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# Reduction of fractionated dissolved organic matter and their trihalomethane formation potential with enhanced coagulation

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**ABSTRACT**: The trihalomethane formation potential (THMFP) of the raw water supply from the U-Tapao Canal, Songkhla, Thailand and the THMFP of the hydrophobic organic fraction (HPO) and hydrophilic organic fraction (HPI) of the raw water supply were determined. The canal has been contaminated with treated and untreated wastewater from communities, agricultural processes, and industrial activities. Water samples were collected 3 times from an intake point of the water treatment plant located downstream of the canal. We found an average dissolved organic carbon (DOC) of 7.4 mg/l and a THMFP of 630 µg/l in the raw water. We also found a $\text{DOC}_{\text{HPO}}$ of 3.3 mg/l, a $\text{DOC}_{\text{HPI}}$ of 3.7 mg/l, a $\text{THMFP}_{\text{HPO}}$ of 281 µg/l, and a $\text{THMFP}_{\text{HPI}}$ of 348 µg/l. Strong fluorescent peaks of tryptophan-like and humic and fulvic acid-like substances were detected in the raw water. The optimal condition of polyaluminium chloride (PACl) coagulation for removing dissolved organic matter was obtained at a PACl of 40 mg/l at pH 7. Under such conditions, it could reduce the average DOC to 55% and THMFP to 48%. The PACl coagulation reduced the fluorescent intensity of humic and fulvic acid-like substances more than tryptophan-like substances. The best reduction observed of DOC was 76% and THMFP was 83%; this was obtained by using a PACl of 40 mg/l with 1 mg/l of polymer and 80 mg/l of powder activated carbon. Under such conditions, there was consistent removal of an average $\text{DOC}_{\text{HPO}}$, $\text{DOC}_{\text{HPI}}$, $\text{THMFP}_{\text{HPO}}$, and $\text{THMFP}_{\text{HPI}}$ by 85, 68, 81, and 79%, respectively. Such a condition was capable of reducing trihalomethanes to meet the World Health Organization standards.

**KEYWORDS**: hydrophilic organic fraction, hydrophobic organic fraction, poly aluminium chloride, polymer, powder activated carbon

## INTRODUCTION

The formation of carcinogenic disinfection by-products (DBPs) through a reaction between natural organic matter (NOM) and chlorine in the water supply process was discovered in the 1970's[1].

A number of researchers have to date focused on NOM characterization, the formation of chlorination DBPs, alternatives disinfectants, and the removal of DBPs precursor and DBPs[2–5].

Dissolved organic carbon (DOC) and UV absorbance at wavelength 254 nm (UV-254) have been used to determine quantities of dissolved organic matter (DOM). Trihalomethane formation potential (THMFP) is used to determine a complete reaction between DOM and chlorine for producing trihalomethanes (THMs). A resin fractionation technique using DAX-8 resin can be used to separate NOM into hydrophobic organic fractions (HPO) and hydrophilic organic fractions (HPI)[6]. By conducting the THMFP test on HPO and HPI, the major THMs precursors can be determined. A three-dimensional fluorescent spectroscopy analysis (the use of fluorescent excitation-emission matrix, FEEM) has been used to classify DOM into tyrosine-like, tryptophan-like, and humic and fulvic acid-like substances[7,8].

In general, it is very important to ensure a safe raw water supply by protecting it from sources of contamination such as industry, community wastage, and agriculture. The development and expansion of communities and industry is continuously increasing leading to an increased discharge of man-made DOM into raw water supply in terms of treated and untreated wastewater.

Novel techniques of water treatment, therefore, must be developed to mitigate these problems. Some research work have focused on characterizing and removing NOM in the raw water supply and related sources of contamination such as from domestic and industrial wastewater[8–11].

Coagulation using aluminium or iron based salts such as $Al_2(SO_4)_3$ or alum, polyaluminium chloride (PACl), ferric chloride, ferric sulphate, and ferrous sulphate has been commonly used by several water supply plants to remove suspended solids and decrease turbidity. Coagulation could further reduce DBPs precursors in the raw water supply and the formation of DBPs and unidentified DBPs in the water supply produced through increasing the coagulant dose[12].

For raw water supply with a high contaminant level, the coagulation of iron based salts could not efficiently remove DBPs precursors at a certain level. A high level of DBPs, therefore, could be formed in the water supply produced. Water supply consumers could be potentially exposed to carcinogenic DBPs by the ingestion, inhalation and dermal contact of the water supply every day.

Enhanced coagulation techniques by polymer and powder activated carbon (PAC) adsorption, therefore, have been studied and developed to produce a safe water supply[13–15].

The U-Tapao Canal is located in Songkhla province in the southern part of Thailand. A water supply of about 100 000–150 000 $m^3$/day is produced using raw water from the canal to serve an approximate population of 421 377 people in four cities in Songkhla province. The raw water is inevitably contaminated with treated and untreated wastewater and considered as a raw water supply with a high contaminant level[15, 16]. This is because the water treatment plant is placed downstream of many communities and industries that are located on upstream and midstream locations.

The main objective of this study was to determine the ability of HPO and HPI in the formation of THMs in the raw water supply from the U-Tapao canal. The optimal condition of PACl coagulation on the removal of DBPs precursor and fluorescent organic matter (FOM) was determined. In addition, the combination of enhanced PACl coagulation using polymer, and PAC for reducing the HPO and HPI and their THMFP, were also examined in this study.

## MATERIALS AND METHODS

### Sample collection and preservation

Water samples were collected 3 times from an intake of a water treatment plant on the U-Tapao Canal, Songkhla, Thailand, in September 2008 (first sampling), April 2009 (second sampling), and July 2009 (third sampling). The sampling period covered approximate a year and was thought to represent the variation of DOM in the canal. Samples for resin fractionation and formation of THMs experiments were prepared by filtering through a GF/F glass micro filter and these were stored in a cold room at a controlled temperature of 4 °C. Samples for experiments of enhanced coagulation were stored in a cold room. The experiments for DOM removal for the first, second, and third water samples were conducted using the common following procedure.

### DOM characterization

Water samples were measured for their pH, turbidity, suspended solids and alkalinity. The filtered water samples were analysed for their UV-254, DOC, specific UV absorption (SUVA), THMFP, and FEEM. The procedure of resin fractionation by using DAX-8 resin was used to fractionated DOM into HPO and HPI[6]. The HPO and HPI were then analysed for their DOC and THMFP.

### DOM removal

The study of DOM removal included 3 experiments: (I) The water sample was coagulated by PACl dosages of 0, 5, 10, 20, 30, and 40 mg/l under controlled pH of 5.5, 7, and 8.5. (II) The enhanced PACl coagulation was conducted using PACl dosage of 5, 10, 20, 30, and 40 mg/l at the optimal pH that was obtained from experiment I with the addition of cationic polymer namely MR FLOC 5000 dosage of 1 mg/l. (III) The enhanced PACl coagulation was performed using optimal conditions from experiment II with the addition of PAC (HRO M325-60 CARBOKARN) of 10, 20, 40, 60, and 80 mg/l.

The coagulated waters were analysed for their DOC, UV-254 and the percentage of DOC and UV-254 reductions for determining the optimal conditions. The coagulated water at the optimal condition in each experiment was analysed for its FEEM. Enhanced coagulation by polymer and PAC were selected in this work because they are convenient for the water treatment plant to employ immediately and they did not require any complicated modification of the water treatment plant.

The coagulated water at optimal conditions in the

**Table 1** Characteristic of the raw water supply from the U-Tapao canal.

| Parameters | First sampling | Second sampling | Third sampling | Average ± SD[†] |
|---|---|---|---|---|
| pH | 6.9 | 6.7 | 6.8 | 6.8 ± 0.1 |
| Alkalinity (mg/l as $CaCO_3$) | 24 | 26 | 26 | 25.3 ± 1.2 |
| UV-254 ($m^{-1}$) | 11.2 | 22.8 | 23.8 | 19.3 ± 7.0 |
| DOC (mg/l) | 10.7 | 6.9 | 4.5 | 7.4 ± 3.1 |
| SUVA (l $mg^{-1}$ $m^{-1}$) | 1.0 | 3.3 | 5.3 | 3.2 ± 2.1 |
| $DOC_{HPO}$ (mg/l) | 4.8 (47) | 3.1 (48) | 2.1 (48) | 3.3 ± 1.4 (48 ± 0.6) |
| $DOC_{HPI}$ (mg/l) | 5.5 (53) | 3.4 (52) | 2.3 (52) | 3.7 ± 1.6 (52 ± 0.6) |

[†] SD = standard deviation.
( ) = percent distribution.

3 experiments was fractionated into HPO and HPI. In the final step, the coagulated water, HPO, and HPI at an optimal condition of 3 experiments were analysed for their THMFP.

### Analytical methods

The DOC was analysed in accordance with the Standard Method 5310D[17] (the wet-oxidation method) using an O.I. analytical 1010 TOC analyser (OI Analytical, College Station, TX). UV-254 was analysed in accordance with the Standard Method 5910B using a UV-Vis spectrophotometer, Genesys 10 UV (Thermoelectron Corp. Madison, WI), with matched quartz cells, that provide a path length of 10 mm. The THMFP measurement was carried out according to the Standard Method 5710B[17]. The chlorination condition for the THMFP test included an incubation time of 7 days in the temperature range of 25 ± 2 °C, pH of 7.0 ± 0.2, and free chlorine residual of 3–5 mg/l at the end of incubation time.

The residual chlorine was measured in accordance with the procedures mentioned in the Standard Method 4500-Cl G[17]. The level of chlorine was measured by the light absorbance at 515 nm (using Genesys 10 UV). The THMs were extracted with pentane in accordance with the Standard Method 6232B before injection to the gas chromatography equipped with an electron capture detector (Agilent Gas Chromatography-6890, Agilent technologies Inc., Wilmington, Delaware, USA). A chromatographic column (Agilent technologies Inc, HP-5, USA), with 0.32 mm × 30 m 0.25 µm film was used to analyse THMs. At least duplicates of each measurement of DOC, UV-254, and THMFP were performed. The FEEM was analysed in accordance with the procedure using a JASCO FP-6200 spectrofluorometer[8].

## RESULTS AND DISCUSSION

### Characteristic of raw water supply from the U-Tapao canal

The pH of the raw water supply was close to neutral and an alkalinity of 24–26 mg/l as $CaCO_3$ was detected (Table 1). Sufficient alkalinity is required in the coagulation process using aluminium salts. Additional chemicals for increasing alkalinity were required during the coagulation experiments. This was because the alkalinity value in raw water was slightly low. Ranges of UV-254, DOC, and SUVA from 11.2–23.8 $m^{-1}$, 4.5–10.7 mg/l, and 1.0–5.3 l $mg^{-1}$ $m^{-1}$ were found, respectively.

The variation of UV-254, DOC, and SUVA in the raw water supply could be because of seasonal change and the discharging of DOM from community, agricultural, and industrial activities at upstream and midstream locations on the canal. UV-254, DOC, and SUVA of the raw water supply from the U-Tapao canal are considered as high values when compared with that of raw water supplies from other sources in Thailand[18, 19].

SUVA is a useful parameter for the measurement of the aromatic content of NOM and the possibility of a coagulation process for NOM removal. When the SUVA was more than 4 l $mg^{-1}$ $m^{-1}$, the composition of NOM mostly consisted of aquatic NOM with high hydrophobicity and molecular weight. Water samples with the SUVA between 2 and 4 l $mg^{-1}$ $m^{-1}$ contained a mixture of aquatic NOM and other NOM (mixture of hydrophobic). When the SUVA was lower than 2 l $mg^{-1}$ $m^{-1}$, the composition of NOM consisted of mostly non-humic substances with low hydrophobicity and molecular weight[20].

A water sample having a high SUVA was easier to remove by coagulation[21]. DOM in the raw water supply in the second and third sampling had a higher potential to be removed by coagulation than that of

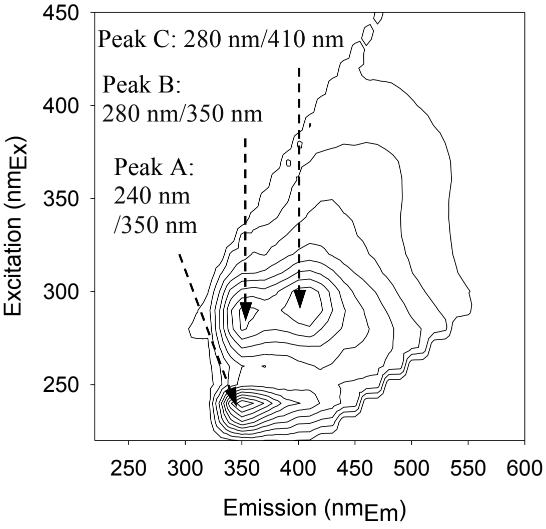


**Fig. 1** FEEM of the raw water supply in the first sampling (Peak A and B: Tryptophan-like substances and Peak C: Humic and fulvic acid-like substances).

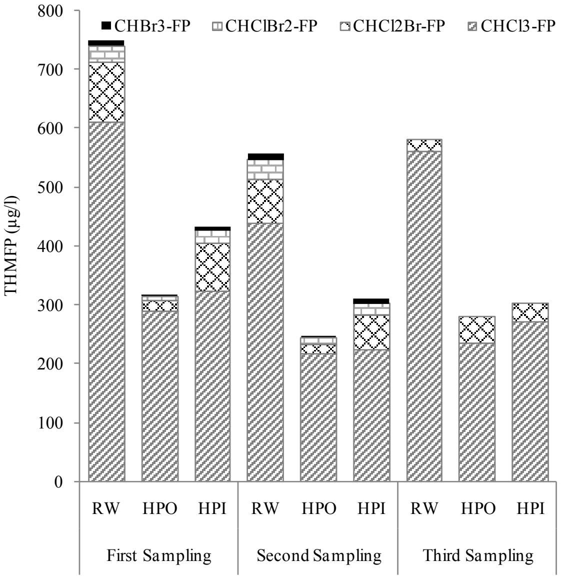


**Fig. 2** THMFP and THMFP species of raw water, HPO, and HPI.

the first sampling. This could be because of the high SUVA in the raw water supply in the second and third samplings that was observed. Given the DOM fraction, the percent distribution of HPI was slightly higher than that of HPO. An HPO and HPI of about 48 and 52% were detected in the raw water supply, respectively.

Three major fluorescent peaks were detected at 240 $\text{nm}_{\text{Ex}}$/350 $\text{nm}_{\text{Em}}$ (peak A), 280 $\text{nm}_{\text{Ex}}$/350 $\text{nm}_{\text{Em}}$ (peak B), and 280 $\text{nm}_{\text{Ex}}$/410 $\text{nm}_{\text{Em}}$ (peak C) (Fig. 1). The putative origin of peak A and B related to tryptophan-like substances whereas that of peak C could originate from humic and fulvic acid-like substances when compared with previous studies[7,8]. The tryptophan-like and humic and fulvic acid-like substances were considered to be the major FOM in the raw water supply from the canal. In general, humic and fulvic acid-like substances could be detected in natural water[19] while the tryptophan-like substances mostly detected in wastewater and treated wastewater[8,22].

A THMFP of as high as 750, 557, and 582 μg/l was detected in the raw water supply from the first, second, and third samplings, respectively (Fig. 2). Chloroform formation potential ($CHCl_3$-FP) of about 83% of total THMFP was detected in the raw water supply, followed by dichlorobromomethane formation potential ($CHCl_2Br$-FP) of about 13%. Dibromochloromethane formation potential ($CHClBr_2$ -FP) and bromoform formation potential ($CHBr_3$-FP) were detected at a level of less than 5%. This observation corresponded with a previous study. This is because $CHCl_3$-FP of about 97% was detected in the raw water supply from Bangkhen Water Treatment plant followed by a $CHCl_2Br$-FP of about 3%[23].

The THMs standard of 80 μg/l in drinking water has been set by US Environmental Protection agency (USEPA)[24]. The World Health Organization (WHO) has set health related guideline values of 200, 60, 100, and 100 μg/l for chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$) and bromoform ($CHBr_3$), respectively[25]. The ratio of THMFP/WHO guidelines of the raw water supply at the first, second, and third samplings were 5.2, 3.8, and 2.9, respectively. It can be stated that the raw water supply had a higher potential to form DBPs than the standard of both USEPA and WHO. The water treatment plant must have a high performance capability in the removal of DBPs precursors which would lower the DBPs level in the water supply and reducing the health effects on consumers of the water supply.

To determine the major THMFP precursor, a THMFP test was conducted for HPO and HPI samples. For the first sampling, $\text{THMFP}_{\text{HPO}}$ and $\text{THMFP}_{\text{HPI}}$ of 317 and 432 μg/l were detected, respectively. Whereas those of the second sampling were 246 and 310 μg/l, respectively. A $\text{THMFP}_{\text{HPO}}$ of 279 μg/l and $\text{THMFP}_{\text{HPI}}$ of 302 μg/l were found in the third sampling. It is clear that HPI was the major

**Table 2** UV-254, DOC, SUVA, and THMFP and their percent reductions.

| Conditions | UV-254 ($m^{-1}$) | | | | Inc. red.† | DOC (mg/l) | | | | Inc. red.† |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1st | 2nd | 3rd | Average | (%) | 1st | 2nd | 3rd | Average | (%) |
| (1) Raw water supply | 11.2 | 22.8 | 23.8 | 19.3 ± 7.0 | N.A. | 10.7 | 6.9 | 4.5 | 7.4 ± 3.1 | N.A. |
| (2) PACl 40 mg/l | 5.6 (50) | 10.7 (53) | 10.9 (54) | 9.1 ± 3.0<br>(52 ± 2.2) | N.A. | 4.9 (54) | 3.0 (57) | 2.1 (53) | 3.3 ± 1.4<br>(55 ± 2.1) | N.A. |
| (3) PACl 40 mg/l, polymer 1 mg/l | 5.2 (54) | 9.8 (57) | 10.7 (55) | 8.6 ± 3.0<br>(55 ± 1.7) | 3 | 4.7 (56) | 2.8 (59) | 2.7 (40) | 3.4 ± 1.1<br>(52 ± 10) | N.A. |
| (4) PACl 40 mg/l, polymer 1 mg/l, and PAC 80 mg/l | 3.1 (72) | 7.1 (69) | 7.1 (70) | 5.8 ± 2.3<br>(70 ± 1.7) | 18 | 1.4 (87) | 1.9 (73) | 1.4 (69) | 1.6 ± 0.3<br>(76 ± 9.5) | 21 |

| Conditions | SUVA (l mg$^{-1}$ m$^{-1}$) | | | | Inc. red.† | THMFP (µg/l) | | | | Inc. red.† |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1st | 2nd | 3rd | Average | (%) | 1st | 2nd | 3rd | Average | (%) |
| (1) Raw water supply | 1.0 | 3.3 | 5.3 | 3.2 ± 2.1 | N.A. | 750 | 557 | 582 | 630 ± 105 | N.A. |
| (2) PACl 40 mg/l | 1.1 (–) | 3.6 (–) | 5.2 (2) | 3.3 ± 2.1 | N.A. | 384 (49) | 241 (57) | 356 (39) | 327 ± 76<br>(48 ± 9) | N.A. |
| (3) PACl 40 mg/l, polymer 1 mg/l | 1.1 (–) | 3.5 (–) | 4.0 (25) | 2.9 ± 2.1 | N.A. | 337 (55) | 231 (59) | 307 (47) | 292 ± 55<br>(54 ± 6) | 6 |
| (4) PACl 40 mg/l, polymer 1 mg/l, and PAC 80 mg/l | 2.2 (–) | 3.7 (–) | 5.1 (4) | 3.7 ± 2.1 | N.A. | 110 (85) | 62 (89) | 139 (76) | 104 ± 39<br>(83 ± 7) | 35 |

† Increase reduction.
( ) = percent reduction.

THMFP precursors in the raw water supply from the U-Tapao canal. In addition, CHCl$_3$-FP of 88 and 78% of total THMFP was the major THMFP species in the HPO and HPI, respectively, followed by CHCl$_2$Br-FP of 9 and 16% in HPO and HPI, respectively.

## DOM surrogates removal by enhanced coagulation

The coagulation, flocculation, and sedimentation followed by sand filtration were considered to be normal and cost-effective processes for the removal of NOM[3]. This section aims to present the optimal condition for the removal of DOM surrogates by enhanced coagulation. The results in detail on PACl coagulation and enhanced coagulation are not shown. In summary, the percentages of both DOC and UV-254 reduction under controlled pH of both 5.5 and 7 were significantly higher than those of pH 8.5 for experiment I. Under controlled pH of 5.5 and 7, the percentages of both DOC and UV-254 reductions were not much different. DOC and UV-254 steadily decreased at a PACl dosage of 5 mg/l and gradually decreased when a PACl dosage was increased from 10 mg/l to 40 mg/l.

In experiment I, a pH of 7 was selected as optimal because the pH of the raw water supply was close to 7. Therefore, it required less chemicals for adjusting the pH. In addition, a PACl 40 mg/l yielded the highest reduction of DOC and UV-254. Therefore, this dosage was selected as the optimal dosage. Under these conditions, the average reductions of UV-254 of 52%, DOC of 55% and THMFP of 48% were obtained (Table 2). The SUVA after PACl coagulation was slightly increased because the percentage of DOC reduction was higher than that of UV-254. An alum of 50 mg/l was the optimal dosage for reducing the TOC in Luanhe river water by 31% and alum of 35 mg/l could reduce the TOC in Yellow River water by 16.8%[26]. The optimal dosage of PACl in this study was compatible to the previous study[26].

In the case of experiment II, the enhanced coagulation by the addition of cationic polymer 1 mg/l under a controlled pH of 7, the DOC and UV-254 steadily decreased at a PACl dosage of 5 mg/l. They gradually decreased when a PACl dosage was increased from 10 mg/l to 40 mg/l. A PACl 40 mg/l yielded the highest DOC and UV-254 reduction; therefore, this dosage was used as the optimal dosage. Under these conditions, the average values of UV-254, DOC and THMFP were reduced by 55, 52, and 54%, respectively. The average value of the SUVA after coagulation slightly decreased.

For experiment III, the enhanced PACl and polymer coagulation was varied by PAC dosage. DOC and UV-254 were steadily decreased at a PAC dosage of 5 mg/l and they gradually decreased when the PAC dosage was increased from 10–80 mg/l. At PAC 80 mg/l, it yielded the highest DOC and UV-254 reduction. Therefore, this dosage was set as the optimal dosage. Under such conditions, the average reductions of UV-254 of 70%, DOC of 76%, and THMFP of 83% were obtained. The average value of the SUVA after coagulation slightly increased. Ferric chloride of 80 mg/l with enhanced coagulation by PAC

**Table 3** Fluorescent intensity of tryptophan-like peak, humic and fulvic acid-like peak and their reductions.

| Condition | Summation of fluorescent intensity of tryptophan-like peak (QSU) | | | | Increase reduction | Fluorescent intensity of humic and fulvic-like peak (QSU) | | | | Increase reduction |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1st | 2nd | 3rd | Average | (%) | 1st | 2nd | 3rd | Average | (%) |
| (1) Raw water supply | 573 | 483 | 503 | 520 ± 47 | N.A. | 235 | 280 | 252 | 256 ± 23 | N.A. |
| (2) PACl 40 mg/l | 461 (20) | 388 (20) | 430 (15) | 426 ± 37<br>(18 ± 3) | N.A. | 106 (55) | 118 (58) | 110 (56) | 111 ± 6<br>(56 ± 2) | N.A. |
| (3) PACl 40 mg/l, polymer 1 mg/l | 390 (32) | 320 (34) | 383 (24) | 364 ± 39<br>(30 ± 5) | 12 | 111 (53) | 113 (60) | 109 (57) | 111 ± 2<br>(57 ± 4) | 1 |
| (4) PACl 40 mg/l, polymer 1 mg/l, and PAC 80 mg/l | 366 (36) | 290 (40) | 311 (38) | 322 ± 39<br>(38 ± 2) | 20 | 98 (58) | 104 (63) | 95 (62) | 99 ± 5<br>(61 ± 3) | 5 |

( ) = percent reduction.

adsorption at 80 mg/l could increase the DOC and THMFP reduction up to 76 and 82%, respectively[13]. In addition, the enhanced coagulation and PAC adsorption was more successful in reducing THMs for meeting the Turkish THMs limit of 150 µg/l than by enhanced coagulation alone. Coagulation using PACl of 20 mg/l and enhanced coagulation with polymer of 0.1 mg/l and PAC of 10 mg/l could reduce DOC by 71%[14].

The fluorescent intensities of the fluorescent peak could be used to determine the quantities of different FOM in the water. The sum of the fluorescent intensities of all outstanding fluorescent peaks in an FEEM has been proposed to determine the quantity of the total FOM in water[8]. The reduction of each FOM, such as tryptophan-like substances, by PACl and enhanced PACl coagulation was evaluated by the reduction of the sum of fluorescent intensities of overall peaks of tryptophan-like substances (Table 3).

By using PACl 40 mg/l at pH 7, the fluorescent intensities of tryptophan-like and humic and fulvic acid-like substances were reduced by 18 and 56%, respectively. The PACl coagulation reduced the fluorescent intensity of humic and fulvic acid-like substances better than tryptophan-like substances.

Enhanced coagulation by both polymers alone and polymers with PAC did not show any significant reduction of fluorescent intensity of humic and fulvic acid-like substances. However, they could reduce total fluorescent intensity of tryptophan-like substances by 30 and 38%, respectively.

The increasing in the reduction of UV-254, DOC and THMFP was considered. The percentage reduction of UV-254, DOC and THMFP by PACl 40 mg/l and controlled pH at 7 was used as the baseline treatment of DOM surrogate removal. In general, the effective aids for enhanced coagulation was cationic polymers. These could improve the performance capability of PACl coagulation by enhancing the neutralization ability of PACl[27]. The enhanced coagulation by polymer alone was not successful in the removal of DOC; however, it increased the UV-254 and THMFP reduction by 3 and 6%, respectively. The polymer selected may not be suitable for the removal of DOM from the U-Tapao canal. To maintain water quality for satisfying DBPs standard, granular or powder activated carbon had been used as additional treatment[13, 28, 29]. The enhanced coagulation with the polymer and PAC in this study successfully increased the UV-254, DOC, and THMFP reductions by 18, 21, and 35%, respectively.

For the raw water supply contaminated with treated and untreated wastewater, enhanced coagulation could increase the THMFP removal better than UV-254 and DOC removal. Disinfection by-products formation potential removal by coagulation and softening was always greater than DOC removal[30]. For the FOM, enhanced PACl coagulation by polymer alone, and polymer with increased PAC, the reduction of total fluorescent intensity of tryptophan-like substances was 12 and 20%, respectively. It can be suggested that enhanced coagulation successfully reduced DOM and FOM in a raw water supply with a high level of contamination.

## HPO and HPI removal by enhanced coagulation

The hydrophobic and hydrophilic characteristics of DOM can affect the formation of DBPs and the removal of DBPs precursors. As can be seen from Fig. 3 and Table 4, the PACl of 40 mg/l and controlled pH at 7 in an experiment I could reduce $DOC_{HPO}$ and $DOC_{HPI}$ by 60 and 48%, respectively. This observation corresponded well with previous work which showed that HPO was found to be more easily removed by coagulation than HPI[14]. Using PACl coagulation, $THMFP_{HPO}$ and $THMFP_{HPI}$ were reduced by 57 and 39%, respectively. The results show that HPI was the major THMFP precursors in the coagulated water, thus the enhanced coagulation technique must be mainly focused on the HPI removal.

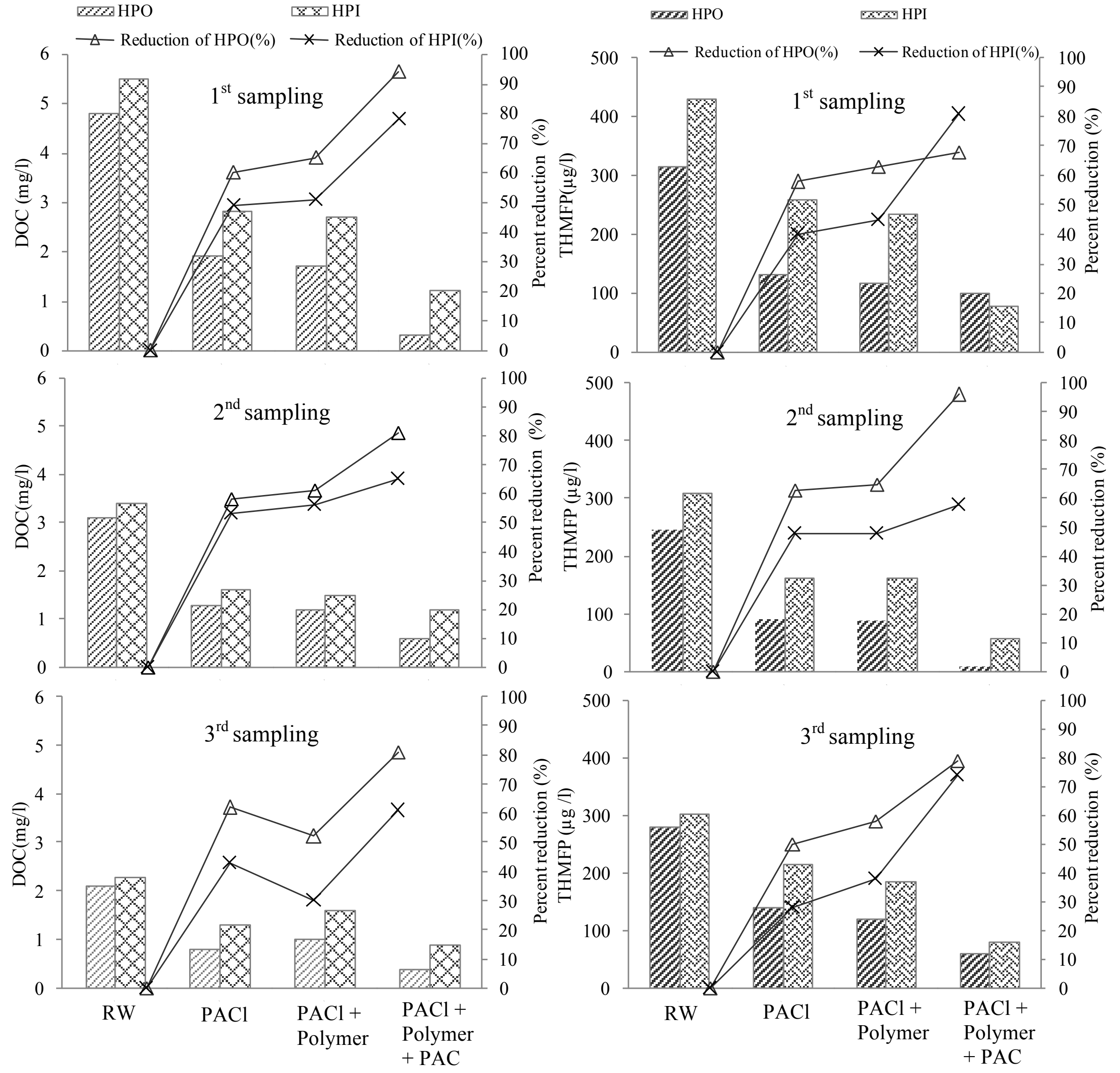


**Fig. 3** Reduction of DOC and THMFP of HPO and HPI by enhanced coagulation.

In experiment II, the enhanced PACl coagulation by the polymer of 1 mg/l, the $DOC_{HPO}$ and $DOC_{HPI}$ were removed by 59 and 46%, respectively. Under these conditions a reduction of $THMFP_{HPO}$ and $THMFP_{HPI}$ of 62 and 44% were obtained, respectively. HPI was still the major THMFP precursor in the coagulated water by PACl and polymer coagulation. The enhanced PACl coagulation by combined polymer 1 mg/l and PAC of 80 mg/l in experiment III, could consistently remove $DOC_{HPO}$ and $DOC_{HPI}$ by 85 and 68%, respectively, and a reduction of $THMFP_{HPO}$ of 81% and $THMFP_{HPI}$ of 79% were achieved. This result corresponds with previous studies. Enhanced coagulation using PACl of 20 mg/l with combined polymer of 0.1 mg/l and PAC of 10 mg/l could reduce $DOC_{HPO}$, $DOC_{HPI}$, $THMFP_{HPO}$, and $THMFP_{HPI}$ by 75, 65, 79, and 77%, respectively[14].

The percentage of DOM fraction reductions and their THMFP by PACl 40 mg/l and controlled pH at 7 was set as the baseline treatment. Enhanced coagulation by polymer alone did not increase the removal of $DOC_{HPO}$ and $DOC_{HPI}$; nevertheless, the percentage of $THMFP_{HPO}$ and $THMFP_{HPI}$ reduction was increased by 5%. The selected cationic polymer

**Table 4** HPO, HPI, $THMFP_{HPO}$, and $THMFP_{HPI}$ reductions.

| Condition | Average reduction (%) | | Increase reduction (%) | | Average reduction (%) | | Increase reduction (%) | |
|---|---|---|---|---|---|---|---|---|
| | HPO | HPI | HPO | HPI | $THMFP_{HPO}$ | $THMFP_{HPI}$ | $THMFP_{HPO}$ | $THMFP_{HPI}$ |
| (1) Raw water supply | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A | N.A. |
| (2) PACl 40 mg/l | 60 | 48 | N.A. | N.A. | 57 | 39 | N.A | N.A. |
| (3) PACl 40 mg/l, polymer 1 mg/l | 59 | 46 | N.A. | N.A. | 62 | 44 | 5 | 5 |
| (4) PACl 40 mg/l, polymer 1 mg/l, and PAC 80 mg/l | 85 | 68 | 25 | 20 | 81 | 79 | 24 | 40 |

may not suitable for removing DBPs precursors. The enhanced PACl coagulation by the combined polymer with PAC greatly increased the reduction of $DOC_{HPO,}$ $DOC_{HPI}$, $THMFP_{HPO,}$ and $THMFP_{HPI}$ by 25, 20, 24, and 40%, respectively. The low molecular weight and uncharged DOC was effectively removed by PAC[13]. A high molecular weight fraction was effectively removed by the coagulation process, while the combined PAC adsorption with coagulation succeeded in the removal of low molecular weight NOM[28]. It can be stated that enhanced PACl and polymer coagulation by PAC adsorption had the ability to remove both HPO and HPI in the raw water supply contaminated with treated and untreated wastewater.

## The ratio of THMFP and standard of treated water

THMFP has been commonly used to determine the THMs at the completion of reaction conditions between DOM and excess amounts of chlorine. The THMFP value of the water sample was inevitably higher than that of THMs in the actual conditions. The treatment process that can reduce THMFP to lower than the THMs standard should be also reduced the THMs to under the acceptable level. The THMs standard in drinking water promulgated by USEPA[24] and WHO[25] were used to compare with THMFP in treated water in order to evaluate the health risks to water consumers in the population of Songkhla province, Thailand.

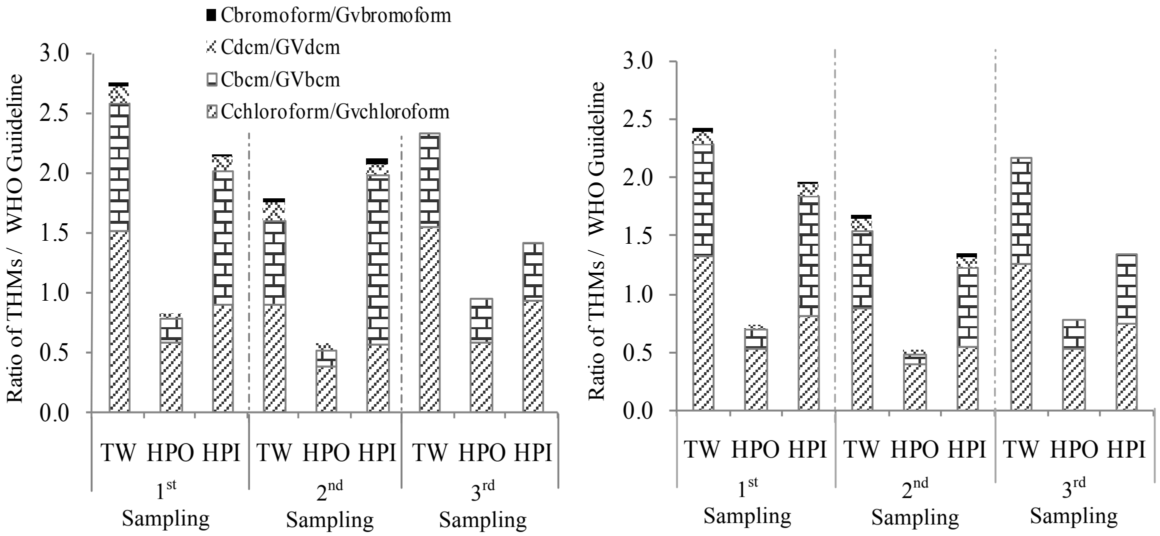
The water treated by PACl coagulation at the first, second, and third samplings had ratios of THMFP/USEPA standard value of 4.8, 3.0, and 3.8, respectively. The enhanced coagulation by polymer had a slightly reduced THMFP/USEPA ratio. The enhanced PACl and polymer coagulation by PAC reduced the THMFP/USEPA ratio of the first, second, and third samplings to 1.4, 0.8, and 1.7, respectively.

The water treated by PACl coagulation had a ratio of THMFP/WHO guideline values of 2.8, 1.8, and 2.3 for the first, second, and third samplings, respectively (Fig. 4). Enhanced coagulation by polymers did not show significant reduction of the ratio of THMFP/WHO Guideline values. For the enhanced PACl and polymer coagulation by PAC, there was a reduce ratio of THMFP/WHO guideline values of the first, second, and third samplings to 0.8, 0.5, and 1.1, respectively.

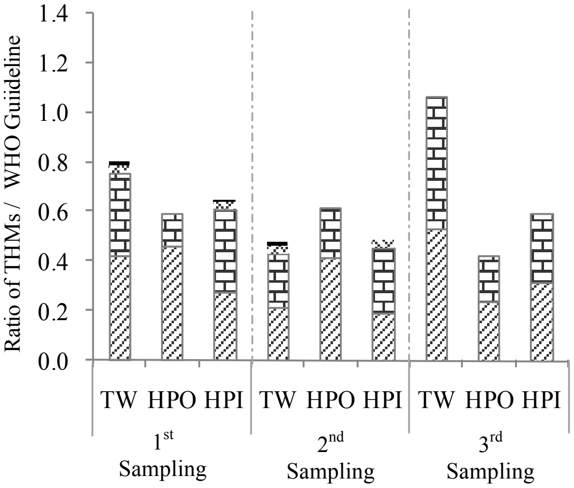
The guideline value of $CHCl_2Br$ was set at the lowest level when compared with that of other THMs species. $CHCl_2Br$ was even present in tiny quantities, and significantly increased the ratio THMFP/WHO guidelines (Fig. 4). Therefore, $CHCl_2Br$ is an important parameter that should be seriously considered. PACl coagulation reduced the $CHCl_2Br$-FP of the first and second samplings by 31 and 42%, respectively. For the third sampling, it did not show any reduction of $CHCl_2Br$-FP.

Enhanced coagulation by polymers slightly increased the percentage of $CHCl_2Br$-FP reduction. The enhanced coagulation by polymers and PAC increased the reduction of $CHCl_2Br$-FP of the first and second samplings by 49 and 40%, respectively. This could be because the PAC can significantly remove the bromide and bromate from a raw water supply due to adsorption. The activated carbon could be used after coagulation and filtration prior to chlorination[31]. For the THMFP/WHO Guideline values of the HPO and HPI, HPI had moderately high ratios of the THMFP/WHO Guideline values than for those of HPO in almost all cases. In addition, the $CHCl_2Br$-FP of HPI was greater than that of HPO. Advanced water treatment techniques, therefore, should focus on HPI removal.

Finally, it can be stated that the enhanced PACl and polymer coagulation by PAC has the capacity to reduce the THMs to meet WHO standards. A water treatment plant, therefore, could employ this enhanced coagulation technique for reducing DOM precursors in order to produce safe water supply for consumers. However, an important barrier is the increased costs of the water supply. In this case a government agency should partially subsidize this cost and provide knowledge of this situation to water consumers.



(1) PACl (2) PACl + Polymer



(3) PACl + Polymer + PAC

**Fig. 4** Ratio of THMFP to WHO Guideline of treated water, HPO, and HPI treated by (1) PACl, (2) PACl + Polymer, (3) PACl + Polymer + PAC.

## CONCLUSIONS

High values of UV-254, DOC, SUVA, and THMFP of a raw water supply from the U-Tapao canal, Songkhla, Thailand were detected. The tryptophan, humic and fulvic acid-like substances were detected as the major fluorescent organic matter. The percentage of HPI was slightly higher than that of HPO. HPI was the major THMFP precursor. A PACl dosage of 40 mg/l under a controlled pH of 7 was the optimal condition and could reduce the averages DOC and THMFP by 55 and 48%, respectively. Under such conditions, the fluorescent intensity of humic and fulvic acid-like substances could be reduced better than tryptophan-like substances. The highest reductions of DOC of 76% and THMFP of 83% were obtained when using PACl 40 mg/l with polymer 1 mg/l and PAC of 80 mg/l. Enhanced coagulation by polymer alone and polymer with PAC could only reduce the total fluorescent intensity of tryptophan-like substances. The enhanced coagulation by PAC was successful in reducing $CHCl_2Br$-FP. Under the optimal PACl coagulation, the averages of $DOC_{HPO}$, $DOC_{HPI}$, $THMFP_{HPO}$, and $THMFP_{HPI}$ were reduced by 60, 48, 57, and 39%, respectively. Enhanced coagulation under the best conditions consistently reduced average $DOC_{HPO}$, $DOC_{HPI}$, $THMFP_{HPO}$, and $THMFP_{HPI}$ by 85, 68, 81, and 79%, respectively. Under such conditions, it is capable of reducing the THMFP in treated water supplies to meet WHO standards.

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