FORMATION OF TRIHALOMETHANES IN SURFACE WATER AND GROUNDWATER BY USING CHLORINE AND CHLORINE DIOXIDE AS DISINFECTANT

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ABSTRAK

Air merupakan unsur yang penting bagi manusia dan alam sekitar. Pencemaran air khususnya air minum disebabkan oleh virus, bakteria patogen dan mikroorganisma yang lain perlu dirawat sebelum disalurkan kepada pengguna. Disinfeksi merupakan satu proses yang penting dalam perawatan air bagi memusnahkan mikroorganisma yang terdapat di dalam air. Hasil daripada proses disinfeksi, pelbagai jenis hasil sampingan disinfeksi (DBP) terhasil dan ianya didapati menjejaskan kualiti air minum dan boleh membahayakan kesihatan manusia dimana ianya bersifat karsinogenik. Selain daripada klorin, penggunaan disinfektan lain seperti klorin dioksida juga didapati mampu membunuh mikroorganisma yang terdapat di dalam air. Oleh itu kajian ini dijalankan bagi membandingkan penggunaan klorin dan klorin dioksida sebagai disinfektan dalam penghasilan trihalometana dan untuk menghubungkaitkan tahap penghasilan THM menggunakan disinfektan klorin dan klorin dioksida terhadap pH. Berdasarkan hasil kajian yang dijalankan, klorin didapati menghasilkan trihalometana yang lebih tinggi berbanding klorin dioksida. Berdasarkan hasil kajian pada air bawah tanah, TTHM maksimum dijumpai pada pH 7 dalam tempoh masa 24 jam dengan jumlah trihalometana sebanyak 49.4 µg/L dengan penggunaan klorin sebagai disinfektan, manakala jumlah TTHM terendah juga berada pada pH 7 dalam tempoh masa 3 jam dengan penggunaan klorin dioksida sebagai disinfektan dengan jumlah TTHM sebanyak 5.4 µg/L. Hubungan disinfektan terhadap pH tidak menunjukkan hubungkait yang jelas memandangkan terdapat penurunan dan penaikan jumlah TTHM yang berbeza pada setiap pH.

ABSTRACT

Water is an important element for human and environment. Water pollution in drinking water which was caused by viruses, bacteria, pathogens and microorganisms need to be treated before being distributed to the consumers. Disinfection is one of the important process in treating water to kill microorganisms. Disinfection process causes the formation of disinfection by products (DBP) which affect the quality of drinking water and can harm human health due to its carcinogenic. The use of other disinfectant such as chlorine dioxide can also be used to kill microorganisms in water. Therefore, this study was carried out to compare the formation of trihalomethanes using chlorine and chlorine dioxide as water disinfectants and to find the relationships between chlorine and chlorine dioxide to pH. Based on the study, chlorine is found out to formed high trihalomethanes compared to chlorine dioxide. Based on the study on the groundwater samples, the maximum TTHM were found at pH 7 in the contact time of 24 hours with the value of 49.4 µg/L with the used of chlorine as disinfectants, while the minimum value of trihalomethanes found is also at pH 7 in the contact time of 3 hours with the used of chlorine dioxide as the disinfectants with the value of 5.4 µg/L. The relationships of disinfectants used in this study to pH does not shows a strong relationship since there were different fall and increment of total trihalomethanes at every pH.

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LIST OF ABBREVIATIONS

BDOC	Biodegradable Dissolved Organic Carbon
$CHBr_3$	Bromoform
Cl_2	Chlorine
ClO_2	Chlorine Dioxide
$CHCl_3$	Chloroform
$CHBrCl_2$	Bromodicholomethane
CHClBr2	Dibromochloromethane
DBPs	Disinfection by-products
DOC	Dissolved Organic Carbon
HOCl	Hypochlorous Acid
MOH	Ministry of Health Malaysia
MRDL	Maximum Residual Disinfectants Level
NOM	Natural Organic Matter
SUVA	Specific Ultra Violet Absorbance
THMs	Trihalomethanes
TOC	Total Organic Carbon
TTHM	Total Trihalomethanes
USEPA	United States Environmental Protection Agency
UV_{254}	UV Absorbance at 254nm
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Water is very important substances on earth which benefits human, plants and animals. Water that is transparent and nearly colorless in physical characteristics are chemical substance that is the main essential constituent of earth's streams, oceans and lakes and the fluids of most living organisms. Drinking water sources which subject to contamination require appropriate treatment to remove disease-causing agents. Public drinking water systems use various methods of water treatment to provide safe drinking water for communities. The quality of drinking water is very important thing in the health aspect for all living beings. The water treatment process may vary slightly in different locations, depending on the technology of the plant and the water it needs to process, but the basic principles are basically the same. Water treatment processes have shown a significant improvement over the past century in an effort to reduce waterborne disease and transmission. Many techniques have been developed in response to local conditions with other various objectives besides disinfection, including colour reduction, softening, turbidity removal, taste and odor control, and corrosion control.

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. Chemical disinfection is used to destroy or control the growth microorganisms present in water that would otherwise cause fouling, corrosion of equipment, or lead to disease from microbial activity (Pandit & Kumar, 2013). Disinfection in drinking water has significantly reduces the risk of pathogenic infection but may cause chemical threat to human health due to disinfection residues and their by-products (DBPs) when the organic and inorganic precursors are present in water. 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 & Rodriguez, 2004).

Trihalomethanes (THMs) formation in treated water is a result of a reaction between the disinfectant such as chlorine and chlorine dioxide used for water disinfection and some natural organic matters. THMs can be form when chlorine is added to water with organic material, such as algae, river weeds, and decaying leaves (Madabhushi, 1999). THMs are formed in drinking water generally as result of chlorination of organic matter occur in raw water supplies. The chlorine, chlorine dioxide, and humic acid concentration, temperature, pH, and bromide ion concentration cause the rate and degree of THMs formation increase (World Health Organization, 2004)

1.2 Problem Statement

A safe drinking water is very important. The quality of water has been associated with health. Drinking water is an important public health issue, state and local officials closely monitor for contaminants and work together to protect water quality (Pandit & Kumar, 2013). Drinking water can be contaminated by two sources either by man-made chemicals or by natural sources, like heavy metals in rock and soil. Natural waters contain impurities. Impurities is harmless. However, in certain levels of microorganisms, minerals, man-made chemicals, or naturally-occurring pollutants in drinking water can be harmful to health.

Chemical disinfectants are known as antimicrobial agents that kill or inhibit the growth of microorganisms. Disinfection in drinking water has relatively reduces the risk of pathogenic infection. However, due to disinfection residues and their by-products (DBPs) when the organic and inorganic precursors are present in water, it may cause chemical threat to human health. 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 & Rodriguez, 2004). The application of disinfection agents to drinking water can reduces microbial risk. However, it also poses chemical risk in the form of their by-products. Disinfectant which reacts with natural organic matter (NOM) and/or inorganic substances present in water may cause the formation on DBPs (Sadiq & Rodriguez, 2004).

Disinfection is well known as the final step in the water treatment process to prevention of secondary pollution due to regrowth of pathogenic microorganism in the water distribution system. (Mohammadi et al., 2015). According to research study in 2006, DBPs may affect health which it have been linked to bladder and rectum cancer, and may also have reproductive and development effects. Besides that, kidney and liver function may affects in humans in both acute and long-term exposures due to chloroform (Bhardwaj, 2006) Thus, this study is carried out to correlate THM formation level from different disinfectants to selected water quality parameters.

1.3 Objectives

The objectives of the study are:

i. To compare THMs formation level from chlorine and chlorine dioxide as disinfectant from surface water and groundwater.

ii. To determine the relationship between THMs formation level using chlorine and chlorine dioxide to pH.

1.4 Scope of Study

The scope of this study are as follows:

i. The water samples were taken at surface water and groundwater. The sample of surface water are from Jalan Baru river, Perak while the groundwater are from the water source at the borehole located in Universiti Sains Malaysia, Engineering Campus. Both of the samples were taken at difference sources to know the formation of trihalomethanes from different characteristics of water sources in different content of organic matter.

ii. The water quality parameter for all samples collected were tested. The parameter tested were pH, dissolved organic carbon (DOC) and UV_{254}.

iii. All of the water samples taken were disinfected by using two disinfectants which are chlorine (Cl_2) and chlorine dioxide (ClO_2) to determine THMs formation.

iv. All of the samples were extracted and analyzed by using gas chromatography to obtain THMs concentrations.

1.5 Importance and Benefit of Study

This study is carry out to make a comparison between the THMs formation level by using different disinfectants which are chlorine and chlorine dioxide from surface and groundwater. The relationship between disinfectants used to pH in the formation of THMs is study since the formation is known to cause negative effects to human health. This study is very important to know the efficiency of using chlorine and chlorine dioxide in reducing the formation of THMs.

Chlorine is one of the most common disinfectant used water treatment. In this study, both chlorine and chlorine dioxide are used as disinfectants. Based from the study, the different results obtained will be compared to the Malaysian Drinking Water Quality Standard and the results can be compared to know the formation of THMs from different disinfectants.

pH is an important parameter to be control in water because the value may effect the formation of trihalomethanes. There is a study saying that DBPs have been linked to bladder and rectum cancer, and may also have reproductive and development effects. Therefore an efficient disinfectant with several parameter value that can control DBPs need to be carry out.

1.6 Dissertation Outline

There are five chapters consists in this dissertation. The first chapter is an introduction to the study which is consists of background study, problem statement, objectives, scope of study and importance and benefits of study.

Next, Chapter 2 is on the literature review. It covers various subtopics that is related to the study. Chapter 2 consists of subtopic of characterization of natural organic matter, disinfectants of chlorine and chlorine dioxide, disinfection by-products (DBPs) and its occurrence in drinking water, potential of DBPs effects on human health, formation of trihalomethanes and also the formation of chlorate and chlorite based on previous study.

Chapter 3 is about the method on how the study was be carried out. Chapter 3 explains on the procedures that were carried out in this study from the beginning until the analysis of THMs. There are explanations about the procedures that were carried out which are to check the water quality parameters for pH, dissolve organic carbon (DOC), temperature and UV_{254}. This chapter also highlights about the procedure carried out to prepare disinfected samples and to prepare the extraction samples until the GC-MS analysis to obtain the formation of trihalomethanes.

Chapter 4 consists of the results and discussion. All of the data obtained will be analyzed and discussed in this chapter. This chapter is very important as it is the final finding results for the study.

Lastly, the final chapter would be chapter 5 which is the conclusion and recommendations for the future studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Characterization of Natural Organic Matter (NOM)

Natural organic matter (NOM) is organic compound that is found in complex mixtures that are present in all fresh water such as surface waters. Fooladvand et al. in 2011 found that DBPs in drinking water were affected by NOM, pH, bromide concentration (Br^-), water temperature, chlorine dosage (Cl_2) and residence time. NOM generally affect water treatment processes such as coagulation, oxidation, adsorption, and membrane filtration. It has to be removed from drinking water for practical and hygienic reasons. NOM are the product of various decomposition and metabolic reactions in the water supply and its surrounding watershed. Solid or liquid separation process to remove particulate material is known to be one of the most basic processes in the treatment of raw water source to meet drinking water standard. Disinfection by-products (DBPs) have been a main indication for specific focus on removal of NOM in water supply. Removal of other particle classes, such as microorganisms and particulate forms of NOM is found to be beneficial for efficient treatment (Au et al., 2011)

The characteristics and amount of NOM in surface water depends on many aspects such as geology, climate and topography. Better drinking water quality requires the removal of organic matter. Thus, designing and operating a drinking water treatment plant requires emphasis on the evaluation of removal technologies for NOM (Matilainen et al., 2011). Typically NOM characteristic is dependent on the biodegradable dissolved organic carbon (BDOC) content in water sources. Autochthonous NOM is a type of NOM that originates from the decay of biota living in water bodies such as algae and bacterias (Ibrahim & Aziz, 2014). According to the past study, characteristics and properties of NOM are based on the origin of water sources (Sharp et al., 2006). Hence different methods were proposed for removing or reducing NOM amount in drinking water sources. Presence of NOM give significant impact to the quality of drinking water sources (Matilainen & Sillanpaa, 2010).

The diversity of molecules that constitute NOM and the relative low concentrations of NOM in water often makes characterization of NOM difficult. Different fractions and the chemical groups involved in NOM structure are summarized in Table 2.1 while the relationships are as shown in Figure 2.1. Based on the Table 2.1 and Figure 2.1, it shows that humic acid, fulvic acid, proteins, aromatic amines, hydrocarbon and ether are from the fraction of hydrophobic acids while sugars, hydroxyl acids, amino acids, ketones and purines are from the fraction of hydrophilic acids.

Table 2.1: Fractions and chemical groups of NOM (Adapted from Bhardwaj, 2006)

Fraction	**Chemical Group**
i) Hydrophobic Acids	
Acid	Humic and Fulvic Acids
Bases	Proteins, Aromatic Amines
Neutrals	Hydrocarbon and Ether
ii) Hydrophilic Acids	
Acid	Sugars, Hydroxy Acids and Carbohydrates
Bases	Amino Acids and Purines
Neutrals	Polysaccharide and Ketones

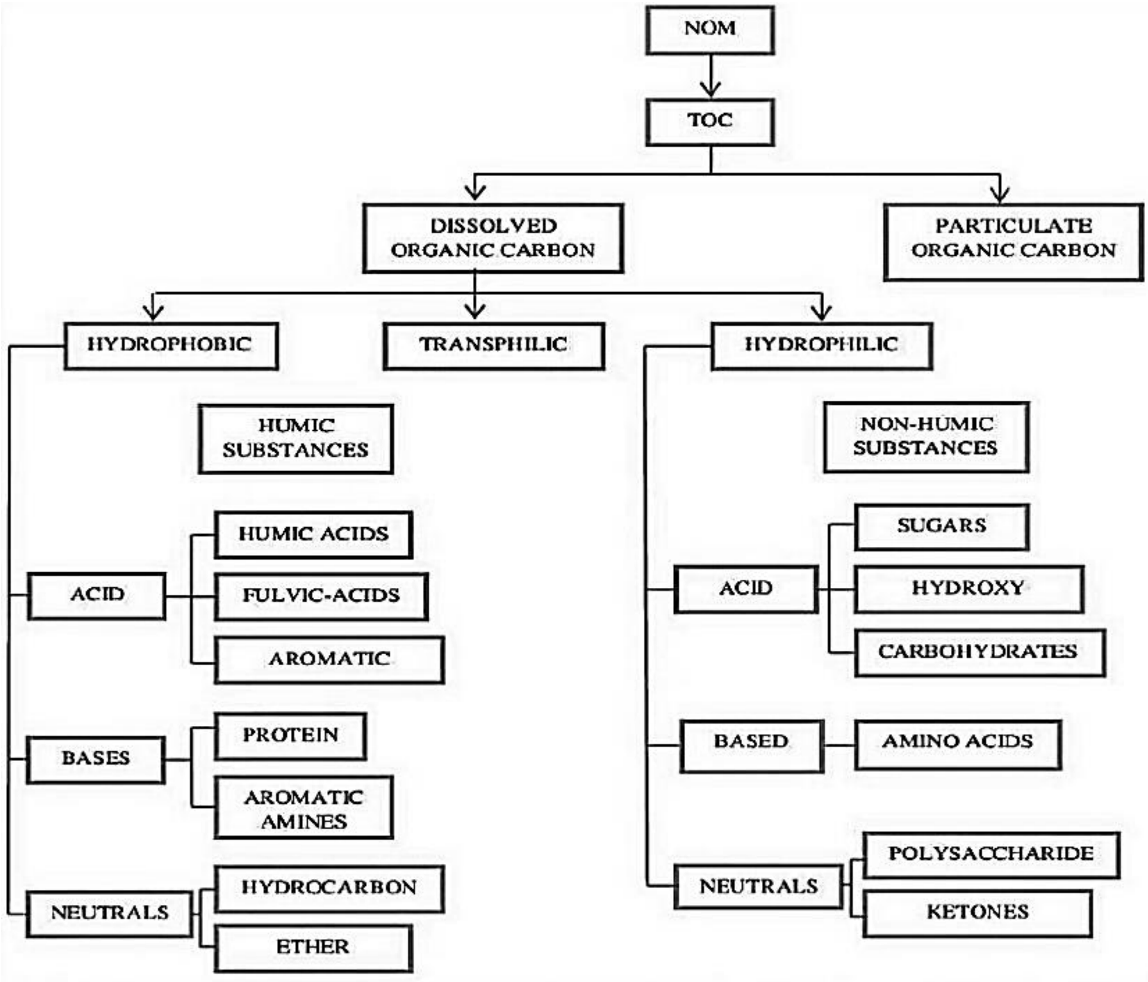

Figure 2.1: NOM fraction and its chemical groups relationships (Ibrahim & Aziz, 2014)

Based on previous study, low specific UV absorbance (SUVA) value indicated that there is less aromatic carbon present in the water. The less aromatic carbon present can be considered as the stronger precursor to trihalomethanes due to the hydrophilic fraction that is isolated from low humic waters if compared to hydrophobic fraction (Croue et al, cited in Ibrahim & Aziz, 2014). Humic acid and Fulvic acid are the fraction of NOM that are considered as reactive fractions in the formation of DBPs (Wang et al,. 2015).

2.2 Disinfectants

Disinfectants are chemical substances used to destroy viruses and microbes (germs), such as bacteria and fungi, as opposed to an antiseptic which can prevent the growth and reproduction of various microorganisms, but does not destroy them. There are many types of disinfectants that can be used in the disinfection process of drinking water such as chlorine, chlorine dioxide, ozone and chloramine.

2.2.1 Chlorine

The application of chlorine is still the most common method of disinfection. It is economical, effective and helpful in controlling tastes and odors, irons and manganese, slime-producing bacteria, cyanides, and phenols. (Sarai, 2006). The advantages of chlorine is that it has effectively proven against bacteria and viruses. Some protozoan cysts are resistant to the effects of chlorine (Safe Drinking Water Foundation, n.d.). Chlorine react with natural organic matter (NOM) (WHO, n.d.). It is available as compressed elemental gas, sodium hypochlorite solution (NaOCl) or solid calcium hypochlorite ($Ca(OCl)_2$.

The purpose of chlorine disinfection is to kill microbes that exist in drinking water. The disinfection by-products (DBPs) formed by the reaction of free chlorine with humic substance in the water (Kim et al., 2003). The disadvantages of chlorine is it is able to react with natural organic matter to produce THMs and other halogenated DBPs. However, the optimization of the treatment system may control the formation of by-product formation (Gorchev & Ozolins, 2011). Table 2.2 shows the physicochemical properties of chlorine.

Table 2.2: Chlorine Physicochemical Properties

(Adapted from Fawell et al.,1996)

Property	**Value**
Boiling point	-34.6^{o}C
Melting point	-101^{o}C
Density	3.214 g/litre at 0^{o}C and 101.3 kPa
Vapour pressure	480 Pa at 0^{o}C
Water solubility	14.6 g/litre at 0^{o}C

Chlorine can produces hypochlorous acid (HOCl) and hydrochloric acid at lower pH. HOCl which is a strong disinfectant, is the principal disinfecting form of chlorine (Sarai, 2006). The pH of the water will affect the dominating chlorine species such that HOCl control at lower pH, while the hypochlorite ion (OCl^-) control at higher pH. HOCl is a stronger oxidant. Therefore, chlorine is more effective as an oxidant and a disinfectant at lower pH. Both forms, HOCl and OCl^-, are referred to as free chlorine (“Chlorine,” n.d.).

The effectiveness of chlorine is pH dependent. Free-residual chlorine is more effective with lower pH. However, Cl_2 is also quite toxic, so pH below 4 should be avoided. 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^{o}C in about 10 minutes (Sarai, 2006).

Table 2.3: Minimum free residual chlorine required at different pH values (Sarai, 2006)

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

2.2.2 Chlorine Dioxide

Chlorine dioxide (ClO_2) is a yellow to red gas and it is a very strong disinfectant. The use of chlorine dioxide 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). ClO_2 dissolves in water even in the absence of oxidizable substances and in the presence of alkali (WHO, n.d.).

ClO_2 does not typically react with NOM or humic substances. Compared to chlorine, its effectiveness is not affected by ammonia and pH, and it does not produce THMs. ClO_2 pre-oxidation is said can minimize THMs and other by-products (Yang et al,. 2013). ClO_2 that is used as alternative to chlorine are said to corresponded to 81% reduction in the THMs concentrations in distribution system (Volk et al., 2002). ClO_2 effectiveness is reported as better than chlorine against *Giardia* and *Cryptosporidium*. Apparently, chlorine dioxide weakens the pathogens, while chlorine or chloramines destroy them (Sarai, 2006).

Based on a previous study, ClO_2 is said to be more efficient in killing bacteria compared to chlorine over a wide pH range and it does not lead to the