

**REDUCTION OF TRIHALOMETHANE FORMATION
POTENTIAL BY COAGULATION WITH
ALUM AND POLYMER**

NUAFUN SUNGCHUM

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OF THE REQUIREMENTS FOR
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MAHIDOL UNIVERSITY
2007**

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ALUM AND POLYMER**

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REDUCTION OF TRIHALOMETHANE FORMATION POTENTIAL BY COAGULATION WITH ALUM AND POLYMER

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ABSTRACT

This research aimed to study the reduction of trihalomethane formation potential (THMFP) from Bangkok Water Treatment plant raw water using alum and alum combined with polymer. An anionic polymer (anionic polyacrylamide, AnPAM) and two cationic polymers (high and low molecular weight of polydiallyl dimethyl ammonium chloride, DADMAC) were investigated. Coagulation experiments were carried out with alum dosages of 15, 30, 45, and 60 mg/L, polymer dosages of 0.05, 0.1, 0.15, and 0.2 mg/L and with uncontrolled and controlled pH at 5.5, 6.0, and 6.5 to treat raw water with different characteristics, i.e. (i) high turbidity and high dissolved organic carbon (DOC), (ii) low turbidity and low DOC, and (iii) low turbidity and high DOC.

Experiments demonstrated clearly that the coagulation by alum alone could reduce THMFP but not as effectively as that by the combination of alum and polymer. The highest efficiency in reduction of THMFP from the coagulation with the combination of alum and polymer could be ordered from high to low as: high molecular weight cationic DADMAC, low molecular weight DADMAC and AnPAM, respectively. Regarding THMFP reduction by the combination of alum and high molecular weight cationic DADMAC coagulation, the optimal condition for the coagulation was at pH 5.5 and alum dosage of 30 mg/L and 0.1 mg/L of high molecular weight cationic DADMAC, which resulted in 44-50% THMFP reduction for high turbidity-high DOC water. With 45 mg/L of alum combined with 0.15 mg/L of high molecular weight DADMAC, THMFP reduction efficiency could be enhanced to 54% for low turbidity-low DOC water and 45% reduction of THMFP for low turbidity-high DOC water with 45 mg/L of alum combined with 0.2 mg/L of high molecular weight DADMAC. On the other hand, the combination of alum and AnPAM did not seem to have significant improving THMFP reduction efficiency.

KEY WORDS: WATER TREATMENT / CARCINOGENIC SUBSTANCE / TAP WATER /
DISINFECTION

107 pp.

การลดศักยภาพการเกิดไตรฮาโลมีเทนโดยกระบวนการโคแอกกูเลชันด้วยสารส้มและโพลิเมอร์
(REDUCTION OF TRIHALOMETHANE FORMATION POTENTIAL BY COAGULATION WITH
ALUM AND POLYMER)

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บทคัดย่อ

การศึกษาในครั้งนี้มุ่งศึกษาประสิทธิภาพของการลดศักยภาพการเกิดไตรฮาโลมีเทน จากการบำบัดน้ำจากจุดรับน้ำของโรงปรับปรุงคุณภาพน้ำบางเขนด้วยสารส้ม และสารส้มร่วมกับโพลิเมอร์ โดยโพลิเมอร์ที่ใช้มี 2 ประเภท คือ ประเภทประจุลบ ได้แก่ anionic polyacrylamide (AnPAM) และประเภทประจุบวก ได้แก่ polydiallyl dimethyl ammonium chloride (DADMAC) ทั้งแบบมวลโมเลกุลสูงและมวลโมเลกุลต่ำ โดยแปรค่าปริมาณสาร โคแอกกูแลนต์ ที่ความเข้มข้นของสารส้มเท่ากับ 15, 30, 45, และ 60 มิลลิกรัม/ลิตร แปรค่าความเข้มข้นของโพลิเมอร์ที่ 0.05, 0.1, 0.15, 0.2, และ 0.5 มิลลิกรัม/ลิตร และแปรค่าพีเอชที่ 5.5, 6.0, และ 6.5 และไม่ควบคุมพีเอช ตามลำดับ เพื่อบำบัดน้ำดิบที่มีลักษณะต่างๆ กัน ได้แก่ น้ำที่มีความขุ่นสูงและสารอินทรีย์คาร์บอนละลายสูง, น้ำที่มีความขุ่นต่ำและสารอินทรีย์คาร์บอนละลายต่ำ และ น้ำที่มีความขุ่นต่ำและสารอินทรีย์คาร์บอนละลายสูง

ผลการศึกษาการเปรียบเทียบประสิทธิภาพการลดศักยภาพการเกิดไตรฮาโลมีเทน ของกระบวนการโคแอกกูเลชันด้วยสารส้มเพียงอย่างเดียว พบว่าประสิทธิภาพต่ำกว่าการใช้สารส้มร่วมกับโพลิเมอร์ โดยประสิทธิภาพของโพลิเมอร์ในการลดศักยภาพการเกิดไตรฮาโลมีเทนเรียงลำดับจากสูงไปหาค่า ได้แก่ DADMAC ชนิดแบบมวลโมเลกุลสูง, มวลโมเลกุลต่ำ และ AnPAM ตามลำดับ และพบว่าพีเอชที่เหมาะสมคือ พีเอช 5.5 โดยในสภาวะที่เหมาะสมสำหรับน้ำที่มีความขุ่นสูงและค่าสารอินทรีย์คาร์บอนละลายสูง คือ เมื่อใช้สารส้มที่ความเข้มข้น 30 มิลลิกรัม/ลิตร ร่วมกับโพลิเมอร์ DADMAC ชนิดมวลโมเลกุลสูง ที่ความเข้มข้น 0.1 มิลลิกรัม/ลิตร ให้ประสิทธิภาพเป็น 44-50% ในขณะที่น้ำที่มีความขุ่นต่ำและสารอินทรีย์คาร์บอนละลายต่ำ สภาวะที่เหมาะสมคือ เมื่อใช้สารส้มที่ความเข้มข้น 45 มิลลิกรัม/ลิตร ร่วมกับโพลิเมอร์ DADMAC ชนิดมวลโมเลกุลสูง ที่ความเข้มข้น 0.15 มิลลิกรัม/ลิตร สามารถเพิ่มประสิทธิภาพเป็น 54% และสำหรับน้ำที่มีความขุ่นต่ำแต่ค่าสารอินทรีย์คาร์บอนละลายสูง สามารถลดการเกิดไตรฮาโล-มีเทนโดยให้ประสิทธิภาพ 45% เมื่อใช้สารส้มที่ความเข้มข้น 45 มิลลิกรัม/ลิตร ร่วมกับโพลิเมอร์ DADMAC ชนิดมวลโมเลกุลสูง ที่ความเข้มข้น 0.2 มิลลิกรัม/ลิตร ส่วนการใช้โพลิเมอร์ ประจุลบ (AnPAM) พบว่าไม่สามารถช่วยลดค่า THMFP อย่างมีนัยสำคัญ

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LIST OF ABBREVIATIONS

Al(OH) ₃	Aluminum hydroxide
AnPAM	Anionic polyacrylamine
ANOVA	Analysis of variance
°C	Degree celsius
C	Carbon
Ca ²⁺	Calcium ion
Ca(OH) ₂	Calcium hydroxide
CatPAM	Cationic polyacrylamide
CHBr ₃	Bromoform
CHClBr ₂	Dibromochloromethane
CHCl ₂ Br	Bromodichloromethane
CHCl ₃	Chloroform
D/DBPrule	Disinfectants and disinfection by-product rule
DADMAC	Polydiallyl dimethyl ammonium chloride
Da	Daltons
DBPs	Disinfection by-products
DOC	Dissolved organic carbon
DPD	N,N-decethyl -p-phenylenediamine
ECD	Electron capture detector
EPA	Environmental protection agency
EpiDMA	Epichlorohydrin dimethylamine
GAC	Granular activated carbon
GC	Gas chromatography
HAAs	Haloacetic acids
HAA ₅	Haloacetic acids at 5
HANs	Haloacetonitriles
HOCl	Hypochlorous acid

LIST OF ABBREVIATIONS (continued)

HMW	High molecular weight
LMW	Low molecular weight
Mg ²⁺	Magnesium ion
MCL	Maximum contaminant level
MF	Microfiltration
MW	Molecular weight
N	Nitrogen
NaHCO ₃	Sodium bicarbonate
NaOH	Sodium hydroxide
NF	Nanofiltration
NonPAM	Nonionic polyacrylamide
NTU	Nephelometric turbidity unit
nm	Nanometer
PAC	Polyaluminium chloride
POC	Particulate organic carbon
rpm	Rotation per minute
RO	Reverse Osmosis
S	Sulphur
SDS	Simulated distribution system
SUVA	Specific ultraviolet absorbance
THMs	Trihalomethanes
TOC	Total organic carbon
THMFP	Trihalomethane formation potential
UF	Ultrafiltration
USEPA	United states environmental protection agency
UV-254	Ultraviolet absorbance at 254 nm

CHAPTER I

INTRODUCTION

1.1 Rationales and Justifications

Nowadays, the raw water source for the water supply come from Choapraya River, the main water source for Thailand. This water source is a surface water which contaminated by organic matter derived both from naturally biological activities and human activities. Furthermore, during disinfection process, disinfectant especially chlorine or chlorinated compounds reacting with organic matter may occur disinfection by-products (DBPs) such as trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs) etc. THMs are the causes of not only a central nervous system depression but also hepatotoxicity, nephrotoxicity, teratogenicity, and carcinogenicity. Thus, the U.S. Environmental Protection Agency (USEPA) proposed the drinking water standard with a THMs Maximum Contaminant Level (MCL) of 80 µg/L for Stage 1 and 40 µg/L for Stage 2 (USEPA, 1998).

Several reports demonstrated that THMs content in Bangkok's tap water are in the range of 17-226 µg/L (Ningnoi et al., 1998; Siriwat and Pavittranon, 2000; Kanokkantapong et al., 2006). Result from preliminary work found that THMFP in raw water from Bangkhen Water Treatment Plant was 224 µg/L (24 hours and residual chlorine 1-2 mg/L), collected in 24 March 2006. As compared to the MCL of Guidelines for Drinking Water Quality of USEPA, they were found that several data exceeded the MCL standard. However, no standard has been set for THMs in Thailand. This finding can imply that citizens in Bangkok could likely be exposed to the potentially harmful substances, therefore the method for controlling DBPs precursor in a water system before the formation of DBPs should be concerned.

Reducing the DBPs formation can be done simply by lowering the level of organic precursor prior to the point of disinfection. Modified coagulation or enhanced coagulation can be used to lower the concentration of DBPs formation in water supply treatment. This method has some important advantages when compared to other treatment techniques such as membrane filtration, adsorption by activated carbon or using alternative disinfectant (USEPA, 1998). During the past few years, efforts have been made to develop technologies for the treatment of water. However, many of these technologies are economically non-viable for the small and medium plants due to high capital costs. Nevertheless, modified coagulation is required for a treatment plant to improve the efficiency in reducing organic contaminants but may require a minute increase in operating costs.

Thus, this work was designed to study the optimum operating condition of the coagulation process with alum and a combination of alum and polymer in controlling THMs formation. The organic polymer of interest in this work are cationic polydiallyl dimethyl ammonium chloride known as: DADMAC), which were reported to be the most widely using in USA (Fielding, 1999) and could also be used effectively for the treatment of water in Thailand (Panyapinyopol, 2004), and anionic polyacrylamide (AnPAM) which is among the most widely used coagulants in water treatment plants in Thailand.

1.2 Research Objectives

1.2.1 General Objectives

The general objective of this study is to compare the efficiency of reducing Trihalomethane Formation Potential (THMFP) by coagulation process between using alum and a combination of alum and polymer for the treatment of raw water from Bangkhen Water Treatment Plant.

1.2.2 Specific Objectives

- To compare the efficiency of coagulation process on THMFP reduction under different pH.
- To compare the efficiency of coagulation process on THMFP reduction under different dosage of alum.
- To compare the efficiency of coagulation process on THMFP reduction under different dosages, types and molecular weights of polymer using with alum.

1.3 Research Hypotheses

1.3.1 The reduction efficiency of the THMFP was changed with different dosages of alum.

1.3.2 The reduction efficiency of the THMFP was changed with different pH values.

1.3.3 The reduction efficiency of the THMFP was changed with different polymer types, molecular weights, and dosages of polymer.

1.4 Research Variables

1.4.1 Independent Variables

- Coagulant dosages
- pH during rapid mixing in coagulation experiment
- Type of polymer (cationic and anionic polymer)
- Molecular weights of polymer
- Polymer dosages

1.4.2 Dependent Variables

- THMFP reduction efficiency
- DOC reduction efficiency

1.4.3 Control Variables

- Jar-test procedure (round per minute and timing)
- THMFP test

1.5 Scope of the Study

1.5.1 Raw water was collected from the intake of Bangkhen Water Treatment Plant, Bangkok, Thailand.

1.5.2 The determination of the optimum dosage of alum and polymer for the maximum reduction of THMFP were achieved through the use of Jar-test.

1.5.3 Polymers used in this experiment were DADMAC (high molecular weight; C-308P and low molecular weight; C-358 (Polydyne, USA)) and AnPAM.

1.6 Limitation of Research

1.6.1 Experiments were setup at the laboratory of the Sanitary Engineering Department at room temperature.

1.6.2 The raw water used in this study was collected by grab sampling. The water was taken and stored in plastic containers and preserved in refrigerator at 4 °C.

1.7 Definition of Keywords

1.7.1 Trihalomethanes (THMs): One of a group of organic compounds named as derivatives of methane. THMs are generally the by-product from chlorination of water that contains organic material. The four common THMs are chloroform, dibromochloromethane, bromodichloromethane and bromoform.

1.7.2 Trihalomethane Formation Potential (THMFP): THMFP is an index of the potential extent of THMs. THMFP test is conducted for a 24 hours-test

and residual chlorine 1-2 mg/L which determined by subtracting the initial THMs concentration from the final THMs concentration.

1.7.3 Coagulation: The process of clumping together of colloids and fine particles into larger particles caused by the using of chemicals. This clumping together makes it easier to separate the solids from the water by settling.

1.7.4 Residual chlorine: The amount of free available chlorine remaining after a given contact time under specified conditions.

1.7.5 Alum: Alum refers to Aluminium sulfate, is commonly used as a coagulant in water treatment systems. In water treatment it is used primarily coagulant for the removal of particles.

1.7.6 Polymer: A chemical formed by the union of many monomers (a molecule of low molecular weight). Polymers are used with other chemical coagulants to aid in binding small suspended particles to form larger and heavier aggregates than individual particles for their removal from water.

1.8 Conceptual Framework

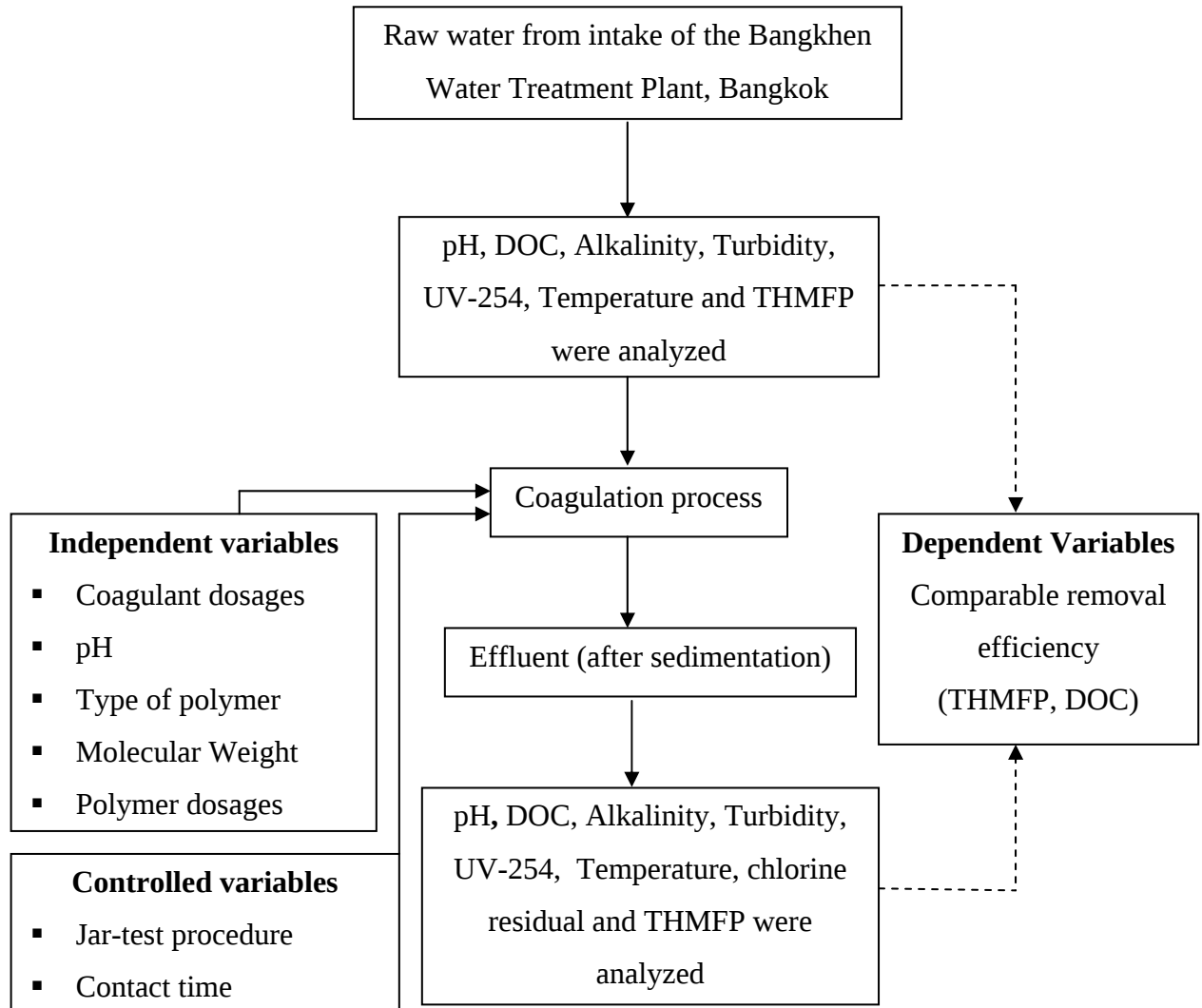


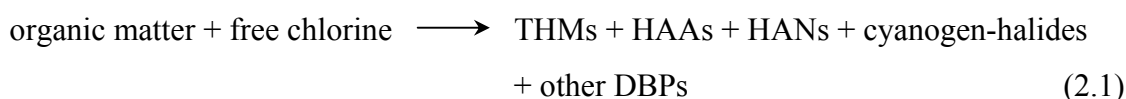
Figure 1.1 Conceptual framework

CHAPTER II

LITERATURE REVIEWS

2.1 Trihalomethanes (THMs)

THMs are organohalogen compounds, named as derivatives of the compound methane. THMs are formed when three of the four hydrogen atoms attached to the carbon atom in the methane compound are replaced with atoms of chlorine, bromine and/or iodine (Vogt and Regli, 1981), when chlorine has a chemical reaction with the organic material (such as humic acids from decaying vegetation) that is already present in the water supply. A general equation for the reaction of organic matter with chlorine is shown in Equation (2.1) (Marhaba et al., 1998).



THMs are composed of 4 organic compounds that include Chloroform (CHCl_3), Bromoform (CHBr_3), Bromodichloromethane (CHCl_2Br), and Dibromochloromethane (CHClBr_2). Characteristics of THMs are presented in Table 2.1. The chemical structures of THMs species are shown in Figure 2.1.

The existence of disinfection by-products, such as chloroform and other trihalomethane compounds, in chlorinated drinking water supplies was first discovered in 1974 (Rook, 1976). Almost all of the disinfection by-products (DBPs) studies in the 1970's were concerned with THMs. Among all four THM species, chloroform was often the most commonly found in drinking water and was usually reported to present in the highest concentration (Vogt and Regli, 1981; and Whitaker et al., 2003). Since THMs were identified and studied long before other types of DBPs, the first DBPs regulations enacted on November 29, 1979, only set a THMs limit of

100 µg/L. On December, 1998. The Stage 1 Disinfectants and Disinfection By-Product (D/DBP) Rule was promulgated by USEPA for a THMs Maximum Contaminant Level (MCL) of 80 µg/L (USEPA, 1998). Stage 2 of D/DBP Rule was anticipated to be more stringent which required lower MCL for DBPs than Stage 1, 40 µg/L.

Table 2.1 THMs characteristics (Artuš, 2004)

Name	Structure	Molecular Weight (g/mol)	Boiling Point (°C)
Chloroform	CHCl_3	119.5	61
Bromodichloromethane	CHBrCl_2	163.9	87
Dibromochloromethane	CHBr_2Cl	208.3	116
Bromoform	CHBr_3	252.7	151

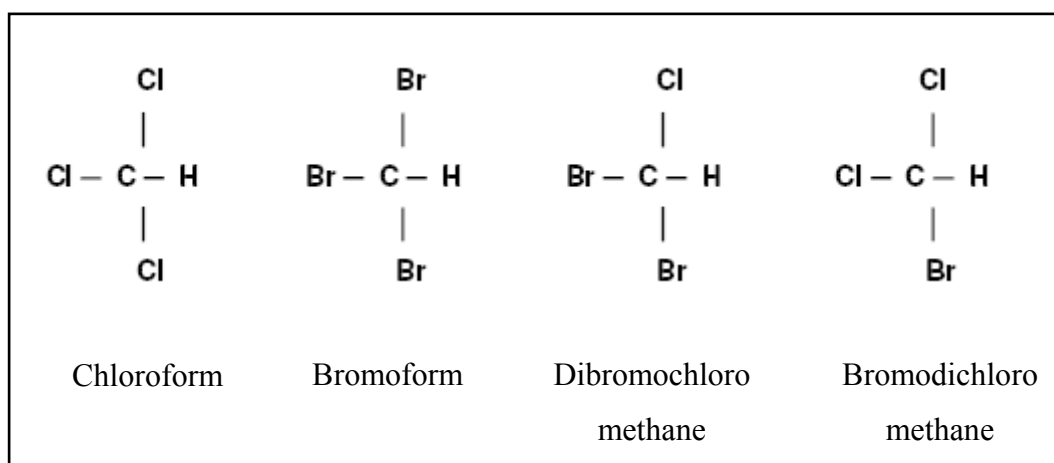


Figure 2.1 Molecular structures of THMs (Artuš, 2004)

2.1.1 Toxicity of THMs

Chloroform and other THMs have been shown to increase tumours of the liver, kidney or large intestine in rats or mice. The risk to human from these contaminants must be assessed carefully since there is considerable benefit associated

with the use of chlorine. Bromodichloromethane has also been shown to increase liver and kidney tumours but bromoform have been shown to increase large intestinal tumours in rats. The weight of evidence is that they are only weak genotoxins and they do not appear to be active in vivo. It is probable that the mechanism for the liver and kidney tumours is the same as for chloroform but the mechanism for the large intestinal tumours is uncertain. The evidence suggests that the use of a threshold approach, based on a tolerable daily intake, would be the most appropriate way of determining safe levels in drinking water (Fawell, 2000; and Rizzo et al., 2005).

2.1.2 Organic Matter

Organic matters are composed of many compounds that contain mainly carbon, hydrogen, oxygen, nitrogen and sulphur. There is a wide compositional range with C 43-62%, O 31-49%, N 1-7% and S 0.1-1.5% (Bolto, 1995). The ratio presents depending on water resources such as from industry or naturally biological activities.

Typical soluble organic matter has a molecular mass range of about 300 to 30,000 unified atomic mass units (or daltons, Da). Common structure of organic matter includes aromatic rings, alkyl chains, carboxylates, phenols, and other alcohols. Polynuclear (polycyclic) aromatic compounds are not generally thought of as making up a significant portion of organic matter. A number of volumes have been dedicated to characterizing organic matter (Chang et al., 2001; and Leenheer and Croué, 2003). Organic matter in surface waters can be at the origin of various problems in drinking water because drinking water sources typically contain 2–10 mg/L of organic matter, of which only 10–30% has been identified. Organic material can be responsible for water taste, odor and color. Organic compounds also lead to the formation of DBPs after reacting with disinfectants during water treatment. Organic matter can be related to bacterial proliferation within distribution systems. Therefore, the control of organic matter has been recognized as an important part of the operation of drinking water plants and distribution systems (Volk et al., 2002; and Bolto et al., 2004). These organic matters include:

- *Humic acid*, which are macromolecular yellow-to-black colored natural organic matter derived from the degradation of plant, algal, and microbial material. Although their formation mechanism and chemical structures are not well understood, they are known to be high in carbon content (50–60%) of both aliphatic and aromatic character and rich in oxygen-containing functionalities such as carboxyl, phenolic, alcoholic, and quinoid groups (Cho et al., 2002). Humic acid can also be classified as those organics that precipitates at acidic conditions ($\text{pH} < 2$) (Chen, 2002; and Leenheer and Croué, 2003).

- *Fulvic acid* is simply those that remained dissolved in the acidified solution. Fulvic acid is of low molecular weight (500–2000) and soluble in water under all pH. Fulvic acid is derived from humus, often found in surface water. Fulvic acids are light yellow to yellow-brown in color that contributes to the formation of trihalomethanes in chlorinated water supplies, and can contribute to organic fouling of ion exchange resin beds (Amy et al., 1992; and Owen et al., 1995).

- *Humin* is a non-soluble part in any condition in fraction of humic substances.

2.1.3 Surrogate Parameters

It is difficult and time-consuming to measure THMs concentrations. Measurements require skilled personnel as well as high technical instrumentation. So, surrogate parameters are used to predict, monitor THMs or represent precursor concentrations.

Surrogate parameter values are linearly proportional to the concentration of the target parameter that is more easily, rapidly, and inexpensively than the parameter of interest. However they have some limitations as they are substitute measurements and are often nonspecific (Edzwald et al., 1985; and Najm et al., 1994). However, it allows on-line monitoring of the operation and performance of water treatment plants. Surrogate parameters used to assess organic matter include:

2.1.3.1 Total and Dissolved Organic Carbon (TOC and DOC)

TOC and DOC are indicators of mass of organic substance. TOC measures the amount of organically bound carbon in water samples. The organic carbon in water is composed of a variety of organic compounds in various oxidation states. TOC is independent of oxidation state of organic matter (APHA, AWWA, and WEF, 2005). DOC is the organic carbon smaller than 0.45 μm membrane filter (USEPA, 2001). DOC is the independent of the oxidation state of the organic matter. Organic carbon in water can be composed in two fractions, particulate organic carbon (POC) and dissolve organic carbon (DOC). In surface water, between 50 and 60 % of humic substances is DOC. Previous works showed that TOC was a good surrogate parameter for THMs (Hubel and Edzwald, 1987; Singer et al., 1995; and Chang et al., 2005).

2.1.3.2 Ultraviolet Absorbance at Wavelength 254 nm (UV- 254)

UV absorption at a wavelength of 254 nm is a useful surrogate measurement of selected organic constituents such as humic substances and various aromatic compounds in water. Strong correlations may exist between UV absorption and organic carbon content, precursors of THMs and other disinfection by-products. UV absorption also has been used to evaluate organic removal by coagulation. Organic compounds are aromatic and have conjugated double bonds which absorb light in the ultraviolet (UV) wavelength region. Therefore, UV absorbance is a well-known technique for measuring the presence of naturally occurring organic matter such as humic substances. However, UV analyses are also affected by pH and turbidity (Edzwald et al., 1985; APHA, AWWA, and WEF, 2005; and USEPA, 2001).

The example of previous work showed that there could be strong correlations (r^2 values between 0.89-0.99) between UV-254 and DBP formation potential for all waters studied, but DOC was less strongly correlated to DBP formation potential (White et al., 2003).

2.1.3.3 Specific Ultraviolet Absorbance (SUVA)

SUVA (L/mg-m) is the ratio of UV absorbance at 254 nm (cm^{-1}) to DOC concentration (mg/L). SUVA is an indicator of organic matter reactivity. SUVA gives a relative indication of the hydrophobic content in water and gives reasonable predictions of THMFP (Krasner et al., 1996). SUVA indicates aromatic compounds in the DOC and can be used to estimate the chemical nature of the DOC at a given location. The water uses SUVA as a surrogate parameter to monitor sites for disinfection by-products precursors. It should be noted that high nitrate content in low DOC waters may interfere in the measurement (USEPA, 2001; and Leenheer and Croué, 2003).

The principle behind this measurement is that UV-absorbing constituents will absorb UV light in proportion to their concentration. Waters with low SUVA values ($\text{SUVA} < 2 \text{ L/mg-m}$) contain primarily non-humic organic matter and are not amenable to enhanced coagulation. On the other hand, waters with high SUVA values ($\text{SUVA} > 2 \text{ L/mg-m}$) generally are amenable to enhanced coagulation (Edzwald, 1993; USEPA, 1999; and Leenheer and Croué 2003).

2.1.4 Trihalomethanes Formation Potential (THMFP)

THMFP is a quantitative measurement of the potential quantity of THMs formed with a high dosage of free chlorine and a long reaction time. THMFP determinations provide a worst-case scenario of the concentration of THMs that may be formed.

The organic precursors in the water source can be indirectly measured by the THMFP test. THMFP is an index of the potential extent of THM formation after the application of chlorine. THMFP test is conducted under standard conditions, samples are buffered at $\text{pH } 7.0 \pm 0.2$, chlorinated with an excess of free chlorine and stirred at $25 \pm 2^\circ\text{C}$ for 7 days to allow the reaction to approach completion. A free residual

chlorine of 3 to 5 mg/L exists at the end of reaction time (APHA, AWWA, and WEF, 2005).

Moreover, the THMFP test, simulated distribution system (SDS) testing method, is also used to provide an estimate of the THMs formed in a distribution system after disinfection by using bench-scale techniques. Chlorine dose and the incubation time are the primary differences between THMFP and SDS testing methods. The disinfectant concentrations and incubation time in SDS test samples are intended to mimic conditions in a distribution system. The chlorine dosage used in this method is the one that results in a chlorine residual at the end of incubation period that is comparable to the chlorine residuals measured in operating full scale distribution systems (commonly between 0.5-2 mg/L) and the incubation period of 12 or 48 hours which is comparable to the average hydraulic residence time in a distribution system. Therefore higher chlorine doses and incubation periods at the standardized formation potential procedures (THMFP testing method) would result in higher THMs concentrations than the ones measured by SDS tests (Najm et al., 1994; and APHA, AWWA, and WEF, 2005).

2.2 Factors Affecting the Formation of THMs

There are several factors affecting the formation potential of THMs. Previous research studies have shown that the major variables that affect THMs formation are: residence time, temperature, pH, disinfectant type and concentration, total organic carbon concentration and bromide concentration.

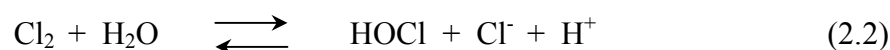
2.2.1 Type of Disinfectants

Each different type of disinfectant has both advantages and disadvantages in drinking water treatment. For instance, free chlorine is very effective in inactivating pathogens but it produces some of the highest concentrations of DBPs (Dojilido et al., 1999). Chloramines are a weaker disinfectant compared to free chlorine but very few DBPs are formed when water treatment plants use chloramination.

2.2.1.1 Chlorine

As the most widely used disinfectant in the United States of America (USA), chlorine is often added to the finished water, even if a different oxidant is used for primary disinfection. Chlorine is added to water in a variety of forms, usually as gas or solid hypochlorite form (Magnuson, n.d.).

Chlorine gas (Cl_2), properly referred as dichloride, and is greenish yellow gas that has familiar and pungent smell. Chlorine (oxidation state: 0) is modestly soluble in water and hydrolyzes rapidly in water to form hypochlorous acid. The following equation (2.2) presents the hydrolysis reaction.



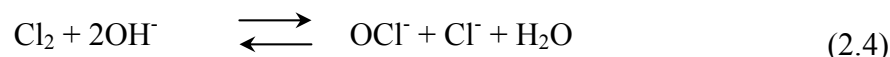
The hydrochloric acid is a strong acid and is completely dissociated into hydrogen and chloride ions. Hypochlorous acid (HOCl , chlorine oxidation state: +1) is a weak acid with a pK_a of about 7.5, and it dissociates into hydrogen and hypochlorite (OCl^-) ions (USEPA, 1999a).



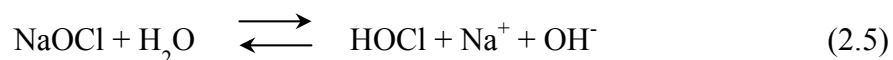
It is believed that chlorine (0) and chlorine (I) compounds work primarily by denaturing enzymes or proteins, thereby inactivating microorganisms. In some cases physical disruption of cell membranes may also contribute. HOCl is thought to be the more active species.

2.2.1.2 Hypochlorite

The equilibrium in Equation (2.2) can be driven forwards using strong base to deprotonate the hypochlorous acid and to neutralize the hydrogen ion.



When sodium hydroxide is used as the base, the familiar sodium hypochlorite, found in household bleach, is formed; this in turn undergoes the following reaction (USEPA, 1999a).



Thus, the same active species, HOCl, is produced from both the reaction of chlorine gas and solid hypochlorite.

The hypochlorous acid may also be produced by addition of solid calcium hypochlorite salt to water. The chemistry of chlorine has practical considerations in this regard: The chlorine (I) cation transfer step means that chlorine and hypochlorous acid both undergo 2-electron reductions. If a reducing agent cannot offer 2 electrons, reactions are generally slow or difficult. The 2-electron reduction can be expressed as follows (Magnuson, n.d.).



Chlorine (I) is unstable and disproportionates thus, hypochlorite solutions are slowly converted to chlorate and chloride, which are not disinfection by-products in the sense that no other reactant is required.



2.2.1.3 Chloramines

Another chlorine-containing disinfectant is chloramine, which is formed from the reaction of ammonia with hypochlorous acid as shown in Equation (2.9) (USEPA, 1999b).



The addition of the ammonia (NH_3) ties up the “free” chlorine, available as HOCl . It also slows down undesirable reactions of “free” chlorine which form disinfection by-product (DBPs). The chemistry of chloramines becomes more complicated as shown in the following equations, in which the chloramine reacts with more hypochlorous acid to tie up more chlorine (USEPA, 1999b).



2.2.2 Disinfectant Concentration

Scientists have been studying how the disinfectant concentration affects THMs formation. The studies have shown that as the disinfectant concentration increases, DBP formation also increases. For example, Singer et al., (1995) conducted a study in North Carolina on eight conventional water treatment plants that practiced chlorine disinfection. The treatment plant that used the largest chlorine dose had average THMs levels higher than the plant which used the smallest chlorine dose.

2.2.3 Residence Time

Several research studies have been conducted to examine how residence time affects DBP formation. The studies have shown that as residence time increases, the concentration of THMs increases and the concentration of HAAs decreases (LeBel et al., 1997; and Chen and Weisel, 1998).

2.2.4 Temperature

Many studies have been conducted to evaluate how temperature affects the rate of DBP formation and the concentration of DBPs that are formed. Some studies

have shown that as the temperature increases, the concentration of THMs also increases. However, the results are not conclusive because conflicting results have been found from different research studies (Nieminski et al., 1993; Chen and Weisel, 1998; and Doijlido et al., 1999). For example, Nieminski et al., (1993) examined THMs and HAA₅ concentrations (during all four seasons) in 14 conventional water treatment plants which disinfect with chlorine. This study showed that the higher THMs concentrations were found in the summer and fall seasons, and the lower THMs concentrations were present in the winter and spring.

2.2.5 pH

Several studies have been done to analyze concentrations of DBPs and how they relate to pH levels of the water supply. The studies have shown that as the pH increases, the concentration of THMs also increases, whereas HAA₅ concentrations were not depend on pH (Nieminski et al., 1993; and Diehl et al., 2000).

2.2.6 Total Organic Carbon Concentrations

Several researchers have studied the impact of total organic carbon concentration on DBP formation. These experiments have found that as the total organic carbon level increased, the DBP formation also increased. Two studies which looked at the total organic carbon levels with respect to THMs and HAAs are discussed in the following paragraph.

Singer et al., (1995) conducted a study on eight North Carolina water supply systems. At a TOC concentration of 5.4 mg/L, an average of 82 µg/L of THMs was produced and an average of 106 µg/L of HAA₅ was formed. At a TOC level of 2.4 mg/L, a mean of 39 µg/L of THMs were created and a mean of 36 µg/L of HAA₅ were produced. These results showed that as TOC concentrations increased so did THMs and HAA₅ levels. Dojilido et al., (1999) also found that HAA formation was depended on the organic matter present in the sample, as higher concentrations of HAAs were formed at higher TOC concentrations.

2.2.7 Bromide Concentrations

Recent studies, which examined the relationship between bromide concentration in a drinking water supply and DBPs formation, have been completed. These studies have shown that as the concentration of bromide is increased, the concentration of THMs and HAAs also increased. When there are high bromide concentrations in a raw water source and chlorine is added to the water supply, more brominated THMs species will be formed because there is more bromide present in the water source for the organics to react with. In typical raw water supplies when chlorine is added, chloroform is the major compound of THMs found in the water supply (Diehl et al., 2000; and Chang et al., 2001).

2.3 THMs Precursors Removal

THMs can be controlled through THMs precursor control and removal or modified disinfection practice. Examples of treatment methods are coagulation, granular activated carbon, membrane filtration that can remove organic matter effectively. Other than through the use of membranes, there is little opportunity to effectively remove bromide. Source water protection and control represent non-treatment alternatives to precursor control. Removal of DBPs after formation is not viable for organic DBPs, whereas bromate and chlorite can be removed by activated carbon or reducing agents. It is expected that the optimized use of combinations of disinfectants, functioning as primary and secondary disinfectants, can further control DBPs. There is a trend towards combination/sequential use of disinfectants; ozone is used exclusively as a primary disinfectant, chloramines exclusively as a secondary disinfectant, and both chlorine and chlorine dioxide in either role. Several methods for the removal of organic matter in the water sources were proposed and they are described below.

2.3.1 Adsorption with Activated Carbon

Granular activated carbon (GAC) has been of special interest due to its ability to remove a wide range of compounds such as organic matter, THMs, odor, and color causing compounds and also other toxic compounds (Nikolaou et al., 1999; and Capar and Yetis, 2002).

2.3.2 Membranes

Membrane processes are rapidly developing water treatment technologies that were initially developed to achieve desalting objectives. There are several types of membrane used for treating water supply treatment. Microfiltration (MF) and Ultrafiltration (UF), due to relatively large pores, MF is effective in turbidity and particulate removal, as well as bacteria, protozoa and algae. UF can also remove viruses and some of the organic matter. Generally UF is effective in high-molecular weight fraction of organic matter removal. Nanofiltration (NF) and Reverse Osmosis (RO) processes are capable of separating almost all organic matter from water (Jacangelo et al., 1995; and Kabsch-Korbutowicz, 2005a). Moreover, these processes have demonstrated capabilities for achieving high levels of removal of disinfection by-product precursors (Chellam et al., 1997).

2.3.3 Ion Exchange

Ion exchange is an effective method for removing organic substances from water (Kim and Symons, 1991; and Collin et al., 1996; and Bolto et al., 2002). The example of previous work studied by Bolto et al., in year 2002 found that anion exchangers can remove organic matter effectively.

2.3.4 Coagulation

Coagulation processes are used to create chemical conditions that facilitate the agglomeration of small colloidal particles into larger particles to improve removals

in settling and filtration. Colloidal particles of natural origin typically have a net negative surface charge that said to be electrostatically stabilized and, therefore, do not aggregate. A primary role of chemical coagulation processes are to neutralizer or reduce the charge-related repulsive forces between particles, thereby allowing the flocculation process to proceed (Bryant et al., 1992; and Faust et al., 1998). Generally, coagulation is a high effectively method in removal of particulate matter but it can be improved and used to remove dissolved organic matter (Cheng et al., 1995; Krasner and Amy, 1995; Vrijenhoek et al., 1998; Panyapinyopol, 2004; Kabsch-Korbutowicz, 2005b; Qin et al., 2005; Rizzo et al., 2005; and Uyak and Toroz, 2005).

2.4 Coagulation of THM Precursors

Coagulation processes can achieve significant removals of precursor compounds, especially those associated with a high molecular weight humic or fulvic fractions. Lower molecular weight fractions are not typically removed to the same degree. Coagulants are usually used for treating drinking water. Examples of frequently used coagulants include (i) metal-salts coagulants such as alum, ferric chloride and ferrous sulfate, (ii) polymerized metal-salts coagulants such as polyaluminium chloride (PAC), and (iii) organic polymers, e.g. cationic, anionic and nonionic.

2.4.1 Aluminium Sulfate

The most widely used coagulant is aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, where $x = 14$ to 18 whose common name is alum. In addition to water aluminum salts dissociate and the Al^{3+} ions undergo typical metal ion hydrolysis reactions. In these reactions, the acidity of the Al cation causes the deprotonation of waters of hydration, as shown in the reaction below:



Upon addition of alum to water in the rapid mixing process, aluminum hydroxide ($\text{Al}(\text{OH})_n^{3-n}$) begins to form. At pH levels less than about 6.5 to 7, n is typically less than 3, resulting in the formation of positively charged dissolved species. The speciation of Al in aqueous solution is highly dependent on pH, a solubility curve as shown in Figure 2.2. This figure illustrates that operational coagulation mechanisms are a function of pH and coagulant concentration. The slow mixing process will allow floc forming or flocculation step, colloid and solid aluminum hydroxide are formed to be a bigger particle that can easily precipitate (Bryant et al., 1992; Faust et al., 1998; and Amirtharajah et al., 1999).

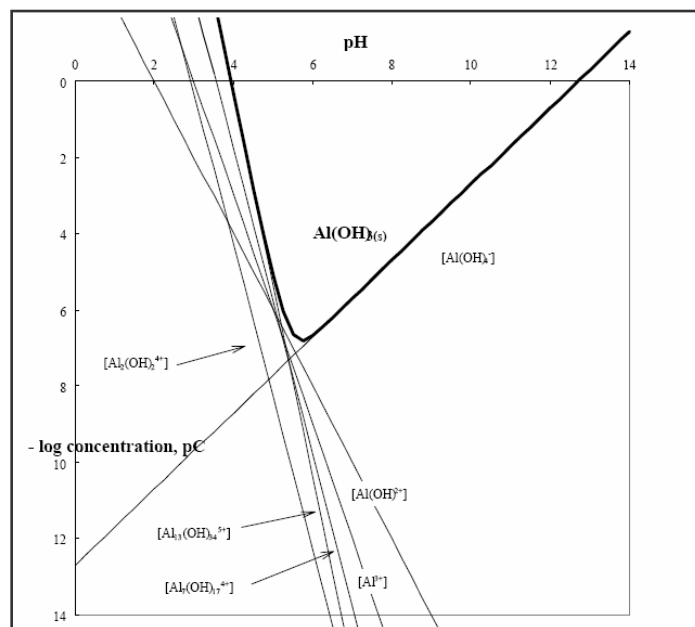


Figure 2.2 Solubility of aluminum hydroxide (Amirtharajah and Mills, 1982)

Mechanism of Organic Precursors Removal by Alum

Alum can remove organic matter by two general mechanisms;

- The first mechanism is adsorption onto aluminium hydroxide ($\text{Al}(\text{OH})_3$) floc. Specific adsorption of cationic coagulant species to the surfaces of particles partially or completely neutralizes the surface charge and decreases repulsive forces. This allows contaminant particles to approach one another closely enough for attractive Van der Waals forces to dominate so that the particles can aggregate and settle out. However, adsorption of excess cationic charge will result in reversal of the

surface charge and subsequent restabilization of the particles (Huang and Shin, 1996; Gregor et al., 1997; Vrijenhoek et al., 1998; Amirtharajah et al., 1999; Nozaic et al., 2001; Duan and Gregory, 2003; Budd et al., 2004; and Uyak and Toroz, 2005).

- The second mechanism is the formation of insoluble complexes in a manner analogous to charge neutralization. The insoluble $\text{Al}(\text{OH})_3$ species forms as a floc, solid precipitate. As the solid is formed and moves through solution, it enmeshes colloidal contaminants, causing their CO-precipitation. This phenomenon is known as sweep coagulation and typically occurs at coagulant doses where the Al concentration is high enough to cause precipitation of $\text{Al}(\text{OH})_3$ (Hubel and Edwald, 1987; Randtke, 1988; Huang and Shin, 1996; Gregor et al., 1997; Vrijenhoek et al., 1998; Amirtharajah et al., 1999; Nozaic et al., 2001; Duan and Gregory, 2003; Budd et al., 2004; and Uyak and Toroz, 2005).

2.4.2 Polymer

The polymers used in water treatment are high molecular-weight, synthetic organic compounds that have a strong tendency to be adsorbed on the surfaces of the particles in an aqueous suspension. Cationic polymers can be classified as primary coagulants, and nonionic and anionic polymers which also can be referred to either as coagulant aids or flocculants (Bolto, 1995; Chang, et al., 1999; and Fielding, 1999).

In general, cationic polymers can be capable of removing organic precursor compounds. However, coagulation with alum may frequently be more effective than with organic polymer alone. The effectiveness of organic polymers is greater for higher molecular weight organics (Bolto, 1995; and Bolto et al., 2001).

In addition, to enhance coagulation process, combinations of alum and polymer is an attractive treatment for removal of THM precursors as it was proved by many previous works (Hubel and Edzwald, 1987; Bolto et al., 2001; and Bolto et al., 2002).

Mechanism of Organic Precursors Removal by Polymer

The small floc formed by coagulation can be built up into larger agglomerates by flocculation with a polymer, with the larger particles formed in this way giving accelerated rates of sedimentation. The process involves polymer bridging, in which polymer bound to looped and chained of the polymer which can attach to nearby particles. This mechanism is favored when long-chain polymers which do not have a high level of charge are used. The nature of the surface charge on the flocs following coagulation will depend on the dose of metal salt used, but the net charge is normally close to zero, with the number of positively and negatively charged sites being almost equal. Often an anionic polymer will increase the size of the flocs by interaction with the positive sites on the floc surface. Bridging will occur when the adsorbed chains interact with another floc in the same way as shown diagrammatically in Figure 2.3 (Bolto, 1995; Chang, et al., 1999; Fielding et al., 1999; and Bolto et al., 2001).

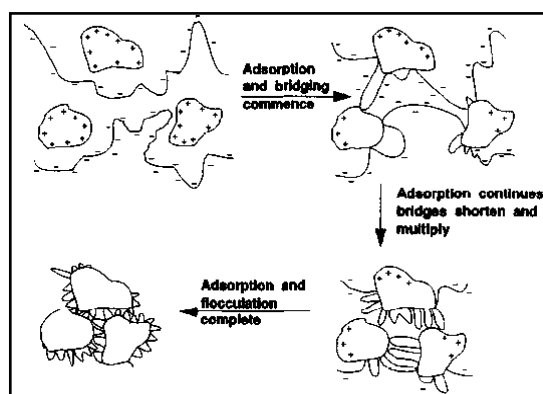


Figure 2.3 The bridging flocculation model (Bolto, 1995)

2.4.3 Chemical and Physical Factors Affecting Coagulation

2.4.3.1 Coagulant Dosage

The optimizing of coagulant dose is important because the coagulant overdosing produces extra amount of sludge and restabilization. Thus, because the metal coagulant addition leads to pH reduction, the addition of alkaline chemicals may

be needed in order to maintain the coagulant pH within an effective range (Budd et al., 2004). The higher dose could improve organic matter removal because it provided more complex for floc formation or positively charged metal hydroxide for charged neutralization (Randtke, 1988; and Dennett et al., 1996). The coagulation conditions on coagulant dose are summarized in Table 2.2. However, overdosing may results in an excess in metal residual in treated water and can cause an increase in processed water turbidity (Hubel and Edwald, 1987; Cheng et al., 1995; Huang and Shin, 1996; Gregor et al., 1997; Vrijenhoek et al., 1998; and Duan and Gregory, 2003).

Table 2.2 Effect of alum dosage on coagulation

Name	Conditions	%Removal		
		Turbidity	Organic Precursors	THMFP
Young and Singer, 1979	0-50 mg/L	70%	40% TOC removal	60%
Chadik and Amy, 1983	1-15 mg/L	67-96%	31-59% TOC removal	36-66%
Edzwald, 1993	0.5-1.0 mg/L	-	80% UV and 72% DOC removal	72%
Cheng et al., 1995	10-40 mg/L	92-96%	20-30% TOC removal	30%
Huang and Shin, 1996	0.5-20 mg/L	-	90% UV removal	-
Gregor, et al., 1997	0-5 mg/L	-	73-87% UV removal	-
Vrijenhoek et al., 1998	0, 3, 5, 10, 20, 40, and 60 mg/L	-	30% TOC removal	67-78%
Bell-Ajy et al, 2000	0-60 mg/L	-	38% TOC and 62% UV removal	51.7%
Qin et al., 2005	1.5, 2.5, 3.5, 4.5, 5.5, 6.5, and 7.5 mg/L	97%	45% DOC removal	-

2.4.3.2 pH

The pH control of coagulation is one of the most important factors. The optimum pH range of 5-7 was often reported for the removal of organic matter by alum (Hubel and Edwald, 1987; Cheng et al., 1995; Gregor et al., 1997; Vrijenhoek et al., 1998; Bell-Ajy et al., 2000; Duan and Gregory, 2003; Rizzo et al., 2005; and Qin et al., 2006). The mechanism of coagulation on pH can be concluded that the removal of humic substances apparently occurs by direct precipitation with monomers and small polymers of aluminium at pH value less than 5.0. On the other hand, at pH values greater than 7.0, removal occurs by adsorption of humic substances on $\text{Al}(\text{OH})_{3(s)}$. In between these pH values, both mechanisms of removal can occur (Dempsey et al., 1984; and Krasner and Amy, 1995). This might be because at pH lower than 5, hydrogen ions out completes the metal hydrolysis products for organic ligands, and poor removal occurs. At pH higher than 7, hydroxyl ions are able to successfully complete with organic matter for the available metal ions. Precipitation of metal hydroxide occurs, shifting the removal mechanisms (Randtke, 1988; Dennett et al., 1996; and Duan and Gregory, 2003). The effect of coagulation conditions on pH are summarized in Table 2.3.

2.4.3.3 Turbidity

Consequently, precipitates often form more easier in high-turbidity waters than in low-turbidity waters. Low-turbidity waters are often found to be difficult to coagulate in the sweep floc region and possibly the adsorption region as well (Randtke, 1988; and Gregor et al., 1997).

2.4.3.4 Organic Matter Concentration (TOC or DOC)

Raw water supplies with low concentrations (less than 10 mg DOC/L) of organic matter are difficult to coagulate (USEPA, 1999). Consequently, the concentration of the organic is significant because of the stoichiometry of the coagulation reaction. When the DOC is low the formation of humic-aluminium

precipitates is favored. When the DOC is high the precipitation of $\text{Al}(\text{OH})_{3(s)}$ is kinetically favored over the formation of humic-aluminium precipitates (Randtke, 1988; Bryant et al., 1992; and Faust et al., 1998).

Table 2.3 Effect of pH on coagulation by alum

Name	Conditions	%Removal		
		Turbidity	Organic Precursors	THMFP
Chadik and Amy, 1983	Ambient pH (8.5) and 6.0	67-96%	30-63% TOC removal	44-65%
Edzwald, 1993	5.5-7.0	-	80% UV and 72% DOC removal	72%
Cheng et al., 1995	5.5, 6.3, 7.0, and ambient	92-96%	20-30% TOC removal	37-38%
Huang and Shin, 1996	3.5-9.0	-	> 81% UV removal	-
Gregor et al., 1997	5.0-7.0	-	73-87% UV removal	-
Vrijenhoek et al., 1998	5.5 and ambient	-	30% TOC removal	67-78%
Bell-Ajy et al, 2000	5.0-8.5	-	38% TOC and 62%UV removal	51.7%

2.4.3.5 Alkalinity

Alkalinity is an extremely important variable for the coagulation process in general, as well as for the removal of organic matter. For the most part, alkalinity controls the pH value, which is achieved without using supplemental addition of acid and base. Excessive alkalinity may increase the coagulant dosage beyond that required for turbidity and organic matter removal. Insufficient alkalinity required the addition of a supplemental base (NaHCO_3 , NaOH or $\text{Ca}(\text{OH})_2$). If the latter situation prevails, the raw water's pH value may be not too low for optimal removal of organic matter. Consequently, the coagulation process for optimal removal of organic matter may

have to be adjusted frequently (Randtke, 1988; Tseng et al., 2000; and Budd et al., 2004).

2.4.3.6 Ions in Solution

The effect of such anion as sulfate on suppression of the charge reversal and acceleration of the kinetics of precipitation of $\text{Al}(\text{OH})_{3(s)}$ have been recognized for a long time. Also, such divalent cations as Ca^{2+} and Mg^{2+} etc. have a significant effect on the coagulation of natural colloidal particles associated with humic acids (Randtke, 1988; and Faust et al., 1998).

2.4.3.7 Mixing

The removal of organic matter is influenced by rapid and slow mixing. When the particulate organic matters are removed via the charge neutralization mechanism, the type of rapid mixing greatly influences this reaction; it is important that the coagulants be dispersed into the raw water stream as rapidly as possible (< 0.1 sec) so that the hydrolysis productions, which develop in 0.01 to 1 sec, will destabilize the colloid. Removal of dissolved organic matter influenced by rapid mixing since it will influence the charge and distribution of the metal hydrolysis products. Aged or recycled coagulant sludge are not very effective for the removal of dissolved organics because these solids will become more crystalline as the age (Randtke, 1988; Bryant et al., 1992; Faust et al., 1998; and Kan et al., 2002).

2.4.3.8 Temperature

In water treatment practice, temperature has an extremely important role in turbidity removal by chemical coagulants. Normally, colder temperatures result in decreased efficiency of turbidity removal. Decreased efficiency at the colder temperature is due to increased viscosity and its effect on particle sedimentation, and because structurally, the aggregates are smaller at the lower temperatures and the kinetics of hydrolysis and precipitation are slower. Some modification can be achieved

by changing coagulant from alum to ferric chloride or to polymeric iron chloride. Another possibility is to switch from sweep coagulation to adsorption-charge neutralization by the addition of sludge from the coagulation process (Bryant et al., 1992; Faust et al., 1998; and Amirtharajah et al., 1999).

2.5 Related Researches

Many researchers studied the efficiency of THM precursors removal on TOC, UV and THMFP removal by alum, polymers and combination of alum and polymer under difference conditions which can be summarized in Table 2.4.

Table 2.4 Review of coagulation condition

Name	Water source	Conditions	%Removal
Chadix and Amy, 1983	Biscayne Aquifer, Edisto, Mississippi, Jame Scioto River, Ilwaco Reservoir and Daytona Beach Aquifer, (USA)	Four cationic polymer at 15-20 mg/L	27-65% THMFP
Hubel and Edwald, 1987	Grasse River (the water supply for Canton, New York, USA)	Alum with cationic polymer and nonPAM	32-66% TOC and 26-70% THMFP removal
Bolto et al., 1999	Moorabool River, Hope Valley, South Australia (reservoir/long river) and Wanneroo, Western Australia (groundwater)	DADMAC 5-8 mg/L, CatPAM 7-8 mg/L, cationic polymethacrylate 7-8 mg/L, and alum 30-60 mg/L	%UV removal 35-70%, 31-69%, 50-75%, and 69-88%, respectively
Panyapinyopol, 2004	Bangkhen Water Treatment Plant, Bangkok Thailand	Combination of - Alum; 15, 30 and 45 mg/L - Polymer type; DADMAC, EpiDMA, CatPAM, and AnPAM - Polymer; 0.1, 0.5, and 1.0 mg/L - pH; 5.5, 7.0, and 8.5	> 40% THMFP removal at Alum 45 mg/L with DADMAC 1 mg/L at pH 5.5

Table 2.4 Review of coagulation condition (continued)

Name	Water source	Conditions	%Removal
Chang et al., 2005	Synthetic water (Humic acid, tannic acid and p-hydroxybenzoic acid)	- Alum 60 mg/L combine with 10 mg/L DADMAC - Alum 20-60 mg/L with CatPAM and NonPAM 2-10 mg/L	- 90% TOC removal of Humic acid - Less than 10% Humic acid removal
Kabsch-Korbutowicz, 2005b	The Great Batorow Peatbag (southwest Poland)	Alum 3.59 gAl/m ³ and pH ranged 5-10	59.9%TOC removal and pH optimal from pH 5–6.
Musikavong et al., 2005	Reclaimed water from treated industrial estate wastewater in northern Thailand	Alum varied from 0, 10, 20, 40, 60 and 80 mg/L and pH : uncontrolled, 5.5, 6 and 6.5	25% removal of THMFP at alum dosage 80 mg/L, pH 5.5
Rizzo et al., 2005	An artificial basin, Salerno (Southern Italy)	Alum dosages 10-80 mg/L	65% of THMFP removal at 60 mg/L
Uyak and Toroz, 2005	Terkos Lake Water (TLW), Istanbul Turkey	Alum dosages 20-200 mg/L	TOC 49% for 160 mg/L, UV-254 59% for 120 mg/L, THMFP 57% for 160 mg/L

Remark polymer summarize: NonPAM = Nonionic polyacrylamide; CatPAM = Cationic polyacrylamide; AnPAM = Anionic polyacrylamide; DADMAC = Polydiallyl dimethyl ammonium chloride; EpiDMA = Epichlorohydrin dimethylamine

CHAPTER III

MATERIAL AND METHODS

The purpose of this research was to find the optimum coagulation conditions, i.e. alum and polymers for the effective reduction of THMFP in the raw water from Bangkhen Water Treatment Plant, Bangkok, Thailand. This chapter explains the experimental plan, sample collection, how each experiment was conducted, and also the analytical procedures that were used in the experiments.

This work was based on a laboratory scale experiment set up at the laboratory room of the department of Sanitary Engineering, Faculty of Public Health, Mahidol University.

3.1 Experimental Procedure

The experiment was conducted step by step as illustrated in Figure 3.1.

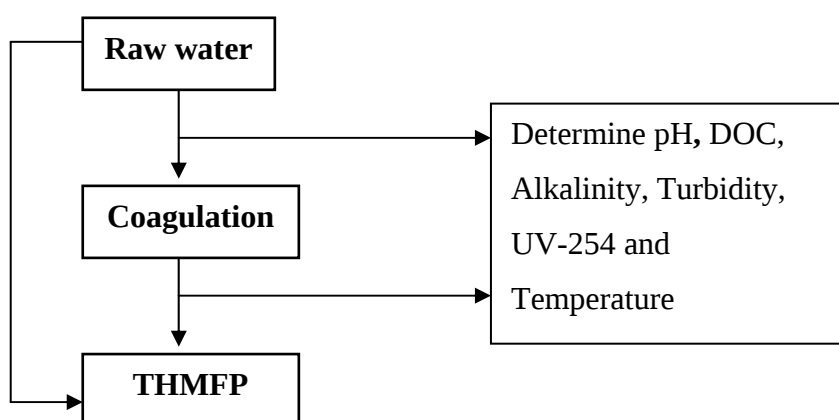


Figure 3.1 Experimental procedure

3.1.1 Raw Water Collection and Storage

Water samples were taken monthly since August to November 2006 from the intake of the Bangkhen Water Treatment Plant, Bangkok and the sampling point is shown in Figure 3.2. Samples were collected in plastic containers by grab sampling and stored in the refrigerator at 4°C without adding any preservatives.



Figure 3.2 Sampling point

3.1.2 Coagulation Experiment

Since the principal factors affecting the coagulation of water are pH and coagulant dosages, the selection of pH and coagulant concentration requires the studies of coagulation in laboratory. Jar-test was used to determine the optimum pH and optimum dosage of coagulant. The procedure of coagulation experiment is as follows:

- Rapid mixing at 100 rpm for 2 minutes
- Slow mixing at 30 rpm for 30 minutes
- Settling for 60 minutes

The coagulation and flocculation experiments were carried out using a Phipps & Bird PB-700 (Cambridge, UK) six-paddle Jar-tester as shown in Figure 3.3.

Samples from each jar were filtered through 0.45 μm membrane filter to remove particulate, and analyzed for those parameters as indicated in Figure 3.1.



Figure 3.3 Jar-test apparatus

3.1.2.1 Coagulation Conditions

Jar-test experiments were carried out under different dosages of alum and polymer, with various controlled pH as shown in Table 3.1. The combination of each condition is illustrated in Figure 3.4.

Table 3.1 Jar-test conditions

Coagulant/ Coagulant aid	Coagulation dosages (mg/L)	pH adjustment
Alum	15, 30 and 45 mg/L	5.5, 6, 6.5 and Uncontrolled
Polymer	0, 0.05, 0.1 and 0.5 mg/L	5.5, 6, 6.5 and Uncontrolled
Cationic		
▪ High MW		
▪ Low MW		
Anionic		

3.1.2.2 Coagulants and Coagulant Aid

▪ Alum

Commercial-grade aluminium sulfate or alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) stock solution was obtained in the liquid form by dissolving in deionized water at 10 mg/mL.

▪ Polymer

Polymers investigated in this experiment were two cationic polydiallyl dimethyl ammonium chloride known as: poly-DADMAC high MW C-308P and low MW C-358 (Polydyne, USA) and anionic polyacrylamide (AnPAM). The characteristics and structure of polymers are shown in Table 3.2 and Figure 3.5 respectively. The first group of organic polymers used in this work, poly-DADMAC, were reported to be the most widely using coagulants in water treatment plants in USA (Fielding, 1999) and could also be used effectively for the treatment of water in Thailand (Panyapinyopol, 2004). The other group is anionic polyacrylamide which is commonly used as coagulant aid in Thailand water treatment plants.

Table 3.2 Characteristics of polymers

Polymer name	C 308P (DADMAC)	C 358 (DADMAC)	AnPAM
Chemical nature	Polydiallyl dimethyl ammonium chloride	Polydiallyl dimethyl ammonium chloride	Acrylamide
Ionic character	Cationic	Cationic	Anionic
Molecular Weight	Low	High	-
Physical form	Clear Amber Liquid	Clear Amber Liquid	Powder
% Active solids	20	20	-

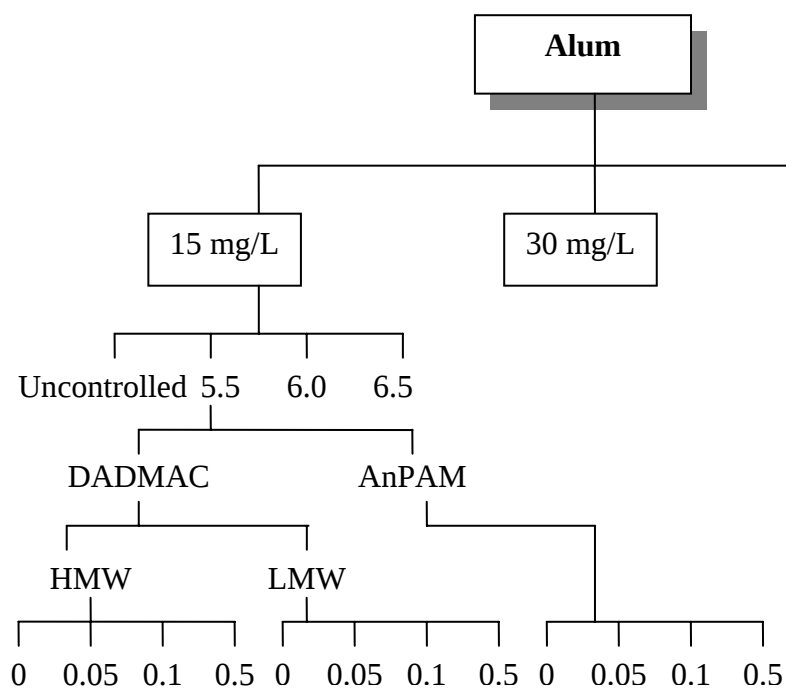


Figure 3.4 Coagulation conditions

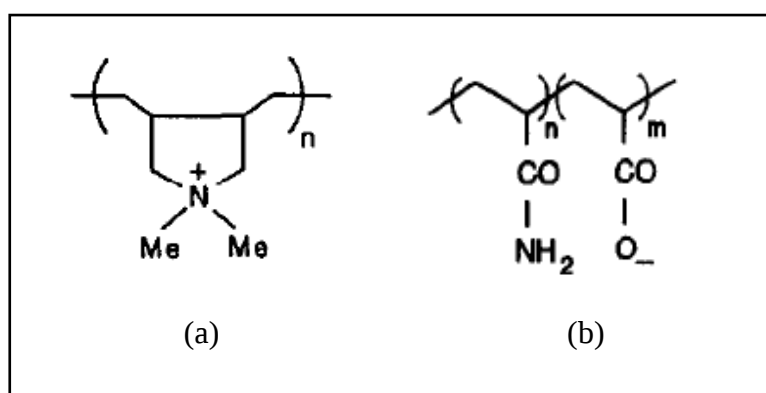


Figure 3.5 Polymer structure (Bolto, 1995)

(a) Poly-DADMAC (b) Polyacrylamide

3.1.3 Trihalomethane Formation Potential (THMFP)

THMFP test was conducted in order to determine the maximum potential of the sample to form THMs. THMFP of a water sample was determined by subtracting the initial THMs concentration from the final THMs concentration. The THMFP in this experiment can be calculated from Equation (3.1).

$$\text{THMFP} = \text{THM}_n - \text{THM}_0 \quad (3.1)$$

THMFP test comprises the following steps:

- Determining of the sample's chlorine demand
- Adjusting pH to 7 by H_2SO_4 or NaOH
- Adding phosphate buffer
- Dosing of excess chlorine
- Incubating the samples at 25 °C till the end of reaction period (24 hours).

The sample must have a residual chlorine between 1-2 mg/L

- Determining of THMs by head space method followed by gas chromatography with Electron Capture Detector (ECD).

3.2 Analytical Methods

This section provides detailed methods used in the experiments.

3.2.1 THMs

THMs was measured by Gas Chromatographic with ECD detector. Measurement of THMs comprises the following steps:

- Pouring 50 mL of the sample in the vial sealed with Teflon sheet and aluminum cap
- Equilibrating at 30°C in water bath for 1 hour
- Taking 0.2 mL of head space in a gas tight syringe, and injecting the sample to the injection port of the GC
- Maintaining the syringe at the injection port until the baseline of chromatogram appears

The operating conditions for GC are shown in Table 3.3.

Table 3.3 Operation conditions for GC

Class	Conditions
GC	Hitachi Model 263-50
Detector	ECD
Column packing	20% SF-96 + 20% Silicone DC 550 (8 : 2) on chromosorb WAW DWCS 80/100 mesh
Column size	3 mm × 3 m
Column temperature	90 °C
Injection temperature	180 °C
Injection volume	0.2 mL
Detector temperature	180 °C
Make-up gas	nitrogen, 50 mL/min

3.2.2 Residual Chlorine

Residual chlorine was measured in accordance with the procedure mentioned in the Standard Method 4500-Cl G DPD Colorimetric Method. The level of chlorine was represented by the light absorbance at 515 nm using Genesys 20 thermo-spectronic.

3.2.3 Ultraviolet Absorption at Wavelength 254 nm (UV-254)

UV-254 of water sample was measured in accordance with standard method 5910 B Ultraviolet Absorption Method at wavelength 254 nm. The samples will be filtered through a 0.45 µm membrane filter prior to the measurement by Genesys 10 UV thermo-spectronic with a 1 cm quartz cell.

3.2.4 Dissolved Organic Carbon (DOC)

DOC of water sample was measured in accordance with standard method 5310 B High-Temperature Combustion Method. DOC of water sample was obtained from the filtrate that passes through the 0.45 μm cellulose acetate membrane, and measured by Shimadzu TOC-500 analyzer (Shimadzu, Milton Keynes, UK).

3.2.5 Specific Ultraviolet Absorbance

Specific ultraviolet absorbance (SUVA) ($\text{L/mg}\cdot\text{m}$) can be calculated as a ratio of the UV absorbance at 254 nm (m^{-1}) with DOC (mg/L).

3.2.6 Alkalinity

Alkalinity of sample was determined by titration with 0.02 N H_2SO_4 according to the standard method 2320 B.

3.2.7 pH

The pH of water sample was measured by Precisa pH 900 with an accuracy of ± 0.1 pH unit.

3.2.8 Turbidity

Measurement of turbidity can be done by HACH model 2100N turbidity meter, using matched cells. The outside of each cell will be cleaned after filling and the samples will be gently mixed prior to measurement. The water turbidity can be expressed in Nephelometric Turbidity Unit (NTU).

3.2.9 Temperature

Temperature of raw water and water sample were directly measured by Thermometer.

The summary of parameters, analytical methods, and instruments in this work are given in Table 3.4.

Table 3.4 Summary of standard methods and instruments

Parameter	Standard Method	Instrument
pH	-	Precisa pH 900
Temperature	-	-
Turbidity	-	HACH, 2100 N Turbidity meter
Alkalinity	Standard Method 2320 B	-
Free Chlorine	Standard Method 4500-Cl G	Genesys 20 thermo-spectronic
THMFP	-	Hitachi Model 263-50
UV-254	Standard Method 5910 B	Genesys 10 UV thermo-spectronic
DOC	Standard Method 5310 B	TOC 500 Shimadzu

3.2.10 Statistical Analysis

1. Descriptive statistics was described as mean value (μ) and standard variation (σ).

$$\mu = \frac{\sum x_i}{N} \quad (3.2)$$

$$\sigma = \sqrt{\frac{\sum (X_i - \mu)^2}{N - 1}} \quad (3.3)$$

Where X_i = Value of samples N = total samples number

2. The k-Way ANOVA (general linear model (Univariation)) was used to test for the difference of statistically significant among the levels of dependent variables.

The significant level in this study was determined at 0.05 (α level = 0.05)

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characteristics of Raw Water

The characteristics of raw water taken from the intake of Bangkhen Water Treatment Plant (Bangkok, Thailand) during August to November 2006 were analyzed for physical and chemical parameters as shown in Table 4.1. The raw water characteristics varied with sampling periods. In August and September, there was an intensive rainy period; turbidity of raw water was about 100 NTU. In October and November, flooding in the northern and central regions of Thailand resulted in low turbidity. Table 4.1 shows that DOC was in the range of 4.0 and 6.5 mg/L, UV-254 0.099 and 0.191 cm⁻¹, and SUVA 2.38 and 3.18 L/mg-m. In addition, THMFP was in the range of 154 to 354 µg/L.

Normally, in rainy season (August and September), the characteristics of raw water, i.e. turbidity and organic matter are higher than that in other seasons because the runoff carries with it particulate matter including organic matter into the water course, thereafter raising THMs formation potential. Flooding in the northern and central regions of Thailand at the end of September caused the particulate organic matter to settle to the bottom of the waterway resulting in all surrogate parameters in October being lower than those in August and September. In subsequent month (November) the water still could not flow out to the sea, and this caused the decomposition of the organic matters in the water source accordingly, thereby increasing the THM precursors. The variation in the water quality i.e. turbidity, DOC and THMFP are illustrated in Figure 4.1.

From this point forward, water quality in August and September is represented as high turbidity-high DOC water sample, in October as low turbidity-low DOC, and in November as low turbidity-high DOC.

Table 4.1 Characteristics of raw water

Parameters	August 2006	September 2006	October 2006	November 2006
pH	8.5	8.0	8.3	8.3
Turbidity (NTU)	110	100	31.7	10.3
Alkalinity (mg/L as CaCO ₃)	79.5	96	84	110
Temperature (°C)	29	28	28	29
UV-254 nm (cm ⁻¹)	0.165	0.150	0.099	0.191
DOC (mg/L)	6.5	6.3	4.0	6.0
SUVA (L/mg-m)	2.62	2.38	2.48	3.18
THMFP at 24 hour (µg/L)	354	238	154	263

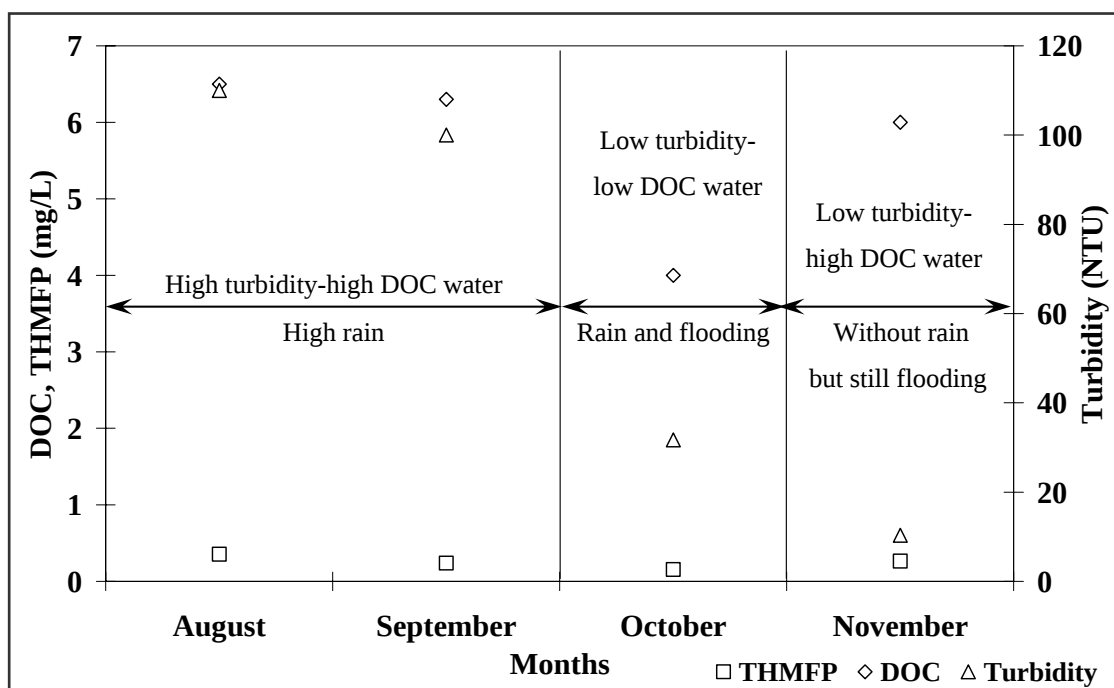


Figure 4.1 Time variation in characteristics of raw water

In the following experimental series, raw water samples were Jar-tested for the optimal coagulation conditions. The parameters of interest are pH (uncontrolled, controlled at 5.5, 6.0 and 6.5), alum doses (15-60 mg/L), and polymer doses (0.05-0.5 mg/L). The analytical parameters included (i) turbidity, (ii) DOC and (iii) THMFP.

4.2 Effect of Alum Dosages on Coagulation

4.2.1 Statistical Analysis

In the event of high turbidity-high DOC raw water (August), the results of dosage of alum on THMFP reduction efficiency from One-Way ANOVA test was significant, $F(2, 117) = 3.979$, $p\text{-value} = 0.021$, the results as shown in Table 4.2. The Least Significance Difference's multiple comparison results of the THMFP reduction efficiency on different alum dosages are shown in Table A-1 of Appendix A (Post Hoc Tests (Multiple Comparisons)). The results showed that the efficiency of THMFP reduction at alum dosage 30 mg/L was significantly higher than at alum dosage 45 and 15 mg/L ($p\text{-value} < 0.05$). At the same time, the efficiency at alum dosage of 45 mg/L was significantly higher than that at alum dosage 15 mg/L.

In case of high turbidity-high DOC water (September), the results of dosage of alum on THMFP reduction efficiency from One-Way ANOVA test was significant, $F(2, 105) = 9.316$, $p\text{-value} = 0.000$ (results as shown in Table 4.2). The Least Significance Difference's multiple comparison results of the THMFP reduction efficiency on different pH values were shown in Table A-2 of Appendix A (Post Hoc Tests (Multiple Comparisons)). The results showed that the efficiencies of THMFP reduction at alum dosages 30 mg/L was significantly higher than between at alum dosage 15 and 45 mg/L ($p\text{-value} < 0.05$), and the efficiency of THMFP reduction at alum dosage of 45 mg/L was significantly higher than an alum dosage of 15 mg/L.

Table 4.2 The results of the ANOVA statistics analysis tests for the THMFP reduction efficiency for different raw water under different of alum dosages

THMFP reduction efficiencies	Alum dosages (mg/L)	Mean	S.D.	ANOVA test	LSD
High turbidity-high DOC water (August)	15	27.883	0.779	DS	30 > 45 > 15
	30	32.281	0.779		
	45	30.623	0.779		
High turbidity-high DOC water (September)	15	28.805	0.679	DS	30 > 45 > 15
	30	35.196	0.679		
	45	34.415	0.679		
Low turbidity-low DOC water (October)	15	29.115	2.739	DS	15 = 30 = 60, 45 > 15, 45 > 30, 45 > 60,
	30	33.707	2.739		
	45	39.957	2.739		
	60	32.156	2.739		
Low turbidity-high DOC water (November)	30	35.152	1.343	DS	30 < 40 = 45 = 60
	40	36.488	1.343		
	45	38.039	1.343		
	60	38.013	1.343		

Remark; DS mean difference significantly among the group

For low turbidity-low DOC water (October), One-Way ANOVA test on the effect of alum dosages on THMFP reduction efficiency was significant, $F(3, 36) = 3.551$, $p\text{-value} = 0.024$, (see Table 4.2). The Least Significance Difference's multiple comparison results of the THMFP reduction efficiency at various pH levels were shown in Table A-3 of Appendix A (Post Hoc Tests (Multiple Comparisons)). The test results indicated that the efficiencies of THMFP reduction at alum dosages 45 mg/L was significantly higher than those at alum dosages of 15, 30, and 60 mg/L, whereas THMFP reduction efficiencies at alum dosages of 15, 30, and 60 mg/L were not significantly different among the group ($p\text{-value} > 0.05$).

For low turbidity-high DOC water (November), the results of alum dosage on THMFP reduction efficiency from One-Way ANOVA test was significant, $F(2, 36) = 7.964$, $p\text{-value} = 0.021$ (Table 4.2). The Least Significance Difference's multiple

comparison results of the THMFP reduction efficiency at various pH levels were shown in Table A-4 of Appendix A (Post Hoc Tests (Multiple Comparisons)). The results showed that the efficiencies of THMFP reduction at alum dosages of 40, 45, and 60 mg/L were significantly higher than that at alum dosage of 30 mg/L (p -value < 0.05). However, the efficiency of THMFP reduction at alum dosage of 40 mg/L was not significantly different from those at 45 and 60 mg/L (p -value > 0.05).

In conclusion, statistics stated that THMFP reduction efficiencies changed with alum dosages.

4.2.2 Discussion

The effects of coagulation at various alum dosages on turbidity, DOC, along with the THMFP reduction efficiency without controlling pH values are shown in Figures 4.2 to 4.4. It can be concluded that the optimum alum dosages were 30 and 45 mg/L for high turbidity-high DOC water, and 45 and 60 mg/L for water sample in low turbidity-low and low turbidity-high DOC waters, were acceptable on removal of turbidity, DOC and THMFP reduction at uncontrolled pH.

In case of high turbidity-high DOC water (water sample in August and September), the removal efficiency of turbidity was about 97% with an alum dose of more than 30 mg/L (see Figure 4.2) where the resulting turbidity was less than 5 NTU. This was considered sufficient for compliance with the standard turbidity requirement in operation of water treatment plant. The alum dosage of 15 mg/L was found to be insufficient for charge neutralization and the attainable residual turbidity was higher than 5 NTU. Meanwhile, in almost all cases, DOC of coagulated waters was gradually reduced with an increase in alum dosage. High reduction of DOC was obtained at alum dosage of 30-45 mg/L (see Figure 4.3) and the efficiency was in the range of 34-52%. Figure 4.4 presents the investigation of THMFP reduction in coagulated water samples by varying different dosages of alum which demonstrates that the alum dosage of 45 mg/L provided the highest THMFP reductions at approximately 25-31%. The results suggested that increasing alum dosage would lead to an increase in

THMFP reduction efficiency. The concentrations in term of microgram per liter of the THMFP in coagulated water were also found that at the maximum reduction of THMFP was observed at alum dosage 30 mg/L and without controlled pH. Due to this condition, THMFP can be reduced from 238-354 $\mu\text{g/L}$ in raw water to the level of 187-259 $\mu\text{g/L}$.

For low turbidity-low DOC water (water sample in October), the experiment showed that the highest turbidity removal efficiency was obtained at approximately 98%. The residual turbidity at the alum dose of 45 mg/L was significantly higher than that at 60 mg/L indicating a potential over-dosing of coagulant. The coagulant overdosing can be the cause of charge reversal and thereby restabilization which led to a higher level of residual turbidity (see Figure 4.2). Figure 4.3 suggests that the percentage of DOC reduction was the highest at approximately 43%, however, an increment in alum dosage from 45 to 60 mg/L led to a slight increase in DOC. The efficiencies of THMFP reduction in this case was approximately 30% with an alum dosage of 45 mg/L. It appears that an alum dosage of 60 mg/L provided lower THMFP reduction efficiency (see Figure 4.4) where the percentage of THMFP reduction was only approximately 20%. As a general observation, DOC removed in a greater extent than THMFP. It was possible that a larger proportion of the less reactive organic matters in forming THMs was removed by chemical coagulation, and the remaining organic matters in solution was highly active to form THMs.

Finally, in case of low turbidity-high DOC water (water sample in November), the percentage of turbidity removal was approximately 91%. The variation in alum dosages from 45 to 60 mg/L did not seem to have significant effect on the turbidity removal efficiency (see Figure 4.2). On the other hand, an increment in alum dosage from 45 to 60 mg/L resulted in a slight increment in DOC reduction. The highest percentage of DOC reduction of approximately 25% was observed. The results showed that THMFP reduced approximately 26 and 28% with an alum dosage of 45 and 60 mg/L, respectively. These observations indicated that, with increasing in alum dosage might slightly would improve the performance of THMFP reduction.

To conclude this section, the coagulation conditions were found to depend significantly on the quality. And even with the same water sample, the coagulation condition was different for different purposes. For the reduction of THMFP, the most suitable coagulation conditions could be summarized as follow;

- High turbidity-high DOC water; the studying with high turbidity-high DOC water was set up the alum dosage between 15-45 mg/L.
- Low turbidity-low DOC water; required higher coagulant doses on removal turbidity and organic matter thus, the alum dosage at 60 mg/L was added up to study.
- Low turbidity-high DOC water; alum dose for 15 mg/L were not significantly improve the removal of THM precursors. Consequently, these characteristics of raw water was not regarding to work on using alum dosage of 15 mg/L and then set of further experiment on the dosage of alum at 40 and 60 mg/L.

It was noted that pH of samples slightly reduced after coagulation. This was because the acidity of the alum which was employed as coagulation aid. The effect of pH on the coagulation was investigated further in Section 4.4.2.

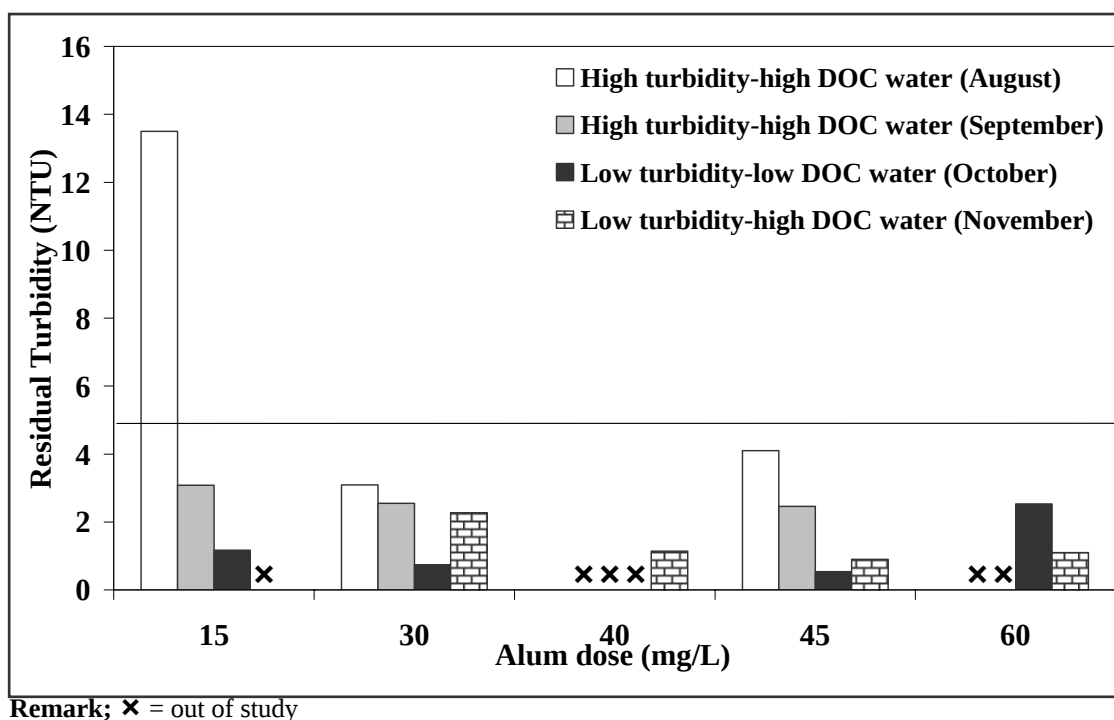


Figure 4.2 Residual turbidity at uncontrolled pH

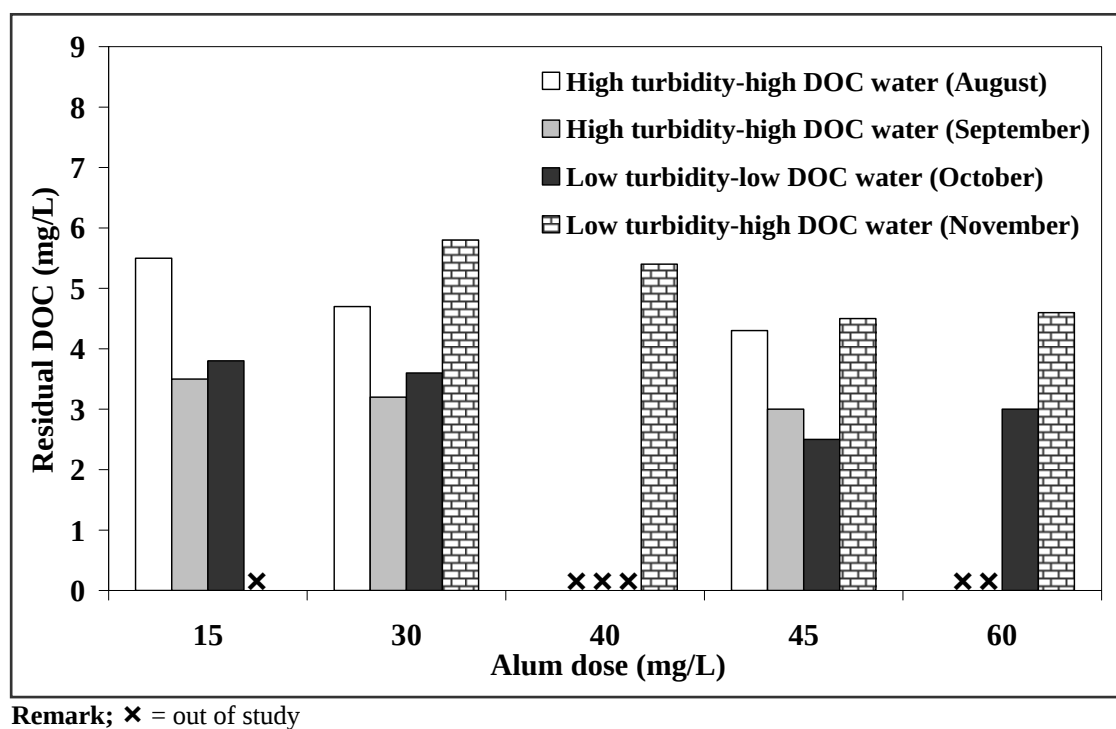


Figure 4.3 Residual DOC at uncontrolled pH

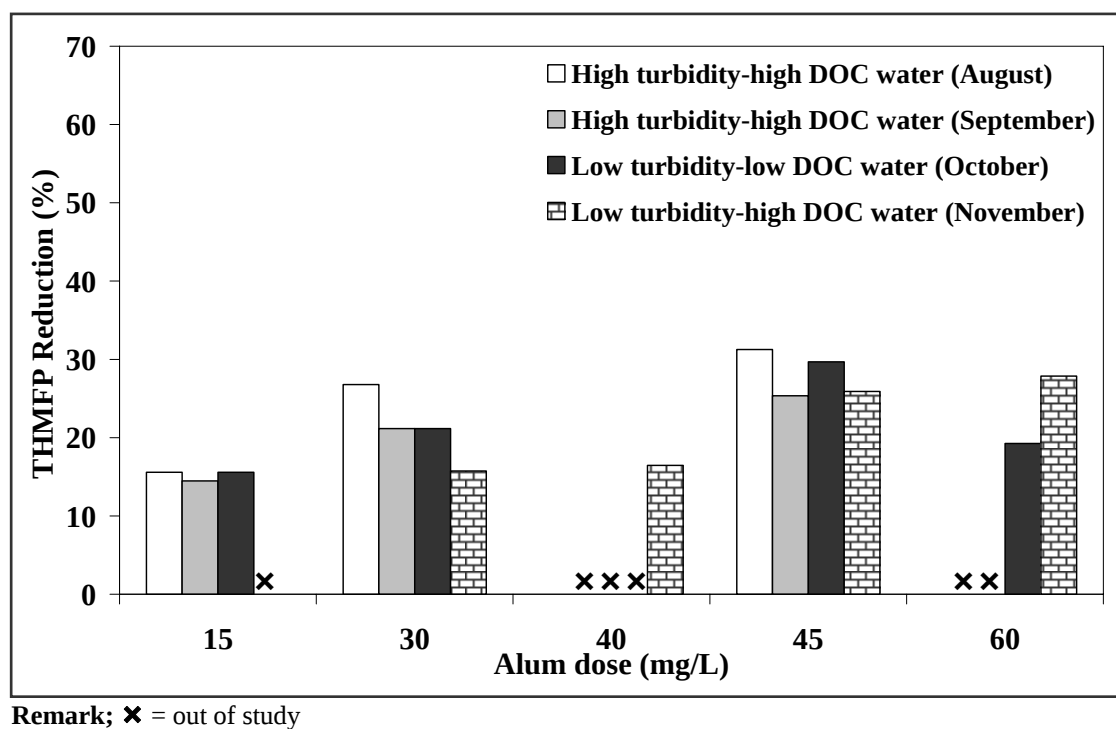


Figure 4.4 THMFP reduction efficiency at uncontrolled pH

4.3 Effect of Polymer Types on Coagulation

4.3.1 Statistical Analysis

The comparison of THMFP reduction efficiency between alum alone and alum combined with different type of polymer found that the comparison between alum alone and alum combined with AnPAM was not significantly different among the group ($p\text{-value} > 0.05$). On the other hand, the comparison among the group of polymer, high molecular weight, low molecular weight DADMAC, and AnPAM found that high molecular weight, low molecular weight DADMAC significantly higher than AnPAM ($p\text{-value} < 0.05$). Accordingly, high molecular weight DADMAC was significantly higher efficiency in THMFP reduction than low molecular weight DADMAC, analysis data as shown in Table A-7 of Appendix A.

The experimental design for another case of high turbidity-high DOC water (September) was not concentrated on AnPAM. Thus, the type of polymer was set for comparison between high molecular weight, low molecular weight DADMAC. The statistical analysis data as shown in Table A-8 of Appendix A. The results indicated that the efficiency of high molecular weight was significant higher than low molecular weight DADMAC and alum alone ($p\text{-value} < 0.05$). Hence, from the statistical analysis was confirmed the experimental results that high molecular weight showed higher efficiency THMFP reduction than low molecular weight DADMAC.

4.3.2 Discussion

Section 4.2.2 suggests that only the two dosages of alum, i.e. 30 and 45 mg/L for high turbidity-high DOC, and 45 and 60 mg/L for low turbidity-low DOC, and low turbidity-high DOC water samples, were acceptable for the removal of turbidity and reduction of THM precursors and THMFP. Hence, this section would only focus on these findings.

Three types of polymers were examined for their effectiveness, i.e. anionic polyacrylamide (AnPAM), high molecular weight and low molecular weight cationic polydiallyl dimethyl ammonium chloride (DADMAC). Figures 4.5 to 4.7 show the comparative performance between the residual turbidity, residual DOC and the percentage of THMFP reduction by using alum combined with polymer for the different water sample.

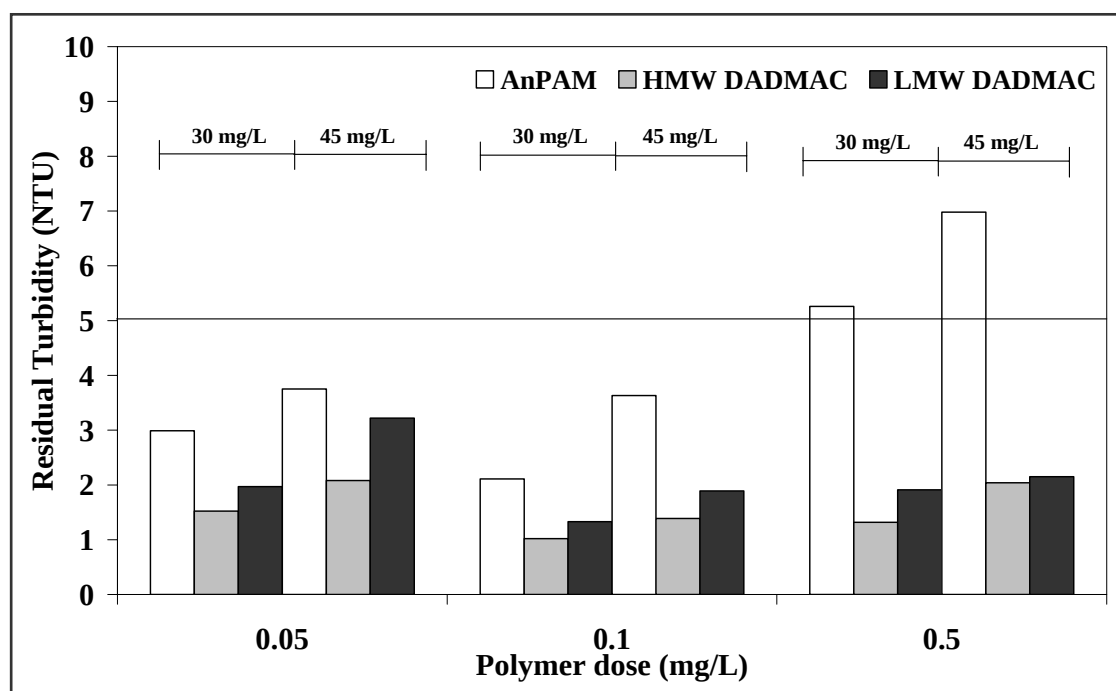
The examination for high turbidity-high DOC water on the changes in turbidity, DOC along with THMFP reduction efficiency can be seen in Figure 4.5 (a-c). The result suggested that coagulation by alum combined with all dosages of high molecular weight DADMAC polymer would achieve better turbidity removal, DOC and THMFP reductions than the use of low molecular weight DADMAC, and AnPAM. These finding were supported by the conclusion from Hubel and Edzwald (1987) who reported that using alum with high molecular weight polymer was more effective than with the low molecular weight. Figure 4.5 (a) illustrates that the residual turbidities from the use of all three types of polymers were less than the standard turbidity requirement (5 NTU). There was an exception at the alum dosages of 30 and 45 mg/L combined with AnPAM (anionic polymer) 0.5 mg/L whereas the residual turbidity was higher than the standard turbidity requirement, (see Figure 4.5 (a)). This was because the excess polymer (0.5 mg/L) caused an uniformed floc formation as shown in Figure 4.6 (a) which was not desirable for coagulation. Figure 4.6 (b) demonstrates the homogeneous floc formation obtained from the use of DADMAC polymer (cationic polymer). Hence, the use of AnPAM with alum was not useful for the reduction of THMFP and the reduction efficiency in this case was only about 24% (from Figure 4.5 (c)). At the optimal condition for this polymer, alum dosage 30 mg/L and polymer dosage of 0.05 mg/L without controlled pH showed worse THMFP reduction than the coagulation by alum alone (27% THMFP reduction) as can be seen in Figure 4.4. As AnPAM was an anionic polymer with the same charge as organic matter presented in water (AWWA, 1971), it did not help charge neutralization of the organic component. Hence, it only offered unattractive DOC reduction efficiency, and a subsequent low THMFP reduction was observed. This finding agreed with the

results from Chang et al., (1999) and Panyapinyopol (2004). Thus, the use of AnPAM will not be further investigated.

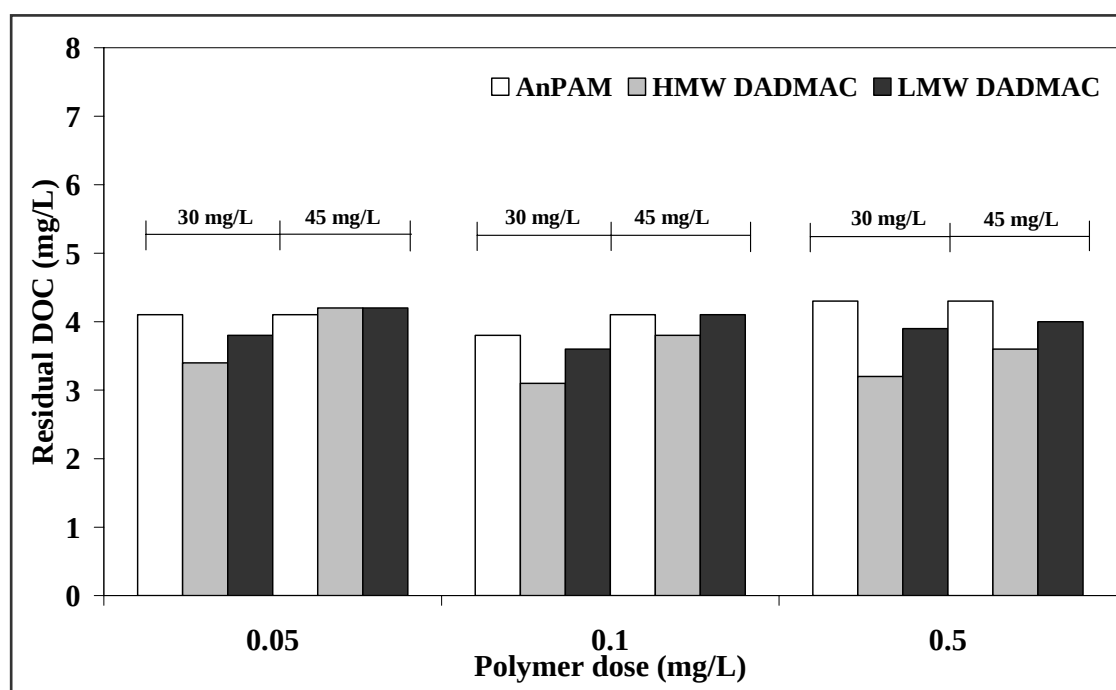
The combination of alum and high molecular weight DADMAC (cationic polymer) can improve turbidity removal and THM precursors reduction at all dosage range as shown in Figure 4.6 (b). DADMAC was explained as a chlorine resistant polymer (Chang et al., 1999) which meant the residual of DADMAC in the water would not easily form THMs. In addition, this polymer has been proven to improve THMFP reduction by strengthening the linkage between particles and flocs, which enlarged the size of floc and accelerated the setting velocity (Chang et al., 2005).

In case of high turbidity-high DOC water experiments were presented in Figure 4.7 (a-c). The residual turbidity, DOC and THMFP reduction efficiency with a combination of alum (30 mg/L and 45 mg/L) and two types of polymer (high and low molecular weight DADMAC) are discussed in this paragraph. The combination of alum and high molecular weight DADMAC exhibited better removal of turbidity, reduction of DOC and THMFP than the use of low molecular weight DADMAC (see Figure 4.5 and 4.7). Therefore, the use of low molecular weight DADMAC was no longer discussed for the cases of low turbidity-low DOC water and low turbidity-high DOC water samples.

While, in cases of low turbidity-low DOC water and low turbidity-high DOC water as shown in Figures 4.8 to 4.9 (a-c), the residual turbidity, residual DOC and THMFP at various high molecular weight DADMAC dosages seemed to be lower with the alum dosage of 45 mg/L than those at 60 mg/L. At the same efficiency of finished water, the combination of alum and high molecular weight DADMAC could reduce the alum dosage from 60 to 45 mg/L for low turbidity-low DOC water and low turbidity-high DOC water samples.

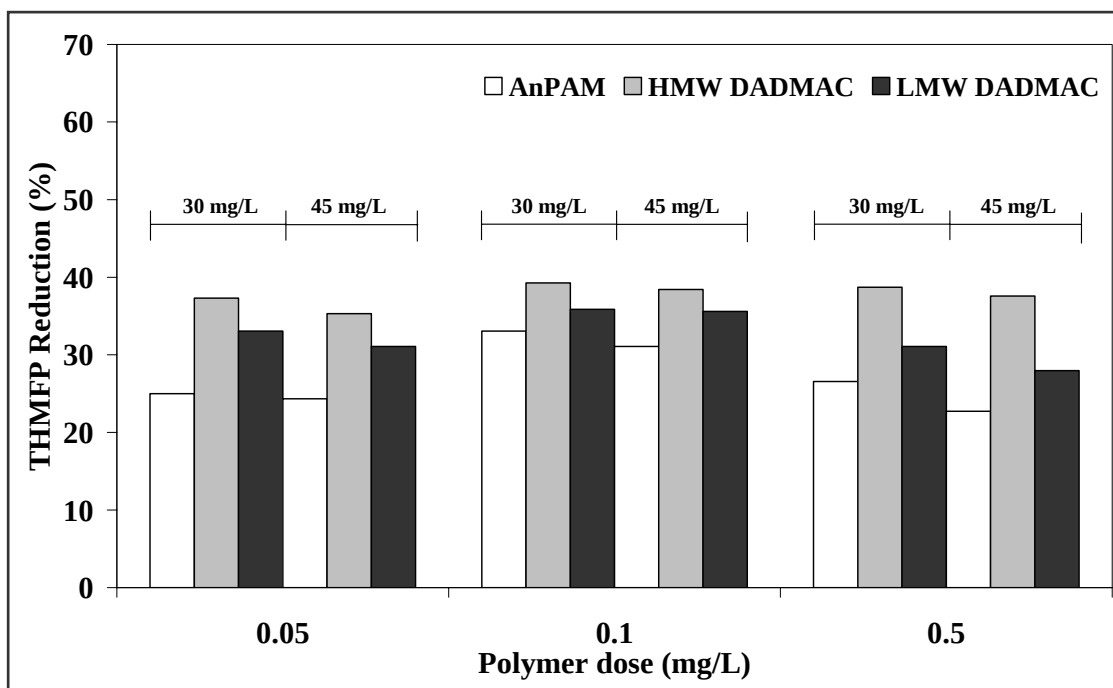


(a) Residual turbidity



(b) Residual DOC

Figure 4.5 Residual turbidity, residual DOC and THMFP reduction at uncontrolled pH for high turbidity-high DOC water (August)



(c) THMFP reduction

Figure 4.5 Residual turbidity, residual DOC and THMFP reduction at uncontrolled pH for high turbidity-high DOC water (August) (continued)

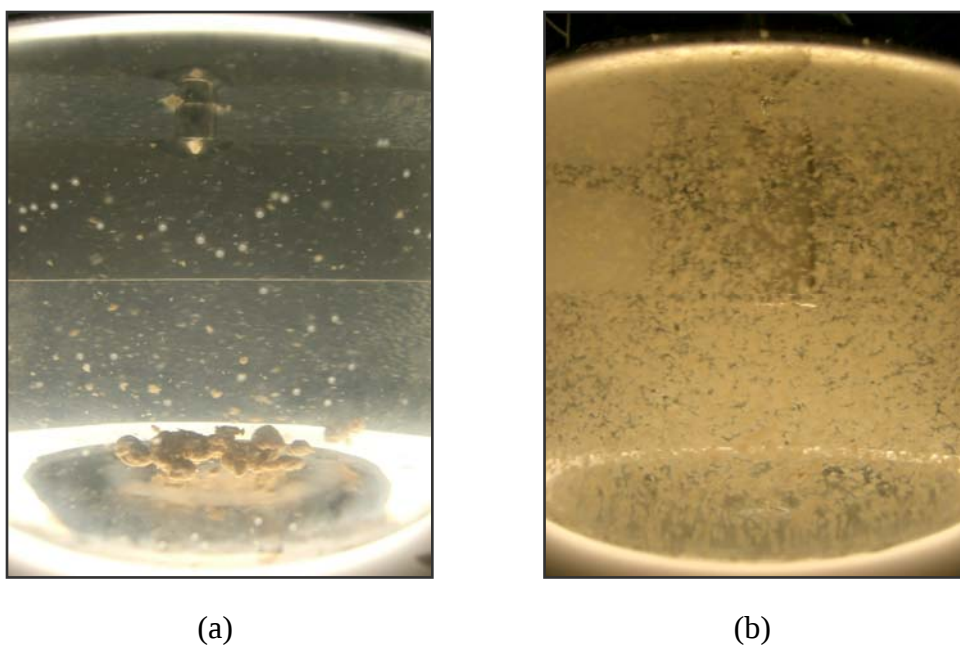
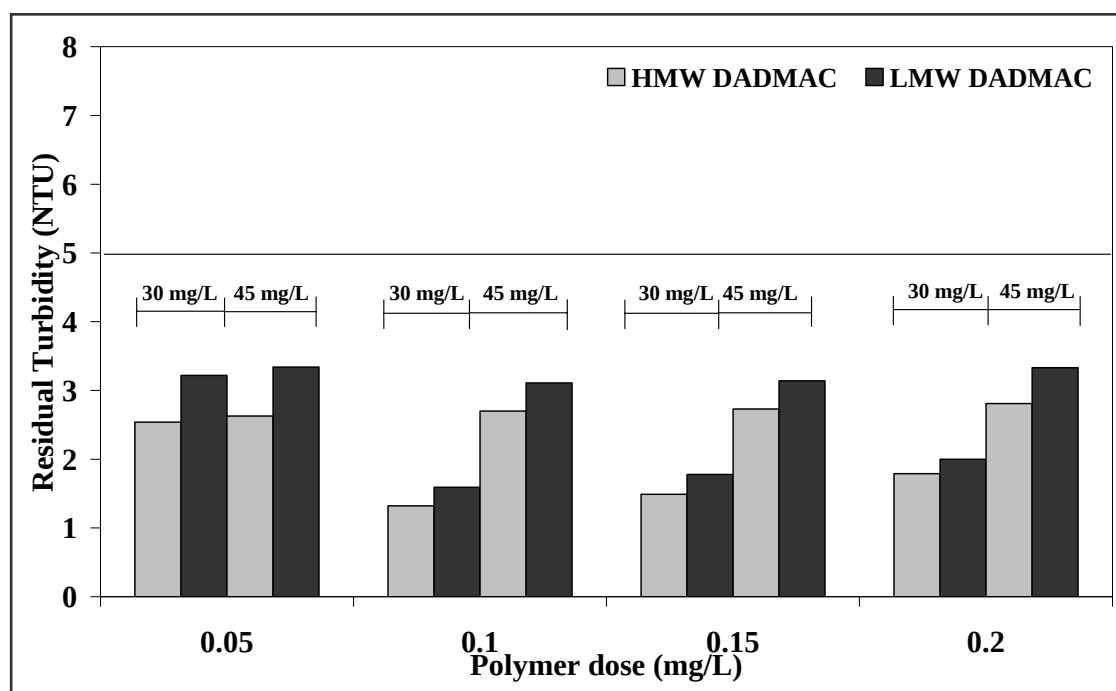
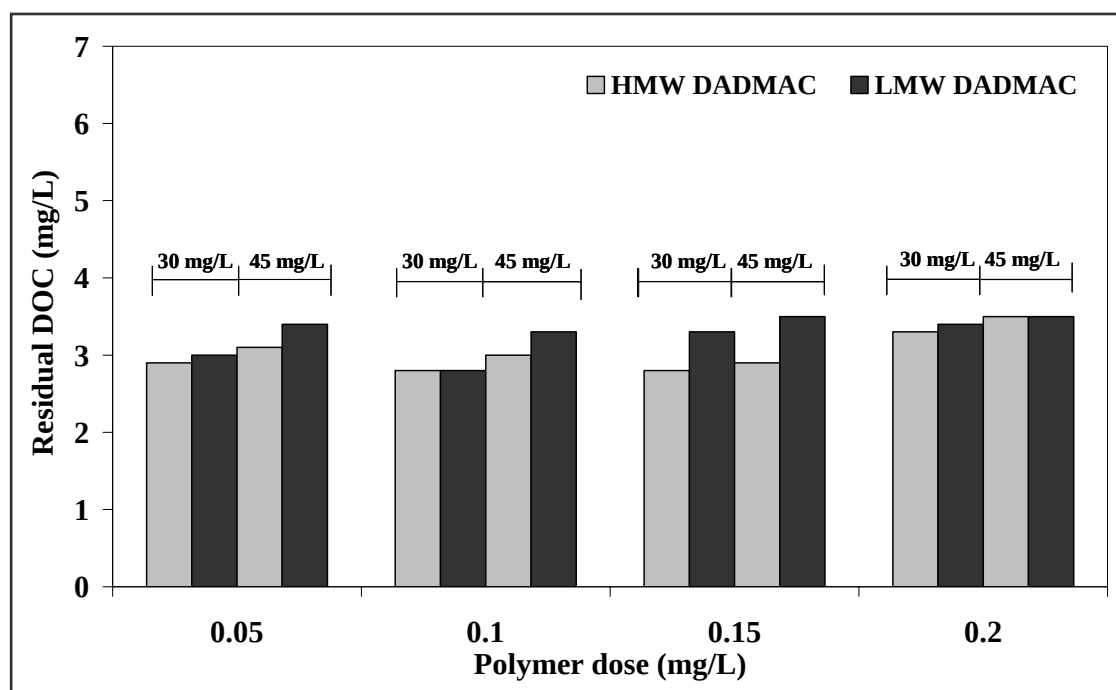


Figure 4.6 Floc forming from coagulation by alum and polymer

(a) alum 45 mg/L and AnPAM 0.5 mg/L (b) alum 45 mg/L and DADMAC 0.5 mg/L

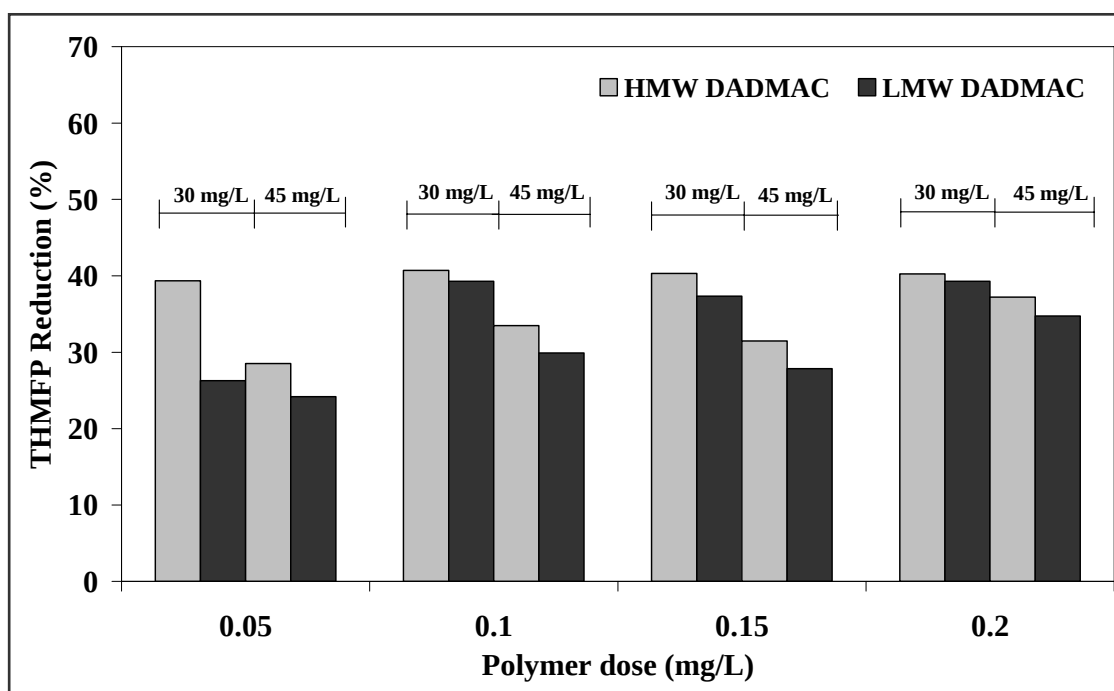


(a) Residual turbidity



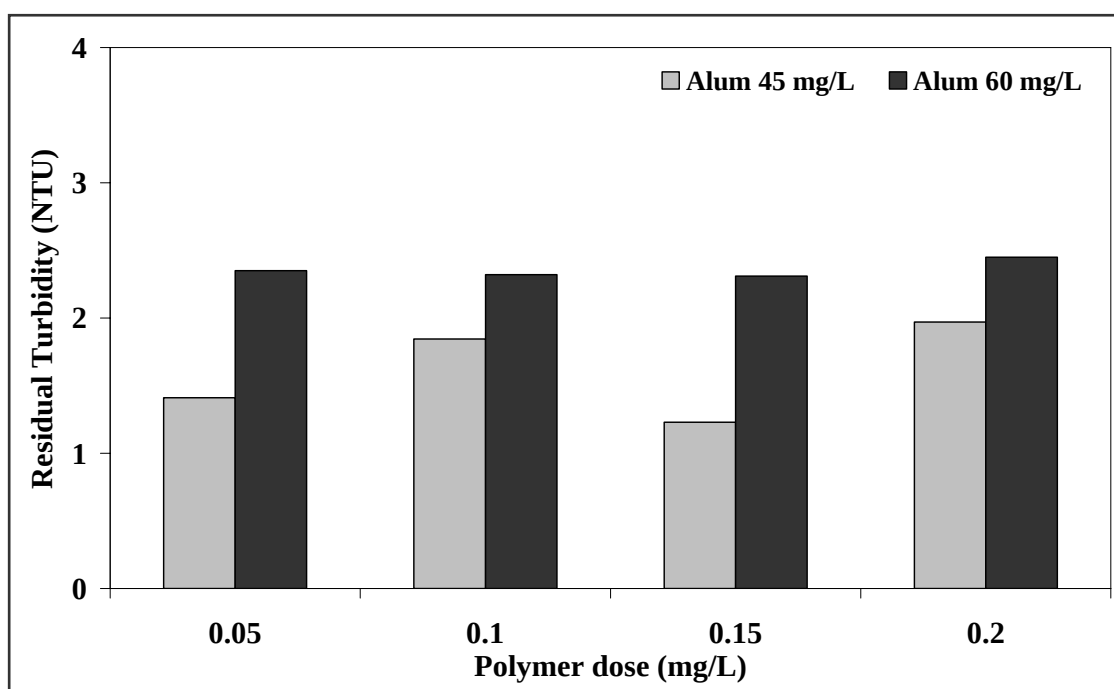
(b) Residual DOC

Figure 4.7 Residual turbidity, residual DOC and THMFP reduction at uncontrolled pH for high turbidity-high DOC water (September)



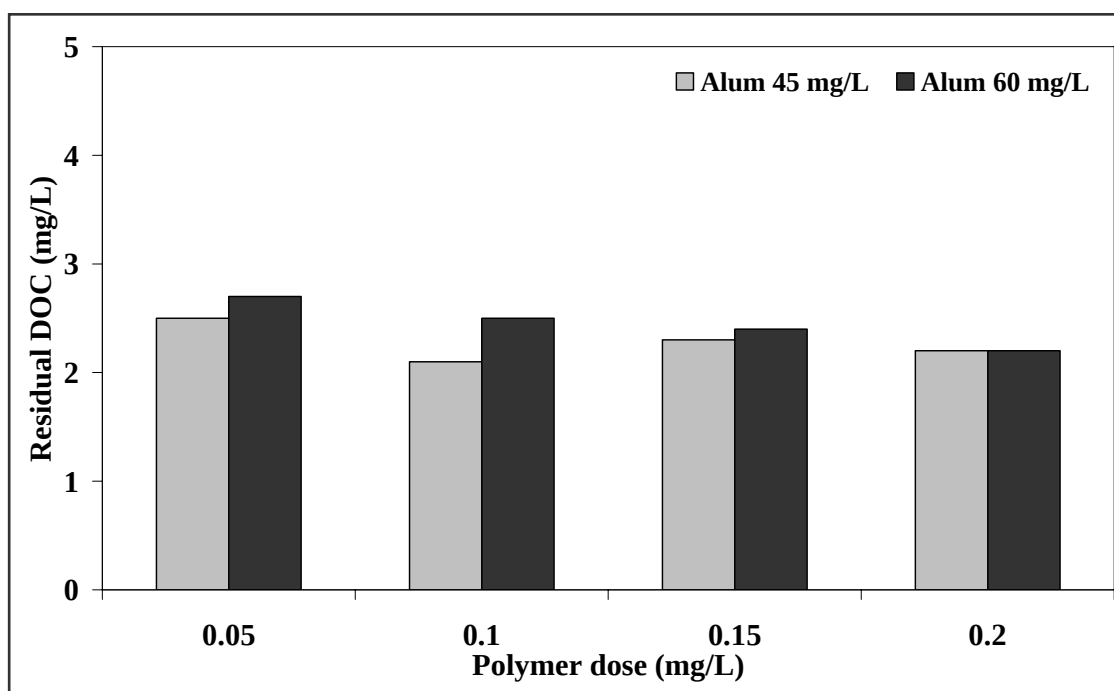
(c) THMFP reduction

Figure 4.7 Residual turbidity, residual DOC and THMFP reduction at uncontrolled pH for high turbidity-high DOC water (September) (continued)

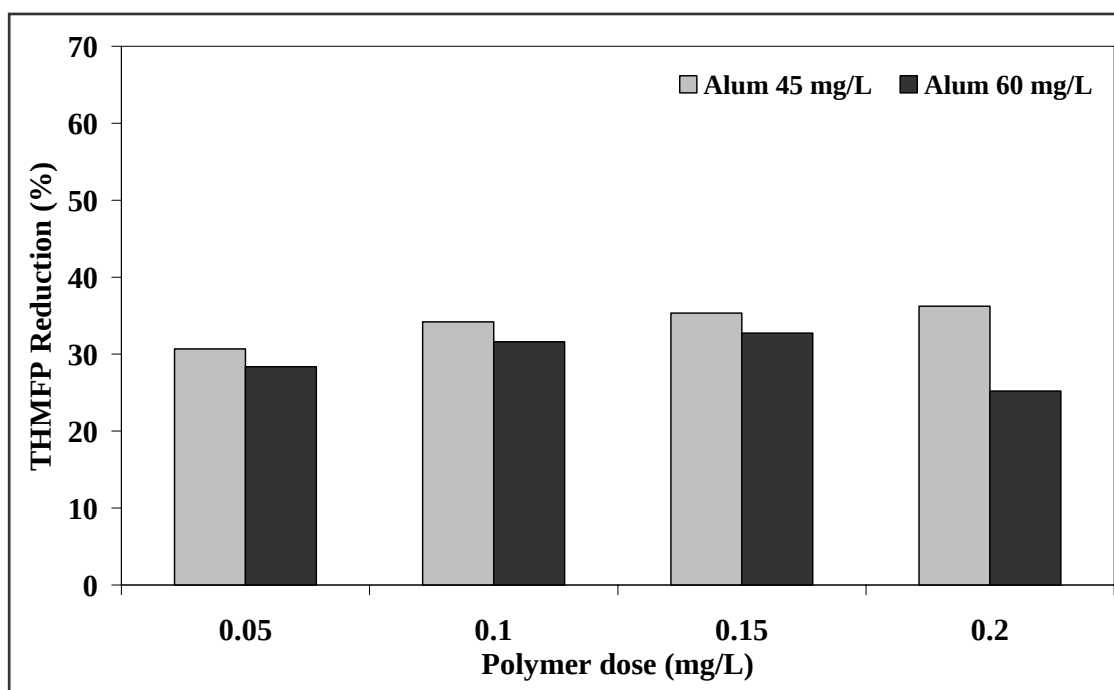


(a) Residual turbidity

Figure 4.8 Residual turbidity, residual DOC and THMFP reduction at uncontrolled pH for low turbidity-low DOC (October)

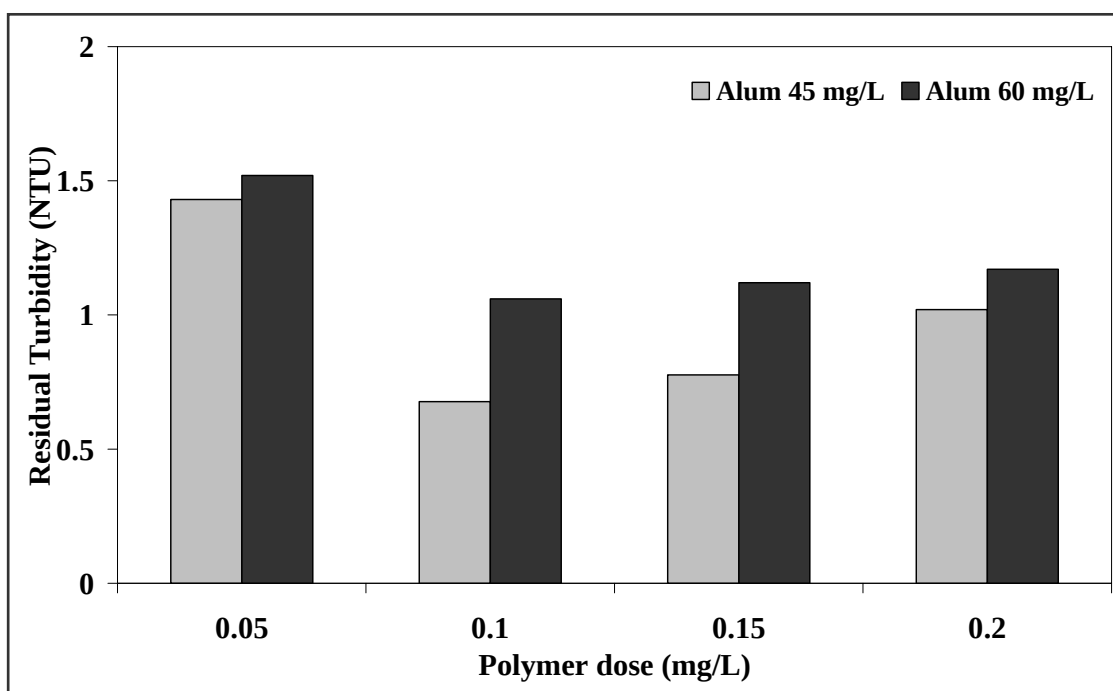


(b) Residual DOC

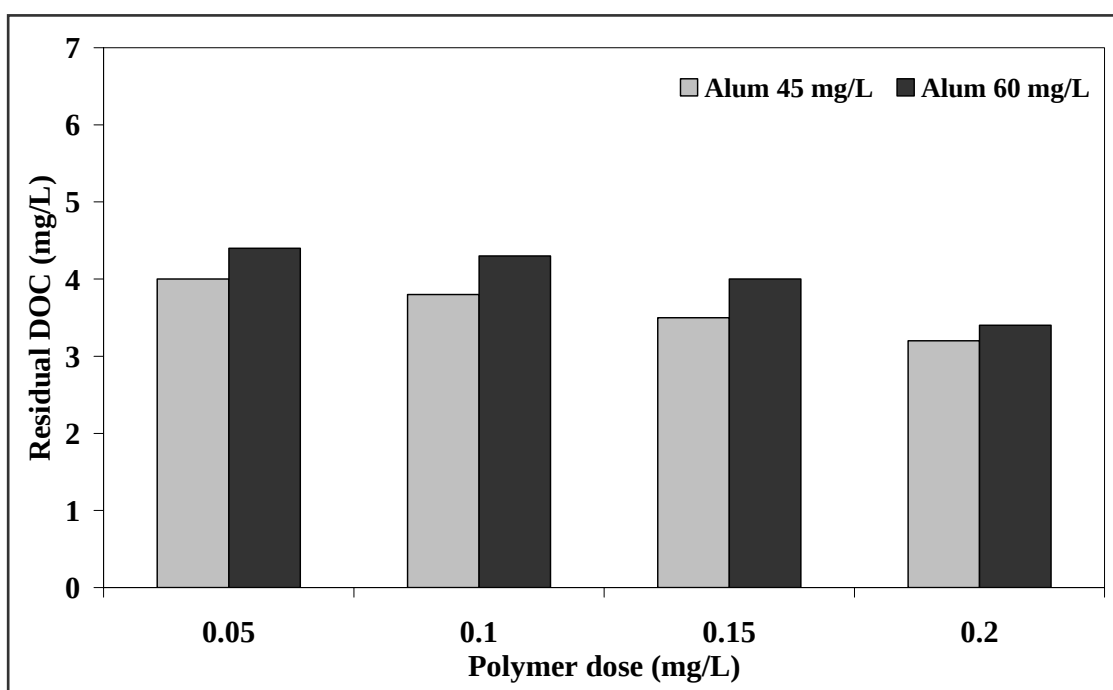


(c) THMFP reduction

Figure 4.8 Residual turbidity, residual DOC and THMFP reduction at uncontrolled pH for low turbidity-low DOC (October) (continued)

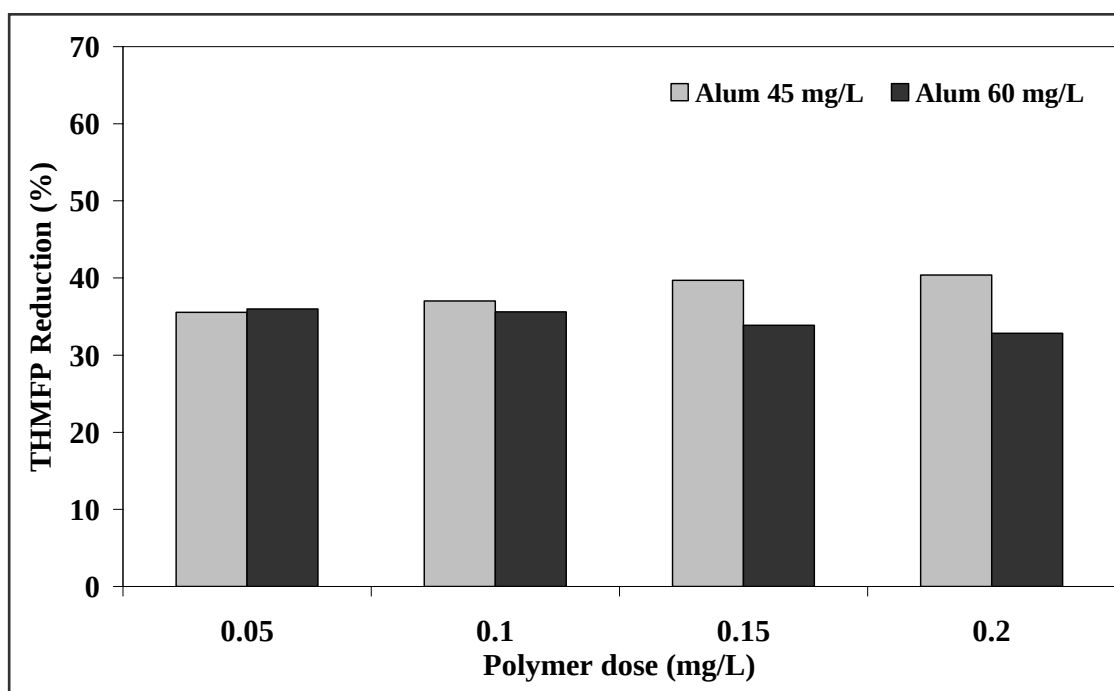


(a) Residual turbidity



(b) Residual DOC

Figure 4.9 Residual turbidity, residual DOC and THMFP reduction at uncontrolled pH for low turbidity-high DOC (November)



(c) THMFP reduction

Figure 4.9 Residual turbidity, residual DOC and THMFP reduction at uncontrolled pH for low turbidity-high DOC (November) (continued)

4.4 Effect of pH Values on Coagulation

4.4.1 Statistical Analysis

In case of high turbidity-high DOC water (water sample in August), the results of pH on THMFP reduction efficiency from One-Way ANOVA test was significant, $F(3, 116) = 8.492$, $p\text{-value} = 0.000$. The results are shown in Table 4.3. The Least Significance Difference's multiple comparison results of the THMFP reduction efficiency on different pH values are shown in Table A-5 of Appendix A (Post Hoc Tests (Multiple Comparisons)). It was found that the efficiency of THMFP reduction at pH 5.5 was significantly higher than from uncontrolled pH, 6.0, and 6.5 ($p\text{-value} < 0.05$). While, at uncontrolled pH, was not different between 6.0 and 6.5 ($p\text{-value} > 0.05$).

Table 4.3 The results of the ANOVA statistics analysis tests for the THMFP reduction efficiency on different of pH values for different raw water

THMFP reduction					
efficiencies	pH	Mean	S.D.	ANOVA test	LSD
High turbidity-high DOC water (August)	uncontrolled pH	29.252	1.032	DS	5.5 >
	5.5	33.451	1.032		(6.0 = 6.5 =
	6.0	29.829	1.032		uncontrolled)
	6.5	27.365	1.032		
High turbidity-high DOC water (September)	uncontrolled pH	27.555	0.784	DS	5.5 >
	5.5	36.841	0.784		(6.0 = 6.5 =
	6.0	34.013	0.784		uncontrolled
	6.5	32.812	0.784		

Remark; DS mean difference significantly among the group

For another case of high turbidity-high DOC water (September) the results of pH on THMFP reduction efficiency from One-Way ANOVA test was significant, $F(2, 36) = 11.259$, $p\text{-value} = 0.000$. The results are shown in Table 4.3. The Least Significance Difference's multiple comparison results of the THMFP reduction efficiency on different pH values are shown in Table A-6 of Appendix A (Post Hoc Tests (Multiple Comparisons)). The results showed that the efficiency of THMFP reduction at pH 5.5 was significantly higher than uncontrolled pH, 6.0, and 6.5 ($p\text{-value} < 0.05$). At the same time, efficiency of THMFP reduction at uncontrolled pH was not different between 6.0 and 6.5 ($p\text{-value} > 0.05$). These results were also consistent with the high turbidity-high DOC water (August) studies. In addition, at pH value of 6.0, 6.5 and uncontrolled pH were significantly difference under conditions of uncontrolled pH.

On the other hand, the statistic analysis for factor of pH values in low turbidity-low DOC water (October) and low turbidity-high DOC water (November) could not calculate because the requirement of the post hoc tests must have more than three groups of independent values.

These results corresponded to the hypothesis, which stated that, the THMFP reduction efficiencies were changed with under different pH values.

4.4.2 Discussion

The effect of pH was investigated only for the coagulation at optimal alum doses. Coagulation experiments on reduction of turbidity, DOC and THMFP reduction efficiency were carried out at alum dosage of 30 mg/L for high turbidity-high DOC, and 45 mg/L for low turbidity-low DOC and low turbidity-high DOC, with an appropriate polymer type (high molecular weight DADMAC) with a dosage of 0.05 mg/L (from Section 4.3.2). Figures 4.10 to 4.12 show the results on the residual turbidity in supernatant, residual DOC and THMFP reduction efficiency versus a combination of alum and polymer at various pH levels (uncontrolled, 5.5, 6.0 and 6.5).

The high turbidity-high DOC raw water sample (August and September) was studied to determine the coagulation efficiency in turbidity, DOC and THMFP reduction. From the experimental results, it was observed that the optimal pH for the coagulation were presented at 5.5 as turbidity, DOC and THMFP were illustrated to be reduced at the greatest extent at this pH. The experimental data on turbidity (Figure 4.10) demonstrated that the maximum turbidity removal efficiency was about 97%. Figure 4.11 illustrates that the reduction efficiency for DOC were observed at 52-58%, whereas the efficiencies of THMFP reduction as shown in Figure 4.12 was in the range of approximately 40-44%.

The optimal pH for the coagulation of high turbidity-high DOC water was observed to be at 5.5 for the raw water samples in August and September. Note that there was no significant improvement in the percentage of THMFP reduction by using the different coagulation pH from 5.5, 6.0, and 6.5. Thus, subsequent studies for low turbidity-low DOC water and low turbidity-high DOC water would not concentrate on the reduction of organic matter and THMFP reduction at coagulation pH 6.0 and 6.5. These experiments results was supported by the conclusion from others researchers (Amirtharajah and Mills, 1982, Duan and Gregory, 2003, and Kabsch-Korbutowicz, 2005b) that with an increase in coagulation pH, the residual DOC increased and this

would lead to a decrease THMFP reduction efficiency. pH level higher than 5.5 is normally not recommended as some alum would turn into an anionic complex not suitable for the removal of anionic compounds which was often the main character of the DOC contaminants.

Similar findings were obtained for other water samples, the results with low turbidity-low DOC water (October) on the removal of turbidity, DOC reduction together with percentage of THMFP reduction are shown in Figures 4.10 to 4.12. The turbidity removal efficiency at pH 5.5 was about 96% (see Figure 4.10). At the same time, residual DOC as shown in Figure 4.11 demonstrated that the percent DOC reduction obtained from the coagulation at pH 5.5 was approximately 55%, and Figure 4.12 shows that the reduction efficiency of THMFP was approximately 39%. For low turbidity-high DOC water (November), the efficiency in turbidity reduction was about 96% (Figure 4.10), the percent DOC reduction approximately 50% (Figure 4.11), and the THMFP reduction was approximately 40% (Figure 4.12).

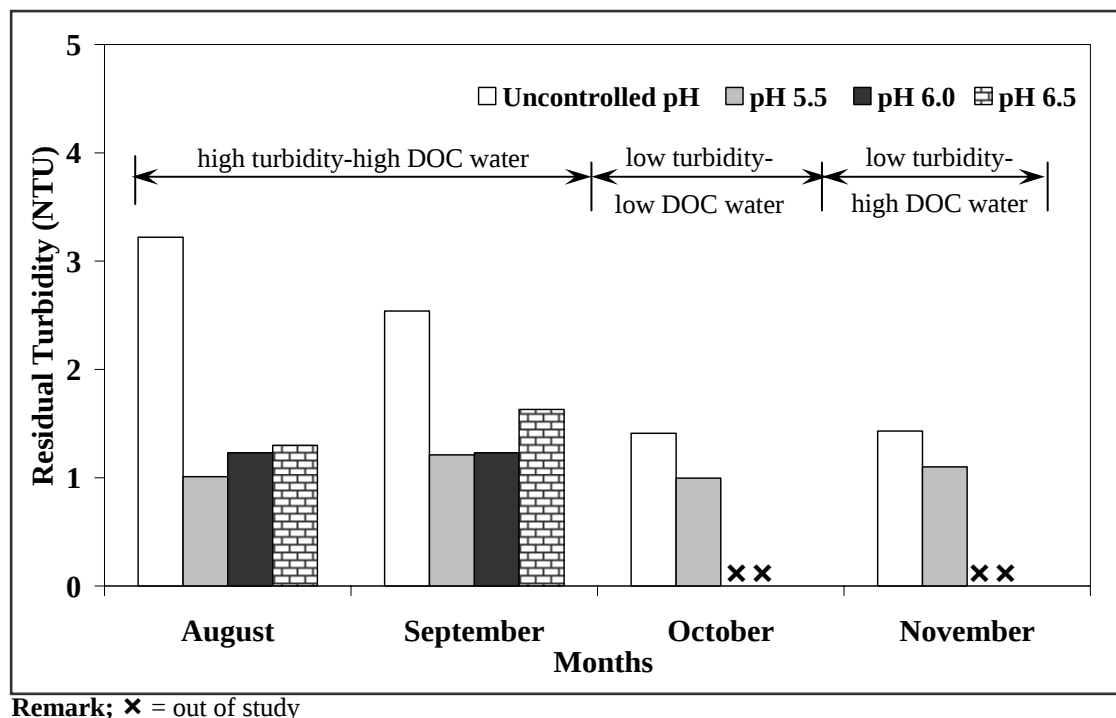
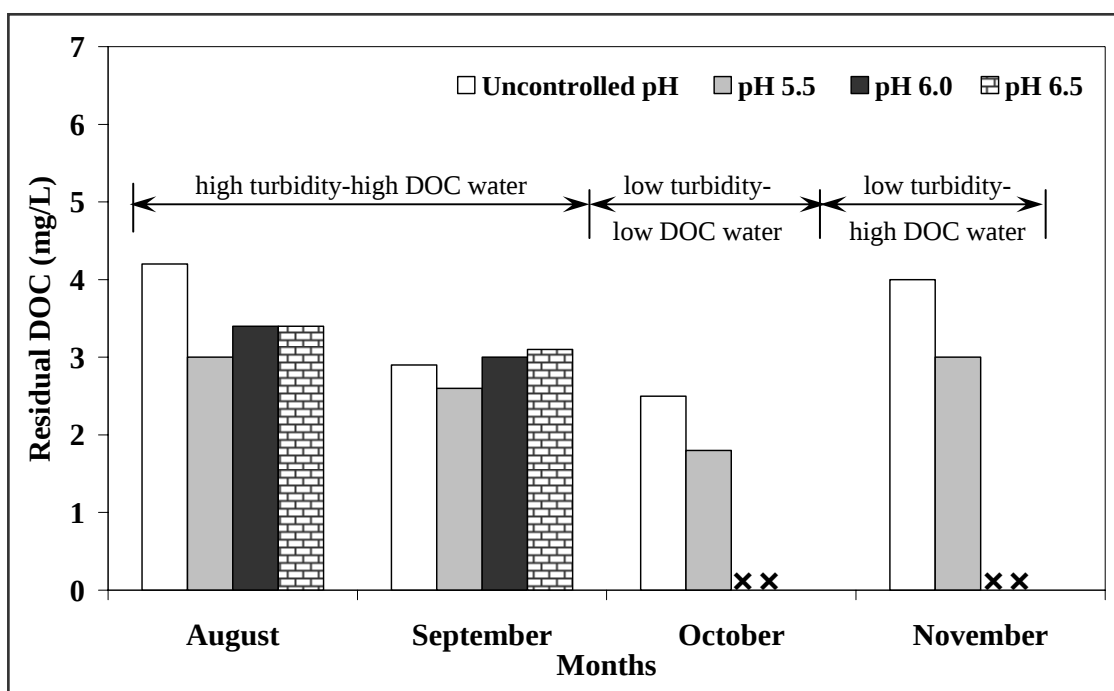


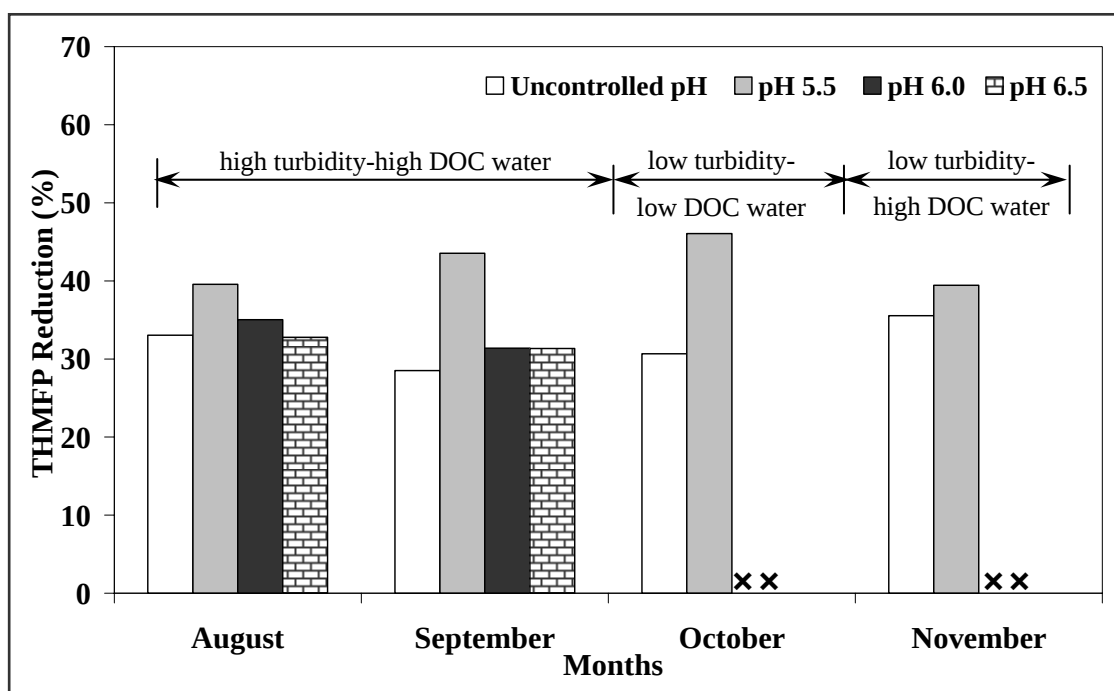
Figure 4.10 Residual turbidity at alum dosage 30 mg/L for high turbidity-high DOC water and 45 mg/L for low turbidity-low DOC water and low turbidity-high DOC water with 0.05 mg/L high molecular weight DADMAC



Remark; X = out of study

Figure 4.11 Residual DOC at alum dosage 30 mg/L for high turbidity-high DOC water and 45 mg/L for low turbidity-low DOC water and low turbidity-high DOC water with 0.05 mg/L high molecular weight DADMAC

These results were also consistent with the reports from previous studies of Hubel and Edzwald, 1987; Vrijenhoek et al., 1998; Panyapinyopol, 2004; Kabsch-Korbutowicz, 2005b; and Musikavong et al., 2005, who found that optimum THM precursors removal was obtained at pH 5.5. This was because at this pH the mechanism was the formation of insoluble aluminum-humates complexes and adsorption to aluminum hydroxide precipitates. At pH lower than 5.5, the hexa aqua cation, $\text{Al}(\text{H}_2\text{O})_6^{3+}$ or simply Al^{3+} is the dominant species (see Figure 2.2), and Al^{3+} was not effective coagulant for organic matters as it was not readily adsorbed on the surface of organic matters (Sanks, 1979).



Remark; x = out of study

Figure 4.12 THMFP reduction efficiency at alum dosage 30 mg/L for high turbidity-high DOC water and 45 mg/L for low turbidity-low DOC water and low turbidity-high DOC water with 0.05 mg/L high molecular weight DADMAC

4.5 Effect of Polymer Dosages on Coagulation

4.5.1 Statistical Analysis for Factors of Dosages, Types and Molecular Weight of Polymer Using With Alum on THMFP Reduction

The multiple analysis was performed to decide the alum dosages, pH values, polymer types, and dosages of polymer that effect to THMFP reduction efficiency by using ANOVA test (Univariate Analysis of Variance). Note that in this study have many data due to the interaction of many independent variables so the calculation of input factors could not be done. Thus, in this calculation can be done at 3 combinations (maximum loading of SPSS program).

The results of analysis for high turbidity-high DOC water (August) were shown in Table A-1 (tests of between-subjects effects) of Appendix A. From the first

analysis was a combination on alum dosages, pH values, and polymer types. The results showed that alum dosages, pH values, and types of polymer were the main effect to the reduction of THMFP ($p\text{-value} < 0.05$). Furthermore, the combinations between alum dosages-pH values, alum dosages-types of polymer, pH values-types of polymer, and alum dosages-pH values-polymer types found that all combinations were significantly in reduction of THMFP that meant 3 factors have interacted on THMFP reduction efficiency ($p\text{-value} < 0.05$, R^2 adjusted = 0.765, $N = 120$). Another analysis, the 3 combinations tested (alum dosages, pH values, and polymer dosage) found that the interaction of 3 factors have interacted ($p\text{-value} < 0.05$, R^2 adjusted = 0.869, $N = 120$).

Thus, each factor i.e. alum dosages, pH values, polymer types, and dosages of polymer were significantly effect to THMFP reduction. Whilst, the combination of these factors also significantly interaction to THMFP reduction.

The results of another case analysis for high turbidity-high DOC water (September) were shown in Table A-2 (tests of between-subjects effects) of Appendix A. From the first analysis was the combination of alum dosages, pH values, and polymer types. The results showed that these factors were the most important effect to reduce THMFP. Furthermore, the combinations between alum dosages-pH values, alum dosages-types of polymer, pH values-types of polymer, and alum dosages-pH values-polymer types found that the combinations were significantly effect to the reduction of THMFP ($p\text{-value} < 0.05$, R^2 adjusted = 0.850, $N = 108$) that meant these 3 factors have interaction to reduce THMFP. Finally, the 3 combinations analysis (alum dosages, pH values, and polymer types) found that the combination of alum dosage-pH value, alum dosage-polymer dosage, pH value-polymer dosage, and alum dosage-pH value-polymer dosage were significantly interaction, that meant the combination of independent variables have relations on THMFP reduction ($p\text{-value} < 0.05$, R^2 adjusted = 0.865, $N = 108$).

Therefore, the factors of alum dosages, pH values, types, and dosages of polymer were the main effect on reduced THMFP, whilst the combination of these

factors from statistical analysis indicated that they were significantly interaction to reduce THMFP.

The statistical analysis for low turbidity-low DOC water and low turbidity-high DOC water could not be calculated because pH values and type of polymer had not sufficient group of data which the constraint of the program.

4.5.2 Discussion

In this section, coagulation experiments were carried out with varying dosages of polymer (high molecular weight DADMAC) from 0.05 to 0.5 mg/L. Other conditions were remained at optimal, i.e. pH 5.5 and alum dosage of 30 mg/L for high turbidity-high DOC water, and 45 mg/L for low turbidity-low DOC water and low turbidity-high DOC water. The effects of coagulation at various dosages of polymer on turbidity, DOC, along with the THMFP reduction efficiency are shown in Figures 4.13 to 4.16.

In the event of high turbidity-high DOC raw water, the residual turbidity at optimal dosage of alum 30 mg/L and pH at 5.5 with high molecular weight DADMAC are illustrated in Figure 4.13, it was found that, in all of cases, the residual turbidity in the supernatant were lower than 5 NTU which corresponds to the maximum removal efficiencies of 99% where the optimal conditions were: alum dosage of 30 mg/L and polymer dosage of 0.1 mg/L. Figure 4.14 illustrates that the reduction efficiency for DOC were observed at 54-60% whereas the efficiencies of THMFP reduction as shown in Figure 4.15 was in the range of approximately 44-50%. This was obtained at the optimal conditions of alum dosage 30 mg/L and polymer dosage 0.1 mg/L. On the other hand, at a polymer dosage of 0.5 mg/L, the residual DOC increased as the floc formation was poor where the undesired pellets were observed. Figures 4.14 and 4.15 illustrate the relationship between DOC and THMFP reduction, where a decrease DOC (THM precursors) increased the removal efficiencies of THMFP. In this experiment, the samples were originally tested with the range of polymer dose from 0.05-0.5 mg/L, as apparent from the results in August. However, it was noticed that this range of dose was too wide and the high dose of 0.5 mg/L did not seem to have

benefits on the coagulation. Subsequent experiments were therefore carried out using a smaller range of polymer dose, i.e. from 0.05-0.2 mg/L.

Coagulation results of low turbidity-low DOC raw water sample showed that the maximum percentage of removal turbidity was approximately 99% as can be seen in Figure 4.13. In case of residual DOC, Figure 4.14 shows that the maximum reduction of DOC was approximately 64% whereas Figure 4.15 reveals that the maximum reduction efficiencies of THMFP of approximately 54% occurred at the polymer dosage of 0.15 mg/L at all parameters.

Experiment on coagulation of low turbidity-high DOC water sample (Figure 4.13) demonstrated that the maximum turbidity removal efficiency was about 94%. Coagulation results of raw water sample showed that the maximum reduction of DOC approximately 58% which occurred at polymer dosage 0.2 mg/L (Figure 4.14). Figure 4.15 shows that the maximum efficiencies of THMFP reductions approximately 45% at dosage of polymer 0.2 mg/L.

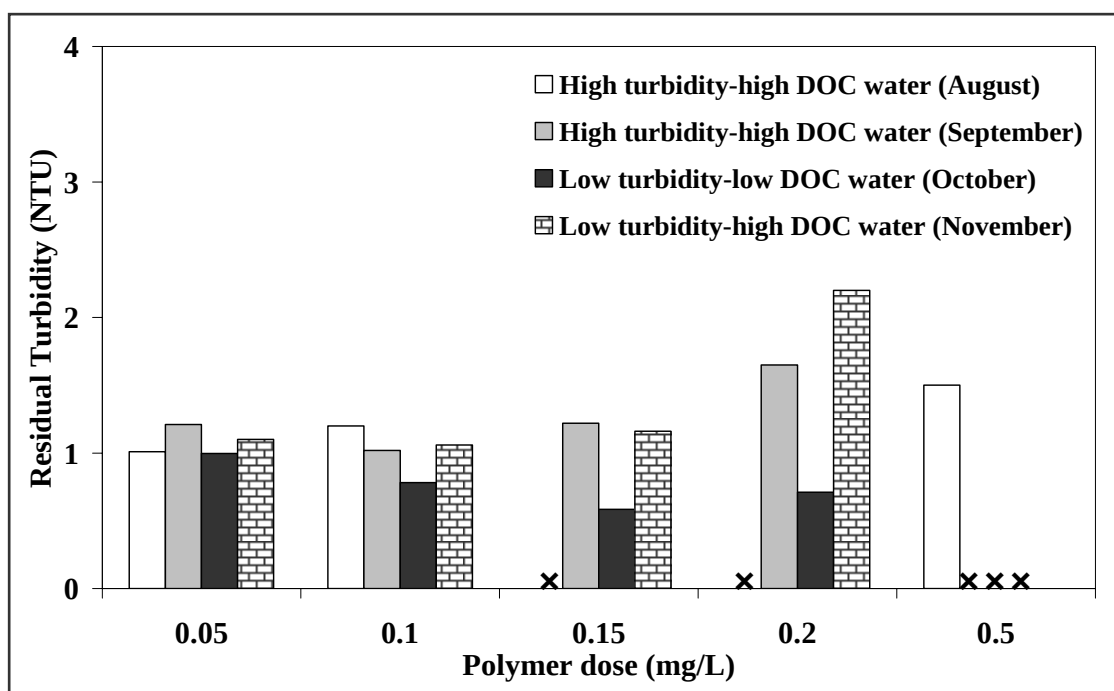


Figure 4.13 Residual turbidity at optimal alum dosage and high molecular weight DADMAC at pH 5.5

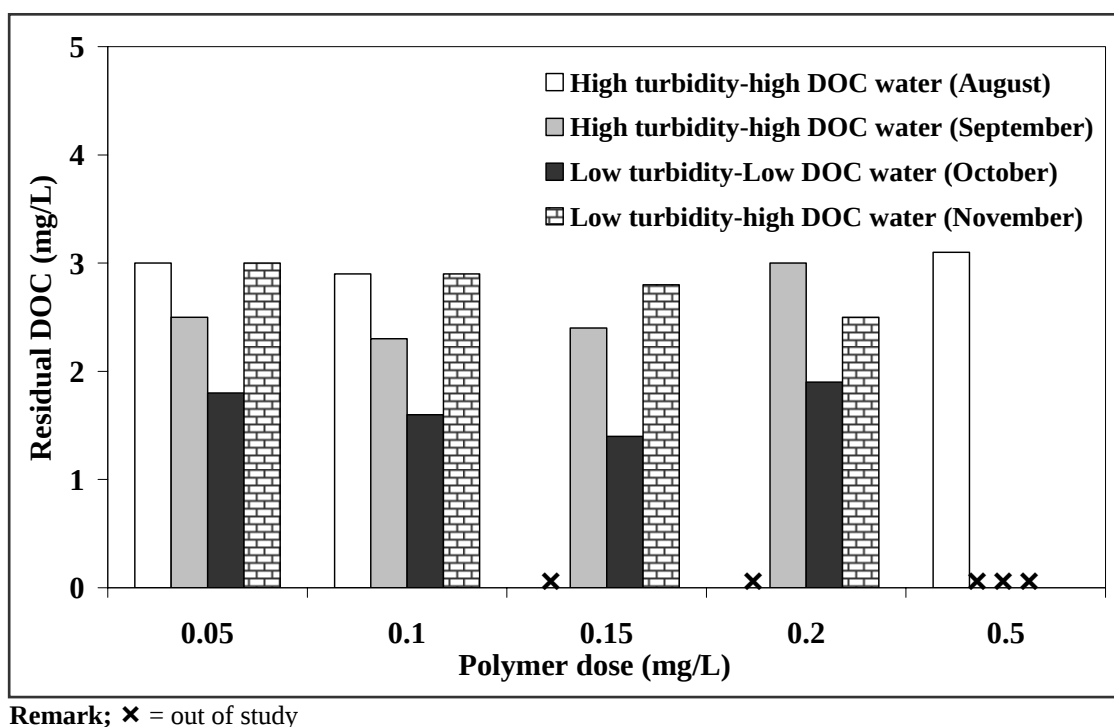


Figure 4.14 Residual DOC at optimal alum dosage and high molecular weight DADMAC at pH 5.5

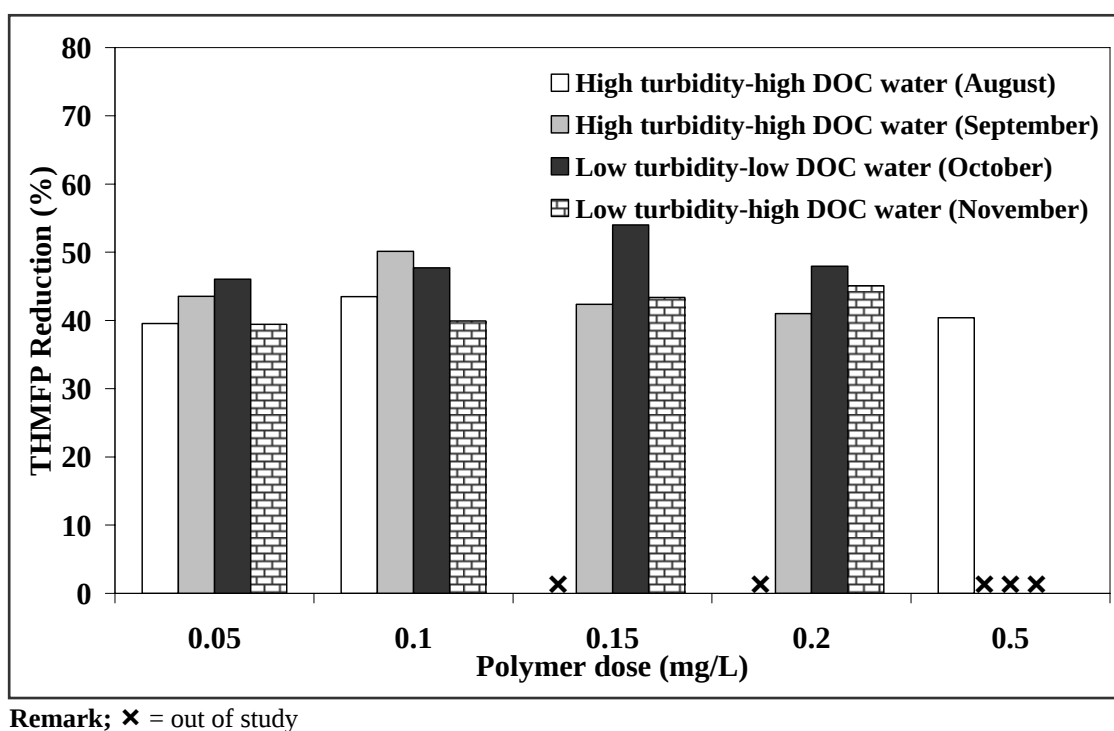


Figure 4.15 THMFP reduction efficiency at optimal alum dosage and high molecular weight DADMAC at pH 5.5

The combinations of alum and high molecular weight DADMAC (cationic polymer) could achieve a better THM precursors removal than alum alone. This also significantly reduced the requirement for alum dosages for THM precursors removal. From the results obtained in Section 4.2.2, if this study focused on the dosage of alum alone, the optimal alum dosages for high turbidity-high DOC water, low turbidity-low DOC water and low turbidity-high DOC water were 45, 45, 45, and 60 mg/L, respectively. However with the cationic polymer used as coagulant aids, the optimum alum dosage was reduced from 45 to 30 mg/L for high turbidity-high DOC water, and from 60 to 45 mg/L for low turbidity-low DOC water and low turbidity-high DOC water with higher efficiency in removal of turbidity, DOC and THMFP reduction than using alum alone. High molecular weight cationic polymer used as coagulant aids can improve turbidity removal by making denser floc and reduce sludge volume, and can be beneficial to THM precursors reductions.

4.6 Economical Evaluation

Chemicals cost was calculated based on the treatment of 1 million cubic meters tap water. Alum cost was calculated from the data obtained from Metropolitan Waterworks Authority, Thailand and polymer cost was from the data obtained from Polydyne, USA, as shown in Table 4.4.

Table 4.4 Economical data used in calculation of chemical costs

Items	Cost (Baht/Ton)
Alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$)	3,860
Poly-DADMAC	60,000
AnPAM	108,000
H_2SO_4	21,000

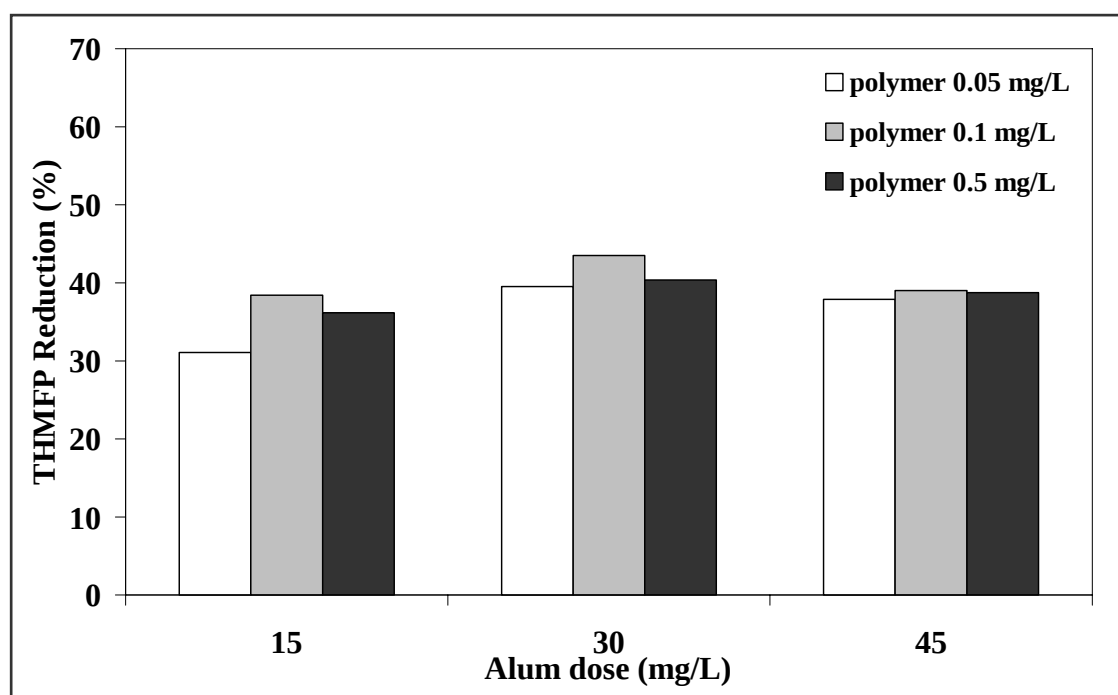
Chemical costs for the treatment at optimal THMFP reduction conditions (pH 5.5 and high molecular weight DADMAC polymer) were compared with those for

the uncontrolled pH conditions for the different raw water samples are shown in Figures 4.16 to 4.19.

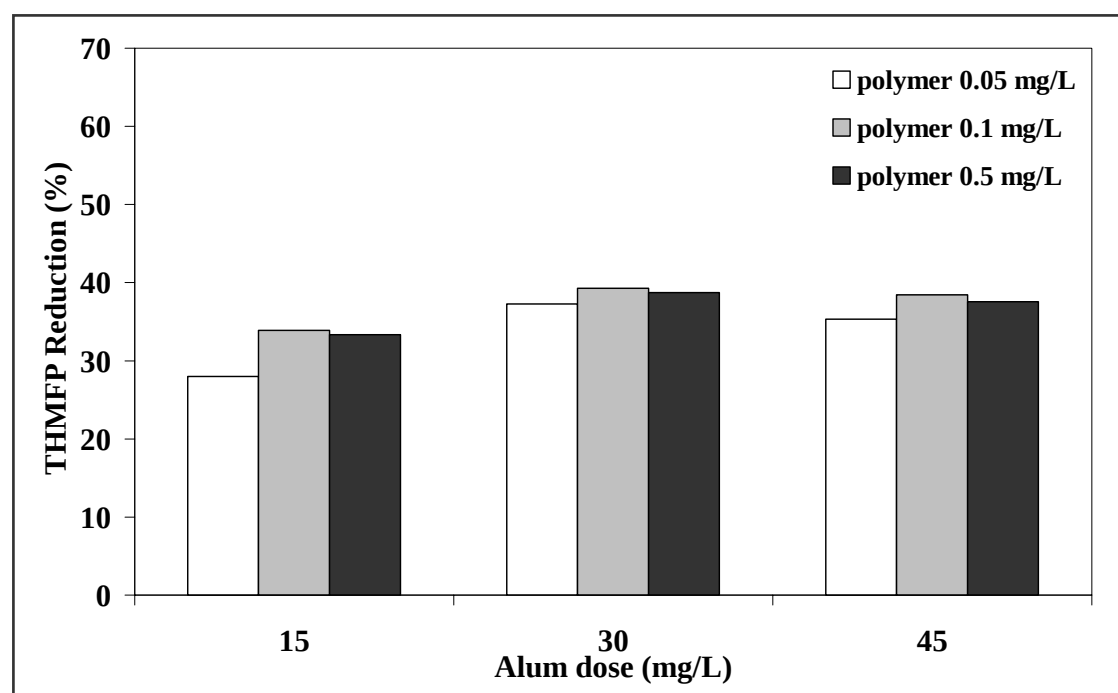
Figure 4.16 (a) shows the optimal conditions for the treatment of high turbidity-high DOC water. The percentage of THMFP reduction was the highest at alum dosage of 30 mg/L and polymer dosage of 0.1 mg/L at pH 5.5. To compare with the uncontrolled pH at the same condition (Figure 4.16 (b)) found that THMFP was not significant different. The chemical cost at pH 5.5 was approximately 142,800 baht per 1 million cubic meter tap water (pH adjustment in this experiment was done by using sulfuric acid) and was approximately 121,800 baht per 1 million cubic meter tap water for the case of uncontrolled pH.

Moreover, for the case of uncontrolled pH, Figure 4.16 (b) illustrates that the alum dosage of 30 mg/L and polymer 0.05 mg/L did not provide significantly different THMFP reduction efficiency when compared with that at optimal condition (pH 5.5, alum 30 mg/L, and polymer 0.1 mg/L). It should therefore be the best choice to select the lower dosage of coagulant aid and uncontrolled pH which yielded the chemical cost of about 118,800 baht per 1 million cubic meter tap water, which was 3,000 baht cheaper than optimum condition at pH 5.5.

Figure 4.17 (a) displays the optimal condition on THMFP reduction (about 50%) which took place at pH 5.5 with high molecular weight DADMAC. The chemical cost for the case of high turbidity-high DOC water at the optimal dosage of alum at 30 mg/L and polymer dosage of 0.1 mg/L was approximately 142,800 baht per 1 million cubic meter tap water. On the other hand, at the condition of no pH adjustment, alum dosage at 30 mg/L and polymer dosage of 0.05 mg/L as shown in Figure 4.17 (b), the chemical cost for the optimal percentage of THMFP reduction (only about 40%) was 118,800 baht per 1 million cubic meter tap water. In this uncontrolled pH case, Figure 4.17 (b) illustrates that, at alum dosage of 30 mg/L, the variation of polymer dosage between 0.05 to 0.2 mg/L did not yield different THMFP reduction efficiency, and therefore the condition at the polymer dose of 0.05 mg/L was selected.

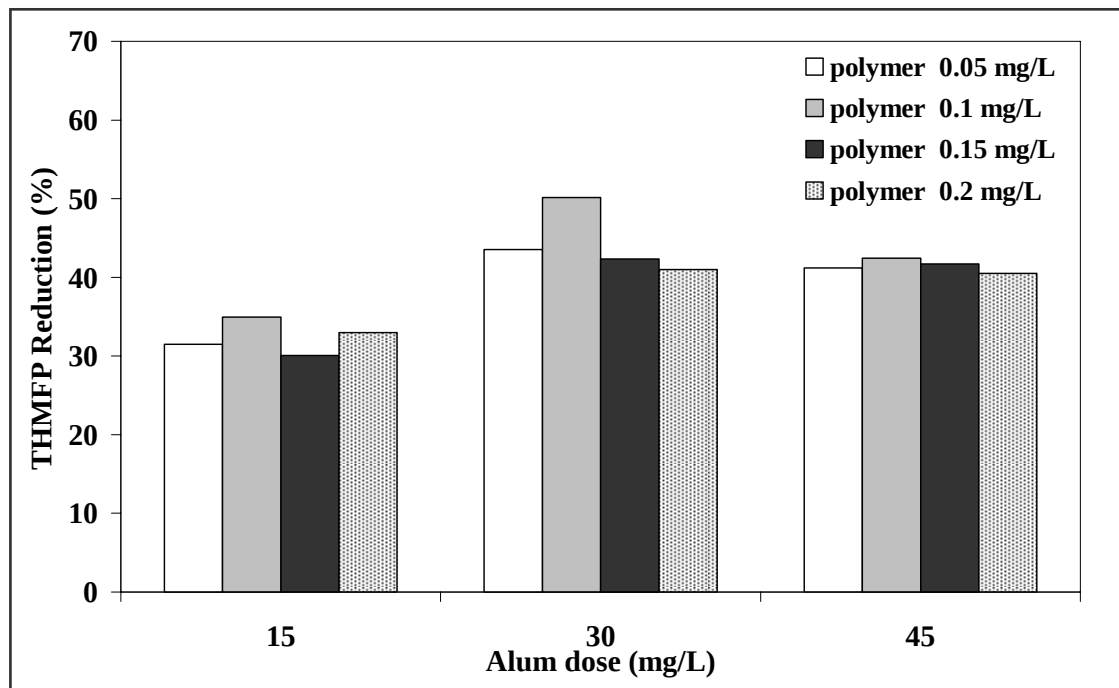


(a) pH 5.5

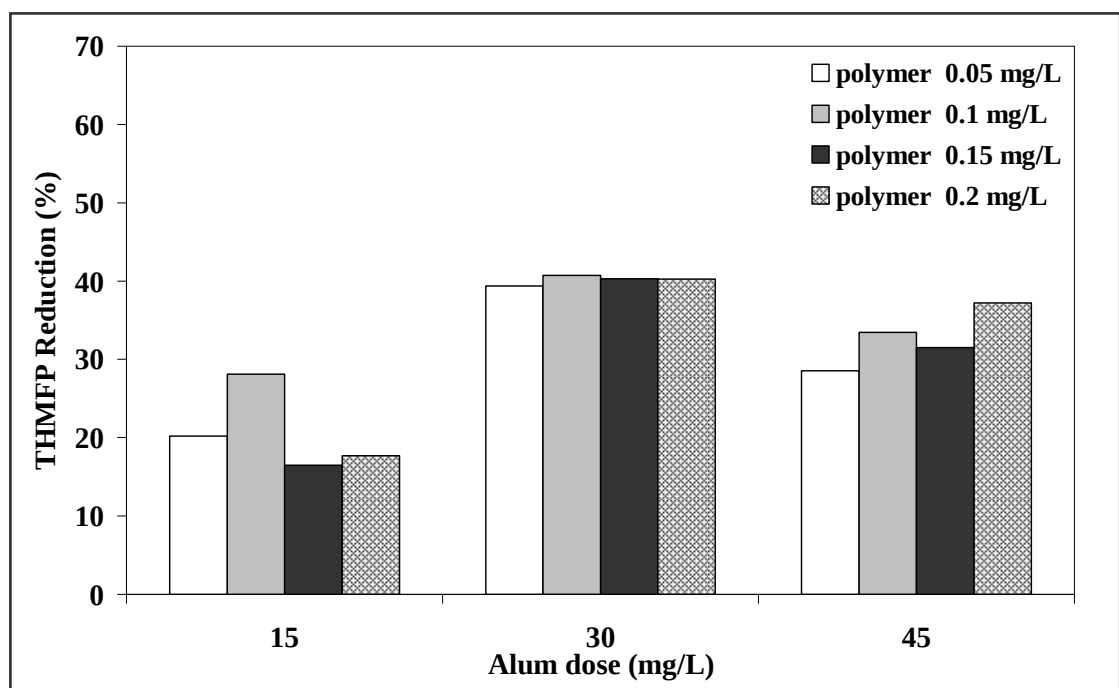


(b) Uncontrolled pH

Figure 4.16 Combination of alum and high molecular weight DADMAC on the percentage of THMFP reduction for high turbidity-high DOC water (August)



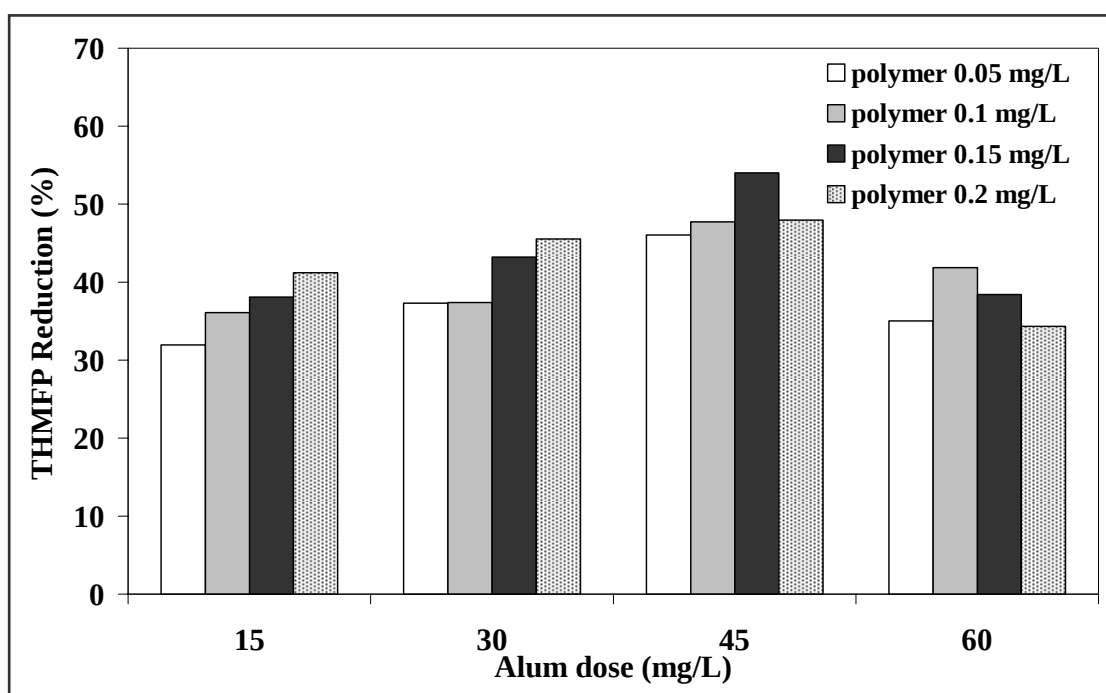
(a) pH 5.5



(b) Uncontrolled pH

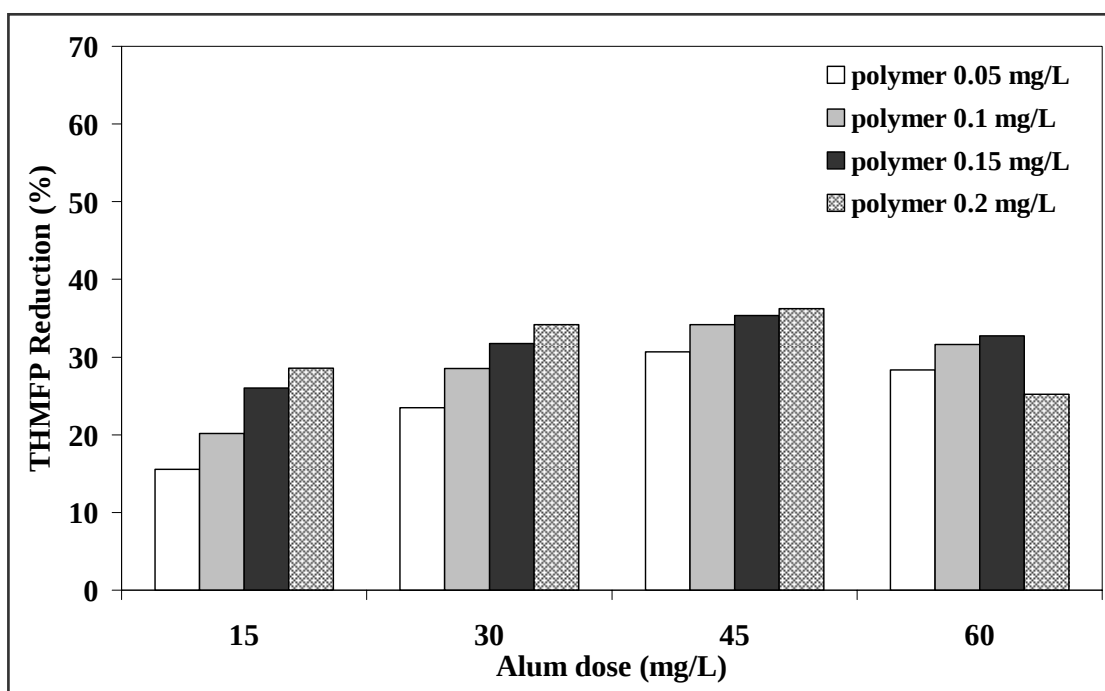
Figure 4.17 Effects of alum and high molecular weight DADMAC dosages on THMFP reduction for high turbidity-high DOC water (September)

For the low turbidity-low DOC water sample, Figure 4.18 (a) demonstrates that the optimal condition for THMFP reduction was clearly identified at alum dosage of 45 mg/L and polymer dosage of 0.15 mg/L at pH 5.5. At this condition, the chemical cost was about 203,700 baht per 1 million cubic meter tap water. On the other hand, the chemical cost of coagulation without pH adjustment was about 182,700 baht per 1 million cubic meter tap water at the same alum and polymer dosages. It was interesting to note that the efficiency of THMFP reduction at the optimum alum dosage of 45 mg/L, and different polymer dosages were not much different as shown in Figure 4.18 (b). For more option in the selection of optimum condition for uncontrolled pH (see Figure 4.18 (b)), at alum dosage of 30 mg/L, polymer dosage 0.2 mg/L and 45 mg/L of alum dosage and 0.1 mg/L polymer dosage, it appeared that the chemical cost was evaluated at approximately 127,800 and 179,700 baht (54,900 baht cheaper) per 1 million cubic meter tap water, respectively, with the same level of THMFP reduction.



(a) pH 5.5

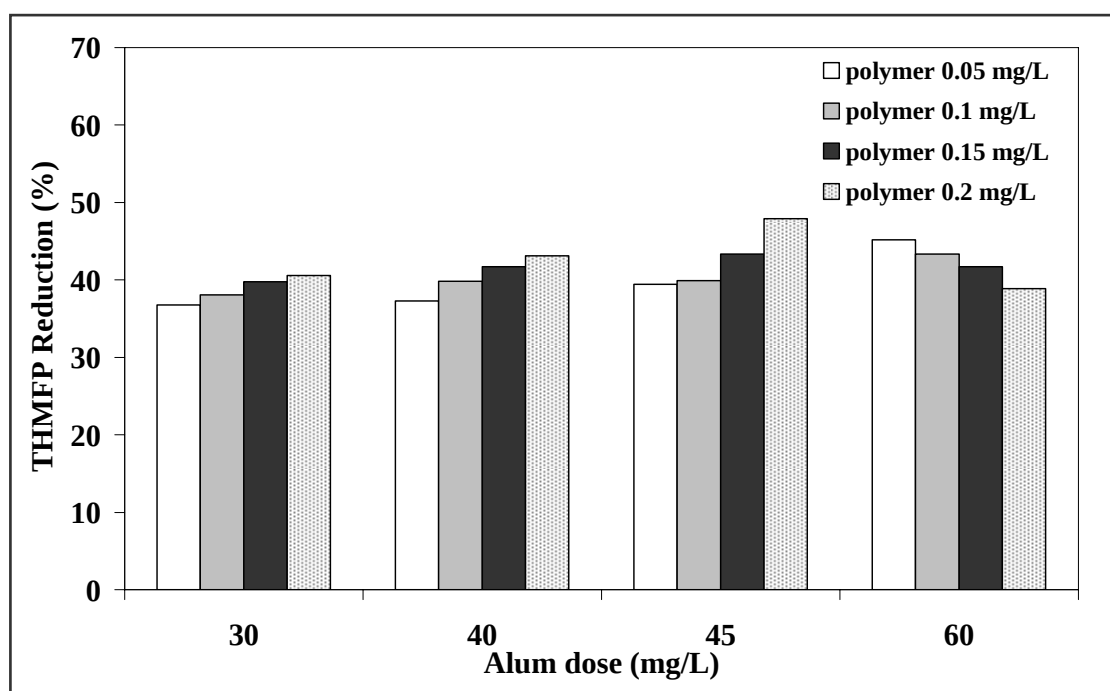
Figure 4.18 Effects of alum and high molecular weight DADMAC dosages on THMFP reduction for low turbidity-low DOC water (October)



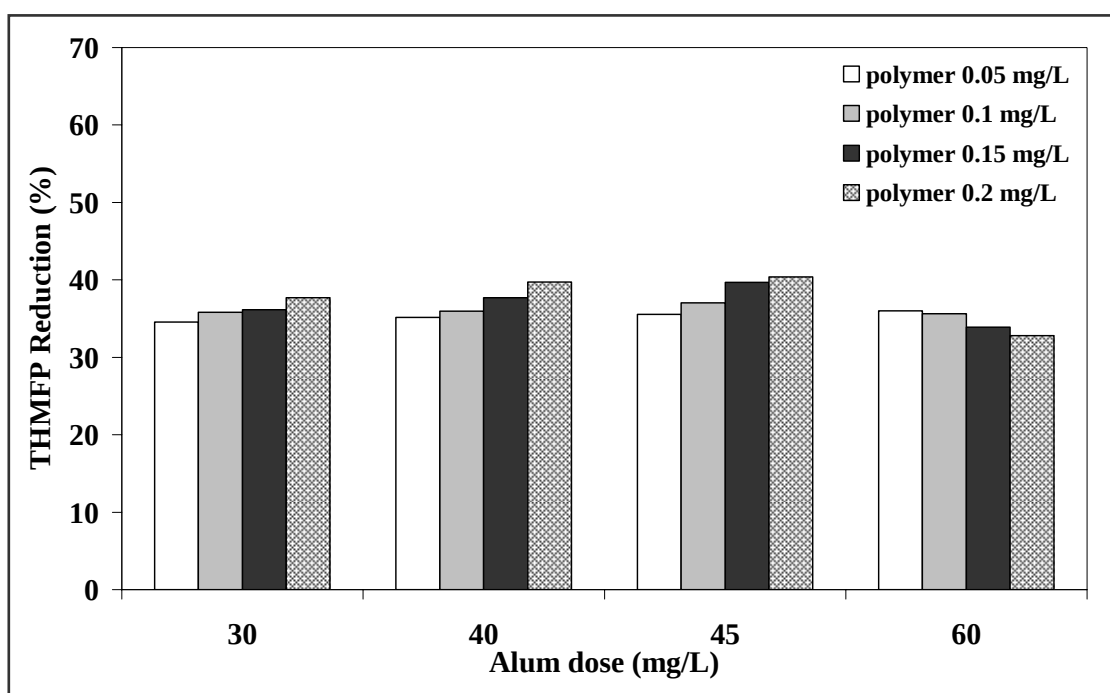
(b) Uncontrolled pH

Figure 4.18 Effects of alum and high molecular weight DADMAC dosages on THMFP reduction for low turbidity-low DOC water (October) (continued)

The chemical cost for low turbidity-high DOC water was evaluated at approximately 206,700 baht per 1 million cubic meter tap water at the optimal condition for THMFP reduction (about 50%), which occurred at 45 mg/L of alum and polymer dosage of 0.2 mg/L. In contrast, Figure 4.19 (b) shows the efficiency of THMFP reduction without controlling of pH that the efficiency was much lower than that at pH 5.5, with only just 40 % reduction. The cost of uncontrolled pH coagulation for the optimal THMFP reduction at alum and polymer dosages of 30 and 0.2 mg/L was about 185,700 baht per 1 million cubic meter tap water.



(a) pH 5.5



(b) Uncontrolled pH

Figure 4.19 Effects of alum and high molecular weight DADMAC dosages on THMFP reduction for low turbidity-high DOC water (November) (continued)

From the results of overall of raw water cases at the optimal condition can be summery about cost analysis in order to compare the overall cost of chemicals (calculated based on 1 million cubic meter tap water). The relationships between the optimal conditions (pH 5.5) on THMFP reduction and without controlled pH among raw water quality were performed also depicted in Table 4.5.

Table 4.5 The conclusion and comparison about cost analysis between uncontrolled pH and pH 5.5 at optimal dosages of alum and polymer on THMFP reduction

Types	Optimal Condition	Cost*	
		pH 5.5	Uncontrolled pH
High turbidity-high DOC water	Alum dosage 30 mg/L and polymer dosage 0.1 mg/L	142,800	121,800
Low turbidity-low DOC water	Alum dosage 45 mg/L and polymer dosage 0.15 mg/L	203,000	182,700
Low turbidity-high DOC water	Alum dosage 45 mg/L and polymer dosage 0.2 mg/L	206,700	185,700

*Unit cost: baht per 1 million cubic meter tap water

Moreover, from the experimental study about coagulation results and economical analysis can be summarized in Table 4.6. It was noted that the chemical cost in Table 4.6 calculated base on the maximum operation in the Bangkhen Water Treatment Plant (Bangkok, Thailand), this plant is the largest water supply facility in Bangkok, and produces tap water at the rate of approximately 3 million cubic meters per day.

Table 4.6 The summary of the results on the reduction efficiency and cost analysis at optimal condition on THMFP reduction

Types	Alum dose (mg/L)	Polymer dose (mg/L)	THMFP Reduction	DOC Reduction	Cost*
High turbidity-high DOC water	30	0.1	44-50%	54-61%	428,400
Low turbidity-low DOC water	45	0.15	54%	64%	609,000
Low turbidity-high DOC water	45	0.20	45%	58%	620,100

*Unit cost: baht per 3 million cubic meter tap water

In all cases, the cost of coagulation with pH adjustment was higher than the cost of coagulation without pH adjustment. Implementation of enhanced coagulation in conventional water treatment plant (optimized for turbidity removal), hence, resulted in an increase in the overall cost of chemicals. This comes to a conclusion that, in normal situation for low DOC raw water, the water treatment facility can be operated at uncontrolled pH but in the case of high DOC level raw water operator should adjust coagulation pH to the level of 5.5 for higher efficiency in organic matters removal.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The aim of this study was to investigate the optimum operating condition of the coagulation process with alum and a combination of alum and polymer in reduction of trihalomethane formation potential (THMFP) in raw water from Bangkhen Water Treatment Plant, Bangkok, Thailand. On the basis of the experimental obtained, the following conclusions;

1. The optimal condition on coagulation pH for DOC and THMFP reduction was observed at a pH 5.5.
2. Coagulation by alum alone can reduce THMFP but not as effectively as the combination of alum and polymer.
3. The highest efficiency in reduction of DOC and THMFP from the coagulation with the combination of alum and polymer could be ordered from high to low as: high molecular weight cationic polydiallyl dimethyl ammonium chloride (DADMAC), low molecular weight DADMAC and anionic polyacrylamide (AnPAM), respectively.
4. The optimal dosage on combination of alum and high molecular weight DADMAC polymer with different raw water characteristics are as follow;
 - High turbidity-high DOC water (August and September), alum dosage of 30 mg/L and polymer dosage of 0.1 mg/L.
 - Low turbidity-low DOC water (October), alum dosage of 45 mg/L and polymer dosage of 0.15 mg/L.
 - Low turbidity-high DOC water (November), alum dosage of 45 mg/L and polymer dosage of 0.2 mg/L.

5. The THMFP reduction efficiencies at optimal coagulation condition for high turbidity-high DOC water, low turbidity-low DOC water, and low turbidity-high DOC water were occurred at 44-50%, 54%, and 45%, respectively. Accordingly, the efficiencies of DOC reduction at optimal condition for these raw water were occurred at 54-61%, 64%, and 58%, respectively.

6. Turbidity could be effectively removed to the level of lower than 5 NTU by coagulation by alum and the combination of alum and polymer.

5.2 Recommendations

Based on the results of this study, some recommendations for further studies can be proposed.

1. Comparison between other coagulants, such as PACl and ferric chloride with high molecular weight DADMAC should be developed to compare the efficiency and cost.

2. Kinetics of THMs formation along the river basin should be studied for longer period (in a year or preferably more than one year) in order to better understand the seasonal changes and its effects on THMs formation kinetics.

3. Experiments should be conducted with different bromide contents to determine the effect of bromide ion concentration on the formation of each THMs species.

4. Due to the high level of THMFP were observed in raw water, this indicated that other chlorinated disinfection by-products (DBPs) in term of haloacetic acids (HAAs), haloacetonitriles (HANs) and cyanogen halides might be formed, thus, others chlorinated by-products should be studied.

5. Residual aluminium concentration in finished water is one of parameters for drinking water standard so, in the next study should include this parameter into the experiment.

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APPENDIX

APPENDIX A

STATISTICAL ANALYSIS

Table A-1 The statistical analysis of THMFP reduction efficiencies at alum dosages of 15, 30 and 45 mg/L (high turbidity-high DOC water-August)

▪ Tests of Normality

	alum	Shapiro-Wilk		
		Statistic	df	Sig.
THMFPeffi	15	0.974	40	0.479
	30	0.960	40	0.165
	45	0.956	40	0.125

▪ Test of Homogeneity of Variance

		Levene			
		Statistic	df1	df2	Sig.
THMFPeffi	Based on Mean	0.117	2	117	0.889
	Based on Median	0.115	2	117	0.892
	Based on Median and with adjusted df	0.115	2	113.387	0.892
	Based on trimmed mean	0.115	2	117	0.891

▪ ANOVA Test

THMFPeffi

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	233.138	2	116.569	3.979	0.021
Within Groups	3428.042	117	29.300		
Total	3661.180	119			

▪ Post Hoc Test (Multiple Comparisons)

Dependent Variable: THMFPeffi

LSD

(I) alum	(J) alum	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Upper Bound	Lower Bound
15	30	-4.025(*)	0.803	0.000	-5.625	-2.425
	45	-2.248(*)	0.803	0.007	-3.849	-0.648
30	15	4.025(*)	0.803	0.000	2.425	5.625
	45	1.777(*)	0.803	0.030	0.177	3.377
45	15	2.248(*)	0.803	0.007	0.648	3.849
	30	-1.777(*)	0.803	0.030	-3.377	-0.177

Based on estimated marginal means

* The mean difference is significant at the 0.05 level.

▪ Tests of Between-Subjects Effects

Dependent Variable: THMFPeffi

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	2918.879 ^(a)	47	62.104	6.024	0.000
Intercept	86252.063	1	86252.063	8366.077	0.000
alum	260.422	2	130.211	12.630	0.000
pH	466.500	3	155.500	15.083	0.000
type	1512.201	3	504.067	48.892	0.000
alum * pH	65.248	6	10.875	1.055	0.004
alum * type	124.057	6	20.676	2.005	0.008
pH * type	200.677	9	22.297	2.163	0.035
alum * pH * type	146.289	18	8.127	0.788	0.007
Error	742.301	72	10.310		
Total	115954.623	120			
Corrected Total	3661.180	119			

^a R Squared = 0.897 (Adjusted R Squared = 0.765)

▪ **Tests of Between-Subjects Effects**

Dependent Variable: THMFPeffi

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	1819.707 ^(a)	47	38.717	1.514	0.056
Intercept	86252.063	1	86252.063	3372.381	0.000
alum	260.422	2	130.211	5.091	0.009
pH	466.500	3	155.500	6.080	0.001
polymer	263.960	3	87.987	3.440	0.021
alum * pH	65.248	6	10.875	0.425	0.009
alum * polymer	332.931	6	55.489	2.170	0.006
pH * polymer	147.133	9	16.348	0.639	0.008
alum * pH * polymer	140.027	18	7.779	0.304	0.010
Error	1841.473	72	25.576		
Total	115954.623	120			
Corrected Total	3661.180	119			

^a R Squared = 0.974 (Adjusted R Squared = 0.869)

Table A-2 The statistical analysis of THMFP reduction efficiencies at alum dosages of 15, 30 and 45 mg/L (high turbidity-high DOC water-September)

▪ **Tests of Normality**

	alum	Shapiro-Wilk		
		Statistic	df	Sig.
THMFPeffi	15	0.946	36	0.079
	30	0.966	36	0.331
	45	0.936	36	0.093

▪ **Test of Homogeneity of Variance**

		Levene			
		Statistic	df1	df2	Sig.
THMFPeffi	Based on Mean	2.675	2	105	0.074
	Based on Median	2.565	2	105	0.082
	Based on Median and with adjusted df	2.565	2	92.564	0.082
	Based on trimmed mean	2.662	2	105	0.075

▪ **ANOVA Test**

THMFPeffi

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	777.188	2	388.594	9.316	0.000
Within Groups	4379.710	105	41.712		
Total	5156.898	107			

▪ Post Hoc Tests (Multiple Comparisons)

Dependent Variable: THMFPeffi

LSD

(I) alum	(J) alum	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Upper Bound	Lower Bound
15	30	-6.01250(*)	1.52227	0.000	-9.0309	-2.9941
	45	-5.30194(*)	1.52227	0.001	-8.3203	-2.2836
30	15	6.01250(*)	1.52227	0.000	2.9941	9.0309
	45	0.71056(*)	1.52227	0.042	-2.3078	3.7289
45	15	5.30194(*)	1.52227	0.001	2.2836	8.3203
	30	-0.71056(*)	1.52227	0.042	-3.7289	2.3078

Based on estimated marginal means

* The mean difference is significant at the 0.05 level.

▪ Tests of Between-Subjects Effects

Dependent Variable: THMeffi

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	3596.130(a)	35	102.747	4.740	.000
Intercept	71791.446	1	71791.446	3311.822	.000
alum	688.384	2	344.192	15.878	.000
pH	777.699	3	259.233	11.959	.000
type	906.015	2	453.007	20.898	.000
alum * pH	218.289	6	36.382	1.678	.001
alum * type	48.608	4	12.152	.561	.007
pH * type	51.360	6	8.560	.395	.009
alum * pH * type	132.718	12	11.060	.510	.009
Error	1560.767	72	21.677		
Total	127262.723	108			
Corrected Total	5156.898	107			

^a R Squared = 0.897 (Adjusted R Squared = 0.850)

■ Tests of Between-Subjects Effects

Dependent Variable: THMFPeffi

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	4419.482 ^(a)	59	74.906	4.876	0.000
Intercept	107620.083	1	107620.083	7005.223	0.000
polymer	1493.923	4	373.481	24.311	0.000
alum	810.166	2	405.083	26.368	0.000
pH	1132.710	3	377.570	24.577	0.000
polymer * alum	103.575	8	12.947	0.843	0.006
polymer * pH	196.463	12	16.372	1.066	0.009
alum * pH	348.599	6	58.100	3.782	0.004
polymer * alum * pH	168.091	24	7.004	0.456	0.010
Error	737.416	48	15.363		
Total	127262.723	108			
Corrected Total	5156.898	107			

^a R Squared = 0.897 (Adjusted R Squared = 0.865)

Table A-3 The statistical analysis of THMFP reduction efficiencies at alum dosages of 15, 30, 45 and 60 mg/L (low turbidity-low DOC water-October)

▪ **Tests of Normality**

	alum	Shapiro-Wilk		
		Statistic	df	Sig.
THMFPeffi	15	0.956	10	0.742
	30	0.967	10	0.864
	45	0.916	10	0.325
	60	0.968	10	0.868

▪ **Test of Homogeneity of Variance**

		Levene			
		Statistic	df1	df2	Sig.
THMFPeffi	Based on Mean	1.172	3	36	0.334
	Based on Median	0.755	3	36	0.527
	Based on Median and with adjusted df	0.755	3	32.122	0.528
	Based on trimmed mean	1.138	3	36	0.347

▪ **ANOVA Test**

THMFPeffi

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	625.517	3	208.506	3.551	0.024
Within Groups	2114.031	36	58.723		
Total	2739.548	39			

▪ **Post Hoc Tests (Multiple Comparisons)**

Dependent Variable: THMFPeffi

LSD

(I) alum	(J) alum	Mean	Std. Error	Sig.	95% Confidence Interval	
		Difference (I-J)			Upper Bound	Lower Bound
15	30	-4.59200	3.42704	0.189	-11.5424	2.3584
	45	-10.8420(*)	3.42704	0.003	-17.7924	-3.8916
	60	-3.04100	3.42704	0.381	-9.9914	3.9094
30	15	4.59200	3.42704	0.189	-2.3584	11.5424
	45	-6.25000	3.42704	0.007	-13.2004	0.7004
	60	1.55100	3.42704	0.654	-5.3994	8.5014
45	15	10.8420(*)	3.42704	0.003	3.8916	17.7924
	30	6.25000(*)	3.42704	0.007	-0.7004	13.2004
	60	7.80100(*)	3.42704	0.029	0.8506	14.7514
60	15	3.04100	3.42704	0.381	-3.9094	9.9914
	30	-1.55100	3.42704	0.654	-8.5014	5.3994
	45	-7.80100(*)	3.42704	0.029	-14.7514	-0.8506

Based on estimated marginal means

* The mean difference is significant at the 0.05 level.

Table A-4 The statistical analysis of THMFP reduction efficiencies at alum dosages of 30, 40, 45 and 60 mg/L (low turbidity-high DOC water-November)

▪ **Tests of Normality**

	alum	Shapiro-Wilk		
		Statistic	df	Sig.
THMFPeffi	30	0.813	10	0.121
	40	0.867	10	0.093
	45	0.922	10	0.375
	60	0.929	10	0.435

▪ **Test of Homogeneity of Variance**

		Levene			
		Statistic	df1	df2	Sig.
THMFPeffi	Based on Mean	0.089	3	36	0.965
	Based on Median	0.064	3	36	0.979
	Based on Median and with adjusted df	0.064	3	30.000	0.979
	Based on trimmed mean	0.096	3	36	0.961

▪ **ANOVA Test**

THMFPeffi

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2062.684	3	687.561	7.964	0.000
Within Groups	3108.136	36	86.337		
Total	5170.819	39			

▪ Post Hoc Tests (Multiple Comparisons)

Dependent Variable: THMFPeffi

LSD

(I) alum	(J) alum	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Upper Bound	Lower Bound
30	40	-15.4950(*)	4.15541	0.001	-23.9226	-7.0674
	45	-17.0460(*)	4.15541	0.000	-25.4736	-8.6184
	60	-17.0200(*)	4.15541	0.000	-25.4476	-8.5924
40	30	15.4950(*)	4.15541	0.001	7.0674	23.9226
	45	-1.55100	4.15541	0.711	-9.9786	6.8766
	60	-1.52500	4.15541	0.716	-9.9526	6.9026
45	30	17.0460(*)	4.15541	0.000	8.6184	25.4736
	40	1.55100	4.15541	0.711	-6.8766	9.9786
	60	0.02600	4.15541	0.995	-8.4016	8.4536
60	30	17.0200(*)	4.15541	0.000	8.5924	25.4476
	40	1.52500	4.15541	0.716	-6.9026	9.9526
	45	-0.02600	4.15541	0.995	-8.4536	8.4016

Based on estimated marginal means

* The mean difference is significant at the 0.05 level.

Table A-5 The statistical analysis of THMFPeffi reduction efficiencies at pH values of uncontrolled pH, pH 5.5, 6.0 and 6.5 (high turbidity-high DOC water-August)

▪ **Tests of Normality**

	pH	Shapiro-Wilk		
		Statistic	df	Sig.
THMFPeffi	uncontrolled	0.952	30	0.197
	5.5	0.947	30	0.141
	6.0	0.960	30	0.301
	6.5	0.936	30	0.071

▪ **Test of Homogeneity of Variance**

		Levene			
		Statistic	df1	df2	Sig.
THMFPeffi	Based on Mean	4.168	3	116	0.008
	Based on Median	3.400	3	116	0.020
	Based on Median and with adjusted df	3.400	3	95.946	0.021
	Based on trimmed mean	3.948	3	116	0.010

▪ **ANOVA Test**

THMFPeffi

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	659.303	3	219.768	8.492	0.000
Within Groups	3001.877	116	25.878		
Total	3661.180	119			

▪ **Post Hoc Tests (Multiple Comparisons)**

Dependent Variable: THMFPeffi

LSD

(I) pH	(J) pH	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Upper Bound	Lower Bound
uncontrolled	5.5	-4.03467(*)	1.31348	0.003	-6.6362	-1.4332
	6.0	-0.06433	1.31348	0.961	-2.6658	2.5372
	6.5	2.51433	1.31348	0.058	-0.0872	5.1158
5.5	uncontrolled	4.03467(*)	1.31348	0.003	1.4332	6.6362
	6.0	3.97033(*)	1.31348	0.003	1.3688	6.5718
	6.5	6.54900(*)	1.31348	0.000	3.9475	9.1505
6.0	uncontrolled	0.06433	1.31348	0.961	-2.5372	2.6658
	5.5	-3.97033(*)	1.31348	0.003	-6.5718	-1.3688
	6.5	2.57867	1.31348	0.052	-0.0228	5.1802
6.5	uncontrolled	-2.51433	1.31348	0.058	-5.1158	0.0872
	5.5	-6.54900(*)	1.31348	0.000	-9.1505	-3.9475
	6.0	-2.57867	1.31348	0.052	-5.1802	0.0228

Based on estimated marginal means

* The mean difference is significant at the 0.05 level.

Table A-6 The statistical analysis of THMFP reduction efficiencies at pH values of uncontrolled pH, pH 5.5, 6.0 and 6.5 (high turbidity-high DOC-September)

▪ **Tests of Normality**

	pH	Shapiro-Wilk		
		Statistic	df	Sig.
THMFPeffi	uncontrolled	0.954	27	0.264
	5.5	0.899	27	0.151
	6.0	0.939	27	0.118
	6.5	0.957	27	0.321

▪ **Test of Homogeneity of Variance**

		Levene			
		Statistic	df1	df2	Sig.
THMFPeffi	Based on Mean	2.270	3	104	0.085
	Based on Median	1.862	3	104	0.141
	Based on Median and with adjusted df	1.862	3	88.941	0.142
	Based on trimmed mean	2.231	3	104	0.089

▪ **ANOVA Test**

THMFPeffi

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1264.235	3	421.412	11.259	0.000
Within Groups	3892.663	104	37.429		
Total	5156.898	107			

▪ **Post Hoc Tests (Multiple Comparisons)**

Dependent Variable: THMFPeffi

LSD

(I) pH	(J) pH	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Upper Bound	Lower Bound
uncontrolled	5.5	-9.286(*)	1.109	0.000	-11.515	-7.057
	6.0	-6.458(*)	1.109	0.000	-8.687	-4.229
	6.5	-5.257(*)	1.109	0.000	-7.486	-3.028
5.5	uncontrolled	9.286(*)	1.109	0.000	7.057	11.515
	6.0	2.828(*)	1.109	0.014	0.599	5.057
	6.5	4.029(*)	1.109	0.001	1.800	6.258
6.0	uncontrolled	6.458(*)	1.109	0.000	4.229	8.687
	5.5	-2.828(*)	1.109	0.014	-5.057	-0.599
	6.5	1.201	1.109	0.284	-1.028	3.430
6.5	uncontrolled	5.257(*)	1.109	0.000	3.028	7.486
	5.5	-4.029(*)	1.109	0.001	-6.258	-1.800
	6.0	-1.201	1.109	0.284	-3.430	1.028

Based on estimated marginal means

* The mean difference is significant at the 0.05 level.

Table A-7 The statistical analysis of THMFP reduction efficiencies under different of types and dose of polymer (high turbidity-high DOC water-August)

Polymer Type

▪ **Tests of Normality**

		Shapiro-Wilk		
	Type	Statistic	df	Sig.
THMFPeffi	alone	0.867	12	0.059
	HDADMAC	0.979	36	0.713
	LADMAC	0.941	36	0.053
	AnPAM	0.973	36	0.523

▪ **Test of Homogeneity of Variance**

		Levene			
		Statistic	df1	df2	Sig.
THMFPeffi	Based on Mean	0.834	3	116	0.478
	Based on Median	0.686	3	116	0.562
	Based on Median and with adjusted df	0.686	3	106.997	0.562
	Based on trimmed mean	0.794	3	116	0.500

▪ **ANOVA Test**

THMFPeffi

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1512.201	3	504.067	27.209	0.000
Within Groups	2148.978	116	18.526		
Total	3661.180	119			

▪ Post Hoc Tests (Multiple Comparisons)

Dependent Variable: THMFPeffi

LSD

(I) type	(J) type	Mean		Sig.	95% Confidence Interval	
		Difference (I-J)	Std. Error		Upper Bound	Lower Bound
HDADMAC	LDADMAC	1.0592(*)	0.75681	0.001	-0.4495	2.5678
	AnPAM	7.9169(*)	0.75681	0.000	6.4083	9.4256
	alone	7.1000(*)	1.07029	0.000	4.9664	9.2336
LDADMAC	HDADMAC	-1.0592(*)	0.75681	0.001	-2.5678	0.4495
	AnPAM	6.8578(*)	0.75681	0.000	5.3491	8.3665
	alone	6.0408(*)	1.07029	0.000	3.9072	8.1744
AnPAM	HDADMAC	-7.9169(*)	0.75681	0.000	-9.4256	-6.4083
	LDADMAC	-6.8578(*)	0.75681	0.000	-8.3665	-5.3491
	alone	-0.8169	1.07029	0.448	-2.9505	1.3166
alone	HDADMAC	-7.1000(*)	1.07029	0.000	-9.2336	-4.9664
	LDADMAC	-6.0408(*)	1.07029	0.000	-8.1744	-3.9072
	AnPAM	0.8169	1.07029	0.448	-1.3166	2.9505

Based on estimated marginal means

* The mean difference is significant at the 0.05 level

Polymer Dosages

▪ Tests of Normality

		Shapiro-Wilk		
	Polymer Dose	Statistic	df	Sig.
THMFPeffi	0.05	0.867	12	0.059
	0.1	0.972	36	0.485
	0.15	0.977	36	0.648

▪ Test of Homogeneity of Variance

		Levene			
		Statistic	df1	df2	Sig.
THMFPeffi	Based on Mean	0.453	3	116	0.716
	Based on Median	0.419	3	116	0.739
	Based on Median and with adjusted df	0.419	3	115.679	0.739
	Based on trimmed mean	0.408	3	116	0.748

▪ ANOVA Test

THMFPeffi

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	263.960	3	87.987	3.004	0.033
Within Groups	3397.219	116	29.286		
Total	3661.180	119			

▪ Post Hoc Tests (Multiple Comparisons)

Dependent Variable: THMFPeffi (LSD)

(I) polymer	(J) polymer	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Upper Bound	Lower Bound
0	0.05	-2.88361	1.80390	0.113	-6.4565	0.6892
	0.1	-4.82278(*)	1.80390	0.009	-8.3956	-1.2499
	0.5	-4.61750(*)	1.80390	0.012	-8.1903	-1.0447
0.05	0	2.88361	1.80390	0.113	-0.6892	6.4565
	0.1	-1.93917	1.27555	0.131	-4.4655	0.5872
	0.5	-1.73389	1.27555	0.177	-4.2603	0.7925
0.1	0	4.82278(*)	1.80390	0.009	1.2499	8.3956
	0.05	1.93917	1.27555	0.131	-0.5872	4.4655
	0.5	0.20528	1.27555	0.872	-2.3211	2.7317
0.5	0	4.61750(*)	1.80390	0.012	1.0447	8.1903
	0.05	1.73389	1.27555	0.177	-0.7925	4.2603
	0.1	-0.20528	1.27555	0.872	-2.7317	2.3211

Based on estimated marginal means * The mean difference is significant at the 0.05 level

Table A-8 The statistical analysis of THMFP reduction efficiencies under different of types and dose of polymer (high turbidity-high DOC water-September)***Polymer Types*****▪ Tests of Normality**

		Shapiro-Wilk		
	Polymer Dose	Statistic	df	Sig.
THMFPeffi	alone	0.947	12	0.594
	HDADMAC	0.954	48	0.059
	LDADMAC	0.931	48	0.080

▪ Test of Homogeneity of Variance

		Levene			
		Statistic	df1	df2	Sig.
THMFPeffi	Based on Mean	0.097	2	105	0.908
	Based on Median	0.076	2	105	0.927
	Based on Median and with adjusted df	0.076	2	100.129	0.927
	Based on trimmed mean	0.090	2	105	0.914

▪ ANOVA Test

THMFPeffi

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	906.015	2	453.007	11.190	0.000
Within Groups	4250.883	105	40.485		
Total	5156.898	107			

▪ Post Hoc Tests (Multiple Comparisons)

Dependent Variable: THMFPeffi

LSD

(I) type	(J) type	Mean Difference (I-J)		Sig.	95% Confidence Interval	
			Std. Error		Upper Bound	Lower Bound
alone	HDADMAC	-9.2792(*)	1.50268	0.000	-12.2747	-6.2836
	LDADMAC	-9.1492(*)	1.50268	0.000	-12.1447	-6.1536
HDADMAC	alone	9.2792(*)	1.50268	0.000	6.2836	12.2747
	LDADMAC	0.1300(*)	0.95038	0.008	-1.7645	2.0245
LDADMAC	alone	9.1492(*)	1.50268	0.000	6.1536	12.1447
	HDADMAC	-0.1300(*)	0.95038	0.008	-2.0245	1.7645

Based on observed means.

* The mean difference is significant at the 0.05 level.

Polymer Dosages

▪ Tests of Normality

	Polymer Dose	Shapiro-Wilk		
		Statistic	df	Sig.
THMFPeffi	0	0.947	12	0.594
	0.05	0.947	24	0.228
	0.1	0.967	24	0.592
	0.15	0.957	12	0.743
	0.2	0.983	24	0.950

▪ Test of Homogeneity of Variance

		Levene			
		Statistic	df1	df2	Sig.
THMFPeffi	Based on Mean	0.387	4	103	0.818
	Based on Median	0.252	4	103	0.908
	Based on Median and with adjusted df	0.252	4	91.462	0.908
	Based on trimmed mean	0.340	4	103	0.851

▪ ANOVA Test

THMFPeffi

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1493.923	4	373.481	10.502	0.000
Within Groups	3662.975	103	35.563		
Total	5156.898	107			

▪ Post Hoc Tests (Multiple Comparisons)

Dependent Variable: THMFPeffi (LSD)

(I) polymer	(J) polymer	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Upper Bound	Lower Bound
0	0.05	-5.015(*)	1.386	0.001	-7.801	-2.229
	0.1	-9.799(*)	1.386	0.000	-12.585	-7.012
	0.15	-11.075(*)	1.386	0.000	-13.861	-8.289
	0.2	-10.968(*)	1.386	0.000	-13.754	-8.182
0.05	0	5.015(*)	1.386	0.001	2.229	7.801
	0.1	-4.784(*)	1.131	0.000	-7.059	-2.509
	0.15	-6.060(*)	1.131	0.000	-8.335	-3.785
	0.2	-5.953(*)	1.131	0.000	-8.228	-3.678
0.1	0	9.799(*)	1.386	0.000	7.012	12.585
	0.05	4.784(*)	1.131	0.000	2.509	7.059
	0.15	-1.276	1.131	0.265	-3.551	0.999
	0.2	-1.169	1.131	0.307	-3.444	1.106
0.15	0	11.075(*)	1.386	0.000	8.289	13.861
	0.05	6.060(*)	1.131	0.000	3.785	8.335
	0.1	1.276	1.131	0.265	-0.999	3.551
	0.2	0.107	1.131	0.925	-2.168	2.382
0.2	0	10.968(*)	1.386	0.000	8.182	13.754
	0.05	5.953(*)	1.131	0.000	3.678	8.228
	0.1	1.169	1.131	0.307	-1.106	3.444
	0.15	-0.107	1.131	0.925	-2.382	2.168

Based on estimated marginal means

* The mean difference is significant at the 0.05 level.

APPENDIX B

CHEMICAL COST ANALYSIS

High turbidity-high DOC water

▪ pH 5.5

30 mg/L Alum dose	=	$3,860 \times 30$	
	=	115,800	baht
0.1 mg/L polymer dose	=	$0.1 \times 60,000$	
	=	6,000	baht
1 N H ₂ SO ₄	=	21,000	baht
	=	21,000	baht
Total	=	142,800	baht

▪ Uncontrolled pH

30 mg/L Alum dose	=	$3,860 \times 30$	
	=	115,800	baht
0.1 mg/L polymer dose	=	$0.1 \times 60,000$	
	=	6,000	baht
Total	=	121,800	baht

BIOGRAPHY

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