İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

REMOVAL OF DISINFECTION BY PRODUCTS PRECURSORS WITH ENHANCED COAGULATION IN İSTANBUL WATER SUPPLIES

Ph.D. Thesis by

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ABBREVIATIONS

AHS	: Aquatic Humic Substances
AMW	: Apparent Molecular Weight
AOX	: Adsorbable Organic Halide
AWS	: American Water Systems
AWWARF	: American Water Works Association Research Foundation
BAT	: Best Available Technology
BCAA	: Bromochloroacetic Acid
BDCAA	: Bromodichloroacetic Acid
BDCM	: Bromodichloromethane
BFM	: Bromoform
BLW	: Buyukcekmece Lake Water
CDBAA	: Chlorodibromoacetic Acid
CFM	: Chloroform
CH	: Chloral Hydrate
CP	: Chloro Picrin
DBAA	: Dibromoacetic Acid
DBCAA	: Dibromochloroacetic Acid
DBCM	: Dibromochloromethane
DBP	: Disinfection By-Products
DBPFP	: Disinfection By-Products Formation Potential
DCAA	: Dichloroacetic Acid
D/DBP	: Disinfectant/Disinfection By-Products
DIUF	: Distilled Ultra Filtered Water
DOC	: Dissolved Organic Carbon
DOX	: Dissolved Organic Halide
DPD	: Diethyl Phenyl Diamine
EC	: Enhanced Coagulation
EPA	: Environmental Protection Agency
EU	: European Union
FAS	: Ferrous Ammonium Sulfate
GAC	: Granular Activated Carbon
GC/MS	: Gas Chromatography/Mass Spectrometry
GPC	: Gel Permeation Chromatography
HAA	: Haloacetic Acids
HAAFP	: Haloacetic Acids Formation Potential
HAN	: Haloaceto Nitriles
HK	: Halo Ketons
HPF	: Hydrophilic Fraction

HPOA	: Hydrophobic Acids
HPON	: Hydrophobic Neutrals
HPSEC	: High Performance Size Exclusion Chromatography
kDa	: Kilo Daltons
MBAA	: Monobromoacetic Acid
MCAA	: Monochloroacetic Acid
MCL	: Maximum Contaminant Level
μECD	: Mikro Electron Capture Detector
MRLs	: Minimum Reporting Levels
MW	: Molecular Weight
MWCO	: Molecular Weight Cutoff
NOM	: Natural Organic Matter
NOMS	: National Organic Monitoring Survey
NORS	: National Organics Reconnaissance Survey
OC	: Optimized Coagulation
OLW	: Omerli Lake Water
PSS	: Poly Styrene Sulfonates
PZC	: Point of Zero Charge
SOM	: Synthetic Organic Matter
SPSS	: Statistical Package for Social Sciences
SUVA	: Specific Ultraviolet Absorbance
TBAA	: Tribromoacetic Acid
TCAA	: Trichloroacetic Acid
THM	: Trihalomethanes
THMFP	: Trihalomethanes Formation Potential
TOC	: Total Organic Carbon
TLW	: Terkos Lake Water
TPHA	: Transphilic Acids
TPHN	: Transphilic Neutrals
TOX	: Total Organic Halide
TOXFP	: Total Organic Halogen Formation Potential
UF	: Ultrafiltration
USA	: United States of America
UV$_{254}$	: Ultraviolet Absorbance at 254 nm

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REMOVAL OF DISINFECTION BY PRODUCTS PRECURSORS WITH ENHNACED COAGULATION IN ISTANBUL WATER SUPPLIES

SUMMARY

Chlorination is the most commonly employed chemical disinfectant in drinking water treatment nowadays. However, several studies reported that chlorination of organic matter in fresh water resulted in formation of disinfection by-products (DBP). Because of concerns over the health effects of organic by-products of chlorination, the use of alternative disinfectants of chloramines, ozone, and chlorine dioxide as primary or secondary disinfection agents is increasing. However, each of these alternatives has also been shown to form its own set of DBP. Concerns regarding the potential health effects of DBP prompted several industrialized countries to develop a number of regulations. The disinfectant/disinfection by-product (D/DBP) regulation in United States of America (USA) has set maximum contaminant levels for trihalomethanes (THM) and haloacetic acids (HAA) of 80 and 60 µg/l, respectively. On the other hand, European Union (EU) regulated THM limit at a 100 µg/L. Moreover, Turkish Government recently regulated 150 µg/L THM limit in drinking water to comply with EU regulations. The USA drinking water regulation mandates water treatment plants using disinfectants to remove predetermined levels of total organic carbon (TOC) as a means of reducing DBP precursors. The US Environmental Protection Agency (EPA) has recognized either enhanced coagulation (EC) or granular activated carbon (GAC) as the best available technology (BAT) for controlling DBP precursors. EC corresponds to the use of coagulant dosages effective for TOC removal.

This study was aimed to investigate the DBP precursors removal with ferric chloride and alum in Istanbul three water supplies. The results of this thesis showed that inorganic coagulants were superior for NOM removal, because one of the major mechanisms of DOC removal involves co-precipitation by adsorption on ferric and alum hydroxides. Furthermore, ferric chloride proved to be consistently more effective than alum in terms of NOM removal. Coagulation pH appeared to be a determining factor for maximum NOM removal. The results of this thesis showed that enhanced coagulation is a valuable means of controlling DBP formation without requiring significant capital investments for TLW and BLW. For OLW, pH optimization was required because of low level of specific ultraviolet absorbance (SUVA) value of OLW.

İSTANBUL İÇME SUYU KAYNAKLARINDA ZENGİNLEŞTİRİLMİŞ KOAGÜLASYON YÖNTEMİ İLE DEZENFEKSİYON YAN ÜRÜNLERİ ÖNCÜ BİLEŞİKLERİ GİDERİMİ

ÖZET

İçme suyu arıtımında klor en yaygın kullanılan bir kimyasaldır. Öte yandan bu konuda yapılan çalışmalar, klorlama işlemi süresince, klor doğal organik maddelerle (DOM) reaksiyona girerek dezenfeksiyon yan ürünleri bileşiklerini (DYÜ) oluşturur. Klorlama yan ürünlerinin sağlık etkisinden dolayı, son yıllarda alternatif dezenfektan olarak klor aminler, ozon ve klordioksit gibi kimyasalların kullanımında artış görülmüştür. Ancak, bu dezenfektanlarda kendi yan ürünlerini oluşturmaktadırlar. DYÜ'lerin sağlık etkilerinden dolayı, gelişmiş ülkelerde bir takım yönetmelikler geliştirilmiştir. Amerika Birleşik Devletlerinde (ABD) Dezenfektan/Dezenfeksiyon Yan Ürünleri (D/DYÜ) yönetmeliği trihalometan (THM) ve haloasetik asit (HAA)'ler için sırasıyla 80 ve 60 µg/L limit getirmiştir. Öte yandan Avrupa Birliği ülkelerinde THM limiti 100 µg/L iken, bu limit ülkemizde 150 µg/L olarak düzenlenmiştir. ABD'deki içme suyu yönetmeliği, DYÜ öncü bileşiklerini gidermek amacıyla, dezenfektan kullanan içme suyu arıtma tesislerinin belirli bir miktarda toplam organik karbon (TOK)'u sudan uzaklaştırmalarını gerektirmektedir. ABD Çevre Koruma Örgütü (EPA) zenginleştirilmiş koagülasyon ve granüller aktif karbon prosesinin DYÜ öncü bileşiklerini giderme konusunda en iyi mevcut teknoloji (BAT) olarak belirlemiştir. Zenginleştirilmiş koagülasyon yöntemi TOK giderimi için efektif bir şekilde koagülant kullanımını kapsamaktadır.

Bu çalışmanın amacı demir klorür ve alüm koagülasyonu ile DYÜ öncü bileşiklerinin giderimini kapsamaktadır. Bu çalışmanın sonuçları inorganik koagülantların DOM

gideriminde verimli bir şekilde kullanılabileceğini göstermiştir. Bu TOK gideriminin en temel mekanizmasını demir ve alüminyum hidroksit flokları üzerindeki adsorpsiyon işlemi oluşturmaktadır. Bunun yanında, demir klorürün alümden daha fazla miktarda DOM giderdiği tespit edilmiştir. Koagülasyon pH'nin maksimum DOM gideriminde belirleyici bir faktör olduğu görülmüştür. Bu çalışmadan elde edilen sonuçlar, zenginleştirilmiş koagülasyon yönteminin çok fazla yatırım maliyeti gerektirmeksizin Terkos ve Büyükçekmece sularında klorlama sonucu oluşabilecek DYÜ oluşum potansiyelini kontrol etmede etkili bir arıtma yöntemi olduğunu göstermiştir. Ömerli suyunun düşük seviyede spesifik ultraviyole absorbans (SUVA) değerine sahip olmasından dolayı, bu suda bu yöntemin etkili bir şekilde uygulanabilmesi için pH optimizasyonu yapılması gerektiği belirlenmiştir.

1. INTRODUCTION

Chlorination is the most commonly employed chemical disinfectant in drinking water treatment nowadays. However, several studies reported that chlorination of organic matter in fresh water resulted in formation of disinfection by-products (DBP) **(Rook, 1974, Krasner and Amy, 1995; Rodriguez and Serodez, 2001)**. Because of concerns over the health effects of organic by-products of chlorination, the use of alternative disinfectants of chloramines, ozone, and chlorine dioxide as primary or secondary disinfection agents is increasing. However, each of these alternatives has also been shown to form its own set of DBP **(Oxenford et al., 1996)**. Concerns regarding the potential health effects of DBP prompted several industrialized countries to develop a number of regulations. The disinfectant/disinfection by-product (D/DBP) regulation in United States of America (USA) has set maximum contaminant levels for trihalomethanes (THM) and haloacetic acids (HAA) of 80 and 60 μg/l, respectively **(USEPA, 1998)**. On the other hand, European Union (EU) regulated THM limit at a 100 μg/l **(EECD, 1998)**. Moreover, Turkish Government recently regulated 150 μg/l THM limit in drinking water to comply with EU regulations **(RCWIHC, 2005)**.

The USA drinking water regulation mandates water treatment plants using disinfectants to remove predetermined levels of total organic carbon (TOC) as a means of reducing DBP precursors **(Bell et al., 2000)**. The US Environmental Protection Agency (EPA) has recognized either enhanced coagulation (EC) or granular activated carbon (GAC) as the best available technology (BAT) for controlling DBP precursors **(Krasner and Amy, 1995)**. EC corresponds to the use of coagulant dosages effective for TOC removal. In USA, EC was selected as the Stage 1 treatment of choice because it was effective for the TOC removal and could be implemented at most water plants treating surface waters using existing treatment processes **(Bell et al., 2000)**. This treatment technique includes two steps of application. Step 1 defines the percentage of influent TOC a plant must remove based on the raw water TOC and alkalinity levels. The step 1 TOC removal requirements increase with increasing raw water TOC levels but decrease with increasing alkalinity. A second step of the D/DPB rule was established to provide

alternate performance criteria when it is technically unfeasible for water utilities to meet the step 1 requirements.

Drinking water in Istanbul is supplied mainly from three big surface water sources of Terkos, Buyukcekmece, and Omerli Lakes. The water is transferred to water treatment plants for treatment operations. In the treatment plants, source waters are treated to comply with EU and Turkish water quality standards. Preoxidation of organic matters in source water occurred with chlorine in Buyukcekmece and Kagithane treatment plants, while Omerli and Ikitelli treatment plants use ozone as a preoxidant agent. The final step of water purification of these treatment plants is disinfection, and in Istanbul, drinking water is always disinfected with chlorine to kill microorganisms that can cause serious illnesses and deaths.

Enhanced coagulation efficiently removes DBP precursors of dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UV_{254}) from source water **(Vrijenhoek et al., 1998)**. The term of enhanced coagulation refers to the modification of the coagulation process to achieve greater DBP precursors treatment **(Bell et al., 2000)**. Reduction in the concentration of organic precursors prior to the application of disinfectant could be expected to result in a decrease in DBP formation.

The approach for THM control employed in this research was enhanced coagulation of precursor removal before chlorination. Several alternatives are available for precursor removal. Removing humic substances with enhanced coagulation may allow the continued use of chlorine as a disinfectant in the water treatment plants and reduce the numbers and amounts of chlorination by-products **(Krasner et al., 1995; Bell et al., 2000)**. Further more, removal of organic compounds can lower chlorine dose required for disinfection purposes because of the reduction of chlorine demand exerted by the organic precursor compounds.

The goal of this research is to increase understanding of both practical and theoretical aspects of DBP control by coagulation so that water utilities will be better equipped to increase precursor removal and reduce DBP formation. The specific objectives of this study are to:

1. Determine the degree of improvement in organic matter (precursors) removal that can be achieved by enhanced coagulation.

2. Examine the use of ultraviolet absorbance (UV_{254}) as a surrogate measure of DBP precursors and the use of specific UV_{254} (SUVA) as the basis for a criterion for enhanced coagulation.

3. Examine the use of multiple linear analyses to model THM formation during enhanced coagulation for Terkos Lake Water (TLW) source.

4. Compare the performance of enhanced and optimized coagulation types for removing DBP precursors.

5. Identify and evaluate benefits and costs associated with enhanced and optimized coagulation.

2. LITERATURE REVIEW

2.1. Disinfection By-Products (DBP)

Disinfection by-products (DBP) are formed by the reaction between disinfectants and naturally occurring organic materials in raw water. Chlorinated DBP include trihalomethanes (THM), haloacetic acids (HAA), haloketones (HK), haloacetonitriles (HAN), chloropicrin (CP), and chloral hydrate (CH) **(Trussell, 1991)**. DBP were first discovered in United States of America (USA) drinking water in 1970's by **Rook (1974)**. Natural sources of humic organic materials were also chlorinated, and all four THM were observed, indicating that chlorination, the most common disinfection practice in the United States, could be exposing the public to THM. After that, **Bellar et al. (1974)** used gas chromatography followed by mass spectrometry (GC/MS) to quantify haloforms in chlorinated drinking water, and chloroform (CFM), bromodichloromethane (BDCM), and chlorodibromomethane (CDBM) were observed. The discovery of haloforms in chlorinated drinking water signaled the USA Environmental Protection Agency (USEPA) and the water utilities to look more detailed for other DBP formed during water chlorination to assess the possible health effects of these compounds.

In 1975, **Symons et al. (1975)** conducted a survey to assess THM occurrence, record various treatment practices and the resulting THM formation, and to monitor the organic content of the finished waters for 80 different water treatment plants in USA. Seventy-five percent of the treatment facilities reported the use of prechlorination. It was noticed that there was a high potential for elevated THM concentrations in finished drinking waters. THM measurements showed that all of the chlorinated waters contained chloroform, and there was a strong correlation between total organic carbon (TOC) concentration and THM formation. Also, higher free chlorine residuals in finished water corresponded to higher THM concentrations **(Symons et al., 1975)**.

It soon became apparent to the water treatment plants that THM were not the only DBP formed during disinfection with chlorine. More than 30 halogenated organic compounds, many of which had aromatic structures, were discovered in a chlorinated secondary effluent from a waste water treatment facility **(Glaze and Henderson, 1975)**. Besides, non-volatile halogenated compounds were detected by monitoring total organic halide (TOX) in four different raw and treated waters **(Glaze et al., 1977)**. These results suggested that a great number of chlorinated organics were being produced during disinfection, and researchers continued to discover and identify DBP in chlorinated water supplies.

Quimby and coworkers (1980) identified phenolic and aromatic carboxhylic acids as halogenated by-products which are formed in addition to THM in 1980. Hundreds of different DBP were detected after chlorination of humic and fulvic acid solutions which were extracted from Black Lake, North Carolina **(Christman et al., 1983)**. CFM, trihloroaceticacid (TCAA), dichloroaceticacid (DCAA) was the most abundant DBP and together they comprised 53 percent of the TOX. More than 500 DBP were detected in chlorinated humic acid solutions by **Stevens et al. (1989)** and approximately 200 of these DBP were found in one or more of ten different finished waters which were analyzed. The reaction between chlorine and natural organic matters clearly forms a wide variety of chlorinated by-products; however, at this time, quantification of all of these DBP is not possible. Researchers can adequately quantify the following DBP: THM, HAA, HAN, CH, and CP.

2.1.1. Physical and chemical properties of DBP

The physical and chemical properties of THM and HAA are very different and are addressed below.

2.1.1.1. THM

THM are volatile organic compounds composed of a carbon atom, a hydrogen atom, and three halogen atoms. Chlorine and bromine are the halogens associated with THM in treated drinking water. THM can also contain iodine; however concentrations of iodine-containing THM are usually insignificant. The structure, molecular weight, and boiling point for each of the THM species are shown in Table 2.1. As the molecular weight of the THM compound increases, the temperature of

the boiling point increases, and this relates to the volatility of compound **(Shorney, 1998)**. Lower boiling points are associated with increased volatility; therefore, chloroform is the most volatile THM. THM volatility is an important characteristic to consider, especially when sampling for THM.

2.1.1.2. HAA

When compared to THM, HAA are considered to be nonvolatile. The structures, molecular weights, and boiling points for six HAA (HAA$_6$) are shown in Table 2.2. The boiling points for the HAA species are higher than for the THM and they are also strongly acidic and dissociate in water; thus, HAA are relatively non-volatile and sampling procedures for HAA are less stringent than for THM **(Shorney, 1998)**.

Table 2.1.: Properties of THM **(Shorney, 1998)**

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

Table 2.2: Properties of HAA **(Singer et al., 2002)**

Name	Abbr.	Structure	Molecular Weight (g/mol)	Boiling Point (°C)
Monochloroacetic acid	MCAA	$CH_2ClCOOH$	94.5	189.3
Monobromoacetic acid	MBAA	$CH_2BrCOOH$	138.9	208.0
Dichloroacetic acid	DCAA	$CHCl_2COOH$	129.0	194.0
Trichloroacetic acid	TCAA	CCl_3COOH	163.5	196.5
Bromochloroacetic acid	BCAA	$CHBrClCOOH$	173.4	215.0
Dibromoacetic acid	DBAA	$CHBr_2COOH$	217.8	128.0
Bromodichloroacetic acid	BDCAA	$CBrCl_2COOH$	207.9	NA
Chlorodibromoacetic acid	CDBAA	$CBr_2ClCOOH$	252.3	NA
Tribromoacetic acid	TBAA	CBr_3COOH	296.7	225

NA: Not available

2.1.2. History of DBP formation in chlorinated water

Determination of the extent of DBP formation in drinking water is essential for evaluating the possible threats to human health and the potential impacts of the planned DBP regulations on future water treatment practices in worldwide. An

assessment of the occurrence of DBP is required to develop reasonable and adequate future regulations. Water treatment plants also may want to know the relative quantities of the individual DBP formed by chlorination so that appropriate control strategies can be implemented.

McGuire and Meadow (1988) compiled the results of three separate large-scale THM occurrence surveys in USA: the National Organics Reconnaissance Survey (NORS); the National Organic Monitoring Survey (NOMS), and the American Water Works Association Research Foundation (AWWARF) Trihalomethane Survey (AWWARF) **(McGuire and Meadow, 1988)**. The mean values of THM ranged from 42 µg/L to 117 µg/L, and the AWWARF study observed the lowest mean THM value, 42 µg/L. This wide range of reported mean THM concentrations is presumed to result primarily from efforts by water plants to control THM formation, because the AWWARF study was conducted approximately twelve years after the NORS and NOMS surveys and approximately 9 years after the promulgation of the THM maximum contaminant level (MCL) of 100 µg/L Thus, it appears that many water treatment plants realized the potential for elevated THM concentrations, modified their treatment practices, and successfully reduced the THM concentrations to below the THM limit of 100 µg/L.

Reckhow and Singer (1990) observed that the THM concentrations in six different treated water supplies of USA ranged from 39 µg/L to 104 µg/L, and the THM concentration in three of the samples was greater than 80 µg/L. This suggests that some water treatment facilities will require additional DBP control strategies to achieve compliance with the proposed THM limit of 80 µg/L in USA.

Krasner et al. (1989) investigated THM and HAA concentrations in clear well effluents from 35 different treatment plants across the USA. THM comprised the largest fraction of DBP by weight (the median of the 35 utilities was approximately 40 µg/L), and the HAA concentrations comprised the second largest fraction by weight (the median of the 35 utilities was approximately 20 µg/L). Overall, of the five individual HAA species tested, TCAA and DCAA were the dominant HAA, except in waters with high bromide concentrations, where monochloro acetic acid (MBAA) and dibromo acetic acid (DBAA) were the greatest. This shift in speciation to brominated compounds was also observed with THM.

Arora et al. (1997) performed a DBP occurrence survey among more than 100 treatment plants of the American Water System (AWS), the largest investor-owned water utility in the United States. The study results show that with existing treatment practices, approximately 20 and 66 percent of the AWS water treatment plants exceeded the proposed Stage I and Stage II THM MCL of 80 and 40 µg/L, respectively. Similarly, approximately 16 and 52 percent of AWS systems studied exceeded the proposed Stage I and II HAA$_5$ limit of 60 and 30 µg/L, respectively. Based on these estimates, it is believed that Stage II requirements may significantly affect future water treatment plants practices and costs.

According to 1999 THM and HAA$_5$ data obtained from Missouri Department of Natural Resources **(Gang, 2001)**, most of the small water systems (population served under 2,000) have THM and HAA problems, especially for the water utilities using surface water as a water sources. For example, among the randomly selected 11 water treatment utilities (small systems, surface water sources), approximately 55 and 91% of the water treatment plants exceeded the proposed Stage I and Stage II THM MCL of 80 and 40 µg/L, respectively. Similarly, approximately 55 and 82% of the plants studied exceeded the proposed Stage I and II HAA$_5$ MCL of 60 and 30 µg/L, respectively. The detailed results are shown in Table 2.3.

Based on reported data regarding the occurrence of DBP in small water systems in Missouri, it appears that some utilities are currently able to achieve compliance with the proposed MCL for THM and HAA$_5$; however, others will have difficulty meeting these MCL without substantial treatment modifications. On the other, up to now, there has no sufficient THM or HAA data in distribution systems of any Turkish city. Thus, it is not possible to make any evaluation regarding DBP formation in Turkish drinking water.

It is important to imply that only a fraction of the compounds which are represented by the TOX measurement have been identified and is quantifiable. This has been shown by **Pourmoghaddas (1991)** that HAA and THM were approximately 55 to 64 percent of the TOX in bromide free water. **Sinsabaugh et al. (1986)** measured a THM formation potential (THMFP) to TOX formation potential (TOXFP) ratio of 0.35 to 0 40 for untreated water supply in Virginia, indicating that over 50 percent of the TOX was comprised of non-THM species. **Rook (1980) and Miller et al. (1982)** found similar results, and observation performed by **Miller et al. (1982)** showed that

chlorination of a humic acid solution at pH 7 produced greater levels of non-volatile DBP than volatile DBP, and TCAA was the major non-volatile compound detected. In a HAA formation study in Dutch surface and ground waters, **Peters et al. (1991)** found the sum of eight HAA (MCAA not detected) to be approximately 15 percent of the TOX in surface waters, while no HAA were detected in ground waters. Disinfection during drinking water treatment is not the sole source of some of these compounds. Herbicides can also be sources of TCAA in water supplies **(Frank et al., 1970)**. The concentration of TCAA in irrigation water ranged from 31 to 128 μg/L after application of 3.8 to 5.9 pounds per acre of sodium salts of TCAA to the banks of an irrigation canal. **Glaze et al. (1993)** indicated that photo degradation of trichloroethylene and tetrachloroethylene produced TCAA and DCAA.

Table 2.3: THM and HAA Data on Small Water Systems in 1999 **(Gang, 2001)**

Water plant name	THM(μg/L)	HAA$_5$(μg/L)
Adrian	204	182
Butler	132	154
Garden City	210	207
Maysville	198	129
Concordia	57	68
Higginsville	56	23
CCWWC	36	32
Louisiana	144	107
Cameron	49	45
Vandalia	81	70
Hamilton	106	58
Shelbina	56	32

2.1.3. Health effects of chlorine, THM, and HAA

The water authorities regulate compounds in drinking water which pose a threat to the health of individuals who utilize public water systems as their source of drinking water. In USA, chemicals are classified by the USEPA based on their carcinogenicity to animals and humans. The alphabetic classification scheme places chemicals in categories ranging from human carcinogen (Class A) to no evidence of carcinogenicity (Class E) **(Clark, 1994)**. Compounds designated as Class B2 (sufficient evidence of carcinogenicity in animals but inadequate evidence of carcinogenicity in humans) and above are typically regulated as carcinogens by the

USEPA **(Clark, 1994)**. The USEPA has classified chlorine as a Class D compound; and the toxicity of low dosages of chlorine, hypochlorous acid (HOCl), and OCl⁻ to humans, via drinking water, has not been proven. Studies involving exposure of rat populations to these chlorine species verified that chlorine ingestion, under normal circumstances, does not increase toxic effects **(Condie, 1987; Daniel et al., 1990)**. However, a separate study has shown that sodium hypochlorite (NaOCl) may be a co-carcinogen or tumor promoter in mice **(Hayatsu et al., 1971)**. Hypochlorite may be associated with sperm head abnormalities in male mice, and chlorine has been linked to chromosome aberrations in mammalian cells **(Meier et al., 1985)**. These effects, however, need further study and verification before chlorine, HOCl, and OCl can be designated as toxic.

After the discovery of THM, the USEPA began assessing the extent of human exposure to THM and the possible health effects associated with THM in drinking water. Data collected by the National Cancer Institute indicated that CFM was carcinogenic to rats and mice **(Shorney, 1998)**. To assess the extent of human exposure, the USEPA measured the THM concentrations in drinking water from 50 cities in the United States and observed finished water THM concentrations ranging from 2 to 269 μg/L. A separate study revealed that the CFM concentrations in the blood of persons who drank un-chlorinated water were less than in persons who drank chlorinated water **(Cotruvo, 1981)**. Due to the toxicity and carcinogenicity of THM as shown by various animal studies, the USEPA classified TTHM as Class B2 compounds (probable human carcinogens) except for CDBM, which was designated as a Class C compound **(Black et al., 1994)**.

2.2. Natural Organic Matter (NOM)

2.2.1. NOM source

There are many types of organic compounds found in natural waters. They are autogenic (natural) origin, referred to as "natural organic matter" (NOM), whereas the anthropogenic is referred to as "synthetic organic matter" (SOM). The quantity of NOM may be represented by the amount of organic carbon in natural waters. NOM is of no significant health concern if consumed by humans, unlike SOM, which can

cause significant negative health effects. However, the amount of SOM present water is usually in low level in comparison to NOM **(Duranceau, 1992)**.

In drinking water, NOM may be responsible for color, and taste-odor problems. It can also be readily adsorbed on to many toxic materials surface that can easily bind to it by ligand exchange **(Rasid, 1985)**. From the utility perspective, NOM can encourage microbial growth and also can increase the chlorine demand within the water distribution system. Finally NOM reacts with chlorine to produce chlorinated DBP, such as THM and other halogenated disinfection by-products **(Rook, 1978)** that are carcinogenic. Thus, understanding of NOM behavior in water can help the water utilities remove it better and minimize DBP formation.

2.2.2. Classification of NOM

NOM is present in practically every water supply and is consisted of mainly humic and non-humic substances. Approximately 50 percent of dissolved organic carbon (DOC) has been identified as humic substances, which is the dominant group of organic compounds in water supplies, and the remainders are non-humic substances. Among the non-humic substances, about 60 percent of the DOC is contained of hydrophilic acids. In the remaining 40% of the non-humic compounds, 20% are carbohydrates, 14% carboxylic acids, 6% amino acids, and less than 1% is hydrocarbons **(Thurman, 1985)**.

Because humic substances are the major constituents of DOC, they are important in water treatment and quality considerations. Since the early 1970's, there has been a major increase in the number of experimental studies dealing with humic substances isolated from water. A significant factor leading to this increased focus on aquatic humic substances was the study report by **Rook (1974)** that chlorination of natural water leads to the formation of chloroform and other potentially hazardous chlorinated by-products. Humic substances are considered a heterogeneous mixture of compounds for which no single structure formula can be given. Over the years, only three general humic substances have been classified as humic acid, fulvic acid, and humin. A major component of aquatic humic substances is fulvic acid **(Fair et al, 1966). Thurman (1985)** observed that aquatic fulvic acids generally have a molecular weight (MW) less than 2,000 Da. Low molecular weight often means that most aquatic humic substances are dissolved, rather than colloidal form. In

comparison, humic acid has a MW of 2,000 Da to 5,000 Da or greater, and is therefore considered to be colloidal.

2.2.2.3. Formation of humic and non-humic substances

It has been found that the humic substances imparting color in water are derived not only from leached soil organic matter, but also from degradation of decaying wood and the aqueous extraction of living plant substances **(Christman and Ghassemi, 1966)**.

The origination of the humic fraction of NOM lies in the humification process, a complex biochemical transformation mediated microbially in plants as well as on its own remains. Thus, the magnitude of humification depends upon the nature of the organic matter present (autocthonous vs. allocthonous), and also upon a number of environmental factors such as the nature of the microbial population. Without living organisms and organic substances, the creation of the humus is not possible. A humic substance that comes from an autocthnous source can, again, have different properties than one originating from an allocthonous source. Such substances may have different physical (e.g., molecular size) as well as chemical (e.g., functional group, aromaticity, and hydrophillicity) properties **(Sinha, 1999)**.

In the initial stages of humic substance formation, a series of enzymatic reactions occur. The simple acids, bases and neutrals such as carbohydrates, proteins, lipids, lignins, tanning, polyphenols, complex polymers, and a variety of pigments are partially transformed into simple monomeric forms. As the first step toward stabilization, these monomers combine and condense to form complexes, or are resynthesized into a variety of new biochemical compounds that interact with each other through various reaction pathways, both systematically and randomly. The products are named humic substances. The whole series of reactions is called the humification process **(Rasid, 1985)**.

Little information is known about the genesis of the non-humic portion. However, it may be accepted that non-humic compounds form concurrently during this humification process. However, their formation paths may be different. The non-humic substances essentially are known to be degradation products of cellular materials and composed of carbohydrates, sugar, proteins, amino acids, fats, oils, and pigments, in biochemically altered or unaltered form **(Rasid, 1985)**. They could be

considered as the precursor of the humic substances. Initially, the concentration of non-humic material may be high, however, as the humification process begins, most precursors are utilized in the synthesis of humic molecules **(Rasid. 1985)**. Thus, the formation of non-humic substances may be closely related to humic substances through the process of humification. NOM is also more likely to become humic substances, whereas protein rich dead microorganism (i.e., autochthonous sources) conversions may lead to the formation of non-humic substances. In addition, these phenomena of forming non-humic and humic compounds can occur simultaneously or separately within the same environment.

2.2.2.4. Characterization of NOM

It is clear from above information that various biochemical processes imply the types of organic matter present in an environment. These differences in physical (i.e., molecular weight, ultraviolet absorbance, etc.) and chemical properties (i.e., humic versus non-humic, various functional groups, i.e., carboxylic, phenolic, etc.) can play an important role in the overall chlorine reactivity. Proper characterization of both the physical and chemical properties of humic compounds is central toward understanding their role in the fate, reactivity, and transport of inorganic and organic pollutants **(Sinha, 1999)**. Measurement of the bulk properties of humic substance such as molecular weight and light absorbance properties can yield important information regarding their chemical reactivity and mobility. The following sections are the brief discussions on the several common NOM characterization techniques.

2.2.2.5. Elemental Analysis

Elemental analysis consists of carbon (C), oxygen (O), hydrogen (H), nitrogen (N), sulfur (S), and ash contents. Analytical results are generally reported as weight (%), and some specific ratios. For example, O/C ratio relates to polarity of NOM, H/C relates to saturation of NOM, and N/C ratio relates to origin of NOM **(Amy, 1999)**. It has been reported that C/N and C/H ratios decreased (thus more nitrogenous and less aromatic) and the type of organic matter present was mostly of an aliphatic nature resembling non-humic substances **(Gang, 2001)**.

As shown in Table 2.4., **Thurman (1985)** studied the elemental composition of aquatic humic substances from different aquatic environments. The values obtained

at this research in Table 2.2.1 are similar to those found from other researchers **(Alderdice et al., 1978; Christman et al., 1980; Wilson et al., 1981)**.

Table 2.4: Elemental Composition of Aquatic Humic Substances **(Gang, 2001)**

Sample	C	H	O	N	P	S	Ash
Groundwater (5 samples mean)							
Fulvic	59.70	5.90	31.60	0.90	0.30	0.65	1.20
Humic	62.10	4.90	23.50	3.20	0.50	0.95	5.10
River water (15 samples mean)							
Fulvic	51.90	5.00	40.30	1.10	0.20	0.60	1.50
Humic	50.50	4.70	39.60	2.00	0.00	0.00	5.00
Lake water (3 samples mean)							
Fulvic	52.2	5.2	39	1.3	0.1	1	5
Humic	0	0	0	0	0	0	0

When compared to humic acid, the low-molecular-weight fulvic acids contain higher oxygen, but lower carbon contents, and they contain considerably more acidic functional groups, particularly COOH **(Gang, 2001)**. Because of its higher oxygen and hydrogen content, the non-humic substance is more polar, and thus, more soluble in water. Conversely, the humic substances are more hydrophobic and of less soluble in water. Due to differences in formation processes, big variations can exist among physical (i.e., molecular weight distributions) and chemical properties within humic or non-humic substances. Therefore, the studies should not only consider the organic carbon concentration (i.e., DOC), but also the nature (i.e., molecular weight distributions) of NOM.

2.2.2.6. Structure of humic and non-humic substances

Another important characterizing technique of humic substances is to have knowledge of its various functional groups. This knowledge has proven valuable in providing an understanding of their geochemical properties. By means of functional groups, the humic substances interact with various organic and inorganic components. Metal chelation and cation exchange are two of the reactions that can happen through the function groups. The most known occurring functional groups are the aliphatic and aromatic carboxyl and phenolic functional groups. Carboxyl

functional (COOH) groups are the most reactive functional groups in humic substances **(Schnitzer, 1978)**. Lower molecular weight fulvic acids are enriched in carboxyl functional groups in comparison to the larger molecular weight humic molecules. The presence of the carboxyl group increases its solubility and is particularly important in cation exchange and chelation interactions. It has also stated that the phenolic functional groups are also reactive components of humic substances.

Schnitzer (1978) stated that the humic molecules were composed of an aromatic core, cross-linking each other with the aliphatic chains in forming the complex polymer. The main types of compounds were aromatic and variously substituted benzene-carboxylic acids. Thus, both aromatic and aliphatic compound formation is important, where the aliphatic provides the necessary linkage in the formation of these macromolecules known as the humic substances.

The relative proportion of the aliphatic and the aromatic compounds depends largely on the nature and composition of the source material. If NOM originates mainly from vegetative decay through microbial activity, it is relatively more aromatic due to the richness of phenolic compounds. However, if they are products of decay, degradation, microbial transformation of proteins, carbohydrates, fats, oils and various types of amino acids **(Rasid, 1985)**, they will be more aliphatic. Further, protein may be the important precursor to the formation of this aliphatic portion of NOM. Amino acids which is products of the decay and hydrolysis of proteins, may participate in various biochemical reactions that may lead to NOM formation.

Many scientists **(Beck et al., 1974; Huizenga and Kester, 1979; Oliver et al., 1983)** have measured carboxyl and phenolic hydroxyl contents in fulvic and humic acid for various water supplies. The results indicated that the average aquatic fulvic acid contains 5.5 meq/g carboxyl and 1.5 meq/g phenolic hydroxyl. **Pomes and coworkers (1999)** reported that aquatic humic substances (AHS) containing meta-dihydroxybenzene (m-DHB) structures might be probable DBP precursors and the compositions of the AHS were also studied. The results reported that the elemental nitrogen content was less than 1%, and phenol content was greater than 0.5 ueq/mg. Non-humic compounds are usually composed of simple organic matter and do not have the complexities of the humic substances. As non-humic substances originate with microbial degradation of proteins, carbohydrates, fats, oils, waxes, etc., their

structural characteristics exhibit the chemical properties of those groups to which they belong.

It has been reported that another important difference between humic and fulvic acids is that nearly all the oxygen in fulvic acids can be accounted for in known functional groups (COOH, OH, OO), whereas a high proportion of the oxygen in humic acids occurs as a structural component of the nucleus (e.g., in ether or ester linkages) **(Gang, 2001)**. The major oxygen containing functional groups in aquatic humic molecules are carboxyl, hydroxyl, carbonyl, and phenolic hydroxyl groups. The sum of the carboxyl and phenolic hydroxyl is called total acidity.

2.2.2.7. Molecular weight and size

Molecular weight (MW) and size properties are not only important in NOM characterization, but are also important in determination of the NOM fraction's chemical reactivity, solubility and precipitation behavior in an aqueous solution. The molecular size of the organic matter present in the natural environment is so much affected by various environmental factors. Organic substances present can differ in its molecular weight and can range from a low of a few hundred to a high of several hundred thousands **(Rasid, 1985)**. Different researchers have used different techniques to characterize the MW of humic substances. The results are variable and are strongly influenced by the technique performed. The most commonly used MW characterizing methods are ultrafiltration (UF), gel permeation, and high performance size exclusion chromatography (HPSEC) techniques **(Rasid, 1985)**.

2.2.2.8. Ultrafiltration

UF technique is a very cheap and convenient method to fractionate NOM into different molecular size ranges. UF membranes with different molecular weight cutoff (MWCO), such as 500, 1,000, 3,000, 10,000, 30,000, and 100,000 Dalton, are commonly used for fractionation of NOM. Many investigators have applied this technique in various studies **(Newcombe et al, 1997; Koechling, 1998; Cai, 1999; Lin et al, 1999)**. They found that fulvic acid MW seldom exceeded 10K (Daltons). Most of the fulvic acid fraction appears to be less than 1K or between 5K to 10K (Dalton) **(Rasid, 1985)**. Besides, humic acid fractions have a larger molecular weight, ranging from 10K to 300K **(Alberts and Schindler, 1976)**.

2.2.2.9. Gel permeation chromatography

Several scientists have used gel permeation chromatography (GPC) techniques to fractionate natural water and to determine molecular size distribution. **Gjessing and Lee (1967)** reported that most fulvic acid fractions were of lower molecular weight, ranging from approximately 0.2K to 1K molecular weight. On the other hand, aquatic humic acids exhibit molecular weights of up to 20K and are of correspondingly larger size.

Vilge-Ritter and colleagues (1999) evaluated the NOM removal in the Seine River water by performing jar tests using three different coagulants. The GPC technique was employed to analyze the mass fractions removed by the coagulants. Further, water samples were evaporated to obtained concentrated solutes. After that, a small amount of the concentrate was injected into a GPC column containing a gel and eluted with ultra-pure water. The gel fractionated the NOM based on molecular weight. Smaller molecules diffused inside the gel particles while larger molecules moved out the gel particles side. GPC profiles were recorded by measuring UV_{254} and DOC parameters. The Seine River water contained 35, 36, and 28% of total organic carbon with MW> 5,000, 1,500 <MW < 5,000, and MW < 1,500 Dalton, respectively. The fraction of MW> 5,000 was the most affected by coagulation procedure. The majority of NOM molecules with MW> 1,500 Dalton was removed by coagulation. Because of the isolation difficulties, little is known about the molecular weight distribution of the non-humic fraction of NOM. On the other hand, like the humic portion of the NOM, non-humic compounds may also be composed of various types of organic matter such as proteins, carbohydrate, fats, oils, and waxes, and also may have a wide distribution in MW. Sinha reported that it may be of smaller molecular weight and of simple aliphatic compounds or may be of long chain, high molecular weight polymers such as proteins **(Sinha, 1999)**.

2.2.2.10. High pressure size exclusion chromatography

High Pressure Size Exclusion Chromatography (HPSEC) separates compounds according to molecular size. NOM samples pass through an analytical column containing porous resin with a controlled pore size distribution. Further, small molecules can penetrate farther into resin pores than can larger molecules. Thus, large molecules elute first followed by the small molecules.

The measurement of molecular weights performing HPSEC has been criticized as a technique that is plagued by artifacts **(Hine and Bursill, 1984)**. On the other hand, humic compounds molecular weights determined by other methods may differ from those measured by HPSEC by as much as 2 orders of the magnitude **(Becher et al, 1985). Chin and coworkers (1994)** found that HPSEC can be used to measure reliably the molecular weight of humic and fulvic acids by the addition of an indifferent electrolyte (e.g., NaCl or KC1). In order to estimate the MW of NOM, referenced compounds with known molecular weight and composition are used for comparisons. **Chin et al. (1994)** investigated that polystyrene sulfonates (PSS) (18K, 8K, 5.4K, 1.8K) could be used as a standard because their coiled configuration and that of Suwannee fulvic acid appeared to be nearly identical. **Pelekani and colleagues (1999)** used HPSEC to characterize two Australian surface waters. Besides, the authors also used PSS as molecular weight standards (1.8K, 4.6K, 8K, 18K, and 35K Dalton) to calibrate their system. Further, **Andersen et al. (2000)** also used PSS with peak molecular weights of 16.9K, 8.K, 3.8K, and 1.37K Dalton, respectively, to calibrate the HPSEC column.

Precautions on selection of gel material should be exercised, since some NOM groups can interact with the gel surface, resulting in transport retardation and disparity elution. Thus, molecular weight distributions can be affected. It has been reported that compounds for MW calibration should mimic the NOM of interest **(Croue et al., 1999)**. However, choosing appropriate compounds is a challenge because of lack of information on the chemical structure of NOM.

2.2.2.11. Molecular dimension orientation

The shape of the humic compounds can also play an important role in organo-metal interaction and chlorination reactions. Various physical parameters of pH, conductivity, etc., can influence the configuration of NOM in the water. It has found that pH has a larger effect on humic substances; at higher pH {i.e., alkaline condition), the acidic functional groups such as carboxylic (-COOH) and phenolic (Ar-OH) deprotonate (or ionize), producing many negatively charged sites, which then repel each other and keep the molecule in a stretched shape **(Gang, 2001)**. On the other hand, under acidic conditions, or with increasing concentration of electrolytes (which causes reduction in intermolecular repulsion force), these

negative charges are neutralized and the geometry from the stretched shaped changes to coiled shaped, which may cause the precipitation of the humic molecule. At low pH conditions, humic substances precipitate, and, however, fulvic acid is still soluble **(Gang, 2001)**.

2.2.2.12. Resins

For chemical characterization (i.e., humic/hydrophobic and non-humic/hydrophilic) of NOM, the two types of resin most often used are the Amberlite XAD-8 and XAD-4 resins. These two resins are chosen because of certain advantages associated with their use. Larger, more hydrophobic fractions can be effectively adsorbed with the XAD-8 resin because of its larger pore size and smaller surface area. On the other hand, XAD-4 has smaller pore size and greater surface area, therefore, is more effective for hydrophilic, smaller molecular weight fractions **(Aiken, 1979)**. The principal of the isolation procedure is to acidify bulk water to lower the pH <2 (becomes more hydrophobic), so that adsorption onto the Amberlite XAD resins can occur. Once adsorbed, it is eluted by adding base solution to pH greater than 11, so that the functional groups are ionized and desorption can take place.

Thurman (1985) and others have successfully used these two resins with humic substances. They reported that these isolation methods had some advantages over other procedures. For example, humic substances can be directly isolated from water (organic solvent is not used in preparation) and the procedure is simple and rapid for large volume samples.

Besides, XAD-8 resin can be used to separate NOM into hydrophobic and hydrophilic fractions **(Harrington et al., 1996; Westerhoff et al., 1996)**. It has been reported under acidic conditions, the hydrophobic NOM is adsorbed onto the XAD-8 resin and the hydrophilic fraction is left behind **(Gang, 2001)**. By using XAD-8 resin, typically, 40 to 60% of NOM can be recovered. Several scientists proposed a two-column array of XAD-8 and XAD-4 resins to isolate and separate the hydrophobic and hydrophilic NOM **(Aiken et al., 1992; Malcolm and McCarthy, 1992)**. Further, using this approach, five fractions of DOC can be obtained:

- Hydrophobic acids (HPOA) including humic and fulvic acids from XAD-8;

- Hydrophobic neutrals (HPON) from XAD-8;

- Transphilic neutrals (TPHN) from XAD-4;

- Transphilic acids (TPHA) from XAD-4; and

- Hydrophilic fraction (HPF) which material passed through both columns.

The HPOA and TPHA fractions accounted for 50 to 90% of the DOC in most water supplies **(Aiken et al, 1992)**. Usually, 20 to 30% of DOC in natural waters was not adsorbed onto XAD-4 or XAD-8 resins. One advantage of the resin fraction is the lack of need for a preconcentration step. On the other hand, the disadvantage of this procedure is the irreversible adsorption of organic matter by the resin. Thus, careful resin cleanup is required. Besides, 20 to 30% of DOC in natural waters did not adsorbed onto XAD-4 or XAD-8 resins, and the lower recovery efficiency of carbon from the resin indicates that this portion can not represent the composition of the total NOM. Further, other considerations are that solute aqueous solubility and resin may affect the efficiency of adsorption of NOM onto XAD resins.

2.3. Chlorination

2.3.1. Chlorine chemistry

For years chlorination has been employed by water treatment plants for disinfection along with iron and manganese oxidation, taste and odor control, and as a treatment to address various other water quality problems. After the discovery of THM in drinking water, water treatment plants examined treatment alternatives to reduce the use of chlorine, especially during pretreatment. Today, chlorine is still the primary chemical agent used for disinfection; however, many water utilities convert free chlorine to chloramines prior to distribution to reduce THM formation.

Chlorine can be applied during water treatment using either chlorine gas, sodium hypochlorite (NaOCl) or calcium hypochlorite ($Ca(OCl)_2$). A detailed description of the chemical equilibrium of chlorination is given below. In each case, the applied chlorine compound disproportionates in water to release HOCl and OCl, which are the reactive forms of chlorine in drinking water. The type of chlorine applied influences pH and alkalinity of water; chlorine gas addition results in a lower pH and alkalinity, while NaOCl and $Ca(OCl)_2$, cause an increase in the pH and alkalinity.

When chlorine gas is added to water, rapid hydrolysis to hydrochloric (HCl) and hypochlorous acid (HOCl) occurs as shown in Equation 2.4.1:

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \qquad (2.4.1)$$

At pH above 4.4, essentially no molecular chlorine remains in aqueous solution. HOCl is a weak acid with a pK. of 7.5, which further hydrolyzes to yield a hydronium ion (H_3O^+) and a hypochlorite ion (OCl^-) according to Equation 2.4.2:

$$HOCl + H_2O \rightarrow H_3O^+ + OCl^- \qquad (2.4.2)$$

With increasing pH value, at a given temperature, the fraction in the anionic form increases. This pH dependence is important because OCl^- is a much less effective oxidant than HOCl **(Gang, 2001)**. One explanation is the higher redox potential of 1.482 V for HOCl as comparing to 0.841 V for OCL^-. The ionic character of OCl^- influences the disinfection effectiveness since neutrally charged molecules, such as HOCl, are more readily transported across cell membranes than the charged OCl^- **(Gang, 2001)**.

Residual chlorine is measured as free chlorine and is the sum of HOCl and OCl values. It has been reported that available chlorine disappears from water by numerous pathways **(Gang, 2001)**. Reactions of organic matter and inorganic water constituents, such as ferrous (Fe^{2+}) and manganous (Mn^{2+}) cation, sulfide (S^{2-}), bromide Br^-, and ammonia, will consume free chlorine. Thus, this demand has to be met before a residual can be provided in the distribution system.

When oxidation of a substance by HOCl happens, the Cl^+ radical in hypochlorous acid takes two electrons from the substance being oxidized to become a chloride ion (Cl^-). This gain of two electrons indicates that the oxidized capacity of HOCl is equal to two equivalents of chlorine or one mole of chlorine **(White, 1999)**. Kinetic studies have demonstrated that both HOCl and OCl^- are the reactive chlorinating agents **(Gang, 2001)** that lead to the formation of the halogenated DBP.

2.3.2. Formation of DBP

Several water quality characteristics influence the DBP formation. The following sections focus on the effects of precursor types and concentration, chlorine dose, contact time, temperature, bromide concentration, and solution pH.

2.3.2.1. Effect of precursor type and concentration

Several scientists have documented increased DBP formation as the precursor concentration increases **(Symons et al., 1975; Kavanaugh, 1978; Shorney, 1998)**. Therefore, removing DBP formation potential (DBPFP) prior to chlorination will clearly reduce subsequent DBP formation if all other factors are held constant.

The type of organic substances present in water has an effect on the extent of DBP formation and the type of DBP produced. Besides, humic acids have usually been found to be more reactive than fulvic acids with chlorine. For example, it has been reported that chlorination of Michigan peat humic and fulvic acid solutions resulted in higher chloroform production in the humic acid solution than in the fulvic acid solution **(Babcock and Singer, 1979)**. **Reckhow and Singer (1984)** chlorinated humic and fulvic acid extracts from five different water sources, and the TOX yield was always greater in the humic acid fraction of these sources than in the fulvic acid fraction. Similar results were obtained by **Trussell and Umphres (1978), and Babcock and Singer (1979)**. On the other hand, **Oliver and Lawrence (1979)** found no appreciable difference in DBP formation between chlorinated humic acid and fulvic acid solutions.

Yeh et al. (1994) chlorinated several fractions of organics extracted from a water supply in Taiwan and observed higher HAA and THM yields (per mg/L DOC) produced by the humic and fulvic acid solutions than by the hydrophilic organic compounds. In an another study, humic and non-humic fractions of three source waters were chlorinated (pH 8, 20 °C, 24 hours contact time) and the TOX, HAA, and THM concentrations were measured **(Dryfuse et al., 1995)**. In the source water with the highest DOC (15.3 mg/L), the humic fraction produced much greater concentrations of TOX, HAA, and THM than the non-humic fraction. However, the other two source waters (DOC concentrations of 2.5 and 5.3 mg/L), the DBP concentrations produced by the humic and non-humic fractions were similar.

The UV_{254} of humic compounds can provide insight into the nature of the organics present, and the potential DBP formation. As reported by **Edzwald et al. (1985)**, humic aromatic compounds and molecules with conjugated double bonds absorb ultraviolet (UV) light, whereas simple aliphatic acids, alcohols, and sugars do not absorb UV light. **Reckhow and Singer (1990)** measured the UV_{254} and DBP

formations of the humic and fulvic fractions of five different water sources. Humic acids were foud to be have greater UV$_{254}$, more aromatic rings, and a higher molecular weight than fulvic acids. As the aromatic content increased (as in humic acids), the percentage of chlorine incorporation also increased; and the higher the specific ultraviolet absorbance (SUVA), the greater the production of DBPFP.

Korshin and collegues found that the change in the UV$_{254}$ has also been correlated to subsequent THM formation and TOX formation **(Korshin and Benjamin, 1997)**. The absorbance change (at 254 nm) resulting from chlorination correlated very well with THM formation in a natural water supply containing 3.6 mg/L TOC. The decrease in UVA (at 272 nm), resulting from chlorination at pH values between 5 and 11, correlated extremely well with TOX formation and was independent of the initial DOC concentration, chlorine dose, water source, and reaction period.

Many scientists investigated the means by which chlorine affects the DBP formation and NOM structure. Chlorine consumption by hydrophobic extracts was found to correlate with the aromatic and phenolic content as well as the subsequent THM and HAA formation **(Singer et al., 1994)**. This implies that the phenolic and aromatic content of the organic substances influenced the chlorine incorporation, and may be associated with precursors to THM and HAA.

Christman et al. (1980) performed chlorination studies on an extracted humic acid solution at pH 12 and identified three major types of compounds: non-chlorinated substituted aromatics, non-chlorinated straight chain acids, and chlorinated straight chain acids. Since no chlorinated aromatics were found, it was hypothesized that at pH 12 value, chlorination caused ring rupture and essentially degraded the aromatic structures. Further, **Bruchet et al. (1985)** monitored DBP formation at two pilot plants and used PY/GC/MS method to identify the DBP. Chlorine was not attached to aromatic rings but was fixed to aliphatic compounds or alkyl chains of more complex molecules. The molecular weight of precursors has also been correlated with DBPFP. **Bell et al. (1996)** reported that organic molecules with molecular weights greater than 1 kilodalton (kD) contributed more DBPFP than did the organics having molecular weights less than 1 kD. However, **Khian et al. (1996)** indicated that dissolved organic halogen (DOX) formation in chlorinated and chloraminated waters was typically greatest in the less 500 kD fraction. Recent study performed by **Sinha (1999)** indicated that THM precursors were predominately

larger molecular weight humic materials, whereas the HAA precursors were large molecular weight humic and non-humic materials.

2.3.2.2. Effect of chlorine dose

As the dosage of applied chlorine to organic solutions increases, the DBP formation concentration increases. This relationship has been observed by many researchers **(Rook, 1974; Oliver and Lawrence, 1979; Young and Singer, 1979; Norwood et al., 1980; Reckhow and Singer, 1984)**. In a study conducted by de **de Leer et al. (1985)**, the concentration of dichloroacetic acid (DCAA), however, was found to be independent of the chlorine dosage

Another issue regarding chlorine dose and DBPFP is the distribution of DBP species formed at varying chlorine dosages, and the oxidative requirements of some DBP during chlorination. **de Leer et al. (1985)** found that the chlorination of humic acid solutions at chlorine to carbon ratios of 0.39 and 3.35 yielded chloroform. In a study by **Norwood et al. (1980)** reported that higher chlorine to carbon ratios favor the formation of chlorinated acids. **de Leer et al. (1985)** found a relationship between the chlorine dosage and the apparent molecular weight (AMW) of the resulting chlorinated organic species. Besides, it has been reported that at the lower chlorine doses, the majority of the chlorinated products had higher molecular weights, whereas, at the higher chlorine doses, the chlorinated products were primarily in the lower molecular weight fractions **(Gang, 2001)**. This trend was also indicated by **Glaze et al. (1980)** and **Johnson and Randtke (1983)**; higher chlorine concentrations sever NOM molecules into lower molecular weight fractions. Related to chlorine dose, the amount of chlorine consumed by the organic substances during treatment is also related to subsequent DBP formation. For example, **Singer et al. (1992)** presented data showing that THM, HAA, and TOX concentrations increased with increased chlorine consumption for six North Carolina water supplies.

2.3.2.3. Effect of chlorine contact time

Increasing contact time between organic substances and chlorine generally results in higher DBP concentrations. This occurrence has been observed by many investigators **(Miller and Uden, 1983, and Reckhow and Singer, 1984)**. On the

other hand, hydrolysis of DBP can occur after extended contact time with chlorine, resulting in an increase or decrease in the concentration of certain DBP.

Addressing the effect of contact time on DBP formation is particularly important when considering the water quality in the water distribution system. **Chen (1993)** monitored THM and HAA concentrations in a distribution system for one year period. The THM concentrations increased with long retention times in the distribution system, whereas the HAA concentrations decreased. These results suggest that a series of reactions was occurring within the distribution system; possibly, certain HAA species were being degraded by microbes attached to the pipe walls **(Gang, 2001)**. Monitoring DBP formation with increased chlorine contact time has provided useful information about the complexity of reactions which are occurring. **Reckhow and Singer (1984)** found that with increased contact time, CFM became a larger percentage of the total TOX, and the concentrations of CFM, TOX, TCAA, and DCAA increased.

2.3.2.4. Effect of solution temperature

Temperature is known to accelerate reaction kinetics; thus, it is not surprising that DBP formation kinetics is faster at higher solution temperature values. Several researchers have observed this trend **(Rook, 1974; Randtke, 1993, Knocke et al., 1986)**. **Stevens et al. (1985)** found an apparent relationship between temperature and pH. At pH 4.7, the organic halogen (AOX) concentration increased with increasing temperature from 4 to 36 °C.

2.3.2.5. Effect of bromide concentration

Water treatment plants located in coastal regions can experience elevated bromide concentrations because of salt water intrusion, while inland water sources, especially ground waters, can have high bromide concentrations due to trapped seawater in sedimentary deposits **(Shorney, 1998)**. **Krasner et al. (1989)** reported that, the bromide concentrations in water from 35 utilities ranged from 0 01 to 3.0 mg/L in USA. It is well known that application of free chlorine to source water supplies containing bromide causes the oxidization of bromide to bromine, which then reacts with precursors to form brominated DBP. The rate of brominated DBP formation is faster than chlorinated DBP **(Symons et al., 1981)** and bromine competes more

effectively than chlorine for reaction with precursors (**Symons et al., 1981; Amy et al., 1985**). **Rook (1978)** observed that OCl⁻ is a stronger oxidant than hypobromite (OBr⁻), which is formed by chlorination of bromide; however, OBr⁻ is a faster substituting agent. The presence of bromide in source waters causes the DBP to be highly brominated rather than chlorinated (**Krasner et al., 1989; Amy et al., 1991; Pourmoghaddas, 1991; Pourmoghaddas et al., 1993**). The THM formed in waters containing high bromide concentrations are typically dominated by BFM and DBCM. It was reported that this shift in speciation towards more brominated compounds also occurs with HAA and HANs (**Pourmoghaddas et al., 1993**). **Symons et al. (1993)** observed that in the presence of bromide and the absence of excess chlorine after chlorination, no CFM is formed; however, when excess chlorine remains in solution. CFM formation occurs, but only after the bromide substitutions are completed.

Higher bromide/DOC (Br/DOC) ratios are responsible for the increased predominance of brominated DBP following treatment to partially remove DBP (**Amy, 1993; Owen et al., 1993**). **Sketchell et al. (1995)** have reported that bromide in source waters increases the molar yield of THM produced during chlorination; but **Cowman and Singer, (1996)** have concluded that the molar yield does not necessarily increase. Further, **Symons et al. (1987)** noted that increasing the bromide to humic acid ratio did not increase the TOX concentration, however, only the speciation of DBP was altered: the presence of bromide caused the yield (weight basis) of brominated THM to increase, while the non-purgeable TOX decreased. In addition, **Pourmoghaddas and Stevens (1995)** found similar results; as the bromide concentration was increased, the percentage of TOX as THM increased, but the TOX concentration did not increase and the percentage of TOX as HAA did not always increase. Bromide was found to have little effect on the total HAA formation with two different water sources studied by **Cowman and Singer (1994, 1996)**. The presence of bromide did produce significant concentrations of mixed bromo-chloro HAA after chlorination process, and the concentration of bromide-containing HAA increased. It was noted that high bromide to chlorine ratios resulted in more brominated DBP (**Pourmoghaddas et al., 1993**). While the bromide to chlorine ratio exceeded 0.1 mg/mg, DBCAA was the dominant HAA, and at bromide to chlorine ratios exceeding approximately 0.27 mg/mg, TBAA was the dominant HAA

(Pourmoghaddas et al., 1993). **Cowman and Singer (1996)** observed that increased bromide concentrations resulted in increased chlorine consumption in two different water sources, they found a 1 μmol demand of HOCl per 1 μmol bromide in both source waters. This is attributed to the fact that bromide exerts a chlorine demand as bromide is converted to hypobromous acid, which reacts much more strongly with NOM than does hypochlorous acid.

2.3.2.6. Effect of solution pH

Solution pH affects the speciation and amount of DBP formed, as well as the rate of DBP formation during chlorination. For example, THM formation is enhanced in alkaline water; however HAA formation is enhanced at neutral to low pH. Some researchers shows the effect of solution pH on CFM formation during chlorination of James River water **(Harms and Looyenga, 1980)**. The concentration of CFM was substantially higher at pH 11 than at pH 7. This relationship between pH and THM formation has been extensively studied **(Wachter and Andelman, 1984; Stevens et al., 1985)**. For conventional coagulation treatment (coagulation, settling, and filtration) at a near neutral pH, **Singer and Chang (1989)** found that the THM accounted for 26 percent of the TOX, on a chlorine equivalent weight basis.

In THM formation studies by **Morns and Baum (1978)** and **Rook (1980)** the chlorine demand was lower in alkaline solutions than in acidic or neutral solutions, yet increased CFM formation occurred in alkaline solutions. This is due to the pH dependent speciation and reactivity of chlorine. A low pH favors the substitution reactions associated with HOCl, resulting in a higher chlorine demand (and increased TOX formation), while a higher pH favors the oxidation and hydrolysis reactions involved in THM formation.

The influence of pH on HAA formation is more complicated because the rate of formation and hydrolysis varies for each individual HAA. **Reckhow and Singer (1984)**, shows that TCAA formation was maximized between pH 4 and 7, while at pH 11, TCAA formation was negligible. Also, the TOX formation decreased with increasing pH. The data presented by **Miller and Uden (1983)** were similar: TCAA formation was greatest at low-to-neutral pH, while DCAA formation only slightly decreased under alkaline conditions. In tests conducted by **Pourmoghaddas et al.**

(1993), concentrations of TCAA, TBAA, BDCAA and DBCAA were much lower at pH 9 4 than at pH 5.

Lower pH (pH 5) was found to promote bromide substitution in THM formation studies of chlorinated 2,4,6-trihydroxyacetophenone monohydrate **(Gould et al., 1983)**. Less bromide incorporation was observed in test solutions at pH 10. In a pilot-scale study using Ohio River water, TOX and DCAA formation was observed to be independent of solution pH (pH values used for testing were 5.7, 7 0, and 9.4), however the concentrations of TOX and DCAA continued to increase with additional contact time **(Stevens et al., 1989)**. The THM concentration increased with increased solution pH., while TCAA formation was lower at pH 9 4 than at pH 5 and 7. A summary of the relationship between pH and DBP formation for various DBP has been presented by **Stevens et al. (1989)** (Table 2.4.). It is clear that there is not an optimum pH which allows for minimal production of all types of DBP. Thus, although individual DBP or classes of DBP can be decreased by means of pH control, it is virtually impossible to comprehensively control DBP formation by adjusting solution pH alone; other methods must be employed to effectively control formation of the broad spectrum of known and unknown DBP.

The solution pH also influences the relative contribution to DBP formation by different organic compounds. **Oliver and Lawrence (1979)** measured CFM formation at pH 7 and pH 11 for a variety of precursor types and the results are shown in Table 2.8. Altering the solution pH changed the relative amount of CFM formed from each type of precursor. At pH 11, aspartic acid produced the greatest concentration of CFM, while at pH 7, aspartic acid produced the least amount of CFM. **Reckhow and Singer (1990)** found that, at high pH, "the tendency for humic acids to have higher specific yields of CFM than their corresponding fulvic acids is less pronounced. These data indicate that the pH used during water treatment will influence which types of precursors contribute the most to DBP formation.

2.3.3. DBP formation by alternative disinfectants

Disinfectants other than chlorine have been found effective for disinfection and DBP control. Chlorine dioxide, ozone, and pre-ozonation to chlorine are alternative disinfectants to chlorine, and a brief discussion of the advantages and disadvantages of each of these oxidants follows. Chlorine dioxide is a strong oxidizer that was

historically used primarily to control tastes and odors in drinking water **(Hoehn et al., 1994)**. Chlorine dioxide does react with organics, however the TOX formed is only a fraction of the TOX formed by chlorine **(Symons et al., 1981; Ravacha, 1984)**. THM are not formed by the reaction between chlorine dioxide and NOM; however chlorine dioxide use is associated with the production of chlorate and chlorite, which are inorganic DBP **(Hoehn et al., 1994)**. Chlorite is the primary end-product of chlorine dioxide reactions **(Hoehn et al., 1994)**, the chlorite concentration is typically 70 percent of the applied chlorine dioxide dosage. Chlorite, as well as chlorate, is also produced during improperly managed chlorine dioxide generation. Chlorate can also be formed during reactions between: 1) chlorite and free chlorine; and 2) chlorine dioxide and free chlorine **(Hoehn et al., 1994)**. Other known sources of chlorate include the disproportionation of chlorine dioxide at high pH and in sunlight. The proposed D/DBP rule does not recommend an MCL for chlorate; however chlorate can be minimized by proper generation of chlorine dioxide. The chlorine dioxide generation process must achieve a 95 percent chlorine dioxide yield and produce no more than 5 percent chlorine. Proper and periodic maintenance, cleaning, and calibration of rotameters is essential for efficient chlorine dioxide generation **(Hoehn et al., 1994)**; the flow rate of the chlorine, sodium chlorite, and ejector water is crucial. The proposed MCL for chlorite is 10 mg/L.

Ozone is a highly reactive oxidant which is a stronger disinfectant than chlorine. Ozone concentrations dissipate quickly, thus requiring a supplemental disinfectant for maintenance of a residual in the distribution system **(Glaze et al., 1989)**. Ozonation and perozonation of waters containing organic material can produce hydrogen peroxide, bromate, BFM, DBAA, glyoxal, methyl glyoxal, aldehydes, fatty acids, and biodegradable matter **(Trussell, 1991)**. In waters with low bromide concentrations, ozone does not react to form halogenated DBP. When bromide concentrations are substantial, ozone reacts to form brominated DBP such as BFM and bromate **(Siddiqui and Amy, 1993)**. The USEPA has proposed an MCL of 0 010 mg/L for bromate. The effect of pre-ozonation followed by chlorination or chloramination appears to be site specific and dependent upon pH and the applied ozone dosage. **Riley et al. (1978)** reported that pre-ozonation followed by chlonnation under alkaline pH conditions produced greater CFM concentrations than chlorination alone: whereas under neutral pH conditions, pre-ozonation followed by

chlorination produced less CFM than chlorination alone. **Siddiqui and Amy (1993)** found that THM and HAA concentrations after treatment were dependent on the type of organic material present and the ozone-to-TOC ratio. Three different source waters were treated with pre-ozonation followed by subsequent chlorination or chloramination. No distinct trends in THM or HAA formation were observed; the concentrations increased, remained the same, or decreased, depending on the treatment. DCAA and TCAA were the primary HAA formed after pre-ozonation/post-chlorination, whereas MCAA and DCAA were the most abundant HAA after pre-ozonation/post-chloramination. No TCAA was detected in the post-chlorammation studies Bench-scale treatment utilizing ozonation prior to $Al_2(SO_4)_3$ coagulation (pH between 5.5 and 7.5, $Al_2(SO_4)_3$, dosages from 15 to 10 mg/L) revealed that the effectiveness of this treatment scheme is site specific.

2.3.4. Reaction of chlorine with aromatic compounds

Denzer indicated that **(Deinzer, et al., 1978)** aromatic compounds with electron donating groups (such as -OH, -OR, -NH$_2$, -R) are more reactive and tend to incorporate chlorine more readily than aromatics with electron-withdrawing groups (such as -NO$_2$, -COOH.). **Carlson et al. (1975)** studied the reaction of chlorine on monosubstituted aromatic compounds with electron-donating groups {e.g., phenol) and electron withdrawing groups (e.g., nitrobenzene, chlorobenzene, benzonitriles) and found that the former are more reactive than the latter class of compounds. This is due to the ability of the electron-donating group in directing the halogen to both oriho and para positions and increasing the electron density in aromatic ring, whereas the electron-withdrawing group direct the halogen only to meta position and reduce the electron density in aromatic ring structure. **Norwood and Christman (1987)** have also showed the importance of phenolic groups as reactive centers for chlorination by-products.

2.3.5. Reaction of chlorine with aliphatic compounds

Chlorine also reacts with an aliphatic compounds structure in the NOM pool of materials. It has been reported that compounds such as methyl-ketone can react with halogens under basic conditions to form chloroform. **Norwood et al. (1980)** reported that chlorination of resorcinol (aromatic compound.) can produce several chlorinated

intermediates, such as methyl ketone (aliphatic compound). The presence of methyl ketone or oxidizable precursors of methyl ketone at higher pH is considered as a potential source of THM formation **(Deinzer et al., 1978)**.

2.4. Coagulation of DBP precursors

2.4.1. Introduction

Coagulation is an old practice in water treatment, a practice that has not changed much over the years. Until recently, coagulation process has been primarily used to remove color and turbidity causing particulate from water. However, with the discovery of THM in 1970's by **Rook (1976)**, more attention has been given to NOM removal from water. This chlorination by-product has been regulated since 1979. On the other hand, in the early 90's, the USEPA proposed Enhanced Coagulation (EC) rule to further reduce health-related risks from these DBP and forced water utilities to apply EC to further remove NOM from water **(Sinha, 1999)**. In enhanced coagulation practices, NOM removal is based on raw water organic carbon content and alkalinity (Table 2.5.). EC has already been evaluated by several investigators and has been found to be effective in both NOM removal and DBP minimization. Other benefits include reduction in chlorine demand in treated water **(Sinha, 1999)**. The main objective of EC process is to achieve 20% to 50% removal of organic matter prior to disinfection. Some of the disadvantages of EC were reported as increased chemical use, which translates into higher operational cost, higher sludge production, and addition chemical costs associated with pH adjustments.

Table 2.5: EPA Alkalinity and total organic carbon (TOC) matrix for percent TOC removal goals by enhanced coagulation

TOC	Alkalinity mg/L as $CaCO_3$		
	0-60	60-120	>120
mg/L	Percent	percent	percent
2.0-4.0	35	25	15
4.0-8.0	45	35	25
>8.0	50	40	30

2.4.2. Coagulant used for NOM removal

Various types of metal coagulants are available for NOM removal. On the other hand, two of the most commonly used conventional metal coagulants in water treatment are aluminum sulfate ($Al_2(SO_4)_3*18H_2O$, commonly referred to as alum) and ferric chloride ($FeCl_3*6H_2O$, commonly referred to as ferric). Alum is currently the most widely used coagulant, but, over the past few years, the use of iron salt as a coagulant has increased dramatically **(Sinha, 1999)**. Other conventional coagulants include aluminum chloride, and ferric sulfate **(Sinha, 1999)**. However, the use of these coagulants in drinking water has been limited. Conventional coagulants are basically a strong acid salts (e.g.. HCI or H_2SO_4) and a weak base ($Al(OH)_3$ or $Fe(OH)_3$). Thus, it is a mixture of a cation (from base) and an anion (from acid) **(Sinha, 1999)**. Various types of organic polymers are also used in water treatment operations as coagulant aids. Usually, cationic polymers are more often used in comparison to the anionic and non-ionic polymers. **Edzwald (1987)** investigated these polymers as primary coagulant and concluded that while these cationic polyelectrolytes could destabilize the particulate matter, a poor settling of flocs was produced. The use of these polymers may be beneficial for turbidity removal in conjunction with metal coagulants, but may not be effective for removal of the dissolved/colloidal organic substances and may have less significance in precursor minimizing **(Sinha, 1999)**.

2.4.3. Metal coagulant chemistry

When a metal coagulant is added to water, it undergoes a series of hydrolysis reactions, resulting in the formation of various monomeric and polymeric metal hydroxide species while releasing protons, behaving as an acid, and, if the dosage is sufficient, precipitating metal hydroxide solids **(Shorney, 1998)**. The relative amount of each species is dependent upon the various important factors of coagulant dosage, solution pH, the initial alkalinity, and temperature. More detailed discussions of the hydrolysis steps of aluminum and iron salt coagulants have been presented by **Stumm and O'Melia (1968)** and **Amirtharajah (1990)**.

The distribution of hydrolysis products formed during coagulation is often summarized graphically, as a function of pH, known as a pC-pH diagram as shown in Figure 2.1 and Figure 2.2 for aluminum and iron, respectively. Such diagrams

provide a useful visual representation of the different metal species present during coagulation process. The metal hydrolysis products formed during coagulation may be monomeric (containing only one mole of metal, $Al(OH)_2^+$, $Al(OH)^{2+}$, Al^{3+}) or polymeric (containing more than one mole of metal; $Al_{13}O_4(OH)_{24}^{7-}$) **(Shorney, 1998)**. Amorphous solids of $Al(OH)_{3(s)}$ or $Fe(OH)_{3(s)}$ precipitate in the shaded area of each diagram. Careful examination of these pC-pH diagrams provides insight into the charge and concentration of dissolved metal species likely to be present and the potential for of metal hydroxide solids precipitation at any given pH value. The species predominating at the lower pH values are positively charged and many are polymeric, whereas the negatively charged tetrahydroxo monomer predominates at higher pH levels. These differences strongly influence the mechanisms responsible for colloid and dissolved organics removal.

2.4.4. Mechanisms for precursor removal by coagulation

The organic precursors present in drinking water exist in particulate or dissolved states, and organic particles can be removed by the same removal mechanisms as inorganic particles. Dissolved organics must first be converted into particles by other mechanisms. For particulate organics, the primary removal mechanisms during coagulation are charge neutralization (by adsorbing coagulant species of opposite charge) and enmeshment mechanisms **(Shorney, 1998)**. Most of the naturally occurring particles, which contribute to both TOC and turbidity, have a net negative charge that causes them to remain in suspension. It has been stated that this net negative charge must be neutralized to permit flocculation of neutral particles into larger, settleable particles **(Shorney, 1998)**.

Randtke (1988) reported that dissolved NOM can be removed from solution during coagulation by precipitation or coprecipitation **(Randtke, 1988)**. Coprecipitation mechanism occurs when a substance is incorporated into a precipitate. This can happen when organic species are adsorbed onto the metal hydroxides as or after they form. Some scientists consider the removal mechanism for dissolved organics to include charge neutralization, accomplished by the interaction of protons and positively charged coagulant species with the negatively charged organic molecules, followed by adsorption of the neutralized or partially neutralized organics onto precipitated metal hydroxides **(Semmens and Field, 1980; Singer, 1989)**. **Randtke**

(1988) reported that removal of a soil fulvic acid at pH 6 corresponded to a 1:1 ratio of aluminum to carboxyl acid functional groups, strongly indicative of a precipitation reaction.
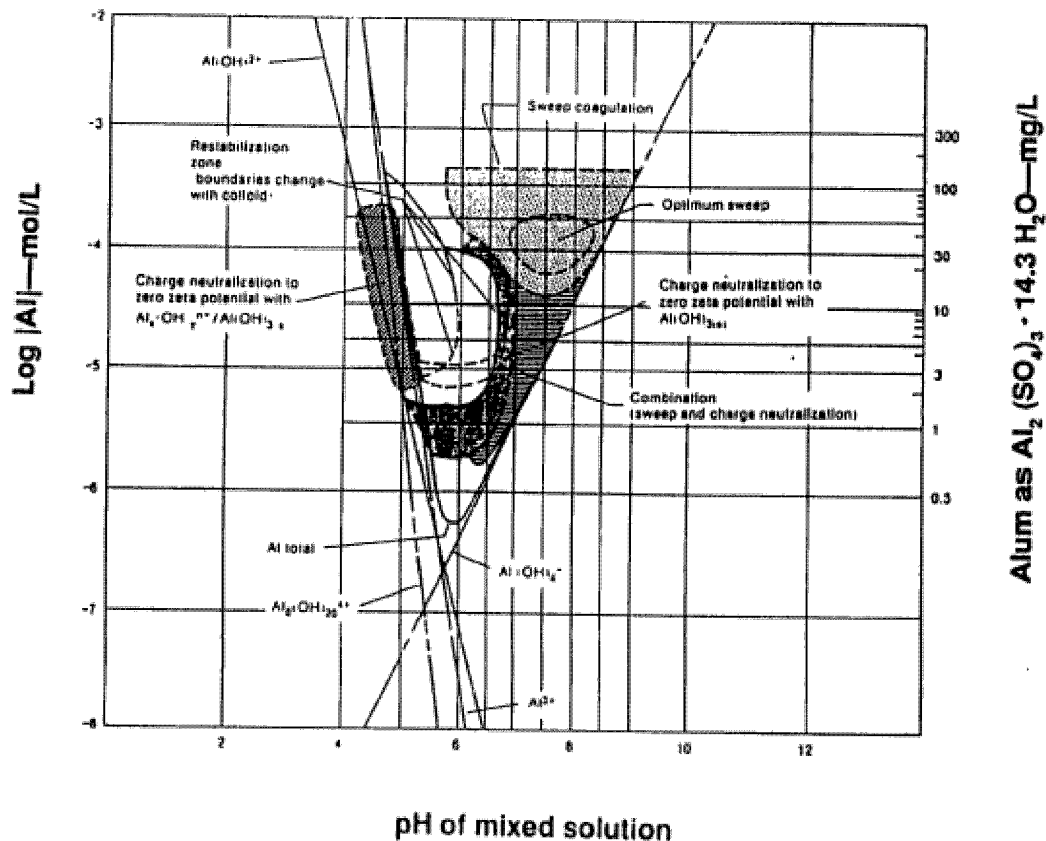
Figure 2.1: pC – pH diagram of aluminum hydroxide (Goodwill, 1997)

Several investigators reported that cationic coagulant species (which predominate at lower pH values) can adsorb to and neutralize these negatively charged particles; but, for this to occur, the amount of metal coagulant added to solution, the resulting solution pH, and the temperature must be conducive to the formation of an appropriate amount of positively charged coagulant species (Shorney, 1998). The conditions for optimum charge neutralization are site specific, and can be determined by a jar-test procedure.

Enmeshment, or sweep flocculation, is another important means of particle removal during coagulation process. When the dosage of metal coagulant is sufficient to form metal hydroxide precipitates, suspended panicles can become enmeshed in the precipitate (the particles serve as nucleation sites for precipitation of the metal

hydroxide solids and are incorporated into the precipitate) **(Shorney, 1998)**. Many conventional water treatment plants effectively use the enmeshment mechanism, especially those treating waters with variable turbidity and NOM concentrations in USA **(Shorney, 1998)**.
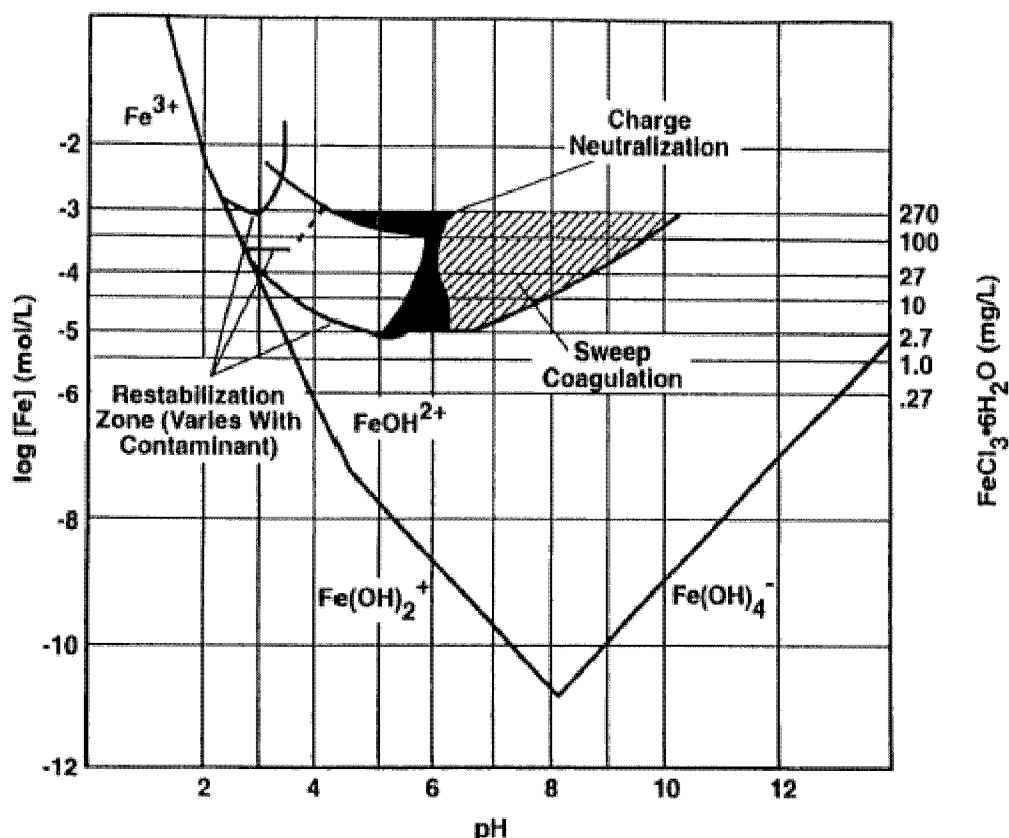
Figure 2.2: pC – pH diagram of ferric hydroxide **(Goodwill, 1997)**

Complexation is the binding of a central atom (metal cation) by a ligand (an organic compound). It has been reported that a complex may be soluble and remain in solution, it may be soluble but able to be removed by adsorption, or it may be insoluble and be incorporated into a homogeneous or heterogeneous precipitate **(Shorney, 1998)**. Complexation of metals by NOM has been studied by several researchers **(Schnitzer, 1971, Stevenson, 1982)**. The extent of complexation is a function of the type and concentration of the ligands and central atoms, as well as the solution pH and ionic strength. **Schnitzer (1971)** reported that one gram of fulvic acid could form soluble complexes with 84 mg of iron or 40 mg of aluminum, thus the potential exists for a significant fraction of the metal in the coagulant to be

complexed by the organics present in solution. While the molar ratio of metal to fulvic acid increases, the complexes become more insoluble and may form a metal fulvate precipitate. It has been determined that soluble aluminum and iron can exist in both inorganic and organic bound forms **(Van Benschoten and Edzwald, 1990)**.

Tadanier et al. (1997) found that that, after coagulation using $Al(SO_4)_3$ dosages less than 50 mg/L and $FeCl_3$ dosages less than 35 mg/L followed by filtration, significant fractions of the aluminum or iron remained in a colloidal state, whereas the remaining organics were in both dissolved and colloidal forms. The water used for experimental work was the hydrophobic acid fraction of organics extracted from Lake Drummond of the Great Dismal Swamp. Under these coagulation conditions, the metals added by the coagulants were "bound" by a fraction of the dissolved organics, which became more colloidal in nature as a result of coagulant addition. As the coagulant dosage approached the highest dosage value tested, the amount of residual colloidal metal decreased, presumably due to the formation of settleable flocs **(Tadanier et al., 1997)**.

Edwards and Benjamin (1997) modeled DOC removal by coagulation using iron or aluminum salts using a semi-empirical model based on a Langmuir adsorption isotherm **(Edwards and Benjamin, 1997)**. The model represents DOC removal as a function of the initial SUVA value of raw water, coagulant dosage, initial DOC concentration, and coagulation pH. The strong correlations found using Edwards' model suggest that adsorption mechanisms, such as those associated with coprecipitation, could be the prevailing removal mechanism for DOC. Further, there is abundant evidence that adsorption plays a major role in DOC removal. Thus, characteristics of metal hydroxide surfaces that influence DOC adsorption, including the surface charge and specific surface area, are of interest **(Shorney, 1998)**.

NOM molecules affect the surface charge of metal hydroxide precipitates. **Pommerenk et al. (1997)** reported that the presence of NOM caused the electrophoretic mobilities of iron flocs formed by $Fe_2(SO_4)_3$, and FeCl3 coagulation to be negative at pH values ranging from 5 to 6, whereas in NOM-free solutions the electrophoretic mobilities were positive.

The specific surface area of metal hydroxide precipitates could influence the amount of organic substances adsorbed during coagulation. **Meng and Letterman (1993)**

found that the specific surface area of $Al(OH)_{3(s)}$ was approximately 109 m^2/g, and for $Fe(OH)_{3(s)}$, 270 m^2/g. Besides, **Crosby (1983)** reported that the specific surface area for $Fe(OH)_{3(s)}$ ranged from 159 to 234 m^2/g. Hence, it appears that $Fe(OH)_{3(s)}$ has a higher specific surface area than $Al(OH)_{3(s)}$ such that it may be a more effective adsorbent for NOM if all other factors are equal **(Shorney, 1998)**.

2.4.5. Factors affecting coagulation

The extent of hydrolysis of all trivalent metal coagulants is dependent on various physical (mixing speed, intensity) as well as chemical (pH, temperature, dose etc.) parameters. The following sections are a brief discussion on these parameters that can affect hydrolysis, and ultimately, coagulation process **(Sinha, 1999)**.

2.4.5.1. Coagulant dosage

Coagulation or destabilization of dissolved/colloidal substances depends on the amount of coagulant added. Usually, inadequate coagulant dose will not effectively destabilized and excessive doses can cause detrimental effects. Therefore, there exists an 'optimal dose' at which coagulation is most effective. Adding coagulants beyond the optimum dose can have an adverse effect on the overall coagulation, where restabilization can happen.

Low coagulant doses cause ineffective coagulation due to insufficient hydroxy-complexes. Moreover, addition of coagulants provide complete destabilization., where effective coagulation occurs due to various monomeric and polymeric hydrolysis species (mechanism known as charge neutralization). Addition beyond this point will result in restabilization because of near complete coverage of colloid/particulates with the hydrolysis product, which then repel one another each other **(Sinha, 1999)**. Excess addition beyond this dose will cause in coagulant-precipitates, such as, $Al(OH)_3$ and $Fe(OH)_3$ solids, to form due to exceeding the solubility products of the coagulants **(Sinha, 1999)**. These bulky precipitates can swallow color and turbidity causing colloid/particulates and removing them as they settle a process the known as sweep flocculation. On the other hand, more coagulant would be demanded in this process, which, from the economical point of view, would be costly. However, at most water treatment plants in USA, coagulation takes place in the sweep floc range, because it is very difficult to coagulate water by an

optimum dose (charge neutralization) when the influent water quality is changing **(Snoeyink and Jenkins, 1980)**.

2.4.5.2. Coagulation of pH

The pH of water during coagulation has a deep influence on the effectiveness of coagulation for colloidal destabilization. The pH controls both the speciation of inorganic coagulants as well as the charge of the organic macromolecules. The pH concentration diagram (solubility diagram) for aluminum and iron hydrolysis (Figures 2.1 and 2.2) that indicates that there is a minimum solubility of these where a solid/precipitation phase predominates (metal-hydroxide present as $Al(OH)_3$ and $Fe(OH)_3$, respectively). For $Al(OH)_3$, this minimum solubility occurs from pH 5.5-6.5, whereas for ferric it occurs at pH >4. However, the solubility of $Al(OH)_3$ increases at lower and higher pH values, and the minimum solubility occurs in between these two extremes (Figure 2.1). This is because of $Al(OH)_3$ amorphoretic behavior where the solubility is controlled by various hydrolyzed species of different solubility.

Here ferric-hydroxide ($Fe(OH)_3$) provides much broader pH range for minimum solubility than $Al(OH)_3$. Hence, $Fe(OH)_3$ precipitates and will exist for a wider pH range than for $Al(OH)_3$ precipitates. Another important difference between $Al(OH)_3$ and $Fe(OH)_3$ is that $Fe(OH)_3$ is less amorphoretic (not as pronounced as $Al(OH)_3$). Thus, at higher pH level, it is less soluble than $Al(OH)_3$.. All of these differences could be significant in organo-metal interactions during water treatment.

2.4.5.3. Raw water alkalinity

Alkalinity is another important factor in coagulation. It gives water its buffering capacity, and in order to form the metal-hydroxide precipitates ($Al(OH)_3$ and $Fe(OH)_3$), the presence of alkalinity is necessary. In the case of the water having low alkalinity, it is necessary to add alkalinity by the addition of lime or soda-ash, such that it will be able to produce metal-hydroxide for effective destabilization. The following equation demonstrates the importance of alkalinity (the formation of metal-hydroxide) **(Knocke et al., 1986)**:

$$Al_2(SO_4)_3*14H_2O + 3Ca(HCO_3)_2 \rightarrow 2Al(OH)_3 + 3CaSO_4 + 14H_2O + 6CO_2$$

$2FeCl_3 + 3Ca(HCO_3)_2 \rightarrow 2Fe(OH)_3 + 3CaCl_3 + 6CO_2$
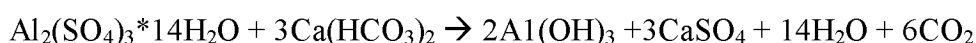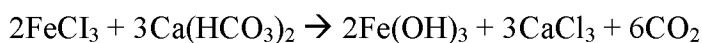
Usually, 0.5 mg/L and 0.62 mg/L of alkalinity are consumed for the addition of each mg/L of alum $(Al_2(SO_4)_3)$ and iron $(FeCl_3)$, respectively. However, waters with higher alkalinity levels may also require greater amounts of coagulant to achieve the optimum pH (pH 5-6 for alum, pH 4-5 for iron) for effective NOM removal, unless acid is added **(Sinha, 1999)**. Further, higher alkalinity also promotes a more of precipitated form of metal hydroxide $(Al_2(SO_4)_3)$ and iron $(FeCl_3)$, which translates into removal by adsorption and *sweep flocculation* than *charge neutralization*. In some water with high alkalinity, adjustment of pH to an optimum level is not feasible: the coagulation/flocculation pH is often near neutral pH where the predominance of hydroxide formation is expected. Hence, for high alkalinity- water, the predominant mechanism is to remove the dissolved/colloidal organic matter by *sweep flocculation* **(Sinha, 1999)**. For low alkalinity water, where the optimum coagulation can easily be reached by polycationicmetal-species, charge-neutralization may be effective. On the other hand, restabilization is more likely to occur for poorly buffered water. For low alkalinity-water, the addition of coagulants can dramatically lower the pH and the hydrogen ion may not compete the metal hydrolysis products for the ligand sites, and poor removal may occur. Therefore, for poorly buffered water additional alkalinity may be required such that appropriate amounts of coagulant doses can be delivered for effective destabilization **(Sinha, 1999)**.

2.4.5.4. Temperature

Knocke et al. (1986) described the effect of temperature on destabilization. Temperature affects viscosity and causes structural changes in floc structure, decreases the hydrolysis and precipitation kinetics, and can thus effect destabilization. It has been noted that lower temperature causes ineffective turbidity removal, although less so for soluble organic matter (DOC) **(Sinha, 1999)**. Among metal coagulants of alum and ferric chloride, alum was found to be less sensitive to temperature than ferric chloride.

2.4.5.5. Type of organic matter

The type of organic matter present can also affect the effectivity of coagulation. There are various types of organic matter in natural water of humic (humic and fulvic acids) and of non-humic (carbohydrates, protein, fats) origin. Because of their color, odor, biodegradation, and capabilities in forming carcinogenic by-products, humic portions (hydrophobic) of NOM have been studied in detail for coagulation. Further, the humic fraction is more favorable (due to hydrophobic) to treatment than non-humic portions (hydrophilic) of the NOM. More researches are still under going to investigate the removal of other fractions, if proven to be important in DBP formation.

Babcock and Singer (1979) showed that, within the humic portion, fulvic acid required about twice the Al^{+3} coagulant doses to achieve 80 percent removal of humic acid. This may be due to higher charge density of fulvic acid (functional groups) that may require higher coagulant dosages. Other research **(Sinsabaugh et al., 1986)** has reported that larger molecular weight more rapidly precipitates than do smaller and more hydrophilic molecules using iron (ferric suifate) as a coagulant. **Knocke et al. (1986)** studied both alum and iron for their effectiveness in molecular weight removal f organic precursors, and he concluded that ferric sulfate was more effective than alum in terms of the removal of the larger molecular weight (> 1.000 Dalton). However, alum is marginally effective in removing smaller molecular weight (< 1,000 Dalton) over ferric sulfate **(Sinha, 1999)**. These results indicated that humic and larger molecular weight NOM will be easier to remove than the smaller molecular weight of hydrophilic fraction by coagulation.

2.4.6. Mechanism of organo-metal interactions

Up to now, the discussion has been primarily focused on hydrolysis and on various factors that affect it. However, it is important also to discuss the interactions between these hydrolyzed species and various types of organic matters. Hydrolysis is a complex process, and the mechanisms by which these hydrolyzed species interact with organic matter are even more complex. On the other hand, it is important to have a generalized conceptual understanding of this complex phenomenon.

Four distinct mechanisms destabilization are (1) compression of the double layer, (2) adsorption to produce charge neutralization, (3) enmeshment for sneep flocailatwn. and (4) adsorption for inter-panicle bridging. Two of these mechanisms, charge neutralization and sweep flocculation **(Crozes et al., 1995)** are particularly important due to their dominance in water treatment. The effectiveness and ultimate removal of the organic substance is very much dependent on the type of binding that forms between the metal and organic matter. It has been reported that these bindings may vary from a weak physical adsorption to a strong chemical bonding involving complexation **(Rasid, 1985)**. The removal of NOM from water by metal coagulants may involve several chemical reactions, some of which are described briefly below.

2.4.6.1. Physical adsorption

Rasid (1985) reported that this phenomenon occurs primarily due to Van der Walls attraction or polarization arising from the rearrangement of macromolecules **(Rasid, 1985)**. Hence, an electrically positive fluctuation in one molecule causes an electrically negative fluctuation in a neighboring molecule, resulting in a net attractive force. But, adsorption of this kind by Van der Walls forces is weak. It has been reported that physical adsorption occurs with larger, more hydrophobic humic molecules, which provide more polarization through orientation to produce the molecular dipole for effective NOM removal, in comparison to lower molecular weight, non-humic molecules **(Rasid, 1985)**.

2.4.6.2. Cation exchange and complexation

This is the most common type of interaction (Figure 2.3) existing between the metal coagulant and NOM molecule. The mechanism involved here (charge neutralization) is the replacement of the dissociable hydrogen of the functional group by the positively charged metal ion (R-COOH + M⁻ → R-COO=M + H⁺). The pH of the media forces the magnitude of this reaction. Under acidic and neutral pH conditions, the hydrogen of the carboxylic group (pKa-4) provides competition for metal ions via protonation (R-COOH) and deprotonation (R-COO⁻). While under alkaline pH conditions, the hydrogen of the phenolic group (pKa~8) offers similar competition for the overall reaction **(Rasid, 1985)**.
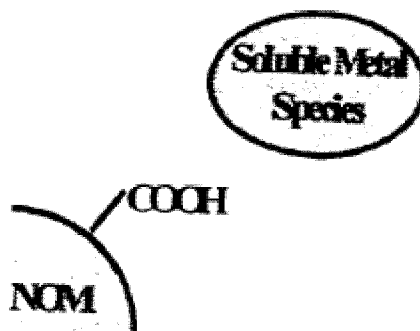
Figure 2.3: Cation exchange and complexation **(Sinha, 1999)**

NOM molecules contain many ligands in which oxygen, nitrogen, and sulfur atoms can act as electron donors **(Rasid, 1985)**. In chelation reactions, the metal ions are bonded to the organic molecules through the transfer of electrons and potential formation of a ring structure around the metal ions. To chelate with metal coagulants, one carboxylic and one phenolic functional group can react to form a bidentate complex **(Schnitzer, 1978)**. It has been found that between humic and non-humic fractions, it is generally believed that the humic fraction is more effective in interacting with the metal coagulants than the non-humic portion of NOM **(Sinha, 1999)**.

2.4.6.3. Surface complexation

Surface complexation may occur when metal concentrations are much larger than the reaction capacity of the functional groups of the organic substances present in the water **(Rasid, 1985)**. This issue can occur over wide pH ranges. However, it is more likely to occur during the sweep coagulation. The presence of metal concentrations, exceeding saturation advances precipitation and the formation of metal hydroxide surfaces. Sorption of this kind is very much dependent on both the properties of the organic matters as well as the physical and chemical properties of the hydroxide surface. Atkinson determined that surface charge develops as a result of deprotonation or protonation of the hydroxylated surfaces **(Atkinson et al., 1967)** and has a point of zero charge (PZC), where the net surface charge is zero; a pH above the PZC of the surface imparts a negative charge (anionic), and below it the surface exhibits a net positive charge (cationic).

3. MATERIALS AND METHODS

3.1. Experimental Procedures

3.1.1. Source water collection procedure

The natural water sources used in this study were Terkos Lake Water (TLW), Büyükçekmece Lake Water (BLW), and Ömerli Lake Water (OLW). Table 3.1 summarizes the average raw water quality data encountered during testing facilities. The raw waters were collected prior to any pretreatment. The raw water samples were collected as grab samples, and they were shipped to Istanbul Technical University, Environmental Engineering Department Laboratory on the same day. They were kept in the refrigerator for 21 days.

3.1.2. Glassware cleaning procedure

All routine glassware used during analysis were placed in a detergent bath over night, rinsed four times with hot tap water, rinsed two times ultra pure water and then placed in an oven at 150 °C for 2 hours. Besides, 2 and 40 mL vials used during THM measurements were placed in a ultra pure water over night, and then they were rinsed several times with hot ultra water, after that they were placed in oven at 550 °C for 1 hour.

3.1.3. Coagulation jar test procedure

Jar tests were performed using Phipps and Bird six paddle jar test apparatus. The jars were round beakers with one liter capacity. The reagent grade ferric chloride ($FeCl_3*6H_2O$) and aluminum sulfate ($Al_2(SO_4)_3*18H_2O$) doses were varied 20 to 160 mg/L. The coagulant dosages calculation was performed based on dry weight of ferric chloride and aluminum sulfate. The jar test mixing conditions were as follows: rapid mix at 150 rpm for 2 minutes, flocculation at 30 rpm for 30 minutes. After coagulation, jars were allowed to settle for 60 minutes prior to filtration through a

0.45 μm membrane filter. The filtrate from each jar was used to perform DOC, UV_{254}, and THM formation potential (THMFP) studies.

3.1.4. THMFP procedure

THM formation potential (THMFP) measurements were conducted in accordance with Standard Methods of 5710 B and EPA 551 **(APHA, 1998 and USEPA, 1990)**. Chlorination of water samples was carried out at pH 7.0 with phosphate buffer solution. An appropriate amount of concentrated sodium hypochlorite dosing solution was added to the raw and coagulated waters to obtain the desired chlorine dose. The chlorinated sample was then incubated in a dark room for 48 h and 7 days at 25 °C. The free chlorine residual was eliminated in the sample bottle, using ammonium chloride solution. Subsequent to both reaction periods, the chlorine residual concentrations were measured using the DPD ferrous titrimetric method in accordance with the Standard Methods 4500 Cl F **(APHA, 1998)**. This method involves addition of an indicator solution of diethylphenyldiamine (DPD) to the sample after addition of a phosphate buffer. The DPD turns red when oxidized by the chlorine. The sample is then titrated with ferrous ammonium sulfate (FAS), which reduces the DPD. The chlorine concentration is determined from the volume of FAS titrant required to return the DPD to colorless form.

3.2. Analytical Methods

3.2.1. DOC analysis

DOC measurements were performed with a Shimadzu TOC-5000 analyzer equipped with an auto sampler, according to the combustion-infrared method as described in the Standard Methods 3510 B **(APHA, 1998)**. The sample is injected into a heated reaction chamber packed with a platinum-oxide catalyst oxidizer to oxidize organic carbon to CO_2 gas. Inorganic CO_2 is measured by non-dispersive infrared analyzers and related to an equivalent concentration of organic carbon. The instrument provided reliable, accurate, and reproducible data with a minimum detection limit of 2 μg/L C. **Edzwald (1994)** suggested that DOC measurements were more representative than TOC for assessing the removal of dissolved DBP precursors by coagulation

3.2.2. UV$_{254}$ analysis

UV$_{254}$ absorbance measurements were performed in accordance with Standard Methods 5910 B **(APHA, 1998)** by a Shimadzu 1601 UV/Vis spectrophotometer at a wavelength of 254 nm with a 1 cm quartz cell. The samples were first filtered through a prewashed 0.45 μm membrane filter to remove turbidity, which can interfere with this measurement, and distilled ultra filtered (DIUF) water was used as the background correction on the spectrophotometer. The cell was rinsed with DIUF water and sample prior to being filled with sample for each absorbance measurement.

3.2.3. THM analysis

THM concentrations were determined with liquid-liquid extraction method according to Standard Methods 6232B **(APHA, 1998)**. The sum of the four trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) mass concentrations was reported as TTHM in μg/L. 35 ml THM samples were pipetted into a 40 ml vials, after that, 3 ml of pentane were transferred to each vial. The vials were then shaken vigorously phase separation. The pentane extract was analyzed by a Agillent Gas Chromatography (6890 Series) with an micro electron capture detector (GC-μECD), auto sampler and capillary column (J&W Science DB-1), 30 m × 0.32 mm I.D.×1.0 μm film thicknesses. The system was supported by a HP Chemstation software. Calibration standards were prepared from primary stock solutions of the analytes in methanol obtained from a commercial source (AccuStandard, Inc. New Haven, CT). Sets of six (including a blank) were prepared for each batch of samples. The carrier gas used was helium and the make-up gas was nitrogen. The injection technique was split/splitless and the carrier gas flow was 1.6 ml/min. The minimum reporting levels (MRLs) obtained with this method are 0.1 μg/L. This procedure allowed for the identification of 17 different volatile organic compounds. For the purposes of this study, interest will be focused strictly on the four THM species **(Uyak et al., 2005)**.

3.2.4. Routine parameters analysis

Alkalinity, pH, and temperature measurements were performed in accordance with Standard Methods **(APHA, 1998)**.

Table 3.1. Average raw waters quality parameters*

Parameters	Unit	TLW	BLW	OLW
pH	-	7.80	8.05	7.05
Turbidity	NTU	3.5	4.8	2.7
Alkalinity	mg/L	115	137	65
Bromide ion	µg/L	180	170	60
Temperature	°C	16.2	17.3	16.4
DOC	mg/L	4.10	4.06	3.66
UV_{254}	1/cm	0.126	0.132	0.083
SUVA	L/mg×m	3.07	3.25	2.27
THMFP	µg/L	285	272	215

*Data obtained during March 2003 and September 2005.

4. ENHANCED COAGULATION OF DBP PRECURSORS REMOVAL

4.1. Objectives

The objectives of this chapter were to evaluate the effect of alum and ferric chloride coagulation dosages on DBP precursors removal. Thus, DOC, UV_{254}, SUVA, and the associated reductions in THMFP removal in TLW, BLW and OLW were investigated.

4.2. Introduction

The disinfection of water with chlorine results in formation of DBP, such as THM and HAA **(Rook, 1974; Crozes et al., 1995; Krasner and Amy, 1995)**. It has been shown that NOM is a likely precursor material for THM and HAA formation. Among DBP found in chlorinated water, THM and HAA have been the focus of particular attention, because they are considered potentially carcinogenic **(Crozes et al., 1995; Vrijenhoek et al., 1998)**. Concerns about health risks associated with DBP have prompted several industrialized countries to establish maximum acceptable levels for THM and HAA concentrations in drinking water. In the USA, more stringent DBP regulations have been promulgated, placing limits on THM and HAA. The USEPA drinking water limits for THM and HAA is 80μg/L, and 60μg/L, respectively **(USEPA, 1998)**. Recently most of the European Countries regulated THM in their water at the level of 100μg/L **(EECD, 1998)**. However, up to 2004, there was no any DBP limit for THM in Turkish Drinking Water Regulation. In 2005, a new drinking water regulation has been ruled by Turkish Ministry of Health, and the THM limit has been regulated as 150 μg/L **(RCWIHC, 2005)**.

Enhanced coagulation efficiently removes DBP precursors of DOC and UV_{254} from source water **(Vrijenhoek et al., 1998)**. The term of enhanced coagulation refers to the modification of the coagulation process to achieve greater DBP precursors treatment. **(Crozes et al., 1995)**. Reduction in the concentration of organic precursors

prior to the application of disinfectant could be expected to result in a decrease in DBP formation.

4.3. Results and Discussion

4.3.1. Effects of coagulant dosage on DOC removal

Data obtained at three source waters were used to compare two types of coagulants of ferric chloride, and alum. Figure 4.1, 4.2, and 4.3 show DOC data for dosage of these two coagulants ranging from 20 to 160 mg/L, when treating TLW, BLW, and OLW. The coagulants dosages calculation was performed based on dry weight of ferric chloride and aluminum sulfate. The points of DOC data shown on the y-axis represent the coagulated raw water DOC at the time of the experiment. It is shown in these figures that, at similar coagulant dosages, ferric chloride consistently outperformed alum in terms of DOC removal from raw waters. As both coagulants dosages increased further, the reduction in DOC also increased gradually. Figure 4.1, 4.2, and 4.3 show that ferric chloride has the maximum DOC removal capacity of 55, 58, and 28% at the dosage of 140, 120, and 120 mg/L, for TLW, BLW, and OLW, respectively. While maximum DOC removals of TLW, BLW, and OLW were obtained at the alum dosages of 120, 120, and 100 mg/L, respectively. The enhanced coagulated DOC with alum coagulation in TLW, BLW, and OLW were as low as 2.06, 2.20, and 3.22 mg/L, representing an overall DOC removal through coagulation approaching 50, 48, and 17%, respectively. Further, ferric chloride lowers the DOC level of TLW, BLW, and OLW to 1.84, 1.78, and 2.80 mg/L. The overall fraction of NOM amenable to coagulation by ferric chloride is greater than for alum. This shows a greater affinity of a fraction of NOM for ferric hydroxide floc than for aluminum hydroxide floc. This difference in adsorption capacity is likely due to more active adsorption sites on the ferric hydroxide flocs **(Crozes et al., 1995)**. Several explanations can be provided for the observation. First, ferric chloride coagulant presents roughly two times more active positive charges than aluminum sulfate **(Crozes et al., 1995)**. Therefore, colloid destabilization and the formation of humates and fulvates can both be expected to be achieved with ferric chloride at half the dosage of alum **(Crozes et al., 1995)**. Also, it is examined that the alkalinity consumed during the formation of the metal hydroxides is two times higher for ferric chloride than alum. Consequently, for a similar coagulant dosage, the coagulation pH

will be lower with ferric chloride than with alum. As mentioned in literature, the lower pH, by increasing the protonation of the humic substances and increasing the positive charge of the coagulating species, reduces the coagulant demand and favors the adsorption of organics onto metal hydroxides **(Edwards and Benjamin, 1997)**.

Ferric hydroxide and aluminum hydroxide flocs are very different in terms of specific surface area, surface charge and extent of active adsorption sites **(Crosby, 1983)**. **Crosby (1983)** determined that the specific surface area of iron hydroxide floc ranges between 160 and 230 m^2/g , while, **Bottero and Bersillon (1989)** determined that aluminum hydroxide flocs are of the same order of magnitude, ranging from 200 to 400 m^2/g. However, due to the higher concentration of active metal in ferric chloride solution and the higher molecular weight of iron, a similar dose of ferric chloride is likely to produce 2.8 times more metal hydroxide by weight than a similar dosage of alum **(Bottero and Bersillon, 1989)**. As a result of the coagulant performance comparison, it appeared that ferric chloride is the better-suited coagulant for enhanced coagulation for TLW and BLW, while for OLW, enhanced coagulation is not suitable alternative. Ferric chloride offered the advantages of reduced sludge production, a greater acidity that would reduce the cost of coagulation pH adjustment, and the potential for removing a greater fraction of NOM amenable to coagulation. An enhanced coagulation primary goal is to achieve DOC removal to allow the use of free chlorine as a primary disinfectant, and potentially as a residual disinfectant in the distribution system.

On the other hand, according to EPA, if you water DOC level is below 2 mg/L, it is expected that the formation of THM is always below the 80 µg/L **(Krasner and Amy, 1995)**. Thus, for our study, ferric chloride reduced the concentration of DOC below 2.0 mg/L in TWL and BLW, while the level of DOC in ferric treated OLW is about 2.0 mg/L. Thus, it can be concluded that ferric chloride coagulation removed grater amount of DOC from these three water supplies, and substantial reductions in DOC concentrations result in low level of THMFP based on EPA and EU THM limit of 80 and 100 µg/L. However, DOC concentrations were found to be 2.06, 2.20, and 2.63 mg/L with alum coagulation in TLW, BLW, and OLW, respectively. All of DOC concentrations are above 2.0 mg/L EPA DOC criteria. Therefore, alum seems to be not suitable coagulant for these water sources under enhanced coagulation

conditions. But, to comply with international THM standards by using alum coagulant, pH optimization seems to be required for these water supplies.

Table 4.1: Average raw waters quality parameters*

Parameters	Unit	TLW	BLW	OLW
pH	-	7.78	8.00	7.15
Turbidity	NTU	1.9	2.3	1.8
Alkalinity	mg/L	115	130	68
Bromide ion	µg/L	120	150	70
Temperature	°C	13.2	14.5	13.4
DOC	mg/L	4.12	4.22	3.89
UV_{254}	1/cm	0.1250	0.1310	0.0820
SUVA	L/mg×m	3.03	3.10	2.11
THMFP	µg/L	295	255	203

*Data obtained during April 2003 and September 2003.
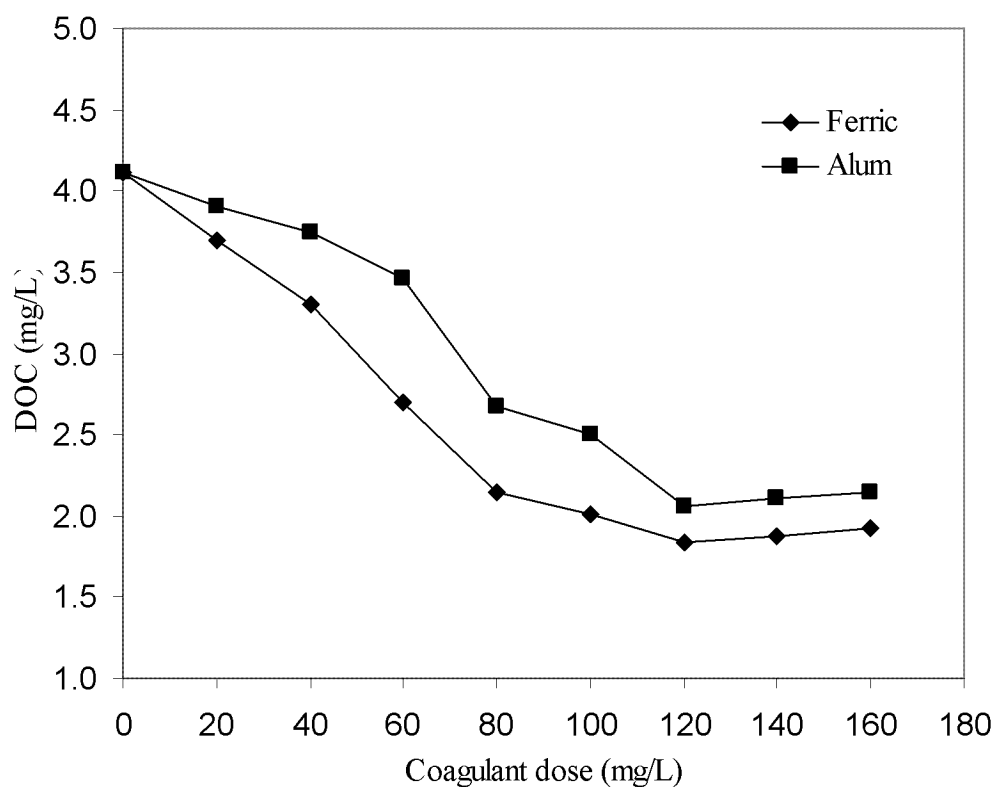
Figure 4.1: Dissolved organic carbon (DOC) removal with alum and ferric chloride in TLW
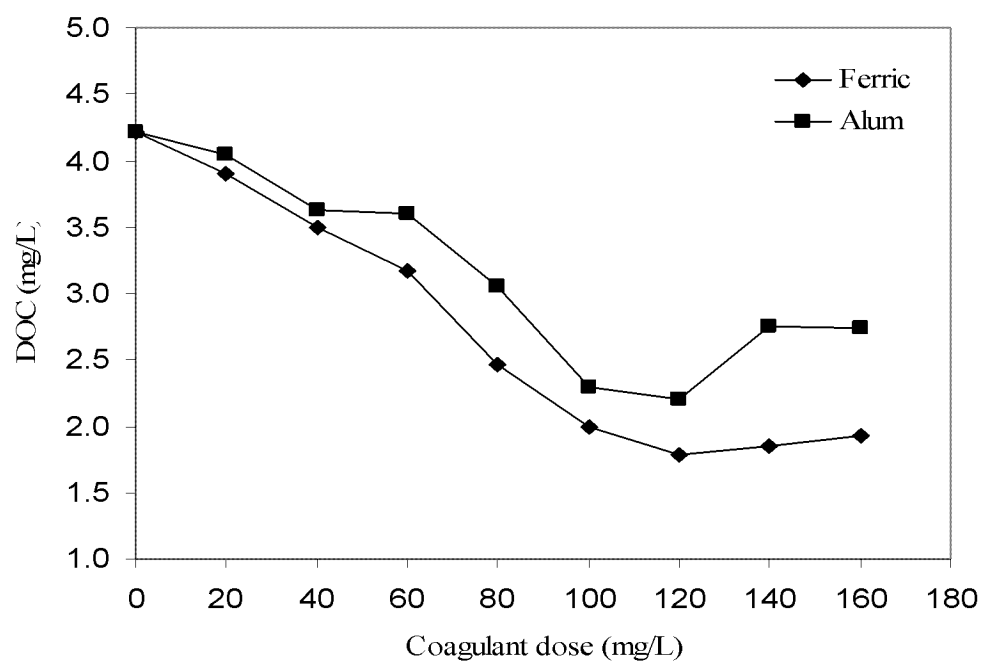
Figure 4.2: Dissolved organic carbon (DOC) removal with alum and ferric chloride in BLW
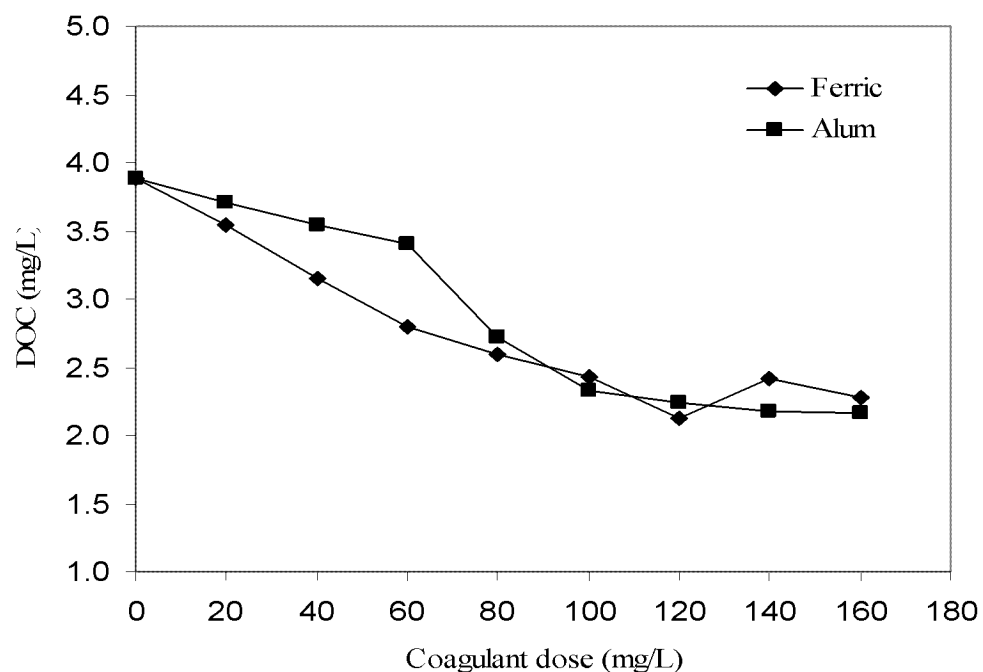
Figure 4.3: Dissolved organic carbon (DOC) removal with alum and ferric chloride in OLW

4.3.2. Effects of coagulant dosage on UV_{254} removal

UV_{254} is an indicator of organic compounds such as benzene rings or unsaturated straight-chain containing compounds with a series of double bonds **(Sawyer et al., 1994)**. Researches have shown that UV_{254} is a good indicator of the humic content of NOM and it is a better surrogate for THMFP **(Uyguner and Bekbolet, 2005)**. A high correlation has been reported **(Owen et al., 1993)**, showing that UV absorbing compounds tend to confirm the presence of THM precursors. Good correlations of UV_{254} absorbance with the aromatic content of NOM have been reported for humic and fulvic acids extracted from various water sources **(Chin et al., 1994)**. UV_{254} of humic materials can provide insight into the nature of the organics present and the potential for THM formation. For this study, Figure 4.4, 4.5, and 4.6 shows the levels of UV_{254} obtained at the various levels of ferric chloride and alum dosage in TLW, BLW, and OLW. Ferric chloride reduced the UV_{254} levels to 0.031, 0.038, and 0.040 cm^{-1} with the dosages of 160, 120, 140 mg/L for TLW, BLW, and OLW, respectively. While, 140, 100, and 140 mg/L alum coagulation of aromatic substances resulted in an UV_{254} levels of 0.041, 0.050, and 0.046 cm^{-1}, for TLW, BLW, and OLW, respectively. The percent removal of UV_{254} with ferric chloride in TLW, BLW, and OLW were about 76, 71, and 54%, respectively. However, alum has the maximum UV_{254} removal capacity of 67, 62, and 44% for TLW, BLW, and OLW respectively. As observed in all the cases, these three figures show that, at similar coagulant dosages, ferric chloride consistently removed more UV_{254} than alum. In this study, the UV_{254} material was generally removed to a greater extent than DOC. In Figure 4.13 and Figure 4.14, a comparison of DOC versus UV_{254} is shown for ferric chloride and alum coagulation in three source waters. It is shown in these figures that the removal amount of UV_{254} were higher than those of DOC for a given jar tests. These results are consistent with literature findings suggesting that aromatic materials are removed more effectively by chemical coagulation than other NOM fractions **(Najm et al., 1994; Edzwald et al., 1985)**. Removal of aromatic substances is not obligator for water utilities. But, Turkey as a candidate country for EU, in order to comply with EU THM limit of 100 μg/L in water distribution system, Istanbul-city water treatment plants using TLW, BLW, and OLW have to remove THM precursors of UV absorbing substances from raw waters during treatment periods. Furthermore, the amount of maximum UV_{254} removal for TLW and BLW

were higher than OLW at all cases. One reason for these differences is that OLW has lower humic content than those of TLW and BLW. As shown in Table 4.1, raw water UV_{254} value of OLW was 0.0820, whereas TLW and BLW raw waters have the UV_{254} level of 0.1250 and 0.1310, respectively. As stated in literature, higher UV_{254} level of raw waters have higher level of hydrophobic substances, thus, hydrophobic content of raw water is effected coagulation more effectively.

4.3.3. Effects of coagulant dosage on SUVA removal

Raw water SUVA values of TLW, BLW, and OLW were 3.03, 3.10, and 2.11, respectively (Table 4.1). **Edzwald et al. (1985)** found that SUVA values higher than 3 describe a relatively hydrophobic DOC, mainly containing aquatic humic material of high molecular weight which is likely to be effectively removed during coagulation. On the contrary, SUVA values of less than 3 indicate that the DOC is hydrophilic, low in molecular weight, low in charge density, and only slightly affected by coagulation. For the 3 water samples studied, SUVA values decreased significantly after coagulation (Figure 4.7, 4.8, and 4.9). The highest DOC removal of 58% was observed for the BLW sample with the highest SUVA (SUVA = 3.10 L/mg*m) treated with ferric chloride. Alternatively, the lowest DOC reduction was observed (17%) for sample OLW, with a SUVA of 2.11 and a raw water DOC concentration of 3.89 mg/L. The average removal of DOC for TLW sample with SUVA value of 3.03 was 55% with ferric chloride coagulation. Several studies have shown that humic substances are preferentially targeted during coagulation **(Randtke, 1988, White et al., 1997; Sinsabaugh et al., 1986)**. For example, the comparison of ^{13}C NMR spectra of water samples before and after chemical coagulation demonstrated that aromatic carbon was preferentially removed **(Harrington and Singer, 1996)**. Furthermore, the nature of humic substances also impacts their removal.

The percent removal of SUVA with ferric chloride in TLW, BLW, and OLW were about 43, 49, and 34%, respectively. However, alum has the maximum SUVA removal capacity of 37, 38, and 32% for TLW, BLW, and OLW respectively. The removal rates of hydrophobic compounds were found to be higher those of hydrophilic compounds **(Tryby et al., 1993)**. **Huang and Yeh (1993)** reported that coagulation removed 50 and 35% of humic and fulvic acids present in colored waters, respectively.
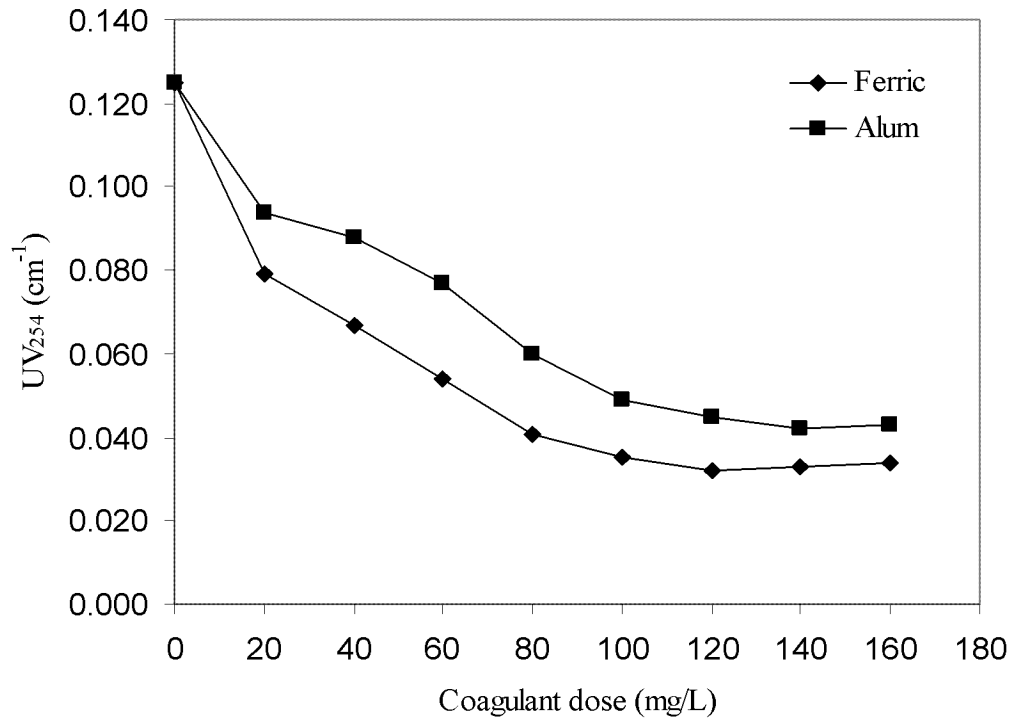
Figure 4.4: UV_{254} removals with ferric chloride and alum in TLW
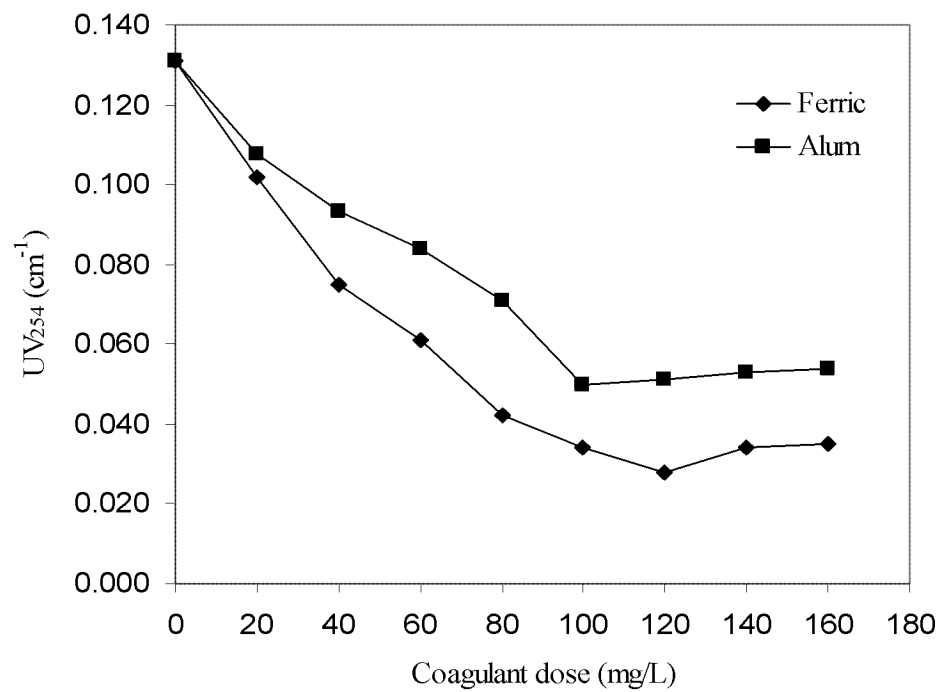
Figure 4.5: UV_{254} removals with ferric chloride and alum in BLW
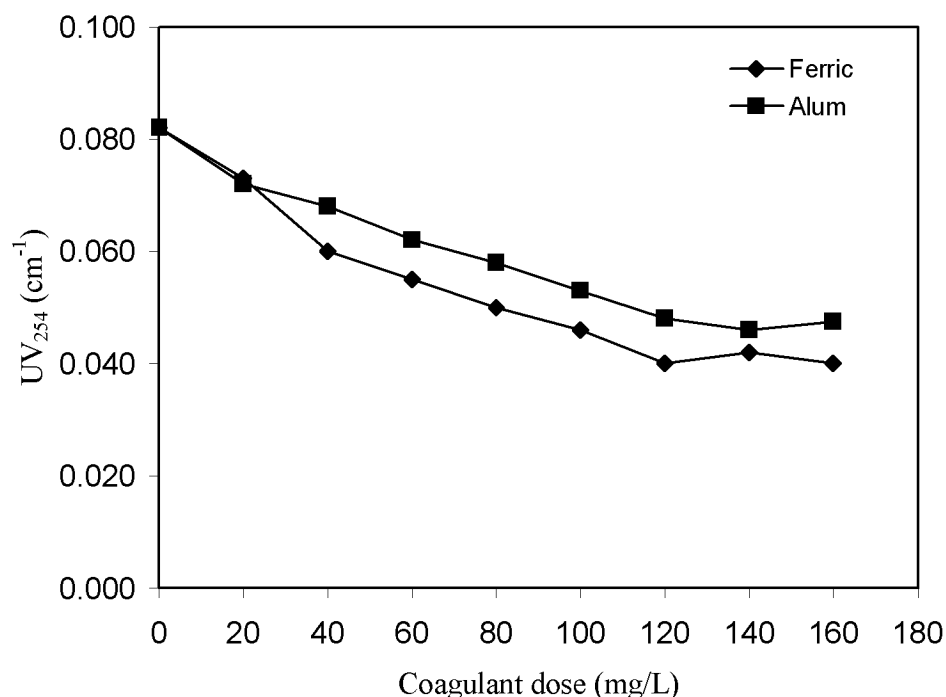
Figure 4.6: UV_{254} removals with ferric chloride and alum in OLW

4.3.4. Effects of coagulant dosage on THMFP removal

The THMFP tests were used to evaluate one aspect of THM formation resulting from precursor removal by enhanced coagulation. The total THM (sum of $CHCl_3$, $CHBrCl_2$, $CHClBr_2$, and $CHBr_3$) formed as a function of ferric chloride and alum dosage are shown in Figure 4.10, 4.11, and 4.12. Reduction in THMFP is attributed to removal of THM precursors. Thus, the trends in THMFP reduction as a function of ferric chloride and alum dosage are similar to those observed with DOC. These three figures show the reduction of THMFP with treatment by ferric and alum coagulants. The jar tests results indicated that ferric chloride was found to be more effective than alum in terms of THMFP removals. Ferric chloride reduced the THMFP level to 71, 73, and 103 µg/L with the dosages of 120, 120 and 100 mg/L for TWL, BLW and OLW, respectively. While, 120 mg/L aluminum sulfate coagulation resulted in a THMFP level of 110, 127, and 125 µg/L in TWL, BLW, and OLW, respectively. Based on 7 day THM formation studies, when consider 80 and 100 µg/L THM limit of EPA and EU, ferric chloride treatment in TLW and BLW meet these international THM regulations, while ferric coagulation of OLW does not meet the any of these THM limits. Thus, enhanced coagulation with ferric chloride appears to be

an effective treatment technique for THMFP removal from TLW and BLW. However, THMFP removal with alum coagulation needs to be modified by arranging pH value of enhanced coagulation. It was concluded that the THMFP was generally removed greater than DOC compounds in the ferric chloride and alum coagulation studies (Figure 4.15 and 4.16). Overall, enhanced coagulation resulted in greater THMFP, and the substantial reductions in THMFP were related to the increased DOC removal. As shown in Figure 4.15 and 4.16, the difference between ferric and alum reduction levels of THMFP is attributed to a greater affinity of a fraction of NOM for ferric hydroxide floc than for aluminum hydroxide floc **(Crozes et al., 1995)**. Moreover, the reduction in THMFP increased with increasing both coagulant dosages.
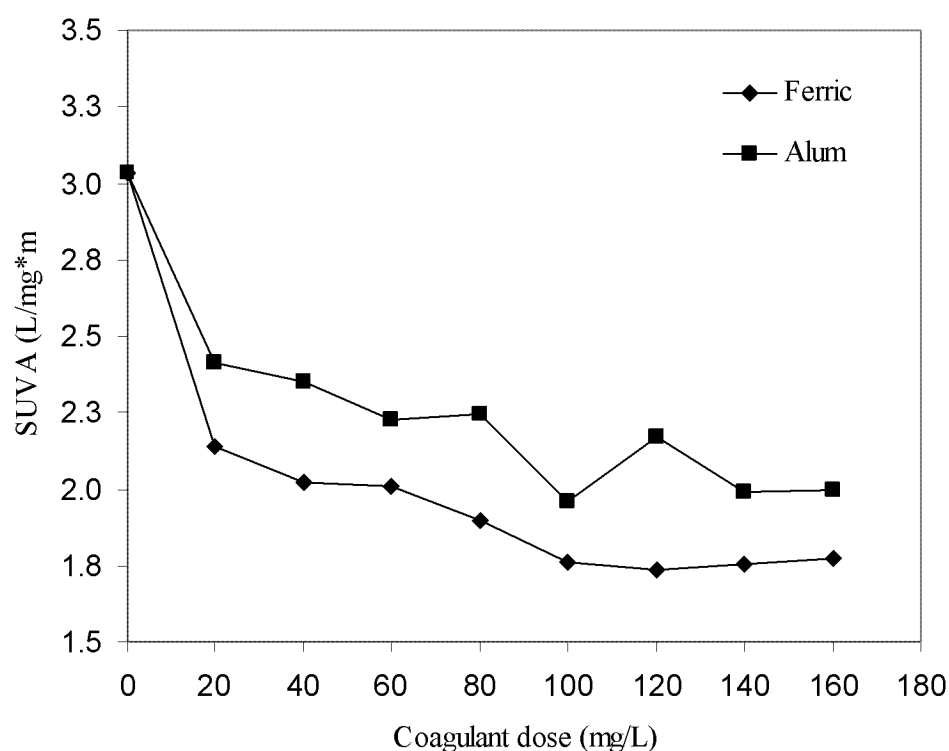
Figure 4.7: SUVA removals with ferric chloride and alum in TLW
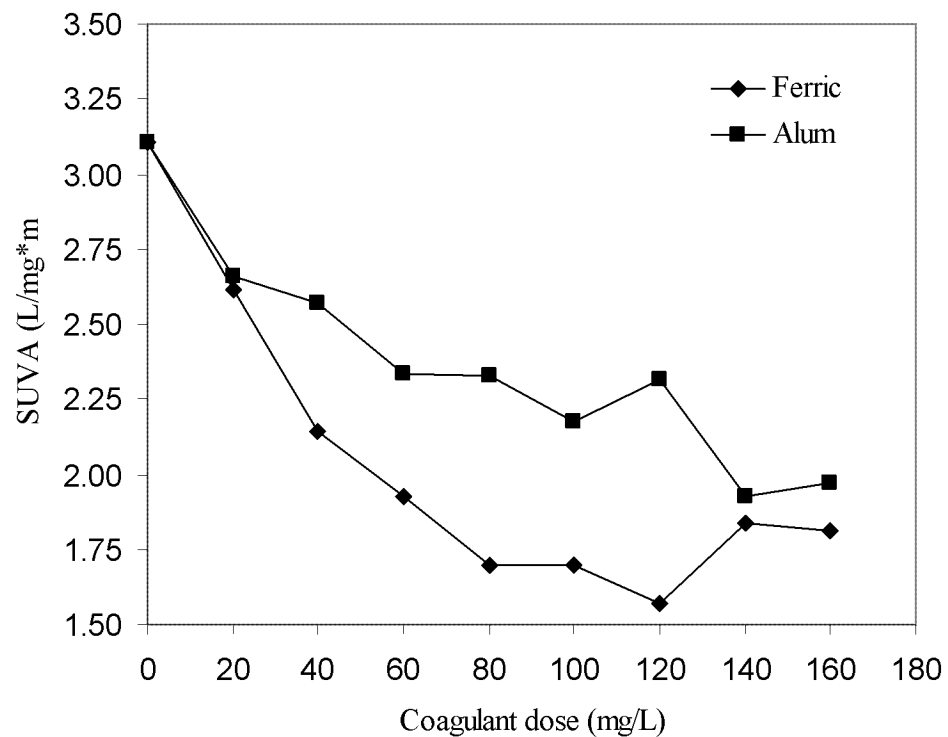
Figure 4.8: SUVA removals with ferric chloride and alum in BLW
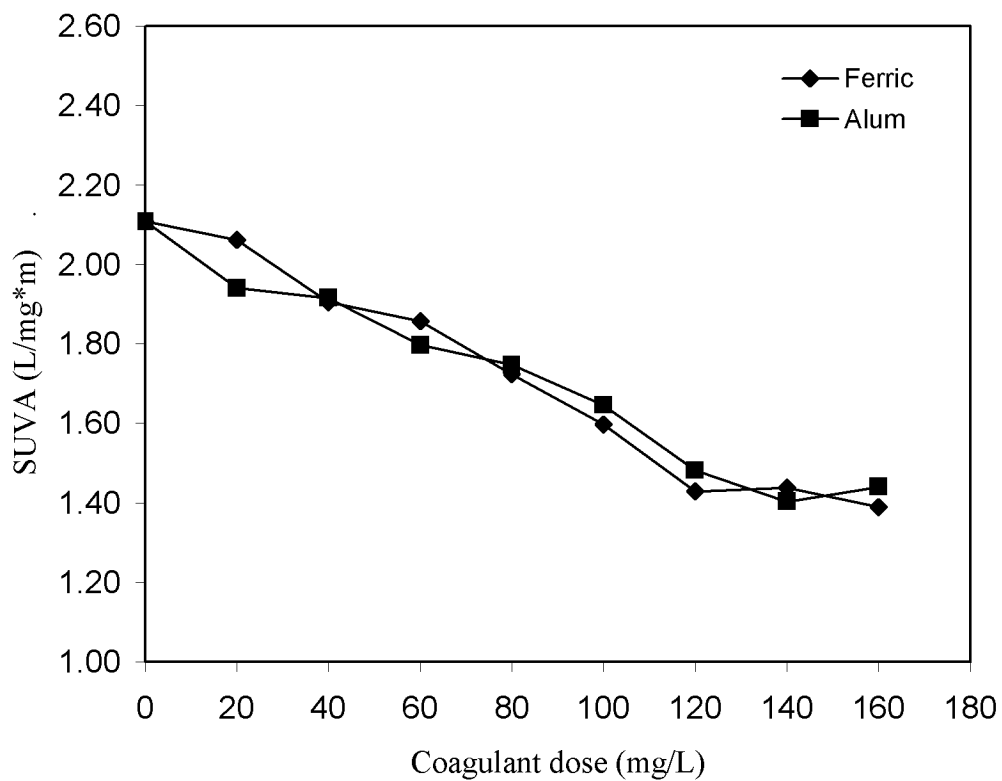
Figure 4.9: SUVA removals with ferric chloride and alum in OLW

57
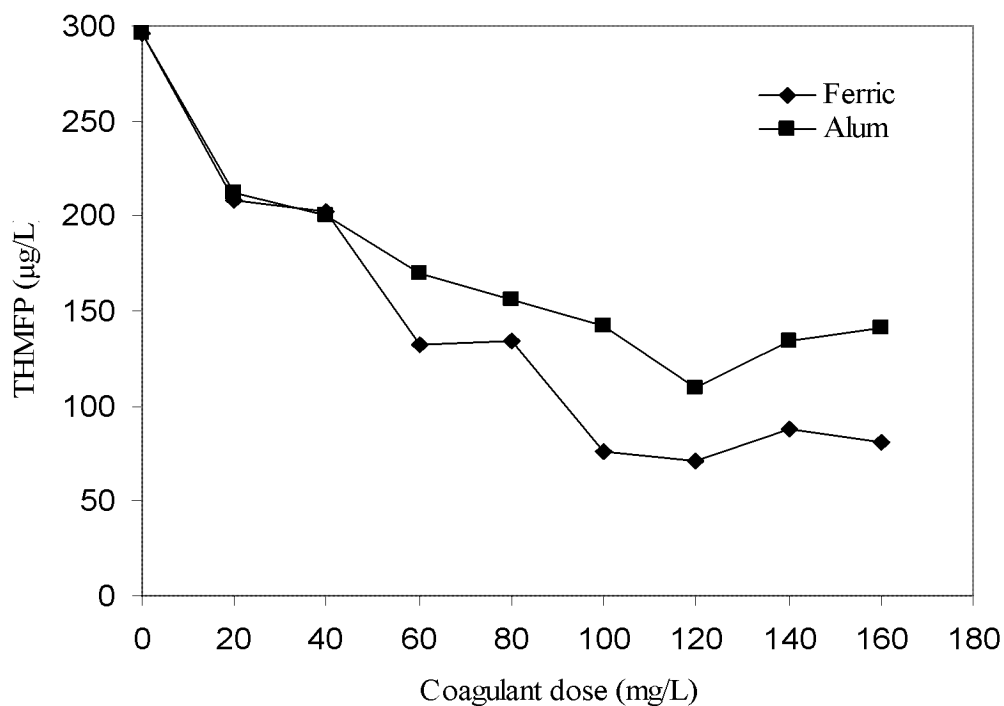
Figure 4.10: Removal of THMFP as a function of ferric chloride and alum dose in TLW
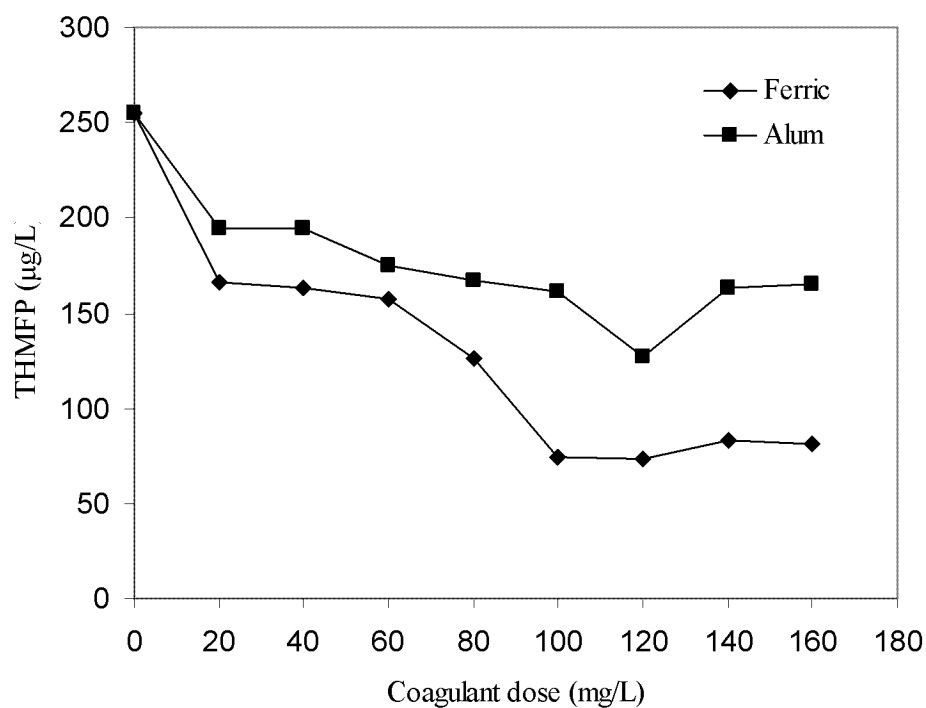
Figure 4.11: Removal of THMFP as a function of ferric chloride and alum dose in BLW
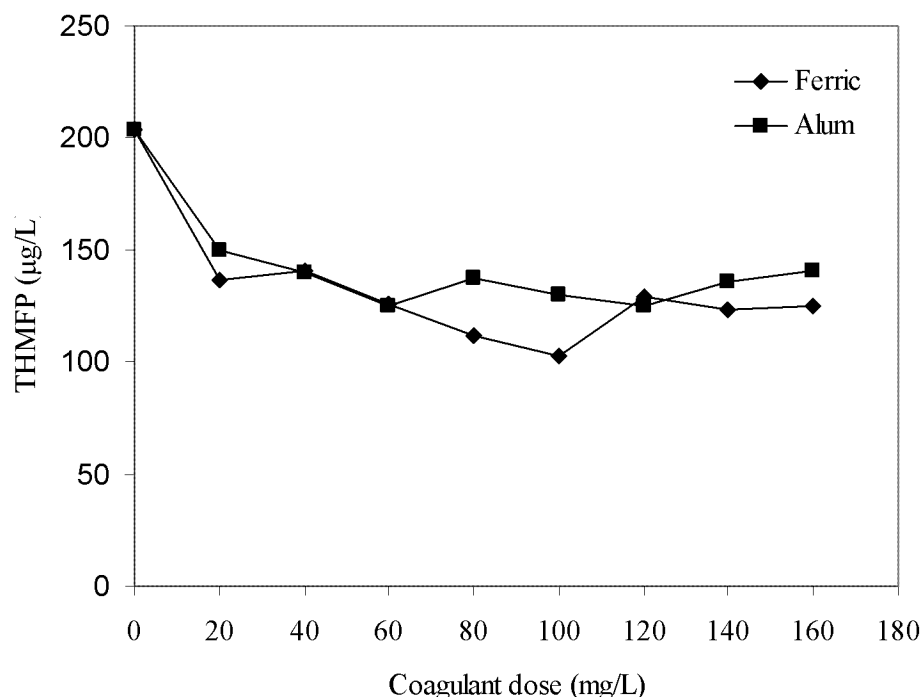
Figure 4.12: Removal of THMFP as a function of ferric chloride and alum dose in OLW

4.3.5. Comparison of THM precursors removal for three water sources

Enhanced coagulation reduced the DOC level by of 55, 58, and 28% and the UV_{254} absorption by 74, 79, and 51% in TLW, BLW, and OLW, respectively, suggesting that enhanced coagulation with ferric treatment preferentially removed organic compounds with higher UV absorption. On the other hand, alum treatment of enhanced coagulation reduced the DOC level in TLW, BLW, and OLW 50, 48, and 17%, and this alum coagulation condition resulted in 66, 62, and 44 % UV_{254} from TLW, BLW, and OLW, respectively. From Figure 4.13 and 4.14, the percent reductions of UV_{254} absorbance with ferric chloride and alum were higher than those of DOC in three surface water supplies. The humic fraction, which absorbs UV light at 254 nm, is more effectively removed by coagulation than the nonhumic fraction **(Edzwald et al., 1985; Najm et al., 1994; Krasner and Amy, 1995)**. This explanation also accounts for the greater percent removal of UV_{254} absorbance in TLW and BLW due to high level of SUVA values. Moreover, **Reckhow and Singer (1990)**, among other researchers, have demonstrated that coagulation removes TOC, UV_{254}, and THMFP in the following order: UV_{254}>THMFP>TOC. Therefore,

enhanced coagulation was deemed best available technology (BAT) for the control of THM and HAA in drinking water **(Krasner and Amy, 1995)**.

As stated in Table 4.1, specific ultraviolet absorbance (SUVA) values were 3.03, 3.10 and 2.11, for TLW, BLW, and OLW, respectively. TLW and BLW represent average humic content, while OLW represents low level of humic content. As shown in Figure 4.13 and 4.14, the moderate humic fraction in TLW and BLW result in greater humic fraction removal and greater overall NOM removal. The low level humic fraction of OLW results in lower humic content treatment and low DOC removal. Overall, the UV_{254} generally decreases with increasing coagulant dose, indicating preferential removal of the humic fraction. This result supports the conclusion that NOM in TLW and BLW was as amenable to chemical coagulation because of their moderate humic fraction. Therefore, enhanced coagulation is very effective for these two water sources. Since OLW has low level of SUVA, the average percent reduction of DOC and UV absorbing substances with enhanced coagulation of ferric chloride was about 28 and 51 %, respectively. Besides, alum removed average 17 and 44 % DOC and UV_{254} from OLW, respectively. Based on EPA TOC removal and Alkalinity matrix table (Table 4.2.), the percent removal of TOC in OLW is expected to be 35%. For ferric chloride coagulation of OLW, EPA requirement was not meet. On the other hand, any of alum dosages meet EPA requirement for OLW as well. Thus, in order to reduce DOC concentration of OLW with enhanced coagulation, a pH optimization studies should be performed. In the next chapter of this study, optimized coagulation issue is explained and studied in detail.

Table 4.2: EPA Alkalinity and total organic carbon (TOC) matrix for percent TOC removal goals by enhanced coagulation

TOC	Alkalinity mg/L as $CaCO_3$		
	0-60.0	60.0-120.0	>120.0
mg/L	percent	percent	percent
2.0-4.0	35	25	15
4.0-8.0	45	35	25
>8.0	50	40	30

As shown in Figure 4.15, increased DOC removal with ferric chloride in enhanced coagulated TLW, BLW and OLW sources resulted in 61, 52, and 45% reduction in THM levels, respectively. Besides, alum treatment of enhanced coagulation reduced the DOC level in TLW, BLW, and OLW 50, 48, and 17%, and this alum coagulation condition resulted in 55, 38, and 39% THMFP from TLW, BLW, and OLW, respectively. Previous studies indicated that DOC may be used as a surrogate of THM precursors because humic substances typically comprise 50% of DOC in surface water supplies. **Adin et al. (1991)** investigated the formation of THM and their experimental results indicated that under fixed chlorine levels and reaction times of 24 hours, THM production increased until the chlorine was depleted and then decreased while fulvic or humic acids concentrations were increasing consistently. However, most investigators found that at low concentrations of humics, in the presence of excess chlorine, THM formation rose with increasing dissolved organic matter with a pseudo first order reaction of DOC **(Kavanaugh et al., 1980; Babcock and Singer, 1979)**.
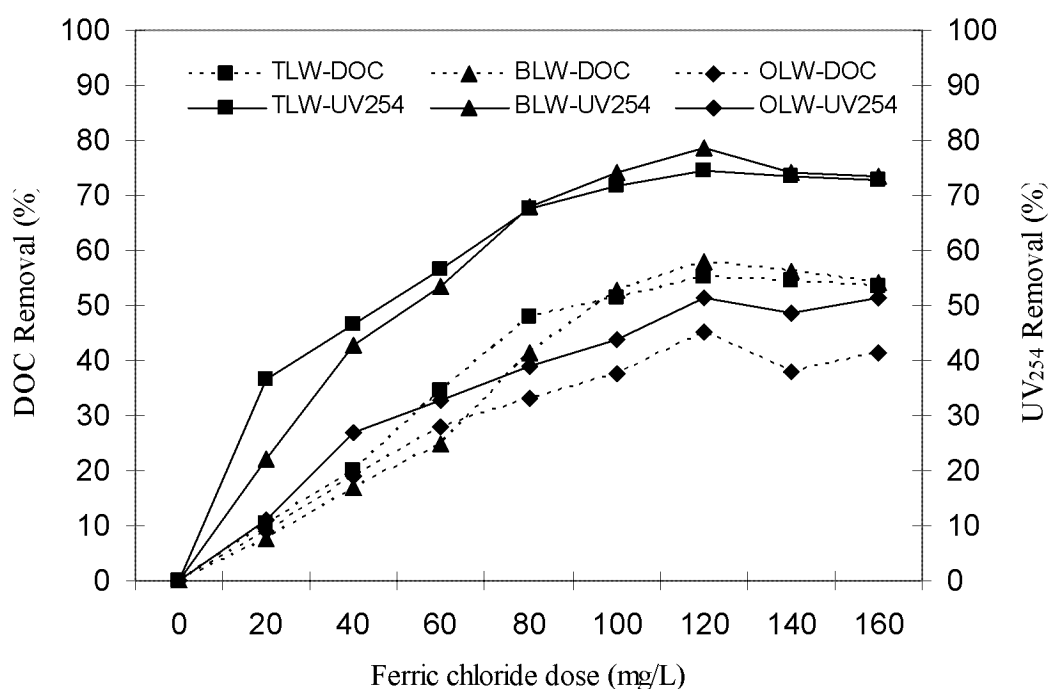
Figure 4.13: Removal of DOC versus UV_{254} as a function of ferric chloride dosages
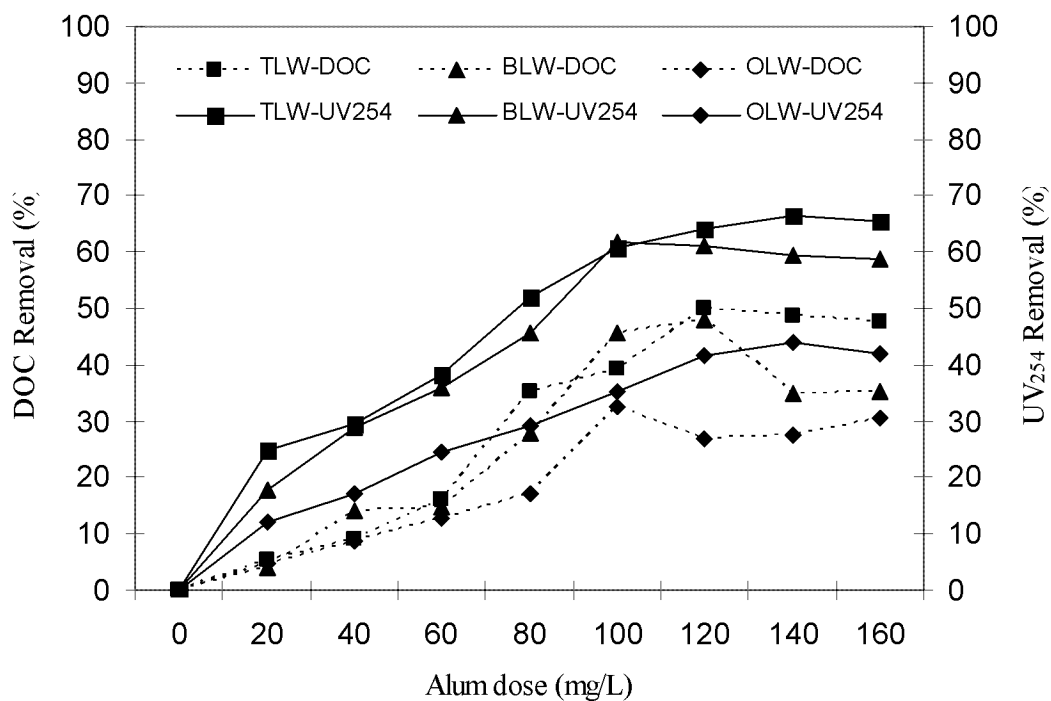
Figure 4.14: Removal of DOC versus UV_{254} as a function of alum dosages
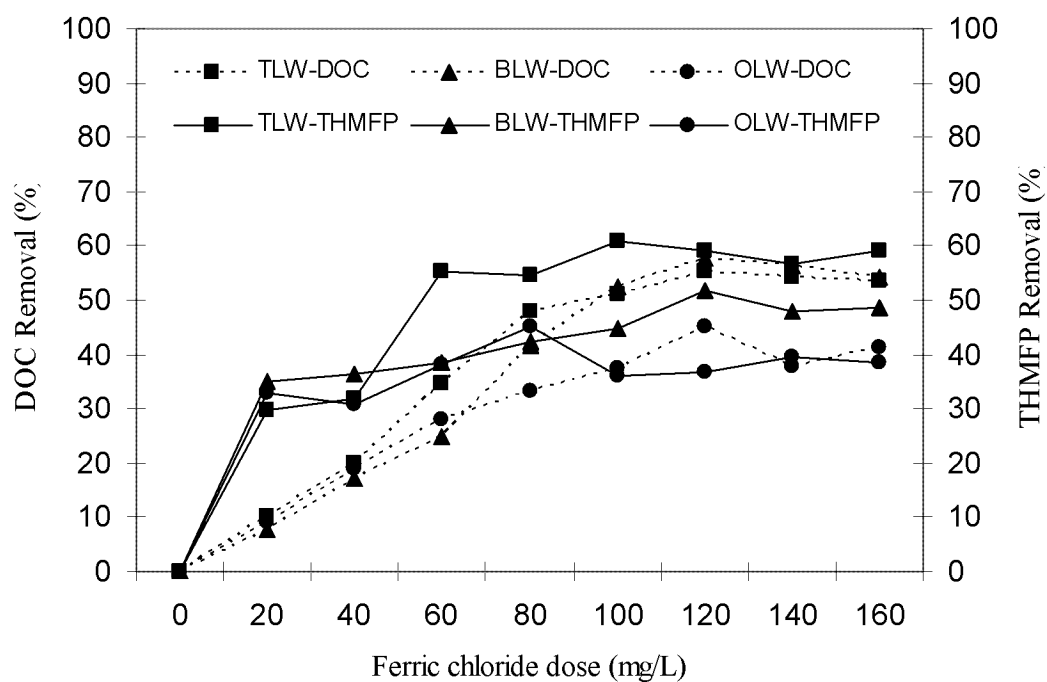
Figure 4.15: Removal of DOC versus THMFP as a function of ferric chloride dosages
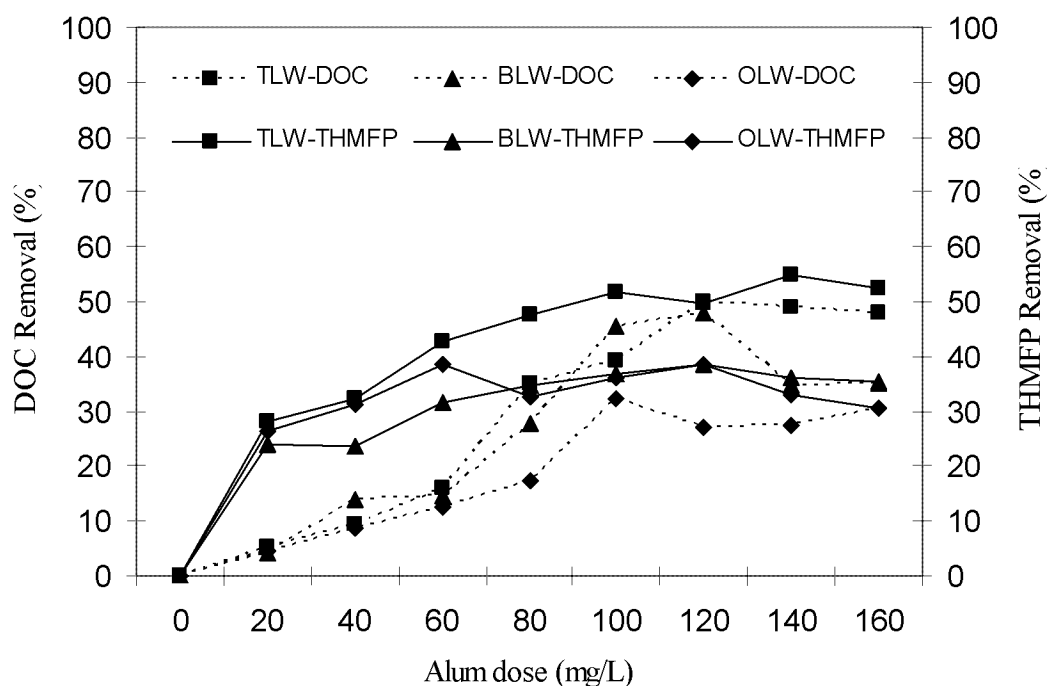
Figure 4.16: Removal of DOC versus THMFP as a function of alum dosages

4.4. Conclusion

This chapter included enhanced coagulation of jar tests procedure of TLW, BLW, and OLW from Istanbul-City. DBP precursors of DOC, UV_{254}, SUVA and THMFP were used to identify the enhanced coagulation treatments. Enhanced coagulation is a DBP precursors treatment technique with the objective of removing DOC to control DBP formation. Jar tests results indicate that enhanced coagulation can increase the removal of DBP precursors from these three water supplies. The results showed that at similar coagulant dosages, expresses as dry weight of coagulant, ferric chloride consistently outperformed alum in terms of DOC, UV_{254}, SUVA and THMFP removals. Enhanced coagulation reduced the DOC level by of 55, 58, and 28% and the UV_{254} absorption by 74, 79, and 51% in TLW, BLW, and OLW, respectively, suggesting that enhanced coagulation with ferric chloride preferentially removed organic compounds with higher UV absorption. On the other hand, alum treatment of enhanced coagulation reduced the DOC level in TLW, BLW, and OLW 50, 48, and 17%, and this alum coagulation condition resulted in 66, 62, and 44% UV_{254} from TLW, BLW, and OLW, respectively. In this study, both UV_{254} and THMFP materials were generally removed to a greater extent than DOC from TLW, BLW, and OLW. These results are consistent with literature findings.

5. OPTIMIZED COAGULATION OF DBP PRECURSORS

5.1. Objectives

This chapter evaluated the effects of different coagulation conditions on the levels of organic matter removal at a bench-scale for three raw water types in Istanbul. In previous chapter, the study was to optimize coagulant dose based upon the optimum removal of DOC. Once the conditions for optimum coagulant dosages had been determined via jar tests, DOC, UV_{254}, SUVA, and THMFP removals were evaluated. In this chapter, optimization of pH levels for two different coagulants of ferric chloride and alum was determined. The purposes of the baseline jar tests were to compare the jar test results to the enhanced and optimized coagulation conditions. The effects of coagulation conditions of pH, coagulant dosage and type, and raw water characteristics were also assessed.

5.2. Materials and Methods

5.2.1. Source waters collection

The natural water sources used in this study were TLW, BLW, and OLW. Quality parameter of these raw waters over 15 month period between June 2004 and August 2005 is summarized in Table 5.1. Daily consumption of 2×10^6 m^3 drinking water is supplied from these surface waters in Istanbul. Plant personnel collected raw water samples as grab samples, and they were shipped to ITU laboratory on the same day. When the samples were received at ITU Department of Environmental Engineering Laboratory, they were kept in the dark in a refrigerator at 4 °C to retard biological activity prior to use.

5.2.2. Jar test coagulation procedure

5.2.2.1. Baseline coagulation (BC)

Baseline coagulation is jar tests that simulated the water treatment plant conditions (coagulation dose) the day that the raw water sample was collected. The purposes of the baseline jar tests were to compare the jar test results with the full-scale plant data, and to serve as a point of comparison to the enhanced and optimized coagulation treatment conditions. Table 5.2 shows the operational parameters of Istanbul water treatment plants.

Table 5.1: Raw waters quality parameters*

Parameters	Unit	TLW		BLW		OLW	
		Range	Aver.	Range	Average	Range	Average
pH	-	7.40-8.10	7.78	7.60-8.50	8.00	6.80-7.60	7.15
Turbidity	NTU	1.3-3.2	2.5	1.2-3.6	2.8	1.8-2.8	2.4
Alkalinity	mg/L	90-145	125	110-153	135	55-76	67
Bromide ion	μg/L	80-460	180	70-530	370	24-120	60
Temp.	°C	15.3-24.8	15.2	10.9-23.2	15.3	11.0-24.2	16.4
DOC	mg/L	3.55-5.85	4.12	3.76-6.25	4.22	3.20-4.80	3.89
UV_{254}	1/cm	0.085-0.165	0.125	0.076-0.153	0.131	0.062-0.098	0.082
SUVA	L/mg×m	2.25-3.64	3.03	2.02-3.76	3.10	1.60-2.80	2.11
THMFP	μg/L	235-412	295	176-345	255	128-245	203

*Data obtained during June 2004 – August 2005

5.2.2.2. Enhanced coagulation (EC)

To determine enhanced coagulation (EC) conditions, a series of bench scale jar tests was used to identify the optimal coagulation dosage. All samples were brought to room temperature (21 °C) prior to jar testing. Experiments on 1 liter samples were performed using a multistage stirrer six paddle jar test apparatus. The reagent grade ferric chloride ($FeCl_3 \times 6H_2O$) and alum ($Al_2(SO_4)_3 \times 18H_2O$) doses were varied 20 to 140 mg/L. The coagulants dosages calculation was performed based on dry weight of ferric

chloride and aluminum sulfate. The standard jar test procedure consisted of a rapid mix at 150 rpm for 2 minutes, flocculation at 30 rpm for 30 minutes. Then the floc was allowed to settle for 60 minutes prior to filtration through a 0.45 μm cellulose acetate membrane filter. The filtrate from each jar was used to perform DOC, UV_{254}, SUVA, and THMFP studies.

Table 5.2: Operational parameters of Istanbul water treatment plants

Water utility	Treatment plants	Source water	Flow rate (m^3/day)	Treatment process
Buyukcekmece	Buyukcekmece	Buyukcekmece Lake	400.000	Pre-chlorination Coagulation Sedimentation Sand filtration Post-chlorination
Kagithane	Celebi Mehmet Han Yildirim Beyazid Han	Terkos Lake Alibeykoy Dam	600.000	Pre-chlorination Coagulation Sedimentation Sand filtration Post-chlorination
Omerli	Ertugrul Gazi Orhaniye Osmaniye Muradiye Emirli	Omerli Lake	1.200.000	Pre-ozonation Coagulation Sedimentation Sand filtration Post-chlorination

5.2.2.3. Optimized coagulation (OC)

Determination of optimized coagulation conditions required evaluation of both the optimum pH and coagulant dosage. To determine the optimum pH for a selected coagulant dose, jar tests were conducted using a constant coagulant dose and varied the pH of coagulation using sulfuric acid. The optimum pH of coagulation was identified as the highest pH at which there was maximum DOC removal. Other parameters including UV_{254}, and THMFP removal were also considered in determining the optimum pH value. To determine the optimum coagulant dosage at the selected pH, coagulant concentrations were varied in each jar while the optimum pH value was maintained constant. This optimum pH/dose condition was defined as the optimized treatment. This series of tests was conducted using two different coagulants for each water type. As mentioned above, coagulants tested included reagent grade alum and ferric chloride. For each raw water sample, DOC,

UV_{254}, SUVA, and THMFP concentrations were assessed before and after treatment under BC, EC, and OC conditions using ferric chloride and alum coagulants.

5.3. Results and Discussion

Removal of organic precursors by coagulation process is impacted by many factors such as coagulation conditions, characteristics of NOM, nature and concentrations of inorganic compounds, and the design and operation of the treatment plant **(Volk et al., 2000)**. Therefore, the removal of organic matter from water with coagulation process varies widely, generally between 10 and 90% **(Randtke, 1988)**. The aim of this chapter was to evaluate how different coagulation conditions impact DBP precursors levels in treated water. Organic precursors removal by BC, EC, and OC treatment techniques were assessed by monitoring raw and coagulated water DOC, UV_{254}, SUVA, and THMFP value. The effects of coagulation pH, coagulant dosage and type, and raw water characteristics were also assessed.

As shown in Figure 5.1, 5.2 and 5.3, coagulation of TLW, BLW, and OLW samples data indicated that as both coagulant dosages increased further, the amount of DOC removal also increased gradually. Ferric chloride reduced the DOC level to 1.78, 1.72, and 2.11 mg/L with the dosage of 140 mg/L for TWL, BLW, and OLW, respectively. While, 140 mg/L aluminum sulfate coagulation resulted in a DOC level of 2.40, 2.50, and 2.82 mg/L in TWL, BLW, and OLW, respectively. As observed in three surface water samples, at similar coagulant dosages, ferric chloride consistently outperformed alum for DOC removal. As a comparison, our results are consistent with other studies **(Edzwald, 1994)**. In this study 40 mg/L coagulant dosage was chosen for BC conditions. Moreover, even though 140 mg/L coagulant dosage resulted in maximum DOC removal in three surface waters coagulation, because of economical and engineering point of view and considerations, 80 mg/L coagulant dosages was selected for EC and OC studies.
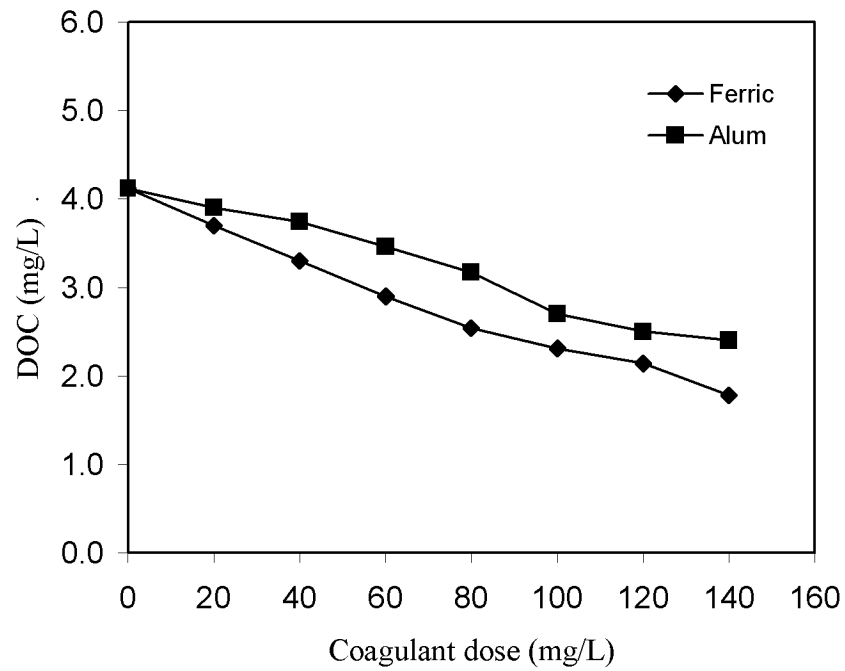
Figure 5.1: DOC Removal with ferric and alum for TLW
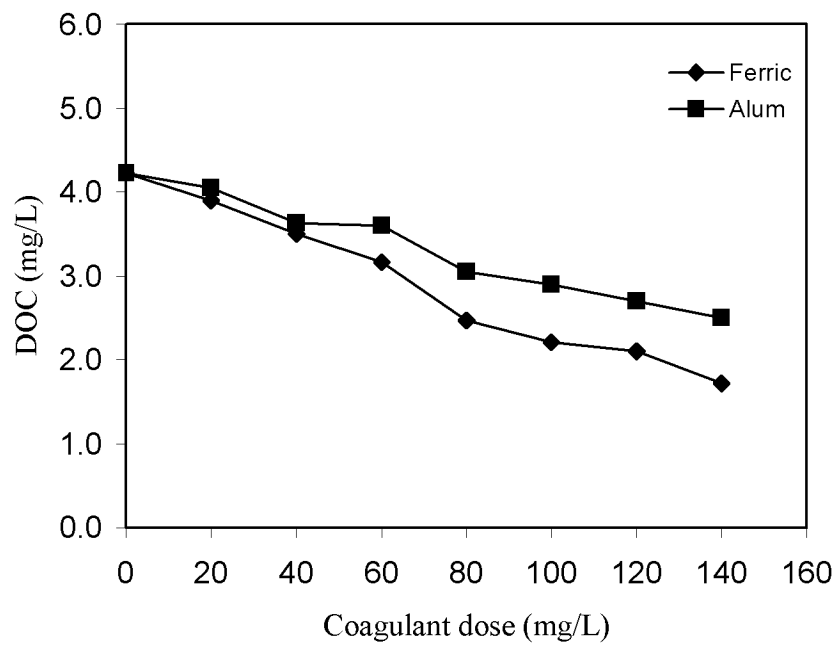
Figure 5.2: DOC Removal with ferric and alum for BLW
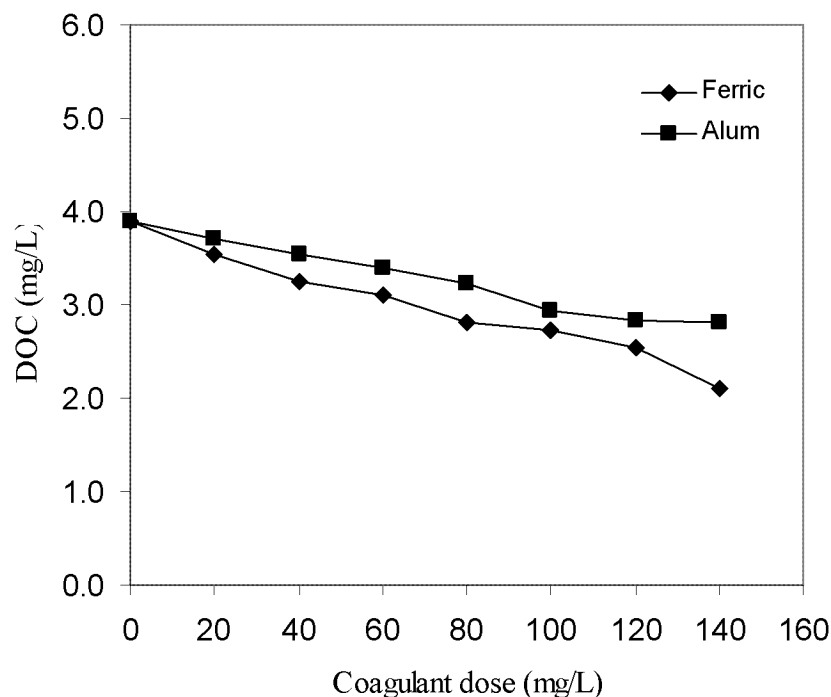
Figure 5.3: DOC Removal with ferric and alum for OLW

5.3.1. Effects of coagulation parameters on DOC removal

5.3.1.1. Coagulation pH

Literature findings reported that the pH of coagulation was dependent on the coagulant type and treated water sample (**Volk et al., 2000**). Numerous researchers have identified coagulation pH as the parameter having a great effect on achieving optimal organic precursors removal by coagulation process (**Randtke, 1988; Crozes et al., 1995; White et al., 1997**). The results of this study support these findings, indicating that the pH of coagulation rather than the coagulant dosage was the determinant factor for DOC removal. For example, 80 mg/L ferric chloride with OC conditions at pH value of 5.25 removed 66% DOC on TLW, while EC of TLW with 80 mg/L alum without pH adjustment resulted in 38% DOC treatment (Table 5.2 and 5.3).

Figure 5.4 shows ferric chloride coagulation of pH scans conducted for TLW, BLW, and OLW with varying DOC and alkalinity levels. Each curve was created with an 80 mg/L

coagulant dosage while the pH of coagulation was varied by addition of H_2SO_4. These data show that the optimal pH was 5.25 for three water sources and DOC removals were varied with pH. For example, for BLW with an alkalinity of 135 mg/L, the optimal pH was 5.25 with 76% DOC removal. For TLW, an optimal pH of 5.25 value resulted in 68% DOC reduction with an alkalinity of 125 mg/L. Finally, in OLW, the optimal coagulation efficiency was 50% at optimal pH of 5.25 with a 67 mg/L alkalinity. It can be concluded that, the DOC removal efficiency with ferric chloride was increasing with increased DOC and alkalinity levels.

As shown in Figure 5.5, the optimal pH for alum coagulation was obtained at 5.50 for TLW and BLW, while, in OLW the optimal pH was 5.25 as in the case for ferric chloride. Optimized conditions with alum removed 52, 67% DOC from TLW and BLW, respectively. For OLW samples, lowering the pH to 5.25 with sulfuric acid led to 45% DOC treatment. As a comparison, **Chowdhury et al. (1995)** reported that baseline plant conditions removed 9% of the total organic carbon (TOC) (TOC = 2.4 mg/L), but TOC removals increased to 25% when carbon dioxide was added to lower the pH from 8.0 to 7.0. **Lind (1995)** also found that TOC removal was improved at lower pH values with alum and ferric chloride coagulation. For this study, the best precipitation pH for DOC substances has been obtained at 5.25 with ferric chloride and alum coagulation. As mentioned in literature, the lower pH, by increasing the protonation of the NOM and increasing the positive charge of the coagulating species, reduces the coagulant demand and favors the adsorption of humics onto metal hydroxides **(Edwards and Benjamin, 1997)**.
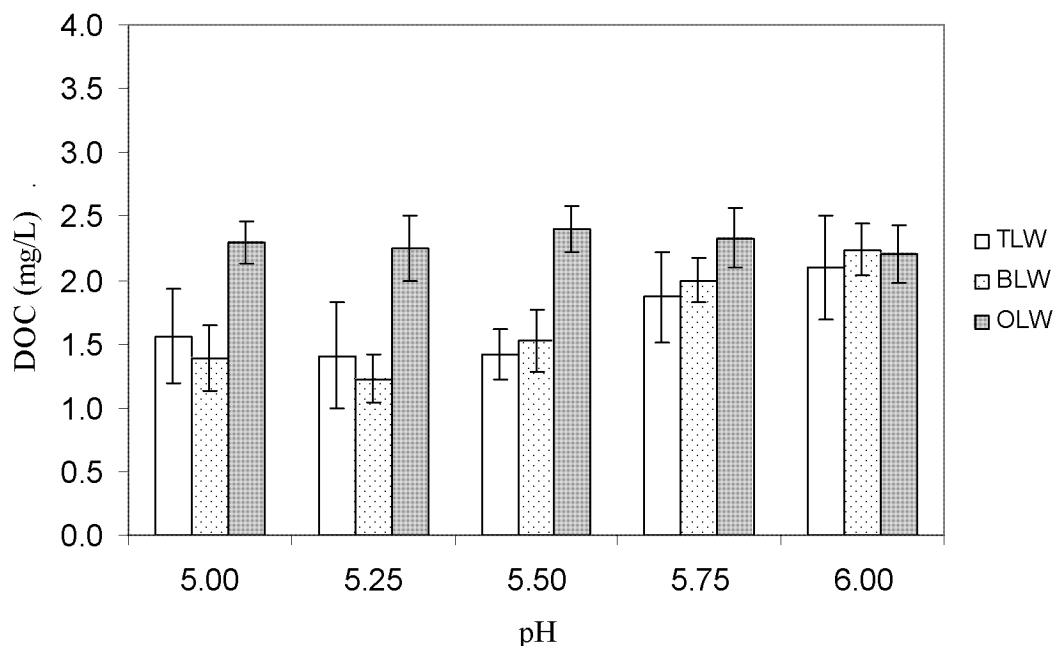
Figure 5.4: Ferric coagulation pH curves on DOC reduction for three water samples

5.3.1.2. Coagulant type

The choice of coagulant was also a factor in the performance of coagulation conditions. The performance of ferric chloride for removal of DOC was compared to alum (Figure 5.1, 5.2, and 5.3). Ferric chloride resulted in better DOC removal than alum. As shown in Table 5.3 and 5.4, BC with ferric chloride removed on average 0.26 mg/L more DOC than alum, while EC with ferric treatment removal resulted in 0.54 mg/L more DOC than alum, and finally OC conditions with ferric chloride removed 0.34 mg/L more DOC than alum. Mainly due to more favorable pH, iron salts typically resulted in greater removal of DOC. Studies reported in the literature are similar, suggesting that the performance of a particular coagulant is dependent upon the specific characteristics of the NOM and the test conditions **(Volk et al., 2000)**. Some investigators have reported that iron was superior to alum salts **(Julien et al., 1994; Randtke, 1993)**. For example, **Crozes et al. (1995)** observed higher removals of DOC when using ferric chloride compared to alum.
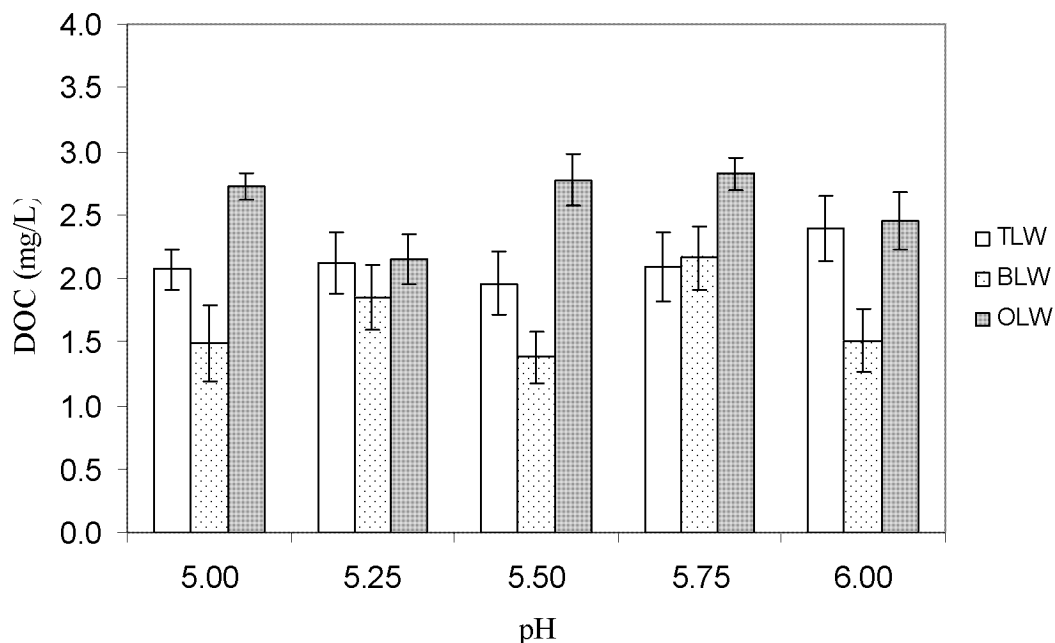
Figure 5.5: Alum coagulation pH curves on DOC reduction for three water samples

5.3.1.3. Coagulant dose

Coagulant dose under BC conditions was 40 mg/L, and EC used 80 mg/L dosage without pH adjustment. Besides, a coagulant dosage of 80 mg/L also was used at selected pH for OC conditions. For all water samples, increasing the coagulant dosage led to an increase in DOC removal. As shown in Table 5.3, BC of 40 mg/L ferric chloride removed 20, 17, and 16% of the DOC on TLW, BLW, and OLW, respectively. While EC with 80 mg/L of ferric chloride yielded a DOC reduction of 38, 41, and 28% for TLW, BLW, and OLW, respectively. Furthermore, OC of TLW, BLW, and OLW with 80 mg/L iron salt at pH value of 5.25 resulted in 66, 71, and 50% DOC reduction, respectively. Table 5.4 also shows that 40 mg/L dosage of alum with BC removed 12, 14, and 9% of DOC on TLW, BLW, and OLW, respectively. Moreover, alum treatment with EC resulted in 23, 28, and 17% DOC removal for TLW, BLW, and OLW, respectively. Finally, the amount of DOC removal with alum OC was 52, 67, and 45% for TLW, BLW, and OLW, respectively. The study results show that at similar coagulant dosages and coagulation techniques, ferric chloride consistently outperformed alum in terms of DOC removal from water samples. **Crozes et al. (1995)** reported that ferric hydroxide floc has a greater affinity of a fraction of NOM

than for aluminum hydroxide floc. This difference in adsorption capacity is likely due to more active adsorption sites on the ferric hydroxide floc **(Crozes et al., 1995)**. Furthermore, ferric chloride presents roughly two times more active positive charges than does aluminum sulfate **(Crozes et al., 1995)**. Therefore, colloid destabilization and the formation of humates can both be expected to be achieved with ferric chloride more effectively than alum.

Table 5.3: THM precursors removal with ferric chloride coagulation under three different coagulation conditions

Source water	Coagulation Techniques	pH	Ferric	DOC	UV$_{254}$	SUVA	THMFP	DOC	UV$_{254}$	SUVA	THMFP
			mg/L	mg/L	1/cm	L/mg×m	µg/L	%	%	%	%
TLW	Raw water	7.78	0	4.12	0.1250	3.03	295	0	0	0	0
	BC	6.94	40	3.30	0.0717	2.17	202	20	43	28	32
	EC	6.57	80	2.54	0.0487	1.92	134	38	61	37	55
	OC	5.25	80	1.41	0.0201	1.43	62	66	84	53	79
BLW	Raw water	8.00	0	4.22	0.1310	3.10	255	0	0	0	0
	BC	7.10	40	3.50	0.0850	2.43	162	17	35	22	36
	EC	6.72	80	2.47	0.0590	2.39	146	41	55	23	43
	OC	5.25	80	1.23	0.0250	2.03	73	71	81	34	71
OLW	Raw water	7.15	0	3.89	0.0820	2.11	203	0	0	0	0
	BC	6.89	40	3.25	0.0670	2.06	141	16	18	2	31
	EC	6.30	80	2.82	0.0560	1.99	112	28	32	6	45
	OC	5.25	80	1.93	0.0438	1.96	83	50	47	7	59

Table 5.4: THM precursors removal with alum coagulation under three different coagulation conditions

Source water	Coagulation Techniques	pH	Alum mg/L	DOC mg/L	UV$_{254}$ 1/cm	SUVA L/mg×m	THMFP µg/L	DOC %	UV$_{254}$ %	SUVA %	THMFP %
TLW	Raw water	7.78	0	4.12	0.1250	3.03	295	0	0	0	0
	BC	6.86	40	3.64	0.0747	2.05	200	12	40	32	32
	EC	6.35	80	3.17	0.0517	1.63	156	23	59	46	47
	OC	5.50	80	1.96	0.0348	1.78	94	52	72	41	68
BLW	Raw water	8.00	0	4.22	0.1310	3.10	255	0	0	0	0
	BC	7.10	40	3.63	0.0932	2.57	195	14	29	17	24
	EC	6.72	80	3.05	0.0804	2.64	167	28	39	15	35
	OC	5.50	80	1.38	0.0406	2.94	82	67	69	5	68
OLW	Raw water	7.15	0	3.89	0.0820	2.11	203	0	0	0	0
	BC	6.92	40	3.55	0.0680	1.92	140	9	17	9	31
	EC	6.40	80	3.22	0.0580	1.80	137	17	29	15	33
	OC	5.25	80	2.15	0.0365	1.43	97	45	55	32	52

5.3.2. Effect of source water characteristics on organic matter removal

Natural organic content and alkalinity level of source water affect the coagulation performance. Usually higher DOC content increases the coagulation efficiency. For this study, moderate variations in organic matter removal were observed between theses three surface water samples tested (Table 5.3 and 5.4). Overall, removal of DOC ranged between 9 and 71%. The removal of humic materials, determined by monitoring the reduction in UV absorbance at 254 nm, ranged between 17 and 84%. THMFP removal amount was in the range of 24 and 79%. Organic precursors are composed of a mixture of compounds varying in size, structure and composition. It was reported that the chemical characteristics of the DOC, as well as other physicochemical properties of the raw water, will determine the degree of removal by coagulation **(Volk et al., 2000)**. Analysis of raw water characteristics showed that both quantity and quality of NOM influenced treatment efficiency. Higher NOM removal was observed for BLW with average DOC value of 4.22 mg/L with a 135 mg/L alkalinity (Table 5.3and 5.4). On average, water sample of TLW with 4.12 mg/L DOC and 125 mg/L alkalinity exhibited DOC removals of 41, and 29% for ferric and alum coagulation respectively. DOC removal of OLW samples with DOC levels below 4 mg/L and 67 mg/L alkalinity resulted in 29 and 20% for ferric and alum coagulants, respectively. Numerous researchers have reported that specific physical and chemical properties of NOM including the molecular weight of organic constituents, the solubility of organic compounds, the charge density of molecules, or the functional group composition, all impact the removal of NOM during coagulation **(Edzwald, 1994; Amy, 1993; Edwards et al., 1994; Harrington and Singer, 1996; Huang and Yeh, 1993; Lefebvre and Legube, 1993; Sinsabaugh et al., 1986)**.

5.3.3. THM precursors removal

5.3.3.1. UV$_{254}$

UV$_{254}$ is an instrumental parameter identifying the aromatic content of water. Figure 5.6 and 5.7 shows the reduction of UV$_{254}$ levels in TLW, BLW, and OLW

with ferric and alum coagulation, respectively. The percent removal of UV_{254} with ferric chloride for TLW, BLW, and OLW samples was about 74, 79, and 53%, respectively. On the other hand, the maximum UV_{254} removals with alum coagulation were 66, 62, and 35% for TLW, BLW, and OLW, respectively. It was concluded that ferric chloride was found to be more effective than alum in terms of UV_{254} removals. In this study, the UV_{254} material was always removed to a greater extent than DOC. In Figure 5.8, a comparison of DOC versus UV_{254} removal is shown. The optimal curve is also shown, and points on this curve indicate equivalent removal of DOC and UV_{254} for three surface water samples. Points above this curve indicate that the percent removal of UV_{254} was higher than the percent DOC removal, whereas the reverse is true for points below the line. As shown in Table 5.3 and 5.4, the average DOC removal for BC was 15% compared with 30% for removal of UV_{254}. For EC, DOC removals averaged 29%, whereas UV_{254} removal increased to 46%, indicating good removal of aromatic compounds. Finally, in OC conditions, the DOC removal amount increased to 59%, while the average UV_{254} removal was 68% with optimal pH values. As a result, when compared UV_{254} to DOC removal, the percentages of UV_{254} reduction were from 1.15 to 1.99 fold higher than DOC reduction, suggesting that coagulation was more effective in removing UV_{254} absorbing materials than DOC **(Edzwald et al., 1985; Najm et al., 1994; Randtke, 1988)**.

5.3.3.2. SUVA

Raw water SUVA values varied between 2.11 and 3.10 (Table 5.1). **Edzwald (1994)** found that SUVA values higher than 3 describe a relatively hydrophobic DOC, mainly containing aquatic humic material of high molecular weight which is likely to be effectively removed during coagulation. On the contrary, SUVA values of less than 3 indicate that the DOC is hydrophilic, low in molecular weight, low in charge density, and only slightly affected by coagulation. For the 3 water samples studied, SUVA values decreased significantly after coagulation (Table 5.3 and 5.4). The highest DOC removal of 71% was observed for the BLW sample with the highest SUVA (SUVA = 3.10 L/mg*m) treated with ferric chloride.

Alternatively, the lowest DOC reduction was observed (9-28%) for sample OLW, with a SUVA of 2.11 and a raw water DOC concentration of 3.89 mg/L. The average removal of DOC for TLW sample with SUVA value of 3.03 was 41% with ferric chloride coagulation. Several studies have shown that humic substances are preferentially targeted during coagulation **(Edzwald, 1994; Randtke, 1988; White et al., 1997; Amy, 1993; Sinsabaugh et al., 1986)**. For example, the comparison of ^{13}C NMR spectra of water samples before and after chemical coagulation demonstrated that aromatic carbon was preferentially removed **(Harrington et al., 1996)**. Furthermore, the nature of humic substances also impacts their removal. The removal rates of hydrophobic compounds were found to be higher those of hydrophilic compounds **(Tryby et al., 1993)**. Huang and colleagues reported that coagulation removed 50 and 35% of humic and fulvic acids present in colored waters, respectively **(Huang and Yeh, 1993)**. In addition, the removal of NOM is affected by other water quality characteristics **(Bell et al., 2000)**.
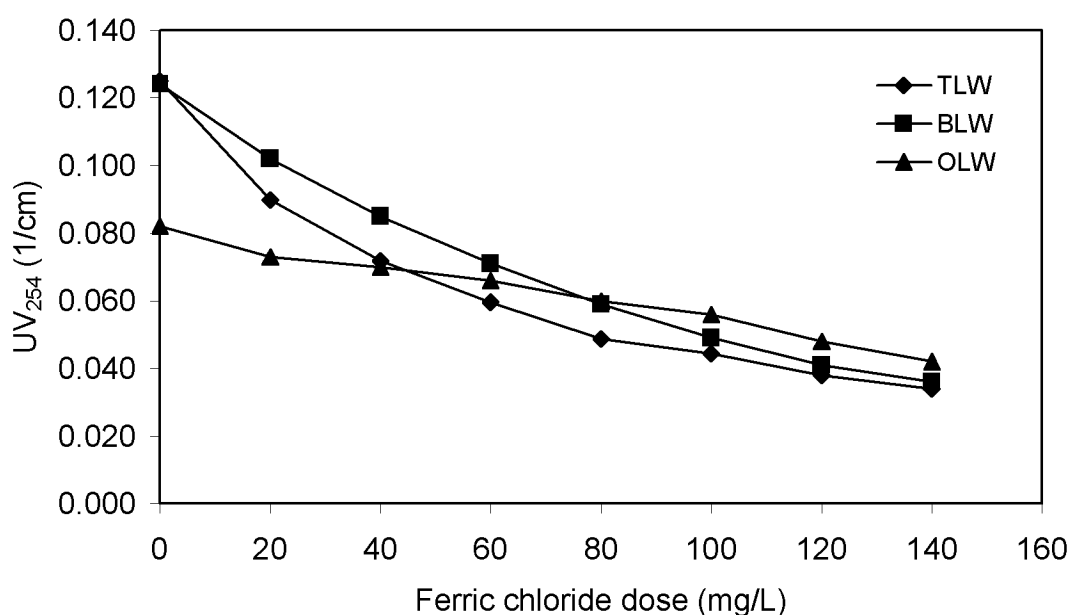
Figure 5.6: UV_{254} removal with ferric for three water samples
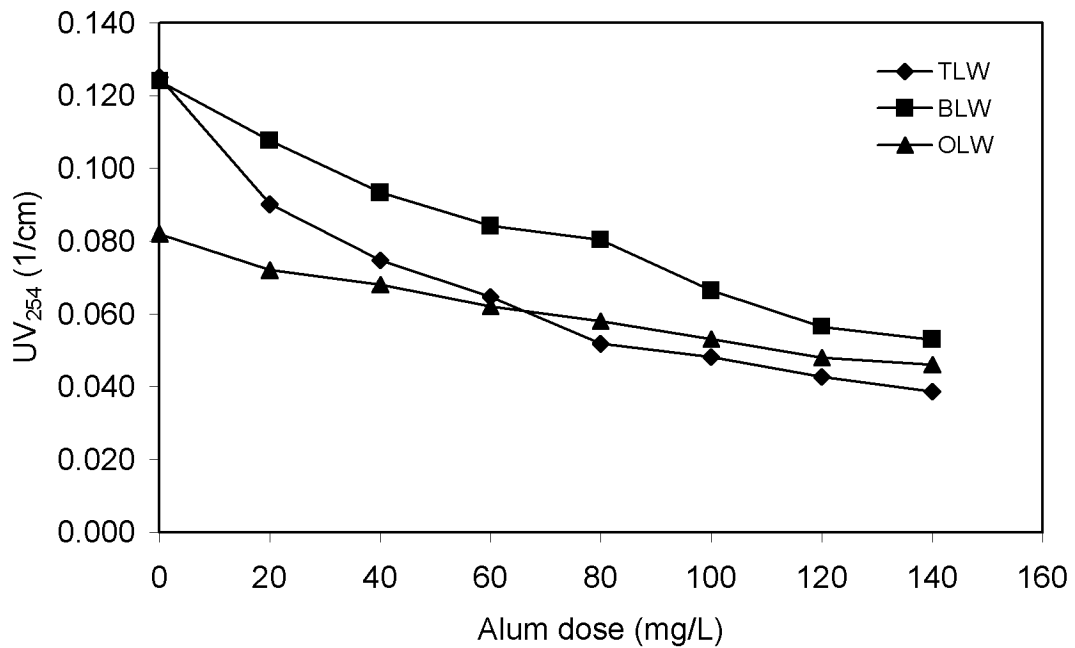
Figure 5.7: UV_{254} removal with alum for three water samples

5.3.3.3. THMFP

Several investigators reported that THMFP reduction is attributed to removal of THM precursors **(Bell et al., 2000; Najm et al., 1997)**. Table 5.3 and 5.4 show the results of jar testing of BC, EC, and OC treatments. Overall, EC and OC resulted in improved seven day THMFP removals compared with the corresponding BC treatments. THMFP values decreased significantly after coagulation (Table 5.3 and 5.4). The highest THMFP removal of 79 was observed for the TLW sample in OC conditions with ferric chloride. Moreover, the moderate THMFP reduction of 55% was observed with EC on TLW sample. It is likely that the improved reductions in THMFP were related to the lower pH of coagulation as well as the increased DOC removal. The average improvement with OC for 3 waters over BC conditions for removal of THMFP was 47%. The jar tests results indicate that ferric chloride was found to be more effective than alum in terms of THMFP removals. Studies conducted by **Crozes et al. (1995)** reported that the difference between ferric chloride and alum reduction levels of THMFP is attributed to a greater affinity of a fraction of NOM for ferric hydroxide floc than for

aluminum hydroxide floc. Moreover, the reduction in THMFP increased with increasing both coagulant dosages and decreasing pH values.

As many people have reported, DOC removal appeared to be a conservative indicator for treatment of THMFP with precursors preferentially removed by OC **(Bell et al., 2000)**. The correlation between DOC removal and THMFP removal was moderate with a R^2 value of 0.77 (Figure 5.9). On the other hand, the relationship between THMFP and UV_{254} absorbing compounds was slightly worse, with a correlation coefficient of 0.66 (Figure 5.10). Even though, literature findings indicate that waters higher in UV_{254} tend to exert a greater THM formation, our study results showed a weak correlation between UV_{254} and THMFP for three water supplies.

5.3.4. Benefits of enhanced and optimized coagulation

EC and OC can be an economical alternative for improved NOM removal from raw water, and they have capabilities to control the THM levels in drinking water of Istanbul. Furthermore, these two modified coagulation techniques can be able to meet the EPA and EC THM limits of 80 and 100 µg/l, respectively. Removal of THM precursors under BC, EC, and OC condition are presented in Table 5.3 and 5.4. Furthermore, Figure 5.11 and 5.12 present the 48 h THMFP results for evaluation of THM levels in distribution systems of Istanbul. OC led to higher removal of DOC than did the BC. For THMFP-48h, Under OC and EC conditions with ferric chloride and alum, all water sources meet the both EPA and EC THM limits, respectively. However, under BC conditions with ferric treatment, just TLW and OLW meet the EC THM limit of 100 µg/l, whereas with alum coagulation, none of three surface water supplies meet the required THM limit of EPA and EC, respectively.
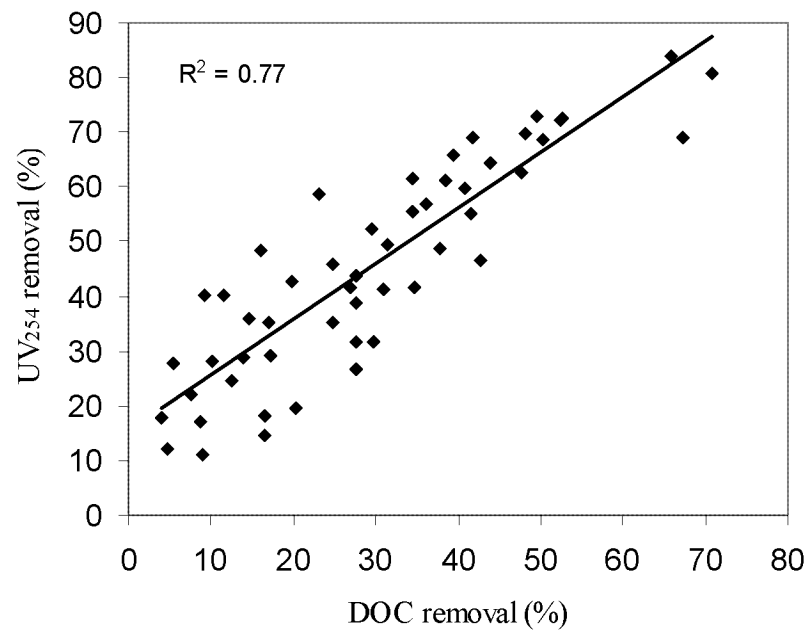
Figure 5.8: Comparison of DOC removal versus UV_{254} removal for three water sources
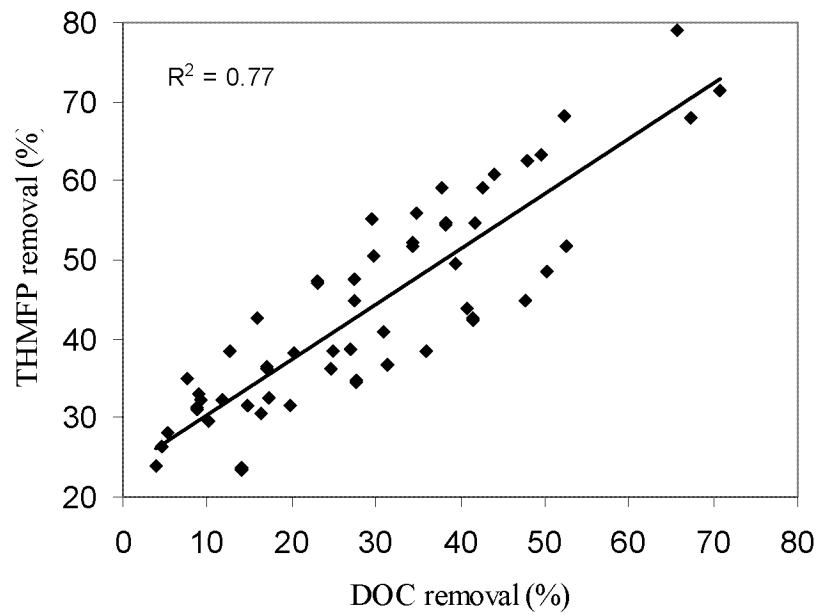
Figure 5.9: Comparison of DOC removal versus THMFP removal for three water sources

The reductions in THMFP for 7 day concentrations under OC conditions were between 52 and 79% (average THMFP reduction of 66%); while DOC removals under OC conditions ranged from 44-71% (average DOC removal of 58%), (Table 5.3 and 5.4) for three surface water. EC and OC would result in an additional DOC removal of 15, and 44%, respectively. This improvement in DOC removal was significant. As a comparison, **Amy (1993)** reported that EC was capable of achieving DOC removals of 50%. Depending on the source water, **Bell et al. (1996)** observed that organic removal could reach 60-80% by OC with ferric chloride. Overall, EC and OC proved to be beneficial for waters of varying water quality. The results indicated that benefits of OC were site specific. To determine how effective EC and OC treatments are under certain conditions, it is necessary to conduct bench scale, pilot or full scale experiments.
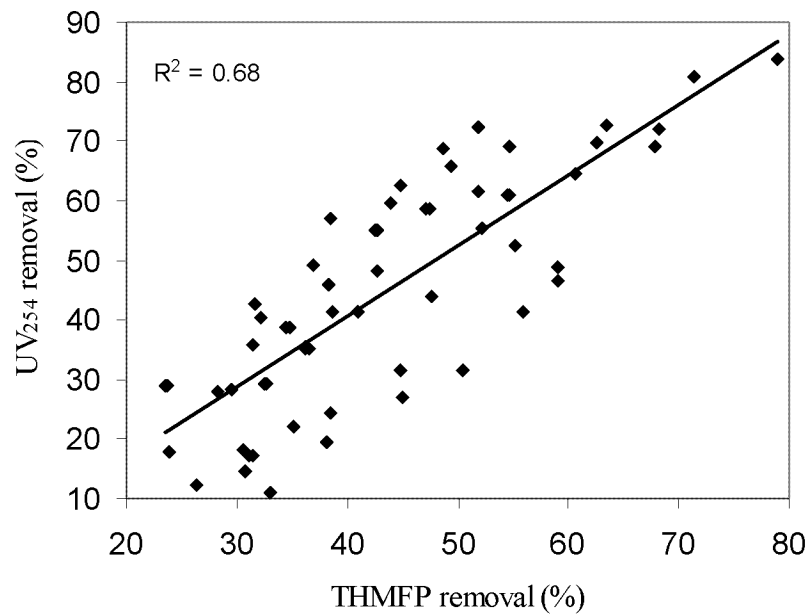
Figure 5.10: Comparison of THMFP removal versus UV_{254} removal for three water sources
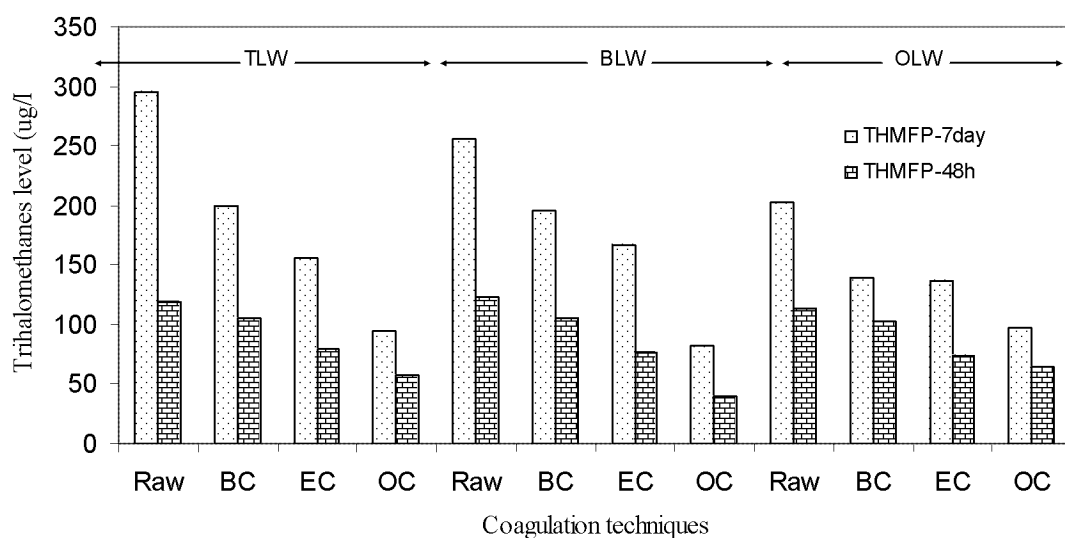
Figure 5.11: Comparison of $THMFP_{48h}$ with $THMFP_{7day}$ for ferric chloride
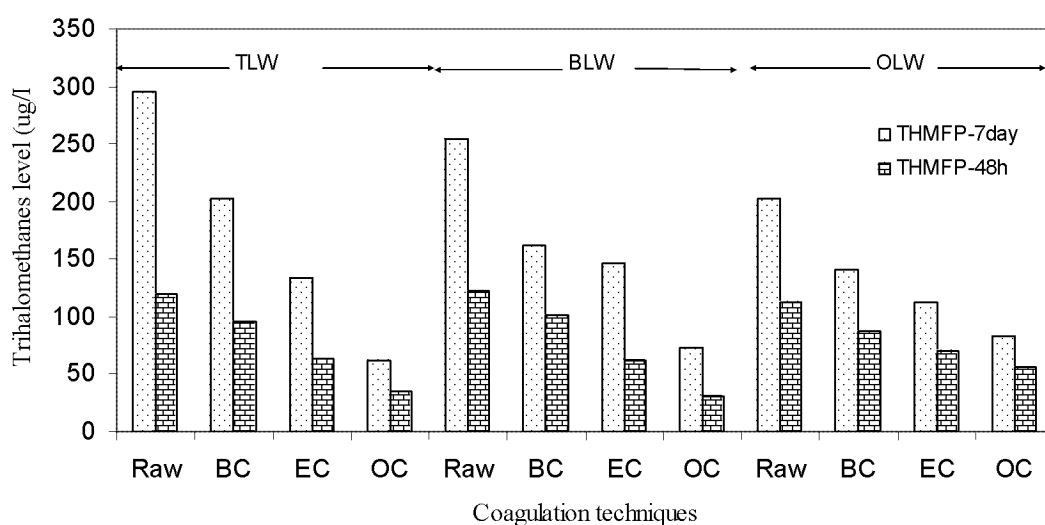
Figure 5.12: Comparison of $THMFP_{48h}$ with $THMFP_{7day}$ for alum

5.4. Conclusions

This chapter investigation included jar tests using 3 raw water supplies in Istanbul. Organic parameters such as, DOC, UV_{254}, SUVA, and THMFP removals were used to identify the BC, EC, and OC treatments. During this study, variations in NOM removal were observed that could be attributable to the coagulation conditions, and the raw water

quality matrices. Compared to conventional treatment practices of BC, EC led to an additional removal of 15% for DOC, 16% UV_{254}, 5% SUVA, and 12% for THMFP. Moreover, OC conditions resulted in extra treatment of 41% for DOC, 38% UV_{254}, 10% SUVA, and 35% for THMFP. OC can be an efficient and inexpensive tool to control NOM in comparison to membrane process and GAC systems in Istanbul water supplies. Overall, when OC was implemented in jar tests, the effectiveness of the treatment program appeared to depend on the pH of coagulation. Jar tests conducted with depressed pH levels at OC conditions removed more DOC than those at moderate pH levels at EC. For low DOC waters, like OLW, additional treatment would be necessary to achieve enhanced removal of NOM. The effectiveness of the treatment process may be different for DOC, UV_{254}, and THMFP. Reduction in one of these parameters does not guarantee that other fractions have been equally affected. It is important, therefore, to monitor each of these fractions to ensure reductions in DBP formation levels.

6. MODELING DBP FORMATION DURING ENHANCED COAGULATION

6.1. Objectives

The objective of this chapter was to examine enhanced coagulation effects on THM formation. Based on THM formation experiments, a data base was established for modeling THM formation during chlorination of enhanced coagulated water. Terkos Lake Water (TLW) in Istanbul city was employed in the jar test experiments. Model variables were coagulant dosage, chlorine dosage, reaction time, and raw water DOC value. The goodness of fit was evaluated through examination of various statistical parameters, including R^2, the F statistic, and α value (significance) for linear regression.

6.2. Material and Methods

6.2.1. Sampling

The natural water source used in this study was TLW, which originates at Terkos watershed delta. The detail of sampling collection procedure was explained in detail in Chapter 3. Further, Table 6.1 summarizes the raw water quality data encountered during testing facilities.

6.2.2. Sample chlorination procedure

After filtration with 0.45 μm membrane filter, chlorination of TLW samples was carried out at pH 7.0 with phosphate buffer solution. An appropriate amount of concentrated sodium hypochlorite dosing solution was added to the raw and coagulated waters to obtain the desired chlorine dose. The chlorinated sample was then incubated in a dark room for 6, 12, and 24 h at 25 °C. The free chlorine residual was eliminated in the sample bottle, using ammonium chloride solution. Subsequent to the reaction period, the chlorine residual concentrations were measured using the DPD ferrous titrimetric method in accordance with the Standard Methods **(APHA, 1998)**.

6.2.3. Experimental analysis

Chlorine, DOC, UV_{254}, and THM measurements were explained in detail in Chapter 3.

6.2.4. Statistical methods

6.2.4.1. Model data base generation

During model construction, TLW was studied in a series of experiments that encompassed the model variables and ranges of conditions. Three values Cl_2 dose was used to represent water treatment plants applied chlorine dose ranges. 2 mg/L was represented as a lower applied dose, while 4 mg/L was used as an average applied chlorine level, and finally 6 mg/L was applied as a higher chlorine dosage for treatment operations. On the other hand, reaction times were varied between 6 h and 24 h. 6 h was represented the minimum time that consumer receive treated water from water treatment plant, while 12 h was used as an average water receiving time for consumer, and finally 24 h was used as higher travel time to consumer from the treatment plant. Moreover, 6 values of ferric chloride dosage were used to represent the water treatment plants coagulation operation ranges. They were 20, 40, 60, 80, 100, and 120 mg/L. 20 mg/L ferric chloride was used as a lower coagulant dosage during treatment operations, and 60 mg/L was used as an average coagulant dosage for coagulation processes, and finally 80, 100, and 120 mg/L ferric chloride dosage were used as an enhanced coagulation dosage conditions for water treatment. The coagulants dosages calculation was performed based on dry weight of ferric chloride and aluminum sulfate

Kinetic experiments were conducted under various combinations of experimental conditions. A base line condition was conventional coagulation with ferric chloride dosages of 20, 40, and 60 mg/L. While, enhanced conditions was enhanced coagulation by ferric chloride dosages of 80, 100, and 120 mg/L.

6.2.4.2. Model development

In this study, multiple linear regression analysis was used to model THM formation during enhanced coagulation process. The general strategy adopted to develop model equation was to describe the roles of DOC precursor, chlorine dose, and reaction

time in formation of THM. The model coefficients obtained were used to predict THM formation. The concentrations of THM are expressed as (μg/L), the DOC as mg/L, the coagulant and chlorine dose as mg/L, while the contact time as hour (h). The model development was based on the THM concentrations from chlorination of coagulated water. Before model construction, log transformations were applied to all data. Then, a multiple linear regression model for THM formation was created using statistical package for social sciences (SPSS) software **(SPSS, 2002)**. Multiple regression analysis was applied to evaluate the statistically significant variables of the system. The level of significance (α) for the inclusion of a variable in the model was 0.05. Throughout the process of model development, several linear and non-linear regression analyses were performed. Independent sets of data from same sources were collected to validate the model. A total 60 samples were collected from raw water for purpose of model development and validation.

Table 6.1: Terkos Lake Water quality parameters*

Variables	Unit	Minimum	Maximum	Averages	Std. Deviation
DOC	mg/L	4.10	5.95	4.66	0.58
UV$_{254}$	1/cm	0.080	0.180	0.127	0.05
SUVA	L/mg-m	1.95	3.02	2.72	0.74
Alkalinity	mg CaCO$_3$/L	98	142	120	31.11
Bromide ion	μg/L	180	360	270	127.27
pH	-	7.65	8.45	8.05	0.57
Temperature	°C	12.30	24.20	18.25	8.41
THMFP	μg/L	182	290	236	78.79

*Data obtained during June 2004 and November 2004

6.3. Results and Discussion

The model building process requires an understanding of the effects of individual parameters of independent variables on total THM formation. The effects of DOC concentration, coagulant dosage, chlorine dose, and reaction time were discussed individually. The characteristics of TLW used in this study are shown in Table 6.1. The raw water DOC concentrations ranged from 4.10 and 5.95 mg/L, and the UV$_{254}$ absorption ranged from 0.080 to 0.180 cm^{-1}. The values are in the range of typical surface waters. Enhanced coagulation reduced the DOC level by 62%, and the UV$_{254}$ absorption by 74%, suggesting that enhanced coagulation with ferric treatment preferentially removed organic compounds with higher UV absorption (Figure 6.1).

From Figure 6.1, the percent reductions of UV$_{254}$ absorbance were higher than those of DOC in TLW. The humic fraction, which absorbs UV light at 254 nm, is more effectively removed by coagulation than the nonhumic fraction **(Edzwald et al., 1985; Najm et al., 1994; Krasner and Amy, 1995)**. This explanation also accounts for the greater percent removal of UV$_{254}$ absorbance and DOC in TLW. As stated in Table 6.1, specific ultraviolet absorbance (SUVA) value was 2.72 representing average humic content for TLW. The moderate humic fraction in TLW results in greater humic fraction removal and greater overall NOM removal. The UV$_{254}$ generally decreases with increasing ferric dose, indicating preferential removal of the humic fraction. As a comparison with **Krasner and Amy (1995)** study, they found that the removal of aromatic substances by alum and ferric chloride coagulation is more effective than the removal of DOC, and it can be concluded from these results that bigger aromatic molecules are removed more effectively than both smaller aromatic molecules **(Krasner and Amy., 1995)**. This result supports the conclusion that TLW's NOM was as amenable to chemical coagulation because of its moderate humic fraction. Therefore, enhanced coagulation is very effective for this water source.
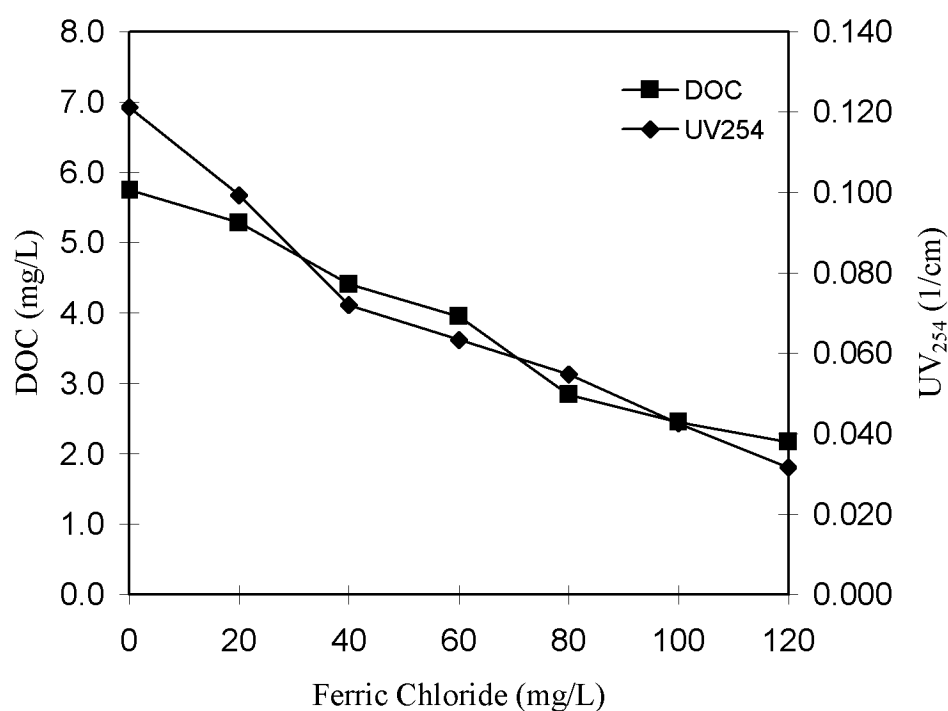
Figure 6.1: THM precursors removal as a function of ferric chloride dose

6.3.1. Effects of DOC concentration on THM formation

Enhanced coagulated samples contained DOC ranging from 5.75 to 2.17 mg/L; Figure 6.1 shows the DOC reduction during enhanced coagulation. Ferric chloride coagulation removed DOC content of TLW 62 %. On the other hand, it is shown in Figure 6.2, a linear relationship (0.732) between DOC and THM formation was obtained with ferric chloride under experimental kinetic conditions (pH = 7.0, Br⁻= ambient, reaction time = 6, 12, and 24 h, and chlorine dose = 2, 4, and 6 mg/L). Most researchers found that THM formation rose with increasing soluble humic substances in surface water supplies **(Uyak et al., 2005)**. Moreover, the rate of THM formation is equal to that of DOC consumption, and a first order reaction was reported with respect to DOC **(Milot et al., 2000)**. In other words, higher level of DOC will provide more THM formation if enough residual chlorine is available. As shown in Figure 6.3 increased DOC removal in enhanced coagulated TLW sources resulted in 61 % reduction in THM levels. Previous studies indicated that dissolved organic (DOC) may be used as a surrogate of THM precursors because humic substances typically comprise 50 % of DOC in surface water supplies. **Adin et al. (1991)** investigated the formation of THM and their experimental results indicated that under fixed chlorine levels and reaction times of 24 hours, THM production increased until the chlorine was depleted and then decreased while fulvic or humic acids concentrations were increasing consistently **(Adin, et al., 1991)**. However, most investigators found that at low concentrations of humics, in the presence of excess chlorine, THM formation rose with increasing dissolved organic matter with a pseudo first order reaction of DOC **(Kavanaugh et al., 1980; Babcock and Singer, 1979)**.

6.3.2. Effects of coagulant dosage on THM formation

Enhanced coagulation of THM formation removal was usually improved by increasing the ferric dosage, and the most effective THM removals (62%) were achieved at the highest ferric dosages of 120 mg/L with a pH value of 6.3 (Figure 6.3) for 24 h reaction time. Increasing the dosage of ferric coagulant not only increases the availability of ferric hydroxides potentially able to adsorb THMFP, but also increase the proton concentration, i.e., decreases the pH. The change in pH may be as or more important in enhancing THMFP removal.
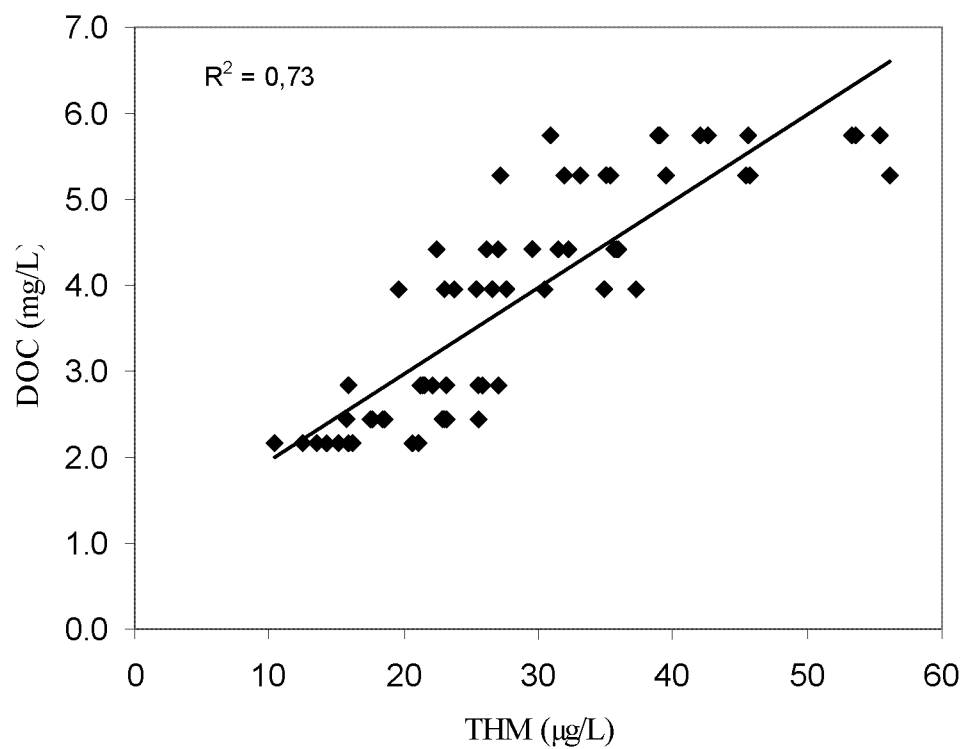
Figure 6.2: Measured THM values versus DOC values in coagulated TLW
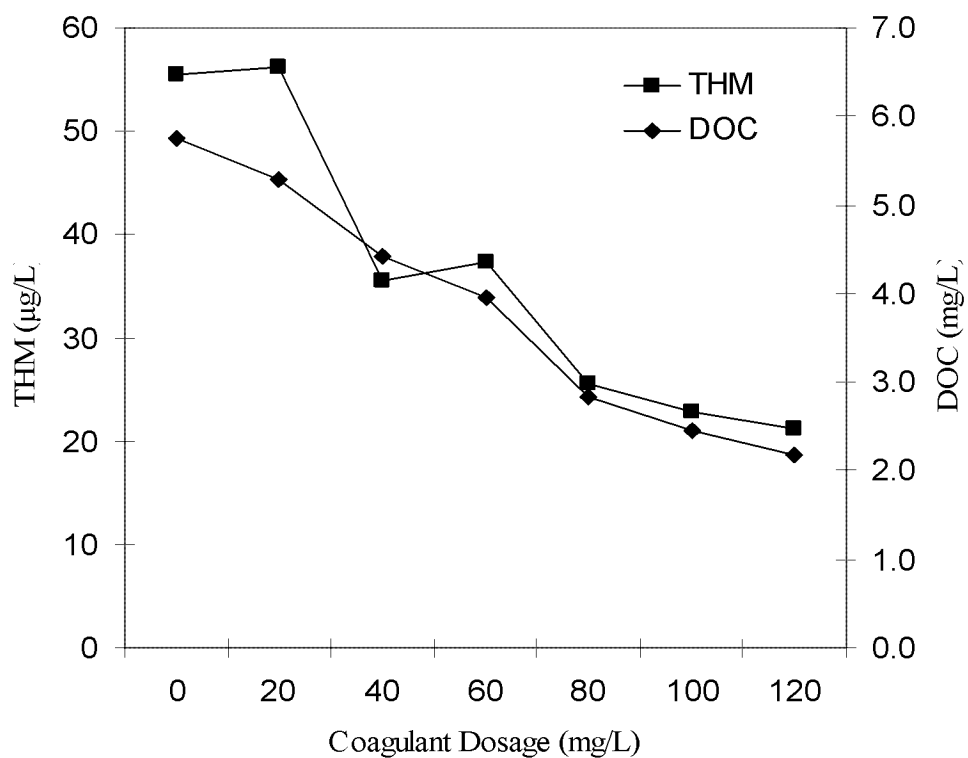
Figure 6.3: DOC removal and THM formation in coagulated TLW

The effect of FeCl₃ dose on the removal of THM species in TLW is shown in Figure 6.4. It was found that, similar to total THM, the percent removals of THM species increase as the FeCl₃ dose increases. From Figure 6.4, the maximum removals attained for chloroform the most dominant specie at 120 mg/L FeCl₃ are 70%. Further, as stated by previous studies **(Toroz and Uyak, 2005; Selcuk et al., 2005)**, the presence of brominated THM in TLW shows the sea water intrusion from Black Sea to TLW source. At maximum ferric dose of 120 mg/L, enhanced removal is due to increased NOM adsorption onto amorphous ferric hydroxide precipitates **(Krasner and Amy, 1995)**.
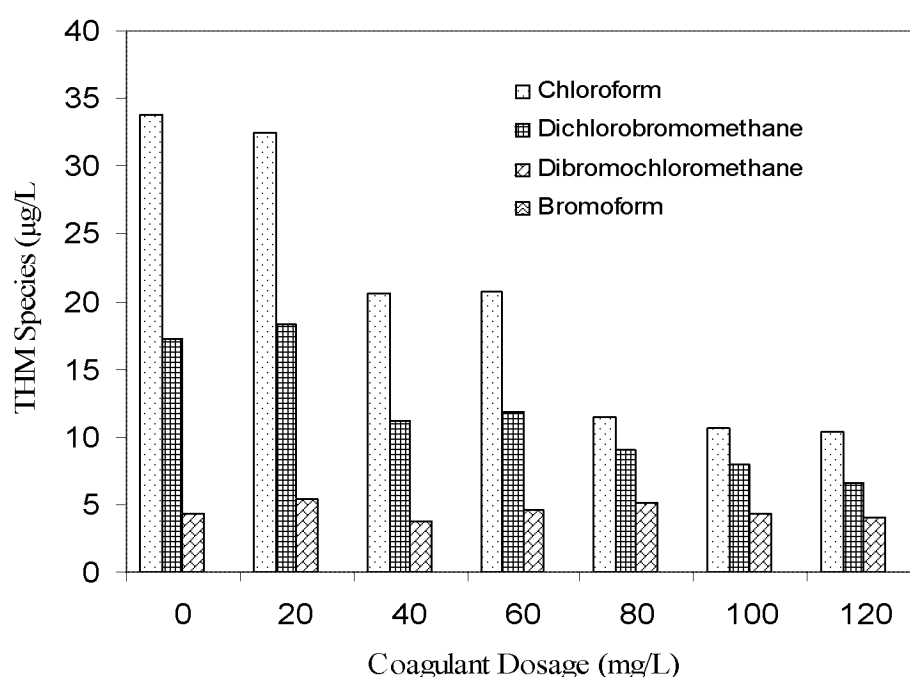
Figure 6.4: THM species formation as a function of ferric chloride dose

6.3.3. Effects of chlorine dosage on THM formation

Attempts were made to determine the effect of chlorination dosage on the production of THM in enhanced coagulated TLW (Figure 6.5). Using Pearson correlation method, a low but definite small relationship (R^2=0.365) was obtained between THM formation and total chlorine dosage for TLW. Table 6.3 shows the regression test for correlation of THM formation with chlorine dosage for this water supply. Addition of chlorine to water leads to the formation of hypochlorous acid (HOCl) and hypochloride ion (OCl⁻). The formation of these species depends on the pH. In acidic

solution HOCl is dominant, whereas in the alkaline solution formation of OCl⁻ dominates. In the case of enhanced coagulation for TLW, the pH value of the drinking water ranges from 8.05 to 6.30. As such hypochlorous acid is more prevalent chlorine specie which is responsible for the formation of THM. As such when THM concentration increases, the concentration of HOCl decreased.
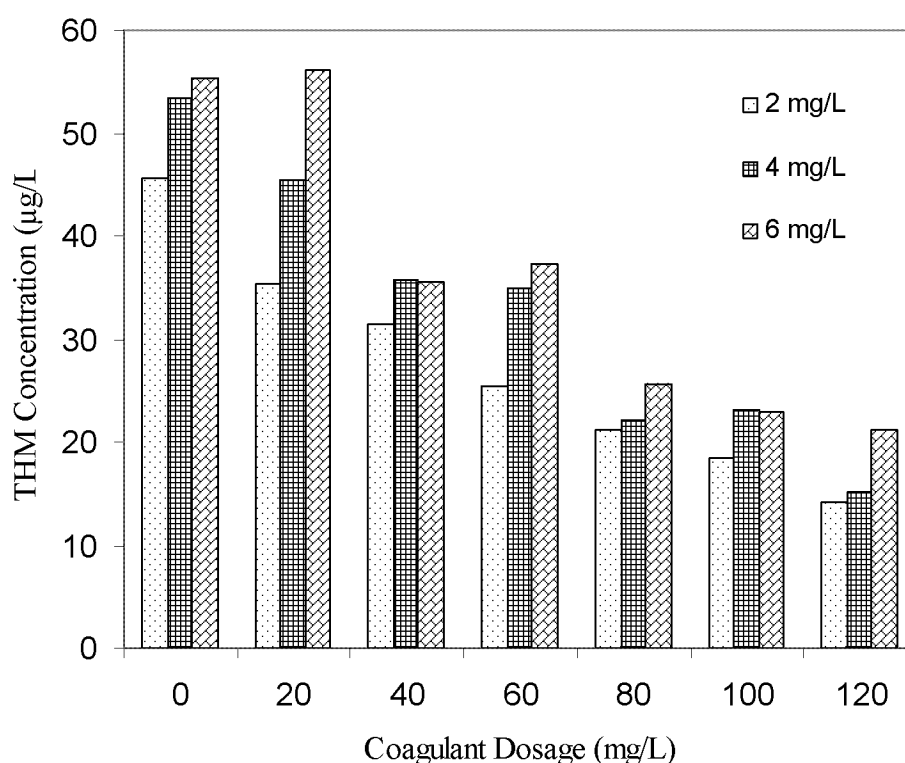
Figure 6.5: THM formation as a function of chlorine dose

6.3.4. Effects of reaction time on THM formation

In this chapter, a series of kinetic experiments was conducted for raw, and each coagulated water samples to provide THM formation versus three reaction times (6, 12, and 24 h) under a chlorine range of 2, 4, and 6 mg/L, and for incremental additions of coagulated water (20 to 120 mg/L). The reaction time value ranged from 6.0 h to 24 h which was associated to the formation of THM values in the range of 10 µg/L - 56 µg/L (Figure 6.6). Since ferric coagulation removed the NOM from raw water, and this influence the amount and rate of THM formation in coagulated TLW (Figure 6.6). Figure 6.6 provides THM data versus reaction time for TLW. THM formation rates were initially rapid, corresponding with the rapid consumption of

chlorine, followed by a slower, declining rate of production. Approximately, 77 % of the THM was formed within the first 6 h, and 94 % of THM formation correspond 12 h reaction time in comparison to final 24 h THM formation potential. These findings are similar to the results of **Krasner et al. (1989)**, and **Sinha (1999)** also reported that about 70 to 90 % of the THM was formed within the first 24 h when compare to 172 h THM formation potential. However, Pearson regression tests indicated weak correlation (r=0.141) between reaction time and the formation of THM for enhanced coagulated water. THM formation is thought to be a multi-stage process. The initial reaction of chlorine with NOM produces intermediates, which react further via various pathways to produce THM, and other final products **(Urano et al., 1983)**. The trends of THM formation depends on some parameters, such as chlorine dose, and the concentration of NOM.
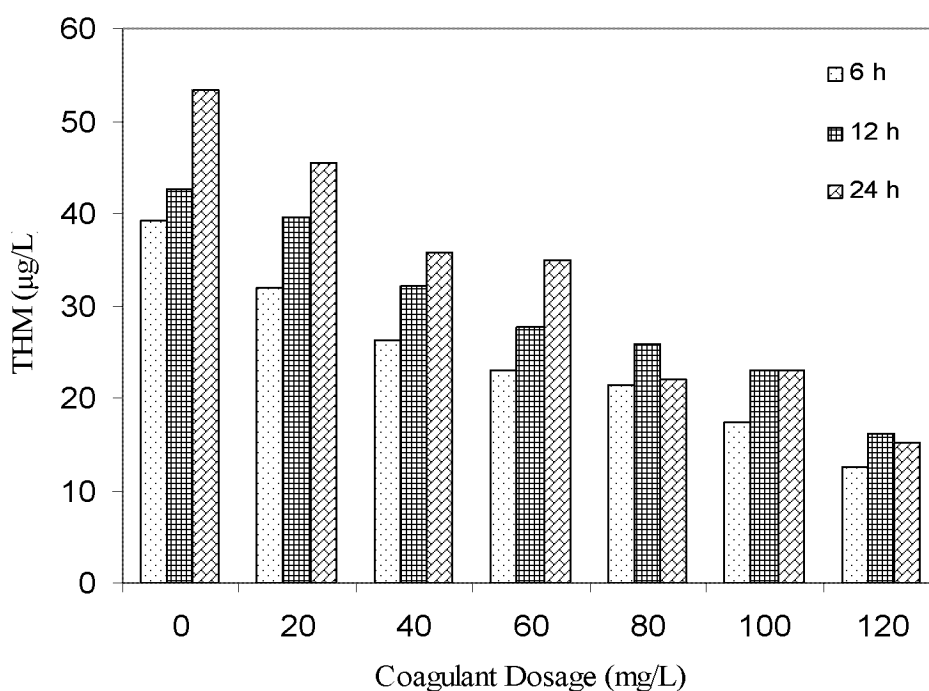
Figure 6.6: THM formation as a function of reaction time

6.3.5. Multiple linear THM formation modeling

Modeling consists of measured THM with the operational and water quality parameters which are responsible for THM formation. The data base created for modeling THM formation in enhanced coagulated samples was based on TLW.

Using a SPSS statistical procedure, THM formation model was developed. THM was predicted from raw and ferric coagulated DOC value, ferric dosage, applied chlorine dose, and reaction time. The predictive linear coagulated water model for THM formation was formulated as shown below. Table 6.2 shows the model accuracy. The R^2 and F value of model were 0.762 and 460, respectively. This model was found to be statistically significant for all four variables (Table 6.3).

$$TTHM = 10^{1.414} \times (DOC-2.1)^{0.199} \times (Ferric+1.56)^{-0.066} \times Cl_2^{0.242} \times Time^{0.210}$$

On the other hand, Figure 6.7 shows the normal probability plot of measured *vs.* the predicted values of THM. In this figure, all the points are near the straight line with a R^2 value of 0.877. Besides, Fig. 5.8 demonstrates the comparison of measured and predicted THM values. As seen in this figure, predicted THM curve overlaps the measured THM curve in most cases. Moreover, model predictions appear to be most accurate for this study.

Table 6.2: Model Summary

R	R^2	Adjusted R^2	F value	Standard error of the estimate
0.873	0.762	0.745	460	0.09459

Table 6.3: Regression Analysis Coefficients

Variables	B	Standard errors	*t*-values	*p*-level
Constant	1.354	0.124	10.921	0.000
log(Ferric+1.56)$^{0.2}$	-0.253	0.100	-2.525	0.014
log(Cl_2)	0.343	0.060	5.704	0.000
log(Time)	0.107	0.049	2.202	0.032
log(DOC-2.1)	0.210	0.025	8.422	0.000

Table 6.4: Pearson correlation matrix for model variables

	Ferric	Cl_2	Time	DOC	THM
Ferric	1.000				
Cl_2	0.000	1.000			
Time	0.000	0.000	1.000		
DOC	-0.563	0.000	0.000	1.000	
THM	-0.563	0.365	0.141	0.763	1.000

6.3.6. Model validation

Validation of a fitted regression model is the confirmation that the model is sound and effective for the purpose for which it was intended. Validation model requires assessing the effectiveness of the fitted equation against an independence set of data, is essential if confidence in the model is to be expected **(Abdullah et al., 2003)**. Analyses were done to determine the mean square error of prediction (MSEP). MSEP is defined as the average square difference between independent observation and prediction from the fitted equation for the corresponding values of the independent variable **(Drapper and Smith, 1981)**. Using independent set of data obtained from experimental chlorinated TLW and based on regression coefficients, and the calculation of percentage error in prediction, it was found that linear model have higher R^2 value of 0.857. Qualitatively, a visual inspection of a plot of measured values vs. predicted values can serve as a measure of model fitness **(Uyak et al., 2005)**. The goodness of the fit was evaluated through examination of various statistical indicators, including R^2, and F-statistic, while validation was focused on the slope and the intercept of predicted versus measured values of R^2 **(Adin et al., 1991)**. The results of the validation analysis are shown in Figure 6.8, which shows measured vs. predicted THM values in chlorinated TLW. The model validation indicates reasonable predictions of THM with R^2 value of 0.857.

6.4. Conclusion

Enhanced coagulation reduced the DOC level by 62 %, and the UV_{254} absorption by 74 % from TLW, suggesting that enhanced coagulation with ferric treatment preferentially removed organic compounds with higher UV absorption. This result supports the conclusion that TLW's NOM was as amenable to chemical coagulation because of its moderate humic fraction. Enhanced coagulation of THM formation removal was usually improved by increasing the ferric dosage, and the most effective THM removals (62%) were achieved at the highest ferric dosages of 120 mg/L with a pH value of 6.3. Increasing the dosage of ferric coagulant not only increases the availability of ferric hydroxides potentially able to adsorb THMFP, but also increase the proton concentration, i.e., decreases the pH. Moreover, increased DOC removal in enhanced coagulated TLW sources resulted in 61 % reduction in THM levels. This chapter discusses the formulation of a model for predicting THM levels in ferric

coagulated TLW in Istanbul. With the use of multiple linear regression techniques, it is possible to develop models for simulating and predicting THM during the enhanced coagulation treatment.
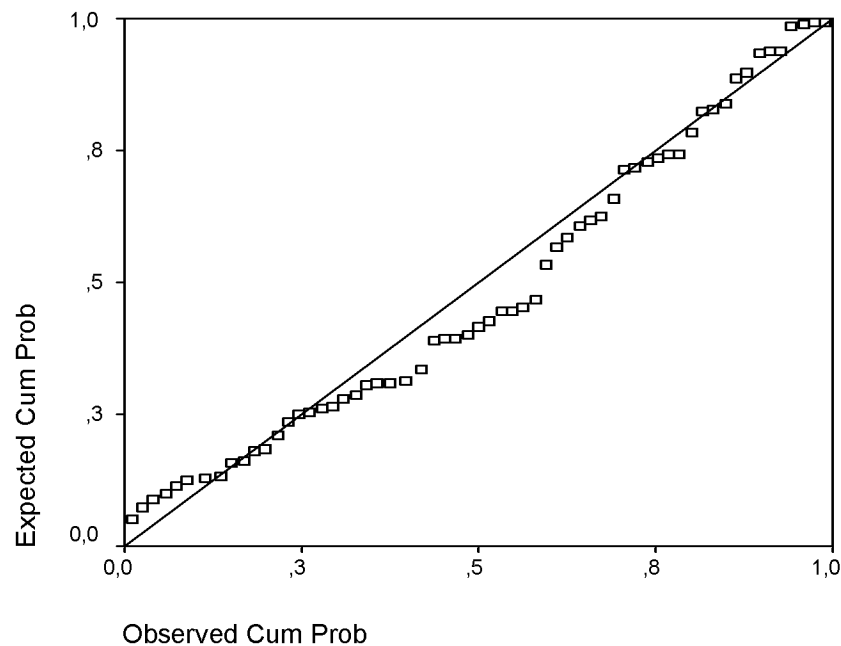
Figure 6.7: Goodness of the fit of the model for predicted and measured values of THM

Based on THM formation experiments, a data base was established for modeling THM formation during chlorination of enhanced coagulated water. The general strategy adopted to develop model equation was to describe the roles of DOC precursor, chlorine dose, and reaction time in formation of THM. The R^2 and F value of model were 0.762 and 460, respectively. This model was found to be statistically significant for all four variables, and model predictions appear to be most accurate for this study. The model validation indicates reasonable predictions of THM with R^2 value of 0.857. Future researches in this area should be directed to formation and modeling of HAA in Istanbul water supplies.
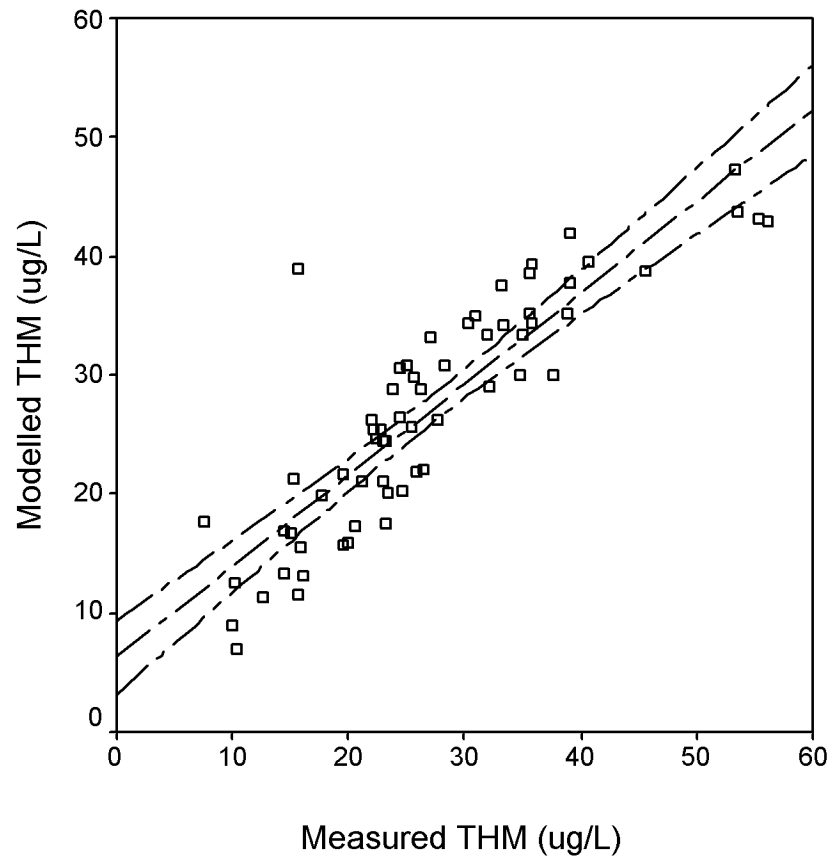
Figure 6.8: Validation of the model for predicted and measured values of THM

7. COST ASSESSMENT OF ENHANCED COAGULATION

7.1. Objectives

The objective of this chapter is to demonstrate how Istanbul water treatment plants can (1) meet current THM limit by using enhanced and optimized coagulation processes, and (2) start to evaluate cost assessment of enhanced and optimized coagulation methods. As currently regulated in our country, Regulation Concerning Water Intended for Human Consumption **(RCWIHC, 2005)** has been effective for water treatment utilities since January 2005. It is important that water authorities begin to evaluate the amenability of water treatment plants to national and international THM limits compliance.

7.2. Introduction

The concept of enhanced coagulation involves a broadening of coagulation objectives from turbidity removal to include NOM removal. These dual objectives require modifying coagulation conditions, with the three principal alternatives being (1) type of coagulant, (2) coagulant dosage, and (3) coagulation pH. The effects of higher dosage are readily apparent, providing more metal for either floc or complex formation. Lower pH reduces the charge density of humic and fulvic acids, making them more hydrophobic and adsorbable. The choice between aluminum and iron simply reflects their different solubilities and coordination chemistry. The practical definition of enhanced coagulation is to provide treatment conditions that still sustain effective turbidity removal while also increasing NOM removal.

The disinfectant/disinfection by-product (D/DBP) regulation in USA mandates water treatment plants using disinfectants to remove predetermined levels of total organic carbon (TOC) as a means of reducing DBP precursors **(Bell et al., 2000)**. The US EPA has recognized enhanced coagulation (EC) as the best available technology (BAT) for controlling DBP precursors **(Krasner and Amy, 1995)**. EC corresponds to the use of

coagulant dosages effective for TOC removal. In USA, EC was selected as the Stage 1 treatment of choice because it was effective for the TOC removal and could be implemented at most water plants treating surface waters using existing treatment processes **(Bell et al., 2000)**. As mentioned preceding chapters, this treatment technique includes two steps of application. Step 1 defines the percentage of influent TOC, a plant must remove based on the raw water TOC and alkalinity levels (Table 7.1). The step 1 TOC removal requirements increase with increasing raw water TOC levels but decrease with increasing alkalinity. A second step of the D/DPB rule was established to provide alternate performance criteria when it is technically unfeasible for water utilities to meet the step 1 requirements.

Table 7.1: EPA Alkalinity and total organic carbon (TOC) matrix for percent TOC removal goals by enhanced coagulation

TOC	Alkalinity mg/L as $CaCO_3$		
	0-60	60-120	>120
mg/L	percent	percent	percent
2.0-4.0	35	25	15
4.0-8.0	45	35 (**TLW** and **OLW**)	25 (**BLW**)
>8.0	50	40	30

In this chapter, based on US water treatment experiences, enhanced coagulation techniques were applied in Istanbul water supplies for NOM removal. In preceding chapters, the work evaluated the coagulation process on the levels of organic matter removal at a bench-scale for TLW, BLW, and OLW. In the 3rd chapter, the study was to optimize coagulant dose based upon the optimum removal of dissolved organic carbon (DOC). In 4th chapter of the study, the conditions for optimum coagulant dosages were determined via jar tests, DOC, UV_{254}, SUVA, and THMFP removals were evaluated, and optimization of pH levels for two different coagulants of ferric chloride and alum was performed. Besides, in 5th chapter, the study was examined the modeling THM formation during enhanced coagulation. In this chapter, cost estimates of four different coagulation techniques were performed. They are base line, enhanced and two optimized coagulation methods. Besides, as it

is the case for all chapters, TOC term was replaced with DOC during this chapter as well.

7.3. Results and Discussion

7.3.1. Titration curves with acids and coagulants

In order to make cost estimates, titration curves for acid and two coagulants were conducted. Titration curves were developed for Terkos, Buyukcekmece and Omerli Lake Waters (TLW, BLW, and OLW) to describe (1) the amount of sulfuric acid necessary to depress the ambient pH to a more optimal pH, and (2) the effects of ferric chloride and alum on pH depression. Titration curves of three water sources for H_2SO_4 are shown in Figure 7.1; the complete titration curves to a pH of 4.3 define the alkalinities of the respective source waters: 125, 135, and 67 mg/L as $CaCO_3$ for TLW, BLW, and OLW, respectively (Table 5.1).

The amount of H_2SO_4 required to reduce TLW to pH levels of 6.5, 6.0, and 5.5, the required optimum pH values for ferric chloride and alum coagulation, was estimated from the titration curves (Figure 7.1). These required amounts of H_2SO_4 for TLW were 60 mg/L for 6.5, 89 mg/L for 6.0, and 102 mg/L for 5.5 pH values. On the other hand, the amount of required H_2SO_4 to reduce BLW to pH levels of 6.5, 6.0, and 5.5, was estimated also from the Figure 7.1. These required amounts of H_2SO_4 for BLW were 70 mg/L for 6.5, 102 mg/L for 6.0, and 118 mg/L for 5.5 pH values. Further, the amount of required H_2SO_4 to reduce pH levels of OLW to 6.5, 6.0, and 5.5, was estimated from the Figure 7.1. These required amounts of H_2SO_4 for OLW were 32 mg/L for 6.5, 49 mg/L for 6.0, and 59 mg/L for 5.5 pH values. On the other hand, the amount of acid required varies with seasonal changes in water quality of alkalinity and pH values.

Ferric chloride and alum exhibit acid properties when added to water. Therefore, coagulant addition will also contribute to pH depression toward more optimal pH conditions. Mineral acid addition before coagulant addition represents a trade off between coagulant costs and acid costs. Coagulant titration curves of ferric chloride and alum for the TLW, BLW, and OLW sources are shown in Figure 7.2 and Figure 7.3.
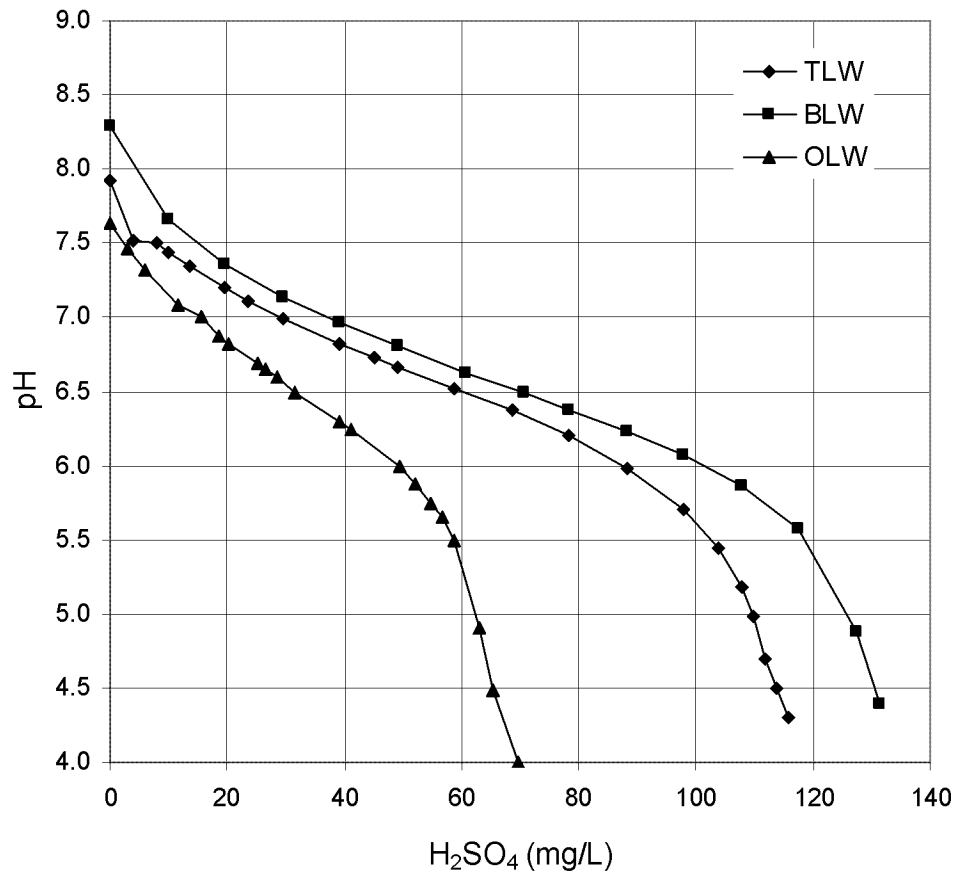
Figure 7.1: H_2SO_4 titration curves of three water sources

7.3.2. Impact of coagulation pH on DOC removal

It is shown in Figure 7.2 that using ferric chloride addition to depress the pH to 6.5, 6.0, and 5.5 for TLW requires 120, 170, and 200 mg/L ferric chloride, respectively. To depress the pH of TLW to 6.5, 6.0, and 5.5 with alum requires 130, 200, and 240 mg/L alum, respectively (Figure 7.3). On the other hand, using ferric chloride addition to depress the pH to 6.5, 6.0, and 5.5 for BLW requires 142, 210, and 245 mg/L ferric chloride, respectively. To depress the pH of BLW to 6.5, 6.0, and 5.5 with alum requires 160, 240, and 290 mg/L alum, respectively. Further, using ferric chloride addition to depress the pH to 6.5, 6.0, and 5.5 for OLW requires 60, 84, and 98 mg/L ferric chloride, respectively (Figure 7.2). To depress the pH of OLW to 6.5, 6.0, and 5.5 with alum requires 68, 102, and 124 mg/L alum, respectively. The shape of the ferric chloride

titration curve parallels that of H_2SO_4 addition, whereas the alum curve is affected, in part, by the pH of minimum solubility of insoluble aluminum hydroxide.
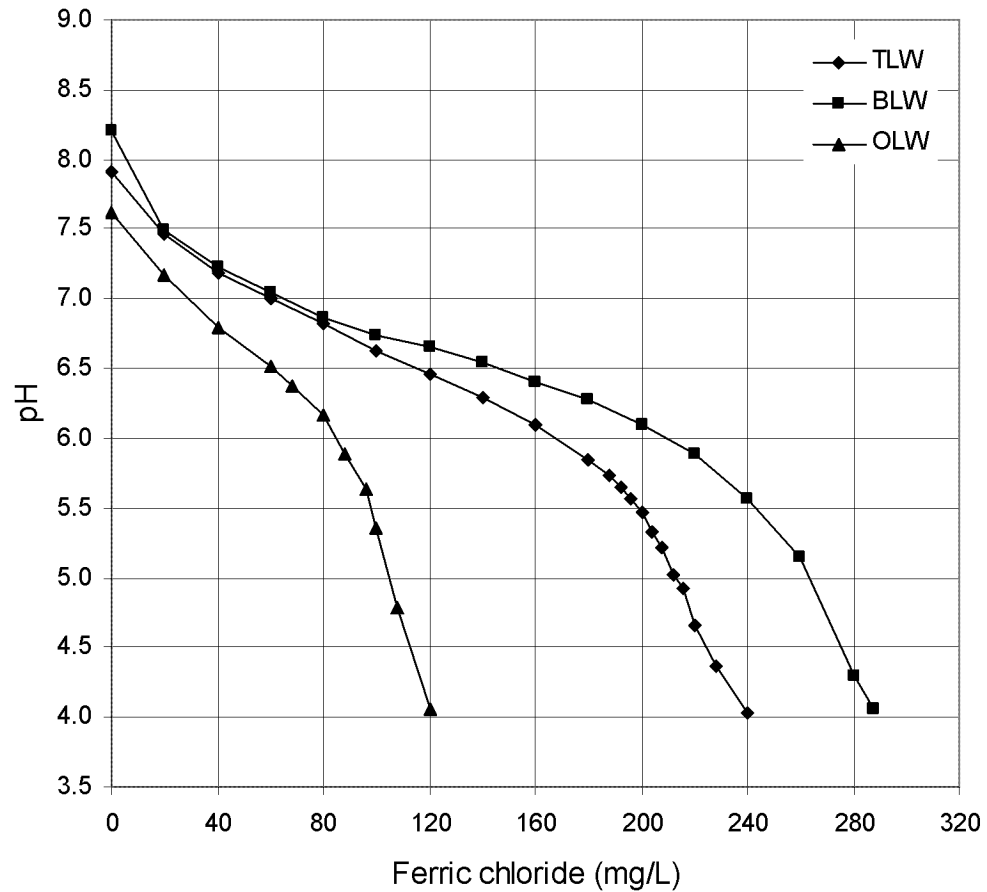
Figure 7.2: Ferric chloride titration curves of three water sources

The TLW experiences moderate DOC variations (3.55-5.85 mg/L) as shown in Table 5.1., and the enhanced coagulation requirement of 35 percent TOC removal was met by using 80 mg/L ferric chloride or 100 mg/L alum without pH adjustment (Figure 7.4). Besides, 35 percent TOC removal could be achieved using 20, 40, and 60 mg/L ferric chloride with reduction of the coagulation pH below 7.0 by addition of acid. As shown in Figure 7.5, 2.68 mg/L TOC level which is 35 percent removal of EPA requirement for TLW source can be met by varying pH and ferric chloride variations. Further, the TOC removal compliance of 35% for alum coagulation with adjusted pH levels is also shown

in Figure 7.6. The 35 percent TOC criteria was met by 4 of 9 columns of alum dose-pH combination for TLW.
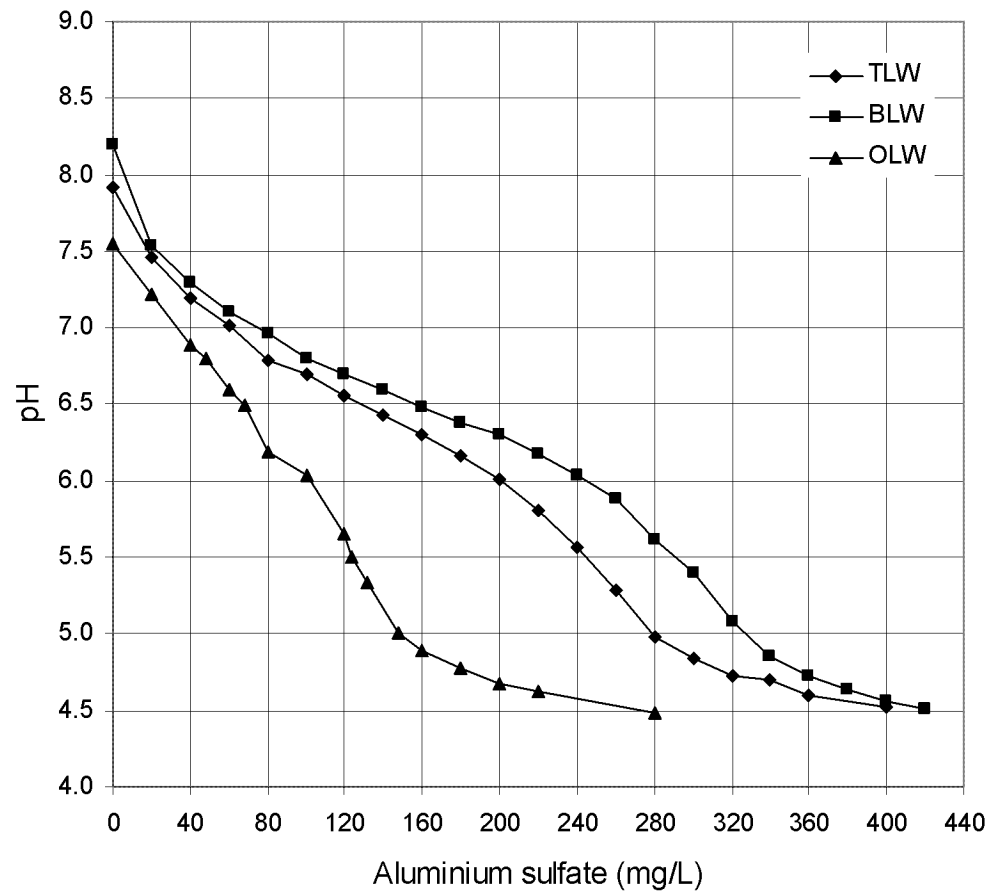
Figure 7.3: Alum titration curves of three water sources
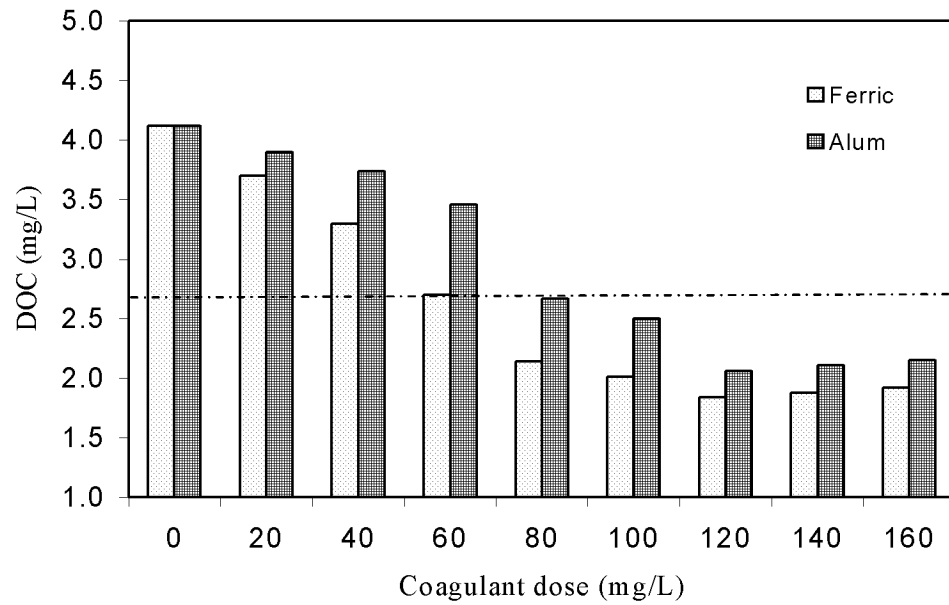
Figure 7.4: Effect of coagulant dose on DOC removal from TLW
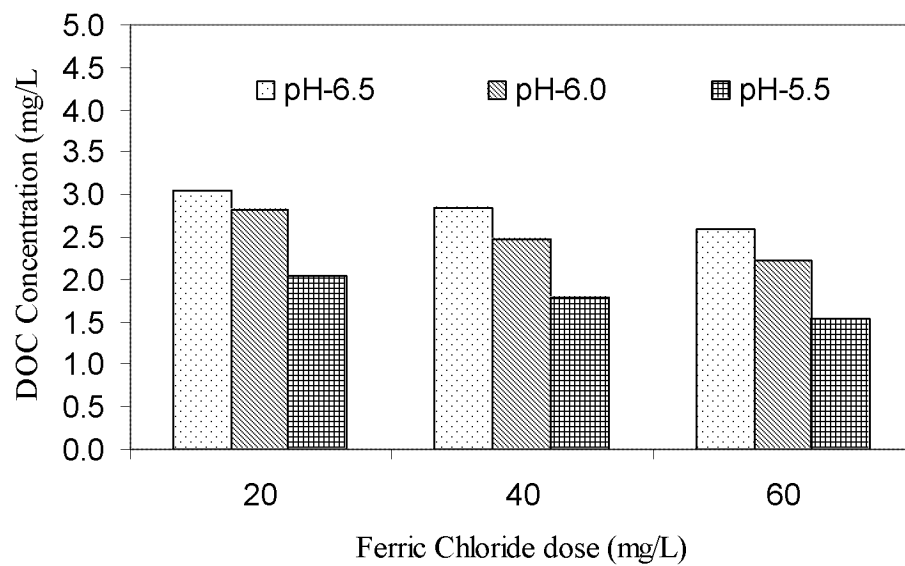
Figure 7.5: Impact of coagulation pH with ferric chloride on DOC removal from TLW

The BLW is typically exhibits a medium level of NOM (3.76-6.25 mg/L) and moderate average alkalinity value of 135 mg/L. DOC removal data in Figure 7.7 shows that the enhanced coagulation requirement of 25 percent could be met at a ferric chloride and alum dose of about 60 and 80 mg/L, respectively. Adjustment of the coagulation pH to 6.5, 6.0, and 5.5 reduced the required coagulant dose by 20 to 40 mg/L. Figure 7.8 shows that 25% TOC removal can be met on BLW source with pH adjustment. Further, except 20 mg/L ferric chloride coagulation at pH 6.5, all of the ferric chloride coagulant dose and pH combinations can meet the TOC removal requirement of 25% for BLW. Besides, alum coagulation with pH adjustment improved the coagulation efficiency of BLW. As summarized in Figure 7.9, 25% TOC removal compliance can be met 6 of 9 columns of alum dose-pH combination for BLW.
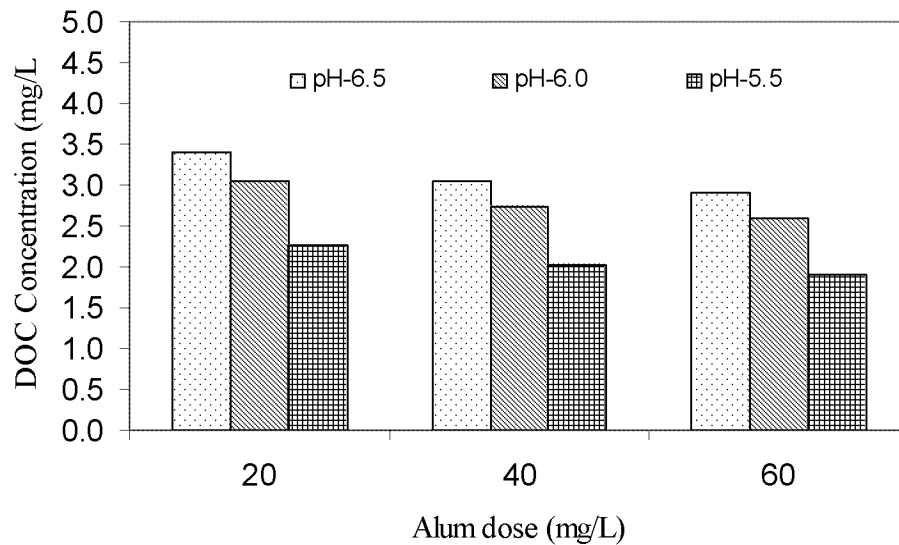
Figure 7.6: Impact of coagulation pH with alum on DOC removal from TLW
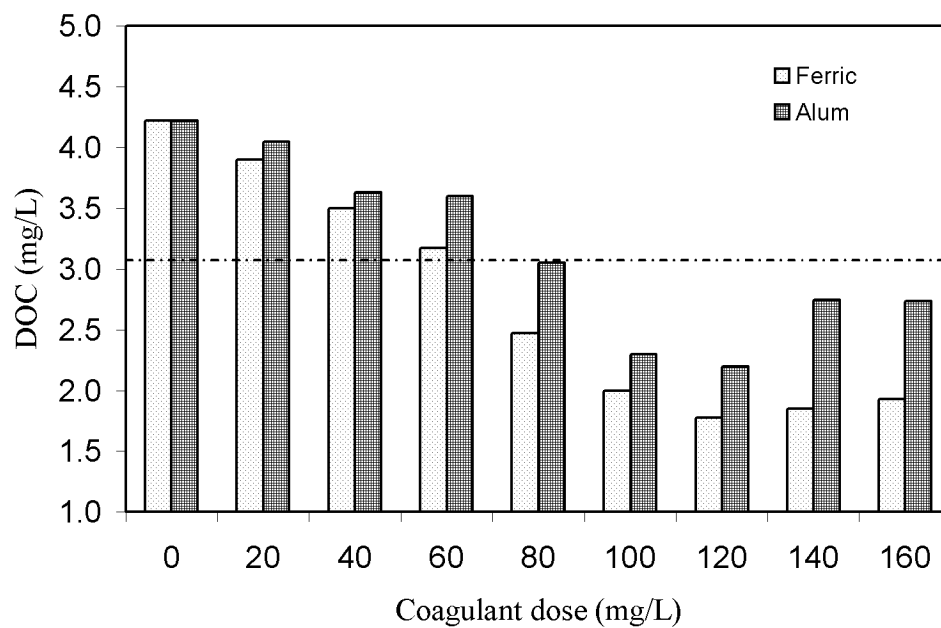
Figure 7.7: Effect of coagulant dose on DOC removal from BLW
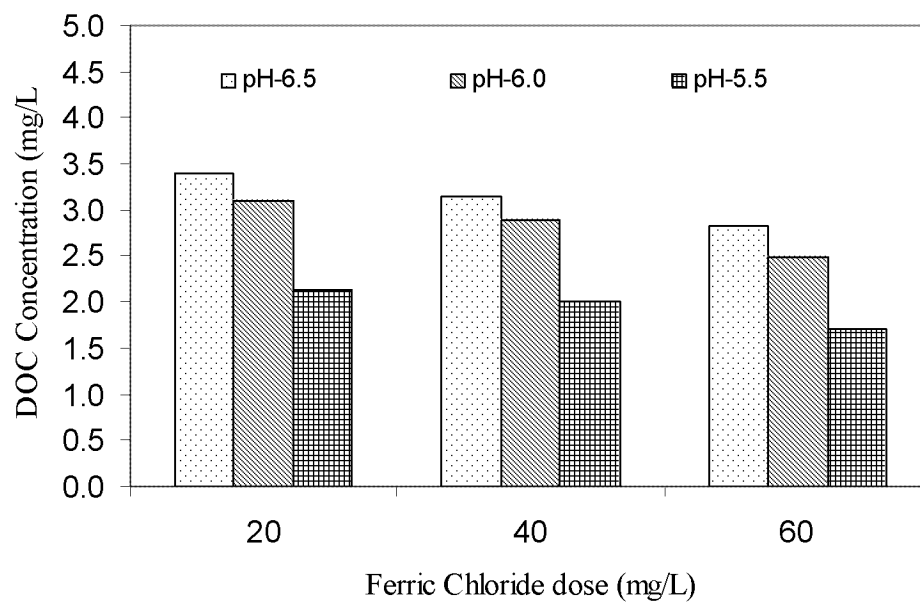
Figure 7.8: Impact of coagulation pH with ferric chloride on DOC removal from BLW
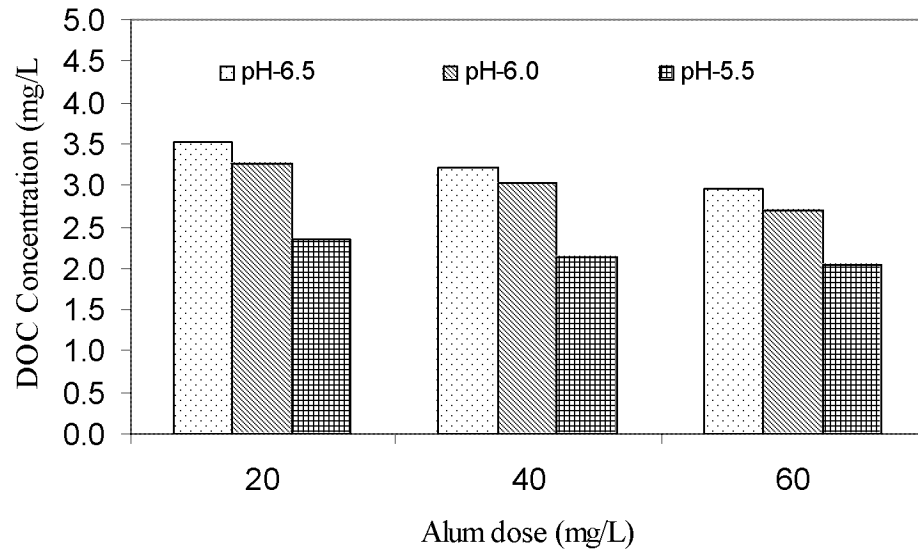
Figure 7.9: Impact of coagulation pH with alum on DOC removal from BLW

The OLW is typically characterized by a medium DOC value between of 3.20 and 4.80 mg/L and low average alkalinity value of 65 mg/L. The required percentage removal of TOC by enhanced coagulation is as high as 35 percent. Figure 7.10 shows that this goal could be met at a ferric chloride dose of 100 mg/L with no pH adjustment. Further, 35% required percent of TOC removal could be achieved at alum dosages of 100 mg/L and above. As shown in Figure 7.11, 2.53 mg/L TOC level which is 35 percent removal of EPA requirement for OLW source can be met by varying pH and ferric chloride variations. Alum coagulation dosages and pH adjustment improved the NOM removal very effectively from OLW. Figure 7.12 shows that 35% TOC removal value of 2.53 mg/L is shown as dashed lines. 4 of 9 columns could comply with TOC requirements criteria of 35% for OLW coagulation with alum.
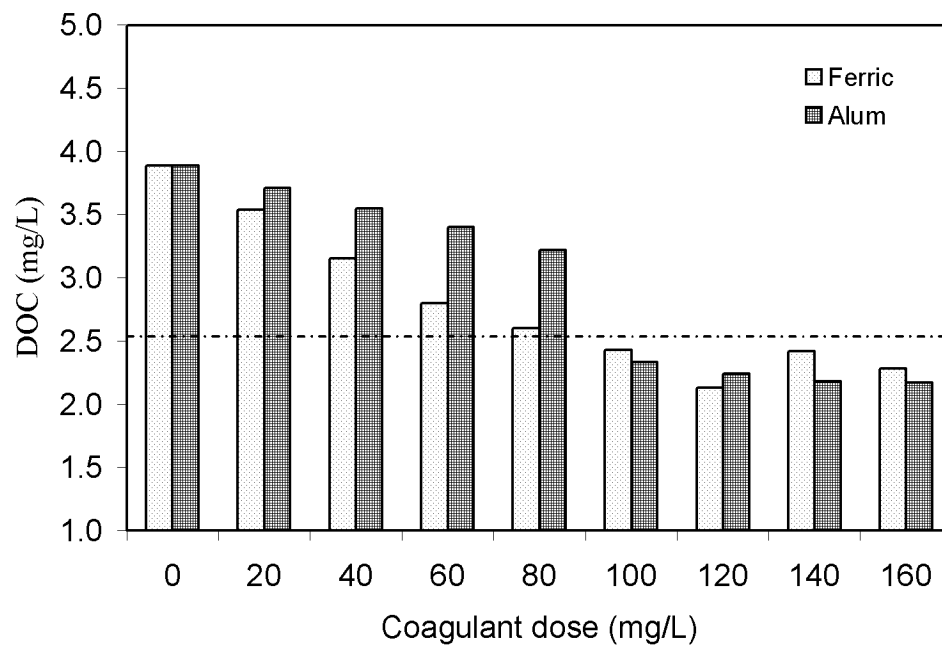
Figure 7.10: Effect of coagulant dose on DOC removal from OLW
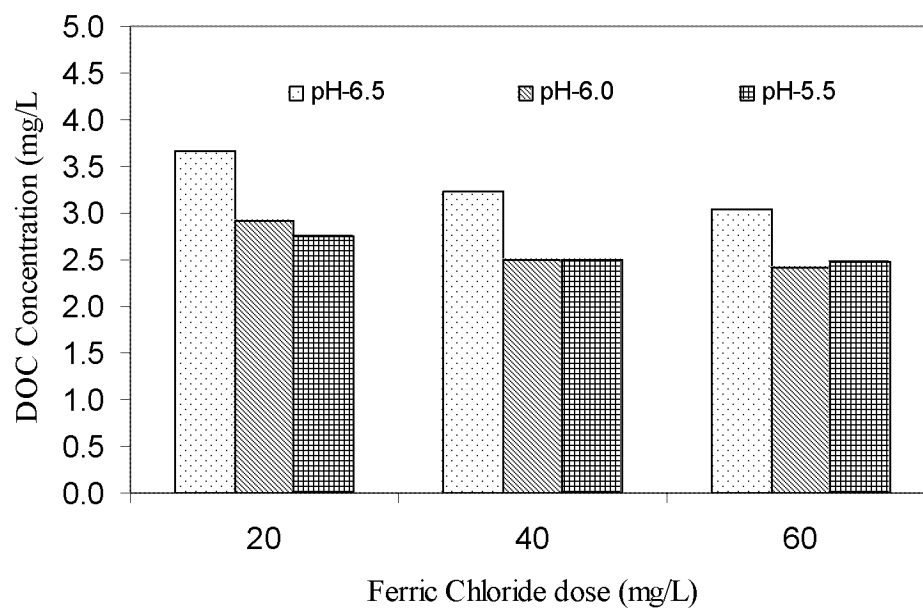
Figure 7.11: Impact of coagulation pH with ferric chloride on DOC removal from OLW
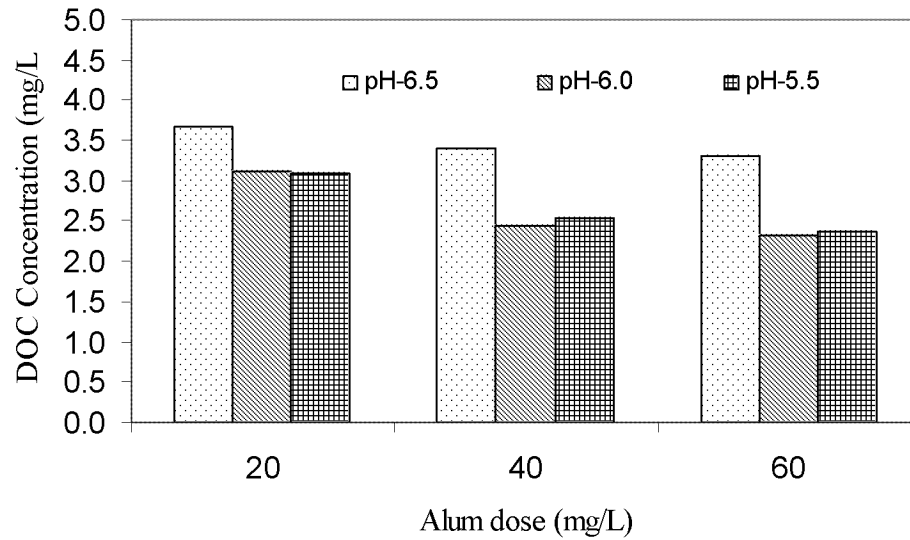
Figure 7.12: Impact of coagulation pH with alum on DOC removal from OLW

7.3.3. Cost assessments of four coagulation techniques

In Istanbul water treatment plants, approximately, the average applied coagulant dosages are 40 mg/L. For this thesis, this amount of coagulant dose was represented as Baseline Coagulation (BC) condition. Furthermore, the optimum coagulant dose for Enhanced Coagulation (EC) method was selected as 80 mg/L. On the other hand, during Optimized Coagulation-I, (OC-I) 40 mg/L coagulant dose was applied at the optimum pH value of 6.0. For Optimized Coagulation-II (OC-II) technique, the optimum ferric chloride coagulation dose and pH values were 80 mg/L and 5.5, respectively. Further, alum coagulation used 80 mg/L coagulant dose and pH 6.0 values for OC-II. When the optimum coagulant conditions were selected, practical applications, engineering points and cost issues were taken into account. For each of three source waters studied, the chemical cost of four coagulation techniques was evaluated, and was compared with each other. Table 7.2 and Table 7.3 show the chemical cost data for all coagulation methods.

Without pH adjustment, BC by ferric chloride costs 7.20 $/1000 m^3 water treated for three water supplies. Further, alum treatment of BC, required 7.40 $ for treatment of

1000 m^3 water for TLW, BLW, and OLW. During coagulant cost calculations, ferric chloride and alum was accounted as 180 and 185 $/ton, respectively.

EC by 80 mg/L ferric chloride costs 14.40 $/1000 m^3 water treated for three water supplies. Further, 80 mg/L alum treatment of EC required 14.40 $ for treatment of 1000 m^3 water for TLW, BLW, and OLW.

With OC-I condition of 40 mg/L ferric coagulation, OC-I type resulted in 18.10, 18.35, and 12.35 $/1000 m^3 water treated cost for TLW, BLW, and OLW, respectively. Besides, 40 mg/L alum treatment at pH 6.0 of OC-I required 19.03, 22.78, and 12.57 $ for treatment of 1000 m^3 water for TLW, BLW, and OLW, respectively. During pH adjustment, sulfuric acid and sodium hydroxide were used to adjust pH value of raw water. Since raw water pH value of BLW was the highest in three water sources, the maximum cost was obtained for BLW. Moreover, the raw water pH value of OLW was around 7.62, the lowest pH value, and the minimum chemical cost was occurred for OLW.

With OC-II conditions of 80 mg/L ferric coagulation at pH 5.5, it was resulted in 24.82, 26.23, and 18.37 $/1000 m^3 water treated cost for TLW, BLW, and OLW, respectively. On the other hand, 80 mg/L alum treatment at pH 6.0 of OC-II required 24.45, 30.00, and 18.98 $ for treatment of 1000 m^3 water for TLW, BLW, and OLW, respectively.

As shown above, since coagulant dose is constant for three waters, the coagulation costs for baseline and enhanced coagulation techniques are same for all three water sources. However, during OC-I and OC-II methods, coagulation cost were varied. The amount of cost discrepancies was caused by different raw water pH values. During the studies, since the highest raw water pH value was belong to BLW, the highest chemical costs for two optimized coagulation methods were happened for BLW. Besides, OLW has the lowest pH value, thus, the lowest chemical costs for occurred for OLW.

Table 7.2: Chemical costs of different coagulation conditions with ferric chloride for Istanbul water supplies

Coagulation Technique	Ferric	H$_2$SO$_4$	NaOH	pH	Q	Ferric	H$_2$SO$_4$	NaOH	COSTS				
	mg/L	mg/L	mg/L		m³/day	ton/day	ton/day	ton/day	Ferric	H$_2$SO$_4$	NaOH	Total	Unit Cost
									$/day	$/day	$/day	$/day	$/1000 m³
TL W													
Baseline Coagulation	40	0	0	7.2	800000	32	0	0	5760	0	0	5760	7.2
Enhanced Coagulation	80	0	0	6.8	800000	64	0	0	11520	0	0	11520	14.4
Optimized Coagulation-I	40	68	60	6	800000	32	54	48	5760	6800	1920	14480	18.1
Optimized Coagulation-II	80	60	73	5.5	800000	64	48	58	11520	6000	2336	19856	24.82

Coagulation Technique	Ferric	H$_2$SO$_4$	NaOH	pH	Q	Ferric	H$_2$SO$_4$	NaOH	COSTS				
	mg/L	mg/L	mg/L		m³/day	ton/day	ton/day	ton/day	Ferric	H$_2$SO$_4$	NaOH	Total	Unit Cost
									$/day	$/day	$/day	$/day	$/1000 m³
BL W													
Baseline Coagulation	40	0	0	7.2	400000	16	0	0	2880	0	0	2880	7.2
Enhanced Coagulation	80	0	0	6.9	400000	32	0	0	5760	0	0	5760	14.4
Optimized Coagulation-I	40	70	60	6	400000	16	28	24	2880	3500	960	7340	18.35
Optimized Coagulation-II	80	70	77	5.5	400000	32	28	31	5760	3500	1232	10492	26.23

Coagulation Technique	Ferric	H$_2$SO$_4$	NaOH	pH	Q	Ferric	H$_2$SO$_4$	NaOH	COSTS				
	mg/L	mg/L	mg/L		m³/day	ton/day	ton/day	ton/day	Ferric	H$_2$SO$_4$	NaOH	Total	Unit Cost
									$/day	$/day	$/day	$/day	$/1000 m³
OL W													
Baseline Coagulation	40	0	0	6.8	1200000	48	0	0	8640	0	0	8640	7.2
Enhanced Coagulation	80	0	0	6.2	1200000	96	0	0	17280	0	0	17280	14.4
Optimized Coagulation-I	40	30	35	6	1200000	48	36	42	8640	4500	1680	14820	12.35
Optimized Coagulation-II	80	18	43	5.5	1200000	96	22	52	17280	2700	2064	22044	18.37

Table 7.3: Chemical costs of different coagulation conditions with alum for Istanbul water supplies

Coagulation Technique	Alum mg/L	H₂SO₄ mg/L	NaOH mg/L	pH	Q m³/day	Alum ton/day	H₂SO₄ ton/day	NaOH ton/day	COSTS				
									Alum $/day	H₂SO₄ $/day	NaOH $/day	Total $/day	Unit Cost $/1000 m3
TLW													
Baseline Coagulation	40	0		7.2	800000	32	0	0	5920	0	0	5920	7.4
Enhanced Coagulation	80	0		6.8	800000	64	0	0	11840	0	0	11840	14.8
Optimized Coagulation-I	40	69		6	800000	32	55	60	5920	6900	2400	15220	19.03
Optimized Coagulation-II	80	48		6	800000	64	38	73	11840	4800	2920	19560	24.45

Coagulation Technique	Alum mg/L	H₂SO₄ mg/L	NaOH mg/L	pH	Q m³/day	Alum ton/day	H₂SO₄ ton/day	NaOH ton/day	COSTS				
									Alum $/ton	H₂SO₄ $/ton	NaOH $/ton	Total $/ton	Unit Cost $/1000 m3
BLW													
Baseline Coagulation	40	0		7.3	400000	16	0	0	2960	0	0	2960	7.4
Enhanced Coagulation	80	0		7	400000	32	0	0	5920	0	0	5920	14.8
Optimized Coagulation-I	40	75		6	400000	16	30	60	2960	3750	2400	9110	22.78
Optimized Coagulation-II	80	60		6	400000	32	24	77	5920	3000	3080	12000	30.00

Coagulation Technique	Alum mg/L	H₂SO₄ mg/L	NaOH mg/L	pH	Q m³/day	Alum ton/day	H₂SO₄ ton/day	NaOH ton/day	COSTS				
									Alum $/ton	H₂SO₄ $/ton	NaOH $/ton	Total $/ton	Unit Cost $/1000 m3
OLW													
Baseline Coagulation	40	0		6.9	1200000	48	0	0	8880	0	0	8880	7.4
Enhanced Coagulation	80	0		6.6	1200000	96	0	0	17760	0	0	17760	14.8
Optimized Coagulation-I	40	32		6	1200000	48	38	35	8880	4800	1400	15080	12.57
Optimized Coagulation-II	80	22		6	1200000	96	26	43	17760	3300	1720	22780	18.98

7.3.4. TOC regulation compliances

Percent Removal of DOC with ferric chloride and alum coagulation of four different coagulation methods and associated THM formation for three water supplies are summarized in Table 7.6 and Table 7.7, respectively. In these tables, comparison with EPA TOC removal requirement and compliance with THM limits in national and international wide were compared. As summarized in Table 5.1, EPA TOC percent removal requirement of TLW, BLW, and OLW are 35, 25, and 35, respectively. However, baseline coagulation studies with ferric chloride showed that EPA TOC removal requirement for all water sources could not be meet. Maximum DOC removals with ferric chloride baseline coagulation were 20, 17, and 19% for TLW, BLW, and OLW, respectively. On the other hand, baseline alum coagulation of DOC from TLW, BLW, and OLW, resulted in 9, 14, and 9% reduction, respectively. Thus, alum coagulation also could not be able to meet EPA TOC limit for three water supplies.

Enhanced coagulation with ferric chloride removed DOC from TLW, BLW, and OLW 48, 41, 33%, respectively. Based on EPA TOC requirement, just only OLW could not be able to meet 35% TOC limit (Table 7.6.). Besides, during alum coagulation at enhanced coagulation mode, DOC removals percent were 35, 28, and 30% for TLW, BLW, and OLW, respectively. In the alum coagulation case, only, TLW source met the EPA TOC limit (Table 7.7.). Based on these results, it was concluded that pH optimization has to be performed to comply with EPA TOC criteria in Istanbul source waters.

Optimized coagulation-I with ferric chloride removed DOC from TLW, BLW, and OLW, 53, 46, 35%, respectively (Table 7.6.). Further, alum treatment of optimized coagulation-I resulted in DOC removal of 38, 49, and 36% for TLW, BLW, and OLW, respectively (Table 7.7.). Based on two coagulant results, all of the water DOC treatment could meet EPA TOC limit. Further, OLW just complied with EPA TOC limit with these two coagulants. Thus, critic TOC removal amount of OLW should be increased by pH optimization studies.

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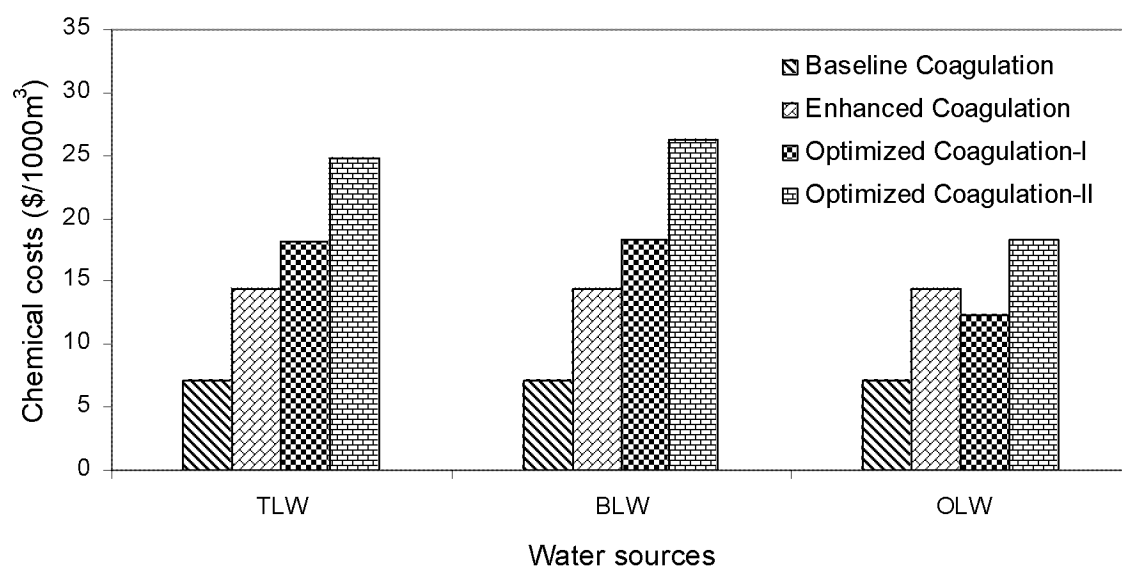
Figure 7.13: Chemical costs of different coagulation conditions with ferric chloride for meeting EPA TOC requirement for three Istanbul water supplies
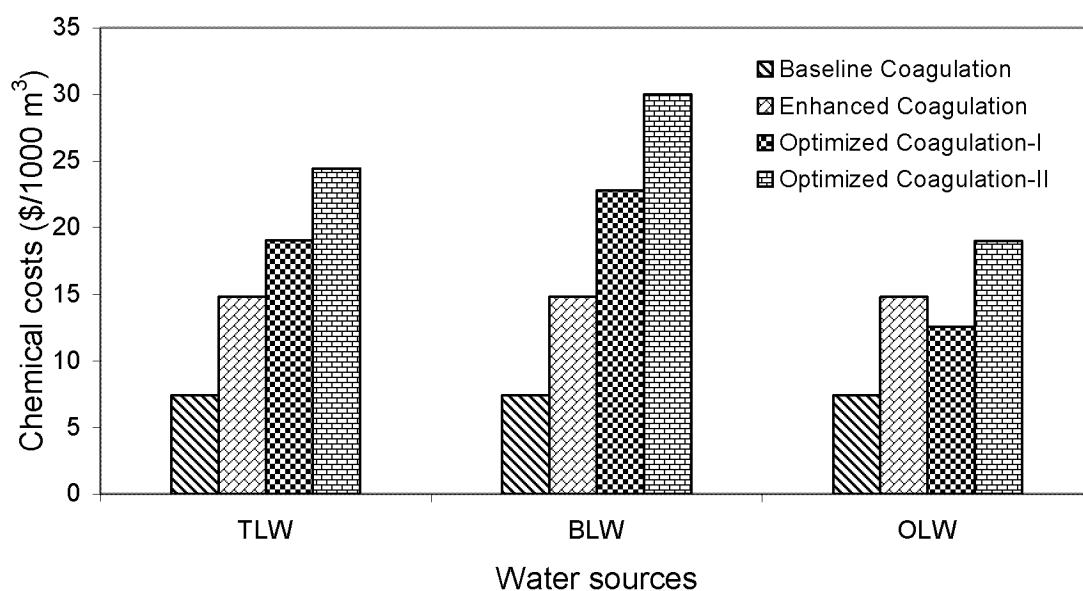
Figure 7.14: Chemical costs of different coagulation conditions with alum for meeting EPA TOC requirement for three Istanbul water supplies

Optimized coagulation-II with ferric chloride resulted in DOC removal of 66, 64, and 41 for TLW, BLW, and OLW, respectively (Table 7.6.). Further, alum coagulation of TLW, BLW, and OLW with optimized coagulation–II technique removed DOC from TLW, BLW, and OLW, 42, 64, and 37%, respectively (Table 7.7.). Based on these results, all of the water DOC removal percent could meet EPA TOC limit. Besides, increasing coagulant dosages from 40 mg/L to 80 mg/L increased the TOC removal amount in addition to pH optimization.

Table 7.4: Total chemical costs of different coagulation conditions with ferric chloride for Istanbul water supplies

Coagulation Technique	Q	Ferric	H_2SO_4	NaOH	COSTS				
	m^3/day	ton/day	ton/day	ton/day	Ferric	H_2SO_4	NaOH	Total	Unit Cost
TLW-BLW-OLW					$/day	$/day	$/day	$/day	$/1000 m^3
Baseline Coagulation	2400000	96	0	0	17280	0	0	17280	7.20
Enhanced Coagulation	2400000	192	0	0	34560	0	0	34560	14.40
Optimized Coagulation-I	2400000	96	118	114	17280	14800	4560	36640	15.27
Optimized Coagulation-II	2400000	192	98	141	34560	12200	5632	52392	21.83

Table 7.5: Total chemical costs of different coagulation conditions with alum for Istanbul water supplies

Coagulation Technique	Q	Alum	H_2SO_4	NaOH	COSTS				
	m^3/day	ton/day	ton/day	ton/day	Ferric	H_2SO_4	NaOH	Total	Unit Cost
TLW-BLW-OLW					$/day	$/day	$/day	$/day	$/1000 m^3
Baseline Coagulation	2400000	96	0	0	17760	0	0	17760	7.40
Enhanced Coagulation	2400000	192	0	0	35520	0	0	35520	14.80
Optimized Coagulation-I	2400000	96	123	155	17760	15450	6200	39410	16.42
Optimized Coagulation-II	2400000	192	88	193	35520	11100	7720	54340	22.64

Table 7.6: Chemical costs of different coagulation conditions with ferric chloride to meet national and international THM requirements for Istanbul water supplies

TLW

Coagulation Technique	Dose	pH	DOC Removal	THMFP-2 day	EPA TOC*	EPA THM	EU THM	TR THM	Unit Cost
	mg/L		(%)	µg/L	%	µg/L	µg/L	µg/L	$/1000 m3
Baseline Coagulation	40	7.18	20	126	35	80	100	150	7.20
Enhanced Coagulation	80	6.82	48	64	35	80	100	150	14.40
Optimized Coagulation-I	40	6.00	53	58	35	80	100	150	18.10
Optimized Coagulation-II	80	5.50	66	32	35	80	100	150	24.82

BLW

Coagulation Technique	Dose	pH	DOC Removal	THMFP-2 day	EPA TOC*	EPA THM	EU THM	TR THM	Unit Cost
	mg/L		(%)	µg/L	%	µg/L	µg/L	µg/L	$/1000 m3
Baseline Coagulation	40	7.23	17	117	25	80	100	150	7.20
Enhanced Coagulation	80	6.86	41	72	25	80	100	150	14.40
Optimized Coagulation-I	40	6.00	46	49	25	80	100	150	18.35
Optimized Coagulation-II	80	5.50	64	39	25	80	100	150	26.23

OLW

Coagulation Technique	Dose	pH	DOC Removal	THMFP-2 day	EPA TOC*	EPA THM	EU THM	TR THM	Unit Cost
	mg/L		(%)	µg/L	%	µg/L	µg/L	µg/L	$/1000 m3
Baseline Coagulation	40	6.80	19	105	35	80	100	150	7.20
Enhanced Coagulation	80	6.16	33	62	35	80	100	150	14.40
Optimized Coagulation-I	40	6.00	35	51	35	80	100	150	12.35
Optimized Coagulation-II	80	5.50	41	27	35	80	100	150	18.37

Table 7.7: Chemical costs of different coagulation conditions with alum to meet national and international THM requirements for Istanbul water supplies

Coagulation Technique	Dose	pH	DOC Removal (%)	THMFP-2 day	EPA TOC*	EPA THM	EU THM	TR THM	Unit Cost
	mg/L			µg/L	%	µg/L	µg/L	µg/L	$/1000 m3
TLW									
Baseline Coagulation	40	7.19	9	145	35	80	100	150	7.40
Enhanced Coagulation	80	6.79	35	72	35	80	100	150	14.80
Optimized Coagulation-I	40	6.00	38	68	35	80	100	150	19.03
Optimized Coagulation-II	80	6.00	42	47	35	80	100	150	24.45

Coagulation Technique	Dose	pH	DOC Removal (%)	THMFP-2 day	EPA TOC*	EPA THM	EU THM	TR THM	Unit Cost
	mg/L			µg/L	%	µg/L	µg/L	µg/L	$/1000 m3
BLW									
Baseline Coagulation	40	7.30	14	137	25	80	100	150	7.40
Enhanced Coagulation	80	6.96	28	73	25	80	100	150	14.80
Optimized Coagulation-I	40	6.00	49	58	25	80	100	150	22.78
Optimized Coagulation-II	80	6.00	64	44	25	80	100	150	30.00

Coagulation Technique	Dose	pH	DOC Removal (%)	THMFP-2 day	EPA TOC*	EPA THM	EU THM	TR THM	Unit Cost
	mg/L			µg/L	%	µg/L	µg/L	µg/L	$/1000 m3
OLW									
Baseline Coagulation	40	6.89	9	121	35	80	100	150	7.40
Enhanced Coagulation	80	6.60	30	70	35	80	100	150	14.80
Optimized Coagulation-I	40	6.00	36	52	35	80	100	150	12.57
Optimized Coagulation-II	80	6.00	37	33	35	80	100	150	18.98

7.3.5. THM regulation compliances

Table 7.6 and Table 7.7 represent also 48 h THMFP results for evaluation of THM levels in three coagulated water supplies. The reason why THMFP$_{48h}$ was chosen is because it was assumed that residents receive water at average time of 48 h after water leave from water treatment plant. As shown at these two tables, under baseline coagulation with ferric chloride and alum, all water sources meet the newly regulated Turkish THM limit of 150 µg/L. Whereas, none of three surface water supplies with base line coagulation conditions for two coagulants meet EPA and EU THM limits of 80 and 100 µg/L, respectively. Thus, there will be a THM compliance problem in Istanbul water supplies with this coagulation method in near future.

Enhanced coagulation treatment with ferric chloride and alum is shown in Table 7.6 and Table 7.7. This treatment technique with ferric chloride removed THM concentrations below Turkish and international THM limits. Besides, alum treatment under enhanced coagulation, meet national and international THM criteria as well. However, all of THM levels with ferric and alum coagulated waters near to EPA THM criteria of 80 µg/L.

As shown in Table 7.6 and Table 7.7, under optimized coagulation-I conditions with ferric and alum, THM levels decreased below half of THM levels of base line conditions for three waters studied. This means, optimized coagulation-I treatment techniques removed 2 times higher THM substances than those of current treatment methods in Istanbul water treatment plants. Consequently, it was concluded that the effects of coagulation pH is stronger than coagulant dosages for THM removal for Istanbul waters. However, all of the THM values with this method are above future 40 µg/L THM limit of EPA.

Percent Removal of THM formation with ferric chloride and alum coagulation of optimized coagulation-II methods are summarized in Table 7.6 and Table 7.7, respectively. In these tables, comparison of compliance with THM limits in national and international wide were compared. All of the THM levels were below Turkish, EU, and EPA THM limits. Further, it was concluded that all of the THM concentrations found to be to be lower than future 40 µg/L of THM limit of US EPA.

As summarized in Table 7.4 and Table 7.5, a cost assessment was carried out based on four typical treatment methods in which ferric chloride and alum were used. For a 2400000 m^3/day plant at a dosage of 40 mg/L ferric chloride and alum, BC chemical costs were estimated to be 7.20 \$/1000 m^3 and 7.40 \$/1000 m^3. Cost for EC with ferric and alum at 80 mg/L were resulted in 14.40 \$/1000 m^3 and 14.80 \$/1000 m^3 water treated. Moreover, cost estimates of OC-I technique at adjusted pH value for ferric chloride and alum coagulation were found to be 15.27 \$/1000 m^3 and 16.42 \$/1000 m^3 water. Finally, cost assessment of OC-II modes at 80 mg/L ferric and alum coagulant with adjusted pH level resulted in 21.83 \$/1000 m^3 and 22.64 \$/1000 m^3 water treated. It was concluded that increasing coagulation dosages raised the chemical cost 100%, and also performing pH adjustment with and without increased coagulant dosages increased chemical cost at an average value of 120 and 200%, respectively. The main factors for increased chemical cost were sulfuric acid and sodium hydroxide prices. One other important point is that ferric chloride treatment resulted in higher level of TOC removal and associated reduction in THM formation and lower chemical cost in comparison to those of alum coagulation.

7.4. Conclusion

In this chapter, four different coagulation techniques were applied in Istanbul water supplies for NOM removal. Further, cost estimates of each technique were also performed. In order to make cost estimates, titration curves for acid and two coagulants were conducted. Titration curves were developed to describe (1) the amount of sulfuric acid necessary to depress the ambient pH to a more optimal pH, and (2) the effects of ferric chloride and alum on pH depression. Titration curves of three water sources for H_2SO_4 were constructed and the complete titration curves to a pH of 4.3 define the alkalinities of the respective source waters: 125, 135, and 67 mg/L as $CaCO_3$ for TLW, BLW, and OLW, respectively. The amount of H_2SO_4 required to reduce TLW, BLW, and OLW to pH levels of 6.5, 6.0, and 5.5, the required optimum pH values for ferric chloride and alum coagulation, was estimated from the respective titration curves. Ferric chloride and alum exhibit acid properties when added to water. Therefore, coagulant addition will also contribute to pH depression toward more

optimal pH conditions. Mineral acid addition before coagulant addition represents a trade off between coagulant costs and acid costs.

On the other hand, the amount of acid required varies with seasonal changes in water quality of alkalinity and pH values. For a 2400000 m^3/day plant at a dosage of 40 mg/L ferric chloride and alum, BC chemical costs were estimated to be 7.20 $/1000 m^3 and 7.40 $/1000 m^3. Cost for EC with ferric and alum at 80 mg/L were resulted in 14.40 $/1000 m^3 and 14.80 $/1000 m^3 water treated. Moreover, cost estimates of OC-I technique at adjusted pH value for ferric chloride and alum coagulation were found to be 15.27 $/1000 m^3 and 16.42 $/1000 m^3 water. Finally, cost assessment of OC-II modes at 80 mg/L ferric and alum coagulant with adjusted pH level resulted in 21.83 $/1000 m^3 and 22.64 $/1000 m^3 water treated. It was concluded that increasing coagulation dosages raised the chemical cost 100%, and also performing pH adjustment with and without increased coagulant dosages increased chemical cost at an average value of 120 and 200%, respectively. The main factors for increased chemical cost were sulfuric acid and sodium hydroxide prices. One other important point is that ferric chloride treatment resulted in higher level of TOC removal and associated reduction in THM formation and lower chemical cost in comparison to those of alum coagulation.

8. CONCLUSION

1. Investigation of DOC, UV_{254}, SUVA and THMFP removals from TLW, BLW, and OLW with ferric chloride and alum coagulants were determined by performing jar tests procedure. The results showed that at similar coagulant dosages, expresses as dry weight of coagulant, ferric chloride consistently outperformed alum in terms of DOC, UV_{254}, SUVA and THMFP removals. Enhanced coagulation reduced the DOC level by of 55, 58, and 28% and the UV_{254} absorption by 74, 79, and 51% in TLW, BLW, and OLW, respectively, suggesting that enhanced coagulation with ferric chloride preferentially removed organic compounds with higher UV absorption.

2. DBP precursors such as, DOC, UV_{254}, SUVA, and THMFP removals were used to identify the BC, EC, and OC treatments. During this study, variations in NOM removal were observed that could be attributable to the coagulation conditions, and the raw water quality matrices. Compared to conventional treatment practices of BC, EC led to an additional removal of 15% for DOC, 16% UV_{254}, 5% SUVA, and 12% for THMFP. Moreover, OC conditions resulted in extra treatment of 41% for DOC, 38% UV_{254}, 10% SUVA, and 35% for THMFP. OC can be an efficient and inexpensive tool to control NOM in comparison to membrane process and granular activated carbon (GAC) systems in Istanbul water supplies. Overall, when OC was implemented in jar tests, the effectiveness of the treatment program appeared to depend on the pH of coagulation. Jar tests conducted with depressed pH levels at OC conditions removed more DOC than those at moderate pH levels at EC. For low DOC waters, like OLW, additional treatment would be necessary to achieve enhanced removal of NOM. The effectiveness of the treatment process may be different for DOC, UV_{254}, and THMFP. Reduction in one of these parameters does not

guarantee that other fractions have been equally affected. It is important, therefore, to monitor each of these fractions to ensure reductions in DBP formation levels.

3. Enhanced coagulation of THM formation removal was usually improved by increasing the ferric dosage, and the most effective THM removals (62%) were achieved at the highest ferric dosages of 120 mg/L with a pH value of 6.3. Increasing the dosage of ferric coagulant not only increases the availability of ferric hydroxides potentially able to adsorb THMFP, but also increase the proton concentration, i.e., decreases the pH. With the use of multiple linear regression techniques, it is possible to develop models for simulating and predicting THMs during the enhanced coagulation treatment. Based on THM formation experiments, a data base was established for modeling THM formation during chlorination of enhanced coagulated water. The general strategy adopted to develop model equation was to describe the roles of DOC precursor, chlorine dose, and reaction time in formation of THM. The R^2 and F value of model were 0.762 and 460, respectively. This model was found to be statistically significant for all four variables, and model predictions appear to be most accurate for this study.

4. Titration curves were developed to describe (1) the amount of sulfuric acid necessary to depress the ambient pH to a more optimal pH, and (2) the effects of ferric chloride and alum on pH depression. Titration curves of three water sources for H_2SO_4 were constructed and the complete titration curves to a pH of 4.3 define the alkalinities of the respective source waters: 125, 135, and 67 mg/L as $CaCO_3$ for TLW, BLW, and OLW, respectively. The amount of H_2SO_4 required to reduce TLW, BLW, and OLW to pH levels of 6.5, 6.0, and 5.5, the required optimum pH values for ferric chloride and alum coagulation, was estimated from the respective titration curves. Ferric chloride and alum exhibit acid properties when added to water. Therefore, coagulant addition will also contribute to pH depression toward more optimal pH conditions. Mineral acid addition before coagulant addition represents a trade off between coagulant costs and acid costs. On the other hand,

the amount of acid required varies with seasonal changes in water quality of alkalinity and pH values. For a 2400000 m^3/day plant at a dosage of 40 mg/L ferric chloride and alum, BC chemical costs were estimated to be 7.20 \$/1000 m^3 and 7.40 \$/1000 m^3. Cost for EC with ferric and alum at 80 mg/L were resulted in 14.40 \$/1000 m^3 and 14.80 \$/1000 m^3 water treated. Moreover, cost estimates of OC-I technique at adjusted pH value for ferric chloride and alum coagulation were found to be 15.27 \$/1000 m^3 and 16.42 \$/1000 m^3 water. Finally, cost assessment of OC-II modes at 80 mg/L ferric and alum coagulant with adjusted pH level resulted in 21.83 \$/1000 m^3 and 22.64 \$/1000 m^3 water treated. It was concluded that increasing coagulation dosages raised the chemical cost 100%, and also performing pH adjustment with and without increased coagulant dosages increased chemical cost at an average value of 120 and 200%, respectively. The main factors for increased chemical cost were sulfuric acid and sodium hydroxide prices. One other important point is that ferric chloride treatment resulted in higher level of TOC removal and associated reduction in THM formation and lower chemical cost in comparison to those of alum coagulation.

The study results showed that inorganic coagulants were superior for NOM removal, because one of the major mechanisms of DOC removal involves co-precipitation by adsorption on ferric and alum hydroxides. Furthermore, ferric chloride proved to be consistently more effective than alum in terms of NOM removal. Coagulation pH appeared to be a determining factor for maximum NOM removal. The results of this thesis showed that enhanced coagulation is a valuable means of controlling DBP formation without requiring significant capital investments for TLW and BLW. For OLW, pH optimization was required because of low level of SUVA value of OLW. The EPA enhanced coagulation requirement of TOC criteria were met with optimized coagulation techniques for all waters. The installation of enhanced coagulation systematically increased the cost of coagulation. In most cases, however, coagulation pH adjustment with sulfuric acid reduced the cost of enhanced coagulation by reducing the required coagulant dose.

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RESSUME

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