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Development of An Analytical Solution for The Parallel Second Order Reaction Scheme for Chlorine Decay Modelling

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Declaration

To the best of my knowledge and belief, this thesis contains no material previously published by any other person except where due acknowledgement has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature: …..  …

Date: 01/11/2010

DEDICATIONS

This dissertation is dedicated to my mother, whom I owe my whole life to, to my sisters and my father for their love and support.

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ABSTRACT

Chlorine is broadly used for water disinfection at the final stage of water treatment because of its high performance to inactivate pathogenic microorganisms, its lower cost compared to other well-known disinfectants and its simple operational needs. However, reaction of chlorine with a wide range of organic and inorganic substances in water causes its decay and formation of chlorinated by-products, which are in some cases carcinogenic and harmful to human health. The major challenge is balancing the risk from these with the cost of operation needed to mitigate the impact. These challenges highlights the importance of having a robust modelling approach for chlorine decay in bulk water as a pre-required step to model the chlorine decay and formation of its by-products in the whole distribution system.

In this study, initially, a comprehensive literature review was conducted to investigate and evaluate all existing modelling approaches for chlorine decay prediction especially in bulk water. Among all existing modelling schemes, three models were paid more attention due to their popularity and/or fundamentally valid background. They are first order model, second order model and parallel second order model.

During the literature review, comparing the effectiveness of the second order model (SOM) proposed by Clark (1998) with the parallel second order model (PSOM) offered by Kastl et al., (1999), the author found that these two models are both fundamentally sound, although the PSOM had better capability in terms of data fitting, and representing the chlorine decay behaviour is much better than SOM. However, non-existence of analytical solution for PSOM was found to be the major negative point for wide adaptation of PSOM compared to SOM.

Trying to understand the basic principles of both models, it was understood that the formulation of SOM was genuine and the researchers who claimed that Clark (1998) made a mistake in deriving the analytical solution were proved wrong. This resulted in having the first publication as a comment in Water Research (Fisher et al., 2010b; Appendix A3).

Further study was performed on how SOM was formulated and attempts were made to apply the same methodology to PSOM in order to arrive at an analytical solution. Consequently, making a reasonable assumption, an analytical solution for the parallel

second order model was formulated and evaluated against the existing numerical method.

As the case study of this research, initially, the previous chlorine decay data from Pilbara Water Treatment Plant was fitted to a first order reaction scheme and it was proved that the data did not comply with it. This was an expected result and the need for other model was validated. For further analysis, fresh water samples were collected from Pilbara Water Treatment Plant to perform chlorine decay tests.

Temperature effect on the behaviour of chlorine decay in the bulk water was investigated by integrating Arrhenius equation with PSOM. Three methods of temperature analysis were compared and the best one was recommended for practical application. It was shown that the model was capable enough to properly display the chlorine decay profile when temperature varies.

The thesis consists of eight chapters. In chapter 1, a brief description of the research background and the overall objectives of the research are given. Chapter 2 focuses on providing a comprehensive literature review about all involved aspects as well as chlorine decay modelling background. Chapter 3 discusses the methodology and analytical methods for conducting laboratory experiments. Chapter 4 gives a prove that the first order decay model does not show accurate results for chlorine decay prediction and the parallel second order model is much more accurate in predicting chlorine concentration. In Chapter 5, the main part of this research, an analytical solution for the parallel second order model is developed. Chapter 6 evaluates the effectiveness of the parallel second order model against the first and second order model. Within chapter 7, temperature effect on the chlorine decay behaviour and the selected modelling approach is evaluated and chapter 8 gives a brief conclusion and recommendation.

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Glossary

The following symbols are used in this thesis:

THM	=	Triahalomethane
TTHM	=	Total Trihalomethane
NDMA	=	Nitrosdimethylamine
DBP	=	Disinfection By-Products
N-DBP	=	Nitrgenous Disinfection By-Products
FRA	=	Fast Reacting Agent
SRA	=	Slow Reacting Agent
NH_3	=	Ammonia
NO_2	=	Nitrite
NO_3	=	Nitrate
NO_x-N	=	Total of nitrite and nitrate
DOC	=	Dissolved Organic Carbon
DON	=	Dissolved Organic Nitrogen
TOC	=	Total Organic Carbon
TON	=	Total Organic Nitrogen
DPD	=	Diethyl-p-Phenylene Diamine
EDTA	=	Ethylenedinitrilotetraacetic Acid
NOM	=	Natural Organic Matter
HAA	=	haloacetic acids
TDS	=	Total Dissolved Solids

1. Introduction

1.1. Background Summary

Safe drinking water and its related issues are of great concern for drinking water supply authorities in every country especially in regions with a high risk of drought. Australia, as one of the driest continents (after Antarctica), is dealing with major challenges in ensuring sustainable water supply in the face of drying climate and rising demand for the safe drinking water. While the demand for the adequately treated drinking water is growing, over-extraction is likely to place pressure on freshwater resources. As a result, the use of alternative sources such as storm, grey and recycled water is being increasingly considered and consequently adequate quality maintenance of these waters will be more appreciated. Furthermore, more tightening water quality restrictions, in response to recently recognised water-related carcinogenic threats, is being introduced by the public health officials; which may result in further attention to the improvement of water quality.

One of the aspects of water quality enhancement in regard to water treatment is disinfection, particularly by chlorination. This is usually done to remove pathogens and other health-threatening micro-organisms. Chlorine is widely chosen as a disinfectant of choice in drinking or recycled water utilities due to its low cost and relative efficacy. Typically, disinfectant, here chlorine, is applied in the clearwell, the final stage of treatment. This disinfectant addition must achieve an adequate inactivation of pathogens before the treated water reaches the first customer (primary disinfection), and be large enough to ensure an adequate residual at the periphery of the distribution system to inhibit microbial regrowth (secondary disinfection). As a result, and according to water quality regulations, it is essential to have a minimum chlorine residual over the whole distribution system and at all times. However, while reacting with different species, depending on the quality of water, the type of treatment processes and the condition of distribution system, chlorine decay behaviour is significantly variable. Thus the chlorine demand, the retention time and its required set point and initial dosing are varied from one water source to another and also over different water networks. On the other hand, the reaction between chlorine and natural organic matters (NOMs) contributes to production of disinfection by-products (DBPs) which has been identified as potentially carcinogenic, mutagenic or toxic substances. The latter, together with the need to

have a maximum allowable chlorine concentration for aesthetic reasons, force operation strategies to enhance the water treatment quality and/or to minimise the chlorine dosing. Consequently, the chlorination strategy is focused on balancing microbiological risks and carcinogenic concerns. In addition, as temperature has been proved to have a significant effect on chlorine decay behaviour, any change in this parameter should also be considered. Effective monitoring, and more importantly, accurate prediction of chlorine decay and controlling DBPs through water systems becomes crucial to our water management. Consequently, the important role of having a robust mathematical modelling approach to address all above-mentioned issues regarding chlorinated disinfection for both planning and management applications is being broadly emphasized.

1.2. The objectives of the research

Generally, the goal of this research was to improve the effectiveness of an existing model (Kastl et al., 1999) in order to predict the chlorine demand and DBPs formation in bulk drinking water. As a case study, however, the research also focused on the decay of chlorine and disinfection by-products formation in the Western Pilbara Water Distribution System.

The overall objectives of the research are as follows:

- To perform a comprehensive literature review in order to fully understand the existing modelling approaches for modelling chlorine decay and DBPs formation.
- Comparing existing chlorine decay modelling methods in terms of their potential to properly predict the chlorine residual in bulk water as well as meeting other planning and management criteria and selection of the best method.
- To further develop the best chosen modelling approach (Kastl et al, 1999) by developing an analytical solution.
- Evaluation of discussed modelling approach by studying the chlorine demand when they are challenged with different chlorine doses and at various temperatures (15-50˚C).

2. Literature Review

2.1. Introduction

Probably one of the most important factors influencing the development of human civilization used to and continues to be adequately supplying the water. The preliminary stage of this development was mostly involved and concerned with the quantity of water supply. Population growing and resulting over-extraction of high-quality surface waters, however, has placed freshwater resources under stress. Moreover, the contamination of water sources with municipal, agricultural, and industrial wastes has led to deterioration in the quality of water in most other existing sources. Simultaneously, by increasing the general public knowledge and discovering more water quality related diseases, water quality regulations have become more rigorous. Therefore, the consideration of water quality can no longer be ignored. Indeed, apparently, all sources of water require some form of treatment before reaching the consumer. This chapter will initially discuss the background information of water treatment processes. The importance and different types of water disinfection as a final step of treatment process will be explained afterwards. The final part of this chapter will summarize the literature review about chlorine decay modelling in distribution systems.

2.2. From Catchment to Tap

Most urban communities collect their water from a natural water body in the catchment, whether a stream, river or an underground aquifer. The water collected may then be stored for some time in a reservoir. Unless it is already of very high quality, the stored water will undergo various treatment processes that remove any chemicals, organic substances or organisms that could be harmful to human health. The water is then delivered to the community through a network of mains and pipes called a distribution system.

2.3. History of Water Treatment

The importance of good drinking water in maintaining health was recognised early in history. However, it took centuries before people understood that their senses alone were not adequate for judging water quality.

The earliest water treatments were based on filtering and driven by the desire to remove the taste and appearance of particles in water. Filtration was established as an effective means of removing particles from water and widely adopted in Europe during the nineteenth century.

Exactly why a clean and reliable water supply was needed, apart from looking and tasting better, was not understood until the second half of the nineteenth century. That was when the nature of infectious disease was recognised and the ability of water supplies to transmit diseases such as cholera and typhoid was first demonstrated.

After this, concerns about the quality of drinking water focused on disease-causing microorganisms (pathogens) in public water supplies.

Scientists discovered that visible cloudiness, or turbidity, not only made the water look unappealing; it could also indicate a health risk. The turbidity was caused by particles in water that could harbour pathogens.

As a result, drinking water treatment systems were designed to reduce turbidity, thereby removing pathogens that were causing typhoid, cholera and other waterborne illnesses.

By the early twentieth century, better protection of water supplies from sewage pollution and simple but effective methods of water treatment (chlorination, sand filtration) had greatly reduced rates of waterborne disease in developed nations. Since then, scientists and engineers have been developing ways of processing water more quickly, more effectively, in a more controlled way and at lower cost.

2.4. Water Treatment Processes

The overall water treatment processes for removing contaminants and improving water quality are similar all around the world. However, the choice of which treatments to use from the variety of processes available depends on the characteristics of the water, the types of water quality problems and the costs of different treatments. The most widely used water treatment process is a combination of some or all of the following:

2.4.1. Coagulation

Coagulation is the process in which the negative charge on particles is neutralized, usually by addition of positive charges such as those provided by alum. The neutralization of particles allows them to clump together forming larger particles which are easier to settle.

2.4.2. Flocculation

Now that the particles have a neutral charge and can stick together. The water flows into a tank with paddles that provide slow mixing and bring the small particles together to form larger particles called flocs. Mixing is done quite slowly and gently in the flocculation step. If the mixing is too fast, the flocs will break apart into small particles that are difficult to remove by sedimentation or filtration.

2.4.3. Sedimentation

Sedimentation is a physical water treatment process used to settle out suspended solids in water under the influence of gravity. The water flows to a tank called a sedimentation basin where gravity causes the flocs to settle to the bottom. Large particles settle more rapidly than small particles. It would take a very long time for all of the particles to settle out and that would mean we would need a very large sedimentation basin. So the clarified water, with most of the particles removed, moves on to the filtration step where the finer particles are removed.

2.4.4. Filtration

Filtration occurs as the water passes through a substance that helps remove even smaller particles. One of the oldest and simplest processes used to treat water is to pass it through a bed of fine particles, generally sand. Sand filtration usually removes fine suspended solid matter as well as some other particles, such as larger microorganisms. Filters can also be made of layers of sand, gravel and charcoal. The development of new synthetic materials has led to an increased range of filter materials and methods, which are being used increasingly to treat water for urban and industrial purposes.

In membrane filtration, water is filtered through tiny holes (pores) in a membrane wall rather than a bed of sand. The smaller the pore size, the more particles are held by the membrane as the water passes through. Of the different kinds of membrane filtration processes, microfiltration is the most widely used in water treatment in Australia, becoming increasingly popular for small-scale water treatment plants supplying smaller communities in rural and regional Australia.

Two other types of membrane filtration, involving membranes with even smaller pores – ultrafiltration and nanofiltration – are not widely used in Australia, because of the lower levels of synthetic chemicals, such as pesticides, present in our water and the high cost of these membrane processes.

2.4.5. Disinfection

Water is disinfected to kill any pathogens that may be present in the water supply and to prevent them from regrowing in the distribution system. Without disinfection, the risk from waterborne disease is increased.

The two most common methods to kill microorganisms in the water supply are oxidation with chemicals such as chlorine, chloramine or ozone or irradiation with ultra-violet (UV) radiation.

The most widely used chemical disinfection systems in Australia are chlorination, chloramination and ozonation.

For a water supplier, the key factors in selecting a disinfection system are:

- Its effectiveness in killing a range of microorganisms
- Its potential to form possibly harmful disinfection by-products
- The ability of the disinfecting agent to remain effective in the water throughout the distribution system
- The safety and ease of handling chemicals and equipment
- Cost

2.5. Different Types of Disinfections

Depending on the quality of water and the size of distribution system (in terms of retention time), different types of disinfectants might be applied in the last part of treatment process.

2.5.1. Chlorine Disinfection (Chlorination)

Chlorine is one of the most commonly used disinfectants for water disinfection. In most water treatment facilities in the world, chlorine is applied as a disinfectant due to its relatively low cost, effectiveness in inactivating pathogenic microorganisms and ability to provide a residual concentration in the network that protects against bacterial regrowth.

2.5.1.1. A Historical Overview

Probably, one of the first known attempts to use chlorine for water disinfection was made by John Snow in 1850. After an outbreak of cholera, he employed chlorine to disinfect the Broad Street Pump water supply in London. In 1897, Sims Woodhead used "bleach solution" as a temporary measure to sterilize potable water in distribution mains at Maidstone, Kent (England) following a typhoid outbreak. The first application of chlorine in water treatment occurred in facilities in England around the 1890's, where its application dramatically reduced the number of typhoid deaths. Soon after this success, chlorination was started in Jersey City, New Jersey, in 1908. Very soon, other cities and towns across the US followed this prosperous disinfection process which resulted in the virtual elimination of waterborne diseases such as cholera, typhoid, dysentery and hepatitis A. By World War II, disinfection with chlorine had become a treatment that was standard worldwide. Before taking the advantage of chlorination for drinking water treatment, typhoid fever killed about 25 out of 100,000 people in the US annually, which is close to the annual death rate associated with car accidents currently happening in the US.

Gradually over time, guidelines have been set for using chlorine for water treatment, and with continual research and development, the chlorination process and its advantages and disadvantages have been more understood.

Briefly speaking, the use of chlorine in the potable water systems seems to be one of the greatest achievements to control disease outbreaks among humans in recent century. It has been advantageous to use chlorine as a disinfectant because:

- It controls pathogenic micro-organisms in water
- It provides a residual in the distribution system which protects the water from re-contamination
- It is better understood than other disinfectants since it has been used for approximately a century in water treatment plants.
- The actual disinfection of water is achieved by the chlorine damaging the cells of micro-organism which disallows them to multiply therefore causing the micro-organisms to die.
- And also chlorine destroys some of the matters which provide food to the microorganisms.

2.5.1.2. Chemistry of Aqueous Chlorine

In the literature, the term aqueous chlorine for water and waste water treatment refers to a variety of chlorine species including elemental chlorine (Cl_2), hypochlorite acid (HOCl), hypochlorite ion (OCl^-) and also chloramine species such as monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and trichloramine (NCl_3).

When pure water is chlorinated, chlorine (Cl_2) hydrolyzes very quickly to produce chloride ion (Cl^-), hypochlorite acid, hypochlorite ion according to the following reactions:

$$Cl_2 + H_2O \leftrightharpoons HOCl + Cl^- + H^+ \quad (2.1)$$

$$HOCl \leftrightharpoons H^+ + OCl^- \quad (2.2)$$

Under typical water treatment conditions in the pH range 6-9, hypochlorous acid and hypochlorite are the main chlorine species (Deborde and vun Gunten, 2007). The type and concentration of chlorine species produced depends on the temperature and pH level. That means the distribution of chlorine into HOCl and OCl^- is pH dependent. Figure 2.1 illustrates the distribution of Cl_2, HOCl and ClO^- as function of pH at 25°C for a chloride concentration of $5x10^{-3}$ M (177.5mg/L) (Deborde and vun Gunten, 2007).

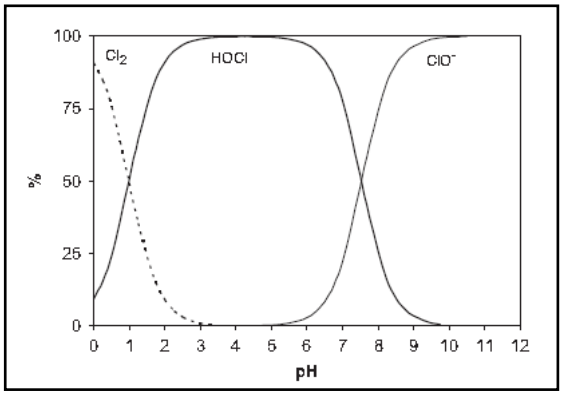

Fig.2.1. : ***Distribution of different chlorine species as function of pH at 25°C for a chloride concentration of $5x10^{-3}$ M (177.5mg/L) (Deborde and vun Gunten, 2007)***

Among the different aqueous chlorine species, hypochlorous acid is the most reactive species while the reactivity of hypochlorite ion is negligible compared to HOCl. Therefore, a lower pH is preferred with disinfection with chlorine in order to produce more HOCl rather than OCl^-.

Hypochlorous acid is a weak acid. It dissociates or ionizes with a dissociation constant ranging from $1.6x10^{-8}$ at 0°C to $3.2x10^{-8}$ at 25°C (Morris, 1966). As can be seen from Figure 2.1, at pH 7.5 and 25°C, the concentration of HOCl and OCl^- are approximately same.

If ammonia is present in or added to the water under chlorination, hypochlorous acid reacts rapidly with ammonia to form chloramines:

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \quad (2.3)$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \quad (2.4)$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \quad (2.5)$$

Depending on the pH, the relative concentration of hypochlorous acid and ammonia, the reaction time and the temperature, some of the above reactions become dominant. Usually monochloramine is the only chloramine that is observed when pH values are more than 8 or when the molar ratio of hypochlorous acid to ammonia is less than 1.0. At higher chlorine-to-ammonia ratios or at lower pH values, dichloramine and trichloramine (also called nitrogen trichloride) are formed. At pH values less than 3, only nitrogen trichloride is ordinarily detected (Morris, 1978b).

The portion of chlorine in aqueous solution formed as hypochlorous acid and hypochlorite ion is called “free chlorine” (free residual chlorine). Chlorine present as monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and organic N-chloro-compounds in which the chlorine-containing compound has a lower oxidation potential than free chlorine is called "combined chlorine" (combined residual chlorine). "Total chlorine" (total residual chlorine) is the sum of the free and combined chlorine.

In other words, free chlorine consists of chlorine which has not reacted in water, therefore determines the disinfection potential reactants of the water. HOCl and ClO^- are considered as free chlorine. Combined chlorine is formed when free chlorine reacts with ammonia and other nitrogenous compounds (organic nitrogen). The combined chlorine, like monochloramine (NH_2Cl), has much less disinfection potential than free chlorine. Finally, total chlorine is free and combined chlorine added together, therefore providing the total disinfection potential of a water sample.

Due to having a strong reaction properties, chlorine reacts with a wide range of organic and inorganic constituents in water. While chlorine reaction with most of inorganic compounds is well enough understood, the reaction pathways between chlorine and inorganic species are still relatively unknown due to the site specific and heterogeneous nature of the natural organic matter (Boccelli et al., 2003).

In general, aqueous chlorine disappears in water due to four kinds of reactions occurring between chlorine and organic and inorganic constituents:

- Oxidation
- Addition
- Substitution
- Light decomposition

Chlorine reaction with inorganic matters such as soluble iron (Fe^{2+}), manganese (Mn^{2+}), ammonia (NH_3 and NH^{4+}) and Halides (SO_3^{2-}, CN^- or sulfide) is only due to oxidation process. In this process, the $Cl^{+\delta}$ radical of the Cl-O bond polarization ($Cl^{+\delta} \rightarrow OH^{-\delta}$) accepts two electrons from the substance being oxidized. In other word, when oxidation reaction occurs, hypochlorous acid or hypochlorite ion will oxidize inorganic species by forcing them to transfer electrons. The oxidation reactions of chlorine with inorganic compounds are usually instantaneous. Some of

the chlorine oxidation reactions with inorganic species in water are as follows (Gang et al., 2003):

$$HOCl + 2Fe^{2+} \rightarrow 2Fe^{3+} + Cl^- + OH^- \quad (2.6)$$

$$HOCl + Mn^{2+} \rightarrow Mn^{4+} + Cl^- + OH^- \quad (2.7)$$

$$4HOCl + S^{2-} \rightarrow SO_4^{2-} + 4Cl^- + 4H^+ \quad (2.8)$$

$$HOCl + Br^- \rightarrow HOBr + Cl^- \quad (2.9)$$

$$3HOCl + 2NH_3 \rightarrow N_2 + 3Cl^- + 3H_2O + 3H^+ \quad (2.10)$$

Reactions of chlorine with organic compounds, however, are more complex. The reaction schemes of hypochlorous acid with organic matters could be described as (i) oxidation reactions, (ii) addition reactions to unsaturated bonds or (iii) electrophilic substitution reactions at nucleophilic sites (Deborde and vun Gunten, 2007). Equations 8 is one of the examples of the oxidation reactions between hypochlorous acid and organic compounds.

$$R - CHO + HOCl \rightarrow R - COOH + Cl^- + H^+ \quad (2.11)$$

In addition and substitution reactions, chlorine is added or substituted into the NOM molecular structure to form chlorinated organic intermediates, which might further decompose to form DBPs (van Hoof, 1992; Gang et al., 2003). Most of the substitution reactions of chlorine with organic compounds consist of a group of parallel and/or serial reactions some of which are fast while some others are slow. In their critical review, Deborde and vun Gunten (2007) concluded that addition and oxidation reactions of chlorine with organic matters are typically slow and only electrophilic attacks of chlorine on the structure of organic compounds are usually fast enough to be significant.

2.5.1.3. Problems Caused by Chlorination

As mentioned, chlorine is a very popular disinfectant in water treatment processes but it has presented some disadvantages as well.

- The first drawback of using chlorine as a disinfectant, as discussed earlier, is that chlorine reaction is pH-dependant. Therefore various forms of chlorine might be present during disinfection (HOCl, ClO- , Cl2) depending on the pH of the water.

The problem with having these different forms of disinfectants is that they all have differing reactivity with the organisms contained in the water. This makes it difficult to achieve consistent results during laboratory experiments. So the pH of the water will have to be monitored closely to ensure the experiments conducted for this project are consistent with one another. In addition, in real treatment process, in order to have the strongest chlorine species (HOCl) among all potentially produced species, lower pH is more desirable.

- The second issue with chlorination is that when chlorine reacts with Natural Organic Matter (NOM) and inorganic compounds in water, it results in the formation of Disinfection By-Products (DBPs). DBPs are the chemical compounds some of which proved to be carcinogenic and harmful to human health. Though this problem is found to be a general issue with all kinds of disinfectants, chlorination has emerged to form more chlorinated by-products.

2.5.2. Chloramine Disinfection (Chloramination)

As explained in previous section, chloramines are some of the products of chlorination when ammonia is present in or added to the water. Due to have the similar disinfection properties with chlorine against bacteria and microorganisms, they are considered as an alternative disinfectants to chlorine.

Although chloramination does not have the taste and odour problems usually experience when chlorine is selected for disinfection, it requires a very large CT (concentration x contact time) value to provide effective disinfection.

In 1908, chloramination was used as disinfectant for the first time in the United States in a water treatment plant in Denver, Colorado but not continuously. The first continuous application of chloramination in the United States occurred at the Greenville, Tennessee water treatment plant in 1926. Disinfection with chloramine became popular between 1929 and 1939 until world war two during which lack of ammonia forced treatment plants to stop disinfecting with chloramine. During 1930s, it was found that chloramine is more stable than free chlorine in the distribution systems. As a result, chloramine was recognized as an appropriate secondary disinfectant to limit bacterial regrowth. During 1980s, the chloramine disinfection

even got more popularity since it was realised that chloramine did not produce as much DBPs as free chlorine did.

As mentioned before, chloramination consists of the reactions between free chlorine and ammonia in the aquatic solution. When chlorine reacts with ammonia, monochloramine (NH_2Cl), dichloramine ($NHCl_2$) or trichloramine (NCl_3) might be formed (equations 3, 4 and 5).

Monochloramine is the best chemical for disinfecting water because unpleasant taste and odors can arise when dichloramines or trichloramines are formed. Moreover monochloramine is more capable of inactivating microorganisms than other two species. A chlorine-to-ammonia ratio of 3:1 to 5:1 is commonly used to limit the production of dichloramines and trichloramines and promote the formation of monochloramines. In addition, these ratios limit nitrification and biofilm growth, which can occur when higher levels of ammonia are used (American Water Works Association, 1999).

As chloramines are not as strong enough as free chlorine to disinfect the water, in order to meet the water quality regulations for primary disinfection of such organisms as Giardia and viruses, long detention times or high chloramine concentrations would be needed. However, since chloramines are capable of producing a stable disinfectant residual, chloramination would be an appropriate secondary disinfectant to control bacterial regrowth in distribution systems.

2.5.3. Chlorine Dioxide Disinfection

Chlorine dioxide (ClO_2) is a disinfectant, which is antimicrobially stronger than chlorine and chloramine species. This strong oxidant can also be used for the control of iron, manganese, and taste and odour causing compounds. It is a yellowish-green gas, which is relatively soluble in water. With an interesting property of having biocidal efficacy over a wide pH range from 3 to 10 (even better at from 4 to 9), chlorine dioxide is more efficient than chlorine against microbial pollutants but produces a smaller microbicidal effect than ozone.

While chlorine reacts with different substances through oxidation, electrophilic substitution and addition reactions, chlorine dioxide reacts only via oxidation. That is the reason for having less THM formation in waters disinfected with chlorine

dioxide. However, chlorites and the chlorates are precisely the most important DBPs produced by the use of this disinfectant. High concentrations of chlorite and chlorate can cause an increase in methemoglobanemia (Korn and Graubard, 2002).

Chlorine dioxide was first used as a water disinfectant in the United States in 1944, at the Niagara Falls, New York water treatment plant. By 1977, about 500 water treatment plants in Europe were reported to use chlorine dioxide as a disinfectant residual for the distribution system (American Water Works Association, 1999).

The main disadvantage of using chlorine dioxide as a water disinfectant compared to chlorine is its high operating costs. This is because the production procedure of chlorine dioxide is far more complex than that of chlorine. Therefore, it is not sold off the shelf and should be generated on-site. As a result, it is only utilised as a primary disinfectant.

2.5.4. Ozone Disinfection (Ozonation)

Ozone is a three-atom molecule of oxygen (O_3), with a delta negative and a delta positive electric charge. It is a powerful oxidizing agent that attacks all "oxidation able" components which come into contact with ozone. Ozone can oxidize wide range of inorganic and organic compounds such as metals like iron and manganese and microorganisms like viruses and bacteria. Ozone's oxidation potential is 2.07 V, compared with HOCl (free chlorine), which has an oxidation potential of 1.49 V (Evans 1972). This property of having a good oxidation potential makes ozone an appropriate option as a drinking water disinfectant. However, because ozone does not have a stable chemical residual, it is not used as a secondary disinfectant (U.S. EPA, 1999a). In addition, its high oxidation capacity demand water treatment equipment be made of corrosion resistant materials.

Ozone is formed when diatomic oxygen (O_2) is broken apart into oxygen free radicals (O•), which bond with O_2, forming ozone. The process works as follows:

$$O_2 + energy \rightarrow 2O\bullet \quad (2.12)$$

$$2O\bullet + 2O_2 \rightarrow 2O_3 \quad (2.13)$$

Briefly, it can be expressed as:

$$3O_2 \rightarrow 2O_3 \quad (2.14)$$

Ozone was first used in water disinfection in 1893 in Oudshoorn in the Netherlands. Soon after that, ozone experienced a great boom in the field of drinking water disinfection. During 1940s, however, an economical way to manufacture chlorine gas was found through development of chemical weapons and this led ozone to give its priority to chlorine.

In past years several other properties of ozone have been discovered related to drinking water treatment. In the 1960s it was discovered that ozone could also be used as a coagulant (Langlais et al. 1991). Ozone is also useful for algal control within the water treatment plant. Ozone destroys algal cells before they have a chance to get into clearwells and clarifiers, where the cells would begin algal growth (Langlais et al. 1991).

There have been concerns about the safety of ozone with regard to DBP formation (other than TTHMs and HAAs). Bromate and formaldehyde can be formed in water after ozone disinfection, if the water has a high bromide ion concentration. Halopropanones and chloral hydrates are some other DBPs that are formed from disinfection with ozone. All of these DBPs are toxic. (Farren, 2003)

2.5.5. Ultraviolet Disinfection

The discovery of ultraviolet light dates back to 1835 and it was first used as a wastewater disinfectant in 1901 in Europe. Since the prediction and its control was difficult at that time, chlorine became more popular disinfectant of choice.

Ultraviolet disinfection is defined as the transmission of electromagnetic energy produced from a mercury arc lamp. As UV radiation penetrates the cell wall of an organism, the UV light destroys the genetic material of the organisms called deoxyribonucleic acid (DNA) or ribonucleic acid (RNA), thus preventing the organism from reproducing.

Pathogens are successfully killed at wavelengths ranging from 245 to 285 nm. Either low-pressure (254 nm) or medium-pressure (180 – 1,370 nm) mercury arc lamps, set at low or high intensities, can be used as the source of UV radiation (U.S. EPA, 1999b).

The effectiveness of a UV disinfection system depends on the characteristics of the water or wastewater, the intensity of UV radiation, the amount of time the microorganisms are exposed to the radiation, and the reactor configuration. For any treatment plant, disinfection success is directly related to the concentration of colloidal and particulate constituents in the wastewater (U.S. EPA, 1999b).

UV disinfection is very effective at inactivating most viruses, spores and cysts. It has shorter contact time compared to other disinfectants. Very small concentrations of DBPs are formed when UV disinfection is used. However, high concentrations of turbidity and certain minerals can decrease the effectiveness of UV (U.S. EPA, 1999b). In addition, this type of disinfection does not produce a disinfectant residual; therefore, it can only be used as a primary disinfectant. As a result, a secondary disinfectant, such as chlorine, in combination with UV radiation should be used when using UV as primary disinfection.

2.6. Disinfection By-Products

Disinfection by-products (DBPs) are described as some chemicals that are formed when disinfectants react with the organic compounds in water. Therefore, DBPs are by-product compounds produced as an desirable result of water disinfection. Some of these compounds are found carcinogenic and some are suspected of causing acute health effects. The chemical compounds of most serious concern contain chlorine and bromine atoms. These compounds have been shown to be carcinogenic, mutagenic or toxic, and have caused negative reproductive or developmental effects in animal studies. Among over 600 DBPs which have been discovered so far, trihalomethanes (THMs) were found in greatest abundance existing in chlorinated drinking water, with lover concentrations of haloacetic acids (HAAs).

2.6.1. History of Disinfection By-Products

Scientists first became aware of DBPs in the early 1970s. In 1974, Rook and others reported the identification of the first DBPs, chloroform, in chlorinated drinking water. Rook (1974) found that chloroform, a known carcinogen, was produced from humic acids by the haloform reaction, the resultant compounds are known as Total Halogenated Compounds (TOX). More specifically, THM was identified as the first

halogenated DBPs in treated water (Rook, 1974). In 1976, the U.S. Environmental Protection Agency (U.S. EPA) published the results of a national survey that showed that chloroform and the other THMs were ubiquitous in chlorinated drinking water. In the same year, the National Cancer Institute published results showing that chloroform was carcinogenic in laboratory animals. Because of these observations, an important public health issue was recognized. In total there have been approximately 600-700 disinfection byproducts (DBPs) that have been reported in the literature for the major disinfectants used in water treatment practices (chlorine, ozone, chlorine dioxide, chloramines) (Krasner et al., 2006). Apart from THMs and HAAs, some of the more recently discovered DBPs which are highly toxic out of the 600-700 DBPs are N-Nitrosdimethylamine (NDMA) (Mitch et al., 2003a and 2003b), chlorinated furanone 3-chloro-4-(dichloromethyl)-5-hydroxy-2-(5H)-furanone or simply put as MX, and halonitromethanes (Krasner et al., 2006).

2.6.2. The Effect of Disinfection By-Products on Humans

As mentioned before, disinfection is very important as it stops the chances of outbreaks of waterborne illnesses, but it also forms by-products during disinfection that can be harmful to humans. The DBPs, such as THMs, HAAs and NDMAs are considered to be carcinogenic, cancer causing, and therefore regulations have been applied to these compounds to reduce the exposure to customers, for example, the United States Environmental Protection Agency (U.S. EPA) set out maximum contaminant levels for these DBPs. Studies on lab animals have shown that these DBPs can cause adverse reproductive or development effects. U.S. EPA states on the website that there have been investigations on the relation between exposure to chlorinated treated drinking water and cancer in human population. Some of these studies have shown a correlation between the consumption of chlorinated treated waters and bladder, rectal, and colon cancers. Also, some of these investigations have shown no correlation between cancer in humans and the consumption of chlorinated water. The World Health Organisation (WHO) states in Volume 52 Chlorinated Drinking water; Chlorination By-products; Some Other Halogenated Compounds; Cobalt and Cobalt Compounds (1997) that overall there is inadequate evidence for the carcinogenicity of chlorinated drinking-water in humans and lab animals. There has been research on individual DBPs like NDMA, THM, HAA, and

the research has proven that they are carcinogenic in higher concentration (EPA IRIS website). So many DBPs are carcinogenic but the concern arises when they are in a high enough concentration in the chlorinated water to cause harm to humans.

2.6.3. Trihalomethanes (THMs)

Trihalomethanes (THMs) are chemical compounds in which three of the four hydrogen atoms of methane (CH4) are replaced by halogen atoms (chlorine, bromine, iodine and/or fluorine). Trihalomethanes with all the same halogen atoms are called haloforms.

Trihalomethanes (THMs) include chloroform ($CHCl_3$), dibromochloromethane ($CHBr_2Cl$), bromodichloromethane ($CHBrCl_2$), and bromoform ($CHBr_3$). Chloroform is the THM most commonly found in drinking water and is usually present in the highest concentration (Vogt and Regli, 1981).

Trihalomethanes are formed as a by-product when chlorine is used to disinfect the drinking water. They result from the reaction of chlorine with organic matter in the water being treated. The THMs produced may have adverse health effects at high concentrations, and many governments set limits on the amount permissible in drinking water. In the United States, the EPA limits the total concentration of chloroform, bromoform, bromodichloromethane, and dibromochloromethane to 80 parts per billion in treated water. These four compounds of THMs are called "total trihalomethanes" (TTHM).

Table.2.1 : Specifications of different compounds of TTHMs

Molecular formula	IUPAC name	CAS registry number	Common name	Other names
CHF_3	trifluoromethane	75-46-7	fluoroform	Freon 23, R-23, HFC-23
$CHClF_2$	chlorodifluoromethane	75-45-6	chlorodifluoromethane	R-22, HCFC-22
$CHCl_3$	trichloromethane	67-66-3	chloroform	methyl trichloride
$CHBrCl_2$	bromodichloromethane	75-27-4	dichlorobromomethane	BDCM
$CHBr_2Cl$	dibromochloromethane	124-48-1	chlorodibromomethane	CDBM
$CHBr_3$	tribromomethane	75-25-2	bromoform	methyl tribromide
CHI_3	triiodomethane	75-47-8	iodoform	methyl triiodide

2.6.4. Haloacetic Acids (HAAs)

Haloacetic acids are carboxylic acids in which a halogen atom replaces the hydrogen atom in acetic acid. Thus, to from monohaloacetic acid, a single halogen would replace a hydrogen atom. For example, monochloroacetic acid would have the structural formula of $CH_2ClCOOH$. In the same manner, in dichloroacetic acid two chlorine atoms would take the place of two hydrogen atoms to form $CHCl_2COOH$. The inductive effect caused by the electronegative halogens often result in the higher acidity of these compounds by stabilising the negative charge of the conjugate base.

Nine years after trihalomethanes were discovered, haloacetic acids (HAAs) as the second most important disinfection by-products were first detected in chlorinated drinking waters by Christman et al. (1983). Haloacetic acids (HAAs) consist of nine different compounds including monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, dibromoacetic acid, tribromoacetic acid, bromochloroacetic acid, dibromochloroacetic acid and dichlorobromoacetic acid). Currently, only monochloroacetic acid ($CH_2ClCOOH$,) dichloroacetic acid ($CHCl_2COOH$), trichloroacetic acid (CCl_3COOH), monobromoacetic acid ($CH_2BrCOOH$) and dibromoacetic acid ($CHBr_2COOH$), all together referred to as HAA5, are regulated. When using a chlorine disinfectant, dichloroacetic and trichloroacetic acids are the most common HAAs. If a water source has high bromide content, bromodichloroacetic acid and bromochloroacetic acid can be found at high levels (Farren, 2003).

2.6.5. N-Nitrosodimethylamine (NDMA)

N-Nitrosodimethylamine (NDMA), also known as dimethylnitrosamine (DMN), is a semi-volatile organic chemical that is highly toxic and is a suspected human carcinogen. The maximum admissible concentration of NDMA in drinking is set to 7 ng L^{-1} by the US Environmental Protection Agency (Andrzejewski et al., 2005). The EPA has not yet set a regulatory maximum contaminant level (MCL) for drinking water. NDMA appears to have a very strong affinity as a poison for the liver and at least one case of poisoning in humans is reported. NDMA is water-soluble, colourless, and has at best a weak taste and odour.

NDMA is an industrial by-product or waste product of several industrial processes. It first came to attention as a groundwater contaminant in California in 1998 and 1999 at several sites that produced rocket fuel. Manufacturing of unsymmetrical dimethylhydrazine (UDMH), which is a component of rocket fuel that requires NDMA for its synthesis, proved to be the culprit in these cases.

In water treatment, however, the formation of NDMA was reported in laboratory experiments during water chlorination in 1980. The formation of NDMA was later documented after chlorination at full-scale drinking water treatment plants and at wastewater treatment plants.

NDMA is a highly toxic DBP, especially in relation to the more common THM and HAA by-products. For example on the US EPA integrated risk information system (IRIS) database classifies NDMA as a probable human carcinogen and lists a drinking water concentration resulting in a 10-6 risk of contracting cancer of 7 ng/L for NDMA and for the same level of risk, the IRIS database provides a 4 µg/L drinking water concentration for bromoform, which is a form of THM. Therefore, the allowable concentration of bromoform is more than one thousand times greater than that of NDMA.

NDMA can be formed due to the nitrosation of secondary amines, like dimethylamine, by nitrite. Also, it has been proposed that formation of NDMA during water and wastewater treatment involving chlorination reactions resulting in the formation and oxidation of 1,1-dimethylhydrazine, which is also known as UDMH, and as mentioned before UDMH results in NDMA when oxidised (Mitch et al., 2003a and 2003b). The formation rate of NDMA is highest between pH 6 and 8,

the pH range over which chlorination is usually conducted (Mitch et al., 2003b). It is also known that NDMA is a DBP when chloramine is used as a disinfectant. The reaction causing the NDMA is the direct reaction between monochloramine and dimethylamine (Choi and Valentine, 2002). Therefore, these reactions are a concern in chlorination because if there is ammonia present during chlorination then inorganic chloramine, which is a form of combined chlorine, can form, which may eventuate into NDMA.

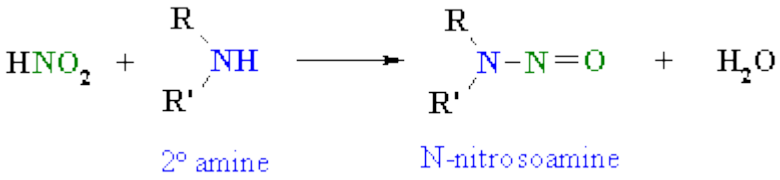

Fig.2.2. : Nitrosamin of secondary amine to form N-nitrosoamine (source: http://www.chem.ucalgary.ca/courses/351/Carey/Ch22/ch22-3-6.html)

Another area of concern with NDMA formation is where recycled water is being pumped into aquifers to replenish existing groundwater sources, which is causing elevated concentrations of NDMA. It is known that NDMA is formed when wastewater is treated with chlorine, so NDMA control is of great concern in areas where recycled water is used for indirect potable reuse (Mitch et al. 2003a).

2.7. Factors Which Influence the Formation of DBPs

Several factors have been reported in the literature to be effective on the formation of DBPs. Previous research studies have shown that the major variables that affect DBP formation are: temperature, pH, disinfectant type, total organic carbon concentration and chlorine to nitrogen levels (for chloramination). Though these factors have been studied to some extent independently from the decay behaviour of disinfectant, for chlorination by-products, it is more advisable to prioritize the effect of chlorine demand on DBPs formation and then draw a relationship between these two and other factors.

2.7.1. Type of Disinfectant

It has been shown that each type of disinfectant would produce a different level of DBPs potential formation. Having said that high level of DBPs formation produced by a disinfectant is a disadvantage, different type of disinfectant has both advantages and disadvantages in drinking water treatment. For example, though free chlorine is very effective at inactivating pathogens, it produces some of the highest concentrations of DBPs compared to other types of disinfectants. Chloramination is a weaker disinfectant compared to free chlorine but fewer amounts of DBPs is produced when using chloramination. Ozone, on the other hand, is an effective disinfectant and does not produce many DBPs of concern. However, ozone is not capable of providing a residual through the distribution system. Similarly, ultraviolet light has been proved effective at inactivating pathogens and it has not shown to form any DBPs that are yet regulated by the U.S. EPA but again it does not maintain a residual for secondary disinfection. Regarding chloramination, the best Cl_2:N ratio for minimizing DBP formation depends on raw water quality. The type and concentration of humic substances present in the raw water source are the most important parameters that dictate which Cl_2:N ratio is the best. In a study examining chloramine disinfection, Diehl et al. (2000) found higher TTHM levels when disinfecting with chloramines at a Cl_2: N ratio of 7:1. They also found that as the Cl_2: N ratio decreased the HAAs decreased. The experiment showed that a Cl_2: N ratio of 3:1 was ideal for controlling DBP formation, but this ratio might not be suitable for controlling bacterial regrowth (Farren, 2003).

2.7.2. Residence Time

Some researchers studied the influence of the residence time on DBPs formation and to examine how it affects the DBPs formation. Some studies have shown that as residence time increases, the concentration of TTHMs increases and the concentration of HAAs decreases. Some others concluded that both TTHMs and HHAs increase when residence time increases. However, THMs and HAAs cannot be consistently related to water age in distribution systems because THMs are known to volatilize and HAAs are known to biodegrade over time when the disinfectant residual is low (Bixiong et al., 2009). Chen and Weisel (1998) performed

experiments to examine the DBPs' concentration in a conventional treatment plant in which chlorine was used for disinfection of the water supply. The average concentrations for TTHMs at days zero, one, two and three or more were 25±14 μg/L, 30±16 μg/L, 29±15 μg/L, and 30±14 μg/L, respectively. The average levels for HAA5 at days zero, one, two and three or more were 24±6 μg/L, 23±7 μg/L, 21±8 μg/L, and 14±6 μg/L, respectively. The reason for increasing the TTHMs with the increase in residence time is explainable due to this fact that chlorine demand increases with time. However, the reason behind the evidences, which have shown the decrease in the level of HAAs with the increase in residence time, is not clearly known.

2.7.3. Temperature

Many studies have been conducted to evaluate how temperature affects the rate of DBP formation and the concentration of DBPs that are formed. Some studies have shown that as the temperature increases, the concentration of TTHMs also increases. However, the results are not conclusive because conflicting results have been found from different research studies (Farren, 2003).

Nieminski et al. (1993) evaluated the effect of seasonal temperature variations on the formation of TTHM and HAAs in 14 conventional water treatment plants in which chlorine was the disinfection of choice. In their study, the mean TTHM levels for summer, fall, winter, and spring were reported as 32.1 μg/L, 28.7 μg/L, 17.6 μg/L, and 16.5 μg/L, respectively. In this study, they showed that the highest TTHM concentrations were found in the summer and fall seasons, while the lowest TTHM concentrations were present in the winter and spring.

Some researches indicated that THMs and HAAs formations have a key temperature (Garcia-Villanova et al., 1997; Abdullah et al, 2003). THMs level is said to be reduced drastically when the temperature is increased above key temperature value. The reason was explained that the rate of THMs formation would rise up with the temperature increase up to a certain level at which the rate of removal of THMs, most likely owing to their volatility, becomes higher than their formation rate (Abdullah et al, 2003).

2.7.4. pH

The related studies have shown that as the pH increases, the concentration of TTHMs also increases. HAA concentrations, however, have not been shown to be consistently dependant on pH. Diehl et al. (2000) conducted a series of experiments to determine the effect of pH on DBP formation in water supplies treated with chloramines. TTHMs were measured at different pH levels of 6, 8 and 10 and the results were reported as 161 μg/L, 259 μg/L, and 295 μg/L, respectively. HAAs were also examined at these pH conditions and the concentrations were 74.5 μg/L, 74.3 μg/L, and 55.5 μg/L, respectively. Diehl et al. (2000) concluded that as pH increases, TTHM levels increase and HAA levels decrease.

In the research conducted by Bixiong et al. (2009) different samples from water treatment plants in six cities in China were tested to examine the effects of different factors on DBPs formation potential. They showed that with increasing pH from 6 to 8.5, the content of THAA does not change significantly. In the pH range from 6.5 to 7.7, however, THAA content increases slowly with pH, but in the pH range of 7.7–8.5, the concentration of THAA decreases instead.

2.7.5. The Concentration of Total Organic Carbon (TOC)

Several researchers have studied the impact of total organic carbon concentration on DBP formation. These experiments have found that as the total organic carbon level increased, the DBP formation also increased.

A study on eight North Carolina water supply systems was conducted by Singer et al. (1995) showing that when TOC concentration was 5.4 mg/L, an average of TTHM and HAA9 level were 82 μg/L and 106 μg/L respectively. At a TOC level of 2.4 mg/L, however, a mean of 39 μg/L for TTHMs and an average of 36 μg/L for HAA9 were reported. These results showed that as TOC concentrations increased so did TTHM and HAA9 levels. Dojilido et al. (1999) also found HAA formation was dependent on the organic matter present in the sample, pointing out that higher concentrations of HAAs were formed at higher TOC concentrations.

2.7.6. Bromide Concentrations

Some of the recent studies have been performed to examine the relationship between bromide concentration in a drinking water supply and DBP formation. These studies have shown that as the concentration of bromide is increased, the concentration of TTHMs and HAAs also increases. Existence of high bromide concentrations in a raw water source when chlorine is added to the water contributes to formation of more brominated THMs as there is more bromide present in the water source for the organics to react with. In a typical raw water supply disinfected with chlorine, chloroform is the major compound of TTHMs formed in the water.

Diehl et al. (2000) examined the effect of bromide concentration on DBP formation in a series of experiments performed for three different water sources. Results showed that as the bromide concentration increased, the TTHM concentration also increased. The study performed by Pourmoghaddas et al. (1993) also concluded that the highest HAA values were formed when the largest amount of bromide was present in the water.

2.8. Chlorine Decay Modelling

Chlorine is broadly used as an effective disinfectant in the final process of the most water treatment schemes, due to its low cost and high efficacy. Chlorine, as a non-selective oxidant, reacts with both organic and inorganic chemical species in water; therefore, it functions as a highly effective antimicrobial agent to reduce the risk of water-born and infectious disease (Jabari Kohapei et al., 2010).

Chlorine reaction with bacteria and micro-organisms leads to inactivate them by totally falling their organic structures apart. This process is quite fast and contributes to death of microorganisms some of which are generally of health concerns to the human. This disinfectant addition, however, must achieve an adequate inactivation of microorganisms before the treated water reaches the first customer (primary disinfection). Besides, most of the time, the condition of the distribution systems makes an ideal environment for microorganisms' regrowth. Therefore, a minimum concentration of disinfectant should always be maintained at the periphery of the distribution system to inhibit microbial regrowth (secondary disinfection). As a result, and according to the water quality regulations, it is essential to have a

minimum chlorine residual over the whole distribution system and at all times. (Jabari Kohapei et al., 2010).

The reaction of chlorine with microorganisms, which are potentially the main sources of water-related health problems, is the main reason of using chlorine as a disinfectant. However, due to have reasonably high oxidation potential, chlorine also reacts with other organic and inorganic matters in the bulk water. This phenomenon of reaction with different species other than microorganisms (bacteria and viruses) is known as the main reason for chlorine decay over time. Therefore, more chlorine is usually required than expected to satisfy the primary and secondary disinfection.

On the other hand, the reaction between chlorine and natural organic matters (NOMs) results in the production of disinfection by-products (DBPs) some of which has been recognised as potentially carcinogenic or toxic substances and harmful to human health. Hence, the chlorine concentration should be limited to order to decrease the disinfection by-products formation potential. In addition, according to the water regulations, chlorine residual should also be limited to a maximum allowable concentration in compliance with aesthetic limitations.

Consequently, considering the minimum required chlorine residual along with the DBPs and aesthetic issues, it is reasonable to enhance the water treatment quality and/or to define a maximum and minimum limit for the chlorine dosage in the water disinfection process.

Furthermore, chlorine decay behaviour has been proved to be significantly affected by water quality characteristics such as total organic carbon (TOC) or dissolved organic carbon (DOC), pH and temperature. There are also several evidences of how different types of treatment processes and also hydraulic and non-hydraulic conditions of the distribution system may influence the chlorine decay profile (Clark and Sivaganesan, 2002). Therefore the chlorine demand, the retention time and its required set point and initial dosing are varied from one water source to another and also over different water networks (Jabari Kohapei et al., 2010).

As a result, in order to address all above-mentioned issues, having a robust mathematical modelling approach to predict the chlorine residual is being broadly emphasized (Fisher et al., 2010a).

So far, several empirical as well as theoretical models for the prediction of chlorine decay in bulk water have been presented. While empirical models are based on the relationship of chlorine consumption with certain water characteristics such as TOC, DOC, pH and temperature, theoretical models attempt to relate the chlorine decay to the time throughout a set of dynamic process equations. These equations are based on physical and chemical principles such as conservation of mass for water and chemical constituents and mass-action kinetics in chemical reactions. The latter (theoretical models) have been presented to be more suitable for both planning and management applications (Fisher et al., 2010a). Therefore, those models, which are dependent on the chemical reactions of chlorine with different constituents in the water, have been paid more attention in the literature.

As mentioned earlier, almost all modelling attempts made so far to predict chlorine decay in bulk waters could be classified into two empirical and theoretical modelling approaches. However, in order to enhance the effectiveness of their models, some of the researchers attempted to combine the attributes of these two categories together.

2.8.1. Empirical Chlorine Decay Models

One of the earliest emprical models to predict bulk chlorine decay in potable water was presented by Feben and Taras (1951). It was an equation which directly described the loss of free chlorine concentration as a power function of time:

$$Cl_t = Cl_0 - kt^n \qquad (2.15)$$

where Cl_t is the chlorine concentration [mg/L] at time t[h] after initial dosing, Cl_0 is the initial chlorine concentration and k and n are coefficients to be estimated for data fitting.

Feben and Tara found that their model needed more than one set of parameters to be estimated to fit the data over whole contact time. The power n should be limited to to the range of 0 to 1 in order to have the shape of a real decay curve. Further, their model suffers from an unwanted feature of C turning negative as t increases, instead of asymptoting towards zero. Because the concept of this empirical model is not based on either the water characteristics nor chemical kinetics of chlorine reactions, recent models have generally avoided to use this kind of modelling approach.

Lyn and Taylor (1993) described the chlorine residual of a particular treated water as an empirical function of chlorine dose, DOC, temperature and time:

$$\mathrm{Cl(t)} = 0.285\mathrm{Cl}_0^{1.631} + \mathrm{DOC}^{-0.313}\mathrm{T}^{-0.176} - \mathrm{DOC}^{-0.241}\mathrm{T}^{0.101}\mathrm{t}^{0.265} \quad (2.16)$$

where Cl_0 is the initial concentration of chlorine or chlorine dosing, DOC is dissolved organic carbon, T is temperature and t is time.

A modified form of saturation type model based on the Michaelis-Menten equation was proposed by Dugan et al. (1995) and developed by Koechling (1998):

$$\frac{\mathrm{dC}}{\mathrm{dt}} = \frac{-\mathrm{k} * \mathrm{TOC} * \mathrm{C_t}}{\mathrm{K} * \mathrm{TOC} + \mathrm{C_t}} \quad (2.17)$$

Integrating from equation 11 yields:

$$\mathrm{C_t} = \mathrm{K} * \mathrm{TOC} * \ln(\mathrm{C_0}/\mathrm{C_t}) - \mathrm{k} * \mathrm{TOC} * \mathrm{t} + \mathrm{C_0} \quad (2.18)$$

where $\mathrm{C_t}$ is chlorine residual at time t, K and k are rate constants for which two emprical relationships with $\mathrm{C_0}$ and TOC were established.

2.8.2. Theoretical (Mechanistic) Chlorine Decay Models

As explained before, modelling chlorine decay with theoretical approaches are based on chemical reactions occurring between chlorine species and all aqueous constituents which are potentially ready to be involved in one type of those reactions with chlorine.

Most of the chlorine reacting in water is consumed by partial oxidation of natural organic and inorganic matters to produce inert products. Most of these reactions would probably are in the form of parallel reactions. Only a small fraction of chlorine participates in the oxidation of organic compounds to form DBPs, whose reaction procedures might be in the format of serial, parallel or a combined and complex pathway (Kastl et al., 1999).

Based on that, It seems reasonable to presume that chlorine disappears in bulk water mostly due to a set of concurrent parallel and serial reactions with a large number of different aqueous substances. Assuming that all chlorine reaction schemes are in the parallel format, each of those reactions could be expressed generally as follows:

$$\mathrm{Cl} + \mathrm{X_i} \xrightarrow{\mathrm{k_i}} \mathrm{P_i} \quad (2.19)$$

where Cl refers to chlorine, X_i is an aqueous compound or molecular site that reacts with chlorine, ki is the rate constant and P_i is the product of this general reaction.

With the assumption that chlorine decays due to n parallel reactions, which are first order with respect to reactants and second order overall, the chlorine decay rate could be described by:

$$\frac{dC_{Cl}}{dt} = -C_{Cl} * \sum_{i=1}^{n} k_i * X_i \qquad (2.20)$$

in which C_{Cl} is chlorine concentration at time t, X_i is the concentration of ith aqueous species at time t that reacts with chlorine and k_i is its corresponding reaction rate constant.

Depending on the nature of the reaction with chlorine, type and amount of X_i in the water and their rate constants, there might be numerous different parallel reactions occurring simultaneously or consecutively. It is unrealistic to consider all those reactions with chlorine in an applicable planning/management modelling even though all reaction characteristics were known (Jabari Kohpaei et al., 2010).

One major attempt to consider all above mentioned reaction pathways with chlorine was made by Jonkergouw et al. (2009). In order to represent the effects of all discussed reactions with chlorine, they defined a different term named as the concentration-weighted average rate coefficient for the entire set of reactions happening between chlorine and other reactants in the aquatic solution.

$$\kappa_t = \frac{\sum_{i=1}^{n} k_i * X_{i,t}}{X_t} \qquad (2.21)$$

$$X_t = \sum_{i=1}^{n} X_{i,t} \qquad (2.22)$$

$$\frac{dC_{Cl}}{dt} = \frac{dX_t}{dt} = -\kappa_t X_t C_{Cl} \qquad (2.23)$$

In this formulation, $X_{i,t}$ is the concentration of each reactants at time t, X_t is the summation of their concentrations and κ_t is the new term defiend as the concentration-weighted average rate coefficient for all reactions.

Having said that there is no analytical solution for equation 17, they proposed an empirical equation for this coefficient with similar mathematical behaviour.

However, the efficiency of this model in accordance with its complexity is being questioned. The most important drawback of their model is about this general concern that if it is acceptable to formulate a model to consider all involving reactions without having any indication of their decay properties (Fisher et al., 2009).

In order to better understand the concept of different mechanistic modelling approaches and compare them together, Fisher et al. (2010a) classified all previously developed theoretical models into three types:

2.8.2.1. Single-Constituent Decay Models

One of the earliest, simplest and initially most popular mechanistic or theoretical approaches for modelling chlorine decay was labelled first order modelling method. According to first order kinetics, there is only one component involved; i.e. compound A is going to be converted to compound B (A→B). The rate of first order reaction is proportional to the first power of the concentration of only one component. Therefore, modelling with first order kinetics, chlorine concentration is assumed to be decreased over time by itself and it does not take into account other species with which chlorine is reacting. The general first order kinetic expressions for chlorine decay in bulk water would be expressed as follows:

$$\frac{dc_{cl}}{dt} = -k * c_{cl} \tag{2.24}$$

$$Cl(t) = Cl_0 \exp(-kt) \tag{2.25}$$

where c_{cl} is chlorine concentration at time t, Cl_0 is initial chlorine concentration [mg/L] and k is the decay constant [h-1].

Figure 2.3 shows the chlorine decay profile of a chlorinated water sample taken from the effluent of water treatment plant in Harding dam, West Pilbara, Western Australia. It expresses the general trend of chlorine decay behaviour which would be observed for most of chlorinated drinking water samples.

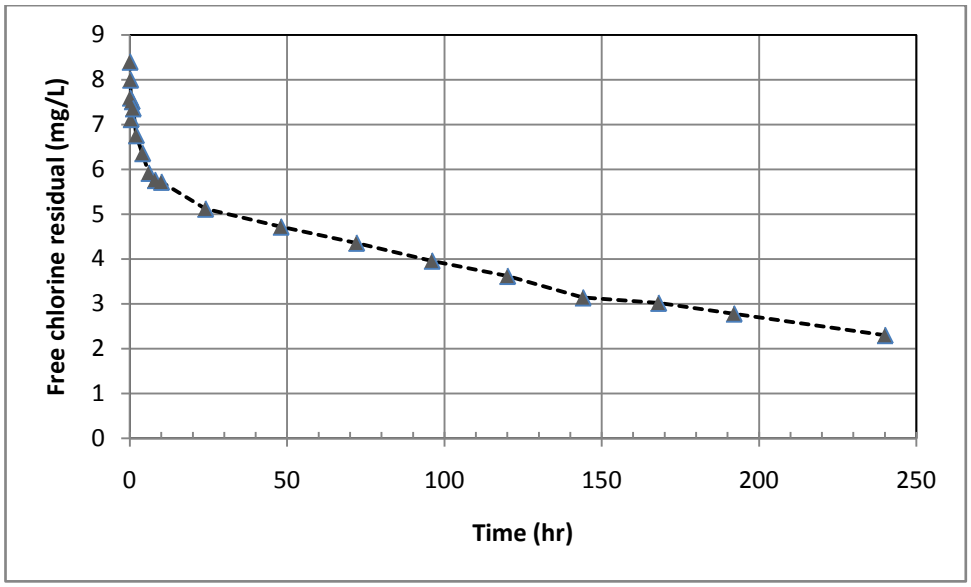

Fig.2.3. : The general trend of chlorine decay behaviour

As can be seen from the figure, a sharp decrease in free chlorine decay immediately after chlorination followed by a much gentler decline after initial time could be observed. If the free chlorine decay were of first order, the curve would be a horizontal straight line in a semi-log plot. Clearly, this is not the case, i.e. the rate is very high initially and continues to fall slowly even after becoming relatively stable at about 30 hours. This is clearer in figure 2.3 when trying to fit the same data with first order model (Fisher et al., 2010a).

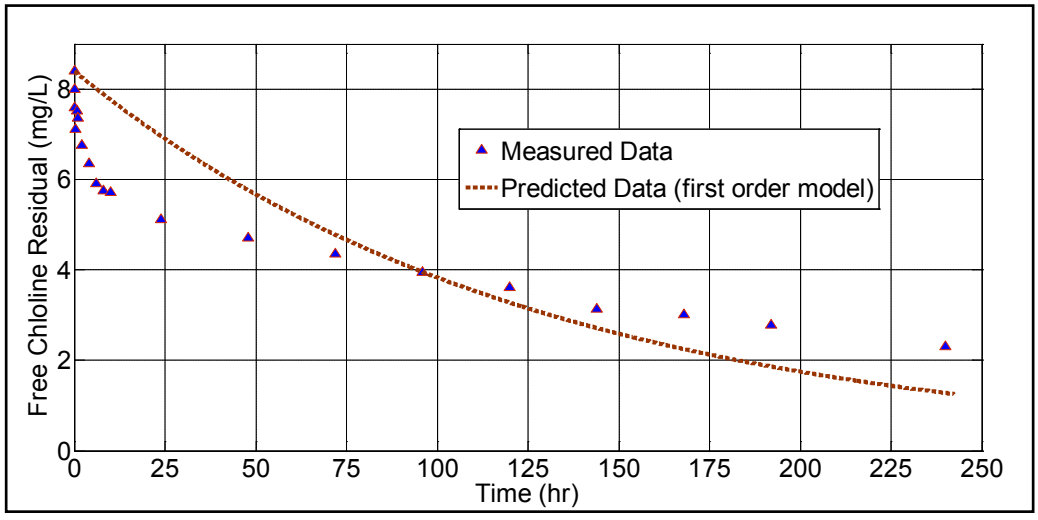

Fig.2.4. : Data fitting for chlorine decay of water sample from Pilbara Water Treatment Plant

Despite the simplicity and easiness of this model, it has not presented a good data fitting in different applications. Additionally, the rate coefficient k is highly

dependent on the water source and the type of treatment process. Furthermore, the model is not capable of reproducing the higher decay rates observed in the initial stages of chlorination nor the slow tailing off at very long reaction times (Jabari Kohpaei et al., 2010; Fisher et al., 2010a; Kastl et al., 1999; Clark et al., 2002).

In all first order kinetic models, only two variables, chlorine concentration and time, are considered. In fact, in these modelling concepts, the effect of reacting agents is either neglected or their amount assumed to be much larger than chlorine. Therefore, it is assumed that the concentration of reacting agents does not significantly change during the reaction with chlorine; and the reaction rate is only proportional to the chlorine concentration. This leads to the so-called pseudo-first-order reaction. However, this assumption is not necessarily valid for all applications.

In some cases, depending on water quality and initial dosing, after first few hours, the assumed condition might be valid (Warton et al., 2006). But even if this makes a reasonable result to properly predict the chlorine demand after the whole retention time in some circumstances, which is not guaranteed, there are still two important defects: one is that there is no proven evidence of the time to consider the starting point of the reaction kinetics; and second, a satisfactory model should not only match the measured data accurately but also it should be able to some extent explain the mechanism of the occurring reactions; which in this case the model fails (Fisher et al., 2010a).

Initially, several attempts were made to compensate the defects of the simple first order model. These attempts, however, were to ignore the role of other important influencing factors on chlorine decay specially reactant species. Hass and Karra (1984) evaluated some of these models against first order and a new method called parallel first order model. The models were labelled as follows:

- Power-law decay model (nth order)
- First-order decay with stable components
- Power-law decay with stable components (nth order)

For the decay models with stable components it was assumed that a portion of the initial chlorine residual is not decaying and only the remainder is subject to decay. They concluded that except for the parallel first order model, all other rate laws resulted in unsatisfactory fits to the data.

In the so-called parallel first order decay model, chlorine is hypothetically divided into two parts, each part is assumed to decay independently according to first order reaction with its own individual decay rate. Hass and Karra (1984) declared that in their assumption, chlorine may decay through two mechanisms, each of first order, and involving a different component of chlorine residual. In other words, component X with concentration C_0x, is assumed to decay according to first order kinetics with a rate constant of k_1 and the remainder, which is the initial chlorine residual without component X, $C_0(1-x)$, is subject to first order decay with a rate constant of k_2. By definition, x is limited to a range between zero and unity.

Gang et al. (2002) used the same method for prediction of chlorine decay but with a different and more specific explanation about the reacting agents. Their initial assumption of separating natural organic matters (NOMs) to "two distinct types of reacting functionalities" which may result in two parallel reactions forming halogenated by-products would be acceptable. Having said that "one fraction of NOM, possibly associated with aldehyde and phenolic hydroxyl, is presumably involved in rapid reaction with chlorine while another fraction results in slow rate of chlorine consumption" might be reasonable. This is because as it is already known many components with different reactivity with chlorine is subject to react with chlorine. Therefore, although it does not represent the exact reaction complex occurring between chlorine and all natural organic matters, the basics of those assumptions would be understandable. Nevertheless, the last part of their assumption, which is the mathematical principle of the first order model, is not fundamentally valid.

Vasconcelos et al. (1996) examined the effectiveness of four different bulk decay models, initially proposed for wastewater by Haas and Karra (1984). The four decay models were: (1) first-order, (2) nth order, (3) limited first-order, and (4) parallel first-order. They suggested that the benefits of using models 2–4 ''were not overwhelming'' when compared to the simpler first-order model (Bocelli et al., 2003).

2.8.2.2. Two-Constituent Decay Models

Considering the effect of reactant constituents, Clark (1998) introduced a two-component second-order chlorine decay model which is based on the concept of reaction between chlorine and another notional substance on the assumption that the balanced reaction equation can be represented by:

$$aA + bB \rightarrow pP \tag{2.26}$$

where A and B are reacting substances; A could be representative for chlorine and B would be a summation of all individual organic and inorganic species which potentially react with chlorine. P is an overall representative for product of the reaction. Clark proposed an analytical solution for this model, which seems to be the first prosperous trial for a second-order model.

$$C_A = \frac{K}{1 - Re^{-ut}} \tag{2.27}$$

where C_A is the initial chlorine concentration and K, R and u is constant parameters to be estimated.

However, since chlorine reacts with lots of organic and inorganic compounds with different complicated mechanisms and stoichiometry, it seems having a and b as stoichiometry parameters, to be estimated, is not appropriate. The Clark's equation can be modified as follows if the simple stoichiometry of the chlorine reaction is assumed:

$$Cl_2 + A \xrightarrow{k} \text{inert product} \tag{2.28}$$

$$C_{Cl}(t) = \frac{C_{Cl_0} - C_{A_0}}{1 - \frac{C_{A_0}}{C_{Cl_0}} * e^{-(C_{Cl_0} - C_{A_0}) * k * t}} \tag{2.29}$$

where C_{Cl_0} and C_{A_0} are initial concentrations of chlorine and notional reactant respectively and k is the rate coefficient. Having just two parameters to be estimated with an explicit solution is one important advantage for Clark's method. Moreover, it perfectly meets different boundary conditions including pseudo-first-order reaction when $C_{Cl_0} \ll C_{A_0}$ is assumed. However, there are some defects as well: one is that the equation is only valid while $C_{Cl_0} \neq C_{A_0}$, and If not, it would be significantly modified to Eq.6:

$$C_{Cl}(t) = \frac{C_{Cl_0}}{1 - C_{Cl_0} * k * t} \quad (2.30)$$

This leads to a calculation problem while data fitting for Eq.30. The second disadvantage is that it considers only one individual species to react with chlorine. This is very prominent as in most cases at least two different reactions with chlorine, the initial fast and the later slow one, have been reported.

Later, trying to compensate the last defect, Clark (2002) extended his model to include these two reaction types (fast and slow) by separating chlorine into two components reacting with two single organic constituents separately. However, the latter suffers from the same theoretically fundamental problem on which parallel first order is based. In other words, they did not give any proof for the assumption of separating chlorine to two different fractions, each one reacting with different notional agents (fast and slow reacting agents).

Huang et al., 2007, attempted to prove that Clark was wrong in deriving the equation correctly and attempted to extract the correct formula. However, after reviewing both papers, it has been revealed that Clark was right and he just made a minor typing error about a negative sign, which did not have any effect on the final result. However, on the other hand, Huang had a serious mistake while deriving the integration, forgetting to consider the boundary conditions while integrating (Fisher et al., 2010b).

2.8.2.3. Multiple Reactive-Constituent Models

Probably, the earliest reactive-constituent model of chlorine decay in natural water was developed by Qually and Johnson (1983). They considered the NOM that reacted with chlorine to be of two types- fast and slow reacting fulvic acids.

Kastl et al. (1999) proposed a parallel second order model by assuming two notional constituents –fast and slow reducing agents- reacting with chlorine. The decay model consists of two simultaneous parallel reactions with the overall second order kinetics as follows:

$$Cl_2 + FRA \rightarrow Cl^- + \text{inert product} \quad (2.31)$$

$$Cl_2 + SRA \rightarrow Cl^- + \text{inert product} \quad (2.32)$$

where FRA is the concentration of Fast reacting Reducing Agents and SRA is the concentration of Slow reacting Reducing Agents in the water.

Kastl et al. (1999) compared the suitability of five represented reaction schemes for describing chlorine decay behaviour in one nominated bulk water sample. They showed that the parallel second order model accurately satisfies the requirements of modelling chlorine decay. They also confirmed that the two parallel reactant model was the simplest one to satisfy the criterion regarding invariance of coefficients in relation to initial dose (up to 4 mg/L), with the smallest weighted error. They also showed that the model well represents re-chlorination.

Trying to involve combined chlorine, Fisher and Kastl (1996) extended the two parallel reactant model to include similar reactions with two nitrogeneous agents in order to make the model capable of predicting nitrogeneous by-products specially NDMAs. In other words, assuming that there is a relationship between the production of nitrogeneous by-products (e.g. NDMA) and the decay rate of combined chlorine, other sets of reaction schemes would be needed to present this relationship. In extended model, there are two additional reactions, representing the reaction between chlorine and nitrogeneous compounds to produce combined chlorine and inert product. The last equation is proposed to include the decay of combined chlorine over the rest of retention time. The reaction scheme for additional reactions can be expressed as:

$$Cl_2 + \text{FRNA} \rightarrow \text{CCl} + \text{inert product} \quad (2.33)$$

$$Cl_2 + \text{SRNA} \rightarrow \text{CCl} + \text{inert product} \quad (2.34)$$

$$\text{CCl} \rightarrow \text{inert product} \quad (2.35)$$

where FRNA is the concentration of Fast reacting Reducing Nitrogeneous Agents, SRNA is the concentration of Slow reacting Reducing Nitrogeneous Agents in the water and CCl is the concentration of combined chlorine.

The second order reaction rates for different reactants and resulting free and combined chlorine rates in this model could be given as follows (Fisher et al, 2010):

$$\frac{dC_j}{dt} = -k_j * C_{Cl} * C_j \quad j = 1, \dots, 4 \quad (2.36)$$

where C_j and k_j are concentration of the four reacting agents and their rate constants respectively.

$$\frac{dC_{Cl}}{dt} = \sum_j \frac{dC_j}{dt} \tag{2.37}$$

$$\frac{dC_{CCl}}{dt} = -k_{CCl} * C_{CCl} - \sum_j \frac{dC_j}{dt} \tag{2.38}$$

where C_{Cl} is free chlorine concentration and C_{CCl} and k_{CCl} are combined chlorine concentration and its rate constant respectively. In this form, the "parallel reactant" model has ten parameters-the decay coefficient (kj) and initial concentration (C_{0j}) of each of the four reducing agents and those of combined chlorine (k_{CCl} and C_{0CCl}).

It is obvious that having more complicated model with more parameters to be estimated results in having more precise decay profile, but makes parameters more difficult to be interpreted and verified. Although the extended model (Equations 2.36, 2.37 and 2.38) has the capability of considering combined chlorine and nitrogeneous compounds and probably present more accurate decay profile because of having more parameters, it is better to understand the strengths and weaknesses of the original model (Kastl et al., 1999) first and then attempt to extend it. Therefore, the original non-extended parallel second order model (Kastl et al., 1999) was selected to be more investigated.

2.8.3. Temperature Effect

Depending on the climate of the network region as well as the type of water storage and distribution system (either over or under ground) and the material used for that purpose, water temperature could vary over the year. For several years, Arrhenius equation has been proposed as the best method to describe the way in which temperature alterations affect the chlorine decay. Fisher and Kastl (1996) preferred to use a relative form of Arrhenius equation to keep the temperature relationship independent of any other variables. They assumed the temperature dependence relationship to be described by a single value of activation energy in this relative form of Arrhenius equation:

$$k_T = k_{T_0} * \exp\left(\frac{-\frac{E}{R}*(T_0 - T)}{(273 + T_0)(273 + T)}\right) \quad (2.39)$$

where k_T and k_{T_0} are the reaction constants at temperatures T and T_0 [˚C] respectively. E/R is the ratio of activation energy to the universal gas constant [K], which expresses the sensitivity of all reactions to the temperature.

2.9. Summary and Conclusion

In this chapter, initially, background information about water disinfection and related treatment processes was briefly discussed. Then different types of water disinfection methods, including chlorination, and their advantages and disadvantages were explained. A comprehensive literature review about chlorine decay modelling and its involving effective factors were discussed afterwards.

Existing methods for chlorine decay modelling in the literature were classified into two categories: empirical models versus theoretical or mechanistic models. Mechanistic models were given more scores due to their more capabilities in predicting chlorine residuals in all planning and management applications.

Among all existing theoretical methods for chlorine decay prediction, the most popular ones in the literature including first order reaction model, second order model, parallel first order and parallel second order modelling approaches were paid more attention and compared more carefully. According to Fisher et al. (2010a), parallel second order model was noticed to be the most effective modelling approaches to meet all considered criteria to predict chlorine residuals in bulk water.

The only shortcoming of the model compared to all above mentioned modelling methods is not having an analytical solution with which the model could be more competitive and user friendly.

3. Materials and Methods

In this chapter, the methods and procedures for analysing the samples and measuring the water quality parameters of interest will be explained.

3.1. Collection of the Samples

All required samples were ordered to be collected from different sections of the Harding Dam Water Treatment Plant in Western Pilbara. Samples were collected from different parts of each section in order to have an acceptable representative of water quality in each part. After the samples were collected, they were stored in cleansed plastic containers of 10 or 20-litre volume, sealed properly and labelled to show all information about their sampling location, date and time. The samples were afterwards sent to Water Laboratory of Civil engineering Department in Curtin University to be tested.

3.2. Storage of the Collected Samples

Once the samples were received, they were carefully poured into smaller chlorine-demand-free amber containers of 5-litre volume. After relabeling the new containers, the prepared samples were then kept in the laboratory fridges at 4ºC for the future use.

3.3. Preparation of the Samples

There are several stages needed to be done for samples during the laboratory experiments for chlorine decay testing. These stages were as follows:

- Filtering
- Making the Accurate Volume of the Samples
- Duplication of the Samples
- pH Adjustment
- Labelling

3.3.1. Filtering

Filtering process was needed when Dissolved Organic Carbon (DOC) measurement was intended. The process started by initially setting up the filtering apparatus and pump. Before any filtering begun, the apparatus must be cleaned to remove any unwanted substances that could contaminate the sample. Then the filter paper, with the size of 0.45μm, was placed into the apparatus. Before using the actual water sample, the filter paper was rinsed with 400mL of deionised water to remove any DOC which might exist in the filter paper. Once all the apparatus is clean and the filter paper rinsed thoroughly, the filtering can begin. To filter the sample, it was poured into the top part of the apparatus where gravity feed the water through the paper. The pump was then applied to create vacuum pressure in the bottom part of apparatus to help filtering process run more smoothly and quickly. This was usually required for the all samples and more specifically when there was large amount of suspended particles. If the filter paper became clogged up with particles then it was replaced with a new paper and then rinsed with 400mL of deionised water for filtering to restart. The filtering process was stopped once there was enough sample for testing.

3.3.2. Volumes of the Sample

Before starting chlorine decay test, the water samples needed to be made into a manageable and accurate volume so it could be dosed with certain amount of chlorine and measured for its decay. Two different methods were examined for chlorine dosing of the samples. In one method, first the volume of the samples were fixed to a certain amount and then the samples were chlorinated using a small amount of condensed chlorine solution. That small amount did not affect the total volume so much. In this method, each sample was made to a volume of 500mL in the 600mL bottle. To measure the volume accurately, the sample were weighed, instead of using a measuring cylinder. In the second method, first, some amount of sample was poured into a volumetric flask, then a certain amount of diluted chlorine solution was added to it and finally the total volume was made to 500mL by adding more sample. During the experiments, the second method for chlorination of the samples was found to be more accurate.

3.3.3. Duplication of the Samples

To avoid significant errors and to reduce the uncertainties during the experiments and to ensure the consistency when measuring the chlorine decay, duplicate samples were made for each sample. The reason is that, during the chlorine decay testing, each sample can be compared to the duplicate sample so any anomalies can be picked up in the results. The anomalies may occur due to the equipment or human error. Therefore, for most of the tests two sets of 500mL sample were prepared.

3.3.4. pH Adjustment

The pH value is the scale by which the acidity or basicity of a solution could be determined. For water samples, it shows if the water is acidic, basic or neutral and also gives an estimation of acidic or basic the water is. To compare the chlorine decay potential of different samples, the pH value of the samples had to be consistent for every sample, because pH can have a significant effect on the rate of the chlorine decay.

In this research, the optimal pH range for chlorine decay was maintained between 7.5 to 8, depending on the water source. Measuring pH was conducted by the HACH HQ30d pH meter. If the pH was not in the intended range, then an acid or base was used to adjust pH to the correct value. The acid used was Sulphuric Acid, and the base used was Sodium Hydroxide, both with a concentration of 1mol/L.

Because each water source has a different initial pH reading and responds differently when acid/base is added to them, the process of pH adjustment should be performed based on trial and error phenomena. That is addition of acid/base and pH measurement should continue until the intended pH value is obtained.

For this purpose, firstly, the initial pH of water sample was measured with the HACH HQ30d pH monitor. Then, depending on whether the pH meter reading is above or below the intended range, an acid or base was added to the water sample, respectively.

Each time the acid or base was added to the samples, they were stirred for some time to allow the acid/base to affect the pH. After stirring, the sample was left to settle for

5-10 minutes, and then the pH was tested again. If the pH was not within the range of interest the process was repeated again until the pH was correct.

A record was kept on how much acid/base was added to the samples. This was done so it was easier to get the duplicate sample to the correct pH as it was already known from the original sample how much acid/base was required to get the pH correct.

For the water samples whose pH constantly fluctuated, meaning the pH was never stabilised, a buffering agent was added to help stabilise the pH and make it simpler to adjust. The buffer agents used for stabilising the pH were Calcium Carbonate or Sodium Carbonate.

3.3.5. Labelling

All water samples were labelled so there was no mix up with other student's samples in the lab.

3.4. Initial Water Quality Testing of the Samples

Before chlorination of water samples, initial water quality testing for each water source was conducted to obtain the water characteristics, which help understand the composition of the water and therefore help explain the chlorine decay behavior for each sample. This step was done before the pH adjustment so the acids and bases added to the sample cannot affect the results. Major experiments to examine the initial water quality characteristics were as follows:

- Total Organic Carbon/Dissolved Organic Carbon (TOC/DOC)
- Ammonia (NH3)
- Nitrate/Nitrite
- Total Organic Nitrogen/Dissolved Organic Nitrogen (TON/DON)
- pH
- UV_{254}

3.4.1. TOC/DOC Analysis

Total organic carbon (TOC) is the amount of carbon bound in an organic compound and is often used as a non-specific indicator of water quality. Dissolved Organic Carbon (DOC) is the organic carbon remaining in a sample after filtering the sample, typically using a 0.45 micrometer filter. The total and dissolved organic carbon were measured using the General Electric Sievers 5310C Laboratory Total Organic Carbon Analyser. For TOC analysis, first, the samples, which were to be tested for the measurement, were poured into 40mL pre-cleaned glass vials. For each water source, three samples were prepared, one original and two duplicate samples. The 40mL of sample is analysed by the machine to give an average TOC and DOC reading in parts per million (ppm) or parts per billion (ppb).

3.4.2. Ammonia and Nitrate/Nitrite Analysis

If necessary, the ammonia, nitrate and nitrite concentrations of the water samples were all obtained using the AQUAKEM 200. The machine required the correct AQUAKEM reagent and a 2mL sample of the water source to test the requested parameters.

3.4.3. TON/DON Analysis

This analysis was outsourced to SGS Company, as the machinery in the Curtin University Civil Engineering Water lab was incapable of measuring these variables.

3.4.4. UV_{254} Measurement

UV absorbance was measured using Helios Gamma Spectrophotometer (Thermoelectron) and measured by filtering the sample through 0.45µm CA filter media. The optical design of this instrument is single beam Seya Namioka monochromator and gives only 0.05% error in measurement.

3.5. Chlorine Induction

One way to induce chlorine for chlorine dosing is using a condensed chlorine solution such as sodium hypochlorite 12% (NaOCl 12%). However, this way forces the examiner to use a small amount of condensed sodium hypochlorite for chlorination of common volume of water samples. As a result, using TRANSPETTE for injecting accurate amount of chlorine solution to the sample is necessary.

The second method for chlorine induction of the samples is to initially dilute the condensed hypochlorite solution to the desired level and then use a reasonable amount of the resulted solution for chlorine dosing of the samples. However, firstly, dilution should be performed using clean deionised water and secondly the concentration of diluted solution should be confirmed. To confirm the concentration of obtained solution, its total chlorine concentration was measured several times to ensure that dilution process was performed properly.

Despite using accurate apparatus for chlorine induction in the first method, it has been found difficult to maintain the high level of accuracy using this method. Therefore, second method of chlorine induction was preferred. According to this method, first, a certain volume of condensed sodium hypochlorite (NaOCl 12%), which contains about 60g of free chlorine, was diluted 1000 times to give only 60mg of free chlorine. As mentioned before, obtained solution was tested several times to confirm its chlorine concentration. This was achieved by dosing a set volume of the sodium hypochlorite into a 10mL vial of deionised water, and then after sufficient mixing the chlorine concentration was checked using the LOVIBOND PCcheckit Chlorine device. Therefore, through back calculations the concentration of the chlorine in the sodium hypochlorite was found. It was essential to check this initial concentration of the sodium hypochlorite as an incorrect initial concentration will lead to errors in the rest of the testing.

The next step was to calculate the volume amount of diluted chlorine solution, which was required for dosing the water samples. The chorine concentrations specified for testing the water sources ranged from 3 to 8.5mg/L of Cl. As a result, for example, 3 mlit of prepared chlorine solution was needed to dose 500 mlit of the sample with the initial concentration of 3mg/L of chlorine.

3.6. Chlorine Decay Testing

All chlorine measurements were conducted with the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method using Lovibond pocket colorimeters.

The LOVIBOND PCcheckit Chlorine device was used to measure the total and free chlorine concentration. To get the concentration, about 10mL of the sample was poured into a 10mL vial, and then a Free or Total LOVIBOND DPD (Diethyl-p-Phenylene Diamine) power pillow was added into the vial. The contents from the powder pillows react with chlorine in the vial to form a pinkish colour. The vial was stirred and left for two minutes. After two minutes, the outside of the vial was wiped clean and placed into the chlorine measuring device which gave the concentration of the chlorine at the time the powder pillow was added. This process was repeated for the whole sample set for the indented times.

Several experiments with de-ionized water were conducted before the main tests to make sure of the initial chlorine concentrations. Before beginning any sampling for the experiments, all involving containers and glassware were cleaned with de-ionized water to ensure that no chlorine demand was present.

Duplicate analysis was performed on each sample, and the average was reported. If the difference between the two values was greater than 10%, a third analysis was performed, and the average of all three values was reported. To minimise the effects of variations in the water quality, repeated tests were done and the results were compared for consistency.

3.6.1. Time intervals

A well defined chlorine decay profile of a water source depends on the appropriate times at which chlorine concentration is measured. Chlorine decays at its quickest rate during the first initial time up to five minutes, then the rate gets to an average from one to five hours, and finally the rate of decay reduces slowly as the chlorine reactants reduce. Therefore, it is important to gather the majority of the chlorine concentration measurements during the first eight hours, especially within the first hour of the chlorine dosing. Thus, the time intervals used to measure the chlorine concentration were 5min, 10min, 20min, 40min, 1hour, 2hr, 4hr, 6hrs and 24hrs after dosing. For the water sources where the chlorine took longer than 24 hours to

completely dissipate, the measurements were taken on a daily basis until the residual chlorine was less than 0.05mg/L of Cl.

3.6.2. Incubation

The water samples were incubated in water baths between chlorine concentration measurements. The samples were examined at the temperatures of 15, 20, 25, 30, 35, 40, 45 and 50˚C.

3.7. Disinfection By-Product Collection and Testing

For testing Disinfection by-Products, especially THMs and HAAs, small 40mL samples were set aside straight after chlorine dosing to be tested for Disinfected By-Product (DBPs) formation, more specifically Trihalomethanes (THMs) formation.

A chlorine quenching agent was added to remove the rest of chlorine in the sample (dechlorinate the sample) when the sampling for THM and HAA was intended in the middle of chlorine decay. The quenching agent used was Sodium Thiosulphate ($Na_2S_2O_3$). A 1% Sodium Thiosulphate was created and used for the all experiments to quench the chlorine residual.

When all stages of chlorine decay had occurred and therefore THM samples were ready, then the 40mL THM samples were sent to SGS to be analysed for the Total Trihalomethane concentration.

3.8. Chlorine Quenching Sample Calculation

According to reaction between Sodium Thiosulphate and chlorine, 316gr of $Na_2S_2O_3$ reacts with 71gr of chlorine to form Sodium Tetrationate and sodium chloride:

$$2Na_2S_2O_3(aq) + Cl_2(aq) \rightarrow Na_2S_4O_6(aq) + 2NaCl(aq) \quad (3.1)$$

So, to quench 1mg/lit of chlorine, 4.45 mg/L (~5 mg/L) of Sodium Thiosulphate is needed. Therefore, if 1% Sodium Thiosulphate solution is prepared, 20 μL of the solution is required to quench 1mg/L of chlorine in a 40mL vial.

4. Proving that the parallel second order model is much more accurate than the first order modelling approach in predicting the chlorine concentration

In this chapter, initially, performing a simple analysis, it will be shown that first-order and even pseudo-first order decay models are not capable of expressing the behaviour of chlorine decay in bulk water properly. For this purpose, the previously collected data from Pilbara Water Treatment Plant was used. Following that, modelling the same data with the parallel second order model, it was shown that the model presents accurate results for prediction of chlorine residuals in bulk water.

4.1. Initial Analysis of the existing data

To examine the potential and credibility of the new formulation against existing numerical methods performed by computer aided programs, five series of chlorine decay data sets were chosen. The data is related to the identical water samples collected from Pilbara Water Treatment Plant at Harding Dam on 23/08/06. The only difference is about different initial chlorine dosing. Table.4.1 shows the readings of chlorine decay tests for different initial chlorine concentrations. Fig.4.1 illustrates the free chlorine residuals for different initial chlorine dosing as well.

Table.4.1 : Chlorine decay results from Pilbara Water Treatment Plant samples on 23/08/06

Initial Dosing (mg/l)	**2.11 (mg/l)**		**4.5 (mg/l)**		**6.7 (mg/l)**		**8.8 (mg/l)**		**11.2 (mg/l)**	
Time (hr)	Free Cl	Total Cl	Free Cl	Total Cl	Free Cl	Total Cl	Free Cl	Total Cl	Free Cl	Total Cl
0	2.11	2.11	4.50	4.50	6.70	6.70	8.80	8.80	11.20	11.20
0.5	1.28	1.42	3.40	3.70	5.50	5.80	7.70	8.00	9.80	10.00
1	1.16	1.28	3.30	3.50	5.40	5.60	7.50	7.90	9.60	10.00
2	1.02	1.15	3.10	3.30	5.20	5.40	7.20	7.60	9.40	9.60
3	0.92	1.08	2.90	3.10	5.10	5.30	7.10	7.50	9.20	9.40
4	0.85	1.01	3.00	3.20	5.10	5.30	7.20	7.50	9.40	9.60
24	0.30	0.45	2.10	2.40	4.10	4.40	6.10	6.40	8.30	8.60
48	0.09	0.26	1.60	1.82	3.60	3.90	5.60	5.90	7.60	8.10
120	0.02	0.09	1.11	1.30	2.90	3.10	4.70	5.00	6.70	7.20
144	0.02	0.08	0.99	1.13	2.70	2.90	4.60	4.90	6.70	7.00
168	0.00	0.00	0.90	1.00	2.60	2.70	4.40	4.70	6.50	6.70

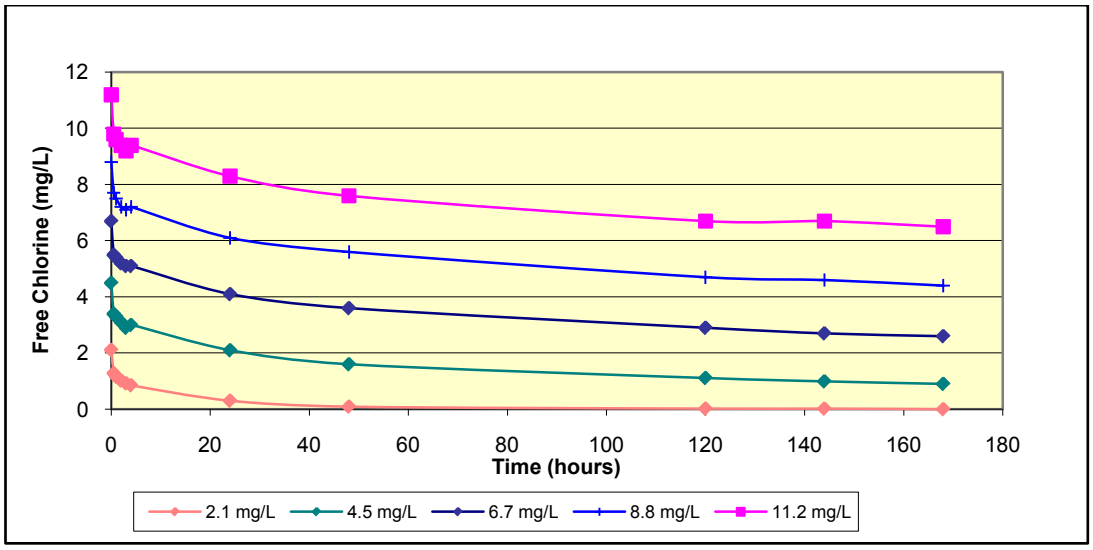

Fig.4.1. : Chlorine decay results from Pilbara Water Treatment Plant samples on 23/08/06

First, applying a very simple technique, it was proved that even after initial period of time, in which the reaction rate is high, the so-called pseudo-first-order decay is not able to properly predict the chlorine decay over the incubation period. For this purpose, assuming that pseudo-first-order decay rate is valid yields:

$$\frac{dCl}{dt} = -k * Cl \qquad (4.1)$$

$$Cl = Cl_0 * \exp(-k * t) \qquad (4.2)$$

$$\ln\left(\frac{Cl}{Cl_0}\right) = -k * t \qquad (4.3)$$

$$\ln Cl = -k * t + \ln Cl_0 \qquad (4.4)$$

Logarithmical concentration of free chlorine was drawn against the time for each group of data sets. It was interestingly revealed that in each figure there is one turning point, separating the curve into two semi-linear ones. Considering the terms in the parallel second order kinetics, the point probably shows the time at which FRAs are depleted. Therefore, after this time there should be only SRAs reacting with chlorine (again it is noticeable that the definition of FRAs and SRAs manifests the dependence of these terms to the relativeness of their average reaction rates to each other). The point would be recognized more accurately by manually drawing two lines over the data points on the both sides of the area in which the point of our

interest is visually residing. Using a trial and error method, this was done by manipulating the range of data covered by linear regression on each side and monitoring the R-Square (R^2) to get the best linear regression. It was shown that the data on the right side of the point of interest is much closer to a linear order. Identifying this initial time and removing it from the figures, they were modified to show only the period of time in which there is only one slope remained. If the assumption of pseudo-first-order reaction, which supposes that the concentration of reactants rather than chlorine is much higher than that of chlorine, is correct, with increasing the initial chlorine concentration the slope of the line should be constant. However, it is seen that, by increasing the chlorine dosing, the slope is being reduced continuously. That means the authenticity of the first order or even pseudo-first-order assumption for the reactions is not valid. Figures 4.2 to 4.6 show the decline in the slopes of the lines resulting from the linear regressions between natural logarithm of residual free chlorine concentration versus time at different chlorine dosing.

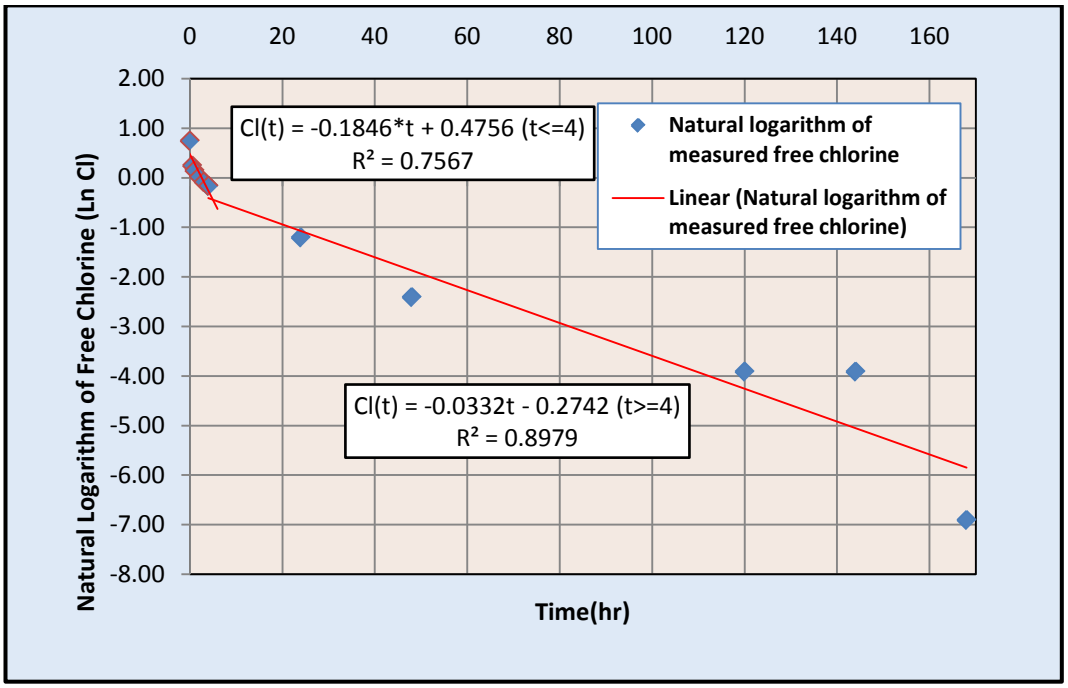

Fig.4.2. : Natural logarithm of free chlorine vs. time for 2.11 mg/l initial dosing for Pilbara Water Treatment Plant samples on 23/08/06

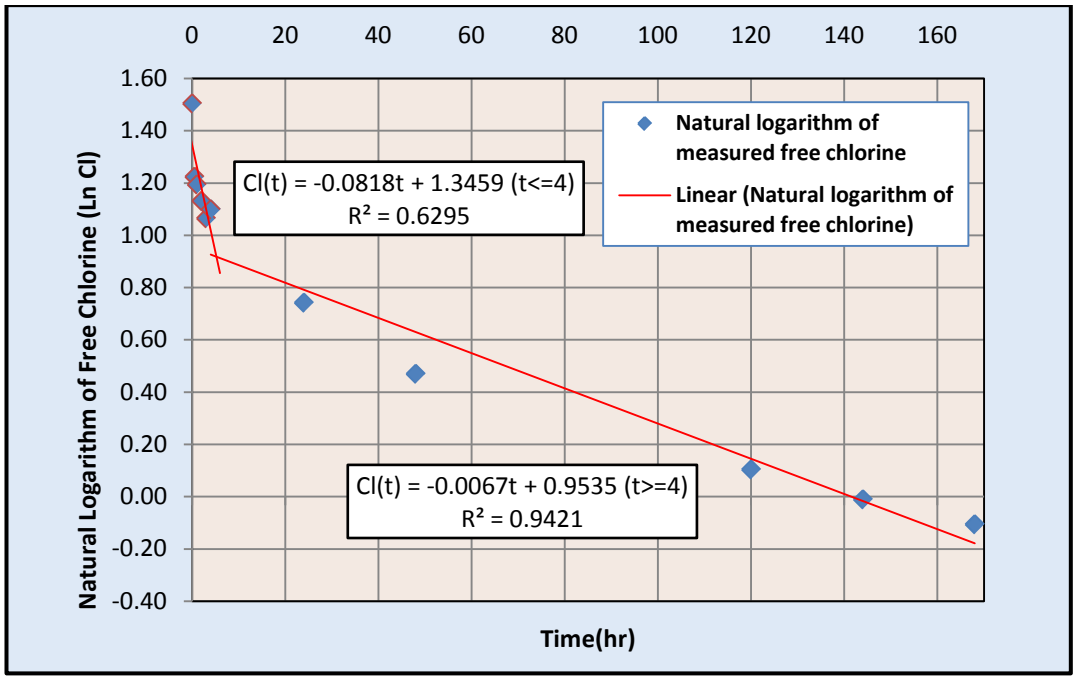

Fig.4.3. : Natural logarithm of free chlorine vs. time for 4.5 mg/l initial dosing for Pilbara Water Treatment Plant samples on 23/08/06

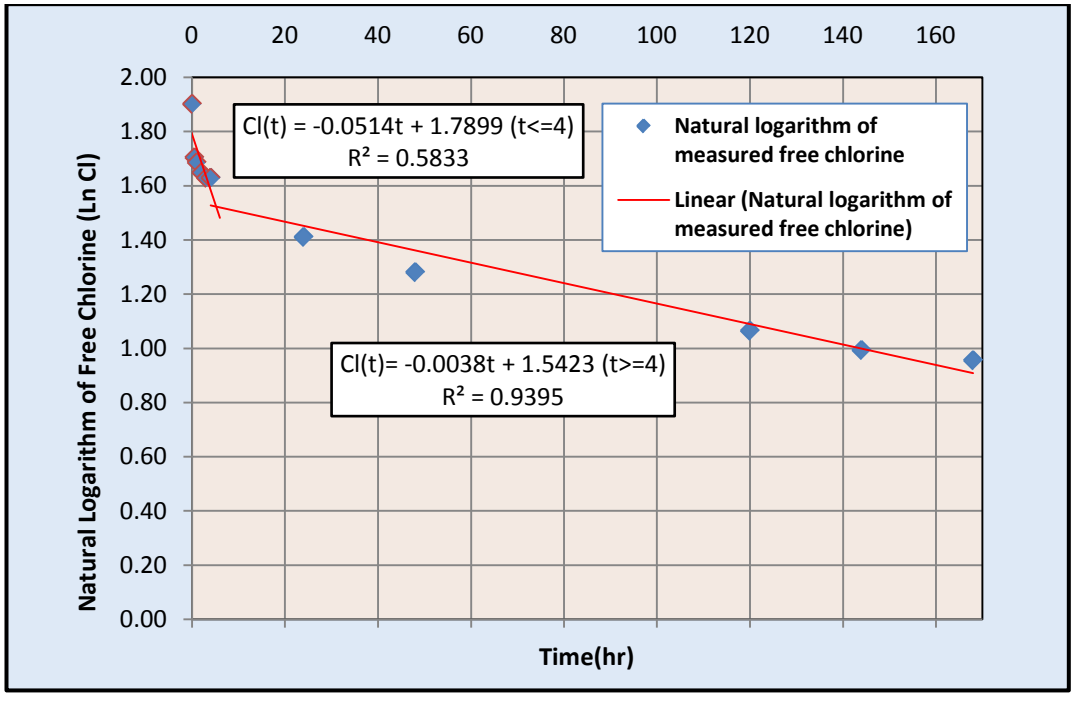

Fig.4.4. : Natural logarithm of free chlorine vs. time for 6.7 mg/l initial dosing for Pilbara Water Treatment Plant samples on 23/08/06

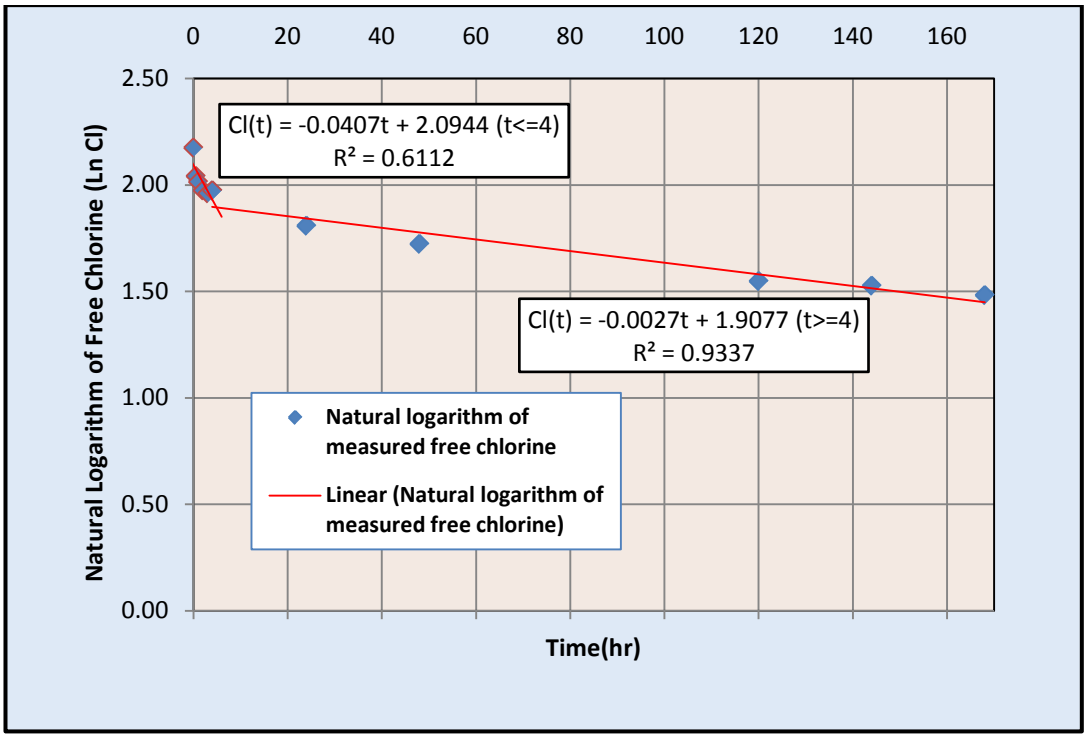

Fig.4.5. : Natural logarithm of free chlorine vs. time for 8.8 mg/l initial dosing for Pilbara Water Treatment Plant samples on 23/08/06

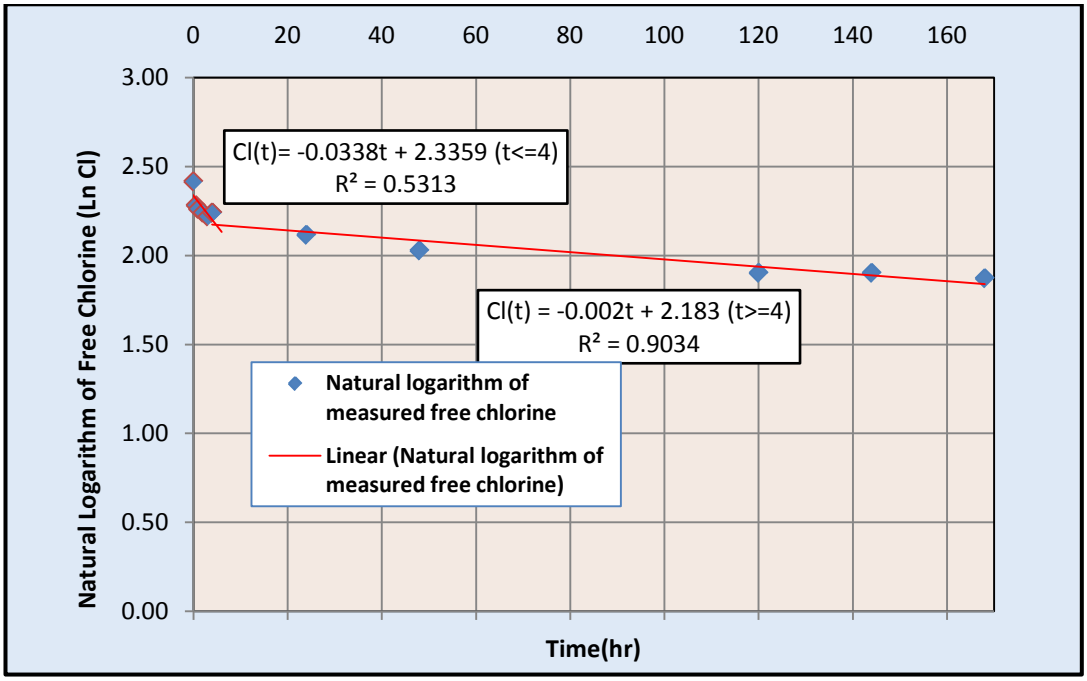

Fig.4.6. : Natural logarithm of free chlorine vs. time for 11.2 mg/l initial dosing for Pilbara Water Treatment Plant samples on 23/08/06

The data of free chlorine readings from all five groups were put into one file to be run in AQUASIM software. For more accuracy, first, parameter estimation for all sets of data was done to have an average value of every parameter within the range of dosing. The results were used afterwards as initial values for every parameter. Table 4.2 shows the parameter estimation when all data sets of different initial dosing is fitted together with one set of parameters (FRA_0, k_{FRA}, SRA_0, k_{SRA}). Figure 4.7 demonstrates the goodness of fit using the above-mentioned parameter estimation.

Table.4.2 : Parameter estimation of data sets of different initial dosing with one set of parameters

Parameter	unit	value
FRA_ini	mg/l	1.4539
SRA_ini	mg/l	3.0640
k_FRA	mg-1lt-1	0.5169
k_SRA	mg-1lt-1	0.0037
Chi^2	---	1.1449
No. of Data Points	---	55

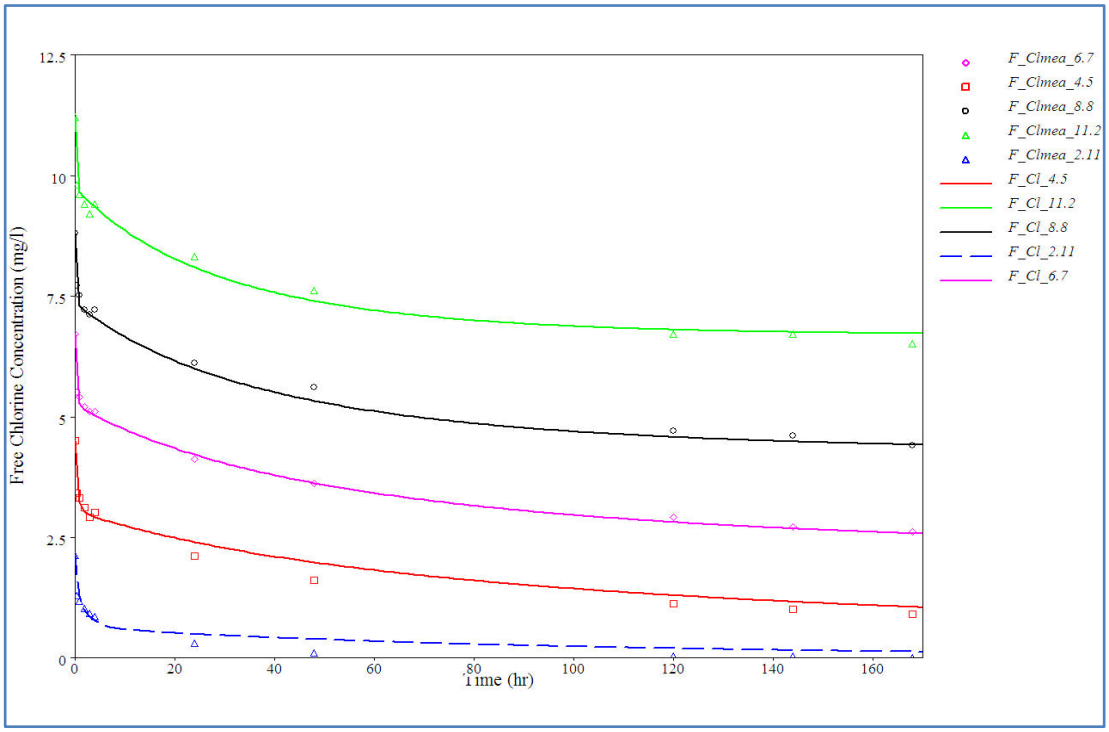

Fig.4.7. : Goodness of data fitting for different initial dosing with one set of parameters for Pilbara Water Treatment Plant samples on 23/08/06

After getting an average estimation for the parameters involved, in another trial, they were used as initial values for parameter estimation of each data set, with particular chlorine dosing, separately. For this purpose, another AQUASIM file, using the same measured data set, was set up. Four program parameters (FRA_0, k_{FRA}, SRA_0 and k_{SRA}), with different indexes, were defined for each data set, related to each chlorine dosing. Then, parameter estimation was conducted for each group of measured data with particular initial chlorine concentration. Table 4.3 shows the parameter estimation with the parallel second order model via AQUASIM software for different chlorine dosing of one water sample taken from Pilbara water treatment plant on 23/08/06. Figure 4.8 illustrates the data fitting of the corresponding data via AQUASIM.

Table.4.3 : The parameter estimation with the parallel second order model (numerical solution) via AQUASIM software for different dosing of one sample taken from Pilbara water treatment plant on 23/08/06

Initial Dosing (mg/L)		**2.11 (mg/L)**	**4.5 (mg/L)**	**6.7 (mg/l)**	**8.8 (mg/L)**	**11.2 (mg/L)**
Parameter		**Estimated parameters with the parallel second order model (Numerical solution)**				
FRA_0	**mg/L**	**0.8394**	**1.2559**	**1.3443**	**1.4425**	**1.6494**
SRA_0	**mg/L**	**1.6139**	**2.5529**	**2.9288**	**3.1498**	**3.1900**
k_{FRA}	**$mg^{-1}Lt^{-1}$**	**2.7566**	**0.8673**	**0.6214**	**0.3024**	**0.3237**
k_{SRA}	**$mg^{-1}Lt^{-1}$**	**0.0689**	**0.0096**	**0.0046**	**0.0029**	**0.0023**
Chi^2	**---**	**0.0019**	**0.0274**	**0.0232**	**0.0416**	**0.0486**
No. of Data Points	**---**	**11**	**11**	**11**	**11**	**11**

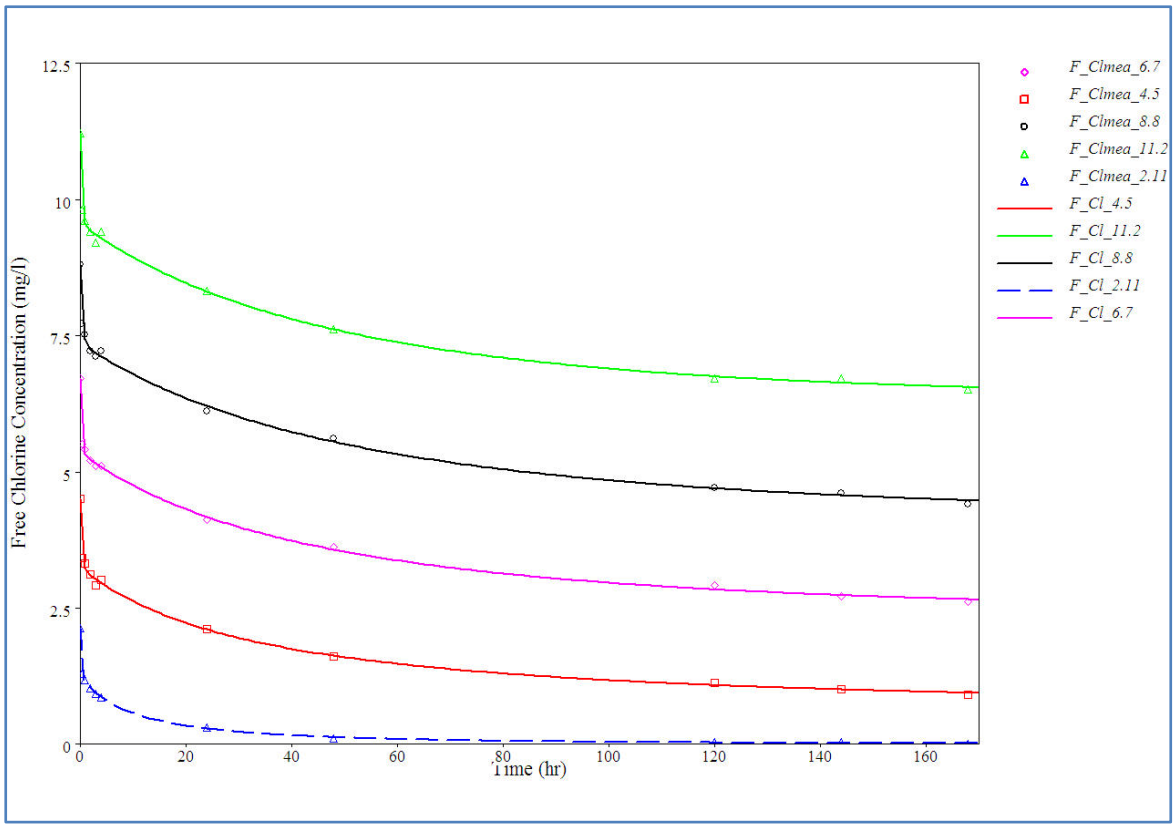

Fig.4.8. : Goodness of data fitting for different initial dosing with different set of parameters; Parallel second order model (numerical solution) with AQUASIM software

As can be seen from the figure 4.8, the parallel second order model represents an accurate prediction of chlorine residual for the selected data. The only problem, which might be noticed from the parameter estimation conducted with this model, is that the estimated parameters are not independent of chlorine dosing. However, part of this inconsistency could be because of the shortage of chlorine concentration in terms of its initial dosing against other reactants' concentrations (FRA and SRA), which contributes to not having a comprehensive observation of the whole involvement of the reactants. Another reason could be the conversion of some parts of SRA to FRA when initial chlorine concentration is increasing. Additionally, as there is no actual limit or boundary for the separation of SRA from FRA or for the definition of k_{FRA} and k_{SRA}, during the parameter estimation, the values would be assigned for these parameters to obtain the best fitting, regardless of their definition. Therefore, it is recommended that the behaviour of the parameters in parallel second order model be more evaluated. However, as performed in the first trial, using one set of parameters for all data sets with different initial dosing could remove the problem while still the accuracy of data fitting is reasonable according to figure 4.7.

4.2. Summary and Conclusion

In this chapter, analysing the existing data obtained from chlorine decay tests of Pilbara Water Treatment samples, it was proved that first order model could not predict chlorine residual properly. It was also shown that the considered assumption for pseudo-first-order was not fundamentally valid. In addition, using the parallel second order model for the same data sets, a very good data fitting for the prediction of chlorine decay in bulk water with this model was presented. Further, it was concluded that using one set of parameters, when having data sets with different initial dosing of one sample, is more appropriate to avoid inconsistency for parameter estimation. However, it was recommended that the behaviour of the parameters in parallel second order model be more evaluated.

5. Development of an analytical solution

5.1. Background

Reviewing the most cited chlorine modelling related publications, Fisher et al. (2010a) concluded that the parallel second order model appropriately summarizes and expresses the effect of different parallel reacting agents, which are simultaneously decaying during their reaction with chlorine. Though the number of parameters in this model is more than that in the first order model or second order model with single reaction scheme, it should be realized that the model is much closer to the nature of reaction schemes (Fisher et al., 2010a; Kastl et al., 1999; Jonkergouw et al., 2009). Moreover, it has been shown that the model has more potential to accurately predict the chlorine decay behaviour in different waters of interest and in variety of planning and management applications (Fisher et al., 2010a; Kastl et al., 1999). Another advantage is that it can be used to understand the performance of treatment process in terms of its effect on chlorine decay (Fisher et al., 2004).

One disadvantage of this model is that there has not been found any analytical or explicit solution for the model so far. Though, without having an analytical solution and by using numerical methods and computer programs, parameter estimation is not impossible, it is clear that having an explicit formulation is still much preferable due to a number of reasons:

- It makes practical to use different, simple and popular computer programs such as spreadsheets and removes the need to acquire and learn specialist and complex software packages for parameter estimation.
- It avoids time-consuming calculations for the parameter estimation due to numerical methods.
- It facilitates manual tuning of the parameters for sensitivity analysis or investigating the methods for the situational effects of any parameter manipulation.
- It enables the operational utilities to have an alternative method in order to evaluate the correctness and accuracy of numerical approaches.

As parallel second order two-reactant model can be easily employed in EPANET-MSX software for network modelling purposes, it makes sense to have an analytical solution that provides a simple approach to parameter estimation.

As mentioned earlier, one of the objectives of the current research is to recognize and remove the potential weaknesses of the parallel second order two-reactant model in terms of utilizing it as a practical method to predict the chlorine residuals in bulk waters. In particular, this chapter is aimed to propose an analytical solution for the discussed model.

Initially, an analytical solution will be proposed for the parallel second order model for chlorine decay prediction in bulk water. The proposed solution will be proved mathematically afterwards by setting some assumptions. Finally, the effectiveness of the discussed analytical solution will be evaluated against the existing numerical method for different sets of data from literature as well as experimental works.

5.2. Analytical Solution Development

It seems reasonable to claim that any modelling development should be headed in the direction of either making an existing model simpler or more accurate or preferably both of them. In this regard, proposing an analytical solution will definitely make the modelling method much simpler to use and to conceptually understand.

An analytical solution for the modelling approach is developed based on the current definition of involving factors (FRAs and SRAs). In this definition, FRAs are the ones whose reaction with chlorine is much faster than that of SRAs. According to this definition and if it is assumed that there is enough chlorine to inactivate all FRAs, it can be said that FRAs are depleted much earlier than the time at which chlorine concentration is zero or be stabilized.

The chlorine reactions with FRA and SRA could be represented by following reactions:

$$\mathrm{CL} + \mathrm{FRA} \xrightarrow{k_{FRA}} \mathrm{P}_1 \tag{5.1}$$

$$\mathrm{CL} + \mathrm{SRA} \xrightarrow{k_{SRA}} \mathrm{P}_2 \tag{5.2}$$

In these reactions, Cl is chlorine concentration; CFRA and CSRA are the concentrations of FRA and SRA respectively. k_{FRA} and k_{SRA} are the rate constants of the reactions. Following Clark's formulation (1998) and according to second order kinetics for both above reactions:

$$\frac{dC_{FRA}}{dt} = -k_{FRA} * C_{CL} * C_{FRA} \quad (5.3)$$

$$\frac{dC_{SRA}}{dt} = -k_{SRA} * C_{CL} * C_{SRA} \quad (5.4)$$

$$\frac{dC_{CL}}{dt} = \frac{dC_{FRA}}{dt} + \frac{dC_{SRA}}{dt} = -k_{FRA} * C_{CL} * C_{FRA} - k_{SRA} * C_{CL} * C_{SRA} \quad (5.5)$$

According to mass balance at time t, the amount of material subtracted from FRA and SRA is equal to that of Cl. So if it is assumed that at time t:

$$C_{Cl} = C_{Cl_0} - x - y \rightarrow \frac{dC_{Cl}}{dt} = -\frac{dx}{dt} - \frac{dy}{dt} \quad (5.6)$$

$$C_{FRA} = C_{FRA_0} - x \rightarrow \frac{dC_{FRA}}{dt} = -\frac{dx}{dt} \quad (5.7)$$

$$C_{SRA} = C_{SRA_0} - y \rightarrow \frac{dC_{SRA}}{dt} = -\frac{dy}{dt} \quad (5.8)$$

where x and y are the chlorine demand at time t by FRA and SRA respectively.

Setting $C_{Cl_0} = a$, $C_{FRA_0} = b$ and $C_{SRA_0} = c$ then (5.3) and (5.4) yield:

$$\frac{dx}{dt} = k_{FRA} * (a - x - y) * (b - x) \quad (5.9)$$

$$\frac{dy}{dt} = k_{SRA} * (a - x - y) * (c - y) \quad (5.10)$$

Before deriving the analytical formulation, in order to fully understand the concept of the model and the mathematical method for deriving its analytical solution, paying attention to the definition of the terms FRA and SRA is very important. In this regard, implying three points is much favourable:

- Though FRA and SRA have been defined as concentration of the notional agents reacting with chlorine, it should be noticed that in this definition, the concentrations of the reactants and stoichiometry of the reactions have been

mixed together. Therefore, the amount of FRA and SRA values would not be the same as fast and slow reacting agents' concentrations.

- No matter what FRA and SRA are, the importance of this definition is that FRA are the parts of fictional agents whose reaction rate with chlorine is much faster than that of SRA. According to this, they could be even different parts of one pure compound reacting with chlorine (Chang et al., 2006) and they are different in terms of their reaction rate constants. As can be seen from the literature, k_{FRA} has been reported much bigger than k_{SRA}. Chang et al. (2006) reported the values between 0.319 and 1.225 for k_{FRA} of the reactions between four pure compounds and chlorine, while the values for k_{SRA} in this research have been reported from 0.006 to 0.028. Similarly, Kastl et al. (1999) reported k_{SRA} as 0.0288 and k_{FRA} as 2.66 h^{-1} mg/L^{-1}. Table 5.1 shows some of the reported values for k_{FRA} and k_{SRA} in the literature. According to the literature, the average ratio of fast and slow reaction rate coefficients ($\alpha=k_{SRA}/k_{FRA}$) is found to be around 0.01. However, the author has found the values between 0.001 and 0.02 for α depending on the quality of the water samples and the chlorine dosing.

Table.5.1 : Some of the Reported Values for k_{FRA} and k_{SRA} in the Literature

Author	year	Reported k_{FRA}	Reported k_{SRA}	$\alpha=k_{SRA}/k_{FRA}$
Chang et al. (*2006*)	2006	0.319-5.051 ($mg^{-1}h^{-1}$)	0.006-0.028 h^{-1}	0.006-0.023
Kastl et al. (*1999*)	1999	2.66 $h^{-1}x$ $(mg/L)^{-1}$	0.0288 $h^{-1}x$ $(mg/L)^{-1}$	0.011
Qualls and Johnson (*1983*)	1983	$6.3x10^{-3}$ $M^{-1}s^{-1}$	$4.2x10^{-5}$ $M^{-1}s^{-1}$	0.007

- Relating the definition of k_{FRA} and k_{SRA} to the reaction time, it is manifested that FRA should be depleted within the short initial time and from then on, it does not have as much significant influence as SRA does on the reaction process.

At time 0 (t=0), x=y=0 and when $t \to \infty$, depending on the amount of the substances, different situations might be considered but for simplicity the following condition is assumed:

$$C_{FRA\,0} < C_{Cl\,0} < C_{SRA\,0} \xrightarrow{t\to\infty} x = C_{FRA\,0}, y = C_{SRA\,0} - C_{Cl\,0}$$

or:

$$b < a < c \xrightarrow{t\to\infty} x = b, y = c - a$$

While if the initial condition is supposed as:

$$C_{FRA\,0} < C_{SRA\,0} < C_{Cl\,0} \xrightarrow{t\to\infty} x = C_{FRA\,0}, y = C_{SRA\,0}$$

or:

$$b < c < a \xrightarrow{t\to\infty} x = b, y = c$$

For solving equations (5.9) and (5.10), it is better to eliminate sections dt and (a-x-y) by dividing (5.9) by (5.10):

$$\frac{(5.9)}{(5.10)} \rightarrow \frac{dx}{dy} = \frac{k_{FRA} * (a - x - y) * (b - x)}{k_{SRA} * (a - x - y) * (c - y)} = \frac{k_{FRA} * (b - x)}{k_{SRA} * (c - y)} \tag{5.11}$$

$$\frac{dx}{k_{FRA} * (b - x)} = \frac{dy}{k_{SRA} * (c - y)} \tag{5.12}$$

integrating (4.12) yields:

$$-\frac{1}{k_{FRA}} * \ln(b - x) + C = -\frac{1}{k_{SRA}} * \ln(c - y) \tag{5.13}$$

knowing that when x=0 and y=0, it yields:

$$-\frac{1}{k_{FRA}} * \ln(b) + C = -\frac{1}{k_{SRA}} * \ln(c) \tag{5.14}$$

$$C = \frac{1}{k_{FRA}} * \ln(b) - \frac{1}{k_{SRA}} * \ln(c) = \ln\frac{b^{1/k_{FRA}}}{c^{1/k_{SRA}}} \tag{5.15}$$

$$-\frac{1}{k_{FRA}} * \ln(b - x) + \ln\frac{b^{1/k_{FRA}}}{c^{1/k_{SRA}}} = -\frac{1}{k_{SRA}} * \ln(c - y) \tag{5.16}$$

$$(b - x)^{\frac{-1}{k_{FRA}}} * \frac{b^{1/k_{FRA}}}{c^{1/k_{SRA}}} = (c - y)^{\frac{-1}{k_{SRA}}} \tag{5.17}$$

$$(c - y) = c * \left(\frac{b - x}{b}\right)^{\frac{k_{SRA}}{k_{FRA}}} \tag{5.18}$$

$$y = c * (1 - \left(\frac{b - x}{b}\right)^{\frac{k_{SRA}}{k_{FRA}}}) \tag{5.19}$$

Or similarly it can be written as:

$$x = b * (1 - \left(\frac{c - y}{c}\right)^{\frac{k_{FRA}}{k_{SRA}}}) \tag{5.20}$$

By substituting y from (4.19) in equation (4.09) produces:

$$\frac{dx}{dt} = k_{FRA} * \left(a - x - c * (1 - \left(\frac{b - x}{b}\right)^{\frac{k_{SRA}}{k_{FRA}}}) \right) * (b - x) \tag{5.21}$$

$$\frac{dx}{\left(a - x - c * (1 - \left(\frac{b - x}{b}\right)^{\frac{k_{SRA}}{k_{FRA}}}) \right) * (b - x)} = k_{FRA} * dt \tag{5.22}$$

Unfortunately there is no explicit integration for the left side of above equation. But considering the definitions of FRA and SRA which indicate $k_{SRA} \ll k_{FRA}$ and examining equation (5.19), the role of slow reacting agents during the short initial time, in which fast reacting agents are being depleted, could be ignored. The reason is that, by definition, $\frac{k_{SRA}}{k_{FRA}} \approx 0$ and during the initial time of reaction, when $t \to 0$, $x \to 0$ then from (5.19) it yields $y \to\to 0$. Figures 5.1 and 5.2 clearly illustrate an example of the specific functional behavior of equations 5.19 and 5.20 for a set of sample parameters.

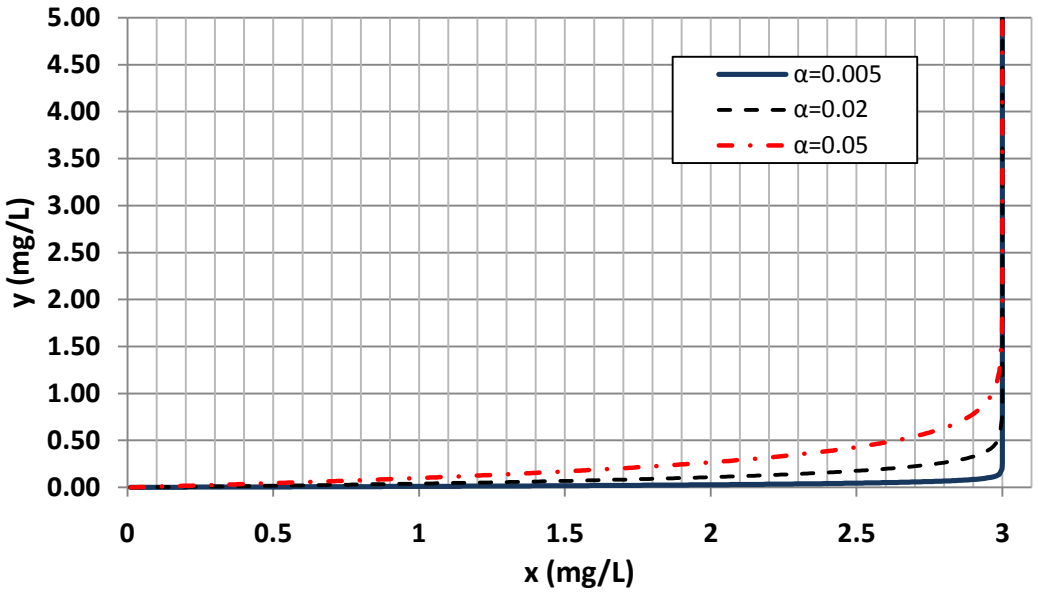

Fig.5.1. : Illustration of the functional behaviour of equation 29 (y as a function of x) for the sample parameters; b=3 (mg/L), c=5 (mg/L), α=0.005, 0.02, 0.05

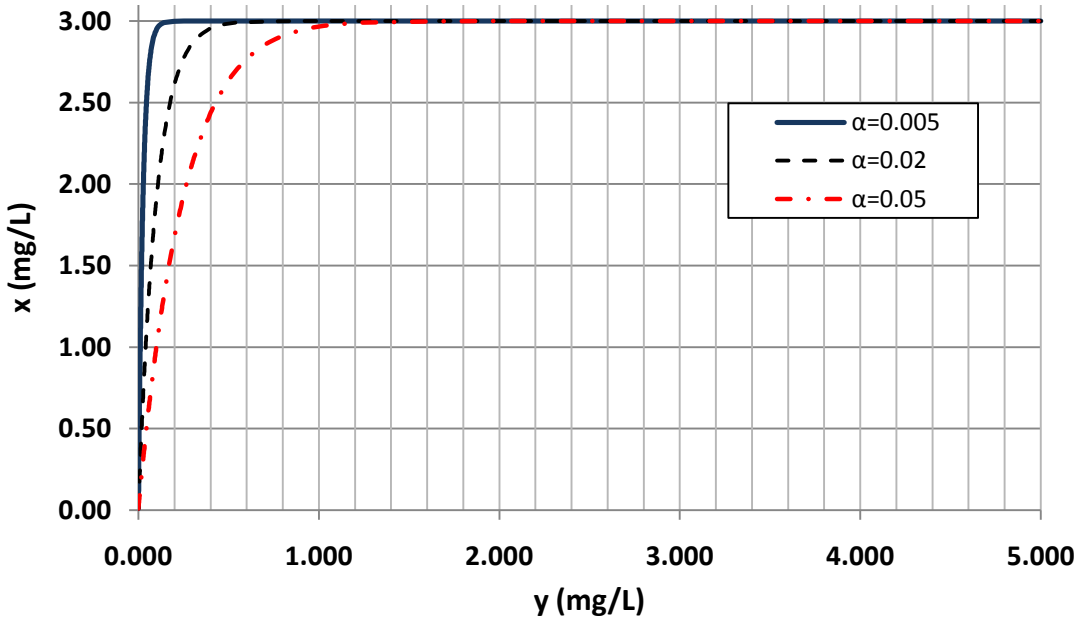

Fig.5.2. : Illustration of the functional behaviour of equation 30 (x as a function of y) for the sample parameters; b=3 (mg/L), c=5 (mg/L), α=0.005, 0.02, 0.05

The important point here is that because of significant difference between the reaction rates of fast and slow reacting agents, the rate at which y is getting far from zero is much less than that of x. In other words, during the initial period of time (when $t \to 0$), due to the specific functional attitude of the equation (5.19), y is much closer to zero than x.

Therefore, equation (5.22) can be reduced to (5.23):

$$\frac{dx}{(a-x)*(b-x)} = k_{FRA} * dt \qquad (4.23)$$

Using the Clark's equation (1998) for equation (5.23), which is same as equation (5.9), x could be calculated as follows:

$$0 < x = \frac{a*b(1-e^{-(a-b)k_{FRA}\,t})}{a-b*e^{-(a-b)k_{FRA}\,t}} < b \qquad (5.24)$$

Similarly, considering equation (5.20), during the initial period of time (when $t \to 0$), noticing that $(\frac{k_{FRA}}{k_{SRA}} \gg 1) \to \infty$ and $0 \ll \frac{c-y}{c} < 1$, it reveals that $x \to b$. Therefore, it means that during the short initial period of reaction time the amount of x value is growing from 0 and in a short time (compared to the whole reaction time) it is getting very close to b, which is the upper limit of this value for the whole reaction time.

Now considering this phenomenon, which is instantaneous jumping of x value from 0 to b, if the effect of x variation on y during the short initial period of time can be ignored, then applying Clark's equation for equation (5.10), it yields:

$$y = \frac{(a-b)*c(1-e^{-(a-b-c)k_{SRA}\,t})}{a-b-c*e^{-(a-b-c)k_{SRA}\,t}} \qquad (5.25)$$

Therefore using equation (4.6) it yields:

$$C_{Cl}(t) = a - \frac{a*b\left(1-e^{-(a-b)k_{FRA}\,t}\right)}{a-b*e^{-(a-b)k_{FRA}\,t}} - \frac{(a-b)*c\left(1-e^{-(a-b-c)k_{SRA}\,t}\right)}{a-b-c*e^{-(a-b-c)k_{SRA}\,t}} \qquad (5.26)$$

Though equation (5.26) is not the exact answer to the problem, keeping in mind the conditions of the reactions and the definition of the terms (FRA and SRA), it seems to be an appropriate approximation of the explicit formulation.

The important point of this formulation is its boundary conditions, which in most of the cases are valid. For instance, to remove the second reaction from the reaction

schemes it is enough to either set c or k_{SRA} to zero. For the first reaction to be eliminated however, only b should be set to zero in order to get the same answer as normal Clark's equation (1998) for one reacting agent. Similarly, at time zero and when $t \to \infty$ the answer is still valid.

In another attempt, a different formulation, which is similar to the last one, could be derived. According to equation (5.24) and considering the explanation and assumption provided before, x is reaching its maximum value in a short initial time. As a result, ignoring the effect of x variation during this initial period, the whole part of $C_{Cl_{FRA}}(t) = a - x$ could be assumed to be constant after the initial period of reaction time. Therefore, according to Clark's formulation (1998) from equations (5.9) and (5.10), the following formulas could be derived:

$$C_{Cl_{FRA}}(t) = \frac{a - b}{1 - \frac{b}{a} e^{-(a-b)k_{FRA}\, t}} \tag{5.27}$$

$$C_{Cl}(t) = \frac{C_{Cl_{FRA}}(t) - c}{1 - \frac{c}{C_{Cl_{FRA}}(t)} e^{-\left(C_{Cl_{FRA}}(t) - c\right)k_{SRA}\, t}} \tag{5.28}$$

It can be seen that for the above formulations, every boundary condition is valid. Basically, what equation (5.27) shows is that because of the nature of FRA, they react fast with chlorine within a short time in which the effect of SRA could be neglected. Then it can be said during the initial time $C_{Cl_{FRA}}(t)$ plays the role of initial chlorine concentration for the equation (5.28). After passing the initial time, FRA are completely depleted and $C_{Cl_{FRA}}(t) \to (a - b)$ so the result of this solution and the previous one, equation (5.26), will be the same.

In a similar way of interpretation for the obtained formulation, by assigning a limit of accuracy, the concentration of FRA, its reacting chlorine concentration and the time of their depletion (t_0) could be calculated by equation (5.27). Then if any chlorine remained after t_0, by applying the Clark's formulation for the remaining chlorine and SRA as the only remaining agent, the rest of chlorine demand could be obtained.

5.3. Verification of the Proposed Analytical Solution

In this section, the proposed analytical formulation for the parallel second order model will be evaluated against the existing numerical solution. To evaluate the accuracy of the developed analytical solution in parameter estimation for different series of chlorine decay data sets, the results of parameter estimation from numerical methods were compared with the ones obtained from the analytical formulation. For this purpose, six set of chlorine decay data were used. Four independent sets of chlorine decay data were obtained from the literature and the other two from the laboratory experiments conducted in Curtin University of Technology. Table 5.2 shows the water quality characteristics of the samples chosen from the literature and the ones used in authors' experiments.

Table.5.2 : Water Quality Characteristics of the Samples

Data source	Sample label	Description	water quality characteristics			
			DOC (mgL^{-1})	UV_{254}	pH	Alkalinity (mgL^{-1})
Literature data no1	A.B.W257	Warton et al. (2006)	1.8	0.058	7.97	95
Literature data no2	LWR	Gang et al. (2003)	9.89	0.1574	---	---
Literature data no3	GWT	Gang et al. (2003)	2.8	0.0284	---	---
Literature data no4	CWT	Gang et al. (2003)	3.09	0.0518	---	---
Experimental data no1	PRW1	Pilbara Raw Water	3.27	---	---	---
Experimental data no2	PPFW1	Pilbara Post Filtration Water	1.96	---	---	---

The literature data is extracted from two research works performed by Warton et al. (2006) and Gang et al. (2003). In the first one, conducted by Warton et al. (2006), a sample of groundwater taken from an artesian aquifer near Wanneroo groundwater treatment plant (GWTP), Perth, Western Australia, was reported to be dosed with chlorine at concentrations of 4, 6, 8 and 10mgL-1 and residual chlorine concentrations were said to be measured periodically over a period of 168 hours. Among all data sets from their work, the one related to 8 mgL-1 chlorine dosing was chosen. In the second research work, performed by Gang et al. (2003), different samples from surface water of the rural Missouri agricultural watersheds (Garden

city, Maysville and Lake Vandalia) and Mississippi River were reported to be dosed by different concentration of chlorine. A 120-hour chlorine demand preliminary study was said to be performed using a series of chlorine dosages based on Cl_2:DOC ratios. Among the data sets of this research work, three of them were selected for the analysis. The data of residual free chlorine concentrations was accurately extracted from the provided figures in these two publications using the graphical methods.

The data obtained from the chlorine decay tests for two water samples, which were taken from Pilbara Water Treatment Plant influent, labelled as "Pilbara Raw Water1 (PRW1)" and "Pilbara Post Filtration Water1 (PPFW1)", were used as experimental data sets.

The data of free chlorine readings from all four groups of chlorine dosing were put into one file to be run in AQUASIM software. In this AQUASIM file, four program parameters (C_{FRA0}, C_{SRA0}, k_{FRA} and k_{SRA}) were defined for each data set related to each chlorine dosing. AQUASIM contains a dynamic equation solver, which is capable of performing parameter estimation to find the best fit of the model output to the experimental data. Parameter estimation was conducted for each group of measured data with particular initial chlorine concentration. The weighted error between experimental and model data (χ^2) can be used as a measure of goodness of fit between experimental and predicted data and can be defined as follows:

$$\chi^2(p) = \sum_{i=1}^{n} \left(\frac{f_{meas,i} - f_i(p)}{\sigma_{meas,i}}\right)^2 \qquad (5.29)$$

where $f_{meas,i}$ is the ith measured value, $f_i(p)$ is the calculated value from the model using parameter values p and $\sigma_{meas,i}$ is the estimated standard deviation of $f_{meas,i}$. During the fitting of the model to the experimental data, the initial concentrations of fast and slow reacting agents (FRA and SRA) along with the reaction rates (k_{FRA} and k_{SRA}) were adjusted by AQUASIM software until χ^2 reaches a minimum value.

To evaluate the proposed analytical solution, using a useful MATLAB application for data fitting, called "cftool", all literature data of free chlorine residuals were stored and categorized into four data groups according to their initial chlorine concentrations. Each group was given an individual fitting name and was allocated an equation as their fitting formula, which was sourced from the new analytical solution (equations 5.25 & 5.26). The fitting formula for each group was produced

according to their initial chlorine concentrations (Cl_0). Appointing the initial values and the boundaries of each parameter (from 0 to infinity), parameter estimation was performed for each data set.

In a similar way of analysis, the data of both samples from Pilbara Water Treatment Plant were inserted into AQUASIM with different sets of parameters to be estimated. Then new explicit formulation was applied to both data sets and parameters were estimated using MATLAB program.

The results of parameter estimation with new explicit formulation for all data sets, conducted by MATLAB program, afterwards, were compared to the ones obtained by parameter estimation using numerical method, performed by AQUASIM software.

Table 5.3 compares the parameter estimation performed by the analytical solution using MATLAB program with numerical method conducted by AQUASIM software for the selected literature and experimental data. Figures 5.3 and 5.4 illustrate the goodness of data fitting for the data from literature as well as experimental data using MATLAB program.

Table.5.3 : Comparison of Parameter Estimations between Two Methods for Literature and Experimental Data; Parallel Second Order Model with AQUASIM Software against New Analytical Solution with MATLAB Program

Data source	Sample label	Initial Dosing (mg/l)	Method	Software	Parameters and results							
					FRA_0	SRA_0	k_{FRA}	k_{SRA}	R^{2*}	SSE^{*}	Chi^{2*}	No. of Data Points
					Unit							
					mg/L	mg/L	$mg^{-1}Lt^{-1}$	$mg^{-1}Lt^{-1}$	---	---	---	---
Literature data no1	A.B.W257	8.00	Numerical solution with parallel second order model	AQUASIM	2.33	2.16	1.907	0.003	---	---	0.095	20
			new analytical solution	MATLAB	2.33	2.16	1.905	0.003	0.995	0.096	---	20
Literature data no2	LWR	12.20	Numerical solution with parallel second order model	AQUASIM	2.68	9.99	0.32	0.004	---	---	0.14	11
			new analytical solution	MATLAB	2.7	9.95	0.316	0.004	0.999	0.141	---	11
Literature data no3	GWT	4.03	Numerical solution with parallel second order model	AQUASIM	1.22	2.89	0.535	0.007	---	---	0.034	11
			new analytical solution	MATLAB	1.23	2.88	0.524	0.007	0.997	0.035	---	11
Literature data no4	CWT	3.62	Numerical solution with parallel second order model	AQUASIM	1.3	3.16	0.557	0.009	---	---	0.021	11
			new analytical solution	MATLAB	1.32	3.12	0.545	0.009	0.998	0.022	---	11
Experimental data no1	PRW1	3.00	Numerical solution with parallel second order model	AQUASIM	1.18	1.84	2.466	0.035	---	---	0.063	15
			new analytical solution	MATLAB	1.19	1.83	2.427	0.035	0.992	0.064	---	15
Experimental data no2	PPFW1	3.00	Numerical solution with parallel second order model	AQUASIM	0.67	2.3	4.817	0.004	---	---	0.076	16
			new analytical solution	MATLAB	0.67	2.3	4.81	0.004	0.993	0.076	---	16

* *R^2: R-Square; SSE: Sum Squared Error; Chi^2: Chi-Square*

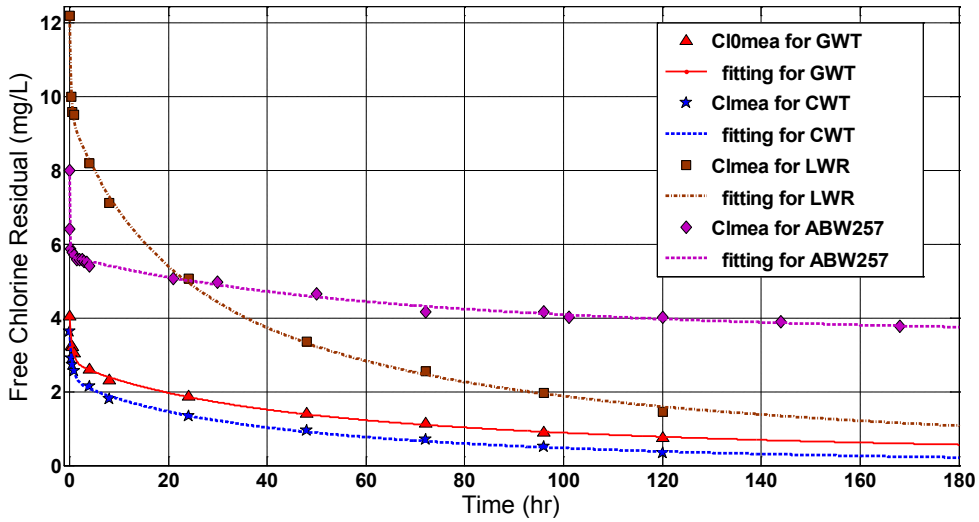

Fig.5.3. : Goodness of data fitting for different initial dosing with different sets of parameters for literature data; new analytical solution with MATLAB program

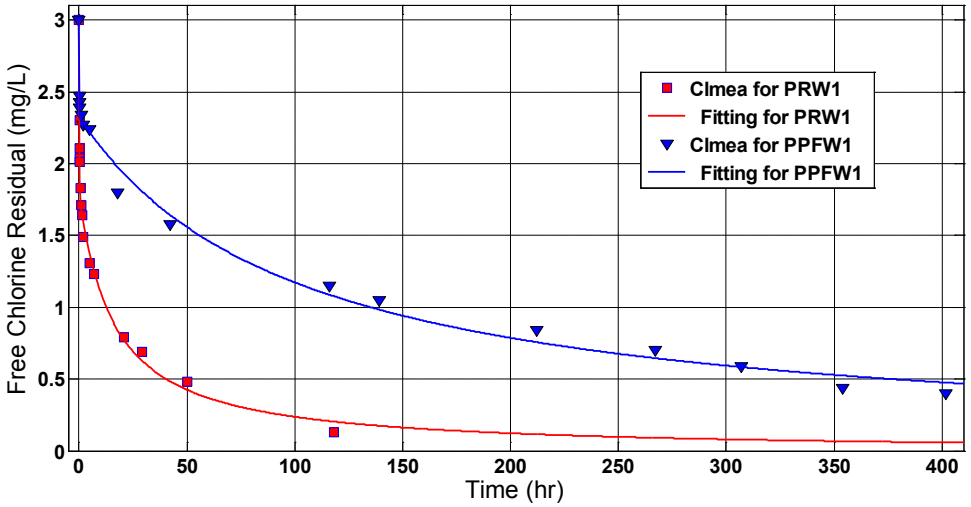

Fig.5.4. : Goodness of data fitting for different initial dosing with different sets of parameters for Pilbara Water Samples; new analytical solution with MATLAB program

As can be seen from Table 5.3, the results of parameter estimation performed with AQUASIM for parallel second order two-reactant model are very close to the ones obtained when the proposed analytical solution is used in MATLAB software. Figure 5.5 compares the predicted chlorine concentrations obtained from numerical method with the ones resulted from new analytical solution for all water samples. The graph expresses an excellent correlation between the values of chlorine residuals predicted by both methods.

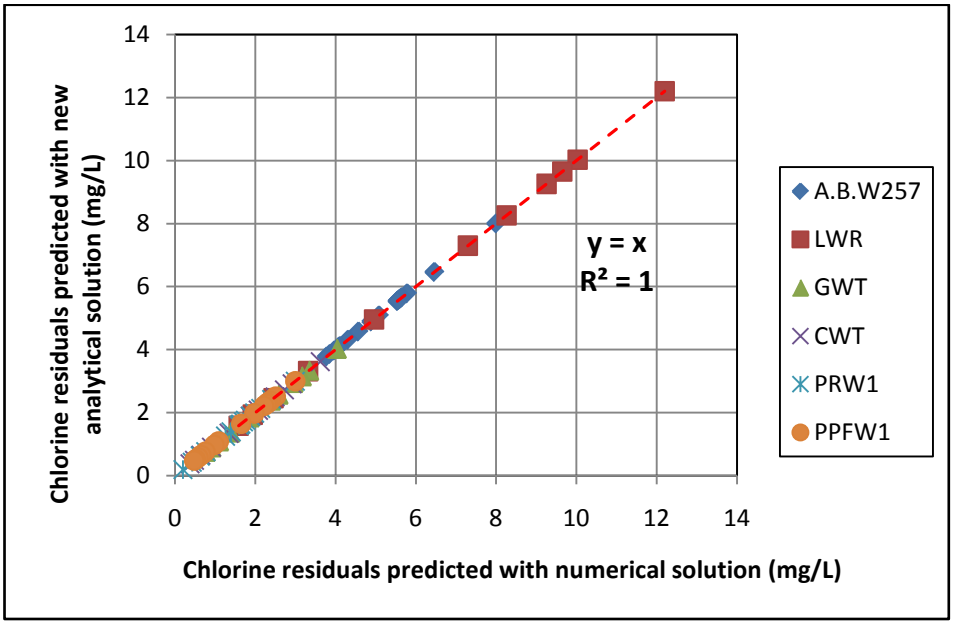

Fig.5.5. : Comparison of chlorine residuals predicted by numerical solution and the ones calculated with new analytical solution

5.4. Assessment of the Effect of α Variation on the Modelling Verification

In order to compare the predicted results of chlorine decay by numerical solution with the ones calculated by presented analytical formulation, a simple programming application in MATLAB software was developed. In this application, initially, after getting the essential parameters such as C_{Cl0}=a, C_{FRA0}=b, C_{SRA0}=c, k_{FRA} and k_{SRA}, chlorine residuals are calculated during the time range between 0 and 200 hours using one of the simplest numerical methods. The method is based on varying the argument (t) from 0 to the end of the considered reaction time (here 200 hours) with very small time steps portions and calculating the corresponding dependent variables (x and y) in equations 5.9 and 5.10. According to the definition of x and y, the initial values of these variables were assigned to be 0 at time 0 ($t = 0 \rightarrow x = 0, y = 0$). The time step (dt) for this purpose is considered to be 0.0075 hour. With this explanation, at time 0 equations 5.9 and 5.10 yield:

$$\text{at } t = 0 \rightarrow \frac{dx}{dt} = k_{FRA} * (a - 0 - 0) * (b - 0) = k_{FRA} * a * b \rightarrow dx$$

$$= k_{FRA} * a * b * dt$$

$$\text{at } t = 0 \rightarrow \frac{dy}{dt} = k_{SRA} * (a - 0 - 0) * (c - 0) = k_{SRA} * a * c \rightarrow dy$$
$$= k_{SRA} * a * c * dt$$

By choosing an appropriate time step (here dt=0.0075 hour), dx and dy will be calculated from above equations. The appropriateness of the selected time step would be verified by changing the time step and comparing the results in a specific time. Then by having dx and dy, the following values of x and y and consequent Cl(t) would be obtained through equation 5.6.

In this method, due to existence of two parallel ordinary differential equations (ODEs), for simplicity, the benefits of using some of the known numerical solutions such as Eulers's method or second or forth order Runge-Kutta methods for numerically solving the equations 5.9 and 5.10 have not been considered.

In the above-mentioned MATLAB software application, an array was allocated to store the results of numerical solution, the ones obtained from analytical solution and their differences at every single time. Then absolute maximum value of the difference column of the mentioned array could be reported as the maximum error between two methods for the individual assigned parameters (C_{Cl0}=a, C_{FRA0}=b, C_{SRA0}=c, k_{FRA} and k_{SRA}). The devised program had also the ability to calculate the first next time step at which the error is smaller than a specific value, e.g. 0.05, after the time at which the maximum error had happened.

Considering the practical range of chlorine dosing and potential values for initial concentration of reacting agents in different waters of interest, the values of 0.5, 1, 2, 5 and 10 for each of the concentration-related parameters of reacting agents (C_{FRA0}=b, C_{SRA0}=c) and the values of 0.5, 1, 2 and 5 for the initial chlorine concentrations (C_{Cl0}=a) were allocated. Similarly, based on the reported values for k_{FRA} and k_{SRA} in the literature, keeping k_{FRA}=1, the values of 0.001, 0.01, 0.1 and 1 for the rate coefficient of the slow reacting agents (k_{SRA}) were considered; making $\alpha=k_{SRA}/k_{FRA}$ ranged between 0.001 and 1. By choosing this broad range for α, the functionality of the analytical formulation can be assessed even when the basic assumption is not met (α=1).

Finally, the previously discussed MATLAB application was run for all considered values of the involved parameters and the absolute maximum error between numerical and analytical solutions were reported.

In the case of having an error more than 0.05, the procedure was repeated by using a smaller time step to ensure that the error was not made by the numerical solution method. If the reported error was still greater than 0.05, the devised program could derive the earliest time at which the maximum error was less than 0.05.

Table 5.4 shows the maximum error between the proposed analytical solution and numerical method for the considered sets of parameters. The table also represents the time at which this maximum error happens.

As can be noticed from this table, when α is small enough such as when it is equal to 0.01 or 0.001, the maximum error is less than 0.05 which is the usual experimental error in chlorine measurement. Further analogous analysis of presented analytical solution against numerical method for a variety of given parameters showed that with every set of individual parameters, there is an unbalanced normal distribution of errors with regard to time, in which maximum error occurrence happens within the short initial time period. Figure 5.6 and 5.7 represent an example illustration of the error function with respect to time for a specific nominated set of parameters.

The maximum absolute error (0.1079), however, is occurring when α is equal to 0.1 which implies a special trend of error occurrence depending on α value. In other words, by increasing α from zero to 0.1 the error tends to increase reaching its maximum at 0.1 and from this point the error seems to be decreasing.

Table.5.4 : Maximum error between the analytical solution and numerical method

C_{Cl0}=a (mg/L)	C_{FRA0}=b (mg/L)	C_{SRA0}=c (mg/L)	k_{FRA} ($mg^{-1}Lt^{-1}$)	k_{SRA} ($mg^{-1}Lt^{-1}$)	α= k_{SRA}/k_{FRA}	Maximum absolute error (mg/L)	Time of Maximum absolute error (hr)
selected value amongst {0.5,1,2,5}	selected value amongst {0.5,1,2,5,10}	selected value amongst {0.5,1,2,5,10}	1	1	1	0.045	0.3045
selected value amongst {0.5,1,2,5}	selected value amongst {0.5,1,2,5,10}	selected value amongst {0.5,1,2,5,10}	1	0.1	0.1	0.1079	1.2543
selected value amongst {0.5,1,2,5}	selected value amongst {0.5,1,2,5,10}	selected value amongst {0.5,1,2,5,10}	1	0.01	0.01	0.0476	3.4125
selected value amongst {0.5,1,2,5}	selected value amongst {0.5,1,2,5,10}	selected value amongst {0.5,1,2,5,10}	1	0.001	0.001	0.0356	0.1275

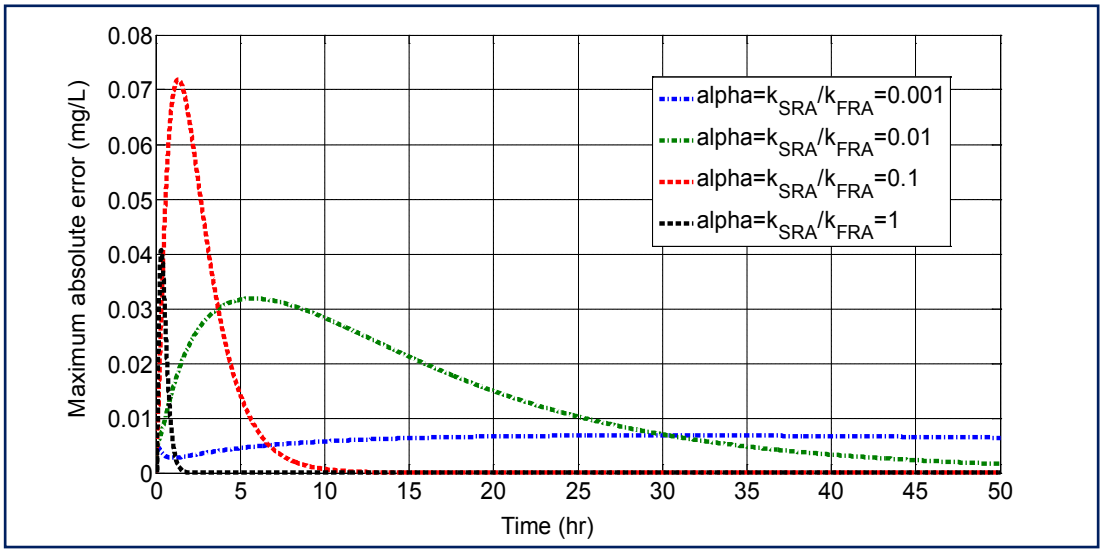

Fig.5.6. : Maximum absolute error vs. time for different α values for the model parameters of Cl0=5, FRA0=5 and SRA0=5

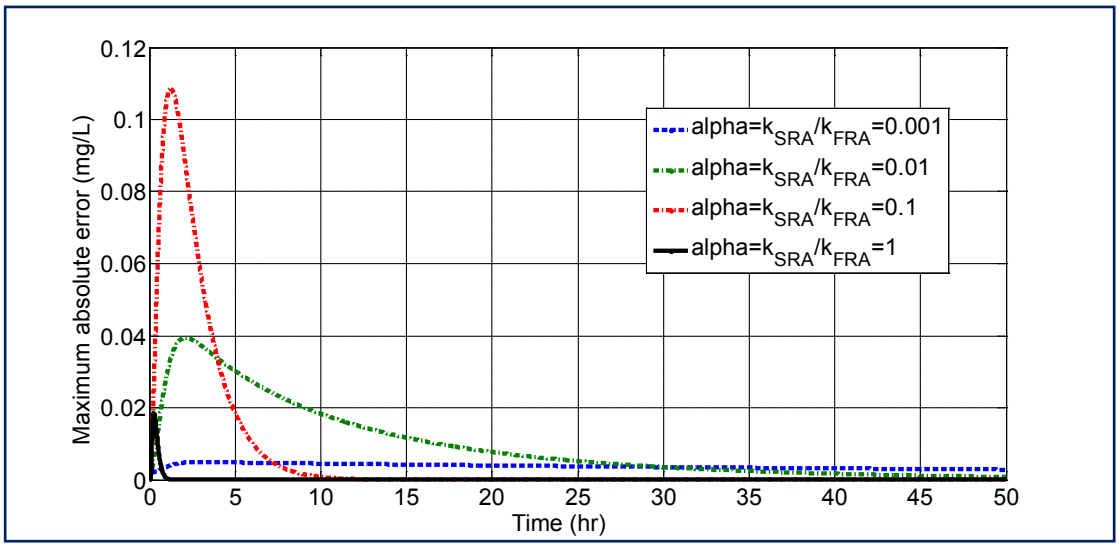

Fig.5.7. : Maximum absolute error vs. time for different α values for the model parameters of Cl0=5, FRA0=2 and SRA0=10

Although performed analysis did not cover all considerable parameter values; which offcourse is not possible; it attempted to visualise the trend of the error function and its probable maximum value within the range of selected values for model parameters. It also shows the time at which the error occurs. With the results of this analysis, it can be concluded that even if the initial assumptions made for mathematically proving the analytical solution is not met, the difference between the results of proposed explicit method and numerical solution is negligible, especially after initial few hours.

5.5. Summary and Conclusion

The aim of this chapter was to develop an analytical solution for the two-reactant parallel second order model as one of the most suitable existing models to predict the chlorine decay in bulk water. Initially, the analytical formulation was mathematically derived from the fundamental reaction schemes by assuming that reaction rate of fast reacting agents are much higher than that of slow reacting ones, which should be true according to the principles of the original model. Comparison between the results of parameter estimation conducted with numerical method and proposed analytical solution for six data sets from independent (the literature) as well as experimental data confirmed that the presented explicit solution presents reliable and accurate results. In addition, the analysis of the results obtained from both methods for different initial conditions showed that the maximum error between two methods is negligible even if the basic assumption ($k_{SRA} \ll k_{FRA}$) is not satisfied. Therefore, it is an appropriate formulation for predicting chlorine decay in bulk water instead of existing numerical solutions, which in most cases are time-consuming and need specialist computer software. As two-reactant parallel second order model could be easily implemented in newly released EPANET-MSX, the easiness of parameter estimation and explicit understanding of effecting parameters provided by the proposed solution would provide an added advantage.

6. Evaluation of the parallel second order kinetics against the first and second order models for the prediction of chlorine residuals in bulk waters

The objective of this chapter is to investigate and to compare the effectiveness of the most popular modelling approaches for the prediction of chlorine decay in the bulk water. For this purpose, initially, performing all necessary laboratory experiments for the nominated water samples, the required chlorine decay data was obtained. Then, considering the most influentially cited criteria for the effectiveness assessment of the chlorine decay models, which are simplicity and accuracy, the efficacy of the three above mentioned modelling methods as the most popular ones was compared against the assigned criteria. However, the focus of this study will be more on the accuracy comparison of three mentioned chlorine decay modelling approaches.

Two other water samples taken from Pilbara Water Treatment Plant, labelled as "Pilbara Raw Water2 (PRW2)" and "Pilbara Post-Filtration Water2 (PPFW2)", were used for the tests. Table 6.1 presents the water quality characteristics of the samples used in authors' experiments.

Table.6.1 : Water Quality Characteristics of the Samples

Sample label	Description	water quality characteristics		
		DOC (mgL^{-1})	UV_{254}	pH
PPFW2	Pilbara Post-Filtration Water2	2.43	0.024	7.78
PRW2	Pilbara Raw Water2	3.87	0.063	8.50

In order to compare the accuracy of parallel second order model with the first and second order modelling methods, the data of free chlorine readings from all laboratory experiments were put into three files to be run in AQUASIM software, each one allocated for one of the methods of modelling. In the first AQUASIM file, which was allocated for the parallel second order model, four program parameters (C_{FRA0}, C_{SRA0}, k_{FRA} and k_{SRA}) and two reaction schemes (fast and slow) were defined for each data set. Similarly, another two AQUASIM files were generated for the first order model (FOM) and the second order modelling method (SOM). Parameter estimation was conducted for each group of measured data and for each modelling methods.

AQUASIM contains a dynamic equation solver, which is capable of performing parameter estimation to find the best fit of the model output to the experimental data (Reichert, 1994).

The fitting procedure, however, is performed based on the numerical solution of all defined reaction schemes.

As mentioned earlier, the weighted error between experimental and model data (χ^2) can be used as a measure of goodness of fit between experimental and predicted data and can be defined as follows:

$$\chi^2(p) = \sum_{i=1}^{n} \left(\frac{f_{meas,i} - f_i(p)}{\sigma_{meas,i}}\right)^2 \quad (6.1)$$

where $f_{meas,i}$ is the ith measured value, $f_i(p)$ is the calculated value from the model using parameter values p and $\sigma_{meas,i}$ is the estimated standard deviation of $f_{meas,i}$.

During the fitting of the model to the experimental data, the initial values of all involving parameters were adjusted by AQUASIM software until χ^2 reaches a minimum value.

Since each selected chlorine decay model has an analytical solution, using MATLAB program, the data fitting performance of the discussed modelling approaches was more rigorously evaluated. With this method of analysis, apart from comparing the results of analytical and numerical solution of each model, more statistical measures such as R-square and SSE (Sum of Squares due to Errors) for the assessment of the correlation between predicted and measured data values were obtained. SSE is a statistical parameter which measures the total deviation of the response values from the fit to the measured data values.

Although considering experimental errors is another method for accuracy assessment of the modelling approaches, since there is not a defined regulation, and further the accuracy of each model is different in different conditions such as in low or high initial chlorine concentration, this method of evaluation for accuracy of the models is not discussed in this chapter. However, conducting a rigorous study to involve the experimental and analysis error for evaluation of chlorine decay models is recommended for the future.

The data of free chlorine residuals from PPFW2 and PRW2 water samples were categorized into different data groups according to their sample names and the methods they were supposed to be analysed with. Each group was given an individual fitting name and was allocated an equation as their fitting formula which was sourced from the analytical solution. The fitting formula for each data set was produced according to its initial chlorine concentration (Cl_0). Appointing the initial values and the boundaries of each parameter (from 0 to infinity), parameter estimation was performed for each data set.

The results of parameter estimation for both data sets from Pilbara Water Treatment Plant (PPFW2 and PRW2) with three most popular chlorine decay models are presented in Tables 6.2, 6.3 and 6.4. Figures 6.1, 6.2 and 6.3 show the goodness of data fitting for the collected

Pilbara water samples analysed with the first order model (FOM), the second order model (SOM) and the parallel second order model (PSOM), respectively.

As can be seen from Figure 6.1, the first order model does not properly express the chlorine decay profile. This would be noticed from the fitting parameters in Table 6.2 as well. According to Table 6.2, the only FOM parameter to be estimated is k (the rate constant), which was found to be $0.088t^{-1}$ for PPFW2 and $0.105t^{-1}$ for PRW2.

According to Table 6.3 and Figure 6.2, the second order model (SOM) represents a much better description of the chlorine decay than FOM in both water samples. SOM contains two parameters to be estimated (the rate constant, k, and the initial concentration of the total reacting agents, RA_0), which gives more freedom degree in chlorine decay prediction compared to FOM. The rate constants obtained from SOM (0.058 $mg^{-1}t^{-1}$ for PPFW2 and 0.036 $mg^{-1}t^{-1}$ for PRW2) are less than those calculated by FOM. However, the difference of the rate constants between these two methods in higher chlorine dosing (for PRW2 sample with 8.4 mg/L chlorine dosing) is less.

Table 6.4 shows the model and fitting parameters estimated by PSOM for both water samples taken from Pilbara Water Treatment Plant (PPFW2 and PRW2). As indicated from Table 6.4, PSOM separates the decay profile into two parts, one with a much higher decay rate than the other ($k_{FRA,PPFW2}$=2.82, $k_{SRA,PPFW2}$=0.014 and $k_{FRA,PRW2}$=1.35, $k_{SRA,PRW2}$=0.007). Moreover, Figure 6.3 illustrates a very good data fitting for the prediction of chlorine decay of both data sets (PPFW2 and PRW2) with the parallel second order model.

Comparing the fitting parameters of three mentioned methods, i.e. Chi^2 (Chi square) and R^2 (R-square), it is clear that PSOM perfectly meets the accuracy criteria compared to FOM and SOM methods. Table 6.5 summarises the comparison of the fitting parameters between these three methods of chlorine decay modelling. As indicated from this table, the R-square parameter for the modelling of PPFW2 sample starts from 0.743 with FOM, increases to 0.867 with SOM modelling approach and gets its highest value of 0.989 using the parallel second order model. However, the improvement of fitting parameters with the change of modelling methods for PRW2 sample with higher initial concentration of chlorine is significantly better than that of PPFW2.

Table.6.2 : The Results of Parameter Estimation for the Experimental Data with First Order Model performed by Numerical Solution (via AQUASIM) and Analytical Solution (via MATLAB)

Sample label	Initial Dosing (mg/L)	Method	Software	Estimated and Fitting Parameters				
				k	R^{2*}	SSE*	Chi^{2*}	No. of Data Points
				Unit				
				t^{-1}	---	---	---	---
PPFW	3.20	Numerical solution with first order model	AQUASIM	0.088	---	---	4.24	18
		Analytical solution (Eq. 19)	MATLAB	0.087	0.743	4.25	---	18
PRW	8.40	Numerical solution with first order model	AQUASIM	0.105	---	---	39.659	18
		Analytical solution (Eq. 19)	MATLAB	0.105	0.58	39.66	---	18

* *R^2: R-Square; SSE: Sum Squared Error; Chi^2: Chi-Square*

Table.6.3 : The Results of Parameter Estimation for the Experimental Data with Second Order Model performed by Numerical Solution (via AQUASIM) and Analytical Solution (via MATLAB)

Sample label	Initial Dosing (mg/L)	Method	Software	Estimated and Fitting Parameters					
				k	RA_0	R^{2*}	SSE*	Chi^{2*}	No. of Data Points
				Unit					
				$mg^{-1}t^{-1}$	mg/L	---	---	---	---
PPFW2	3.20	Numerical solution with second order model (Eq. 22)	AQUASIM	0.058	2.92	---	---	2.189	18
		Analytical solution (Eq. 23)	MATLAB	0.058	2.92	0.867	2.199	---	18
PRW2	8.40	Numerical solution with second order model (Eq. 22)	AQUASIM	0.036	7.10	---	---	19.469	18
		Analytical solution (Eq. 23)	MATLAB	0.035	7.10	0.794	19.47	---	18

* *R^2: R-Square; SSE: Sum Squared Error; Chi^2: Chi-Square*

Table.6.4 : The Results of Parameter Estimation for the Experimental Data with Parallel Second Order Model performed by Numerical Solution (via AQUASIM) and Analytical Solution (via MATLAB)

Sample label	Initial Dosing (mgL)	Method	Software	Estimated and Fitting Parameters							
				FRA_0	SRA_0	k_{FRA}	k_{SRA}	R^{2*}	SSE*	Chi^{2*}	No. of Data Points
				Unit							
				mg/L	mg/L	$mg^{-1}Lt^{-1}$	$mg^{-1}Lt^{-1}$	---	---	---	---
PPFW2	3.20	Numerical solution with parallel second order model	AQUASIM	0.89	2.99	2.82	0.014	---	---	0.167	18
		New analytical solution	MATLAB	0.89	2.96	2.79	0.014	0.989	0.177	---	18
PRW2	8.40	Numerical solution with parallel second order model	AQUASIM	2.71	5.86	1.35	0.007	---	---	0.561	18
		New analytical solution	MATLAB	2.71	5.85	1.35	0.007	0.994	0.563	---	18

** R^2: R-Square; SSE: Sum Squared Error; Chi^2: Chi-Square*

Table.6.5 : The Comparison of fitting parameters for the discussed chlorine decay modelling methods

Sample label	Method	R^{2*}	SSE^{*}	Chi^{2*}
PPFW2	FOM	0.743	4.25	4.24
	SOM	0.867	2.199	2.189
	PSOM	0.989	0.177	0.167
PRW2	FOM	0.58	39.66	39.659
	SOM	0.794	19.47	19.469
	PSOM	0.994	0.563	0.561

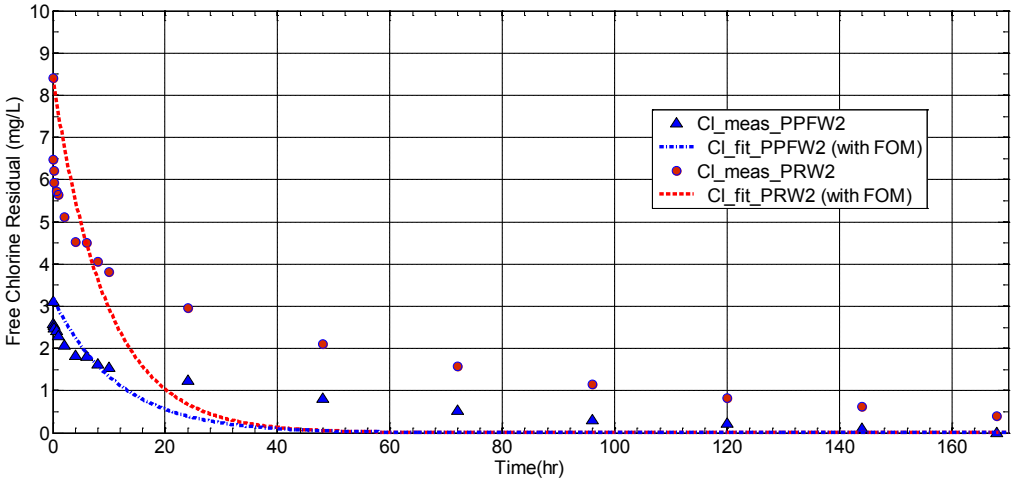

Fig.6.1. : Goodness of data fitting for Pilbara Water Samples with first order model (FOM); Analytical solution with MATLAB program

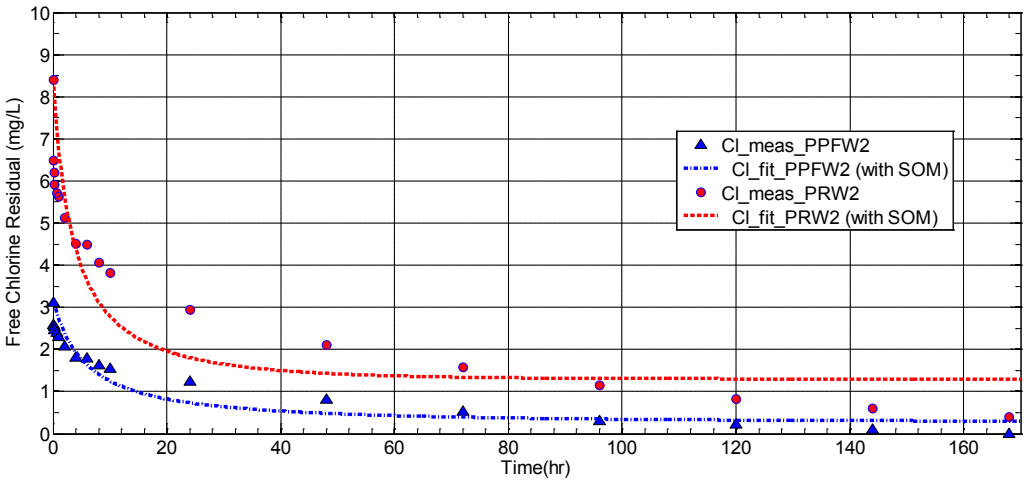

Fig.6.2. : Goodness of data fitting for Pilbara Water Samples with second order model (SOM); Analytical solution with MATLAB program

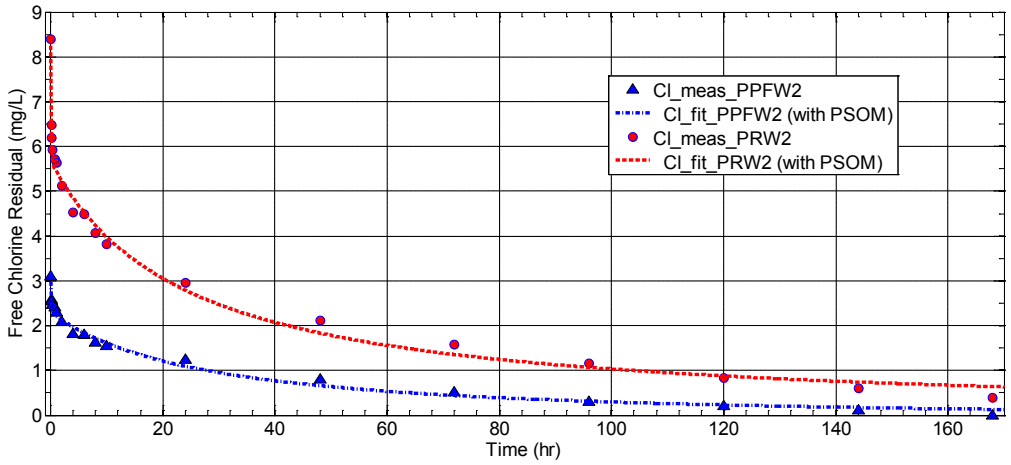

Fig.6.3. : Goodness of data fitting for Pilbara Water Samples with parallel second order model (PSOM); New analytical solution with MATLAB program

6.1. Summary and Conclusion

The aim of this chapter was to compare the accuracy performance of the three most popular modelling approaches for the prediction of chlorine decay in bulk water. Applying all these methods to the chlorine decay data obtained from the laboratory experiments for two water samples, collected from Pilbara Water Treatment Plant, the goodness of data fitting using the fitting parameters calculated by different methods of analysis (analytical solution with Mathlab and Numerical solution with AQUASIM) was compared. It was concluded that the parallel second order model is the most accurate modelling method among the three mentioned chlorine decay models.

CHAPTER 7

7. Temperature Effect on Chlorine Decay Modelling

In this Chapter, temperature effect on chlorine decay behaviour with parallel first order model is evaluated.

The material and methods to obtain the required data are explained in Chapter 3. Obtained raw data for this analysis is presented in Appendix A1.

Three different methods of analysis for the involvement of temperature variation were exercised. The reason for considering these methods was due to their broadly used applications in the literature.

In the first modelling procedure, assuming the least temperature (15°C) as the base, simulation and parameter estimation were performed for all data sets related to each temperature. In this stage, because more temperature should result in higher rate coefficients, it is important to set an appropriate minimum value for the rate coefficients while using AQUASIM. Then deriving the decay estimated parameters from individual decay tests, via Excel spreadsheet, a linear regression between the rate constants and temperature was attempted. The slopes of the lines were calculated as temperature dependence factors (E/R) for both fast and slow reacting reactions.

In the second method of analysis, one single temperature dependence parameter for both fast and slow reactants, defined as the ratio of activation energy to the universal gas constant (E/R), was added to other parameters in AQUASIM. Using this method the software (AQUASIM) itself was trying to make a linear relationship between rate coefficients according to Arrhenius equation.

In the last modelling attempt, however, two different E/R parameters were defined for the involving reactions; one for fast reacting agents labelled as $(E/R)_{FRA}$ and another for the slow ones labelled as $(E/R)_{SRA}$.

Parameter estimation and results of the first modelling procedure for Pilbara Raw Water sample are presented in Table 7.1 as well as in Figures 7.1 and 7.2. Similarly, Tables 7.2 and 7.3 show the parameter estimation of the second and third modelling approaches performed for the same sample. Data fittings of this exercise are shown in figures 7.3, 7.4 and 7.5. Likewise, the results of the parameter estimation of all analysis methods for Pilbara Post Filtration Water sample are shown in Tables 7.4, 7.5 and 7.6 and figures 7.6, 7.7, 7.8, 7.9 and 7.10.

Comparing the three mentioned temperature analysis methods in terms of easiness and accuracy, it is noticeable that in the first modelling method, for each temperature, individual parameter estimation should be performed. Parameters to be estimated in the base temperature (16) would be FRA_0, SRA_0, k_{FRA} and k_{SRA}. However, for other temperatures, keeping the same initial values of FRA_0 and SRA_0 as in base temperature, the only parameters left to be estimated were k_{FRA} and k_{SRA}.

In contrary, in second and third modelling methods of temperatures analysis, because of having only one step for analysing all data and parameters to be estimated, there is no need to manipulate the process in between. However, the results of the first modelling procedure were used in others as initial values for parameter estimation afterwards.

Moreover, in the first method, after parameter estimation, there should be an extra step for deriving the temperature dependence factor for each reactant by using a linear regression amongst rate constants for different temperatures. This would be a disadvantage for the first method compared to the second and third ones, as they do not need extra procedures.

In terms of accuracy however, the third method appeared to be more precise. This could be understood by comparing the chi-square factors. Nonetheless, while comparing, it has to be noticed that the average chi-square factors should be considered for each method. While the average chi-square value of the first approach for Pilbara Raw Water sample is the mean of eight reported chi-square constants (0.0909), for the second and third method it is calculated by dividing the values by 8 (0.11 for the second method and 0.0789 for third one).

Referring back to the first method, however, according to the results from figure 5.14, a very good linear relationship and R-square for deriving E/R value for SRA were observed (R^2=0.994 for k_{SRA}). However, for FRA fraction, it seems that it is not as sensitive enough as SRA fraction to the temperature increase.

The second method is suffering from an accuracy deterioration resulted from an over extra parameter reduction (using only one temperature dependence factor, E/R, for both reactants). In fact, having a close look at the results, as can be seen from the numbers in Table 7.2, the rate constant of slow reacting agents (k_{SRA}) seems to be more sensitive to temperature than that of fast reacting ones (k_{FRA}).

The temperature dependence constant in the first method of analysis is shown to be 3110˚K and 8090˚K for FRA and SRA respectively. This difference implies that there should not be considered only one temperature dependence parameter for both FRA and SRA when directly involving E/R parameter into model.

Comparing the results of the tables, it is realised that the first and third modelling methods are more likely to give the close results, however, in the first one the k_{SRA} values appeared to be twice bigger than those in the third modelling attempt are.

Looking at the results of Pilbara Post Filtration Water sample, however, it is realised that none of the methods is functioning as well as them upon another sample. The issue is more transparent when comparing the data fittings of two water samples. The reason for this might be that for water samples with fewer DOCs and better quality the method is not working properly when temperature is involved. This is something that should be investigated more during the rest of study.

Table.7.1 : Parameter estimation for the first modelling procedure (Pilbara Raw Water Sample)

Parameter	unit	value							
		temperature							
		15	20	25	30	35	40	45	50
FRA_ini	mg/l	1.1497	1.1497	1.1497	1.1497	1.1497	1.1497	1.1497	1.1497
SRA_ini	mg/l	2.0207	2.0207	2.0207	2.0207	2.0207	2.0207	2.0207	2.0207
k_FRA	$mg^{-1}lt^{-1}$	3.4071	6.0644	6.0644	6.0644	8.7948	11.4614	11.4614	11.4614
k_SRA	$mg^{-1}lt^{-1}$	0.0326	0.0516	0.0731	0.1064	0.1877	0.2842	0.4038	0.7171
Chi^2	---	0.1265	0.1008	0.1043	0.0629	0.0360	0.1024	0.1089	0.0851
$(E/R)_{FRA}$	$˚K^{-1}$	3110	3110	3110	3110	3110	3110	3110	3110
$(E/R)_{SRA}$	$˚K^{-1}$	8090	8090	8090	8090	8090	8090	8090	8090

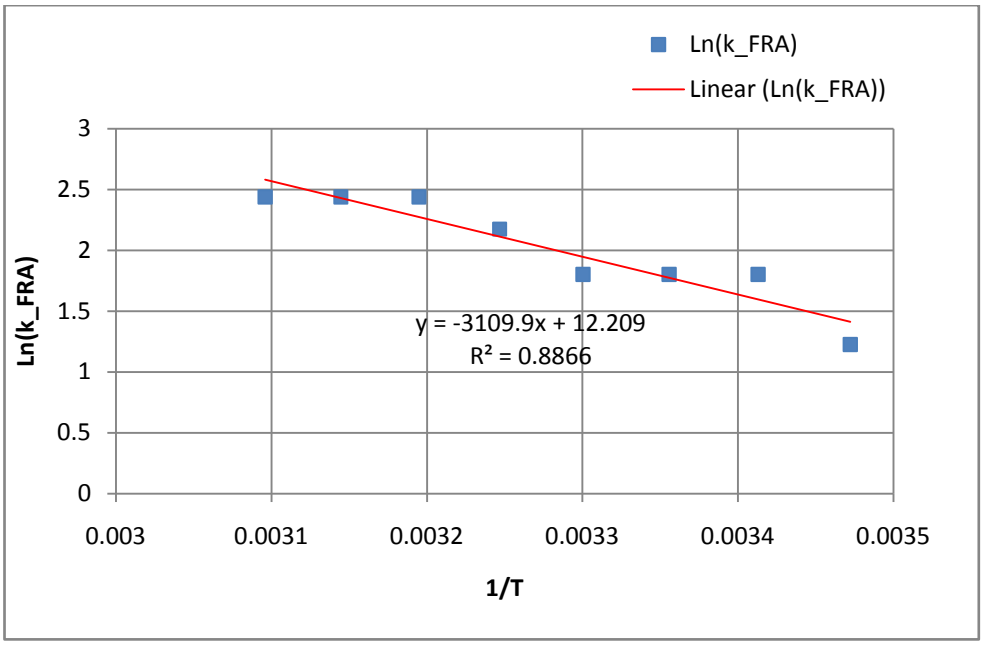

Fig.7.1. **:Linear regression of FRA rate constants vs. time for the first modelling procedure (Pilbara Raw Water Sample)**

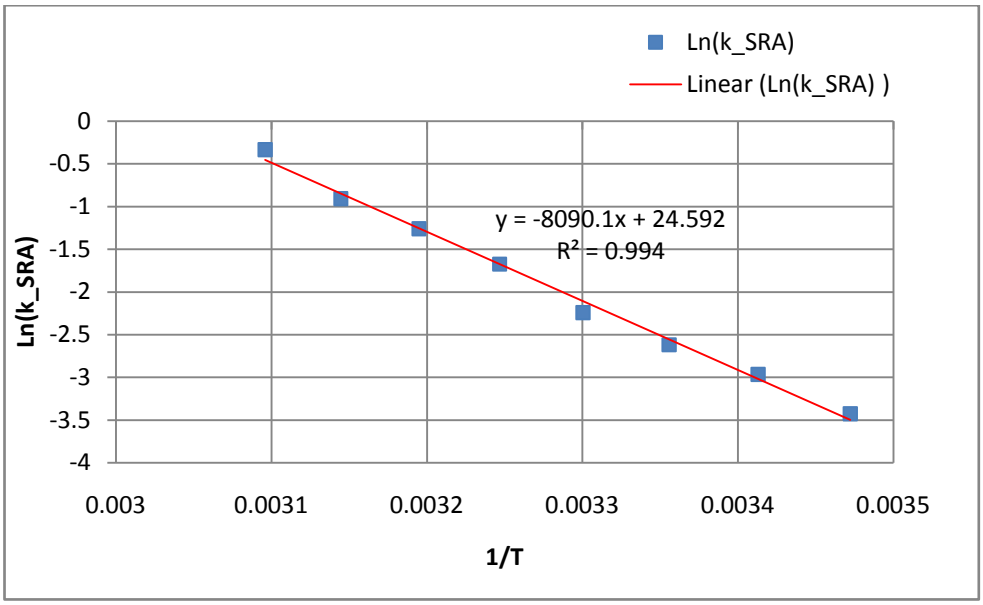

Fig.7.2. **: Linear regression of SRA rate constants vs. time for the first modelling procedure (Pilbara Raw Water Sample)**

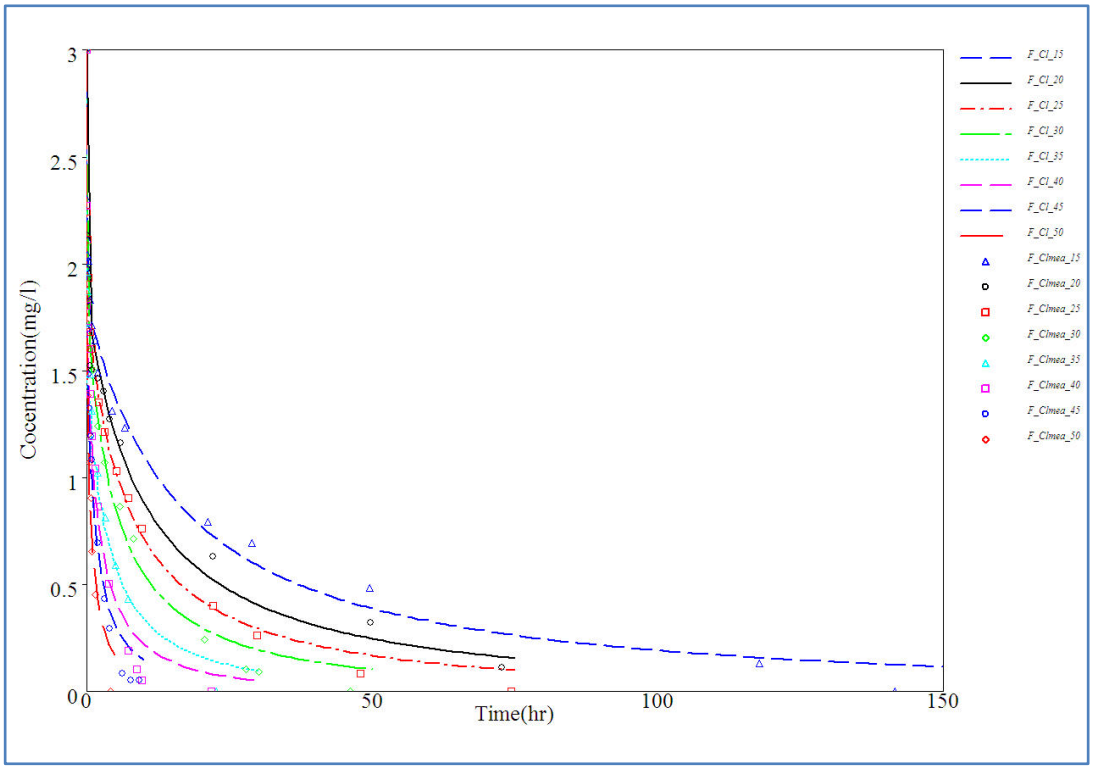

Fig.7.3. : Data fitting for the first modelling procedure (Pilbara Raw Water Sample)

Table.7.2 : Parameter estimation for the second modelling procedure (Pilbara Raw Water Sample)

Parameter	unit	value							
		temperature							
		15	20	25	30	35	40	45	50
FRA_ini	mg/l	1.1064	1.1064	1.1064	1.1064	1.1064	1.1064	1.1064	1.1064
SRA_ini	mg/l	2.4483	2.4483	2.4483	2.4483	2.4483	2.4483	2.4483	2.4483
k_FRA	$mg^{-1}lt^{-1}$	2.7610	4.4451	7.0431	10.9912	16.9063	25.6496	38.4077	56.7974
k_SRA	$mg^{-1}lt^{-1}$	0.0242	0.0390	0.0617	0.0963	0.1482	0.2248	0.3366	0.4978
E/R	$^{\circ}K^{-1}$	8037	8037	8037	8037	8037	8037	8037	8037
Chi^2	---	0.8797	0.8797	0.8797	0.8797	0.8797	0.8797	0.8797	0.8797

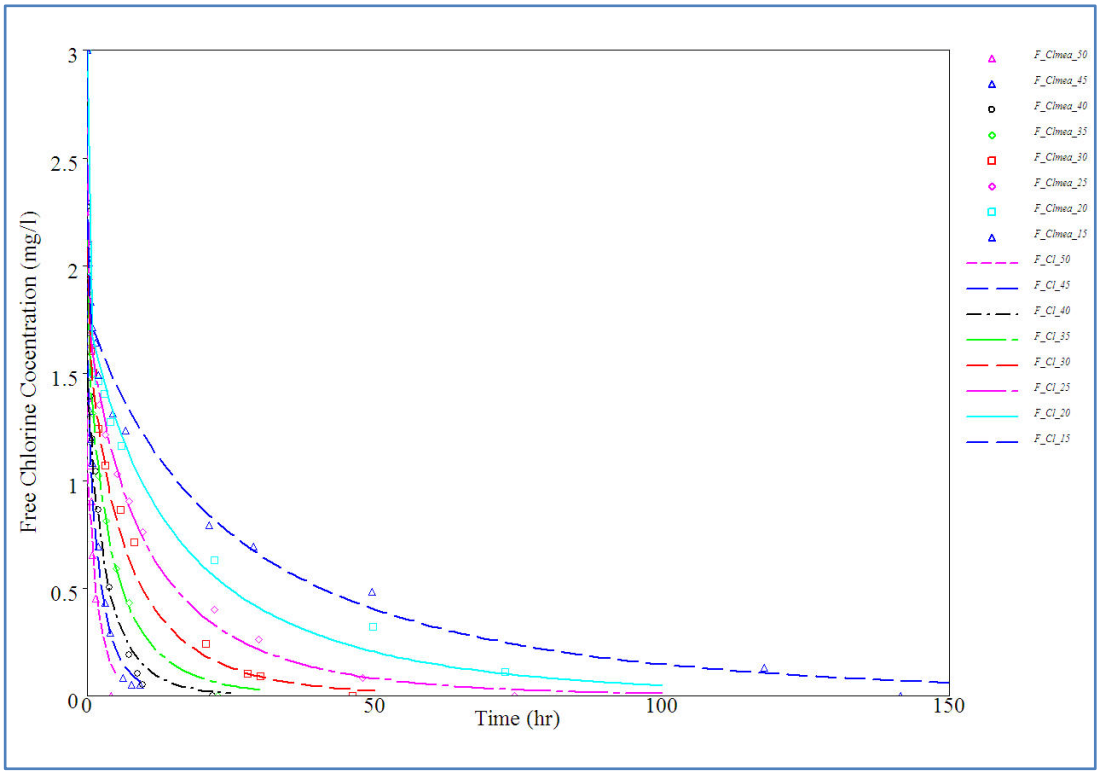

Fig.7.4. : Data fitting for the second modelling procedure (Pilbara Raw Water Sample)

Table.7.3 : Parameter estimation for the third modelling procedure (Pilbara Raw Water Sample)

Parameter	unit	value							
		temperature							
		15	20	25	30	35	40	45	50
FRA_ini	mg/l	1.1998	1.1998	1.1998	1.1998	1.1998	1.1998	1.1998	1.1998
SRA_ini	mg/l	2.8546	2.8546	2.8546	2.8546	2.8546	2.8546	2.8546	2.8546
k_FRA	$mg^{-1}lt^{-1}$	3.3515	3.9688	4.6732	5.4730	6.3769	7.3938	8.5332	9.8045
k_SRA	$mg^{-1}lt^{-1}$	0.0157	0.0258	0.0417	0.0663	0.1039	0.1604	0.2443	0.3672
$(E/R)_{FRA}$	$^{\circ}K^{-1}$	2853	2853	2853	2853	2853	2853	2853	2853
$(E/R)_{SRA}$	$^{\circ}K^{-1}$	8374	8374	8374	8374	8374	8374	8374	8374
Chi^2	---	0.6283	0.6283	0.6283	0.6283	0.6283	0.6283	0.6283	0.6283

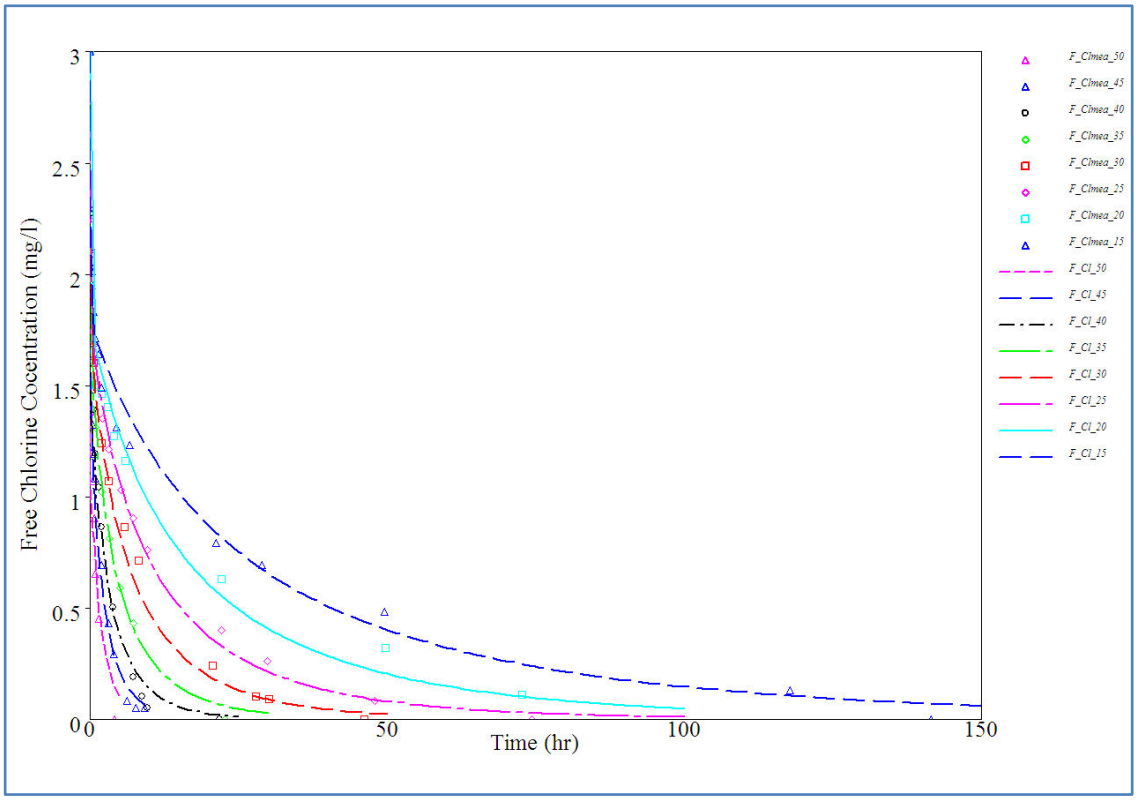

Fig.7.5. : Data fitting for the third modelling procedure (Pilbara Raw Water Sample)

Table.7.4 : Parameter estimation for the first modelling procedure (Pilbara Post Filtration Water Sample)

Parameter	unit	value							
		temperature							
		15	20	25	30	35	40	45	50
FRA_ini	mg/l	0.6686	0.6686	0.6686	0.6686	0.6686	0.6686	0.6686	0.6686
SRA_ini	mg/l	2.2972	2.2972	2.2972	2.2972	2.2972	2.2972	2.2972	2.2972
k_FRA	$mg^{-1}lt^{-1}$	4.9379	5.1516	5.1516	5.1516	10.0000	10.0	10.0	10.0
k_SRA	$mg^{-1}lt^{-1}$	0.0043	0.0131	0.0200	0.0386	0.0680	0.0781	0.1179	0.1576
Chi^2	---	0.0765	0.1962	0.2674	0.2516	0.1244	0.1370	0.3195	0.1026
$(E/R)_{FRA}$	$°K^{-1}$	2417	2417	2417	2417	2417	2417	2417	2417
$(E/R)_{SRA}$	$°K^{-1}$	9095	9095	9095	9095	9095	9095	9095	9095

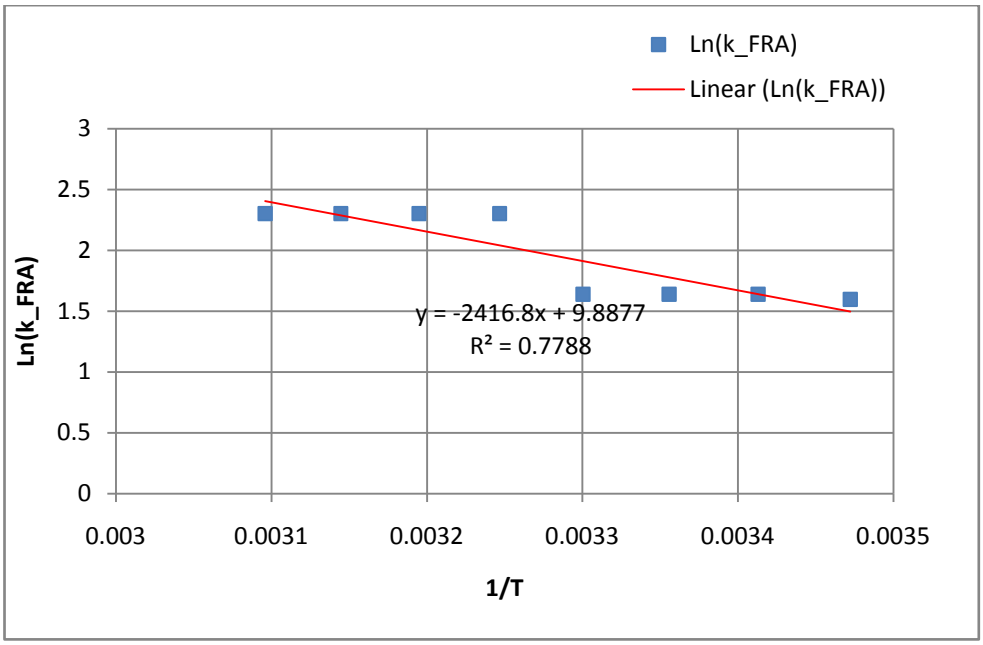

Fig.7.6. : Linear regression of FRA rate constants vs. time for the first modelling procedure (Pilbara Post Filtration Water Sample)

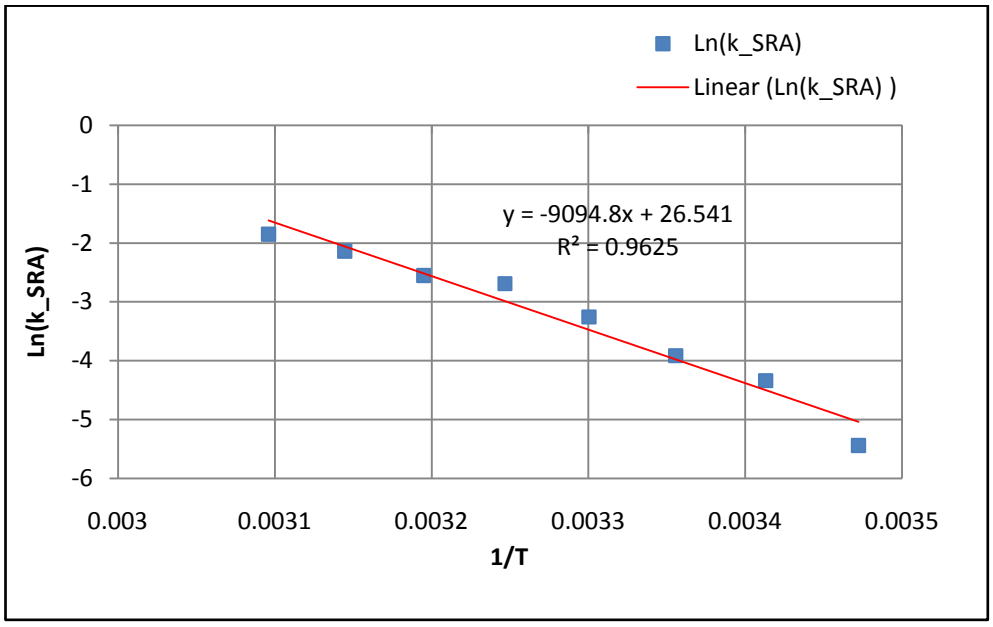

Fig.7.7. : Linear regression of SRA rate constants vs. time for the first modelling procedure (Pilbara Post Filtration Water Sample)

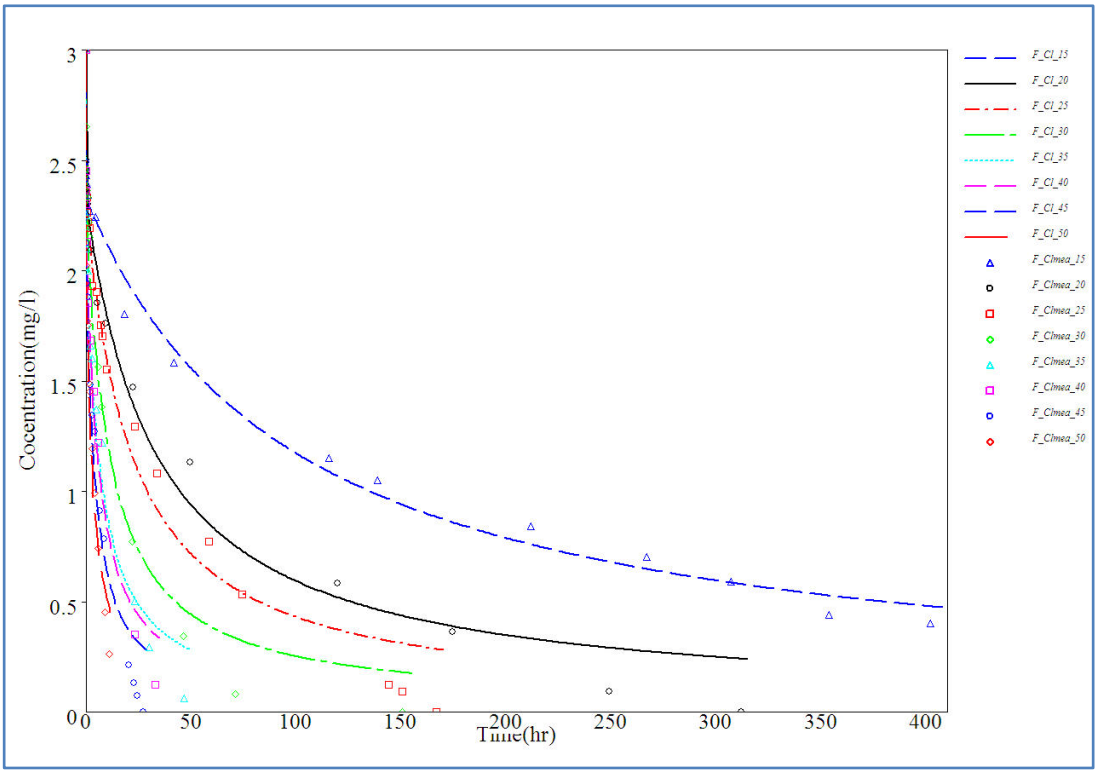

Fig.7.8. : Data fitting for the first modelling procedure
(Pilbara Post Filtration Water Sample)

Table.7.5 : Parameter estimation for the second modelling procedure
(Pilbara Post Filtration Water Sample)

Parameter	unit	value							
		temperature							
		15	20	25	30	35	40	45	50
FRA_ini	mg/l	0.6784	0.6784	0.6784	0.6784	0.6784	0.6784	0.6784	0.6784
SRA_ini	mg/l	3.0031	3.0031	3.0031	3.0031	3.0031	3.0031	3.0031	3.0031
k_FRA	$mg^{-1}lt^{-1}$	2.6811	4.6398	7.8830	13.1610	21.6102	34.9259	55.6007	87.2492
k_SRA	$mg^{-1}lt^{-1}$	0.0038	0.0066	0.0113	0.0188	0.0309	0.0500	0.0796	0.1249
E/R	$^{\circ}K^{-1}$	9256	9256	9256	9256	9256	9256	9256	9256
Chi^2	---	1.8428	1.8428	1.8428	1.8428	1.8428	1.8428	1.8428	1.8428

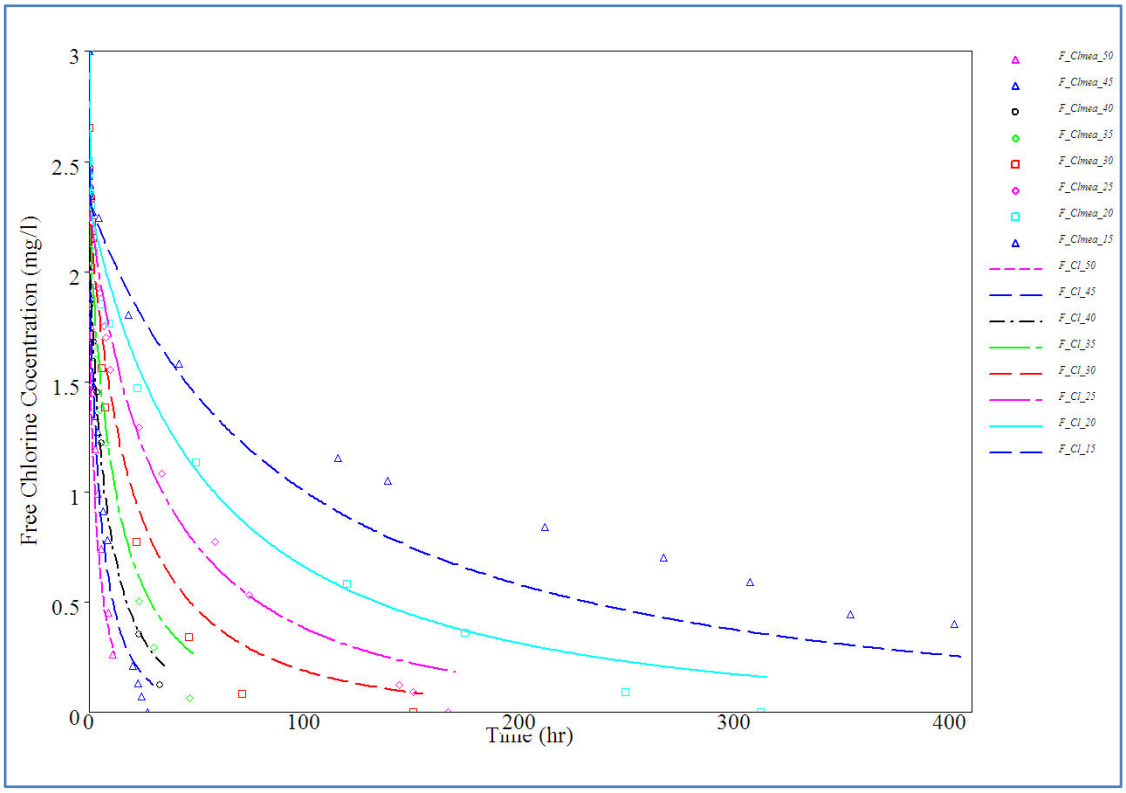

Fig.7.9. : Data fitting for the second modelling procedure
(Pilbara Post Filtration Water Sample)

Table.7.6 : Parameter estimation for the third modelling procedure
(Pilbara Post Filtration Water Sample)

Parameter	unit	value							
		temperature							
		15	20	25	30	35	40	45	50
FRA_ini	mg/l	0.7381	0.7381	0.7381	0.7381	0.7381	0.7381	0.7381	0.7381
SRA_ini	mg/l	3.3200	3.3200	3.3200	3.3200	3.3200	3.3200	3.3200	3.3200
k_FRA	$mg^{-1}lt^{-1}$	3.1464	3.4862	3.8495	4.2368	4.6485	5.0851	5.5471	6.0348
k_SRA	$mg^{-1}lt^{-1}$	0.0030	0.0053	0.0091	0.0152	0.0251	0.0409	0.0654	0.1031
$(E/R)_{FRA}$	$^{\circ}K^{-1}$	1731	1731	1731	1731	1731	1731	1731	1731
$(E/R)_{SRA}$	$^{\circ}K^{-1}$	9359	9359	9359	9359	9359	9359	9359	9359
Chi^2	---	1.6830	1.6830	1.6830	1.6830	1.6830	1.6830	1.6830	1.6830

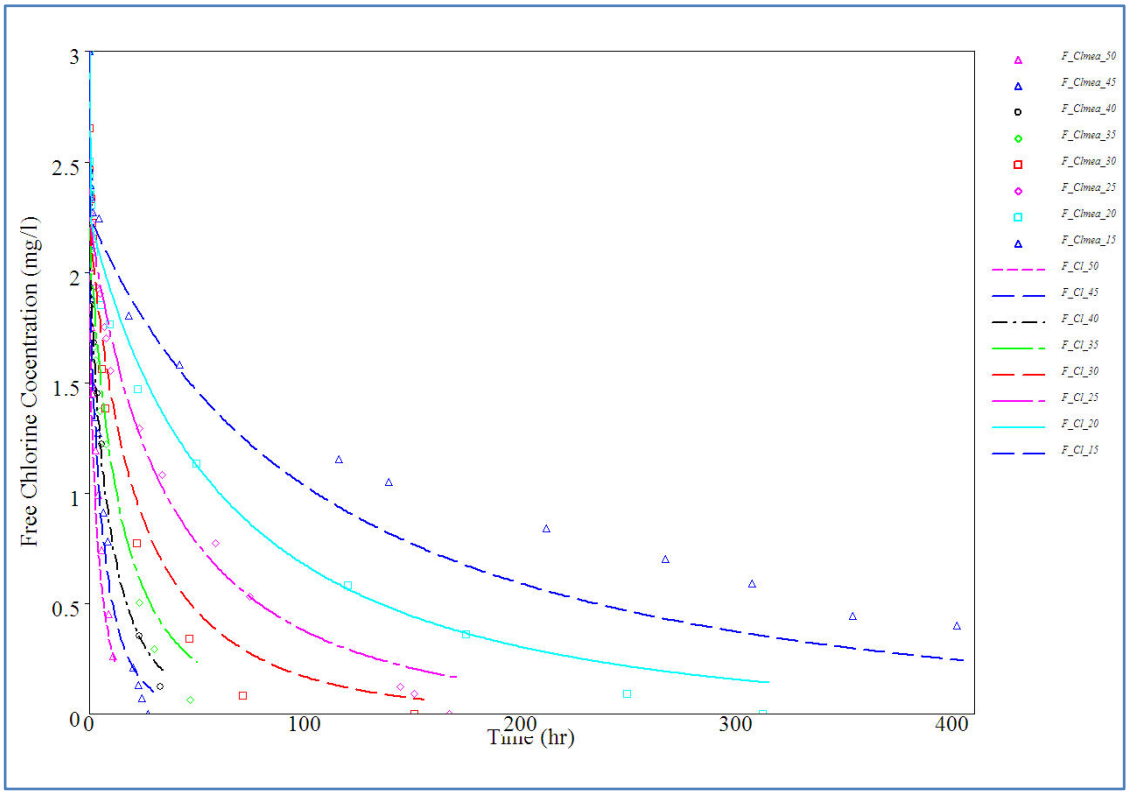

Fig.7.10. : Data fitting for the third modelling procedure
(Pilbara Post Filtration Water Sample)

7.1. Summary and Conclusion

In this chapter, analysing the existing data obtained from chlorine decay test of Pilbara Water Treatment samples, it was proved that first order model could not predict chlorine residual properly. Additionally, it was shown that the considered assumption for pseudo-first-order was not fundamentally valid.

Temperature influence on chlorine decay and different methods for its involvement with parallel second order model were explained in detail later in this chapter as well. It was concluded that considering two different temperature dependence factors (E/R) for fast and slow reactions was more likely to give better results, however, it was recommended that temperature analysis with parallel second order model would rather more investigate.

CHAPTER 8
8. Conclusion

During this research, several modelling approaches for prediction of chlorine decay and its by-product formation were studied and compared. The fist order model, which has been commonly used over several decades, was not found to be capable enough to meet the criteria for chlorine residual prediction. Second order model also cannot represent the chlorine decay profile appropriately since it is not competent to consider the fast reaction rate during the initial period of reaction time. There has been concluded that those approaches that are initiated from parallel first order model are not fundamentally valid, however, in some applications their representation of chlorine decay behaviour is satisfactory. Among all discussed models, the best one in terms of two important factors, which are simplicity and accuracy in different planning and management application, was recognised as parallel second order model.

Extensive effort has been put to develop the mentioned model for proposing an analytical solution for it, which has not existed before. The results of proposed analytical solution for parallel second order model evaluated against its numerical solution for different data sets from literature as well as experimental data. Therefore, its credibility has been proven mathematically as well as practically.

The only problem for the parallel second order model was found to be inconsistency of its estimated parameters while the chlorine dosing varies. This problem, however, was found to be removed if only one set of parameters is applied to all data sets of different chlorine dosing. Although this minor problem is common amongst all other existing models, to have a strong model, it was concluded that the issue should be more investigated.

Finally, the influence of the temperature on the behaviour of chlorine decay and its impact on parallel second order model was studied. Three methods for involving the temperature effect in the modelling procedure were evaluated. It was concluded that considering two separate temperature dependence factors, E/R, for both fast and slow reacting agents led to have more accurate results while the simplicity of the method was kept.

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10. Appendices:

Appendix A1: chlorine decay tests in different temperatures

Table A1.1: Chlorine decay test results for Pilbara Raw Water sample (PRW3-1) at 15˚C

No.	Date & Time	Time (hr)	Total Chloruine (mg/l)	Free Chlorine (mg/l)	Combined Chlorine (mg/l)
1	30/09/2009 12:25	0.00	3	3	0.00
2	30/09/2009 12:29	0.07	2.55	2.3	0.25
3	30/09/2009 12:35	0.17	2.44	2.11	0.33
4	30/09/2009 12:42	0.28	2.34	2.04	0.30
5	30/09/2009 12:50	0.42	2.24	2.01	0.23
6	30/09/2009 13:05	0.67	2.13	1.83	0.30
7	30/09/2009 13:25	1.00	1.97	1.71	0.26
8	30/09/2009 13:58	1.55	1.92	1.64	0.28
9	30/09/2009 14:25	2.00	1.79	1.49	0.30
10	30/09/2009 17:00	4.58	1.53	1.31	0.22
11	30/09/2009 19:10	6.75	1.44	1.23	0.21
12	1/10/2009 9:45	21.33	1.04	0.79	0.25
13	1/10/2009 17:25	29.00	0.88	0.69	0.19
14	2/10/2009 14:05	49.67	0.67	0.48	0.19
15	5/10/2009 10:15	117.83	0.29	0.13	0.16
16	6/10/2009 10:00	141.58	0.19	0	0.19
17	7/10/2009 9:25	165.00	0.15	0	0.15
18	9/10/2009 10:52	214.45	0.1	0	0.10

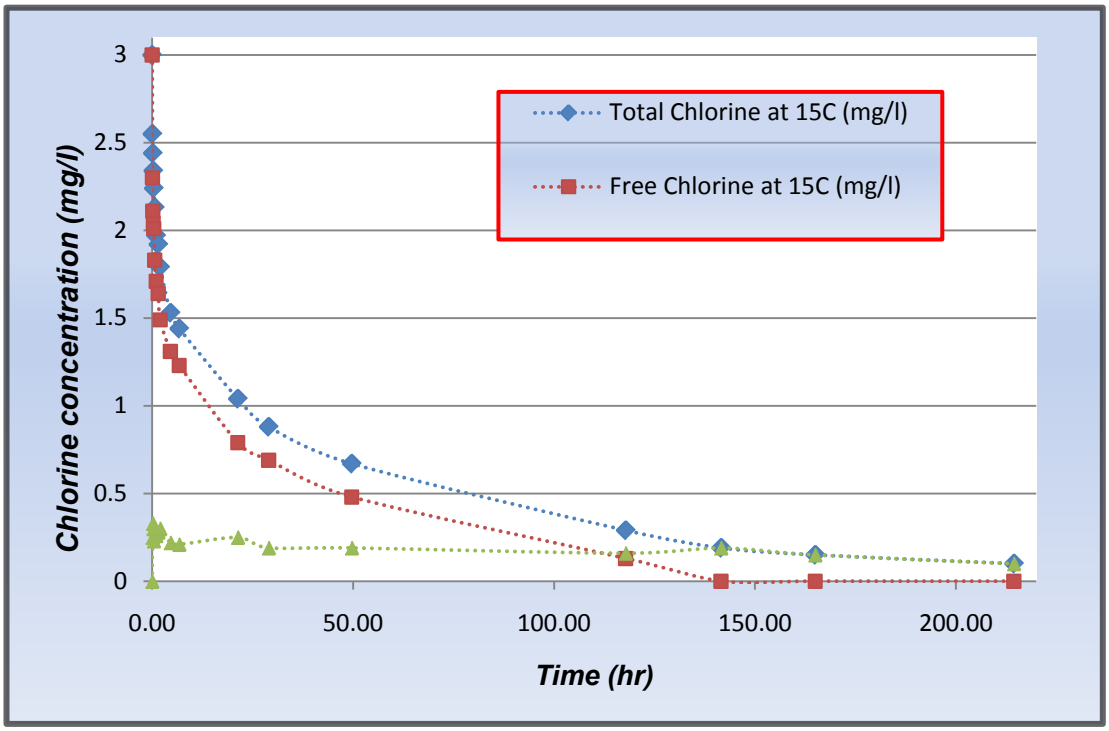

Fig. A1.1: Chlorine decay test results for Pilbara Raw Water sample (PRW3-1) at 15˚C

Table A1.2: Chlorine decay test results for Pilbara Raw Water sample (PRW3-2) at 20˚C

No.	Date & Time	Time (hr)	Total Chloruine (mg/l)	Free Chlorine (mg/l)	Combined Chlorine (mg/l)
1	24/12/2009 11:00	0.00	3	3	0.00
2	24/12/2009 11:05	0.08	2.47	2.13	0.34
3	24/12/2009 11:11	0.18	2.3	1.97	0.33
4	24/12/2009 11:20	0.33	2.08	1.82	0.26
5	24/12/2009 11:40	0.67	1.97	1.52	0.45
6	24/12/2009 12:00	1.00	1.92	1.5	0.42
7	24/12/2009 13:00	2.00	1.74	1.46	0.28
8	24/12/2009 14:00	3.00	1.63	1.4	0.23
9	24/12/2009 15:05	4.08	1.51	1.27	0.24
10	24/12/2009 17:00	6.00	1.4	1.16	0.24
11	25/12/2009 9:15	22.25	0.87	0.63	0.24
12	26/12/2009 12:45	49.75	0.49	0.32	0.17
13	27/12/2009 11:48	72.80	0.3	0.11	0.19

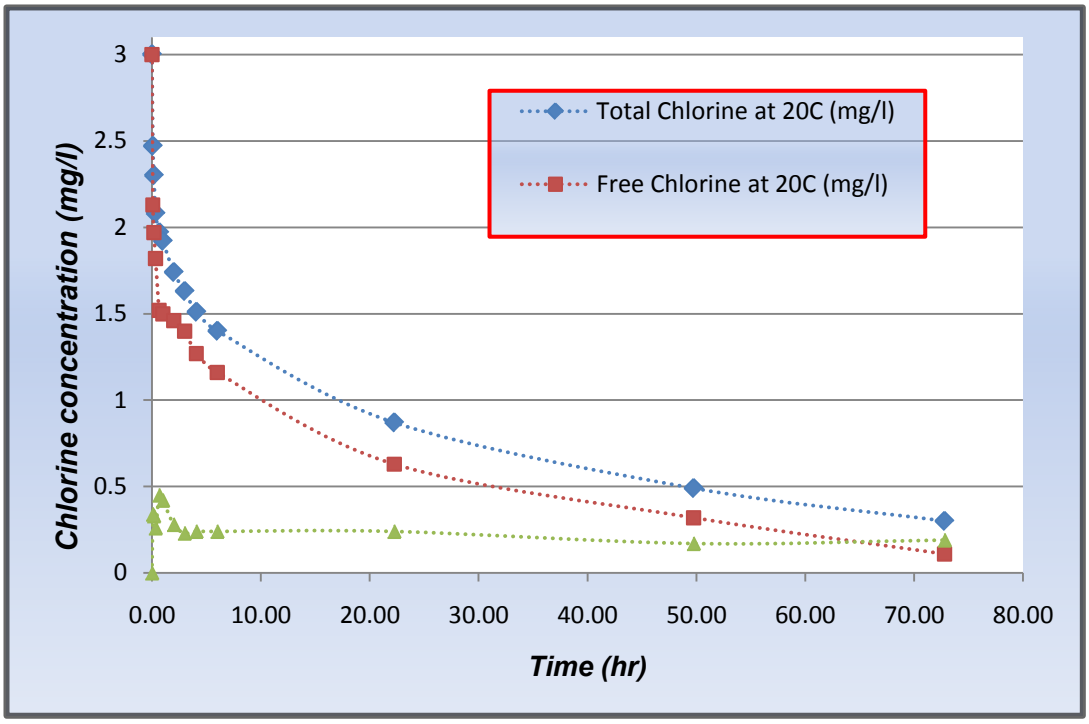

Fig. A1.2: Chlorine decay test results for Pilbara Raw Water sample (PRW3-2) at 20˚C

Table A1.3: Chlorine decay test results for Pilbara Raw Water sample (PRW3-3) at 25˚C

No.	Date & Time	Time (hr)	Total Chloruine (mg/l)	Free Chlorine (mg/l)	Combined Chlorine (mg/l)
1	6/11/2009 11:06	0.00	3	3	0.00
2	6/11/2009 11:11	0.08	2.47	2.24	0.23
3	6/11/2009 11:17	0.18	2.28	2.11	0.17
4	6/11/2009 11:27	0.35	2.15	1.93	0.22
5	6/11/2009 11:46	0.67	1.99	1.68	0.31
6	6/11/2009 12:06	1.00	1.82	1.6	0.22
7	6/11/2009 13:15	2.15	1.59	1.35	0.24
8	6/11/2009 14:15	3.15	1.47	1.21	0.26
9	6/11/2009 16:25	5.32	1.27	1.03	0.24
10	6/11/2009 18:25	7.32	1.11	0.9	0.21
11	6/11/2009 20:53	9.78	1	0.76	0.24
12	7/11/2009 9:20	22.23	0.6	0.4	0.20
13	7/11/2009 17:03	29.95	0.44	0.26	0.18
14	8/11/2009 11:06	48.00	0.23	0.08	0.15
15	9/11/2009 13:29	74.38	0.13	0	0.13
16	10/11/2009 12:25	97.32	0.09	0	0.09

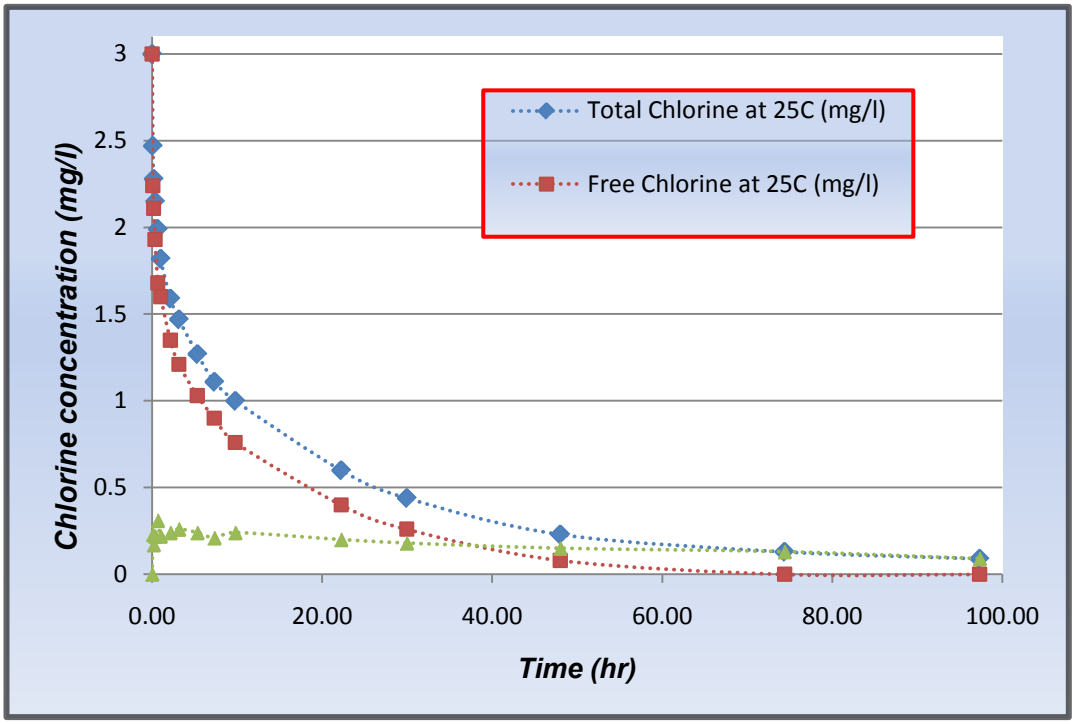

Fig. A1.3: Chlorine decay test results for Pilbara Raw Water sample (PRW3-3) at 25˚C

Table A1.4: Chlorine decay test results for Pilbara Raw Water sample (PRW3-4) at 30˚C

No.	Date & Time	Time (hr)	Total Chloruine (mg/l)	Free Chlorine (mg/l)	Combined Chlorine (mg/l)
1	6/11/2009 12:45	0.00	3	3	0.00
2	6/11/2009 12:51	0.10	2.39	2.09	0.30
3	6/11/2009 12:57	0.20	2.25	1.93	0.32
4	6/11/2009 13:05	0.33	2.1	1.81	0.29
5	6/11/2009 13:25	0.67	1.89	1.6	0.29
7	6/11/2009 13:52	1.12	1.71	1.5	0.21
8	6/11/2009 14:48	2.05	1.49	1.24	0.25
9	6/11/2009 16:00	3.25	1.31	1.07	0.24
10	6/11/2009 18:34	5.82	1.06	0.86	0.20
11	6/11/2009 21:00	8.25	0.9	0.71	0.19
12	7/11/2009 9:30	20.75	0.41	0.24	0.17
13	7/11/2009 16:45	28.00	0.25	0.1	0.15
14	7/11/2009 18:55	30.17	0.23	0.09	0.14
15	8/11/2009 10:55	46.17	0.1	0	0.10

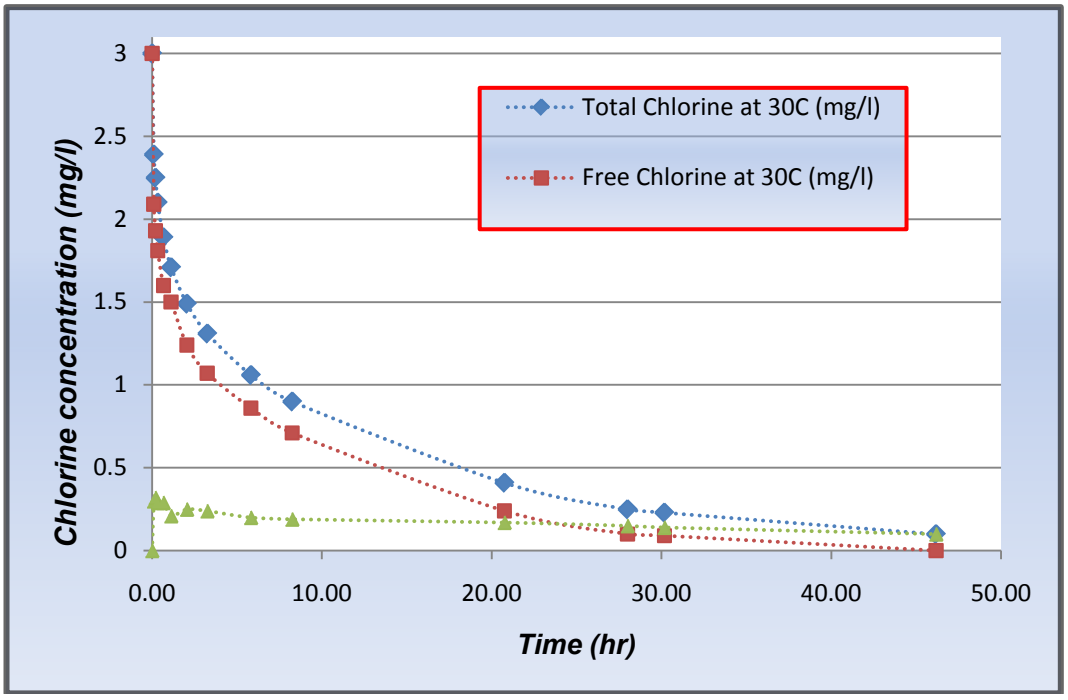

Fig. A1.4: Chlorine decay test results for Pilbara Raw Water sample (PRW3-4) at 30˚C

Table A1.5: Chlorine decay test results for Pilbara Raw Water sample (PRW3-5) at 35˚C

No.	Date & Time	Time (hr)	Total Chloruine (mg/l)	Free Chlorine (mg/l)	Combined Chlorine (mg/l)
1	10/11/2009 11:09	0.00	3	3	0.00
2	10/11/2009 11:14	0.08	2.33	1.96	0.37
3	10/11/2009 11:19	0.17	2.16	1.87	0.29
4	10/11/2009 11:29	0.33	2.01	1.7	0.31
5	10/11/2009 11:49	0.67	1.75	1.48	0.27
6	10/11/2009 12:09	1.00	1.54	1.31	0.23
7	10/11/2009 13:09	2.00	1.27	1.02	0.25
8	10/11/2009 14:30	3.35	1.01	0.81	0.20
9	10/11/2009 16:15	5.10	0.78	0.59	0.19
10	10/11/2009 18:30	7.35	0.61	0.43	0.18
11	11/11/2009 9:58	22.82	0.12	0	0.12

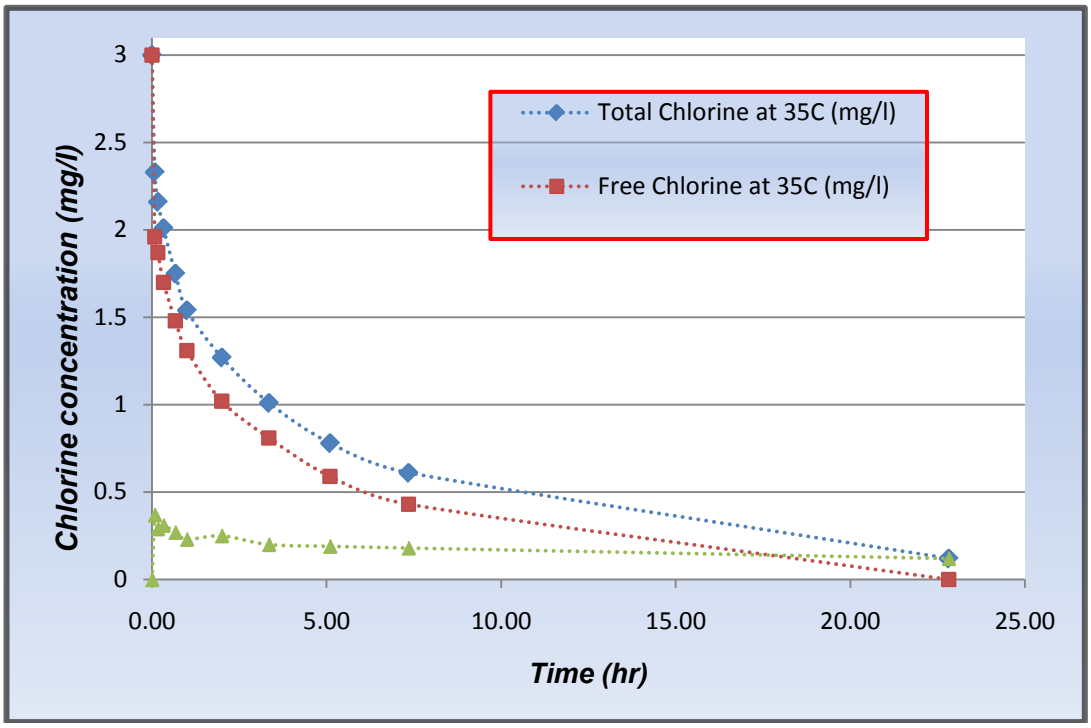

Fig. A1.5: Chlorine decay test results for Pilbara Raw Water sample (PRW3-5) at 35˚C

Table A1.6: Chlorine decay test results for Pilbara Raw Water sample (PRW3-6) at 40˚C

No.	Date & Time	Time (hr)	Total Chloruine (mg/l)	Free Chlorine (mg/l)	Combined Chlorine (mg/l)
1	15/10/2009 12:15	0.00	3	3	0.00
2	15/10/2009 12:17	0.03	2.71	2.27	0.44
3	15/10/2009 12:23	0.13	2.41	1.8	0.61
4	15/10/2009 12:30	0.25	2	1.7	0.30
5	15/10/2009 12:35	0.33	1.85	1.6	0.25
6	15/10/2009 12:55	0.67	1.6	1.39	0.21
8	15/10/2009 13:15	1.00	1.49	1.19	0.30
9	15/10/2009 13:45	1.50	1.25	1.04	0.21
10	15/10/2009 14:16	2.02	1.07	0.86	0.21
11	15/10/2009 16:15	4.00	0.68	0.5	0.18
12	15/10/2009 19:35	7.33	0.34	0.19	0.15
13	15/10/2009 21:05	8.83	0.25	0.1	0.15
14	15/10/2009 22:00	9.75	0.2	0.05	0.15
15	16/10/2009 10:10	21.92	0.07	0	0.07

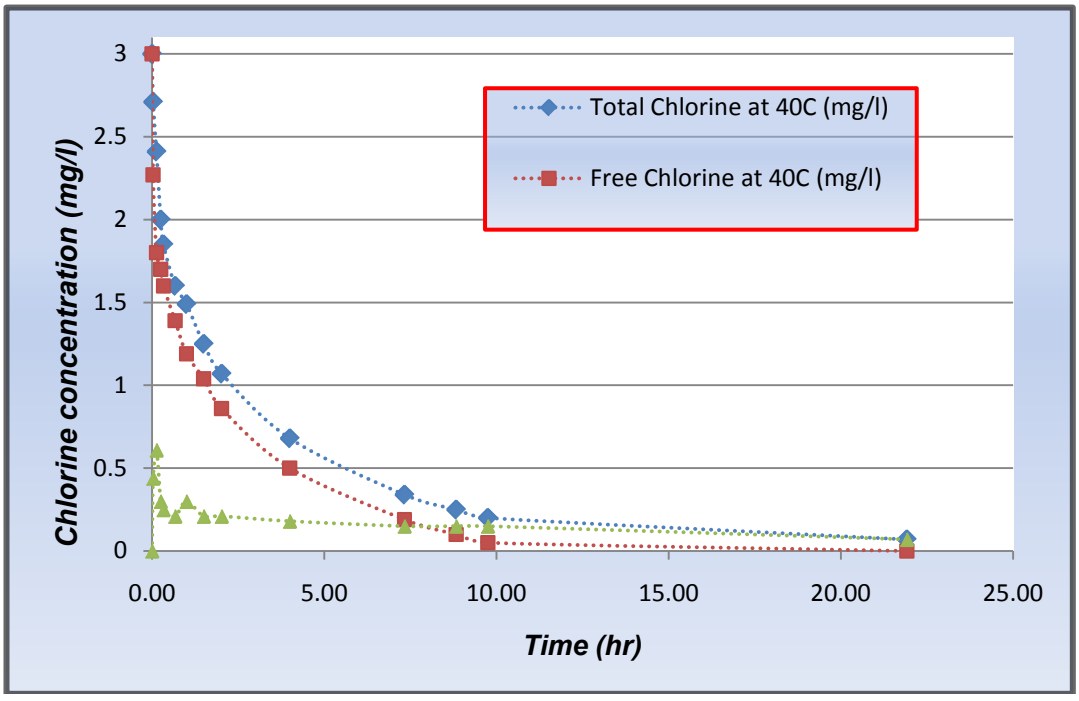

Fig. A1.6: Chlorine decay test results for Pilbara Raw Water sample (PRW3-6) at 40˚C

Table A1.7: Chlorine decay test results for Pilbara Raw Water sample (PRW3-7) at 45˚C

No.	Date & Time	Time (hr)	Total Chloruine (mg/l)	Free Chlorine (mg/l)	Combined Chlorine (mg/l)
1	9/11/2009 12:23	0.00	3	3	0.00
2	9/11/2009 12:28	0.08	2.26	1.97	0.29
3	9/11/2009 12:34	0.18	1.93	1.69	0.24
4	9/11/2009 12:43	0.33	1.75	1.48	0.27
5	9/11/2009 12:53	0.50	1.58	1.32	0.26
6	9/11/2009 13:08	0.75	1.39	1.19	0.20
7	9/11/2009 13:23	1.00	1.27	1.08	0.19
8	9/11/2009 14:26	2.05	0.87	0.69	0.18
9	9/11/2009 15:30	3.12	0.6	0.43	0.17
10	9/11/2009 16:30	4.12	0.47	0.29	0.18
11	9/11/2009 18:38	6.25	0.22	0.08	0.14
12	9/11/2009 20:08	7.75	0.16	0.05	0.11
13	9/11/2009 21:35	9.20	0.14	0.05	0.09

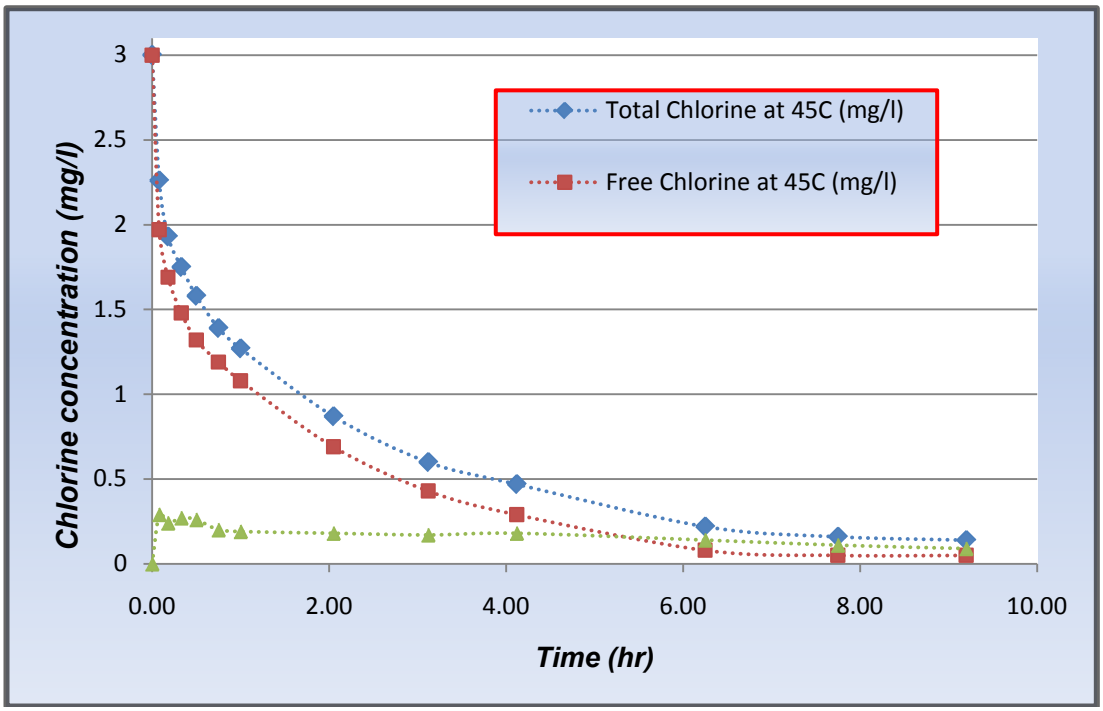

Fig. A1.7: Chlorine decay test results for Pilbara Raw Water sample (PRW3-7) at 45˚C

Table A1.8: Chlorine decay test results for Pilbara Raw Water sample (PRW3-8) at 50˚C

No.	Date & Time	Time (hr)	Total Chloruine (mg/l)	Free Chlorine (mg/l)	Combined Chlorine (mg/l)
1	7/11/2009 12:25	0.00	3	3	0.00
2	7/11/2009 12:30	0.08	2.2	1.83	0.37
3	7/11/2009 12:35	0.17	1.84	1.61	0.23
4	7/11/2009 12:40	0.25	1.74	1.38	0.36
5	7/11/2009 12:45	0.33	1.6	1.2	0.40
6	7/11/2009 12:55	0.50	1.4	1.07	0.33
7	7/11/2009 13:10	0.75	1.21	0.9	0.31
8	7/11/2009 13:25	1.00	1.08	0.65	0.43
9	7/11/2009 13:56	1.52	0.84	0.45	0.39
10	7/11/2009 16:35	4.17	0.22	0	0.22
11	7/11/2009 18:45	6.33	0.11	0	0.11

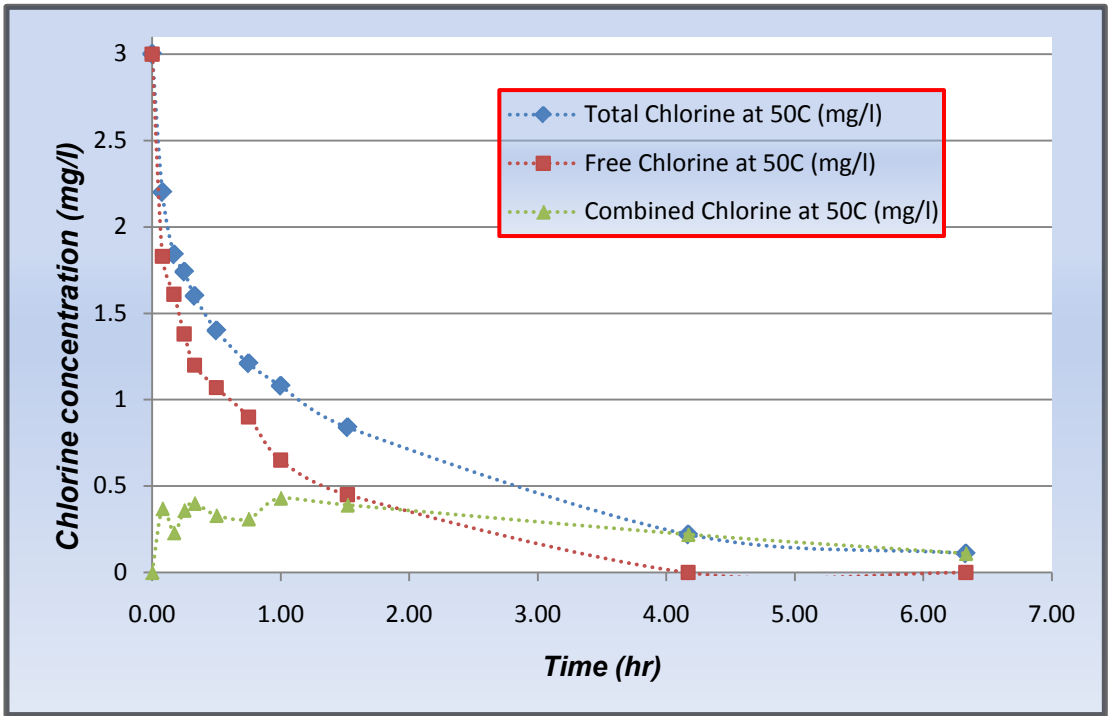

Fig. A1.8: Chlorine decay test results for Pilbara Raw Water sample (PRW3-8) at 50˚C

Table A1.9: Chlorine decay test results for Pilbara Post Filtration Water sample (PPFW3-1) at 15˚C

No.	Date & Time	Time (hr)	Total Chloruine (mg/l)	Free Chlorine (mg/l)	Combined Chlorine (mg/l)
1	20/10/2009 16:02	0.00	3	3	0.00
2	20/10/2009 16:08	0.10	2.8	2.47	0.33
3	20/10/2009 16:16	0.23	2.72	2.43	0.29
4	20/10/2009 16:27	0.42	2.69	2.39	0.30
5	20/10/2009 17:02	1.00	2.66	2.34	0.32
6	20/10/2009 18:00	1.97	2.54	2.27	0.27
7	20/10/2009 20:35	4.55	2.42	2.24	0.18
8	21/10/2009 10:18	18.27	2.07	1.8	0.27
9	22/10/2009 10:03	42.02	1.82	1.58	0.24
10	25/10/2009 11:52	115.83	1.41	1.15	0.26
11	26/10/2009 10:55	138.88	1.31	1.05	0.26
12	29/10/2009 11:50	211.80	1.06	0.84	0.22
13	31/10/2009 19:05	267.05	0.89	0.7	0.19
14	2/11/2009 11:15	307.22	0.75	0.59	0.16
15	4/11/2009 9:55	353.88	0.61	0.44	0.17
16	6/11/2009 10:12	402.17	0.54	0.4	0.14

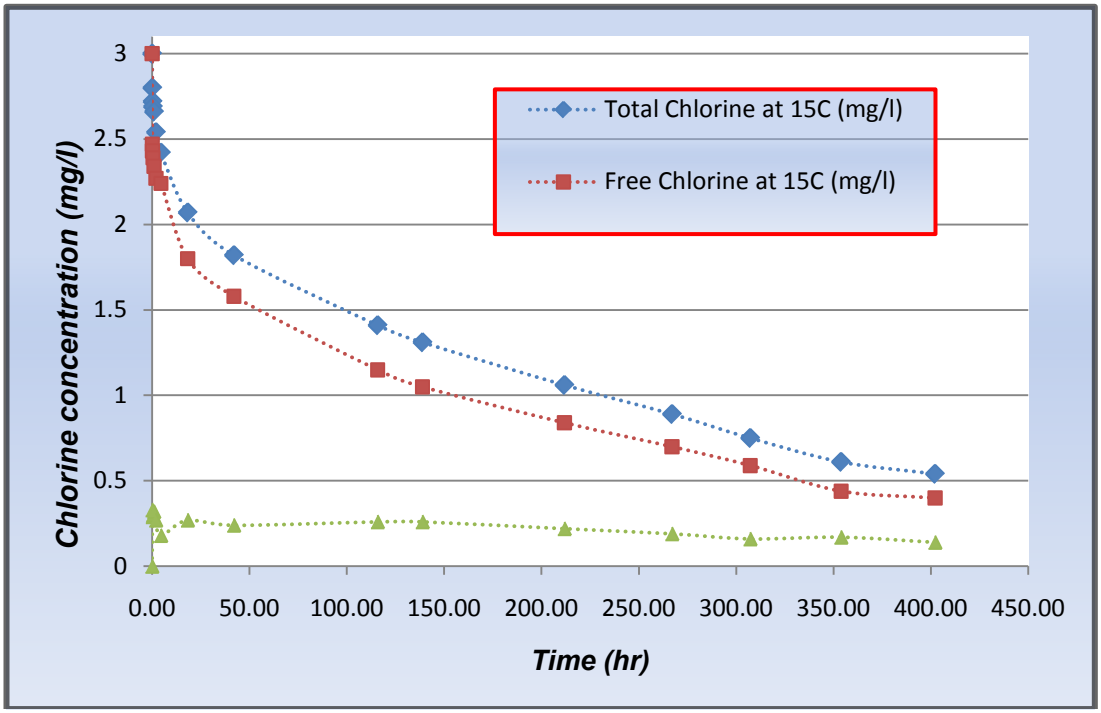

Fig. A1.9: Chlorine decay test results for Pilbara Post Filtration Water sample (PPFW3-1) at 15˚C

Table A1.10: Chlorine decay test results for Pilbara Post Filtration Water sample (PPFW3-2) at 20˚C

No.	Date & Time	Time (hr)	Total Chloruine (mg/l)	Free Chlorine (mg/l)	Combined Chlorine (mg/l)
1	9/12/2009 10:40	0.00	3	3	0.00
2	9/12/2009 10:45	0.08	2.85	2.5	0.35
3	9/12/2009 10:51	0.18	2.77	2.44	0.33
4	9/12/2009 11:00	0.33	2.68	2.35	0.33
5	9/12/2009 11:26	0.77	2.65	2.37	0.28
6	9/12/2009 11:40	1.00	2.54	2.3	0.24
7	9/12/2009 12:58	2.30	2.4	2.09	0.31
8	9/12/2009 16:00	5.33	2.23	1.85	0.38
9	9/12/2009 20:07	9.45	2.08	1.76	0.32
10	10/12/2009 9:15	22.58	1.78	1.47	0.31
11	11/12/2009 12:28	49.80	1.37	1.13	0.24
12	14/12/2009 10:28	119.80	0.77	0.58	0.19
13	16/12/2009 17:15	174.58	0.51	0.36	0.15
14	19/12/2009 20:00	249.33	0.22	0.09	0.13
15	22/12/2009 10:52	312.20	0.1	0	0.10

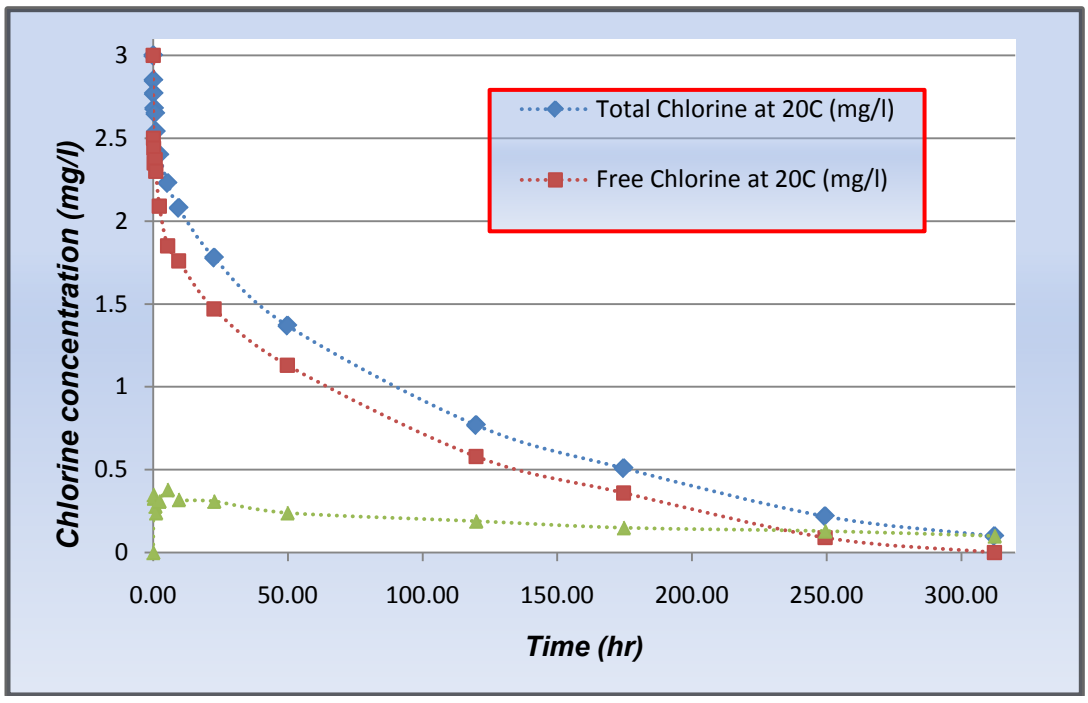

Fig. A1.10: Chlorine decay test results for Pilbara Post Filtration Water sample (PPFW3-2) at 20˚C

Table A1.11: Chlorine decay test results for Pilbara Post Filtration Water sample (PPFW3-3) at 25˚C

No.	Date & Time	Time (hr)	Total Chloruine (mg/l)	Free Chlorine (mg/l)	Combined Chlorine (mg/l)
1	8/12/2009 10:06	0.00	3	3	0.00
2	8/12/2009 10:20	0.23	2.76	2.45	0.31
3	8/12/2009 10:33	0.45	2.6	2.33	0.27
4	8/12/2009 10:47	0.68	2.56	2.26	0.30
5	8/12/2009 11:06	1.00	2.5	2.22	0.28
6	8/12/2009 11:45	1.65	2.4	2.19	0.21
7	8/12/2009 13:08	3.03	2.24	1.93	0.31
8	8/12/2009 15:05	4.98	2.16	1.9	0.26
9	8/12/2009 17:00	6.90	2.07	1.75	0.32
10	8/12/2009 17:55	7.82	2.06	1.7	0.36
11	8/12/2009 20:00	9.90	1.87	1.55	0.32
12	9/12/2009 9:25	23.32	1.52	1.29	0.23
13	9/12/2009 20:00	33.90	1.29	1.08	0.21
14	10/12/2009 20:30	58.40	0.93	0.77	0.16
15	11/12/2009 12:20	74.23	0.75	0.53	0.22
16	14/12/2009 10:15	144.15	0.23	0.12	0.11
17	14/12/2009 16:45	150.65	0.2	0.09	0.11
18	15/12/2009 8:55	166.82	0.13	0	0.13

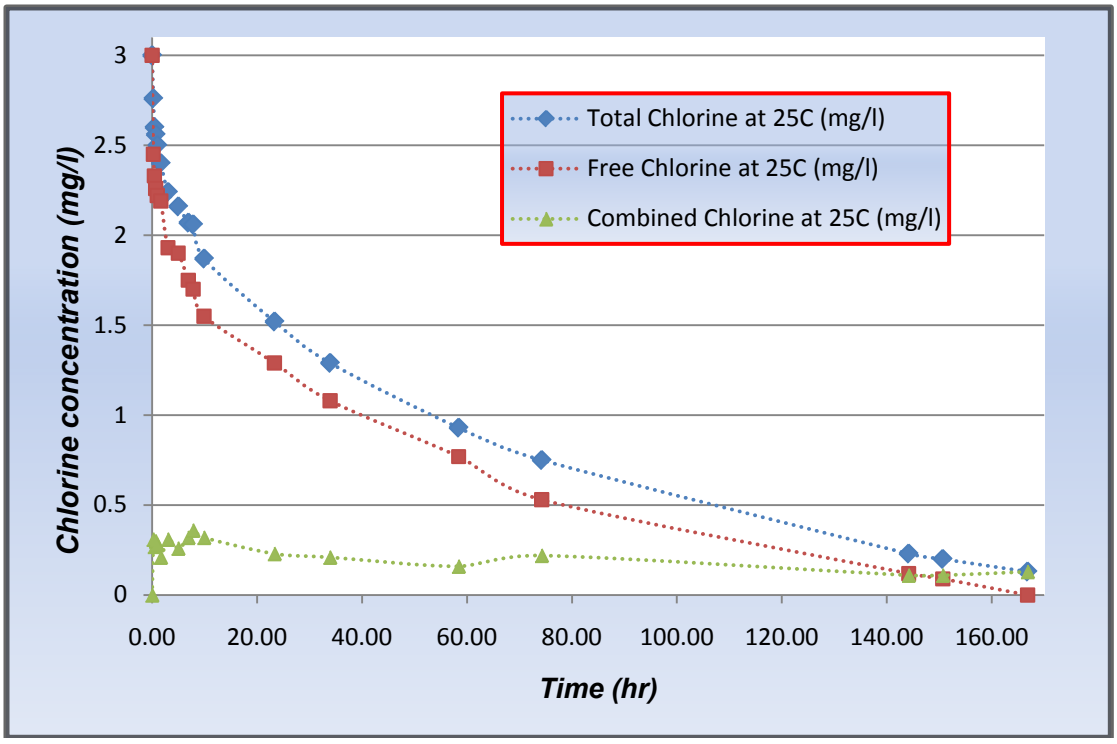

Fig. A1.11: Chlorine decay test results for Pilbara Post Filtration Water sample (PPFW3-3) at 25˚C

Table A1.12: Chlorine decay test results for Pilbara Post Filtration Water sample (PPFW3-4) at 30˚C

No.	Date & Time	Time (hr)	Total Chloruine (mg/l)	Free Chlorine (mg/l)	Combined Chlorine (mg/l)
1	6/10/2009 11:28	0.00	3	3	0.00
2	6/10/2009 11:32	0.07	2.91	2.65	0.26
3	6/10/2009 11:39	0.18	2.75	2.46	0.29
4	6/10/2009 12:08	0.67	2.69	2.36	0.33
5	6/10/2009 12:28	1.00	2.63	2.33	0.30
6	6/10/2009 12:58	1.50	2.49	2.22	0.27
7	6/10/2009 13:28	2.00	2.4	2.15	0.25
8	6/10/2009 17:15	5.78	1.8	1.56	0.24
9	6/10/2009 19:00	7.53	1.63	1.38	0.25
10	7/10/2009 9:45	22.28	0.97	0.77	0.20
11	8/10/2009 10:00	46.53	0.5	0.34	0.16
12	9/10/2009 10:40	71.20	0.22	0.08	0.14
13	12/10/2009 18:00	150.53	0.09	0	0.09

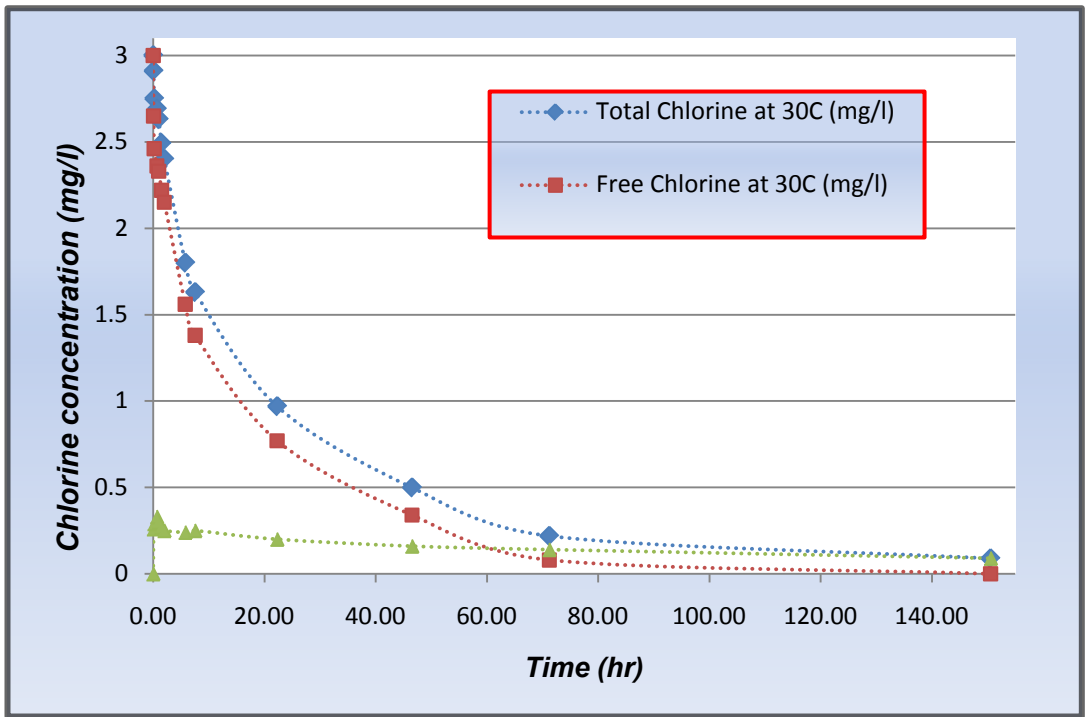

Fig. A1.12: Chlorine decay test results for Pilbara Post Filtration Water sample (PPFW3-4) at 30˚C

Table A1.13: Chlorine decay test results for Pilbara Post Filtration Water sample (PPFW3-5) at 35˚C

No.	Date & Time	Time (hr)	Total Chloruine (mg/l)	Free Chlorine (mg/l)	Combined Chlorine (mg/l)
1	15/12/2009 10:59	0.00	3	3	0.00
2	15/12/2009 11:04	0.08	2.69	2.25	0.44
3	15/12/2009 11:09	0.17	2.62	2.2	0.42
4	15/12/2009 11:19	0.33	2.59	2.25	0.34
5	15/12/2009 11:39	0.67	2.4	2.1	0.30
6	15/12/2009 11:59	1.00	2.35	2	0.35
7	15/12/2009 13:05	2.10	2.11	1.66	0.45
8	15/12/2009 14:05	3.10	1.94	1.6	0.34
9	15/12/2009 16:08	5.15	1.7	1.37	0.33
10	15/12/2009 18:50	7.85	1.43	1.22	0.21
11	16/12/2009 10:25	23.43	0.65	0.5	0.15
12	16/12/2009 17:10	30.18	0.45	0.29	0.16
13	17/12/2009 9:52	46.88	0.18	0.06	0.12

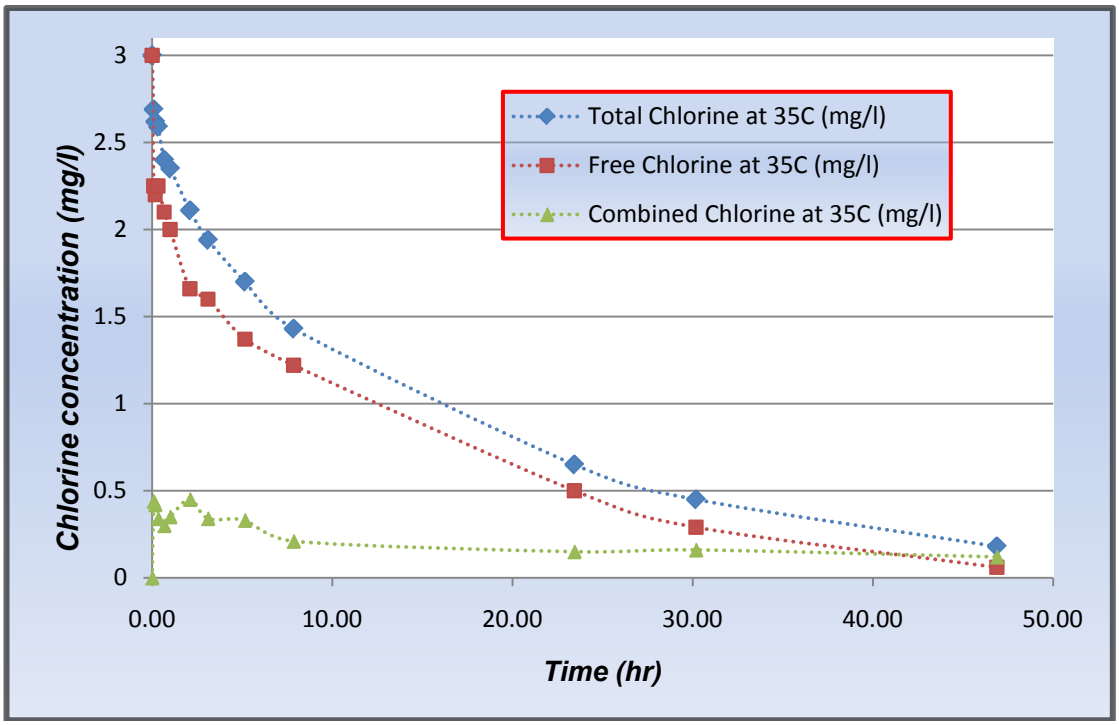

Fig. A1.13: Chlorine decay test results for Pilbara Post Filtration Water sample (PPFW3-5) at 35˚C

Table A1.14: Chlorine decay test results for Pilbara Post Filtration Water sample (PPFW3-6) at 40˚C

No.	Date & Time	Time (hr)	Total Chloruine (mg/l)	Free Chlorine (mg/l)	Combined Chlorine (mg/l)
1	17/12/2009 10:30	0.00	3	3	0.00
2	17/12/2009 10:35	0.08	2.76	2.45	0.31
3	17/12/2009 10:40	0.17	2.72	2.36	0.36
4	17/12/2009 10:50	0.33	2.57	2.3	0.27
5	17/12/2009 11:10	0.67	2.44	2.13	0.31
6	17/12/2009 11:34	1.07	2.26	1.85	0.41
8	17/12/2009 12:38	2.13	2	1.68	0.32
9	17/12/2009 14:30	4.00	1.72	1.45	0.27
10	17/12/2009 16:30	6.00	1.46	1.22	0.24
11	18/12/2009 9:45	23.25	0.49	0.35	0.14
12	18/12/2009 19:45	33.25	0.24	0.12	0.12

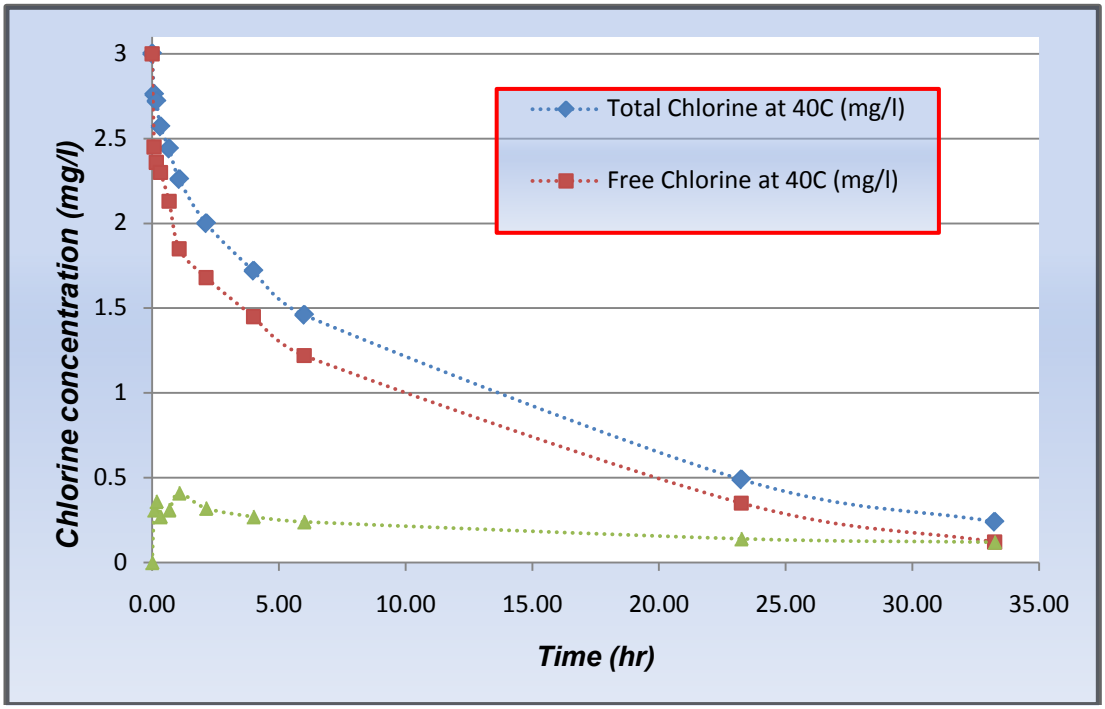

Fig. A1.14: Chlorine decay test results for Pilbara Post Filtration Water sample (PPFW3-6) at 40˚C

Table A1.15: Chlorine decay test results for Pilbara Post Filtration Water sample (PPFW3-7) at 45˚C

No.	Date & Time	Time (hr)	Total Chloruine (mg/l)	Free Chlorine (mg/l)	Combined Chlorine (mg/l)
1	22/12/2009 11:25	0.00	3	3	0.00
2	22/12/2009 11:30	0.08	2.74	2.49	0.25
3	22/12/2009 11:35	0.17	2.6	2.36	0.24
4	22/12/2009 11:45	0.33	2.54	2.12	0.42
5	22/12/2009 12:05	0.67	2.28	1.94	0.34
6	22/12/2009 12:27	1.03	2.2	1.88	0.32
8	22/12/2009 13:31	2.10	1.86	1.48	0.38
9	22/12/2009 14:27	3.03	1.67	1.34	0.33
10	22/12/2009 15:30	4.08	1.49	1.27	0.22
11	22/12/2009 18:15	6.83	1.13	0.91	0.22
12	22/12/2009 20:08	8.72	0.97	0.78	0.19
13	23/12/2009 7:45	20.33	0.34	0.21	0.13
14	23/12/2009 10:29	23.07	0.24	0.13	0.11
15	23/12/2009 12:00	24.58	0.18	0.07	0.11
16	23/12/2009 14:55	27.50	0.13	0	0.13

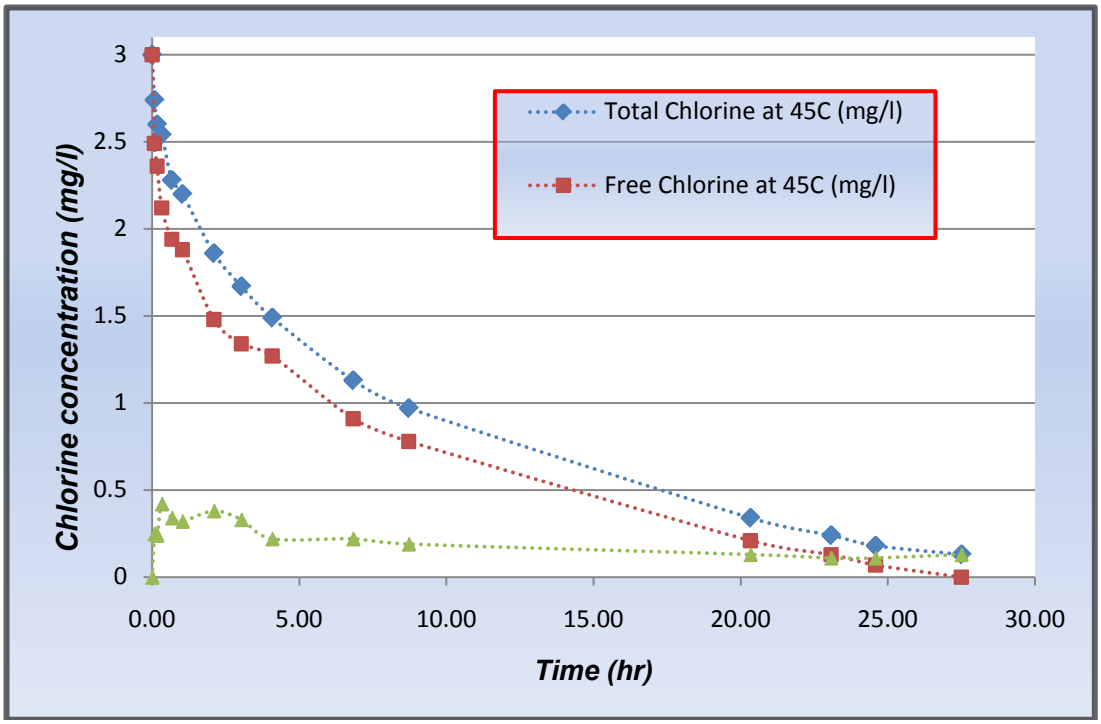

Fig. A1.15: Chlorine decay test results for Pilbara Post Filtration Water sample (PPFW3-7) at 45˚C

Table A1.16: Chlorine decay test results for Pilbara Post Filtration Water sample (PPFW3-8) at 50˚C

No.	Date & Time	Time (hr)	Total Chloruine (mg/l)	Free Chlorine (mg/l)	Combined Chlorine (mg/l)
1	23/12/2009 8:44	0.00	3	3	0.00
2	23/12/2009 8:49	0.08	2.74	2.36	0.38
3	23/12/2009 8:54	0.17	2.5	2.19	0.31
4	23/12/2009 9:04	0.33	2.34	2.02	0.32
5	23/12/2009 9:24	0.67	2.19	1.77	0.42
6	23/12/2009 9:44	1.00	2.09	1.75	0.34
8	23/12/2009 10:21	1.62	1.81	1.49	0.32
9	23/12/2009 10:44	2.00	1.63	1.45	0.18
10	23/12/2009 11:51	3.12	1.42	1.19	0.23
11	23/12/2009 12:55	4.18	1.23	0.99	0.24
12	23/12/2009 14:46	6.03	0.95	0.74	0.21
13	23/12/2009 17:40	8.93	0.6	0.45	0.15
14	23/12/2009 20:01	11.28	0.41	0.26	0.15

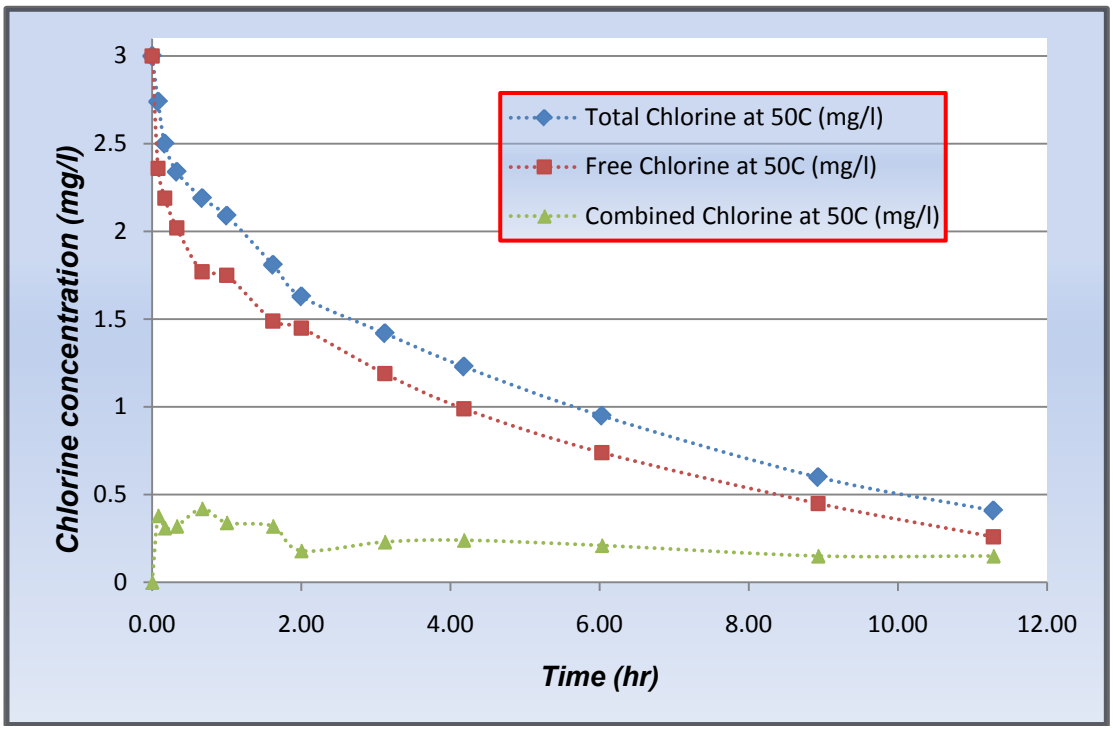

Fig. A1.16: Chlorine decay test results for Pilbara Post Filtration Water sample (PPFW3-8) at 50˚C

Appendix A2:

Comparison of Parameter Estimations and Chlorine Decay Prediction between Two Methods for Literature and Experimental Data No1; Parallel Second Order Model with AQUASIM Software against New Analytical Solution with MATLAB Program

Table A2.1: Comparison of Parameter Estimations and Chlorine Decay Prediction between Two Methods for Literature Data No1; Parallel Second Order Model with AQUASIM Software against New Analytical Solution with MATLAB Program

Literature data no1			
Sample name	Parameters	Modelling method	
		Numerical solution with parallel second order model (Eq. 16 & 19 & 20) using AQUASIM	New analytical solution (Eq. 37 & 38) using MATLAB
A.B.W257	FRA_0	2.33	2.33
	SRA_0	2.16	2.16
	k_{FRA}	1.907	1.905
	k_{SRA}	0.003	0.003
Time (hr)		Chlorine residual (mg/L)	
	Measured	Predicted with numerical solution (parallel second order model; Eq. 16 & 19 & 20) using AQUASIM	Predicted with new analytical solution (Eq. 37 & 38) using MATLAB
0	8	8	8
0.08	6.42	6.46	6.46
0.25	5.86	5.78	5.78
0.5	5.78	5.66	5.66
1	5.69	5.64	5.64
1.5	5.58	5.62	5.62
2	5.58	5.6	5.6
2.5	5.58	5.59	5.59
3	5.54	5.57	5.57
3.5	5.5	5.55	5.55
4	5.41	5.54	5.54
21	5.06	5.08	5.08
30	4.98	4.89	4.89
50	4.66	4.57	4.57
72	4.17	4.31	4.31
96	4.17	4.11	4.11
101	4.01	4.08	4.08
120	4.01	3.97	3.97
144	3.89	3.86	3.86
168	3.77	3.78	3.78

Table A2.2: Comparison of Parameter Estimations and Chlorine Decay Prediction between Two Methods for Literature Data No2; Parallel Second Order Model with AQUASIM Software against New Analytical Solution with MATLAB Program

Literature data no2			
Sample name	Parameters	Modelling method	
		Numerical solution with parallel second order model (Eq. 16 & 19 & 20) using AQUASIM	New analytical solution (Eq. 37 & 38) using MATLAB
LWR	FRA_0	2.68	2.7
	SRA_0	9.99	9.95
	k_{FRA}	0.32	0.316
	k_{SRA}	0.004	0.004
Time (hr)		Chlorine residual (mg/L)	
	Measured	Predicted with numerical solution (parallel second order model; Eq. 16 & 19 & 20)	Predicted with new analytical solution (Eq. 37 & 38) using MATLAB
0	12.2	12.2	12.2
0.4	10	10.03	10.03
0.6	9.57	9.65	9.65
1	9.5	9.26	9.26
4	8.19	8.26	8.26
8	7.12	7.3	7.3
24	5.06	4.96	4.96
48	3.35	3.32	3.32
72	2.56	2.46	2.46
96	1.96	1.94	1.94
120	1.46	1.59	1.59

Table A2.3: Comparison of Parameter Estimations and Chlorine Decay Prediction between Two Methods for Literature Data No3; Parallel Second Order Model with AQUASIM Software against New Analytical Solution with MATLAB Program

Literature data no3			
Sample name	Parameters	Modelling method	
		Numerical solution with parallel second order model (Eq. 16 & 19 & 20) using AQUASIM	New analytical solution (Eq. 37 & 38) using MATLAB
GWT	FRA_0	1.22	1.23
	SRA_0	2.89	2.88
	k_{FRA}	0.535	0.524
	k_{SRA}	0.007	0.007
Time (hr)	Chlorine residual (mg/L)		
	Measured	Predicted with numerical solution (parallel second order model; Eq. 16 & 19 & 20)	Predicted with new analytical solution (Eq. 37 & 38) using MATLAB
0	4.03	4.03	4.03
0.4	3.23	3.34	3.34
0.6	3.2	3.16	3.16
1	3.04	2.95	2.95
4	2.61	2.58	2.58
8	2.3	2.39	2.39
24	1.86	1.86	1.86
48	1.41	1.38	1.38
72	1.13	1.1	1.1
96	0.9	0.91	0.91
120	0.75	0.77	0.77

Table A2.4: Comparison of Parameter Estimations and Chlorine Decay Prediction between Two Methods for Literature Data No4; Parallel Second Order Model with AQUASIM Software against New Analytical Solution with MATLAB Program

Literature data no4			
Sample name	Parameters	Modelling method	
		Numerical solution with parallel second order model (Eq. 16 & 19 & 20) using AQUASIM	New analytical solution (Eq. 37 & 38) using MATLAB
CWT	FRA_0	1.3	1.32
	SRA_0	3.16	3.12
	k_{FRA}	0.557	0.545
	k_{SRA}	0.009	0.009
Time (hr)		Chlorine residual (mg/L)	
	Measured	Predicted with numerical solution (parallel second order model; Eq. 16 & 19 & 20)	Predicted with new analytical solution (Eq. 37 & 38) using MATLAB
0	3.62	3.62	3.62
0.4	2.89	2.92	2.92
0.6	2.71	2.73	2.73
1	2.56	2.5	2.5
4	2.13	2.08	2.08
8	1.8	1.88	1.89
24	1.34	1.35	1.35
48	0.94	0.91	0.91
72	0.7	0.65	0.65
96	0.5	0.49	0.49
120	0.32	0.38	0.38

Table A2.5: Comparison of Parameter Estimations and Chlorine Decay Prediction between Two Methods for Experimental Data No1; Parallel Second Order Model with AQUASIM Software against New Analytical Solution with MATLAB Program

Experimental data no1			
Sample name	Parameters	Modelling method	
		Numerical solution with parallel second order model (Eq. 16 & 19 & 20) using AQUASIM	New analytical solution (Eq. 37 & 38) using MATLAB
PRW	FRA_0	1.18	1.19
	SRA_0	1.84	1.83
	k_{FRA}	2.466	2.427
	k_{SRA}	0.035	0.035
Time (hr)		Chlorine residual (mg/L)	
	Measured	Predicted with numerical solution (parallel second order model; Eq. 16 & 19 & 20)	Predicted with new analytical solution (Eq. 37 & 38) using MATLAB
0.0	3	3	3
0.1	2.3	2.41	2.42
0.2	2.11	2.14	2.14
0.3	2.04	1.99	1.99
0.4	2.01	1.89	1.89
0.7	1.83	1.76	1.76
1.0	1.71	1.71	1.71
1.6	1.64	1.64	1.64
2.0	1.49	1.6	1.6
4.6	1.31	1.4	1.4
6.8	1.23	1.26	1.26
21	0.79	0.77	0.77
29	0.69	0.63	0.63
50	0.48	0.43	0.43
118	0.13	0.2	0.2

Table A2.6: Comparison of Parameter Estimations and Chlorine Decay Prediction between Two Methods for Experimental Data No2; Parallel Second Order Model with AQUASIM Software against New Analytical Solution with MATLAB Program

Experimental data no2			
Sample name	Parameters	Modelling method	
		Numerical solution with parallel second order model (Eq. 16 & 19 & 20) using AQUASIM	New analytical solution (Eq. 37 & 38) using MATLAB
PPFW	FRA_0	0.67	0.67
	SRA_0	2.3	2.3
	k_{FRA}	4.817	4.81
	k_{SRA}	0.004	0.004
Time (hr)		Chlorine residual (mg/L)	
	Measured	Predicted with numerical solution (parallel second order model; Eq. 16 & 19 & 20)	Predicted with new analytical solution (Eq. 37 & 38) using MATLAB
0.0	3	3	3
0.1	2.47	2.51	2.51
0.2	2.43	2.38	2.38
0.4	2.39	2.32	2.32
1.0	2.34	2.3	2.3
2.0	2.27	2.28	2.28
5.0	2.24	2.22	2.22
18.0	1.8	1.98	1.98
42.0	1.58	1.65	1.65
116.0	1.15	1.09	1.09
139.0	1.05	0.98	0.98
212	0.84	0.76	0.76
267	0.7	0.65	0.65
307	0.59	0.58	0.58
354	0.44	0.52	0.52
402	0.4	0.48	0.48

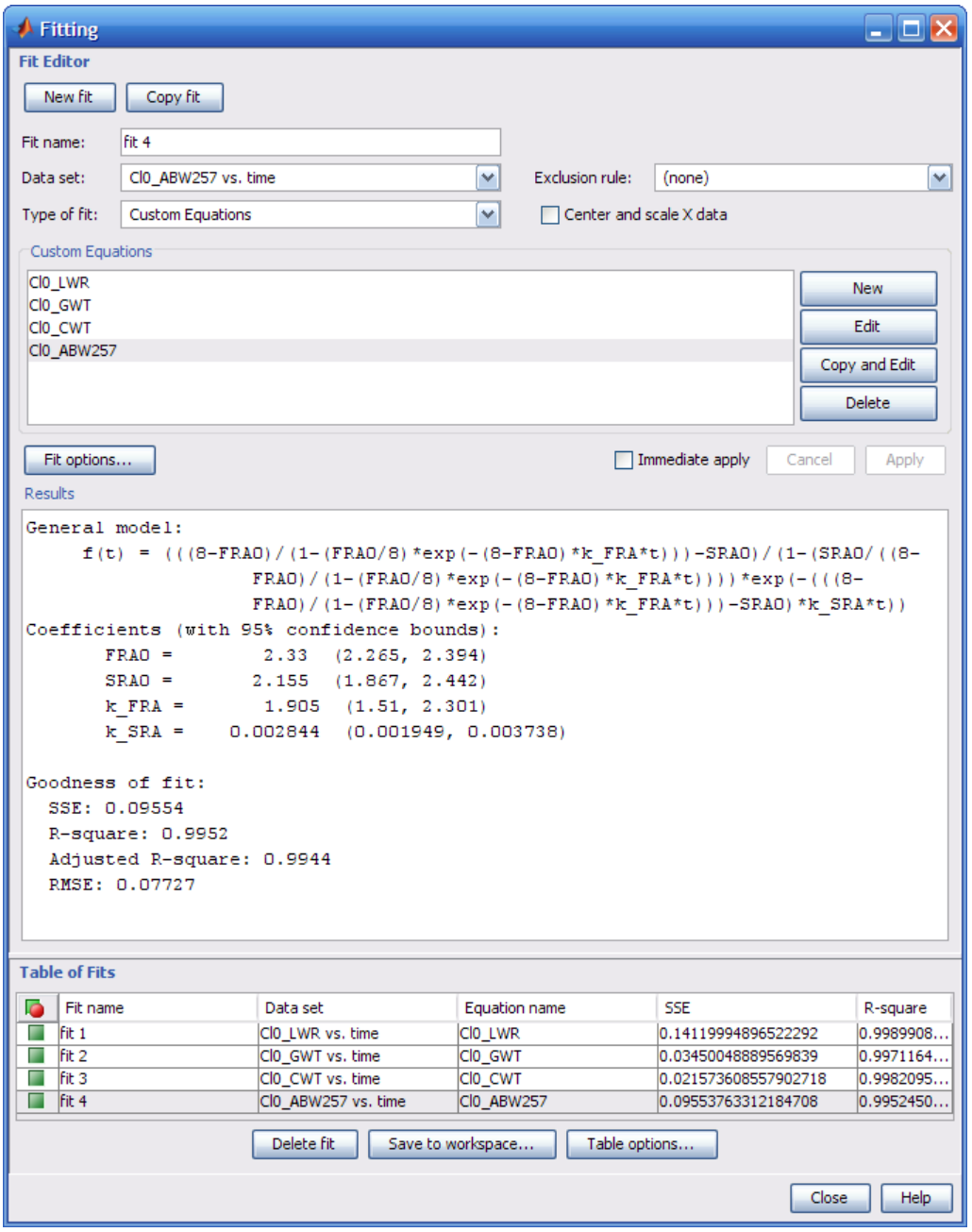

Figure A2.1: Parameter estimation for different initial dosing with different sets of parameters for Literature Data; new analytical solution with MATLAB program

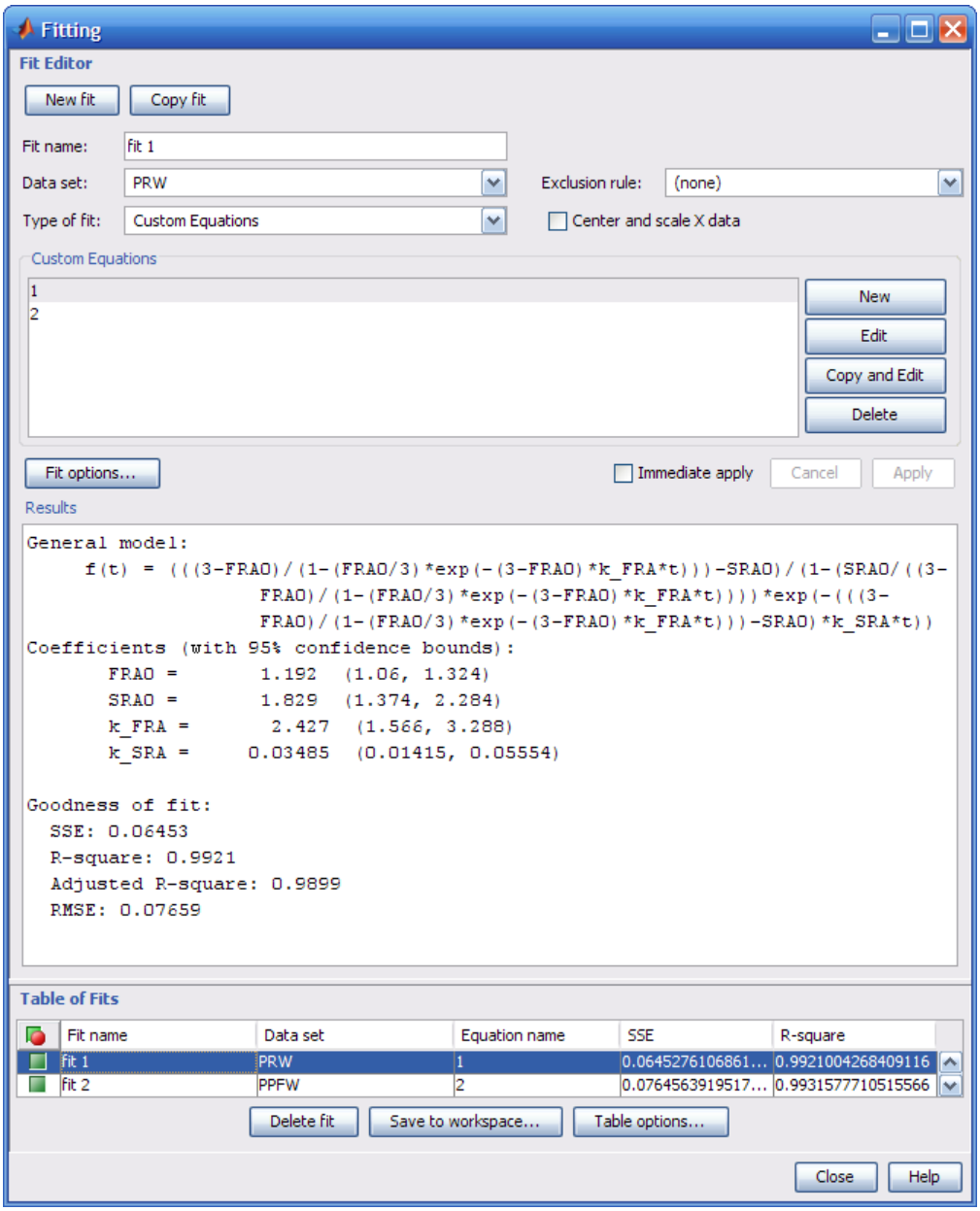

Figure A2.2: Parameter estimation for different initial dosing with different sets of parameters for Pilbara Water Samples; new analytical solution with MATLAB program

Appendix A3: Publications

1- Comment on ''Using Bayesian statistics to estimate the coefficients of a two-component second-order chlorine bulk decay model for a water distribution system'' by Huang, J.J., McBean, E.A. Water Res. (2007)

Ian Fisher [a,*], ***Ahmad Jabari Kohpaei*** [b], *Arumugam Sathasivan* [b]

[a] Watervale Systems P/L, PO Box 318, Potts Point, NSW 1335, Australia
[b] Department of Civil Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

2- Chlorine decay modelling in waters at high temperature

Ahmad Jabari Kohpaei [1], *Arumugam Sathasivan* [2], *Ian Fisher* [3], *Paul Nolan* [4]
1. Research student, Curtin University of Technology, Department of civil engineering, Perth, WA
2. Senior Lecturer PhD, Curtin University, Department of civil engineering, Perth, WA
3. PhD CPEng, Watervale Systems Pty Ltd, Sydney, NSW
4. CPEng, Research and Development, Water Corporation, Perth, WA

3- An analytical solution for the chlorine decay modelling with the parallel second order kinetics

Ahmad Jabari Kohpaei*, Arumugam Sathasivan*
Department of Civil Engineering, Curtin University,
GPO Box U1987, Perth,WA 6845, Australia.

4- Evaluation of the parallel second order kinetics against the first and second order models for the prediction of chlorine residual in bulk waters

Ahmad Jabari Kohpaei*, Arumugam Sathasivan, Hanieh Aboutalebi*
Department of Civil Engineering, Curtin University,
GPO Box U1987, Perth,WA 6845, Australia.

5- Evaluation of the temperature analysis for the chlorine decay modelling using the second order model (SOM) and the parallel second order method (PSOM) in bulk water

Ahmad Jabari Kohpaei*, Arumugam Sathasivan, Hanieh Aboutalebi*
Department of Civil Engineering, Curtin University,
GPO Box U1987, Perth,WA 6845, Australia.