



# Control of Trihalomethane Precursors by Alum Coagulation

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## Abstract

Natural organic matters (NOM) contamination is a worrisome challenge to water treatment plants. The use of alum and alum with PAC are common in treating surface water for household consumption. This study investigated the effect of coagulation by alum and alum with PAC on NOM, focusing on organic fractions and trihalomethane formation potential (THMFP). Water sample was collected from raw water reservoir for Bangkhla water treatment plant. It was found to contain 21.78 mgDOC/L with hydrophilic (HPI) fraction of 58.26% and hydrophobic (HPO) fraction of 41.74%. The presence of NOM was confirmed by FEEM technique where humic-like, fulvic-like and tryptophan-like substances were detected. Coagulation using alum (60 mg/L) and alum with PAC (60 + 60 mg/L) gave comparable results. DOC removal of 38.48% and 39.36% were achieved, respectively. The HPI and HPO fractions remained essentially the same as those of raw water. THMFP was reduced by 13.85 and 19.73%, respectively.

**Keywords :** Natural Organic Matters; organic fractions; Trihalomethane formation potential

## Introduction

Characteristics and quality of surface water vary with topography, season, population and land use (industry and agriculture). Human activities result in contamination of biological and chemical waste. Surface water in urban or populated area is usually high in dissolved organic matter (DOM) and natural organic matter – (NOM). When surface water is used as raw water for water supply, NOM reaction with chlorine leads to formation of health hazard products. NOM also contributes to biological regrowth in the distribution system and producing color, taste and odor [1].

NOM is derived from the degradation of complex organic compounds and can be found in abundance in natural water. NOM can be broadly divided into 2 fractions; hydrophobic (humic) and hydrophilic (non-humic) substances [2]. Humic substances, dominating component in NOM, are comprised of humic and fulvic acids while non-humic substances include carbohydrates (polysaccharide), lipids and amino acids [1, 3]. Humic substances are mostly in soluble form but some maybe found as suspended particulate or adsorbed on the surface of other particles. NOM is not health hazard but when reacts with chlorine may form disinfection by product (DBP) such as trihalomethane (THMs) and haloacetic acid (HAA), known to be

carcinogenic [4]. Factors influencing formation of DBPs are concentration and composition of NOM and water treatment methods [5]. Hydrophilic NOM was a more important source of the formation of THMs and HAAs than the corresponding hydrophobic NOM. Knowledge of NOM fractions is useful in identifying potential precursors of DBPs and the treatment strategies.

The content of dissolved organic carbon (DOC) is not sufficient for the characterization of NOM. Ultraviolet spectrum at 254 nm. is greatly absorbed by aromatic structure and is thus used for the determination of humic substance because aromatic carbon contents in humic are greater than those in non-humic materials [4]. Characterization of NOM by size, structure, functionality, hydrophobicity of NOM were suggested for DBPs study [6, 7].  $UV_{254}$  and SUVA (Specific UV Absorbance, ratio of UV and DOC) is a good indicator of aromaticity of NOM and correlated with the formation of DBPs [8-10]. Fluorescence spectroscopy, size exclusion chromatography, polar fractionation have been utilized to provide insight into a better understanding of NOM characteristic and its tendency to form DBPs [11].

The results from previous studies have shown that in conventional treatment process (coagulation - flocculation / sedimentation / filtration / disinfection) organic matters are removed in the coagulation - flocculation step. Metal salt coagulant, provide positive ions, attract to negative charges on NOM [12]. Organic coagulants are effective for the removal of aromatic hydrocarbon. Aliphatic hydrocarbon is the most difficult to be removed by the method [13]. Removal of low molecular weight NOM can be enhanced by the use of coagulant together with Powder Activated Carbon (PAC). The porous structure of PAC provides higher surface area for adsorbing contaminant [14, 15].

This study investigated the control of THMs formation by alum coagulation. Raw water for Bang Khla water treatment plant was treated by alum and alum with PAC. The effects on NOM were compared, focusing on organic fractions and trihalomethane formation potential (THMFP). Organic content was determined as DOC. Organic components and structures were analyzed by  $UV_{254}$  absorption, SUVA, Fluorescence Excitation-Emission Matrix (FEEM). Resin fractionation of NOM based on the separation of hydrophilic and hydrophobic was also conducted.

## Material and Methods

### Water sample and analytical methods

Water samples were collected from raw water reservoir for Bang Khla water treatment plant, once a month from May 2019 to September 2019. The samples were used for coagulation-flocculation test. Raw and treated samples were analyzed for organic contents, analytical methods are as shown in Table 1.

### Coagulation – Flocculation Test

Water sample was treated by coagulation process, using alum and alum with PAC at the optimal dosage obtained from pretest (60 mg-alum/L and 60 mg PAC/L). Alum [ $Al_2(SO_4)_3 \cdot 18H_2O$ ] and PAC were obtained from Bang Khla water treatment plant, Provincial Waterworks Authority (PWA). Test condition was as employed by Bang Khla water treatment plant ; 30 sec. of rapid mix at 100 rpm followed by 3 steps of slow mix (7.5 min at 60 rpm, 7.5 min at 45 rpm and 5 min at 25 rpm) then left to stand for settling for 30 min. Supernatant was collected and filtered through GF/c filter (0.45 micrometer pore size). Filtrate was analyzed for DOC,  $UV_{254}$  absorbance, Resin fractionation, FEEM and THMFP.

**Table 1** Analytical methods for organic contents and organic fractions

	Analytical method	method No.*
DOC	TOC Analyzer, Shimadzu	5310 B
UV <sub>254</sub>	Ultraviolet absorption	5910 B
SUVA	$SUVA (L \cdot m^{-1} \cdot mg^{-1}) = 100 \times \left\{ \frac{UV_{254} (cm^{-1})}{DOC (mg/l)} \right\}$	5910 B
FEEM	Excitation Emission Matrix spectroscopy Excitation @ 200-500 nm.; Emission @ 250-550 nm	**
THM	GC, Perkin Elmer Clarus600, ECD, Rtx-1701 column	6232 D

\*APHA & AWWA Standard Methods for the Examination of Water and Wastewater [16]

\*\* Park et al. 2019 [15]

### Resin fractionation

The fractionation of NOM was achieved using the resin Nonionic DAX-8 (Supelite DAX-8, Supelco) type and the procedure adopted from Marhaba et al. (2003) and Chow et al. (2004) [17]. Prior to column packing, DAX-8 was washed with 0.1N NaOH for 1 day, then transferred to soxhlet extraction to extract contaminants in the resin with acetone (24 hr.) and then with hexane (24 hr.). The cleaned resin (approx. 15 mL) was soaked in methanol and packed in the glass column (10 mm.diameter x 500 mm.high) with glass fiber at the top and the bottom. To remove remaining contaminants, the column was rinsed sequentially (2 cycles) with 2.5 bed volume of 0.1N NaOH and 0.1N HCl followed by repeated rinsing with Milli-Q water until DOC of the effluent was less than 0.3 mg/L and EC of the effluent less than 10  $\mu$ s/cm.

Water sample (500 mL), prefiltered with GF/c, was acidified to pH 2.0 with 0.1 N HCl and passed through the column at 3.0 mL/min flow rate to separate NOM into fractions. DAX-8 adsorbed strong Hydrophobic acids (HPO) while Hydrophilic (HPI) were eluted out in the effluent. The strong HPO acids was later eluted by rinsing the column with 0.1N NaOH. Both HPI and HPO fractions were analyzed for DOC, UV<sub>254</sub>

absorbance and FEEM. DOC of the DAX-8 effluent represented HPI fraction, DOC of final wash represented strong HPO acid fraction. HPO fractions was also estimated by calculation from DOC of raw sample where (strong HPOacid = DOC of raw water – HPI fraction).

### Trihalomethane Formation Potential (THMFP)

THMFP is used to estimate the amount and reactivity of THM precursors in the water. It is defined as the total concentration of THMs (TTHM) formed when chlorine reacts with NOM present in water under specific test condition. TTHM is the sum of the concentrations of all the four regulated THM species: chloroform (CF), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform (BF). (APHA 2005).

Under standard test condition, water sample was filtered, pH was adjusted and buffered to  $7 \pm 0.2$  and dosed with appropriate amount of chlorine. After dosing, the sample was incubated for 7 days. THMs were purged from the sample and collected on an adsorbent trap and thermally desorbed into the inlet of a GC for analysis of the four THM species (CF, BDCM, DBCM, BF).

## Results

### Raw water characteristics

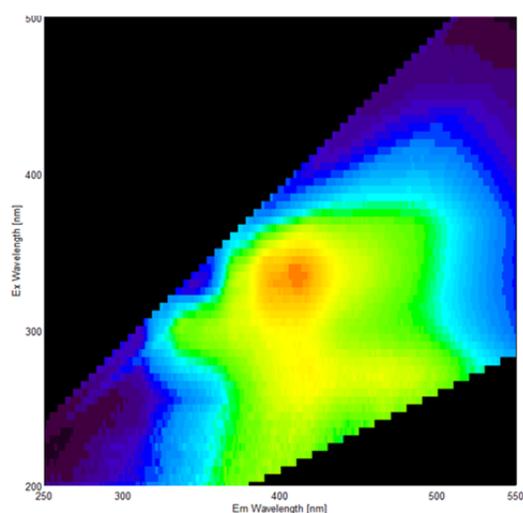
Water sample used in this study was from the water reservoir for Bang Khla water treatment plant. The reservoir is located adjacent to a shrimp farm causing contamination of dissolved organic matter (DOM) and natural organic matter (NOM). Table 2 shows analytical results of organic content in the raw water. DOC varied in a narrow range (16.81-24.75 mg/L), with the HPI fraction of 58.265 larger than that of HPO (41.74%). Organic content in surface water in Bang Khla was comparatively higher than in other regions. A study of water quality in Teharan surface water showed a very low DOC of 0.79-4.598 mg/L [18]. Water from a source in North England was reported to have 7.8-11.2 mgDOC/L [19].

The organic fractions distribution in Bang Khla reservoir was in agreement with those from the study conducted in Bangkok by Panyapinyopol *et al.* (2005), with HPI (66%) as the dominating fraction [20].

Considering the component of organic matter in the sample, UV<sub>254</sub> absorbance indicated the presence of aromatic structure. The FEEM results in Figure 1 showed 3 peaks relevant to the target compounds. Peak A (Ex260-290 nm, Em 400-430 nm), peak C (Ex310-360 nm, Em 390-430 nm.) and peak T (Ex280-310 nm. Em 330-360 nm.) represent humic-like substance, fulvic-like substance and tryptophan-like substance, respectively [15, 21]. The highest intensity was observed at peak C, meaning that fulvic-like substance was present at the highest ratio.

**Table 2** Analytical results of organic content in raw water for Bang Khla water treatment plant

	Unit	Range
DOC	mg/L	16.81 – 24.75
HPI	mg/L	12.69
HPO	mg/L	9.09
UV <sub>254</sub> absorbance	cm <sup>-1</sup>	0.191 – 0.348
SUVA	L/mg-m	1.14 – 1.41
THMs	µg/l as CHCl <sub>3</sub>	0.716 – 0.922

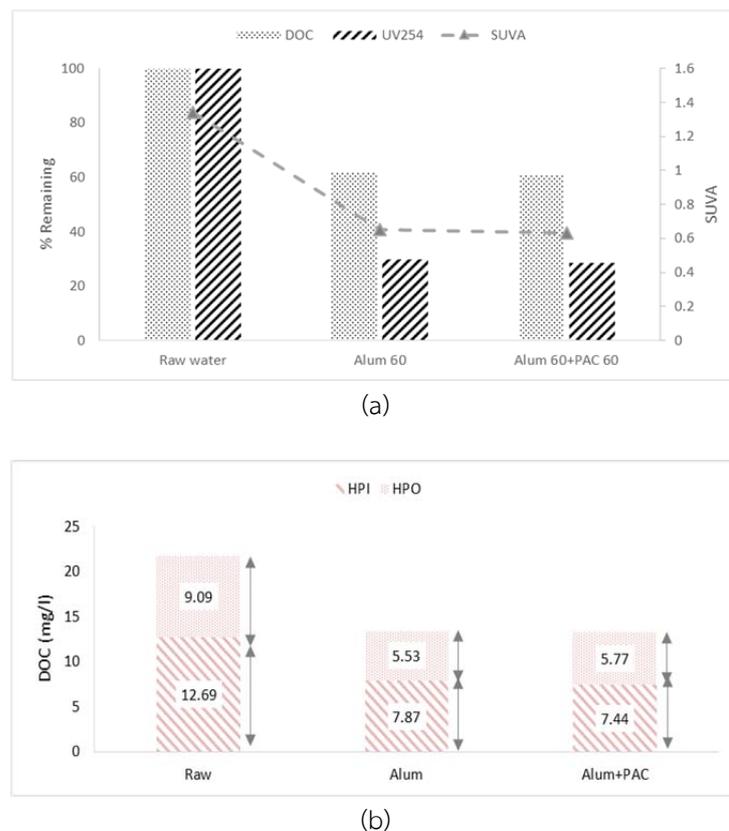


**Figure 1** Fluorescence Excitation Emission Matrix of raw water for Bang Khla water treatment plant

**The effects of alum coagulation on organic fractions**

Raw water sample was treated by coagulation using alum (60 mg/L) and alum with PAC (60+60 mg/L). The doses applied were the optimal doses obtained from the pretest. The results in Figure 2 compare the amount of organic matter remaining in the treated samples. The decrease in DOC and UV<sub>254</sub> absorbance revealed that dissolved organic matter and aromatic compounds were removed by coagulation. The addition of PAC yielded little changes. The small enhancing effect of PAC was

also reported by Park et al. (2019) [15]. Comparison of the 38.48% and 39.35% DOC removal achieved by alum and alum with PAC to the 70.21% and 71.58% decrease in UV<sub>254</sub> absorbance showed that aromatic compounds were more subjected to alum coagulation than the total organic matter. This was in agreement with the decrease in SUVA from 1.34 in raw water to 0.65 and 0.63 by alum and alum with PAC, respectively. This was because both alum and PAC have cationic functional groups while NOM has negative charge on the surface [22].



**Figure 2** The organic contents of raw water and treated water (by alum coagulation and alum with PAC coagulation) a) DOC, UV<sub>254</sub> absorbance and SUVA b) HPO and HPI fractions

The results from DAX-8 fractionation in Figure 2 b) shows that the fractions in treated water remain essentially the same as those in raw water.

### THM Formation Potential

The results of THM analysis in Table 3 showed that in all samples the amounts of the 4 THM species followed the same trend.

Chloroform was found to be formed in the highest amount while bromoform was the lowest. THMFP varied with the amount of precursors (DOC and NOM). THMFP decreased when NOM was removed. Coagulation with alum decreased THMFP by 13.85% (from 180.78 to 155.47  $\mu\text{g/L}$ ). PAC gave a better result, THMFP decreased by 19.73%.

**Table 3** Trihalomethanes formation after 7 days of chlorine exposure.

THM ( $\mu\text{g/L}$ )	Raw water	Alum	Alum + PAC
CF	83.77	68.90	60.30
BDCM, $\mu\text{g/L}$	39.22	37.18	36.47
DBCM, $\mu\text{g/L}$	54.72	46.70	43.10
BF, $\mu\text{g/L}$	3.07	2.96	2.81
THMFP, $\mu\text{g/L}$	180.78	155.74	142.68

### Conclusion

1. Organic content in raw water for Bang Khla water treatment plant was found to be 21.78 mgDOC/L, an average value obtained during May to September 2019. SUVA of 1.34 L/mg-m and FEEM analysis indicated contamination by NOM and humic substances. Resin fractionation by DAX-8 showed that hydrophilic (HPO) fraction was greater than hydrophobic (HPO) one at the rate of 58.26% to 41.74%.

2. NOM was removed by coagulation process, using alum at 60 mg/L, 38.48% DOC removal and 70.21% decrease in NOM (determined by  $\text{UV}_{254}$  absorbance) were achieved. HPO and HPI fractions remained essentially the same as in the raw water. Addition of PAC (60 mg/L) yielded no significant difference in organic removal by alum.

3. Trihalomethane formation potential was found to be related to DOC and NOM. THMFP of the treated sample was decreased by 13.85% by alum and 19.73% by alum with PAC.

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