ELECTROCHEMICAL GENERATION OF CHLORINE FOR DISINFECTION IN CONTINUOUS FLOW PROCESS

ABDUL GHAFAR BIN ABD HALIM

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By

ABDUL GHAFAR BIN ABD HALIM
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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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(ASSOC. PROF. DR. MOHAMED HASNAIN ISA)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

ABDUL GHAFAR BIN ABD HALIM

ABSTRACT

In-situ generation of chlorine was obtained by electrochemical process using Metal Oxides - coated titanium as anode and Titanium as cathode. In this process, its effect will be mainly based on the electrochemical production of hypochlorite and/or hypochlorous acid from the chloride content of the water. Brine solutions which consist of different concentration of sodium hydroxide (NaCl) were being prepared for electrolysis at different conditions such as flow rate of brine solution entering reactor (4 mL/min – 12 mL/min), electrodes configurations, brine solution pH (2 - 7), chloride concentrations (3.6 mg/L – 100 mg/L) and current densities (1.33 mA/cm^2 – 4 mA/cm^2) in a continuous flow process. The system was running for 5 minutes before the 1 litre of sample taken so that the system was stabilized. Two conditions that have been identified to produced optimum value of free available chlorine (FAC) was at pH 5 which yield as high as 800 mg/L and electrodes configuration that produce optimum FAC was arrangement B, which produced 640 mg/L of FAC. From the 3D surface plot, it was found that FAC production increases with increase in chloride concentration and current density but reduces with increase in flow rate. Furthermore at 3.6 mg/L chloride concentration, sufficient amount of FAC was produced for disinfection where 0.23 mg/L, 1.98 mg/L and 2.38 mg/L of FAC was produced at current densities of 4 mA/cm^2 and flow rate of 4 mL/min, 8 mL/min and 12 mL/min respectively.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Chlorine is one of the most commonly used disinfectants throughout the world. The principle chlorine compounds used at wastewater-treatment plants are gaseous chlorine (Cl_2), sodium hypochlorite ($NaOCl$), calcium hypochlorite [$Ca(OCl)_2$], and chlorine dioxide (ClO_2) (Kraft, 2008). Many large cities have switched from chlorine gas to sodium hypochlorite because of the safety concerns related to handling and storage of liquid chlorine (Kraft, 2008).

Although the use of chlorine for the disinfection of both potable water supplies and treated wastewater has been of great significance from a public health perspective, serious concerns have been raised of its continued use. Important concerns include (Metcalf and Eddy, 2004):

1. Chlorine is a highly toxic substance that is transported by rail and truck, both of which are prone to accidents.
2. Chlorine is a highly toxic substance that potentially poses health risks to treatment plant operators and the general public if released by accident.
3. As chlorine is a highly toxic substance, stringent requirements for containment and neutralization must be implemented as specified in the Uniform Fire Code (UFC).
4. Chlorine reacts with the organic constituents in wastewater to produce odorous compounds.
5. Chlorine reacts with the organic constituents in wastewater to produce by products, many of which are known to be carcinogenic and/or mutagenic.
6. Concerns exist over the discharge of chloro-organic compounds to the environment whose long-term effects are not known.
7. Residual chlorine in treated wastewater effluent is toxic to aquatic life.

Thus, one of the ways to make chlorination safer for disinfection is by eliminating the hazards related to transportation and storage of chlorine. This could be done by producing it in-situ. In-situ chlorine generation for water disinfection can be done by using electrochemical process. Different terms have been in use to describe this type of water treatment process or the water produced by this process, such as 'electrolytic disinfection', 'electrochemical disinfection', 'anodic oxidation', 'functional water' and 'electrochemically activated water' (Kraft, 2008).

Electrochemical water disinfection is a rarely used but convenient and highly efficient way to produce germ-free water. The technique works without the addition of chemical compounds to the water to be treated, but is nevertheless based on the biocidal action of various chemical substances (Kraft, 2008).

A batch study (Yusoff, 2008) on electrochemical water disinfection was conducted in the last Final Year Project (FYP) and the optimum criteria for hypochlorite production in a batch system were found. A continuous study will be done in this project to search for the optimum criteria when the electrochemical water disinfection process is applied to a continuous flow.

1.2 PROBLEM STATEMENT

1.2.1 PROBLEM IDENTIFICATION

Chemical agents that have been used as disinfectants such as chlorine introduce hazards to the environment. Many safety concerns related to the transport, storage, and feeding of liquid-gaseous chlorine can create a dangerous situation such as the potential discharge of a toxic vapour cloud due to accident while it is transported or due to leakage at the chlorine storage site.

1.2.2 SIGNIFICANCE OF THE PROJECT

The hazards related to transport and storage of chlorine can be eliminated by generating it in-situ. Further study on in-situ chlorine generation will help in terms of minimizing the hazards towards people and environment, reducing maintenance such as to test leakage from the storage tanks.

1.3 OBJECTIVES

The main objectives of this project are:

1. To determine the effectiveness of in-situ free available chlorine (FAC) generation using low chloride concentrations.
2. To determine the flow rate, pH, concentration of electrolyte, current density and suitable arrangement of the electrodes for the optimum production of (FAC).

1.4 SCOPE OF STUDY

The study will focus on the in-situ hypochlorite ion generation using Metal Oxide-coated Titanium electrodes which have been found to produce optimum FAC (Yusoff, 2008), and Sodium Chloride (NaCl) brine solution electrolyte in a continuous flow system. The amount of free available chlorine generated will be monitored. Effect of the process on electrodes will also be studied.

CHAPTER 2

LITERATURE REVIEW

2.1 SCENARIO ON CHLORINE TRANSPORTATION

Chlorine is one of many industrial agents that are harmful, yet used extensively in processing and transported in bulk. Chlorine gas is so deadly that it was used as a chemical weapon in the trenches of World War I. Yet chemicals like chlorine are essential to modern life and supplies are needed in every city. Chlorine is used as a key disinfectant for the water supply in cities, and is commonly used in cleaning and bleaching agents, for paper production, and to manufacture plastic products (NTSB, 1998).

Chlorine ranks eighth in terms of the quantities of chemicals manufactured in the U.S., and is transported across the nation in more than 100,000 shipments each year (NTSB, 1998). Chlorine shipments probably have no more or fewer accidents than other hazardous materials per mile of transportation, but a number of recent accidents have highlighted the danger chlorine poses when released near populated areas (NTSB 1998). Cases involving chlorine transportation are discussed in Section 2.1.1.

Chlorine is transported and stored as liquid under high pressure. If it was released in the atmosphere, it could quickly vaporize into a toxic gas cloud nearly 500 times its pressurized volume (Gautrin et al., 1999). The trend is now for on site generation.

2.1.1 METRA TRAIN (CHICAGO) CRASHED WITH CHLORINE TANKER

On June 2000, the commuters on the 7:30 am METRA train from Chicago's western suburbs into Union Station crashed into cars and also a tanker containing 90 tons of pressurized liquid chlorine, splitting one of them open and damaging a second one. A jet of chlorine gas exploded out through the rupture. It took fifteen minutes for the tanker to empty (NTSB, 1998).

The sub-zero temperature outside was 34 degrees warmer than chlorine's boiling point. A plume of yellow-green gas reached 50 feet (15 meters) into the air.
The billowing cloud filled the railway tracks. Three commuter trains were halted on the approaching tracks to the accident, each crowded with more than 400 people on board. Within minutes the trains are full of the lethal gas (NTSB, 1998).

The chlorine gas was blown away carrying it to North West area in which the gas entered the air heating system in buildings in which nearly all the workers or students were. Figure 1.1 shows area in Chicago that was affected by chlorine gas while Figure 1.2 shows clouds of chlorine vapours at the scene. Hundreds of workers choked to death in minutes as the dense chlorine poured in through the air heating system. Others suffer permanent lung damage and skin burns. In a nine-storey office building nearby, the chlorine filled the bottom two floors, killing many occupants, but workers who manage to get up above the third floor survived (NTSB, 1998).

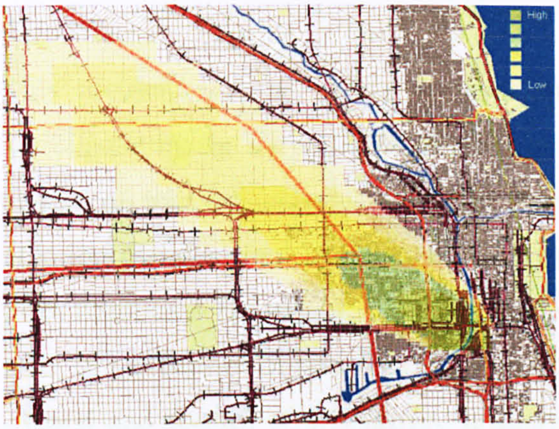


Figure 1.1: Area in Chicago that Is Affected by chlorine gas, Source: (NSTB, 1998)

Figure 1.2: Clouds of chlorine vapours seen at the scene, Source: (NSTB, 1998)

2.1.2 MASSIVE LEAK OF LIQUEFIED CHLORINE GAS, HENDERSON, NEVADA

Massive leaks of liquefied chlorine gas that occured created a dangerous cloud of poison gas over the city of Henderson, Nevada, in the early morning hours of May 6, 1991. Over 200 persons were examined at a local hospital for respiratory distress caused by inhalation of the chlorine and approximately 30 people were admitted for treatment. Approximately 700 individuals were taken to shelters. It is estimated that from 2,000 to 7,000 individuals were taken elsewhere (Routley, 1991).

Chlorine gas was released caused by leak of brine from heat exchanger mixing with liquefied gas. Mixture created corrosive acid which ate through pipes when product was transferred from storage tank. Leak increased as acid ate larger hole in pipe. Approximately 70 tons of chlorine escaped. Chlorine gas cloud dissipated with morning heat and winds (Routley, 1991).

This accident was so crucial because this plant is located Clark County Island surrounded by the City of Henderson. Thus the population at the city were primarily at risk of inhaling chlorine gas. Fire fighters and plant personnel overcome when chlorine cloud moved in unexpected direction. Command Post had to be relocated three times to avoid moving cloud. Some residents exposed during evacuation;
over 200 examined at hospitals; 30 admitted. Citizens evacuated as leak continued to expand and control efforts proved unsuccessful. Approximately 700 people taken to shelters; 2,000 to 7,000 taken elsewhere. Police officers who was assisting with evacuation and traffic control was also exposed to chlorine gas cloud (Routley, 1991).

2.1.1.3 CHLORINE TANKER RUPTURED IN ALBERTON, MONTANA

In 1996, a train derailed in a sparsely populated stretch of line near Alberton, Montana Tanker cars ruptured, venting at least 17,000 gallons (64,000 litres) of chlorine as a dangerous plume of gas, although some reports estimate up to 100,000 gallons (378,000 litres) were lost. This plume was mainly directed across the Clark Fork River. Fortunately, there was not a major town in the vicinity, but 352 people were hospitalized and one person died (NTSB 1998).

2.2 BASIC PRINCIPLES OF DISINFECTION

Disinfection in water and wastewater treatment systems may be defined as the destruction of pathogens (e.g., bacteria, viruses, protozoan, or amoebic cysts) to provide public health protection (Metcalf and Eddy, 2004). Disinfectant chemicals for use in water, wastewater, and cooling tower applications include chlorine and its compounds (e.g., chloramines, sodium hypochlorite, and chlorine dioxide) (Metcalf and Eddy, 2004).

Design considerations and operational factors for disinfectant systems are as follows (Casson and Bess, 2003):

1. The microorganisms to be inactivated
2. The concentration of microorganisms in the water
3. The water quality in which disinfection will occur
4. The variability of the water quality
5. The type of disinfectant chosen for application
6. The dose or concentration of the disinfectant applied
7. The contact time of the disinfectant with the microorganisms

2.3 ELECTROCHEMICAL WATER DISINFECTION

Compared to other chemical disinfection methods, the advantages of electrochemical water disinfection are obvious: no transport, storage and dosing of disinfectants are required. The disinfecting effect can be adjusted according to on-site demand. Electrochemical water disinfection shows a reservoir effect and is often more cost effective and requires less maintenance than other disinfection methods. Photovoltaic power supply makes it possible to use electrochemical water disinfection far from the electrical supply grid and this may be important for its application to drinking water in developing countries (Kraft, 2008).

In electrochemical water disinfection, electrodes (at least one cathode and one anode) are inserted either directly into the volume of water to be disinfected, or into a bypass pipe (Kraft, 2008). A Direct Current (DC) voltage is applied between the electrodes, leading to the electrolysis of the water. At the anode, the main product is oxygen (Equation 2.1) and accompanied by an acidification of the water in the vicinity of the anode. At the cathode, hydrogen is formed (Equation 2.2) (Kraft, 2008):

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.1)$$

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.2)$$

2.4 FREE AVAILABLE CHLORINE

In the nomenclature of water disinfection, the sum of concentrations of molecular chlorine (Cl_2), hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) concentrations is usually termed ‘free chlorine’ or ‘active chlorine’(Metcalf and Eddy, 2004). Free available chlorine or FAC in these forms has a strong tendency to gain electrons to obtain a more stable minus one (-1) oxidation state, as found in chloride. In this reaction, FAC serves as an oxidizing agent, and chloride is the ground state that is no longer very reactive. Many of reactive properties of free chlorine are a result of the strong tendency to return to this ground state (Bryant et al., 1992).

2.5 PRODUCTION OF FREE AVAILABLE CHLORINE FROM THE CHLORIDE CONTENT OF WATER

If electrochemical disinfection is applied to drinking water, industrial water, or other solute-containing water, its effect is mainly based on the electrochemical production of hypochlorite and/or hypochlorous acid from the chloride content of the water (Kraft, 2008).

The disinfectants or the free available chlorine is produced at the anode in a side reaction to oxygen evolution. The following simplified reaction mechanism describes the process. First, chlorine is produced electrochemically from chloride ions dissolved in the water (Equation 2.3) (Khelifa et al., 2004):

$$2Cl^- \longrightarrow Cl_2 + 2e^- \ldots\ldots\ldots\ldots\ldots\ldots (2.3)$$

Chlorine hydrolyses in water and hypochlorous acid (HClO) is formed (Equation 2.4):

$$Cl_2 + H_2O \longrightarrow HClO + HCl \ldots\ldots\ldots\ldots\ldots (2.4)$$

Hypochlorous acid and the hypochlorite anion form pH dependant equilibrium (Equation 2.5):

$$HClO \rightleftharpoons ClO^- + H^+ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.5)$$

The disinfecting effect of free available chlorine is based on the release of atomic oxygen according to Equations (2.6) and (2.7):

$$HClO \longrightarrow O + Cl^- + H^+ \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.6)$$

$$ClO^- \longrightarrow O + Cl^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.7)$$

During the disinfection, chloride ions which have been consumed by electrochemical free chlorine production are reformed. Thus there is no overall change in the chemical composition of the water during electrochemical water disinfection (Khelifa et al, 2004).

2.6 EFFECTIVENESS OF HYPOCHLORITE GENERATION FOR WATER DISINFECTION

The effectiveness of this method has always been accepted for water which contains higher concentrations of chloride ions (Kuhn and Lartey, 1975), such as seawater with about 19 g/l chloride (Adamson et al., 1963), or where large amounts of sodium chloride have been added, for instance to swimming pool water (chloride concentrations here are usually about (2 – 5 g/l) (Kuhn and Lartey, 1975)

For the disinfection of drinking water and other waters with much lower chloride content, the effectiveness of the method was not clear for a long time (Kraft, 2008). It was eventually demonstrated that even at very low chloride concentrations (less than 100 mg/l) sufficient free chlorine can be produced to efficiently disinfect water. Table 2.1 shows comparison of sodium hypochlorite with other commonly used disinfectants.

A research showed on the efficiency of an electrochemical disinfection technology against a range of pathogens such as *Escherichia coli* and bacteriophage *MS2.* Disinfection of *E. coli* was shown to increase with increasing chlorine generation. After treatment for 60 minutes and a chlorine residual concentration of 1.6 mg/L, total measurable inactivation (7 log) of E. coli was achieved (Kerwick et al., 2005). Figure 2.1 shows the effectiveness of generated chlorine species for disinfection.

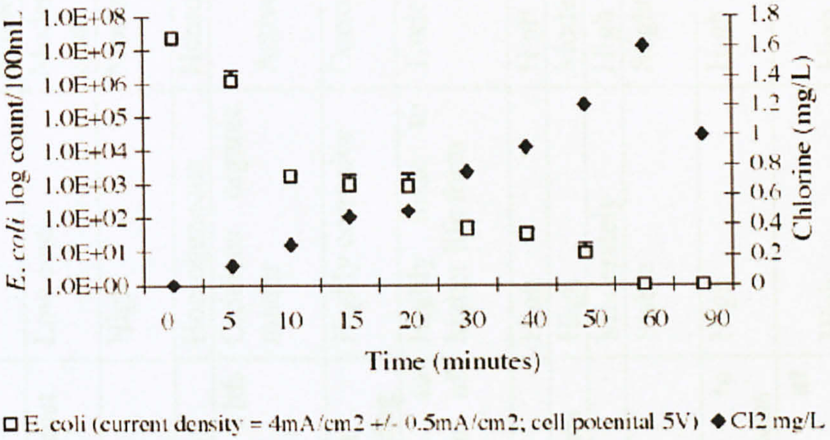


Figure 2.1: *E.coli* inactivation in a 0.01 M sodium chloride electrolyte at current densities of ± 0.5 mA/cm^2 (Kerwick et al., 2005).

Table 2.1: Comparison of ideal and actual characteristics of sodium hypochlorite and other commonly used disinfectants [a, b]

Characteristic [a]	Chlorine	Sodium hypochlorite	Calcium hypochlorite	Chlorine dioxide	Ozone	UV radiation
Availability/cost	Low cost	Moderately low cost	Moderately low cost	Moderately low cost	Moderately high cost	Moderately high cost
Deodorizing ability	High	Moderate	High	High	High	na
Homogeneity	Homogeneous	Homogeneous	Homogeneous	Homogeneous	Homogeneous	na
Interaction with extraneous material	Oxidizes organic matter	Active oxidizer	Active oxidizer	High	Oxidizes organic matter	Absorbance of UV radiation
Noncorrosive and nonstaining	Highly corrosive	Corrosive	Corrosive	Highly corrosive	Highly corrosive	na
Nontoxic to higher form of life	Highly toxic to higher life form	Toxic	Toxic	Toxic	Toxic	Toxic
Penetration	High	High	High	High	High	Moderate
Safety concern	High	Moderate	Moderate	High	Moderate	Low
Solubility	Moderately	High	High	High	High	na
Stability	Stable	Slightly unstable	Relatively stable	Unstable, must be generated as used	Unstable, must be generated as used	na
Toxicity to microorganisms	High	High	High	High	High	High
Toxicity at ambient temperature	High	High	High	High	High	High

[a] See Table A1 for description of each characteristics; [b] na = not applicable (Metcalf and Eddy, 2004)

2.7 EFFECTS OF FLOW RATE, SALT CONCENTRATIONS AND TEMPERATURE ON FAC GENERATION

Flow rate of brine solution, salt concentrations and temperature affect the production of total residual chlorine. (Hsu, 2005) stated that the total residual chlorine increased with increased of salt concentration and decreases of water flow rate. Figure 2.2 and Figure 2.3 show the effects of flow rate as it decreases which produce the highest residual chlorine and also effects of salt concentration and temperature on residual chlorine production.

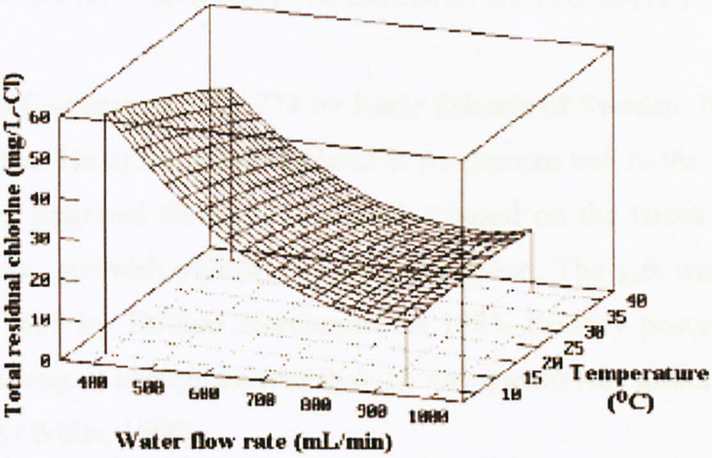


Figure 2.2: Total residual chlorine concentrations of electrolyzed oxidizing water with respect to water flow rate and temperature of input solution

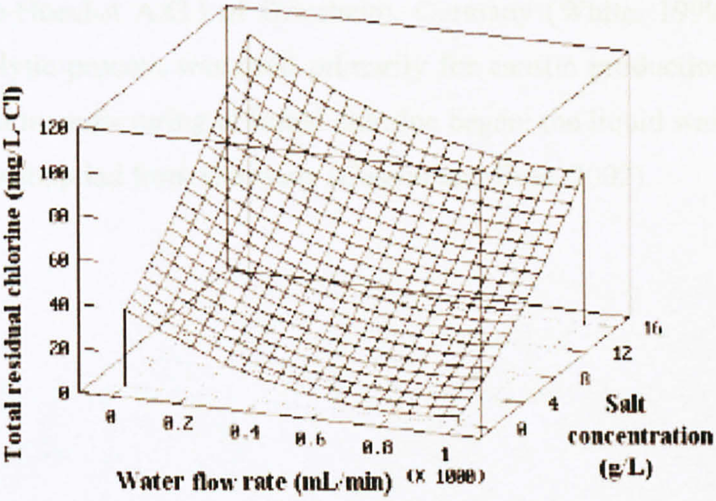


Figure 2.3: Total residual chlorine concentrations of electrolyzed oxidizing water with respect to salt concentrations and temperature of input solution

2.8 SODIUM HYPOCHLORITE (NaOCl)

Sodium hypochlorite solution is usually selected because safety in transport and handling are prime considerations. Chlorine is contained in a solution as hypochlorite, there by reducing risks of accidental release of chlorine gas. Sodium hypochlorite is also selected at many smaller installations since it can be fed using relatively simple methods that include solution feed pumps, hydraulic eductors, or simply gravity flow (Bryant et al., 1992).

2.8.1 ORIGIN OF SODIUM HYPOCHLORITE GENERATION

Chlorine gas was first prepared in 1774 by Karle Scheele of Sweden. It was not until 1810, however, that Humphry Davy declared it an element before the Royal Society of London. Davy proposed the name of chlorine based on the Greek word *chloros* translated to green, greenish yellow, or yellowish green. The gas was liquefied by compression in 1805 by Thomas Northmore. In 1883, Faraday postulated the laws governing the passing of electric current through an aqueous salt solution, coining the word electrolysis (White, 1999).

The first commercial production of chlorine began in 1890 by the Elektron Company (now Fabwerke-Hoechst A.G.) of Griesheim, Germany (White, 1999). At first, the original electrolytic process was used primarily for caustic production. In 1909, the first commercial manufacturing of liquid chlorine began; the liquid was stored in 100-pound cylinders supplied from Germany (Casson and Bess, 2002).

2.8.2 ON SITE GENERATION OF SODIUM HYPOCHLORITE

On-site sodium hypochlorite generation was feasible at the turn of the 20th century; the limitation was the electrode materials, carbon or platinum, which would dissolve in the electrolyte and caused cell damage, poor product quality and it is too expensive for practical use. No cell was developed during this period to provide reliable on-site sodium hypochlorite generation (White, 1999).

Not until the development of the dimensionally stable anode for the chlorine industry in 1967 by an independent Belgian scientist, Henry Beer, was a reliable economic on site generation cell practical. In 1971 J.E. Bennet, using the dimensionally stable anode, developed an unseperated electrolytic cell that was patented by Diamond Shamrock Corporation. Many variations in the electrodes and cell configuration have become available in the marketplace during the ensuing 25 years for electrolysis of both dissolved salt solution and seawater as the system feed stock (White, 1999).

Several proprietary systems are available for the generation of sodium hypochlorite from sodium chloride (NaCl) or seawater. These systems are electrical power intensive and, in the case of the generation from seawater, result in a very dilute solution, a maximum of 0.8 percent hypochlorite. (Metcalf and Eddy, 2004).

2.9 HYPOCHLORITE SYSTEM

Hypochlorite systems can be classified into two basic types, brine electrolysis and seawater electrolysis. The basis for classification is the feed stock derived from either crystallized salt brine systems or seawater feed for seawater electrolysis system (Casson and Bess, 2002).

In on site generation, sea water systems tend to be less efficient, thereby resulting in excess sodium in the hypochlorite solution; brine solutions are preferable, especially where sodium levels must be limited in water (Bryant et al., 1992).

Basic components of hypochlorite systems include provisions for the delivery and unloading, storage facilities and feed tanks, and solution feed equipment and piping. Dilution tanks maybe required where low dosages would otherwise reduce the feed volume below levels that can be reasonably controlled with available metering systems (Bryant et al., 1992).

Although the product of each system is the same sodium hypochlorite disinfectant, differences in the electrolysis method exists as a result of the variations in the calcarious hardness and other properties of the feed material (Casson and Bess, 2002). For brine system, crystallized salt were being used for electrolysis and the calcarious component can be controlled using water softening in order to remove calcium or magnesium from the feed water (Casson and Bess, 2002).

In design of hypochlorite systems, there are several factors that need to be considered such as corrosivity and degradation of the hypochlorite. Hypochlorite can be extremely corrosive to wood and most metals. As such, solutions are normally stored in plastic, fibreglass or rubber lined containers or tanks. All hypochlorite degrade over time, resulting in reduction in solution strength. Factors that can affect the actual rate of hypochlorite degradation are listed below (Bryant et al., 1992):

1. Solution impurities: hypochlorite degradation can be accelerated in the presence of some impurities such as iron, copper, nickel, and cobalt. (White, 1999) suggest that copper and iron should not present at levels greater than 0.5 mg/L and 1.0 mg/L respectively.
2. Storage time: Many sodium hypochlorite suppliers recommend a maximum shelf life of 60 to 90 days (Laurer et al, 1986) but this depends on the storage conditions (eg: tank material and environment the tank located).
3. Sunlight: Hypochlorites should be protected from ultraviolet wavelength since it can reduce the life of hypochlorite solutions strength.
4. Temperature: Degradation of hypochlorite solutions increases rapidly with increase temperature. A common practice is to try to limit temperatures to 80˚F.

2.9.1 BRINE SYSTEM

Brine systems can be used for any application requiring chlorine or chloramines as part of the disinfection regimen. These systems are nearly always installed inland and are designed to provide substantial quantities of stored sodium hypochlorite. Brine system is designed with excess product storage to assure that disinfection capacity is always available to the end user (Casson and Bess, 2002).

To accommodate these requirements, systems are generally configured with the following components and operate in a manner described below (Casson and Bess, 2002):

1. Water softener: Essential for removal of calcium and magnesium from the feed water
2. Salt dissolver: Provides the required salt solution for electrolysis
3. Electrolyzer cell or cells: Electrolyzes the dilute brine solution
4. DC power rectifier: Provide the direct current for electrolysis
5. Storage tanks: Product storage to meet dosing requirements as well as any excess capacity essential to assure continuous dosing capabilities
6. Hydrogen dilution blowers: Provided to dilute the by-product hydrogen produced during the electrolysis process
7. Dosing pumps with dosing controls: Provide the needed disinfection dose based upon the chlorine residual or flow rate at the point of disinfection
8. Cell cleaning system: Used to remove the calcarious material deposited on the cell cathodes during the production process
9. Central control panel: Performs the system production control function

2.9.2 SEAWATER SYSTEM

Seawater electrochlorination utilize high seawater feed flow rates to help control cathode fouling from the naturally occurring magnesium and calcium in seawater (Casson and Bess, 2002). As a result, the product concentrations of sodium hypochlorite are low and operating current efficiency is high. Since seawater provides a 'free' source of salt, these systems contain smaller equipment of less variety than brine electrolysis system (Casson and Bess, 2002). The equipment for a sea water system is listed below, and generally operates in the manner described (Casson and Bess, 2002):

1. Inlet water strainers: Essential for removing particulate material from the seawater feed stream
2. Seawater booster pumps: Provide seawater at the appropriate pressure and flow to the electrolyser system
3. Electrolyzer cell or cells: Electrolyzes the seawater feed to sodium hypochlorite
4. DC power rectifier: Provides the current for electrolysis
5. Hydrogen degassing storage tanks: For removing by-product hydrogen and product storage to meet shock dosing requirements
6. Hydrogen degassing cyclone: An alternate degassing method were only continuous disinfectant dosing is required and hydrogen removal is desirable
7. Hydrogen gas seal pot: Used with the cyclone where hydrogen is vented to the atmosphere without dilution
8. Hydrogen dilution blowers: Provided to dilute the by-products hydrogen produced during the electrolysis process. These blowers may be applied to either tank or cyclone hydrogen removal systems
9. Dosing pumps: Provide the needed disinfection dose to distance or high pressure applications. Direct current variation controls the dose rate rather than control the pump flow
10. Cell cleaning system: Used to remove he calcareous material deposited on the cathode

2.10 APPROXIMATE COST BETWEEN HYPOCHLORITE SYSTEM AND OTHER ALTERNATIVE DISINFECTION TECHNOLOGIES

There was an estimation of cost done by (Leslie et al, 1998) in order to evaluate alternatives of water disinfection system including chlorine gas, sodium hypochlorite (on-site/off-site), calcium hypochlorite, mixed oxidant, chlorine dioxide, ozone and UV light. The cost estimation was done to represent order of magnitude and comparatives estimates and not from detailed design. Table 2 shows the approximate cost for alternatives disinfection technologies. The cost was estimate for:

1. A potable water plant.
2. Capacity of 1.2 million gallons per day (MGD).
3. Operating 24 hours a day.
4. Chlorine dose of 1 ppm.
5. Electricity rates of $0.042 per kilowatt hour (for Washington State).

Table 2.2: Approximate Costs for Alternative Disinfection Technologies (1.2 MGD, 1 ppm chlorine dose) sources: (Leslie et al, 1998)

	Cl_2[1]	Cl_2[2]	NaOCl[3]	On-site NaOCl[4]	$Ca(OCl)_2$[3]	MIOX^{tm}[5]	ClO_2[7]	O_3[8]	UV[9]
Capital	65000	15000	2500	18000	2500	21000	30000	75000	42000
Operating	3600	3600	4400	1500	10000	2200	10000	1000	1000
Maintenance	2600	2600	5000	1600	4600	1300[6]	2500	1600	5000

1. 150# cylinders with scrubbers – prices from Matheson Gas Products.
2. 150# cylinders without scrubbers – prices from Matheson Gas Products.
3. Prices from Van Waters and Roges.
4. Prices from TMG Services, Maple Valley, WA.
5. Prices from MIOX^{tm} Company, Albuquerque, NM.
6. Maintenance is generally cheaper than onsite NaOCl, since these cells do not require acid washing

From the cost estimation, the capital cost for hypochlorite system were initially high but for operating and maintenance cost, hypochlorite system were among the lowest thus logically, in long period of time, the running cost will overcome the capital cost and make hypochlorite system is the best choice for disinfection system.

CHAPTER 3

METHODOLOGY

3.1 GANTT CHART

A Gantt chart was prepared in the planning stage to keep track of what was planned and executed in order to complete this project. The Gantt chart is shown in Appendix (Table A-1) and the red boxes indicate what should have been completed up to week 15.

3.2 PROJECT FLOW

Generally, this project was divided into the following 5 stages as been described in (Figure 3.1):

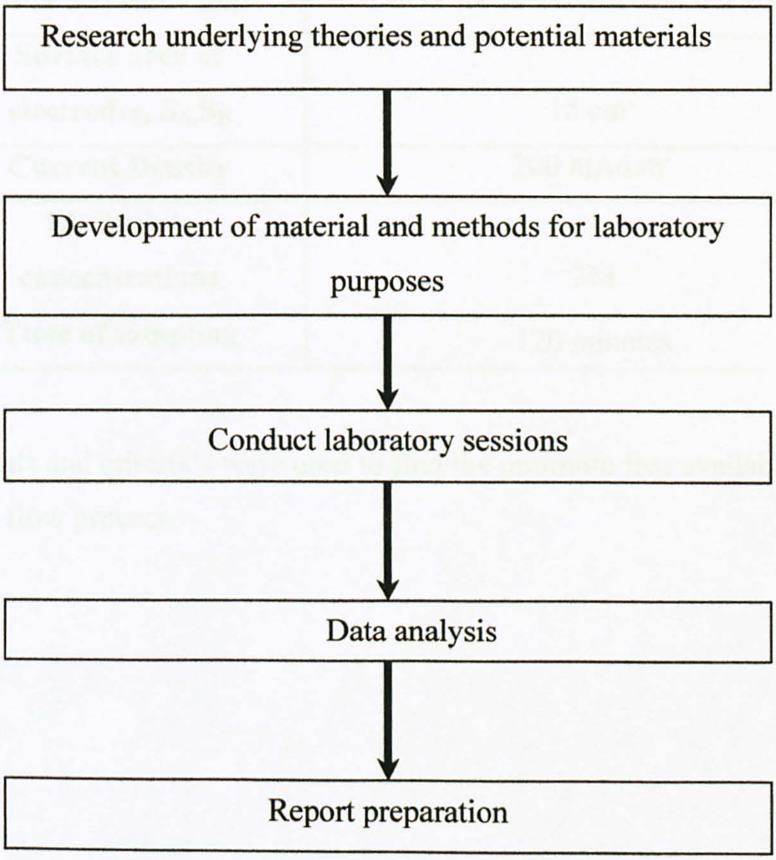


Figure 3.1 Project flow

3.3 PROJECT PROGRESS

Various experiments to determine operating parameters optimum production of FAC were conducted and the results are discussed in the Results and Discussion section. Besides that, journals and reading materials related to electrochemical water disinfection, on site hypochlorite generation and other related topics were studied in order to understand the theory or background about the project. There are some criteria that have been proved to be the optimum to achieve the highest amount of free available chlorine. Since this project was in continuation of a previous Final Year Project (FYP), the material and criteria that was found to produce optimum amount of free available chlorine are stated below (Table 3.1):

Table 3.1: Data from previous study

Electrodes	Anode: Metal Oxide - coated titanium Cathode: Titanium
Inter electrode gap	0.5 cm (between cathode and anode)
Surface area of electrodes, S_A,S_B	15 cm^2
Current Density	200 mA/cm^2
Electrolyte concentrations	2M
Time of sampling	120 minutes

These materials and criteria's were used to find the optimum free available chlorine in a continuous flow process.

3.4 Design Expert 6.0

The Design Expert 6.0 software was used to design and optimize the experimental conditions. Features of the software were:

- Two-level factorial screening studies – Identify the vital factors that affect the process for the improvements.
- General factorial studies – Discover the ideal combination of categorical factors and identify the vital factors that affect the process or product.
- Response Surface Method (RSM) – Find the ideal process settings in order to achieve an optimal performance.
- Mixture Design Techniques – Discover the optimal formulation.
- Combination of process factors, mixture components, categorical factors – Tailor DOE to what information required.

Design Expert software offers rotatable 3D plots for visualization of response surfaces. It also set the flags and explores the contours on interactive 2D graphs. The numerical optimization function finds maximum desirability for up to dozens of response simultaneously. Table 3.2 shows different factor levels that will be used and analyzed using the Design Expert software.

Table 3.2 Factors that will be used for the continuous flow experiment

Variable	Factor	Level (-1)	Level (0)	Level (+1)
A	flow rates (ml/min)	4	8	12
B	current densities (mA/cm^2)	1.3 mA/cm^2	2.7 mA/cm^2	4 mA/cm^2
C	Chloride concentrations (mg/l)	3.6	51.8	100

Three factors will be considered with each having the low, medium and high levels designated by (-1), (0), and (+1) respectively that defined the domains of the variations. The three levels factorial appeared to be most appropriate for this particular study.

3.5 MATERIAL

3.5.1 SODIUM CHLORIDE

This chemical was used to prepared the brine solution for the electrolysis process.

3.5.1.1 PHYSICAL DATA

- Molecular weight: 58.44
- Chemical formula: $NaCl$
- Colour: white
- Physical form: powder
- Common synonyms: Salt, rock salt, Saline

3.5.1.2 Toxicology

- May caused irritation to respiratory tract is inhaled
- Causes irritation, redness and pain to eyes
- Very large dosage can caused vomiting, diarrhoea, and prostration if inhaled

3.5.1.3 Occupational release

- Keep in tightly closed container, stored in a cool, dry and ventilated area
- Observed all warnings and precautions listed for the product
- Protect against physical damage

3.5.2 ELECTRODES

Mixed Metal Oxide - coated titanium will be used as anode because it has been shown that it has high current efficiency and could resist corrosion, while titanium will be used as cathode in this electrolysis process. 4 pairs of electrodes will be used for this experiment. The properties of electrodes are shown below:

Table 3.3: Surface area and positions of electrodes

Electrodes	Surface area/electrode	positions
Mixed oxide-coated titanium	23.6 cm^2	anode
Titanium	17.3 cm^2	cathode

3.5.3 ELECTROLYTIC CELL

Perspex is used to fabricate the electrolysis tank in which electrodes will be installed. The cell was designed to contain 1 litre of water. The dimension of the cell is 0.29 m x 0.05 m x 0.07 m.

3.6 METHODS

This study will determines the effects of 4 factors that will generate optimum value of free available chlorine. The factors are flow rates of brine solution entering the reactor, pH of brine solution, current densities and electrolyte concentrations. The sequence of activities carried in laboratory session and data analysis were described in Figure 3.1

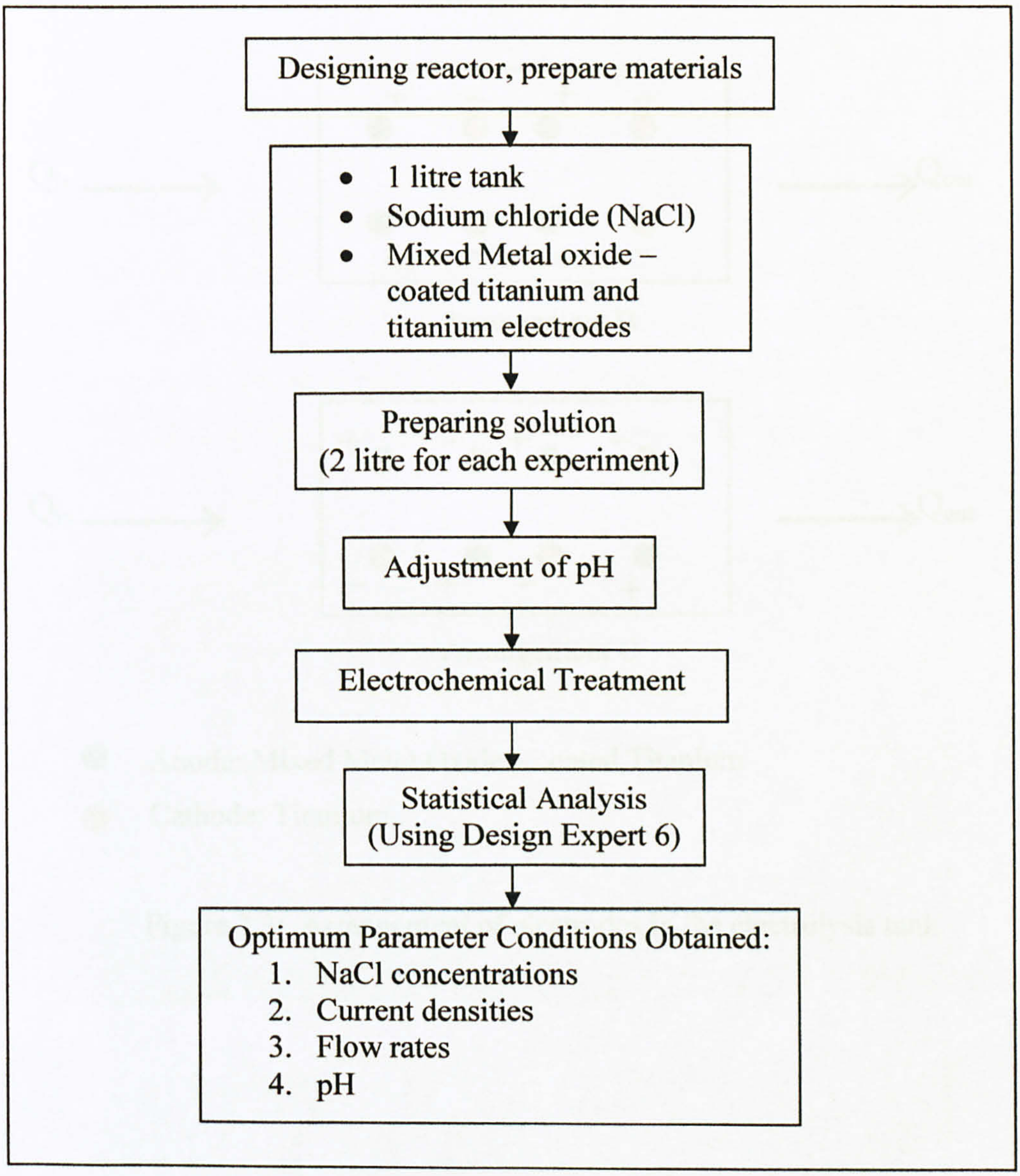


Figure 3.2: Sequence of activities

The experiment will be conducted with different flow rates, pH, current densities, electrolyte concentrations and electrode arrangements (as shown in Figure 3.2) to observe the effect on free available chlorine production. The arrangement of the electrodes is shown below:

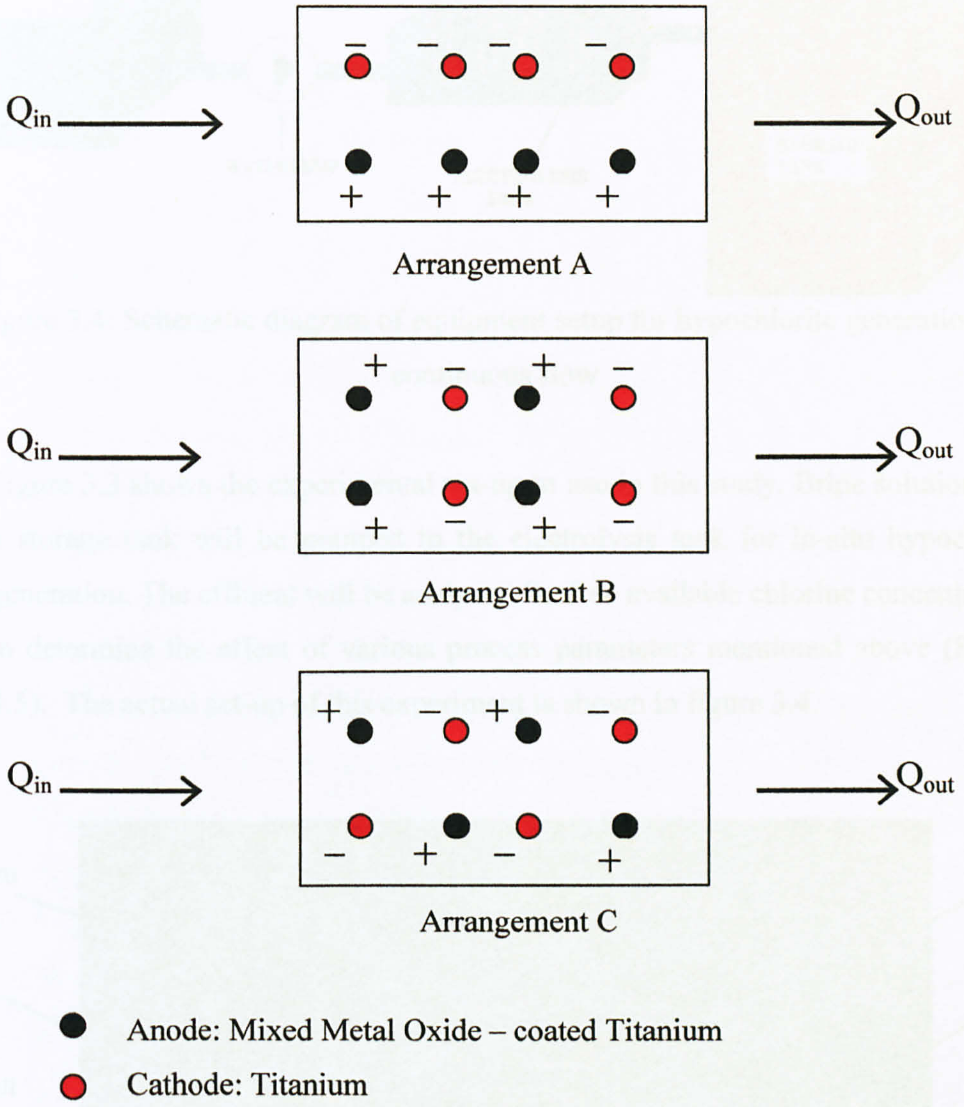


Figure 3.3: Arrangement of electrodes in the electrolysis tank

3.6.1 EQUIPMENT SETUP

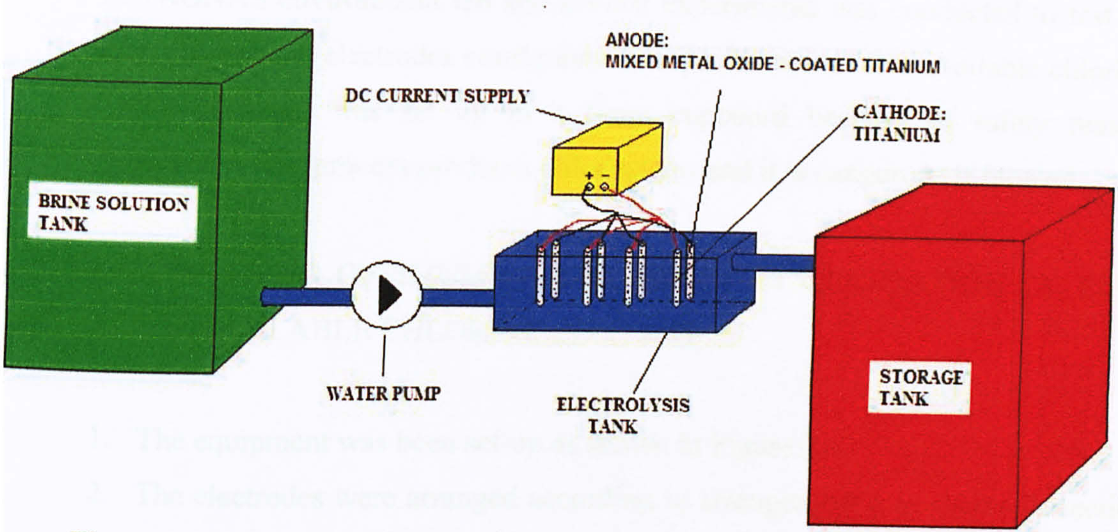


Figure 3.4: Schematic diagram of equipment setup for hypochlorite generation in continuous flow

Figure 3.3 shows the experimental set-up to use in this study. Brine solution from a storage tank will be pumped to the electrolysis tank for in-situ hypochlorite generation. The effluent will be analyzed for free available chlorine concentrations to determine the effect of various process parameters mentioned above (Section 3.5). The actual set-up of this experiment is shown in figure 3.4.

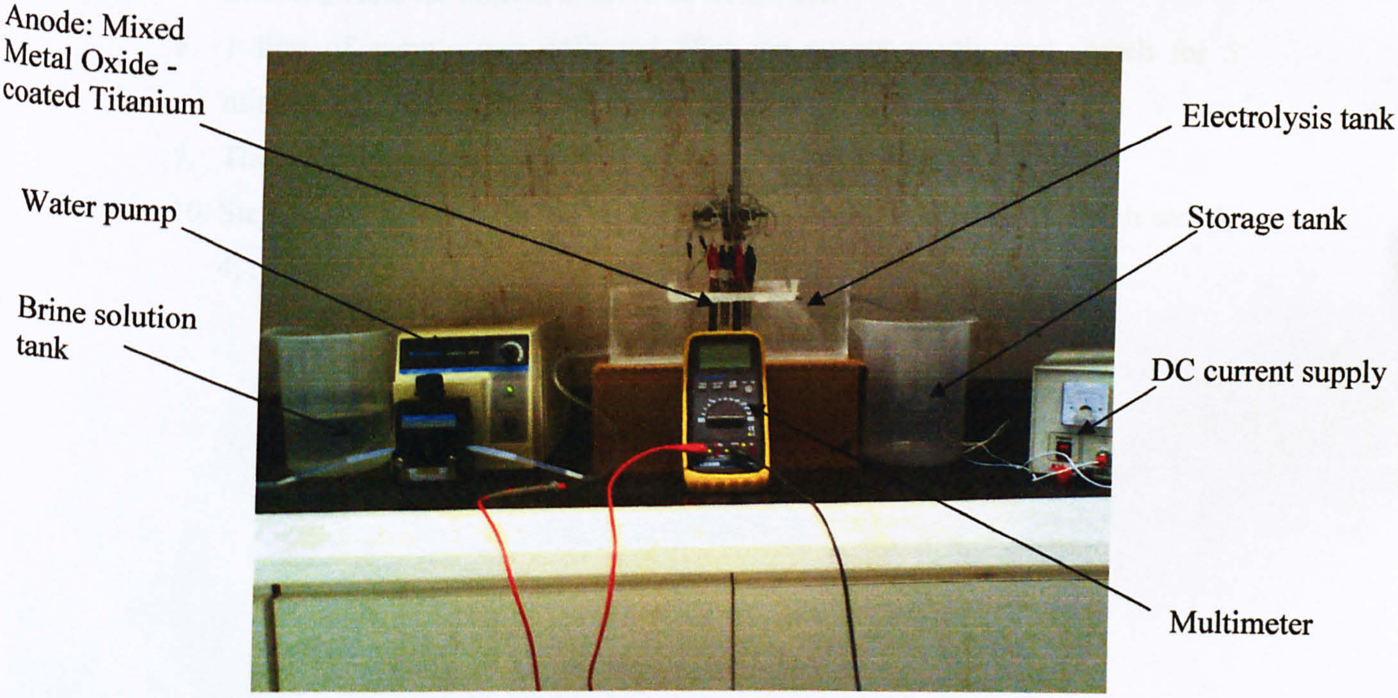


Figure 3.5: Actual equipment setup for hypochlorite generation in continuous flow

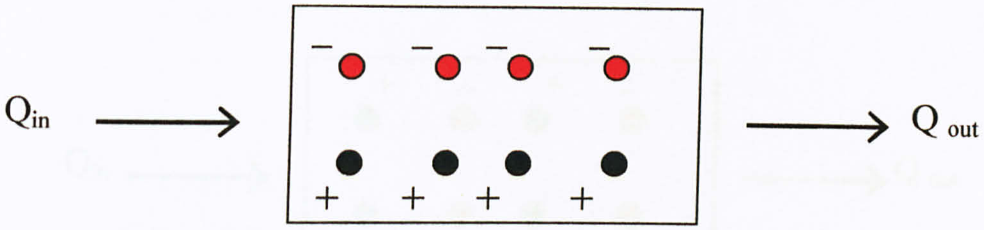
The equipment was set-up in a fume cupboard in Universiti Teknologi PETRONAS environment lab and several experiments was conducted to test the effect of pH and electrodes configuration in production of free available chlorine. The experiment was set up in a fume cupboard because of safety reason. Electrochemical process produces chlorine gas and it is dangerous if inhaled.

3.6.2 FINDING OPTIMUM pH FOR OPTIMUM GENERATION OF FREE AVAILABLE CHLORINE CONTENT

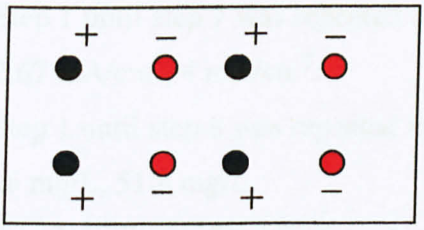
1. The equipment was been set-up as shown in Figure 3.4.
2. The electrodes were arranged according to arrangement 1 as shown in section 3.5.
3. A brine solution of NaCl having concentrations of 1 g/l was prepared in the storage tank.
4. The water pump was set to a flow rate of 10 ml/min.
5. The pH of the electrolyte was adjusted to 2.
6. The water pump nozzle was connected to the electrolytic cell and the pump was switch on.
7. After the electrolyte comes out through the outlet pipe, the power supply is switch on and the current is set to be 2 Ampere.
8. 1 litre of sample was collected after the power supply was switch for 5 minutes in order for the electrolytic cell becomes stable.
9. The sample is tested using DPD method for Free Available Chlorine.
10. Step 1 until 8 was repeated but using different pH of electrolyte which was 3, 4, 5, 6 and 7.

3.6.3 FINDING SUITABLE ELECTRODE ARRANGEMENTS TO GENERATE FREE AVAILABLE CHLORINE

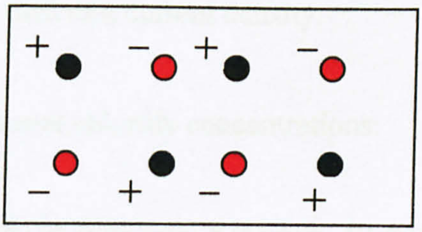
1) The brine solution pump was set to be 12 mL/min.
2) 2 litres of brine solution having concentrations of 1mg/L of NaCl was prepared.
3) The electrodes was arranged as shown in figure 3.5:



4) The brine solution pump nozzle was connected to the electrolytic cell and the pump was switched on.
5) The system was left until a continuous flow developed (a constant flow at output) and the DC power supply was switched on.
6) The current density for the system is adjusted to be 10 mA/cm^2.
7) 1L of sample was collected from the outlet after the system had stabilized and DPD method was used to measure the amount of FAC.
8) Step 1 until 6 but was repeated using different current density which was 20 mA/cm^2 and also 30 mA/cm^2.
9) Step 1 until 8 was repeated but using different arrangement of electrode as shown below:



Arrangement B



Arrangement C

10) A graph of Free Available Chlorine (FAC) and current density was plotted

3.6.4 PROCEDURE FOR ELECTROCHEMICAL PROCESS IN CONTINUOUS FLOW

1) The brine solution pump is set to be 4 mL/min.
2) 2L of brine solution having chloride concentrations of 100 mg/L was prepared.
3) The electrodes was arranged as shown in figure 3.5:

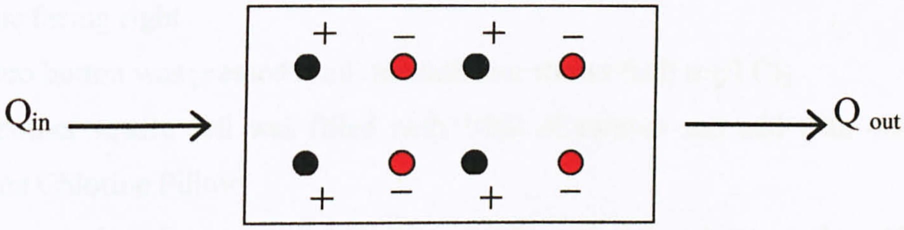


Figure 3.6: Electrodes configuration (arrangement B)

4) The brine solution pump nozzle was connected to the electrolytic cell and the pump was switched on.
5) The system was left until a continuous flow developed (a constant flow at output) and the DC power supply was switched on. The Current density was set to be 1.33 mA/cm^2.
6) 1L of sample was collected from the outlet after 5 minutes and DPD method was used to measure the amount of FAC.
7) Water pumped and power supply was switch off and the electrolyte in the cell was discharge by disconnecting the pump nozzle from the cell.
8) Step 1 until step 7 was repeated but using different current density: 2.67 mA/cm^2, 4 mA/cm^2.
9) Step 1 until step 8 was repeated using different chloride concentrations: 3.6 mg/L, 51.8 mg/L.
10) Step 1 until step 8 was repeated using different flow rate: 8 ml/min, 12 ml/min.
11) Results were analysed using 3-level factorial design using Design Expert 6.0

3.6.5 DPD METHOD

This method uses HACH spectrophotometer (DR 2800) for testing free chlorine (hypochlorous acid and hypochlorite ion) in water and treated water.

1. The program was stored: test number 80 chlorine, F&T PP
2. Blank preparation was prepared
3. The surface of blank was wiped and inserted into the cell holder with the fill line facing right
4. Zero button was pressed until the indicator shows 0.00 mg/l Cl_2
5. Another square cell was filled with 10ml of sample and add with one DPD Free Chlorine Pillow
6. The sample cell was swirled for 20 seconds until pink colour developed*
7. The sample was inserted into the cell holder within 1 minute of adding reagent. Press the read button
8. Results shows reading in mg/l Cl_2

*If the pink colour fades away after DPD Free Chlorine Pillow been added, the sample should be diluted and test the sample again using DPD method.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 FINDING OPTIMUM pH FOR FREE AVAILABLE CHLORINE GENERATION

An experiment was conducted to find the optimum pH to generate Free Available Chlorine. The experiment was done because there was no data regarding pH in order to generate optimum free available chlorine. Table 4.1 and figure 4.1 show the results of the experiment which show that pH 5 is the optimum pH for FAC production.

Table 4.1: Concentrations of FAC* at different value of electrolyte's pH

Electrolyte concentrations: 1 g/l		
Flow rate: 10 ml/min		
Current Densities: 33 mA/cm^2		
Electrode's configuration: Arrangement A		
pH		Concentrations of FAC* (mg/l)
Before Electrolysis	After Electrolysis	
2.17	2.61	200
3.14	8.31	540
4.15	8.77	670
5.16	8.74	800
6.11	8.73	630
7.13	8.22	620

*Free Available Chlorine

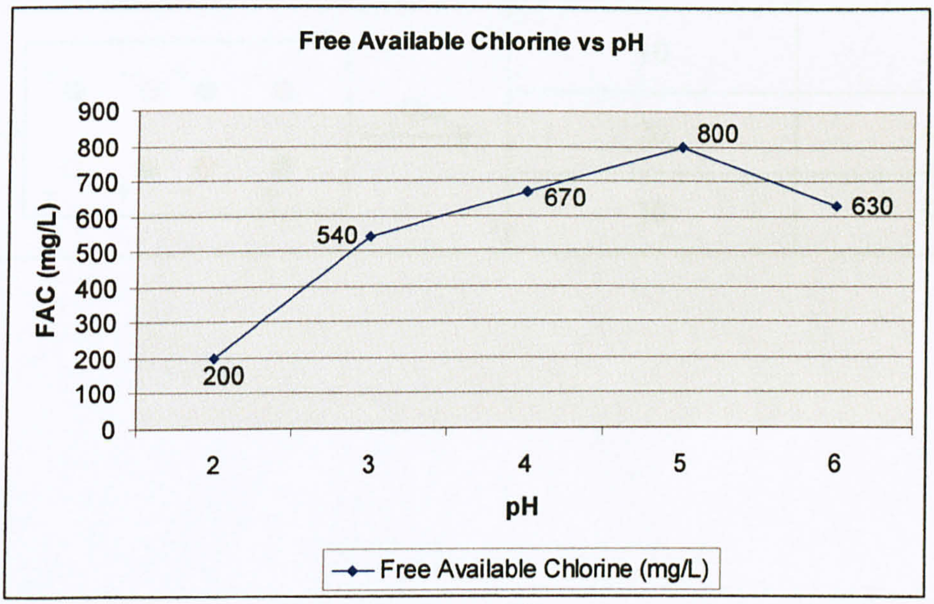
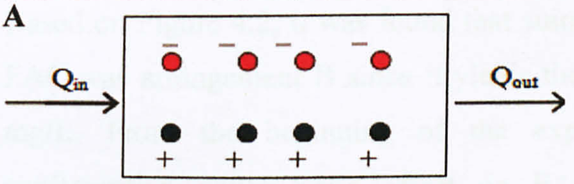
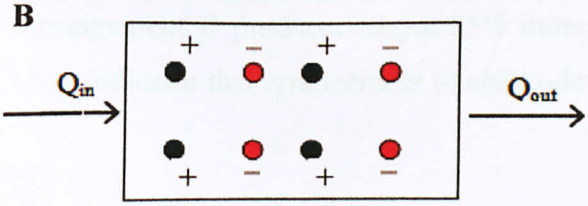
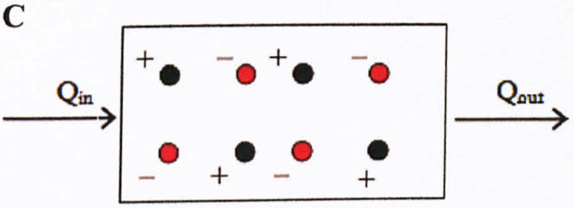


Figure 4.1: Concentrations of FAC* at different value of electrolyte's pH

4.2 FINDING SUITABLE ELECTRODES CONFIGURATIONS FOR OPTIMUM FREE AVAILABLE CHLORINE GENERATION

An experiment was conducted to relate between electrodes configuration and production of FAC. It was found that arrangement B is the best configuration among the three configurations as it produced the highest amount of FAC which was 640 mg/L at current density of 30 mA/cm^2. Table 4.2 and Figure 4.2 shows the concentrations of FAC been produced at different electrodes arrangement at 3 different level of current densities.

Table 4.2: Concentrations of FAC* at different arrangement of electrodes

<table>
<tr><td colspan="3">Electrolyte concentrations: 1 g/l</td></tr>
<tr><td colspan="3">Flow rate: 12 ml/min</td></tr>
<tr><td>Electrodes configuration</td><td>Current densities (mA/cm^2)</td><td>Concentrations of FAC (mg/l)</td></tr>
<tr><td rowspan="3">**A**
 </td><td>10</td><td>100</td></tr>
<tr><td>20</td><td>330</td></tr>
<tr><td>30</td><td>520</td></tr>
<tr><td rowspan="3">**B**
 </td><td>10</td><td>260</td></tr>
<tr><td>20</td><td>480</td></tr>
<tr><td>30</td><td>640</td></tr>
<tr><td rowspan="3">**C**
 </td><td>10</td><td>320</td></tr>
<tr><td>20</td><td>460</td></tr>
<tr><td>30</td><td>590</td></tr>
</table>

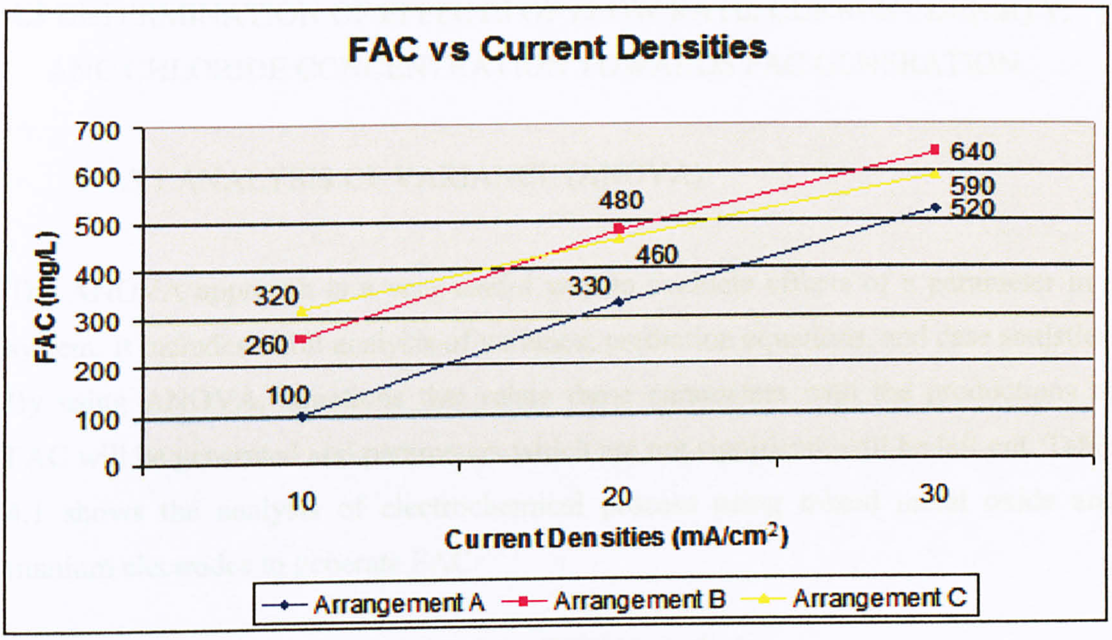


Figure 4.2: Concentrations of FAC* at different arrangement of electrodes

Based on Figure 4.2, it was found that suitable arrangement of electrodes to produce FAC was arrangement B since it yields the highest amount of FAC which was 640 mg/L. From the beginning of the experiment, never expect that electrodes configuration could bring affect on FAC generation. From the graph above, Arrangement B produced about 25% more FAC than Arrangement A and this is a clear indicator that arrangement of electrodes do affects FAC production.

4.3 DETERMINATION OF EFFECTS OF FLOW RATE, CURRENT DENSITY, AND CHLORIDE CONCENTRATION TOWARDS FAC GENERATION.

4.3.1 ANALYSIS OF VARIANCE (ANOVA)

The ANOVA approach is a very useful way to evaluate effects of a parameter in a system. It includes a full analysis of variance, prediction equations, and case statistics. By using ANOVA, equations that relate these parameters with the productions of FAC will be generated and parameters which are not significant will be left out. Table 4.1 shows the analysis of electrochemical process using mixed metal oxide and titanium electrodes to generate FAC.

Table 4.3: ANOVA analysis

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	
Model	3084.39	9	342.71	9.23	< 0.0001	*significant*
A	288.72	*1*	*288.72*	*7.77*	*0.0107*	
B	1091.53	*1*	*1091.53*	*29.39*	*< 0.0001*	
C	591.11	*1*	*591.11*	*15.91*	*0.0006*	
A_2	1.34	*1*	*1.34*	*0.036*	*0.8513*	
B_2	0.43	*1*	*0.43*	*0.012*	*0.9155*	
C_2	313.71	*1*	*313.71*	*8.45*	*0.0082*	
AB	160.16	*1*	*160.16*	*4.31*	*0.0497*	
AC	82.95	*1*	*82.95*	*2.23*	*0.1493*	
BC	518.37	*1*	*518.37*	*13.96*	*0.0011*	
Residual	817.21	22	37.15			
Lack of Fit	786.87	*17*	*46.29*	*7.63*	*0.0169*	*significant*
Pure Error	30.33	*5*	*6.07*			
Cor Total	3901.59	31				

For ANOVA, if the value of "Prob > F" less than 0.05, it indicates that the term is significant. Thus, by looking at the ANOVA of the system, the model (experiment) is significant or in other word meaning that the experiment results can be accepted. From the experiment results, it is also indicated by using Design Expert software that factor A (flow rate), B (current density), C (chloride concentrations) are significant in this model. Changing in this parameter would obviously change the amount of FAC produced. The relationship between factor AB and BC have been identified as significant towards the production of FAC.

The ANOVA also create an equation to simulate the significant terms towards the production of FAC. The Final equation in terms of coded factors is shown in eq.[1]

Free Available Chlorine = 13.59 – 4.00(A) + 7.79(B) + 5.73(C) – 6.62(C^2) – 3.65 (AB) + 6.57 (BC) ....eq [1]

4.3.2 MODEL DIAGNOSTIC PLOTS

The plot of actual and predicted values, student residual, cook's distance and outlier T were termed as model diagnostic plots. These models were used to determine the quality of the points taken into analysis. Table A2 shows the diagnostic case statistics for this system using mixed metal oxide and titanium as electrodes.

Predicted value in table A2 were generated using Prediction equation which shown in equation 1 while "residual" are the difference between actual and predicted point. "Leverage" is a numerical value between zero and one that indicates the potential for a design point to influence the model. As an example, a value of one means that the predicted value will be forced to be exactly equal to the actual value, with zero residuals.

For student residual, cook's distance and outlier T plots can be briefly describe as below (Yusoff, 2008):

1) Student Residual: is the residual divided by the estimated standard deviation (Std Dev) of that residual. It measures the number of standard deviations separating the actual and predicted values.
2) Cook's distance: is a measure of how much the regression changes if the case is deleted. The regression does not change much since the statistics is in average region. Relatively large values are associated with cases with high leverage and large studentized residuals.

3) Outlier T: is the number of standard deviations between actual data point and the predicted value at that point using a model based on all the data expect this point. The statistics shows that data point fits in with the other points for this mode, therefore there is no outlier.

4.3.2.1 *NORMAL PLOT OF RESIDUALS*

Normal plot of residuals can show wether the results have abnormalities or not. The residuals plot should yield straight line. From the normal plot of residuals as shown in figure 4.1, ideally this will be a straight line, indicating no abnormalities. Furthermore, it also indicates that only minor tranformation of the response needed to provide better analysis.

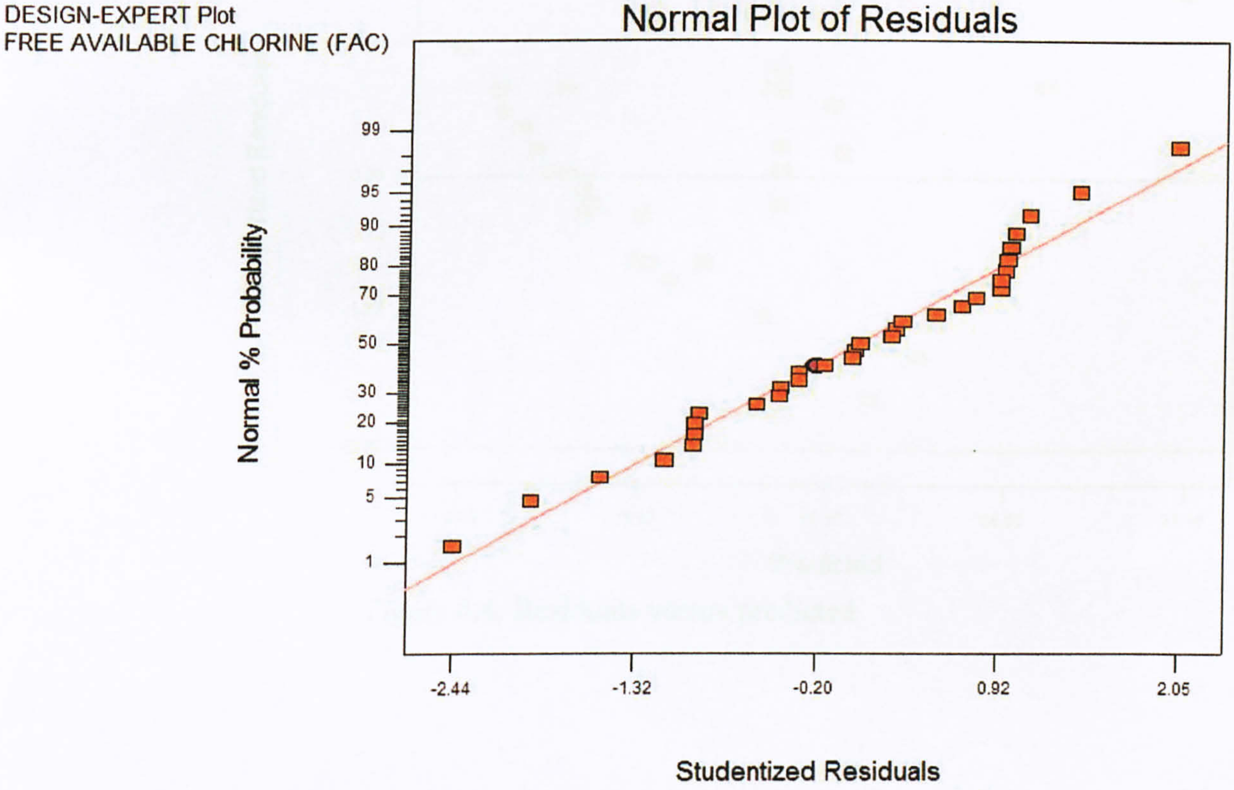


Figure 4.3: Normal Probability versus Studentized Residuals

4.3.2.2 *RESIDUALS VERSUS PREDICTED*

The size of the studentized residual should be independent of its predicted value. In other word, the spread of the studentized residuals should be approximately the same across all levels of the predicted values. In this case, the residuals were distributed within constant variance and if there were residuals expanding the constant variance, a transformation is needed where it is not implies for this experiment. All data were in between the constant range of residuals. Figure 4.2 shows the plot of the residuals versus the predicted response values for the electrochemical process.

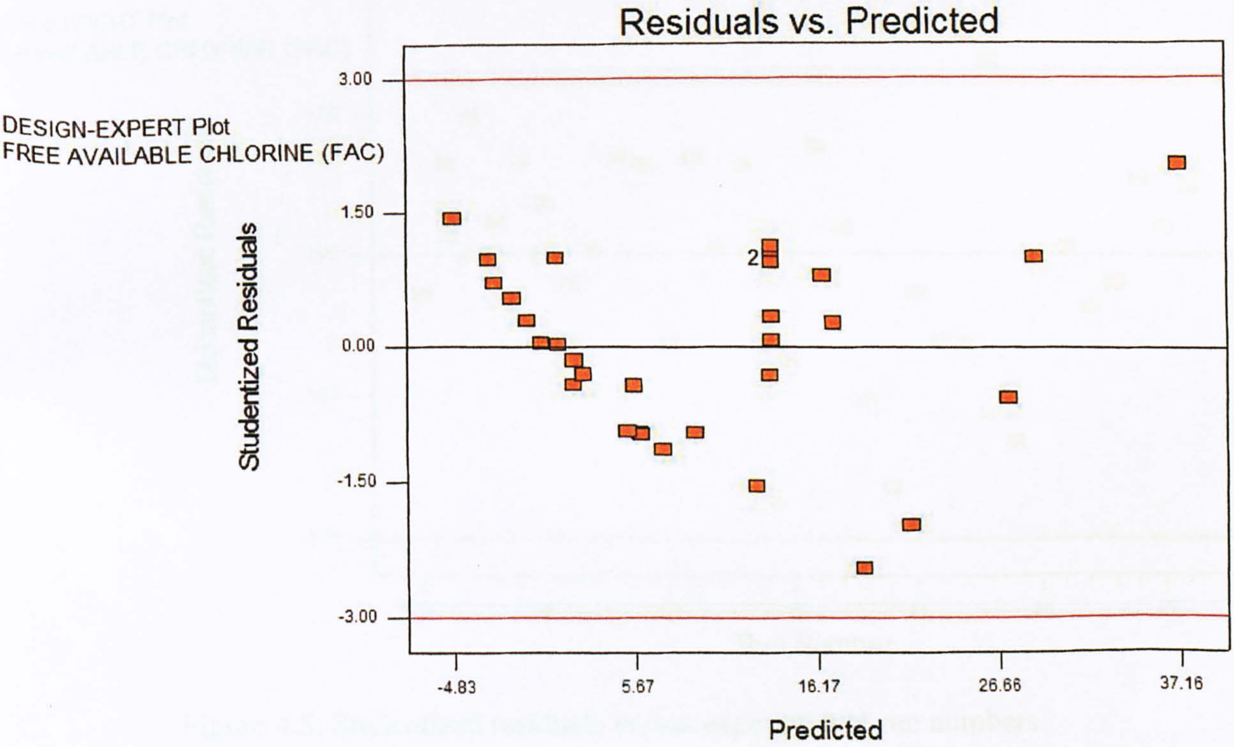


Figure 4.4: Residuals versus predicted

4.3.2.3 *RESIDUALS VERSUS RUN NUMBERS*

For this plot of residual versus run numbers, the spread of the studentized residuals should be approximately the same across all levels of the run numbers. Besides that it also should be within the constant range of residuals. For this experiment, the data point were evenly distributed and been plotted within the constant range of residuals. Figure 4.3 shows the plot of studentized residuals versus the experimental work order.

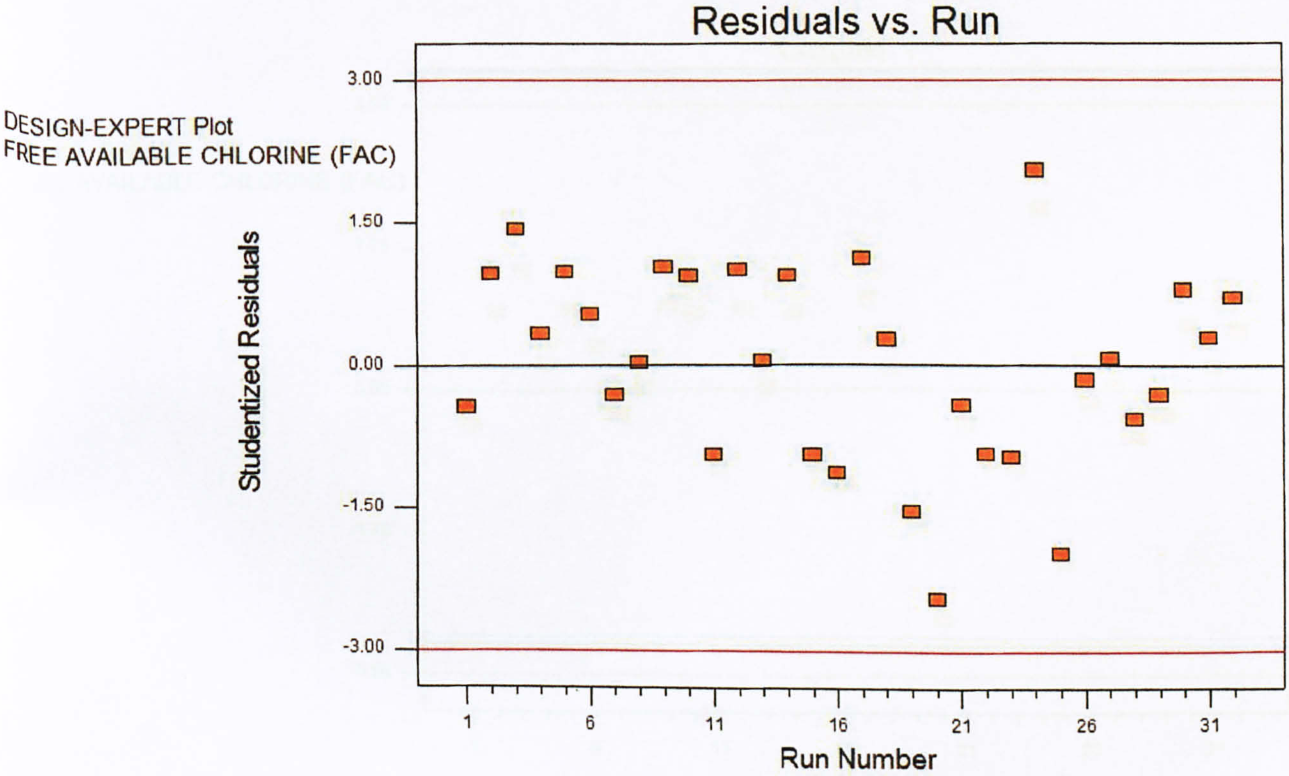


Figure 4.5: Studentized residuals versus experimental run numbers

4.3.2.4 *OUTLIER T VERSUS RUN NUMBERS*

Observations that differ considerably from the main body of the data are called an outlier. Residuals that are far outside this interval may indicate the presence of an outlier; that is, an observation that is not typical of the rest of the data. (C. Montmogery et al., 2007). Indication of an outlier is important to make better analysis of a group of data. For this outlier plot, all the points fall well within the red lines set at plus or minus 3.5. Thus there is no outlier for this experiment data.

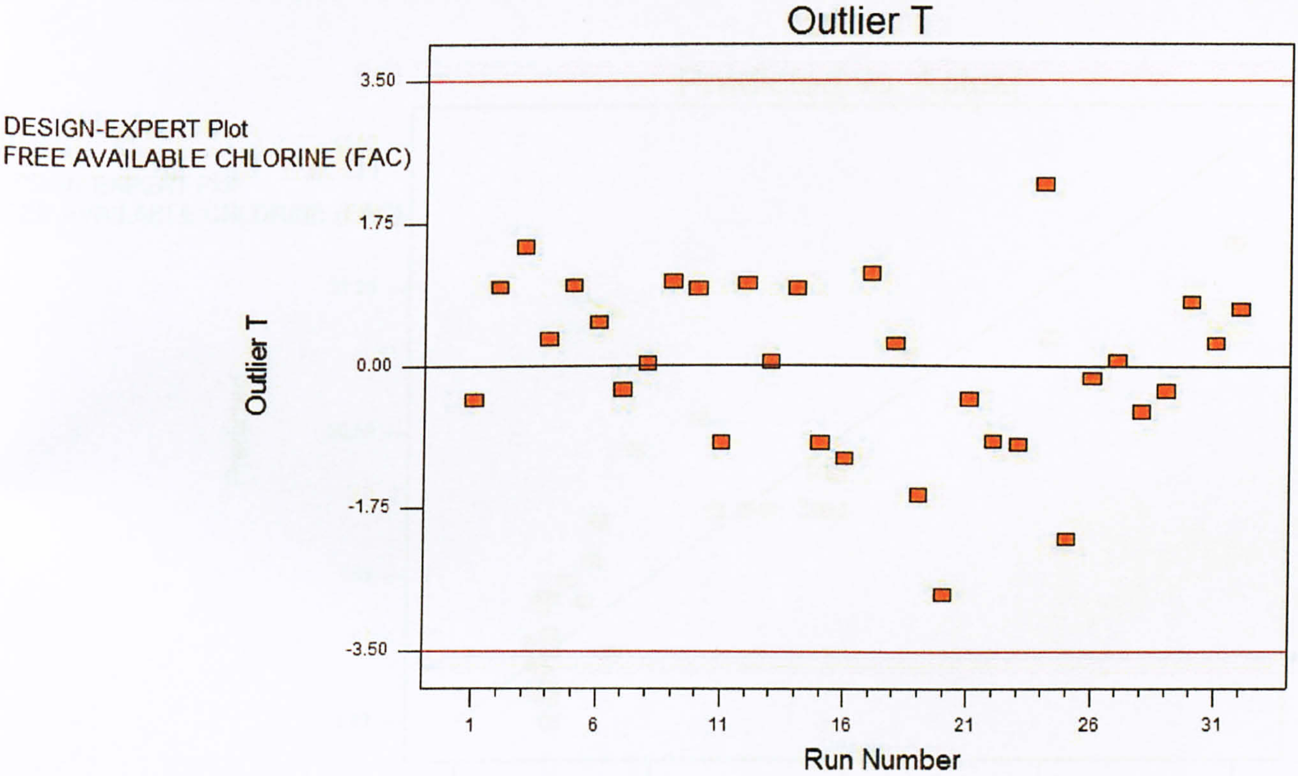


Figure 4.6: Outlier T versus Run numbers.

4.3.2.5 *PREDICTED VERSUS ACTUAL PLOT*

In the ANOVA plot analysis, the square of the correlation coefficient, R^2, always indicates the proportion of the total variance in one variable that is predictable from its relationship with other variables. The higher the R-squared values (closed to 1) means the better will be the goodness of fit (Yusoff, 2008). For this experiment, the value for R-squared is 0.7905 and adjusted R-squared is 0.7049 which is quite near to one. Figure 4.5 shows the plot of actual response values versus the predicted response values for the electrochemical process.

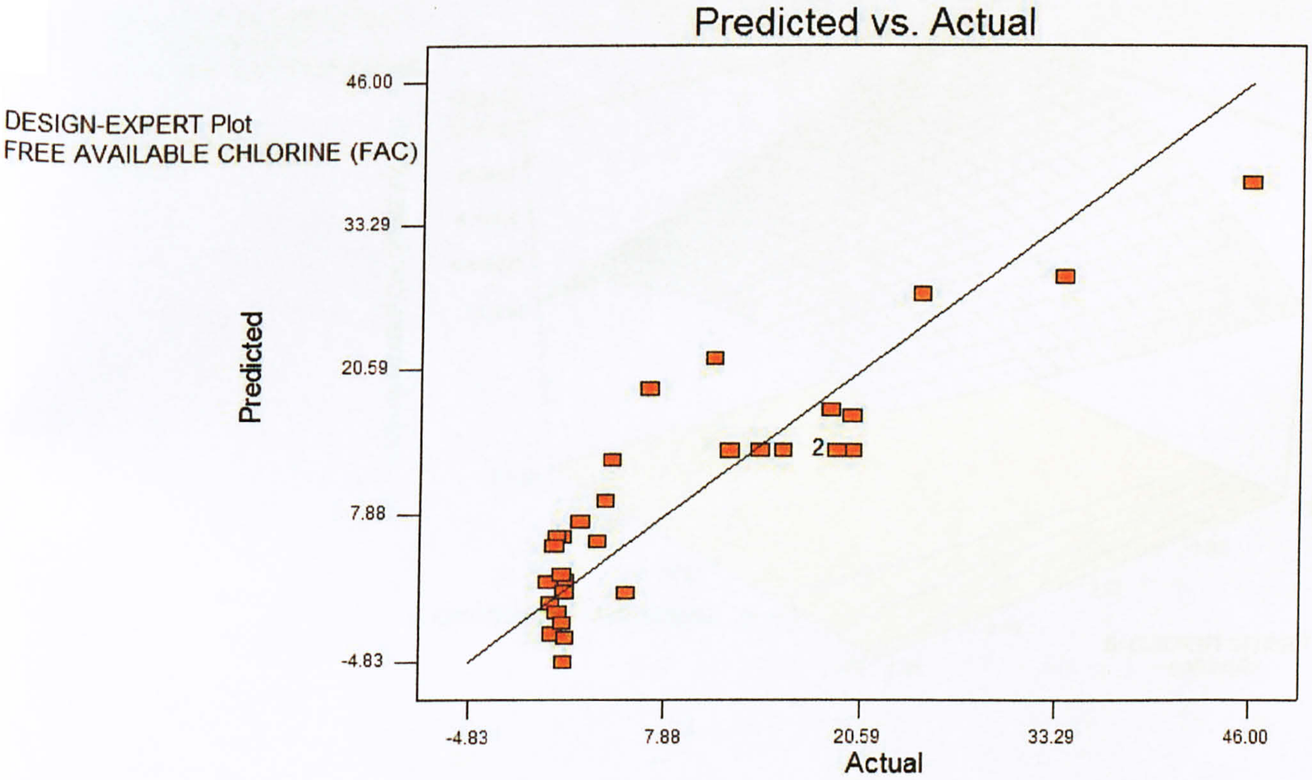


Figure 4.7: Predicted versus actual values

4.3.3 3D SURFACE PLOTS

From 3D surface plots, the suitable condition to produce sufficient FAC can be determined. Figure 4.6, Figure 4.7 and Figure 4.8 shows 3D surface plot for this experiment which been done in different flow rate, 12 mL/min, 8 mL/min and 4 mL/min respectively. From the 3D plots, it can be concluded that FAC production increase as the current density and chloride density were increase and the highest amount of FAC that can be produced was 17.1 mg/L at 12 mL/min (as in Figure 4.6).

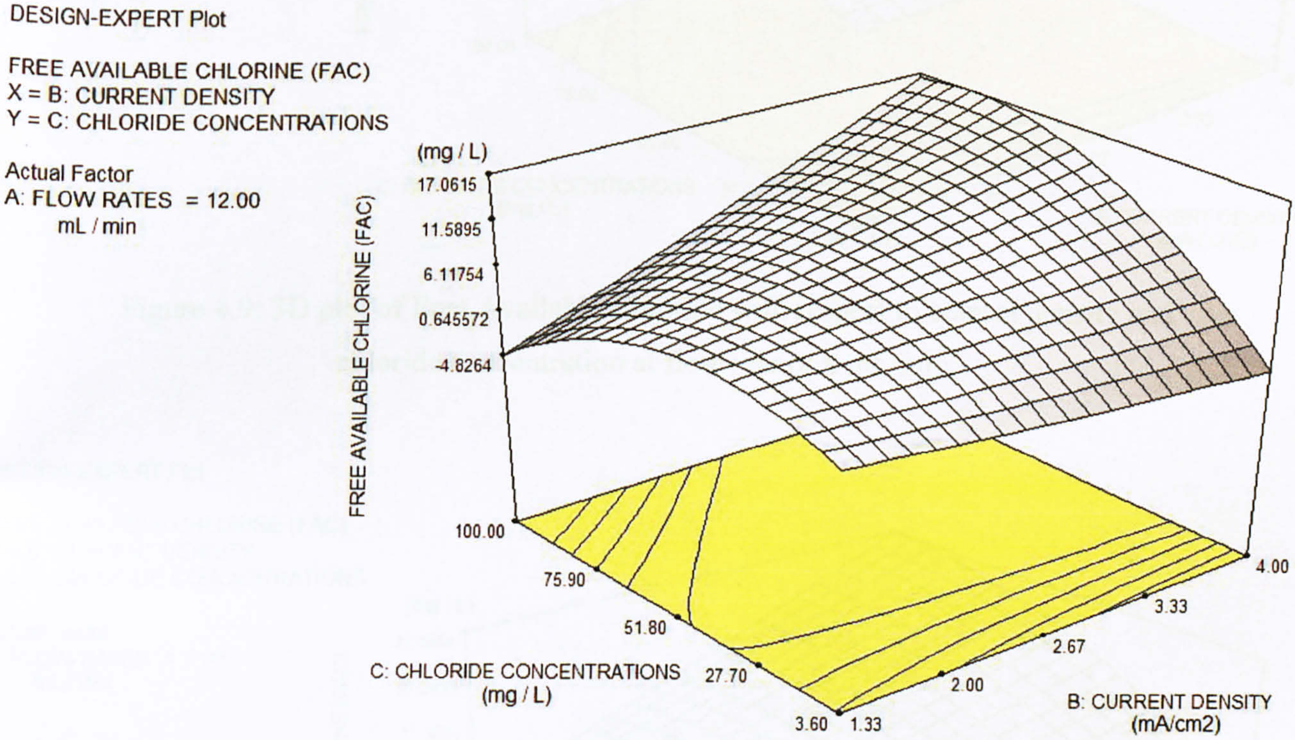


Figure 4.8: 3D plot of Free Available Chlorine with respect to current density and chloride concentration at flow rate of 12 mL/min.

It is also indicated that as the flow rates reduce, the amount of FAC generated was also reduce. Besides that, it is proven that although the electrolysis was done in low concentrations of chloride, but still sufficient amount of FAC can be produced. From the 3D plots, at 3.6 mg/L chloride concentrations, 0.23 mg/L, 1.98 mg/L and 2.38 mg/L of FAC were produced at current density of 4 mA/cm^2 and flow rate of 12 mL/min, 8 mL/min and 4 mL/min.

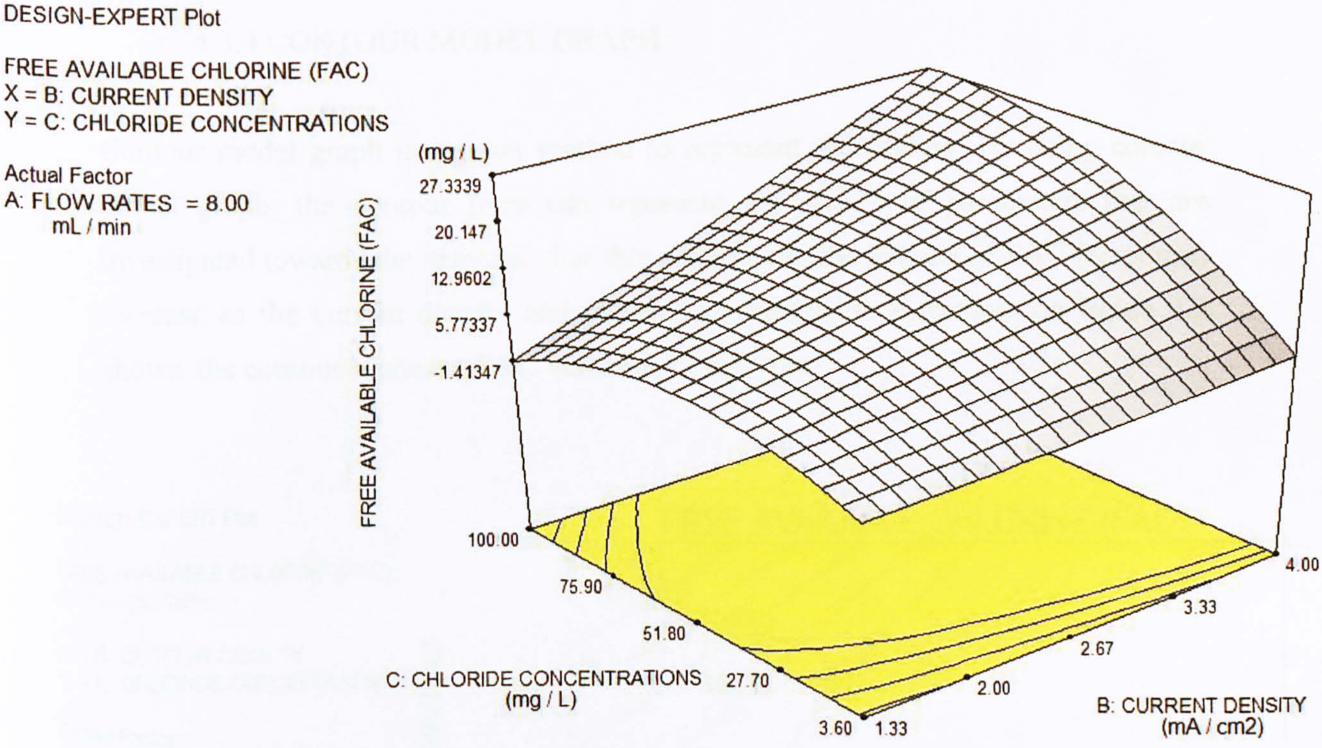


Figure 4.9: 3D plot of Free Available Chlorine with respect to current density and chloride concentration at flow rate of 8 mL/min.

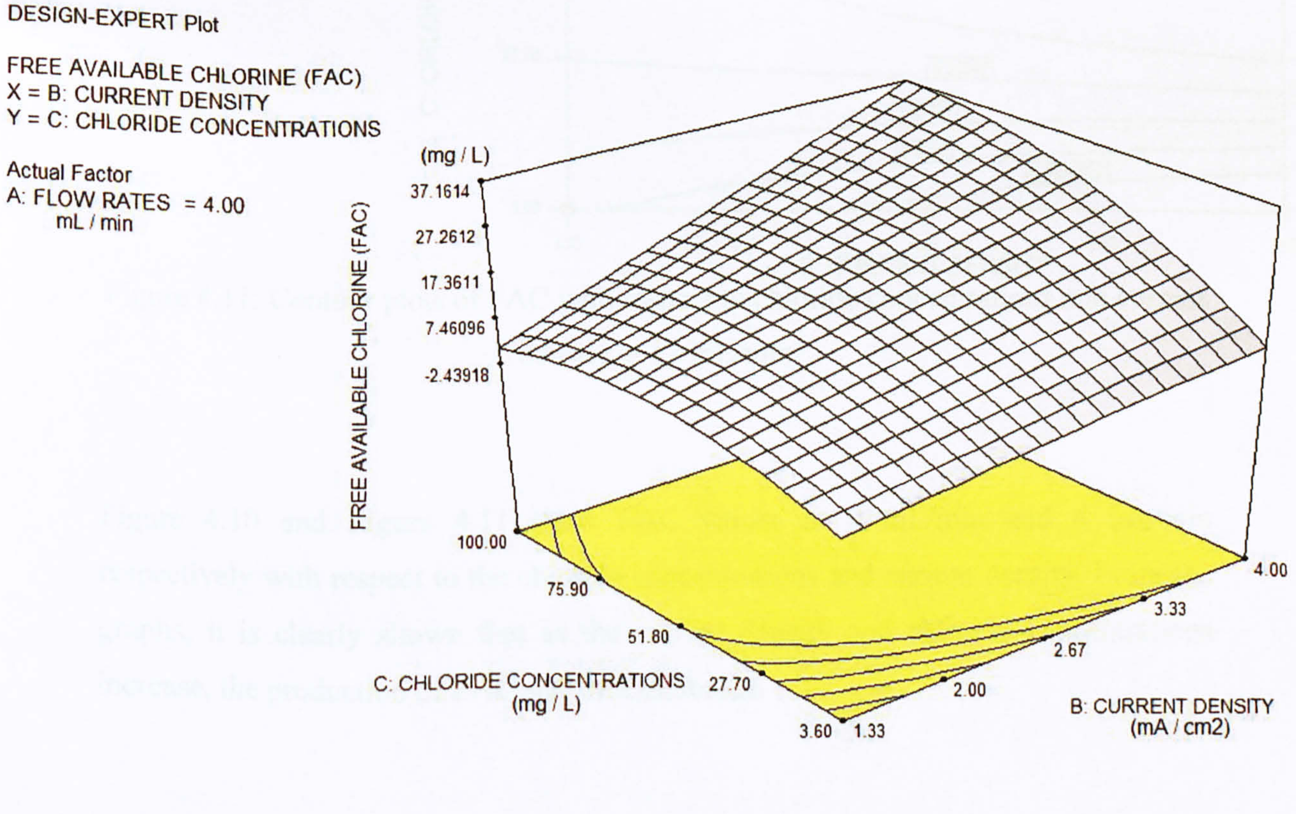


Figure 4.10: 3D plot of Free Available Chlorine with respect to current density and chloride concentration at flow rate of 4 mL/min.

4.3.4 CONTOUR MODEL GRAPH

Contour model graph is another method to represent the finding. By using contour model graph, the contour lines can represent the effects of parameters that are investigated towards the response. For this experiment, the amount of FAC (response) increase as the current density and chloride concentration increases. As figure 4.9 shows, the contour represent FAC values at 12 mL/min.

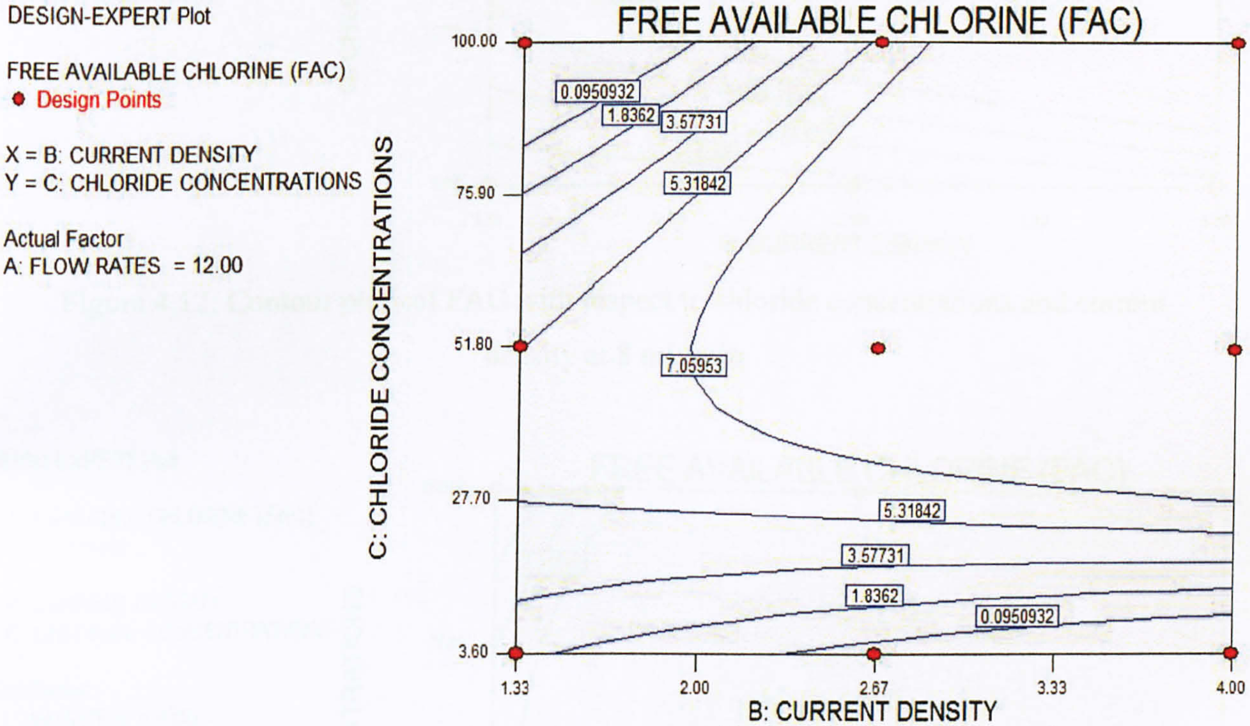


Figure 4.11: Contour plots of FAC with respect to chloride concentrations and current density at 12 mL/min

Figure 4.10 and Figure 4.11 show FAC values at 8 mL/min and 4 mL/min respectively with respect to the chloride concentrations and current density. From the graphs, it is clearly shown that as the current density and chloride concentrations increase, the production of FAC also will increases.

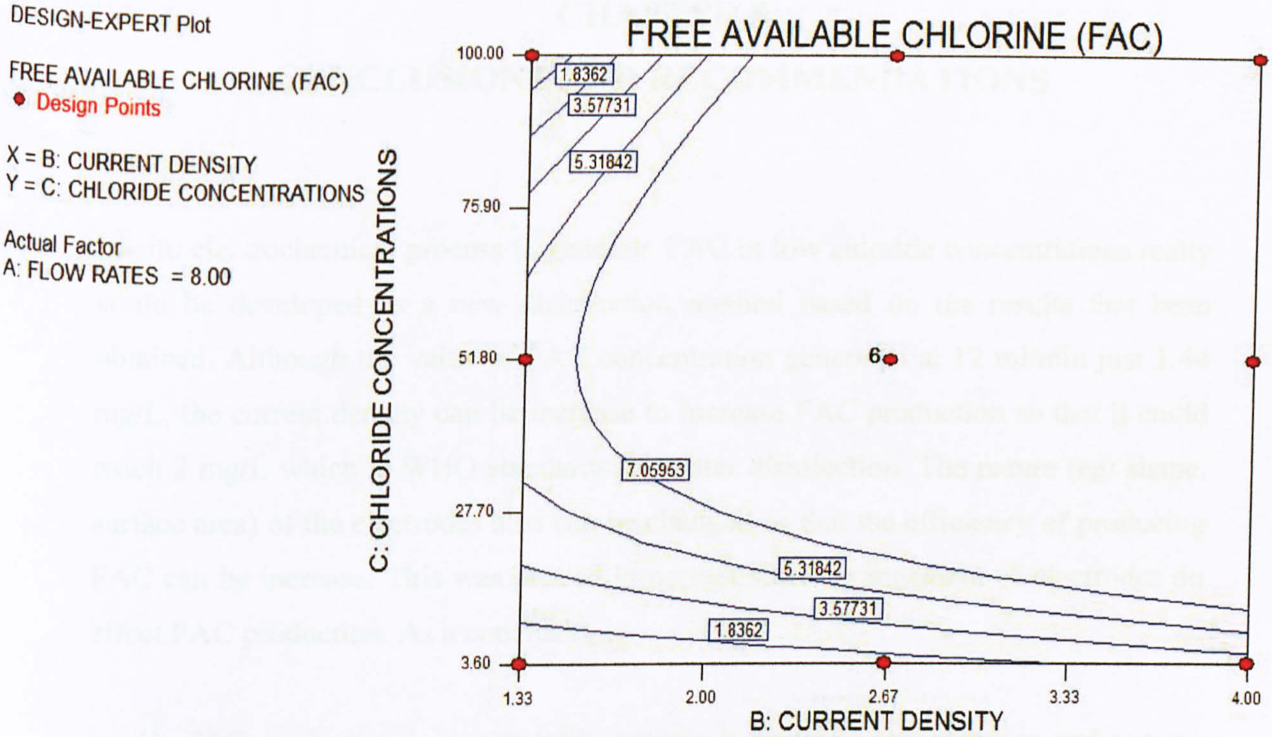


Figure 4.12: Contour plots of FAC with respect to chloride concentrations and current density at 8 mL/min

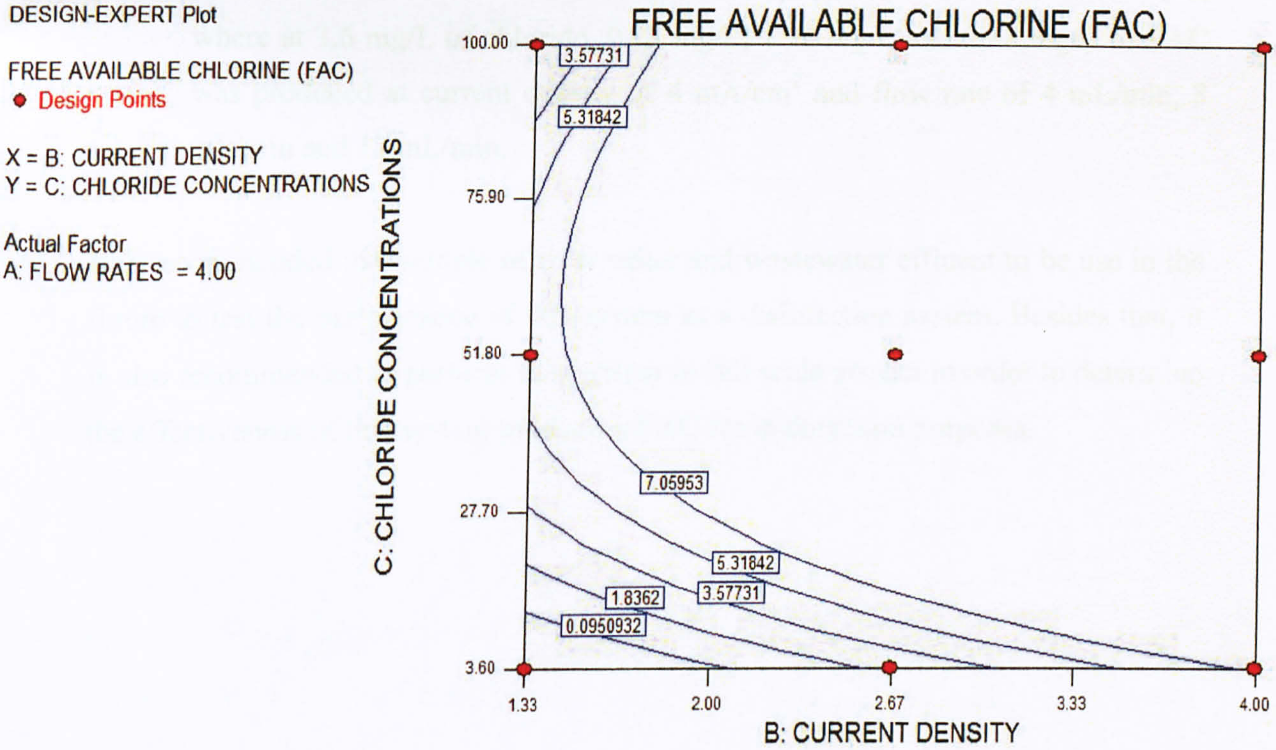


Figure 4.13: Contour plots of FAC with respect to chloride concentrations and current density at 4 mL/min

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

In-situ electrochemical process to generate FAC in low chloride concentrations really could be developed as a new disinfection method based on the results that been obtained. Although the value of FAC concentration generated at 12 ml/min just 1.44 mg/L, the current density can be increase to increase FAC production so that it could reach 2 mg/L which is WHO standards for water disinfection. The nature (eg: shape, surface area) of the electrodes also can be changed so that the efficiency of producing FAC can be increase. This was proved important since arrangement of electrodes do effect FAC production. As a conclusion:

1) FAC production increases with increase in chloride concentration and current density
2) FAC production reduces with increase of flow rate
3) Sufficient amount of FAC can be produced at low concentration of chloride, where at 3.6 mg/L of chloride, 0.23 mg/L, 1.98 mg/L and 2.38 mg/L of FAC was produced at current density of 4 mA/cm^2 and flow rate of 4 mL/min, 8 mL/min and 12 mL/min.

It is recommended that sample of river water and wastewater effluent to be use in the future to test the performance of this system as a disinfection system. Besides that, it is also recommended to perform this system in full scale project in order to determine the effectiveness of this system producing FAC for disinfection purposes.

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APPENDIX

Appendix A

Appendix C

Appendix D

Table A-1
Suggested Milestone for the Second Semester of 2-Semester Final Year Project

No	Detail/Week	1	2	3	4	5	6	7	8	9		10	11	12	13	14	15	16
1	**Project Initiation**										Mid-semester break							
	i) Project Briefing	Y																
	ii) Topic Selection	Y																
	iii) Proposal Draft	Y																
	iv) Submission of Proposal	Y																
2	**Research/Project Development**																	
	i) Get information, Flow progress	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥		🟥	🟥					
	ii) Preparation & submission Prelim Report					🟥	🟥	x		🟥								
	iii) Preparation & submission Progress Report					🟥	🟥	x										
	iv) Seminar				🟥		🟥											
3	**Laboratory**																	
	i) Method/procedure					🟥	🟥											
	ii) Survey materials, tools & equipments					🟥	🟥	🟥										
	iii) Setup, run & testing							🟥	🟥	🟥		🟥						
	iv) Analysis & Finalize data											🟥	🟥					
4	**Project completion**																	
	i) Preparation and poster presentation											🟥	x					
	ii) Preparation & submission Interim Report											🟥	🟥	x				
	iii) Preparation & oral presentation																	
	iv) Submission of dissertation ()															x		

x = proposed week of submission / presentation Y= done in the first semester

Table A2 **Performance of Disinfection Technologies on Key Characteristics**

	Baseline	**Alt. 1**	**Alt. 2**	**Alt. 3**	**Alt. 4**	**Alt. 5**	**Alt. 6**	**Alt.7**
	Cl_2	**NaOCl/ On-site- NaOCl**	**$Ca(OCl)_2$**	**MIOX™**	**ClO_2**	**Chloramines**	**O_3**	**UV**
Disinfection Capability:[1] Bacteria	Good	Good	Good	Good	Good	Poor	Very Good	Very Good
Viruses	Poor	Poor	Poor	Good	Good	Poor	Very Good	Fair
Cysts	Poor	Poor	Poor	Fair[1]	Fair[1]	Poor	Good	No effect
Generation of Hazardous Disinfection by-products	Yes - THMs And HAA5	Yes- THMs and HAA5	Yes- THMs and HAA5	Yes, but less THMs than Cl_2	Yes, but less THMs than Cl_2 Chlorite/ chlorate produced	Yes, but less THMs than Cl_2	Yes, Bromine Insig. Levels THMs formed	None
Persistent Residual	Good	Good	Good	Good- (longer than Cl^2)	Fair	Very Good	None (good for ww)	None (good for ww)
Safety Concerns	High	Low (for on-site)- Medium	Low	Low	Medium-High[2]	Medium	Medium	Low
Complexity of Operations/ Maintenance)	Minimal	Minimal	Moderate[3]	Moderate	Moderate	Minimal	Moderate	Minimal
Size Applicability	All sizes	All sizes	Small-medium (cost)	All sizes	Small-medium	All sizes	Medium-large	Small-medium
Relative Cost	Low	Low	Moderate	Low	Moderate	Low	High	Moderate
Long Term Applicability For:[5] Potable Water	Low (safety issues)	Medium	Medium	Medium	Medium	Effective only for residual purposes	Medium- must have residual	Medium- must have residual
Waste-water	Medium	Medium	Medium	Medium	Low (cost)	None	High	High

Sources: (Leslie et al, 1998)

---

1. Still may require filtration prior to discharge of wastewater.
2. Depending on the method used to generate chlorine dioxide, safety concerns can range from high to moderate.
3. Handling of Ca(OCl)2 is generally more labor-intensive than liquid (i.e. NaOCl)
4. From USEPA Wastewater Disinfection Manual (1986) and communication with equipment manufacturers/vendors.
5. Ability to meet upcoming standards.

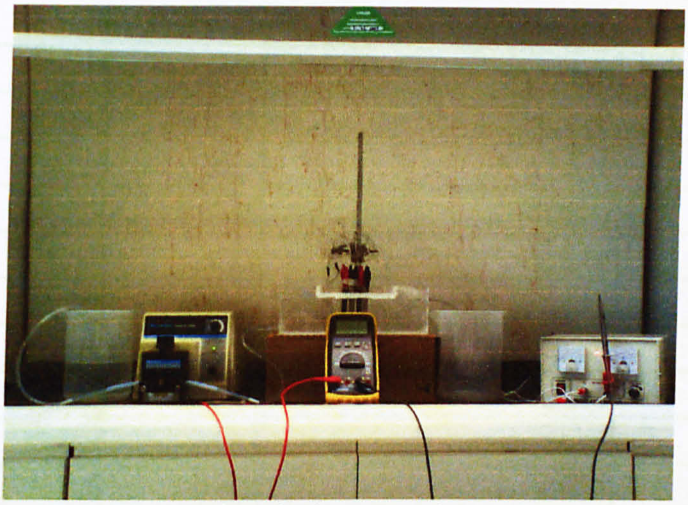


Figure B.1: Electrochemical process in the fume cupboard

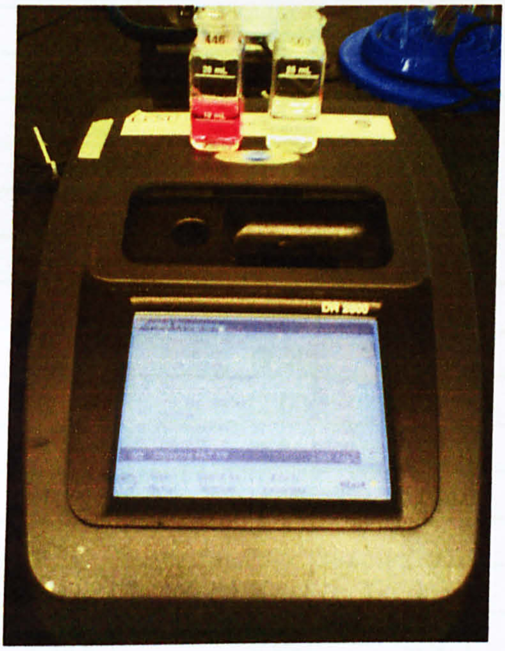


Figure B.2: Pink colour will developed if there is FAC after adding DPD free Chlorine reagent

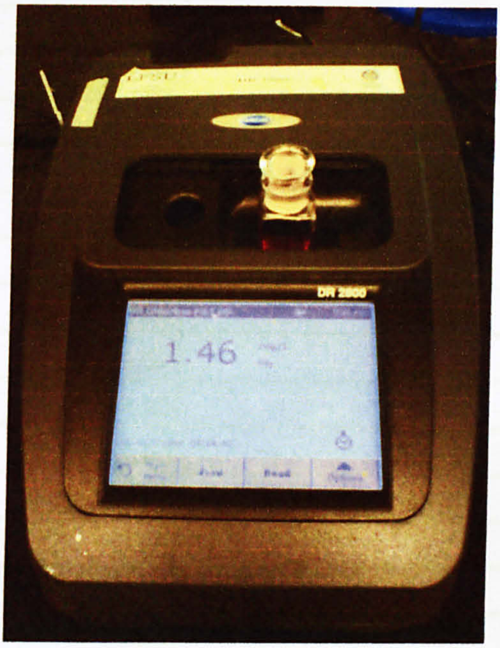


Figure B.3: Spectrophotometer DR 2800

Figure B.4: DPD pillow, Free Chlorine Reagent

Std	Run	Block	Factor 1 A:FLOW RATE mL / min	Factor 2 B:CURRENT mA/cm2	Factor 3 C:CHLORIDE CONCENTRAT mg / L	Response 1 FREE AVAILABLE CHLORINE (FAC mg / L
24	1	Block 1	12.00	2.67	100.00	3.5
9	2	Block 1	12.00	4.00	3.60	1.44
21	3	Block 1	12.00	1.33	100.00	1.35
14	4	Block 1	8.00	2.67	51.80	15.5
19	5	Block 1	4.00	1.33	100.00	5.38
20	6	Block 1	8.00	1.33	100.00	1.26
18	7	Block 1	12.00	4.00	51.80	12
5	8	Block 1	8.00	2.67	3.60	1.37
30	9	Block 1	8.00	2.67	51.80	19.5
32	10	Block 1	8.00	2.67	51.80	19
10	11	Block 1	4.00	1.33	51.80	1.25
16	12	Block 1	4.00	4.00	51.80	33.8
2	13	Block 1	8.00	1.33	3.60	0.47
28	14	Block 1	8.00	2.67	51.80	19
15	15	Block 1	12.00	2.67	51.80	4
7	16	Block 1	4.00	4.00	3.60	2.38
31	17	Block 1	8.00	2.67	51.80	20
13	18	Block 1	4.00	2.67	51.80	18.6
23	19	Block 1	8.00	2.67	100.00	4.4
22	20	Block 1	4.00	2.67	100.00	6.8
3	21	Block 1	12.00	1.33	3.60	0.3
12	22	Block 1	12.00	1.33	51.80	0.67
11	23	Block 1	8.00	1.33	51.80	0.86
25	24	Block 1	4.00	4.00	100.00	46
17	25	Block 1	8.00	4.00	51.80	11
4	26	Block 1	4.00	2.67	3.60	1.43
29	27	Block 1	8.00	2.67	51.80	14
26	28	Block 1	8.00	4.00	100.00	24.5
8	29	Block 1	8.00	4.00	3.60	1.18
27	30	Block 1	12.00	4.00	100.00	20
6	31	Block 1	12.00	2.67	3.60	0.88
1	32	Block 1	4.00	1.33	3.60	0.59

```
Report date:          08/09/2009 09:49:59
Printed by:           Lab

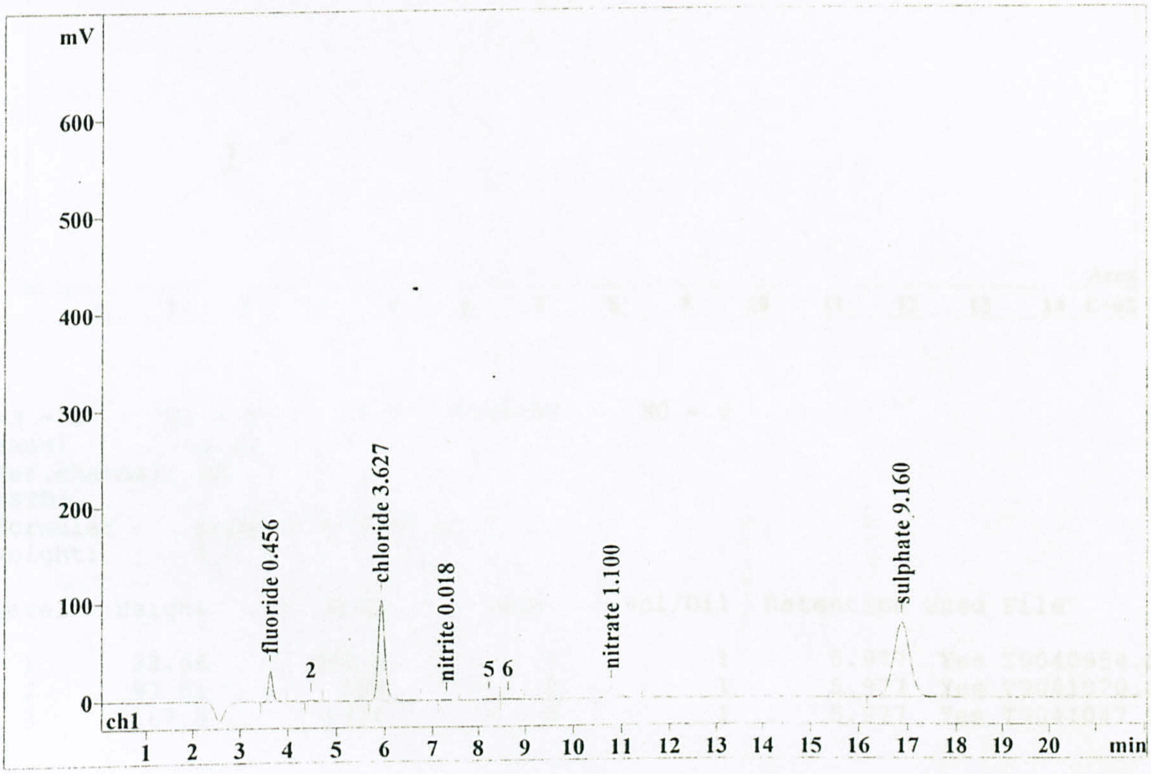
Ident:                TAP WATER
Analysis from:        05/09/2009-03:55:39
File:                 t9050355.chw              Last save: 05/09/2009 04:17:39

Method:               ASUPP5_150_135.mtw             Last save: 04/09/2009 11:0
Run operator:         Lab
Analysis number:      499

COLUMN:               METROSEP A SUPP 5 - 150 (6.1006.520)
Size:                 4.0 x 150 mm
Number:
Part.size:            5.0 µm

ELUENT:               3.2 mM Na2CO3 / 1.0 mM NaHCO3


Flow:                 0.70 mL/min
Temperature:          20.0°C
Pressure:             7.3 MPa
```



```
Quantitation method:   Custom

 No  Retention   Height       Area        Conc.    Name
           min       mV    mV*sec         mg/L
  1       3.63    30.84   203.415        0.456    fluoride
  2       4.48     0.96     7.862        0.000
  3       5.92   103.72   986.823        3.627    chloride ✓
  4       7.29     0.26     3.026        0.018    nitrite
  5       8.22     0.49     6.981        0.000
  6       8.64     0.49     6.603        0.000
  7      10.78    10.15   156.957        1.100    nitrate
  8      16.88    76.72  1764.436        9.160    sulphate
_______________________________________________________
  8      22.00   223.63  3136.102       14.362
```

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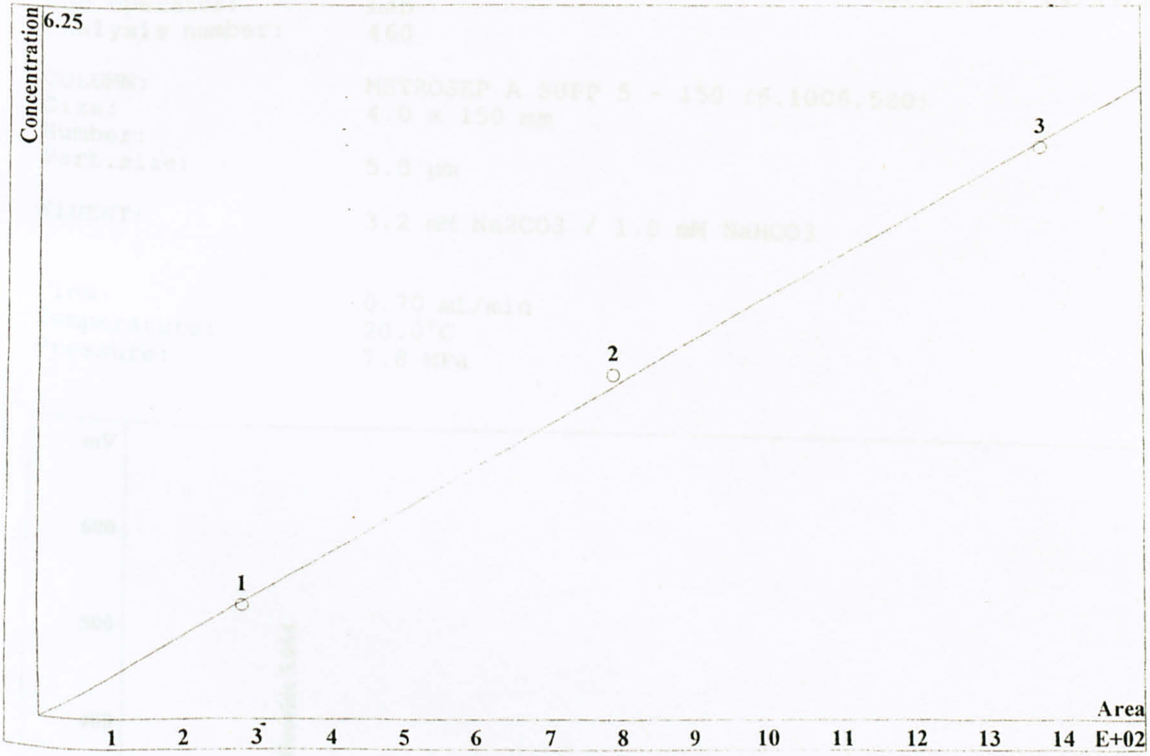
METROHM LTD

CALIBRATION OF COMPONENT chloride

```
Method:                      ASUPP5_150_135.mtw
Equation:                      Q = 0.0036758·A
RSD:                         2.761 %
Correlation coefficient:     0.999165
```



```
K3 = 0       K2 = 0       K1 = 0.0036758       K0 = 0
Base:          Area
Ref.channel: ch1
ISTD:
Formula:       Linear through zero
Weight:        1

Level    Height        Area       Conc.     Vol/Dil  Retention Used File

  1       32.66       281.5           1           1       5.977   Yes T9040954.CHW
  2       93.61         789           3           1       5.977   Yes T9041020.CHW
  3       167.5        1374           5           1       5.977   Yes T9041047.CHW
```

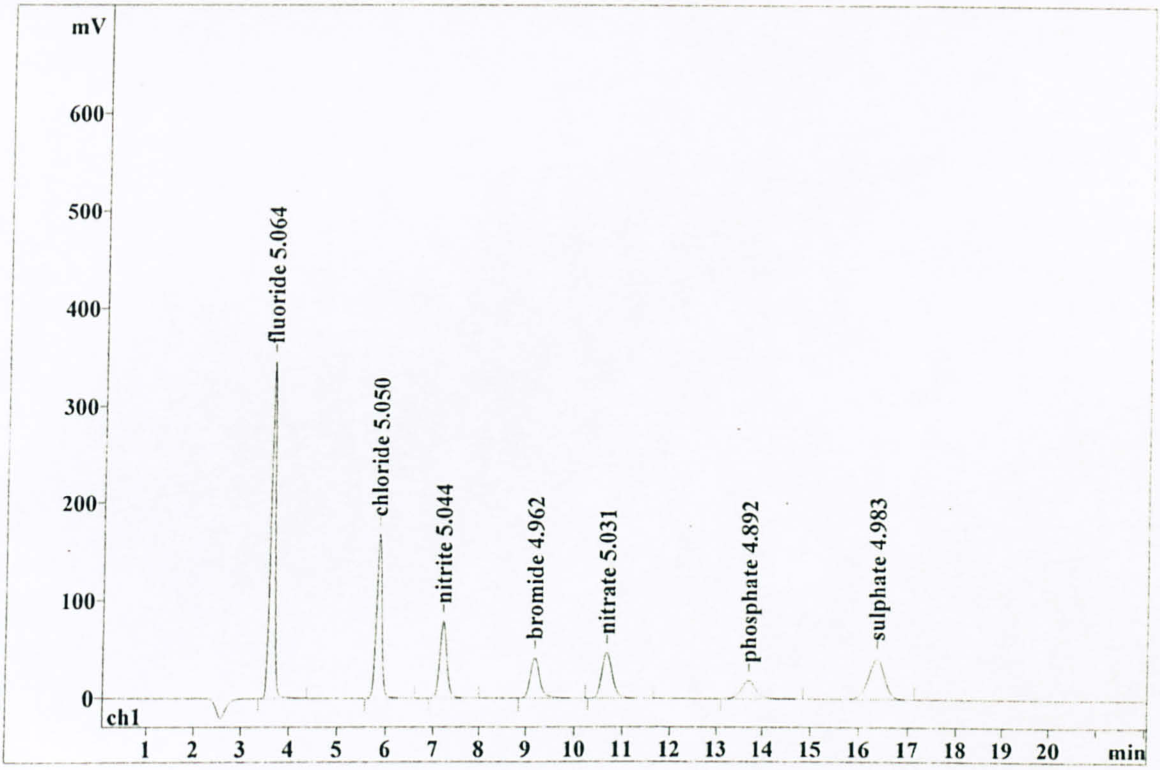
```
Report date:               08/09/2009 09:51:52
Printed by:                Lab

Ident:                     STD3
Analysis from:             04/09/2009 10:47:08
File:                      t9041047.chw              Last save: 04/09/2009 11:09:09
Modified!
Method:                    ASUPP5_150_135.mtw            Last save: 04/09/2009 10:4
Run operator:              Lab
Analysis number:           460

COLUMN:                    METROSEP A SUPP 5 - 150 (6.1006.520)
Size:                      4.0 x 150 mm
Number:
Part.size:                 5.0 µm

ELUENT:                    3.2 mM Na2CO3 / 1.0 mM NaHCO3


Flow:                      0.70 mL/min
Temperature:               20.0°C
Pressure:                  7.8 MPa
```



```
Quantitation method:    Custom

 No  Retention   Height        Area        Conc.    Name
           min       mV     mV*sec         mg/L
  1       3.62   346.33   2259.092        5.064    fluoride
  2       5.82   167.53   1373.912        5.050    chloride
  3       7.20    77.79    830.241        5.044    nitrite
  4       9.16    41.29    591.988        4.962    bromide
  5      10.66    46.49    717.913        5.031    nitrate
  6      13.69    18.42    409.129        4.892    phosphate
  7      16.36    41.98    959.840        4.983    sulphate
______________________________________________________
  7      22.00   739.84   7142.115       35.027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