DISINFECTION BY-PRODUCTS PRECURSORS REMOVAL BY SIMULTANEOUS COAGULATION AND DISINFECTION IN RIVER WATER

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SCHOOL OF CIVIL ENGINEERING
UNIVERSITI SAINS MALAYSIA
2018

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By

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This dissertation is submitted to

UNIVERSITI SAINS MALAYSIA

As partial fulfilment of requirement for the degree of

BACHELOR OF ENGINEERING (HONS.)
(CIVIL ENGINEERING)

School of Civil Engineering,
Universiti Sains Malaysia

June 2018

UNIVERSITI SAINS MALAYSIA

SCHOOL OF CIVIL ENGINEERING
ACADEMIC SESSION 2017/2018

FINAL YEAR PROJECT EAA492/6
DISSERTATION ENDORSEMENT FORM

Title: Disinfection By-Products Precursors Removal by Simultaneous Coagulation and Disinfection in River Water

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I hereby declare that all corrections and comments made by the supervisor(s)and examiner have been taken into consideration and rectified accordingly.

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Date : 13th June 2018

ACKNOWLEDGEMENT

This dissertation would not have been possible without the guidance and the help of several individuals who in one way or another contributed and extended their valuable assistance in the preparation and completion of this research project.

First and foremost, I would like to express my sincere and deep sense of gratitude towards my supervisor, Dr. Nurul Hana Mokhtar Kamal, lecturer from School of Civil Engineering, Universiti Sains Malaysia for her exemplary guidance, creative suggestions and tremendous support throughout this final year project. Her persistent advice and encouragement in improving the research helped me in many ways.

I extend my sincere thanks to all the technical and administrative staff from School of Civil Engineering, Universiti Sains Malaysia for allowing me to use the equipment and facilities. I greatly acknowledged the help and guidance from the staff in Environmental Laboratory especially Mr. Muhammad Zaini Mohd Zuki, Mrs. Samsiah Mohamed Ali, Mr. Mohammed Nizam Mohd Kamal and Mr. Mohad Shukri Zambri throughout my research work.

My deepest gratitude goes to my family for providing unfailing support and giving a continuous encouragement to me throughout the difficult times in the progress of my research. I would also like to thank my friends for their help and support during the laboratory work and thesis writing. Last but not least, thanks to those who were directly or directly involved in the completion of this project.

ABSTRAK

Air adalah komponen yang paling penting dalam evolusi dan kehidupan seharian. Kekurangan bekalan air bersih oleh kerana kehadiran bahan kimia bertoksik dan bakteria berbahaya boleh mendedahkan hidupan kepada penyakit bawaan air yang disebabkan oleh penggunaan air yang tercemar. Pembasmian kuman dalam air minuman mampu mengurangkan risiko penyakit patogenik namun boleh menyebabkan ancaman kimia kepada kesihatan manusia kerana pembentukan produk sampingan disinfeksi (DBPs) dengan kehadiran bahan organik semulajadi (NOM) dalam air. Kehadiran NOM telah menyebabkan banyak masalah dalam air minuman di mana ini boleh disingkirkan melalui beberapa pilihan rawatan seperti penggumpalan. Objektif utama kajian ini adalah untuk mengkaji keupayaan penyingkiran punca DBPs apabila proses penggumpalan dan pembasmian kuman digabungkan. Kajian ini dibahagikan kepada dua bahagian; bahagian pertama melibatkan perbandingan keberkesanan antara dua penggumpal berasaskan ferik untuk proses penggumpalan manakala bahagian kedua melibatkan keberkesanan penyingkiran punca DBPs melalui proses penggumpalan serentak dengan pembasmian kuman. Beberapa parameter seperti tahap kekeruhan, UV_{254}, warna dan karbon organik terlarut (DOC) telah diuji ke atas sampel mentah air sungai dan sampel air selepas dirawat untuk melihat kadar pengingkiran punca DBPs. Penggumpal yang digunakan dalam kajian ini adalah ferik klorida ($FeCl_3$) dan ferik sulfat ($Fe_2(SO_4)_3$) manakala klorin (Cl_2) dan klorin dioksida (ClO_2) telah digunakan sebagai disinfektan. Berdasarkan kajian, peratusan tertinggi penyingkiran tahap kekeruhan adalah 98.03% dengan $FeCl_3$ pada 20 mg/L dan kondisi pH 6.0. Penyingkiran UV_{254} yang terbaik telah dicapai pada 20 mg/L $FeCl_3$ dengan kondisi pH 6.0 (87.91% penyingkiran). Pengurangan warna optimum adalah 98.92% pada pH 5.0 dengan 10 mg/L $FeCl_3$. $FeCl_3$ telah terbukti sebagai penggumpal yang lebih baik

berbanding dengan $Fe_2(SO_4)_3$ dalam menyingkirkan punca DBPs. Menurut dapatan daripada bahagian kedua kajian ini, gabungan antara $FeCl_3$ sebagai penggumpal dan Cl_2 sebagai disinfektan menyebabkan penyingkiran tahap kekeruhan dan UV_{254} yang tertinggi masing-masing pada 97.11% dan 79%. Walau bagaimanapun, gabungan antara $Fe_2(SO_4)_3$ dan Cl_2 mempunyai penyingkiran DOC yang tertinggi iaitu sebanyak 25.5%. Gabungan antara $FeCl_3$ dan Cl_2 menyebabkan penyingkiran tahap kekeruhan dan UV_{254} yang tertinggi manakala gabungan antara $Fe_2(SO_4)_3$ dan Cl_2 mempunyai penyingkiran DOC yang tertinggi dari sampel air.

ABSTRACT

Water was the most important component in our evolution and daily lives. Depletion of clean water supply due to presence of toxic chemicals and harmful bacteria may expose living things to waterborne diseases caused from the consumption of contaminated water. Disinfection in drinking water had significantly reduces the risk of pathogenic diseases but may cause chemical threat to human health due to disinfection by-products (DBPs) formation in the presence of natural organic matter (NOM) in water. The presence of NOM had caused many problems in drinking water, which can be removed by several treatment options such as coagulation. The main objective of this research is to study the ability of DBPs precursors removal when combining coagulation and disinfection process. This study was divided into two parts; the first part involved the comparison between effectiveness of two ferric-based coagulants for coagulation process while the second part involved the efficiency of DBPs precursors removal by using simultaneous coagulation and disinfection. Selected water quality parameters such as turbidity, UV_{254}, colour and dissolved organic carbon (DOC) were tested for raw and treated water samples to observe the DBPs precursors removal. The coagulants used in this study were ferric chloride ($FeCl_3$) and ferric sulphate ($Fe_2(SO_4)_3$) while chlorine (Cl_2) and chlorine dioxide (ClO_2) were used as disinfectants. Based on the study, the highest percentage of turbidity removal was 98.03% with $FeCl_3$ dosage at 20 mg/L and pH condition 6.0. Best UV_{254} removal was achieved at 20 mg/L $FeCl_3$ dosage with pH condition 6.0 (87.91% removal). The optimum colour reduction was found to be 98.92% at pH 5.0 with $FeCl_3$ dosage of 10 mg/L. $FeCl_3$ was proven to be a better coagulant compared to $Fe_2(SO_4)_3$ in removing DBPs precursors, when used alone. According to the result from the second part of this study, the combination between $FeCl_3$ as coagulant and Cl_2 as disinfectant had the highest turbidity and UV_{254} removal

at 97.11% and 79% respectively. However, the combination between $Fe_2(SO_4)_3$ and Cl_2 had the highest DOC removal from the water sample at 25.5%. The combination between $FeCl_3$ and Cl_2 resulted in the highest turbidity and UV_{254} removal while the combination between $Fe_2(SO_4)_3$ and Cl_2 had the highest DOC removal from the water sample.

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LIST OF ABBREVIATIONS

$Ca(OCl)_2$	Calcium Hypochlorite
$CHBr_3$	Bromoform
$CHCl_3$	Chloroform
$CHClBr_2$	Dibromochloromethane
$CHCl_2Br$	Bromodichloromethane
Cl_2	Chlorine
ClO_2	Chlorine Dioxide
DBPFP	Disinfection By-Products Formation Potential
DBPs	Disinfection By-Products
DOC	Dissolved Organic Carbon
$FeCl_3$	Ferric Chloride
$Fe_2(SO_4)_3$	Ferric Sulphate
HMM	High Molar Mass
HOCl	Hypochlorous Acid
HPSEC	High Pressure Size Exclusion Chromatography
IC	Ion Chromatography
MCL	Maximum Contaminant Level
MM	Molar Mass
MOH	Ministry of Health Malaysia
MRDL	Maximum Residual Disinfectants Level
MWD	Molecular Weight Distribution
NaOCl	Sodium Hypochlorite
NOM	Natural Organic Matter

SUVA	Specific Ultra Violet Absorbance
THMs	Trihalomethanes
TOC	Total Organic Carbon
TTHMs	Total Trihalomethanes
USEPA	United States Environmental Protection Agency
UV_{254}	UV Absorbance at 254 nm
WHO	World Health Organisation

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Water is essential to living things including human, animals and plants. Preserving the quality of fresh water is important for the drinking-water supply, food production and recreational use (WHO, 2011). However, in presence of toxic chemicals and harmful bacteria due to human activities, living things may be exposed to waterborne diseases causing from consumption of contaminated water. Contaminated drinking water is a major carrier of disease-causing organisms; these pathogenic organisms may pose a serious threat to human health (Ashbolt, 2004). Depletion of clean water supply may adversely affect the quality of human life. Hence, appropriate water treatment is required to remove the disease-causing agents in drinking water sources which are being subjected to contamination. The most common steps in water treatment used by community water systems include flocculation, sedimentation, filtration and chlorination to provide safe drinking water to the communities.

Since the 1970s, research in the drinking water field has focused on documenting and understanding the occurrence of disinfection by-products (DBPs) in drinking water. Disinfection in drinking water by using chlorine or chlorine dioxide has significantly reduces the risk of pathogenic diseases but may cause chemical threat to human health due to DBPs in the presence of natural organic matter (NOM) in water. NOM has a significant impact on many aspects of water treatment, including the performance of unit processes, necessity for and application of water treatment chemicals, and the biological stability of the water. As a result, NOM affects potable water quality as a carrier of metals and hydrophobic organic chemicals and by contributing to undesirable colour, taste, and odour problems (Sillanpaa, 2014). Besides, NOM or organic precursors may exist in different forms; either dissolved or particulate form, but in another recent studies found that NOM can also occur in an intermediate colloidal state (Beckett and Ranville, 2006).

Chlorinated drinking water may from DBPs such as trihalomethanes (THMs) which comprised of four compounds; chloroform ($CHCl_3$), bromoform ($CHBr_3$), bromodichloromethane ($CHCl_2Br$) and dibromochloromethane ($CHBr_2Cl$) (Hua and Reckhow, 2007). Environmental Protection Agency (EPA) has specified THMs as carcinogenic group (Chang et al., 2010). Ministry of Health Malaysia stated that the maximum allowable limit for TTHMs in drinking water should not exceed 1 mg/L (MOH, 2010). Organic precursors which characterised by total organic carbon (TOC), dissolved organic carbon (DOC), UV absorbance at 254 nm wavelength (UV_{254}) and specific UV absorbance (SUVA) parameters should be removed during water treatment to limit the occurrence of THMs in drinking water. According to USEPA, the percentage removal for TOC to control THMs formation by enhanced coagulation involved pH control (Rizzo et al., 2005).

Water treatment techniques can be applied by water treatment plant to maximise potable water safety and quality while minimising the risk of DBPs. The best approach to reduce DBPs formation is by removing natural organic matter prior to disinfection. EPA has published a guidance document for water system operators entitled, Controlling Disinfection by-products and Microbial Contaminants in Drinking Water as guidelines for water treatment plant operators. According to EPA (2011), one of the processes stated to effectively remove organic matter is coagulation. Coagulation is a process where the repulsive potential of electric double layers of colloids is reduced in such a way that micro-particles can be produced. These micro-particles collide with each other and from larger structures called flocs in the flocculation process.

Coagulation has been employed in water treatment system to decrease turbidity, colour and remove pathogens (Abebe et al., 2016). Ferric salts commonly used in coagulation process include ferric chloride ($FeCl_3$) and ferric sulphate ($Fe_2(SO_4)_3$) (Budd et al., 2004). Many studies have been carried out to compare the effectiveness of one coagulant with another. According to these studies, ferric-based coagulants have been generally noted to remove NOM, measured as DOC and UV_{254}, more effectively than aluminium-based and found to be less sensitive to low temperatures than alum in regard to turbidity removal (Sharp et al., 2006). Most treatment plants optimise their coagulation process for turbidity removal. Coagulation processes can be optimised for natural organic matter removal with higher doses of inorganic coagulants such as ferric-based salts and optimisation of pH (World Chlorine Council, 2008).

Drinking water sources are subject to contamination which leads to waterborne diseases. Hence, an appropriate water treatment is needed to provide safe drinking water to communities. However, in case of disaster such as tsunami and floods, simultaneous coagulation and disinfection is proposed to replace the typical water treatment process. An instant water treatment mix of coagulant-disinfectant can be created in one package to remove heavy metals, chemicals and bacteria by simultaneous coagulation and disinfection within a short amount of time.

1.2 Problem Statement

Chemical disinfectant is being used to kill bacteria and microorganisms in treated water apart from reducing the risk of pathogenic infection. However due to the formation of disinfection-by-products (DBPs) when disinfectant come into contact with natural organic matter present in water, human health may be at risk. The application of disinfection agents to drinking water reduces the microbial risk but lead to chemical risk in the form of their by-products (Sadiq and Rodriguez, 2004). Besides, kidney and liver function may affect human in both acute and long-term exposures due to chloroform (Bhardwaj, 2006). Previous research have been carried out to reduce DBPs in water by using alternative disinfectant such as chloramines and chlorine dioxide which resulted to a lower chlorinated DBPs formation (Hua and Reckhow, 2007).

A safe, reliable, affordable, and easily accessible water supply is essential for good health. Hence, inadequacies in clean water supply during natural disasters may affect health adversely. Lack of clean water supply impacts health by causing acute infectious diarrhoea and non-diarrhoeal disease, which can arise from chemicals such as arsenic and fluoride. An inadequate water supply also prevents good sanitation and hygiene. Consequently, improvements in various aspects of water supply need to be made to prepare for any mishap in the future. An instant water treatment formula which combined coagulant and disinfectant at certain ratio/dosage can be created to replace the typical water treatment process which takes longer time to be completed. This coagulant-disinfectant has distinct advantages of providing microbial quality improvement and turbidity reduction. In case of emergencies such as disasters, water need to be treated in a fast manner due to time constraint. Hence, this treatment formula will be useful for people to treat water in small scale.

1.3 Objectives

The objectives of this research are:

1. To determine the water quality parameters of river water
2. To compare the effectiveness of two ferric-based coagulants, ferric sulphate and ferric chloride for coagulation process
3. To determine the DBPs precursors removal when using simultaneous coagulation and disinfection

1.4 Scope of Work

This study focuses on the DBPs precursors removal by using simultaneous coagulation and disinfection in river water. The surface water sample was taken from the source of Sungai Dua Water Treatment Plant. The water quality parameters tested on the water samples during water sampling at site were pH and temperature. The water quality parameters tested on the water samples in the laboratory were turbidity, UV_{254}, colour and DOC. The effectiveness of ferric sulphate and ferric chloride for coagulation process were studied to determine the optimum dosage and pH. The effectiveness of simultaneous coagulant and disinfectant for water treatment was further discussed in this study. The treated water samples' anions contents were measured by using ion chromatography.

1.5 Importance of Study

This study was carried out to determine the effectiveness in removing DPBs precursors by treating surface water with simultaneous coagulant and disinfectant. The purpose of coagulation and disinfection is to neutralise the charges on particles and deactivate or killing of pathogenic microorganisms respectively. The effectiveness between two types of ferric-based coagulants in removing DBPs precursors is compared between each other. DBPs precursors need to be removed from drinking water since DBPs is a carcinogenic group which gives adverse effects on human health.

Apart from that, ion chromatography was conducted on treated water samples to measure the concentration of anions after coagulation and disinfection were completed. Ministry of Health Malaysia (MOH) had specified the anions contents in drinking water to certain limit. According to the Drinking Water Quality Standards by MOH, maximum acceptable values for chloride, nitrate and sulphate are 250 mg/L, 10 mg/L and 250 mg/L respectively. The guidelines should be adhered for safe and reliable water consumption.

Drinking water sources are subject to contamination which leads to waterborne diseases. Hence, an appropriate water treatment is needed to provide safe drinking water to communities. However, in case of emergencies such as natural disasters, simultaneous coagulation and disinfection is proposed to replace the typical water treatment process.

1.6 Dissertation Outline

This dissertation comprises of five chapters; Chapter 1-Introduction, Chapter 2-Literature Review, Chapter 3-Methodology, Chapter 4-Results and Discussion and Chapter 5-Conclusions and Recommendations.

Chapter 1 outlines overview of the thesis followed by the problem statement to identify and understand why this research was carried out and its relevance to current time followed by the objectives of this research in order to set the desired target of work and finally the justification of this research.

Chapter 2 consists of literature review which explains various subtopics from previous research that is related to the study. Literature review in this dissertation focuses on characterisation of natural organic matter (NOM), coagulation, flocculation, disinfection, type of coagulants and disinfectants, disinfection by-products (DBPs) and potential effects of DBPs on human health.

Chapter 3 explains the research methodology for this study in details. This chapter highlights the procedures that were carried out in this study which consists of water sampling and laboratory work. Methodology of coagulation jar test, water quality parameters and ion chromatography were explained in this chapter.

In Chapter 4, the results are presented in tables and graphs to be further analysed and discussed thoroughly. Effect of combination of coagulants and disinfectants on each water quality parameters and DBPs precursor's removal are discussed in this chapter.

Chapter 5 includes the conclusion and recommendations for future studies based on the results and discussion obtained from this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Characterisation of Natural Organic Matter (NOM)

Natural organic matter (NOM) is defined as a complex matrix of organic materials present in natural waters. As a result of the interactions between the hydrological cycle and the biosphere and geosphere, the water sources used for drinking water purposes generally contain NOM. Thus the amount, character and properties of NOM differ considerably in waters of different origins and depend on the biogeochemical cycles of the surrounding environments (Fabris et al., 2008).

NOM has a significant impact on many aspects of water treatment, including the performance of unit processes, necessity for and application of water treatment chemicals, and the biological stability of the water. As a result, NOM affects potable water quality as a carrier of metals and hydrophobic organic chemicals and by contributing to undesirable colour, taste, and odour problems (Sillanpaa, 2014).

The characterisation of the NOM can be made by high performance size exclusion chromatography (HPSEC) analysis, where the molecular weight distribution (MWD) of NOM can be determined (Chow et al., 2008). Apart from that, fractionation technique where the mixture of organic compounds of NOM are divided into hydrophilic and hydrophobic fractions with resins can be used (Sharp et al., 2006).

The hydrophobic fraction of NOM are composed of humic and fulvic acids (humic substances) and is rich in aromatic carbon, phenolic structures and conjugated double bonds while hydrophilic fractions consist mainly of aliphatic carbon and nitrogenous compounds such as carboxylic acids, carbohydrates and proteins (Świetlik et al., 2004). The humic substances generally account over half of the total organic carbon (TOC) content in water (Matilainen et al., 2010). Humic substances can be regarded as natural anionic polyelectrolytes, with anionic charge at pH values higher than 4. A hypothetical molecular structure of humic acid is shown in Figure 2.1, where important functional groups are illustrated (Duan and Gregory, 2003).

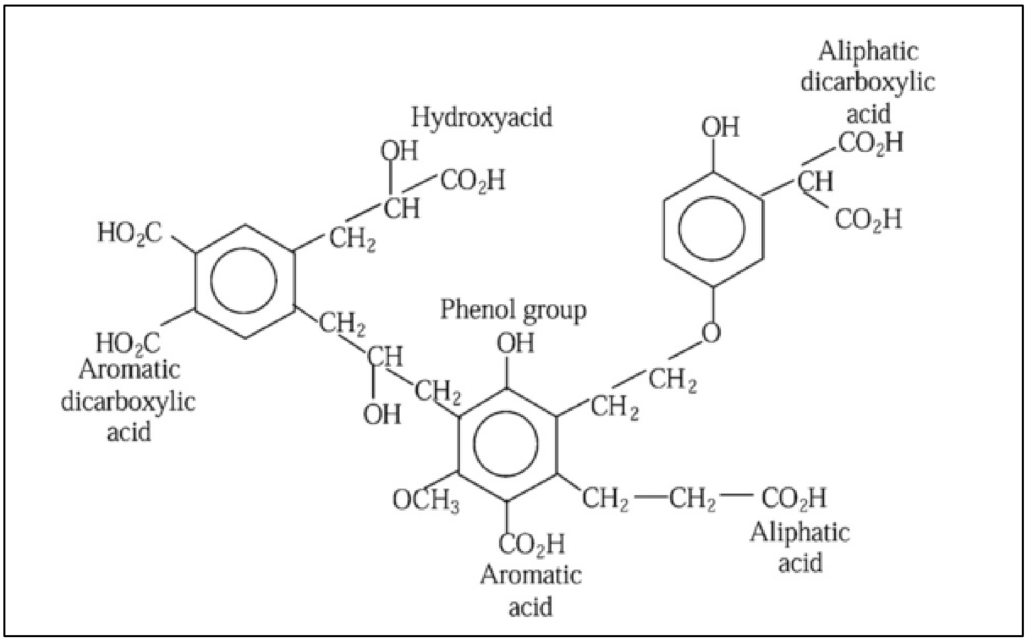

Figure 2.1: Hypothetical Molecular Structure of Humic Acid (adapted from Duan and Gregory, 2003)

Another approach to define hydrophobicity is to determine the SUVA value (i.e. UV_{254} absorbance divided by the TOC concentration). High SUVA value indicates that the organic matter is largely composed of hydrophobic, high MM organic material. Low SUVA value indicates that water contains mainly organic compounds which are hydrophilic, of low MM and have low charge density (Sharp et al., 2006). The different NOM fractions exhibit different properties in terms of treatability by coagulation, coagulant demand, chlorine and ozone reactivity and disinfection by- product formation potential (DBPFP) (Matilainen et al., 2010).

2.2 Coagulation and Flocculation

Coagulation and flocculation are the methods used for aggregating suspended solids into larger and denser particles that will settle and become more filterable. Basically, coagulation is a physical-chemical process aiming at reducing the repulsive potential of electrical double layer of colloids using various coagulants. As a result, colloidal microparticles start to develop and then agglomerate into larger particles or floc (Sillanpää et al., 2018). Flocculation is the process of bringing together the microfloc particles to form large agglomerations by physically mixing or through the binding action of flocculants, such as long chain polymers (Ebeling et al., 2003). Figure 2.2 shows the schematic presentation of a pilot-scale setup used for a coagulation-based water treatment system.

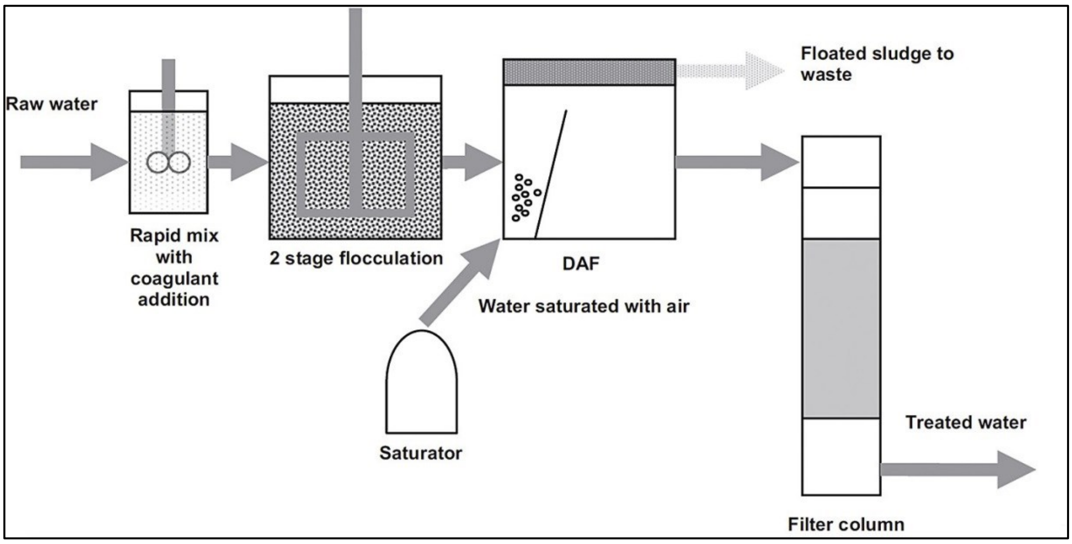

Figure 2.2: Schematic Representation of a Pilot-Scale Setup Used for a Coagulation-Based Water Treatment System (adapted from Jarvis et al., 2012)

This agglomeration phenomenon includes various mechanisms such as charge neutralisation, entrapment, adsorption and complexion with the coagulant's metal ions into insoluble aggregates (Henderson et al., 2006). As far as NOM in concern, and considering the high variability of its organic components in term of molecular and electrical properties, the combined removal mechanisms will substantially differ from one water source to the other and within the same source due to seasonal variations. The result will therefore be a variable removal efficiency of coagulation and the formation of flocs with different sizes and structures (Sharp et al., 2006), which constitutes a serious challenge for the application of coagulation in the treatment of drinking water supplies.

Coagulation has been conventionally applied in water treatment to decrease turbidity and colour and remove suspended particles and pathogens (Volk et al., 2000). The optimum operating conditions to remove turbidity or colour by coagulation are not necessarily the same conditions for NOM removal (Yan et al., 2008). In practice, water treatment by coagulation is carried out by the addition of a determined amount of coagulants (mostly inorganic coagulants such as aluminium or iron salts), which, in the water solution, are dissociated into their trivalent ionic form (Al^{3+} and Fe^{3+}), hydrolysed and end up forming positively charged complexes highly interactive with the negatively-charged colloids (Duan and Gregory, 2003).

The two main operating conditions affecting the overall efficiency of any coagulation process are pH and coagulants' type and dosage. In this regard, when the reaction pH is higher than the minimum solubility of the coagulant (5.8 and 6.3 for ferric chloride and aluminium chloride, respectively), the process generates high molar mass (HMM) polymers or colloidal/precipitated species. In case the pH is lower than the minimum solubility of coagulant, then medium polymers or monomers (Yan et al., 2008). Regarding the effect of coagulants dosage, determining the right amount is a prerequisite for an optimised efficiency (Sillanpää et al., 2018). Thus, overdosing the coagulant results in a substantial increase in the amount of generated sludge and a decrease in pH, while under dosing is generally the cause for the residual metals remaining in treated water (Ibrahim and Aziz, 2014).

2.3 Coagulants

2.3.1 Ferric-Based Coagulants

Ferric salts commonly used in coagulation process such as ferric chloride ($FeCl_3$) and ferric sulphate ($Fe_2(SO_4)_3$) (Abebe et al., 2016). Both coagulants are commercialised either in solid or liquid formulations (Sillanpää et al., 2018). Ferric salts act similarly as aluminium salts once it added in water and form different hydrolysis products. In many research, it has been proved that ferric salts was better in removing NOM compared with aluminium salts especially in removing middle size of NOM fractions. In addition, ferric salts was less sensitive to temperature changes (Matilainen et al., 2010).

Many investigations have been made to compare the effectiveness of different coagulants. According to these studies, ferric-based coagulants have been generally noted to remove natural organic matter (NOM), measured as DOC and UV_{254}, more effectively than aluminium-based one (Sharp et al., 2006).

The application of ferric coagulants is gaining ground over the aluminium counter parts mainly due to the suspected health risks associated with residual aluminium (Flaten, 2001) and the better NOM removal capacities of ferric coagulants. Many studies reported that ferric salts were able to remove more NOM than aluminium salts, under same optimum conditions (Budd et al., 2004; Uyak and Toroz, 2007; Umar et al., 2016). From a mechanistic perspective, several comparative studies pointed out the modus operandi differences between metallic coagulants, mainly ferric and alum ones. In this regard, it was reported that during the coagulation process, ferric chloride ($FeCl_3$) was more effective in removing NOM in comparison with aluminium sulphate ($Al_2(SO_4)_3$), especially for high molecular mass compounds (above 3000 g/mol) (Matilainen et al., 2005).

Application of $FeCl_3$ and $Fe_2(SO_4)_3$ dosages into the water can vary from 5 to 150 mg/L and from 20 to 250 mg/L, respectively (Crittenden et al., 2012). Such variation was due to the spatiotemporal variations of NOM concentrations in the one hand, and the characteristics of the raw water on the other. In this regard, one of the key operating factors was pH, and the various studies conducted to assess its effects on the ferric-based coagulation process showed that the optimum pH range was between 4.5 and 7 (Jarvis et al., 2012; Umar et al., 2016; Zhao et al., 2014). This was slightly lower that the optimum range for aluminium-based coagulants (5.5-7.7 for alum). In practice, determining the optimum pH and dosage of the ferric coagulant is a task that need to be performed on a periodic basis, as the NOM content tends to vary from one water source to the other and within the same water source seasonally. Such effort will help rationalising the use of coagulants chemicals, controlling the amount of generated sludge, and thus optimising the overall coagulation process (Yan et al., 2009). Table

2.1 overviews the operating conditions and the main findings of selected R&D studies conducted around the world between 2010 and 2016 on the removal of NOM from natural waters or synthetic aqueous solutions using ferric-based coagulants.

Table 2.1: Selected Research Studies of the Removal of NOM by Coagulation Using Ferric-Based Coagulants

References	Targeted Organic Compounds	Water Sources and Characteristics	Main Operating Conditions	Monitored Parameters	Optimum Removal Efficiencies	Other Key Results
(Zhao et al., 2014)	NOM	Natural water from the Xiaoqing river (China) Turbidity: 6.20-9.44 NTU pH: 7.95-8.46, DOC: 3.90-4.55 mg/L UV254: 0.067-0.073 cm^{-1}	Coagulant: ferric chloride ($FeCl_3$) Dosage: 15 -90 mg/L pH: 5-10	% removal of DOC and UV_{254}	A reduction of 47.6% in UV_{254} and 57.9% in DOC were reported.	The optimum pH and dose of coagulant were 7 and 65 mg/L respectively.
(Jarvis et al., 2012)	NOM	Natural water from a reservoir (Northern UK) Turbidity: 3.5 NTU DOC: 12.9 mg/L Specific UV absorbance (SUVA): 4.8 L/mg-m	Coagulant: Ferripol XL, a ferric sulphate based coagulant Dosage:5 -15 mg/L pH: 4-8 Reaction time: around 30 min Stirring rate: 30 -200 rpm	Removal of DOC and turbidity	A DOC removal of 80.5% was reported, along with a turbidity residual of 1.15 NTU, at pH 4.5-5 and a dose of 5 mg/L.	The optimum pH was between 4.5 and 5 for the three tested coagulant concentrations (5, 10 and 15 mg/L)

References	Targeted Organic Compounds	Water Sources and Characteristics	Main Operating Conditions	Monitored Parameters	Optimum Removal Efficiencies	Other Key Results
(Chekli et al., 2017)	Algal Organic Matter	Algal turbid water Turbidity: 20 NTU pH:8.7	Coagulant: $FeCl_3$ Dosage: 0.03-0.02 mmol/L pH: 5-9 Reaction time: 40 min Stirring rate: 40-200 rpm	Turbidity Floc formation size	Turbidity removal efficiency was around 97%	The optimum dosage of $FeCl_3$ was 15mg/L
(Tubić et al., 2013)	NOM	Source water from the Vojvodina region (Serbia) pH: 7.5 DOC: 3.9 mg/L UV254: 0.45 cm^{-1} Turbidity: 15 NTU	Coagulant: $FeCl_3$ Dosage: 18-300 mg/L pH: 7 Reaction time: 32 min Stirring rate: 120 rpm	DOC, UV_{254}, SUVA, trihalomethanes formation potential (THMFP) and haloacetic acid formation potential (HAAFP).	The application of the Fe-based coagulant enabled a substantial removal of NOM, with a reduction of DOC, UV_{254} and SUVA by 51%, 70% and 30%, respectively.	Comparing the DOC species in the raw and coagulated water, the hydrophobic fraction was significantly lowered by the coagulation process, along with the complete removal of the HA fraction.

2.4 Disinfection

Chemical disinfection is used to destroy or control the growth of microorganisms present in water that would otherwise cause fouling, corrosion of equipment or lead to diseases from microbial activity (Kumar and Pandit, 2012). In Malaysia, chlorination has been used as primary disinfectant to manage and reduce formation of pathogens in drinking water and water treatment plant (Chang et al., 2010). Disinfection in drinking water by using chlorine or chlorine dioxide has significantly reduces the risk of pathogenic diseases but may cause chemical threat to human health due to disinfection by-products (DBPs) in the presence of natural organic matter (NOM) in water (Hrudey, 2008). The toxic effect of total residual chlorine on fresh water organisms has been confirmed at low concentrations. Residual chlorine and bromine can combine with organics in a receiving water to form halogenated organic compounds which may be carcinogenic to humans (Alley, 2007).

2.5 Disinfectants

Chemicals used for disinfection include halogens such as chlorine, bromine and iodine, metallic ions such as silver or copper as well as ozone, hydrogen peroxide, acids and bases (Alley, 2007). Almost all water systems that disinfect their water use some type of chlorine-based process, either alone or in combination with other disinfectants (World Chlorine Council, 2008). Table 2.2 shows the percentage of drinking water systems using each of these methods.

Table 2.2: Disinfection Methods for U.S. Drinking Water Systems (adapted from World Chlorine Council, 2008).

Disinfectant	Large Systems (>10,000 persons)	Small Systems Using Groundwater (<10,000 persons)	Small Systems Using Surface Water (<10,000 persons)
Elemental Chlorine	84%	61%	82%
Sodium Hypochlorite	20%	34%	17%
Calcium Hypochlorite	<1%	5%	9%
Chloramines	29%	-	2%
Ozone	6%	-	-
UV	-	-	-
Chlorine Dioxide	8%	-	6%

Elemental chlorine (chlorine gas) was mostly used in disinfection of U.S. drinking water systems followed by sodium hypochlorite (bleach) and dry calcium hypochlorite. Each of the disinfectant has its own advantages and limitations for particular applications.

2.5.1 Chlorine

The application of chlorine is still the most common method of disinfection. It is economical, effective and helpful in controlling tastes and odours, irons and manganese, slime-producing bacteria, cyanides, and phenols (Sarai, 2005a). Chlorine can be applied in many forms such as gaseous chlorine (Cl_2), sodium hypochlorite solution ($NaOCl$) or calcium hypochlorite ($Ca(OCl)_2$) (USEPA, 1999a).

When gaseous chlorine (Cl_2) is added into the water, hypochlorous acid (HOCl), hydrogen ion (H^+) and chloride ion (Cl^-) would be produced. The reaction is as in Equation 2.1:

$$Cl_2 + H_2O \longleftrightarrow HOCl + H^+ + Cl^- \qquad [2.1]$$

The two most common compounds of chlorine used for disinfection are calcium hypochlorite and sodium hypochlorite. Calcium hypochlorite reacts in water as in Equation 2.2 to disinfect:

$$Ca(OCl)_2 + H_2O \longrightarrow 2\ HOCl + Ca(OH)_2 \qquad [2.2]$$

Sodium hypochlorite is produced in white powder or tablet form and is completely soluble in water. It is available in up to 70 % available chlorine and can cost much as twice the chlorine gas.

On the other hand, sodium hypochlorite reacts in water as in Equation 2.3 as a disinfectant:

$$NaOCl + H_2O \longrightarrow HOCl + NaOH \qquad [2.3]$$

Sodium hypochlorite is usually produced in clear liquid form and is completely soluble in water as well. It has from 5% to 15% available chlorine and can decompose with exposure to light and heat, especially at higher concentrations. The 15% concentration is the maximum practical for stability reasons. Sodium chlorite is more costly than chlorine gas (Alley, 2007).

The decomposition of HOCl and OCl^- are depending on pH (Durmishi et al., 2015). HOCl which is a strong disinfectant, is the principal disinfecting form of chlorine (Sarai, 2005a). Both of HOCl and OCl^- are good disinfecting agents but HOCl is more effective than OCl^-. The ratio of HOCl to OCl^- is determined by the pH balance and water temperature (Summerhayes, 2014). HOCl is a weak acid which is dominant at pH between 5.5 and 7.5 while OCl^- in pH greater than 7.5. Therefore, the pH level influences the effectiveness of chlorine disinfectants. Since chlorine is more effective as a disinfectant at lower pH, water utilities with chlorinated systems need to maintain the pH for the effectiveness of disinfection with chlorine (Durmishi et al., 2015).

Since the effectiveness of chlorine is pH dependent, free residual chlorine is more active at lower pH. Table 2.3 shows the suggestion of the minimum free residual chlorine required at different pH values for disinfection. The amounts shows will satisfactorily disinfect water at 20^oC in about 10 minutes (Sarai, 2005a).

Table 2.3: Minimum Free Residual Chlorine Required at Different pH Values (Sarai, 2005a)

pH value	**Free Residual Chlorine**
6-8	0.2 ppm
8-9	0.4 ppm
9-10	0.8 ppm

Note: Conversion factor in air: 1 ppm = 2.9 mg/m^3

Among the advantages of chlorine is chlorine disinfectant can reduce the disease-causing microorganisms level in the drinking water. Besides, disagreeable taste and odour can be reduced since chlorine can oxidise many naturally occurring substances such as foul-smelling algae secretions, odours and sulphides from decaying vegetation. Chlorine disinfectant can also eliminate slime bacteria, molds and algae that commonly grow in water supply reservoirs, on the walls mains and in storage tanks. Apart from that, iron and manganese can be removed from raw water with the application of chlorine as disinfectant (World Chlorine Council, 2008).

Chlorine disinfectant has several limitations in disinfection of water system. According to USEPA (1999b), the chlorine residuals even at low concentrations is toxic to aquatic life and may require dechlorination. All forms of chlorine are highly toxic. Hence, storage, handling and transportation of chlorine need to be adhered to the safety regulations. Reaction of free chlorine with humic substances in water may form disinfection by products (DBPs) (Kim et al., 2003). However, the optimisation of the treatment system may control the formation of disinfection by-product formations (Gorchev and Ozolins, 2011).

2.5.2 Chlorine Dioxide

Chlorine dioxide is another bactericidal agent whose disinfectant power is equal to or higher than chlorine. Chlorine dioxide is a yellow-green gas with a pungent smell, water-soluble, but very unstable (Collivignarelli et al., 2018). It is usually produced by sodium hypochlorite and hydrochloric acid according to the reaction in Equation 2.4:

$$5\ NaClO_2 + 4\ HCl \longrightarrow 4\ ClO_2 + 5\ NaCl + 2\ H_2O \qquad [2.4]$$

Chlorine dioxide is characterised by high oxidising power, which is the cause of its high germicidal potential. Due to the high oxidative power, possible bacterial elimination mechanisms may include inactivation of enzymatic systems or interruption of protein synthesis (Cho et al., 2010). The use of chlorine dioxide (ClO_2) as a water disinfectant has widely being used because it is stable either in neutral or acidic dilute aqueous solutions if kept cool. ClO_2 is widely being used in Europe, United State and Canada (Li et al., 1996).

In comparison to Cl_2, ClO_2 did not typically react with NOM or humic substances. Its effectiveness was not affected by ammonia and pH conditions. ClO_2 pre-oxidation can minimise THMs and other disinfection by-products (Yang et al., 2013). ClO_2 that was used as alternative to Cl_2 corresponded to 81% reduction in the THMs concentrations in distribution system (Volk et al., 2002). Apparently, chlorine dioxide weakens the pathogens, while chlorine or chloramines destroy them (Sarai, 2005b).

According to Pereira et al. (2008), ClO_2 was more efficient in killing bacteria compared to Cl_2 over a wide range of pH and did not lead to formation of DBPs. ClO_2 is a more effective bactericide than Cl_2 due to its higher oxidation capacity under pH, temperature, and turbidity ranges depending on the source of raw water that was expected in the treatment of potable water (Pandit and Kumar, 2013).

Maximum residual disinfectants level (MRDL) in drinking water was very important to ensure the safety of a drinking water. Thus, Environmental Protection Agency (EPA) and Ministry of Health Malaysia (MOH) had adopted standards to limit the level of residual disinfectants in drinking water. Both agencies had set regulations for maximum residual disinfectant level for three types of disinfectants namely chloramine, chlorine and chlorine dioxide as shown in Table 2.4.

Table 2.4: Maximum Residual Value for Chloramine, Chlorine and Chlorine Dioxide (USEPA, 2012; MOH, 2010)

Disinfectant	MRDL (USEPA)	MRDL (MOH)
Chloramine	4 mg/L or 4 ppm	-
Chlorine	4 mg/L or 4 ppm	5 mg/L or 5 ppm
Chlorine Dioxide	0.8 mg/L or 800 ppb	-

WHO had set a guideline value for chlorite in drinking water of 0.2 mg/ L. In the UK a limit for combined residual concentrations of chlorine dioxide, chlorite and chlorate had been set at 0.5 mg/ L as ClO_2 in treated water, with a corresponding maximum contaminant level (MCL) of 1.0 mg/ L set by the USEPA. In practice, these limit values restricted chlorine dioxide doses to 0.75 and 1.5 mg/ L in the UK and USA, respectively. Such limits mean that the use of chlorine dioxide as a main disinfectant for drinking water was no longer possible. However, it was still widely used prior to treatment for pre-disinfection or as a pre-oxidant for the removal of taste, odour, colour, phenol, iron and manganese (WHO, 2011). The use of chlorine dioxide as disinfectant create highest disinfection-by-products of chlorite (ClO_2^-) and chlorate (ClO_3^-) ions (Sorlini et al.,2014).

2.6 Disinfection-by Products

DBPs were formed when disinfectants react with natural organic matter (NOM) in water. Formation of DBPs may affect from various factors such as pH, temperature, disinfectant concentration, contact time, NOM and precursor properties (Yang et al., 2013). Table 2.5 shows the common characteristics of DBPs.

Table 2.5: Common Characteristics of DBPs (Adapted from WHO, 2008)

Disinfection-by-Products (DBPs)		Commonness	Effects on Health
Trihalomethanes	Chloroform	High	Carcinogenic
	Bromoform	Moderate	Carcinogenic, Genotoxic
	Dibromochloromethane	Moderate	Carcinogenic, Genotoxic
	Bromodichloromethane	Moderate	Carcinogenic, Genotoxic

Chlorinated drinking water may form DBPs such as THMs which consist of four compounds and it is widely known that THMs is the most prevalent group formed during chlorination process (Hua and Reckhow, 2007). THMs comprised of four compounds; chloroform ($CHCl_3$), bromoform ($CHBr_3$), bromodichloromethane ($CHCl_2Br$) and dibromochloromethane ($CHClBr_2$). THMs is categorised as carcinogenic group; specified by EPA (Chang et al., 2010). According to Ministry of Health, Malaysia, the maximum allowable limit for TTHMs in drinking water is 1 mg/L and it should not exceed the limit in order to have a safe-reliable drinking water (MOH, 2010).

In order to limit the occurrence of THMs in drinking water, organic precursors should be removed during water treatment; this is usually characterised by TOC, DOC, UV_{254} and SUVA parameters. According to USEPA, the percentage removal for TOC to