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Original research article

Removal of Natural Organic Matter from Water by Coagulation and Flocculation to Mitigate the Formation of Chlorine-Disinfection By-Products at the Thu Duc Water Treatment Plant in Vietnam

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ABSTRACT

In this study, removal of NOM to prevent the potential formation of DBP at Thu Duc Water Treatment Plant (TDWTP) in Vietnam was investigated using coagulation-flocculation. Coagulants poly-aluminium chloride (PAC), aluminium sulphate $Al_2(SO_4)_3$, and ferric chloride ($FeCl_3$) – with polyacrylamide (PAM) as the flocculant were examined. The efficiency was characterized by turbidity, total organic carbon (TOC), and total trihalomethane (TTHM). Results showed that the optimal dosage of PAC, $Al_2(SO_4)_3$, and $FeCl_3$ was 20, 10, and 20 mg/L, respectively, while a 0.05 - 0.15 mg/L of PAM was effective dosage. The optimal pH was 7.0 (PAC), 6.0 ($Al_2(SO_4)_3$), and 8.0 ($FeCl_3$). Under optimal conditions, the turbidity removal was almost 99% with all coagulants while a maximum TOC removal of 26.6% was found with $Al_2(SO_4)_3$. In all cases, TTHM was not detected. Hence, $Al_2(SO_4)_3$ accompany with PAM are suggested to replace PAC which is currently used at TDWTP. Although a low efficiency in TOC removal was found, it is significant to raise a suggestion to TDWTP since the water quality monitoring now does not examine NOM and DBPs issues. Furthermore, this study provides useful information for other local water plants which employ similar raw water source and treatment processes.

Keywords: Coagulation; Disinfection by-products (DBPs); Natural organic matter (NOM); Total organic carbon (TOC); Trihalomethanes (THMs); Removal efficiency

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1. Introduction

The Thu Duc Water Treatment Plant (TDWTP) is the main water supply source to Ho Chi Minh City (HCMC), Vietnam. It is also the oldest and largest plant in the area and is administered by the Saigon Water Corporation (SAWACO) – the overall management agency of the HCMC water supply system. The TDWTP is currently operating with the total capacity expanded to 750,000 m^3/day to supply clean water to the urban districts of HCMC [1]. A conventional water treatment process (Fig.1) is run at the TDWTP, in which raw water is collected from the Dong Nai River – upstream of the Sai Gon River – at the Hoa An water intake and pumping station (Fig. 2). The treatment process focuses only on common parameters, such as turbidity, color, and microorganisms by using traditional technologies including coagulation-flocculation, sedimentation, rapid sand filtration, and disinfection. Most municipal water supply systems in Vietnam now use chlorine (Cl_2) for water disinfection [2]. The existing water quality produced by the TDWTP satisfies the national technical regulation on drinking water quality (i.e., Standard No. QCVN 01-1:2018/MOH issued by The Ministry of Health in 2018 [3]). However, the use of chlorine in purifying water poses potential health risks because of its role in the formation of carcinogenic halo-organic compounds called disinfection by-products (DBPs), such as trihalomethanes (THMs), which are formed from the chemical reactions between natural organic matter (NOM) existing in raw water and Cl_2 as shown in Eq. (1.1).

$$\text{Organic matter} + \text{Free Chlorine} \rightarrow \text{THMs} + \text{HAAs} + \text{cyanogen-halides} + \text{Other DBPs} \quad (1.1)$$

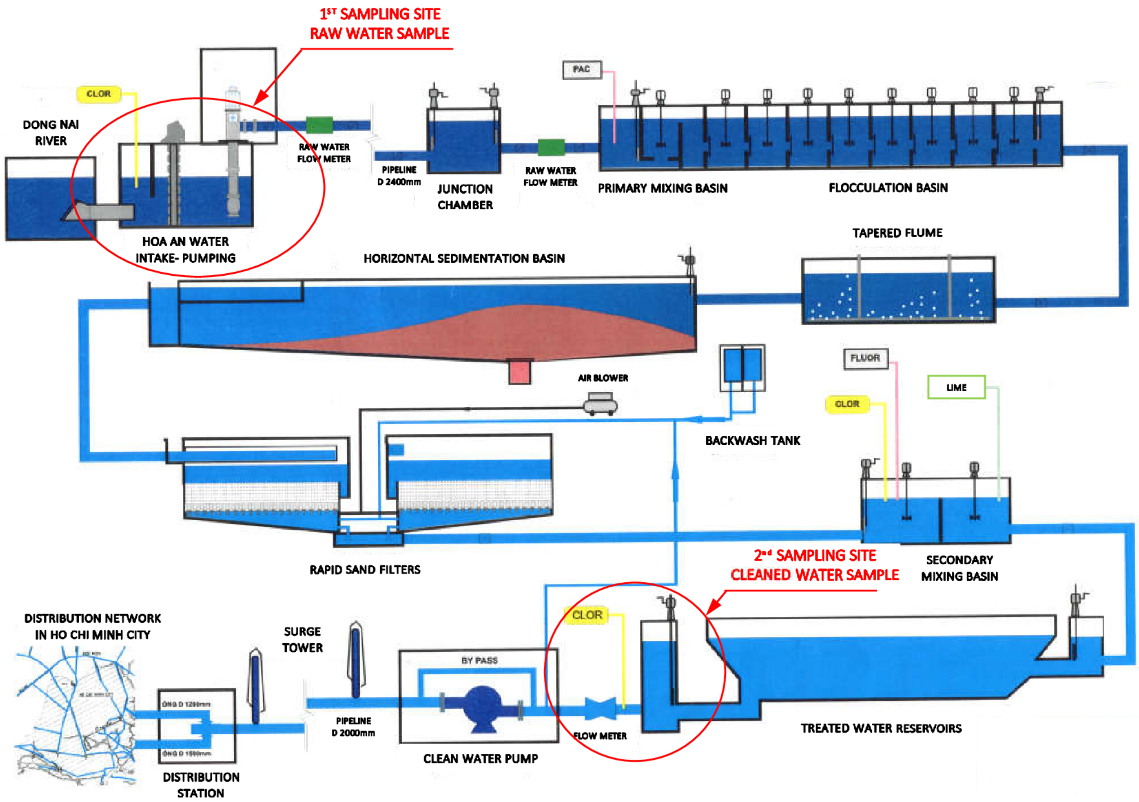


Fig. 1. Flow diagram of the treatment process at the TDWTP.

Fig. 2. Location of the Hoa An Water Intake and Pumping Station.

Unfortunately, the formation of THMs is not monitored in most water treatment plants in Vietnam. At the TDWTP, regular water quality parameters, namely color, turbidity, TSS, hardness, N-based compounds, and pathogens (E. coli and coliform), are monitored but NOM and DBPs are not taken into consideration. This situation is common in most developing countries in the Asia-Pacific region which raises concerns about water quality and sustainability. The increasing pollution of surface water sources in this area, especially caused by organic contaminants, puts pressure on the conventional water process. Thus, it is important to carry out the investigation of NOM removal and DBPs formation in water treatment plants (WTPs) to highlight the necessity of upgrading the treatment process. Furthermore, SAWACO, the authority of TDWTP, is also the owner of more than 7 surface WTPs with different capacities, 4 of which also use raw water from Dong Nai River for the treatment process. Thus, this study can provide useful information for SAWACO to upgrade the existing treatment plants for water security and to protect the health of consumers.

The periodic monitoring report issued by SAWACO for the period of 2017-2018 showed that the pollution levels of surface water are increasing because of run-off which affects the operation and performance of existing treatment processes in HCMC [1]. Specifically, water samples collected from the Saigon and the Dong Nai River are seen to be contaminated with organic matter and microorganisms, which causes lower dissolved oxygen (DO) concentration. Furthermore, the presence of residuals of antibiotics, fertilizer, and pesticides also has been reported in these water sources, which significantly influences the output water quality. Moreover, the increase in organic matter concentration in raw water sources leads to considerable risks of DBPs formation [4]. Thus, the treatment system at the TDWTP should be upgraded to remove NOM and ensure good water quality for the consumers.

NOM is commonly described as a complex mixture of organic compounds occurring naturally in water bodies, and is typically of two types: humic acids and fulvic acids [5]. The chlorination of water containing NOM is reported to be the main reason for THMs formation and for microbial recontamination in the treatment units and/or distribution systems [6, 7]. The four main types of THMs are chloroform ($CHCl_3$), bromodichloromethanes ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) [8]. The concentration of total THMs (TTHMs) and each individual species strongly depends on the concentration and properties of the NOM, type and dosage of chlorine, and operational conditions (reaction time, temperature, and pH). The TTHMs' maximum allowable level is strictly regulated in developed countries: 80 µg/l in the US, 250 µg/l in Australia, 100 µg/l in Canada, 10 µg/l in Germany, and 100 µg/l in the EU [9]. In addition, according to the World Health Organization (WHO) and the United States Environmental Protection Agency (US EPA), permissible HAAs concentrations in drinking water are 60 µg/l [10].

Several methods have been investigated for NOM removal to mitigate the formation of DBPs during water treatment. These methods include coagulation, activated carbon adsorption, ion exchange, electro-coagulation, bio-filtration, membrane filtration, advanced oxidation, and combinations of these techniques [4, 11, 12]. Among these technologies, conventional processes such as coagulation-flocculation and enhanced coagulation are considered effective and economically feasible for NOM removal, especially in the case of large-capacity water treatment plants [13-17]. It has also been reported that NOM removal efficiency in the coagulation-flocculation process is strongly affected by the physical and chemical characteristics of raw water (e.g., the nature and properties of NOM particles) and operational conditions (e.g., type and dosage of coagulants/flocculants, pH, ionic strength, temperature, and turbidity) [13, 18]. The properties of NOM with respect to coagulation and the influence of either NOM or turbidity on the coagulant dosage can be characterized by the specific ultraviolet absorbance (SUVA) concept developed by Edzwald (19). Different coagulants have been studied, such as $Al_2(SO_4)_3$ [5, 20], poly-aluminum chloride (PAC) [21], and ferric chloride ($FeCl_3$) [22, 23]. Studies on coagulation-flocculation [23, 24] and its combination with other processes [20] for NOM removal in water treatment have been carried out and applied in several developed countries. Basically, metal ions $Al^{3+}$and Fe^{2+} introduced from coagulants participate in hydrolysis reactions during the coagulation – flocculation process. Both Al^{3+} and Fe^{2+} salts are amphoteric; thus, they can form complexes substance with both cations and anions. The reaction then leads to the formation of both positively and negatively charged compounds and flocs (i.e., Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_4^-$ and $Al(OH)_3$ in case of Al-based coagulants and amorphous form ($Fe(OH)_3$ in case of Fe-based coagulants), which can be removed by gravity settling [25]. Factors influencing the coagulation process and NOM removal efficiency also have been examined in specific cases [21, 26]. However, in developing countries like Vietnam, there are still few studies on this issue. Specifically, at the TDWTP, no study on the removal of NOM has been conducted so far. Thus, it becomes important to explore the appropriate methods for removing NOM with minimum interference in the current system.

This research aimed to investigate the factors influencing the coagulation and flocculation process for removing NOM at the TDWTP. Different types of coagulants were employed at different pHs in Jar-test experiments to find the optimal conditions. The possibility of the formation of DBPs was also considered and investigated by measuring TTHMs concentration. Experimental parameters were based on the current operational conditions at the Hoa An water intake station. This study aims to find an effective solution for NOM removal and TTHMs control, which can be applied at the TDWTP.

This work is case-study research to show the feasibility of a conventional water treatment plant in removing NOM and preventing DBPs formation. The study is carried out based on the real water samples and operational parameters (i.e., mixing speed of coagulant and flocculant; settling time) currently applied at the treatment system, thus, the practical applicability is high. Specifically, the results and findings obtained from this study can be used directly as a scientific basis for SAWACO in the control, assessment, and assurance of water quality of the TDWTP and the other WTPs under SAWACO administration. It can also provide useful information for the decision makers to upgrade the existing treatment process. In addition, this study may help local authorities in forecasting the negative effects due to the changes or fluctuations in raw water quality due to environmental pollution. This will raise awareness and encourage specific activities to control waste discharge into raw water areas.

2. Materials and Methods

2.1 Water samples collection

Raw water samples were collected from the Hoa An water intake - pumping station of the TDWTP (the first sampling site, Fig.1). At the pumping station, chlorine at 0.1-0.3 mg/L is currently being used for the pretreatment of raw water to reduce microbial contamination and the overgrowth of algae, which may affect the piping system and the pumps. During the raw water collection stage, a composite sampling method was followed to obtain representative water samples [27]. Ten high-density polyethylene (HDPE) tanks (20 L/ tank) were used for two sampling times with an interval of 16 hours, and the experimental water samples were produced from mixed samples. The sampling was taken at a specific time when the pumping station was operating at the average daily flow rate. Parameters such as temperature, pH, DO, and conductivity were measured on-site by using a water monitoring system (HACH, 85490 BASIC01).

The raw water is transported from the Hoa An pumping station located in the Dong Nai province (Fig. 2) to the TDWTP (Ho Chi Minh City) by a reinforced concrete pipeline (with a diameter of 2400 mm and length of 10.8 km). The cleaned water samples were also collected at the output of the water treatment of TDWTP, after disinfection by chlorine of 2-3 mg/L (the second sampling site, Fig. 1).

All the samples were preserved and transferred immediately to the research laboratory at the Ton Duc Thang University (TDTU, Ho Chi Minh City, Vietnam). The properties of water samples were then characterized by turbidity, TOC, and TTHMs. Due to the heterogeneous and undefined character of NOM, surrogate parameters (e.g., TOC and ultraviolet absorbance at a wavelength of 254 nm (UV-254)) are normally used for measurement [8].

2.2 Jar-test experimental design and operation

2.2.1 Jar-test apparatus

A common Jar-test system containing six paddles (JLT6, Velp, Italia) was used. An rpm gauge at the top-centre of the system allows the control of mixing speeds in all the beakers (i.e., 105 rpm in 2.0 mins for initial rapid mixing of coagulant, 50 rpm in 1.0 mins, and 26 rpm in 19 mins for slow mixing flocculation). These control speeds are based on the real operational parameters at the TDWTP since the experiments were designed to simulate the actual coagulation and flocculation process and to investigate the practicability of removing suspended colloids and organic matter from raw water.

2.2.2 Preparing the coagulants and flocculants

For the Jar-test, poly-aluminum chloride (PAC), aluminum sulfate ($Al_2(SO_4)_3$), and ferric chloride ($FeCl_3$) were used as coagulants, while polyacrylamide (PAM) was used as the flocculant. The preparation of these reagents is described below.

- Coagulants (PAC, $Al_2(SO_4)_3$, and $FeCl_3$) at different dosages were prepared from dry chemicals and distilled water. Specifically, the coagulant dosage was varied as below:

+ For PAC: 0, 10, 20, 40, 60, 80, and 100 mg/L, corresponding to 0, 2.02, 4.04, 8.08, 12.13, 16.18, and 20.22 mg/L Al

+ For $Al_2(SO_4)_3$: 0, 10, 20, 40, 60, 80, and 100 mg/L, corresponding to 0, 1.57, 3.14, 6.28, 9.42, 12.56, 15.79 mg/L Al

+ For $FeCl_3$: 0, 10, 20, 40, 60, 80, and 100 mg/L corresponding to 0, 3.44, 6.88, 13.76, 20.64, 27.52, 34.46 mg/L Fe

- The flocculant, PAM, at different dosages (0.05, 0.10, 0.15, 0.20, 0.25 and 0.30 mg/L) was prepared from a 0.01% (100 mg/L) stock solution. PAM is an anionic organic polymer used widely in water treatment to enhance flocculation performance due to its high molecular weight and long polymer chains, which facilitate the formation of floc.

2.2.3 Preparing the water samples

Water samples were filled in 6 beakers of the Jar-test system (B1-B6, 01 liter of sample/ 1 beaker) to test with all three coagulants ($Al_2(SO_4)_3$, PAC, and $FeCl_3$) in different sets of duplicate experiments, as shown in Table 1. A blank sample (beaker B0) without adding any coagulant and flocculant was always performed with other samples during the Jar-test. The original pH of all the samples was measured first and then pH adjustment was carried out to the desired values by using 1 N NaOH and 1 N HNO_3 solutions.

2.2.4 Design and operation of the Jar-test experiments

A detailed design of all Jar-test investigations is presented in Table 1; each coagulant was divided into 3 experiments to (1) investigate the optimal coagulant dosage, (2) optimum initial pH, and (3) optimum PAM dosage.

The experiments were conducted by varying the dosage of the 3 coagulants in a range of 10-100 mg/L and the dosage of the flocculant in a range of 0.05- 0.30 mg/L for the investigated initial pH range of 4.0-9.0.

Table 1. Summary of the experimental design.

Beaker No.	Jar-test experiment stage									Evaluation stage		
	Experiment 1			Experiment 2			Experiment 3					
	Coagulant dosage (mg/L)	Initial pH	PAM dosage (mg/L)	Coagulant dosage (mg/L)	Initial pH	PAM dosage (mg/L)	Coagulant dosage (mg/L)	Initial pH	PAM dosage (mg/L)	Op. Coagulant dosage (mg/L)	Op. initial pH	Op. PAM dosage (mg/L)
1	10	7.0	0.10	a	4.0	0.10	a	b	0.05	a	b	c
2	20	7.0	0.10	a	5.0	0.10	a	b	0.10			
3	40	7.0	0.10	a	6.0	0.10	a	b	0.15			
4	60	7.0	0.10	a	7.0	0.10	a	b	0.20			
5	80	7.0	0.10	a	8.0	0.10	a	b	0.25			
6	100	7.0	0.10	a	9.0	0.10	a	b	0.30			

Note: Coagulants: PAC, $Al_2(SO_4)_3$, and $FeCl_3$; Flocculant: anion polymer (PAM); a: optimal coagulant dosage obtained from Experiment 1; b: optimal pH obtained from Experiment 2; c: optimal flocculants dosage obtained from Experiment 3.

At the end of each experiment, water samples in all the beakers were maintained for static settling for 30 mins before analysis. Turbidity, TOC, and THM concentration were then measured and studied to determine the input values for the next step. In the evaluation stage, all the parameters were simultaneously evaluated to compare the treatment efficiency of the different coagulants. The cleaned water samples were characterized by turbidity, TOC, and TTHMs to examine the water quality of the existing treatment system. The results were compared with the Jar-test experiments to confirm the overall efficiency of these experimental procedures.

The Jar-test operation was conducted at room temperature (20°C) in a duplicate-mode experimental design at the research laboratory. The temperature of water samples was then maintained to minimize the effects of temperature during the experiment. All the chemicals used are of analytical grade and the solutions or reagents were prepared using distilled water.

2.3 Analytical methods and calculation

All the samples before analysis were preserved according to the standard methods [27]. The physical and chemical parameters were then analysed and measured under laboratory conditions. pH was determined using a pH meter (WTW pH 3110, Germany); turbidity was measured using a turbidity meter (HACH 2100 Q, USA), and TOC measurement was performed with a TOC analyser (SHIMADZU-$V_{CPH/CPN}$, Japan). The analysis was according to the combustion-infrared method and the national standard TCVN 6634 : 2000 for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC) in the water [28]. For THM, the total concentration of four THMs (i.e., chloroform, bromodichloromethane, dibromochloromethane, and bromoform) was reported as TTHMs in units of µg/l. The measurement of TTHMs was carried out by a headspace gas chromatograph ECD detector (Gas Chromatography GC-MS Thermo, Trace 1310, USA) and the method is based on EPA Method 508 [29]. All the analyses and measurements were performed in triplicate. The results obtained are average values; standard deviation was also derived.

3. Results and Discussion

3.1 Properties of raw water

The properties of raw water collected from the Dong Nai River at the Hoa An water intake and pumping station are presented in Table 2. The temperature was 25 - 27°C. The pH values were in a range of 6.85-7.14 and turbidity was 20.60-21.00 NTU. TOC were 1.92 mg/L. However, TTHMs was not detected (Limit of Detection, LOD = 5 µg/L) in the raw water samples since the Cl_2 concentration used during the pre-treatment was still low (0.1-0.3 mg/L), indicating the reaction between organic substances and Cl_2 may not have resulted in enough THM traces for the detection limit of the measurement method.

As per the Vietnam National Standard of Raw Water Sources (i.e., TCXDVN 233:1999 [30]), the water quality at the water intake and pumping station satisfies the set standard. For NOM parameters (i.e., TOC) and DBPs (i.e., THMs), there is no standard for raw water in Vietnam at present. The results of raw water characteristics were then used as background data to evaluate the removal efficiency during the coagulation – flocculation process simulated by the Jar-test experiments conducted in this study.

Table 2. Characteristics of raw water collected at the Hoa An water intake and pumping station.

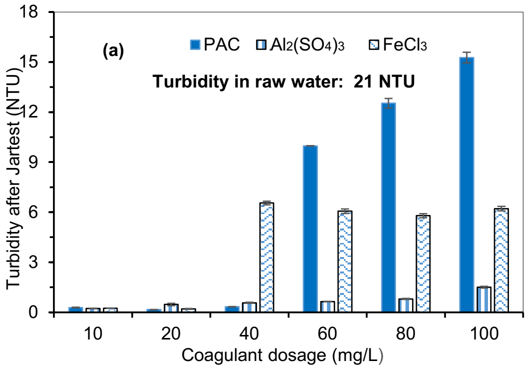
Parameter	Unit	Raw water	Vietnam National Standard TCXDVN 233 - 1999
pH(*)		6.85 - 7.14	6.5 - 8.5
Temperature(*)	°C	25 - 27	-
Conductivity(*)	µS/cm	73.98 - 80.6	-
Dissolved oxygen (DO)(*)	mg/L	6.04 - 8.75	-
Turbidity	NTU	20.6 - 21.0	<20
Total organic carbon (TOC)	mg/L	1.92	4(3)
TTHMs(1)	µg/l	ND(2) (LOD = 5)	-

Note: (1) Total THMs were measured and calculated by the concentration of $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$; (2) ND= Not detected due to the detection limit of the analysis method; (3) According to WHO standards.
(*) The value was obtained directly at sampling site from the monitoring devices installed at pumping station

3.2 Determination of optimal conditions for coagulation – flocculation

3.2.1 Optimal dosage of the coagulants

In Experiment 1, the concentration of each coagulant ($Al_2(SO_4)_3$, PAC, and $FeCl_3$) was varied in a range of 10-100 mg/L for each set of experiments. The initial pH of 7.0 and PAM polymer dosage of 0.10 mg/L were kept uniform for all the experiments (Table 1).



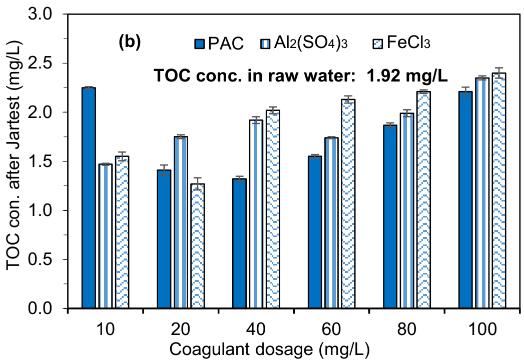


Fig. 3. Effects of coagulant concentration on (a) turbidity and (b) TOC removal.

Fig. 3a shows that coagulant dosages in the range of 10-20 mg/L were the most effective since the turbidity of water samples after static settling was very low (< 0.5 NTU), corresponding to the turbidity removal of > 99% for all three coagulants. When the coagulant dosage was increased to 40 - 100 mg/L, the water quality did not improve as the turbidity increased sharply. This phenomenon can be explained by the fact that the excessive dosage of coagulants caused "unreal turbidity", which probably affected the measurement. Also, the final pH at the end of experiments decreased in the range of 6.9 – 6.4 along with the increase of coagulant dosage of 10-100 mg/L. The excess coagulant dosage (> 40 mg/L) led to an acidic pH environment which may cause the re-stabilization of colloids and ineffective coagulation – flocculation. This resulted in high turbidities found for high coagulant dosages (Fig. 3a).

In terms of TOC removal, different trends were found when the coagulant dosage was varied in the range of 10 - 100 mg/L (Fig. 3b). Specifically, in the case of PAC, the lowest TOC concentration was 1.32 mg/L when PAC dosage of 40 mg/L was used. On the other hand, with $Al_2(SO_4)_3$, a dosage of 10 mg/L was effective to decrease TOC concentration from 1.92 mg/L in raw water to 1.47 mg/L after Jar-test and settling. For $FeCl_3$, the optimal dosage was found to be 20 mg/L, corresponding to the lowest TOC concentration of 1.27 mg/L. In some cases, the TOC concentration in the water samples after the Jar-test was found to be higher than TOC in raw water. It is possible that the use of an organic polymer like PAM as a flocculant may have slightly impacted TOC measurement. Although a similar dosage of PAM was added in all the beakers during this stage, different amounts of coagulants were present and this may have caused PAM to form floc in some cases. In addition, the TOC concentration in all samples was in the low range (i.e., about 2 mg/L) which may affect the accuracy of TOC analysis although all the analyses/measurements were performed in triplicate and the average standard deviation was 0.02-0.04.

The THMs (µg/L) were also examined; however, the results showed that no trace concentration was found because it was under the detection limit of the analysis method (LOD = 5 µg/L) which was adopted. Some studies in the past have also investigated the removal of NOM and DBPs. In the Tigris River (Baghdad), this was done using $Al_2(SO_4)_3$ and $FeCl_3$ via Jar-tests [20]. A different trend was found in their study: an increase in $Al_2(SO_4)_3$ and $FeCl_3$ dosage resulted in linear decrease in turbidity and NOM. Similarly, another study also showed that when the $FeCl_3$ dosage was increased from 10 to 80 mg/L, the removal efficiency of NOM increased accordingly [31].

When taking all results (turbidity, TOC, and TTHMs) and the cost aspect into consideration in this study, the optimal PAC, $Al_2(SO_4)_3$, and $FeCl_3$ dosages were found to be 20, 10, and 20 mg/L, respectively. At the chosen PAC dosage of 20 mg/L, the TOC concentration was 1.41 mg/L which was slightly higher than the 1.3 mg/L obtained at PAC dosage of 40 mg/L. However, the cost of the coagulant is also an important consideration since it will increase total operational costs. The chosen optimal values were then applied for the next set of experiments.

3.2.2 Optimal pH

The adjustment of pH is an important factor that strongly affects the performance of the coagulation and flocculation process. The optimal dosage of PAC (20 mg/L), $Al_2(SO_4)_3$ (10 mg/L), and $FeCl_3$ (20 mg/L) obtained from the results of Experiment 1 (Section 3.2.1), and PAM polymer dosage of 0.10 mg/L, were added similarly to all the beakers to investigate the effects of pH.

Results showed that the turbidity of the settled water in all three cases of coagulants fluctuated when initial pH was increased (Fig. 4a). A similar trend was observed, wherein the lowest turbidity values were found with a neutral range (pH of 6.0 -7.0). Also, initial pH < 6.0 was not effective as turbidity was high in all cases. In contrast, when pH increased to 8-9, different changes were noticed. Specifically, turbidity did not change much when pH was varied from 6-9 in the case of $FeCl_3$, but it did increase when pH was within the basic range (> 7.0) with PAC and $Al_2(SO_4)_3$. Accordingly, with PAC and $Al_2(SO_4)_3$ as coagulants, the highest turbidity removal efficiency was obtained when initial pH was adjusted to be neutral (i.e., 6.0-7.0), while $FeCl_3$ worked most effectively as a coagulant for a wide range of pH, from neutral to basic value (i.e., 6.0-9.0). These findings are in line with the theoretical mechanism of coagulation - flocculation with different coagulants [32]. Basically, $Al_2(SO_4)_3$ has low solubility in a pH range of 5.7-6.2. When $Al_2(SO_4)_3$ is added as a coagulant, it forms $Al(OH)_3$ precipitant, which enhances turbidity removal. In contrast, when the pH level is below 5.7, $Al_2(SO_4)_3$ dissolves in water in the form of cations such as Al^{3+}, $Al(OH)_2^+$, and $Al(OH)^{2+}$, which are not favorable for precipitation. Similarly, if pH is within the basic range, the cationic states will change to $Al(OH)_4^-$. This anion form also does not aid the removal of turbidity.

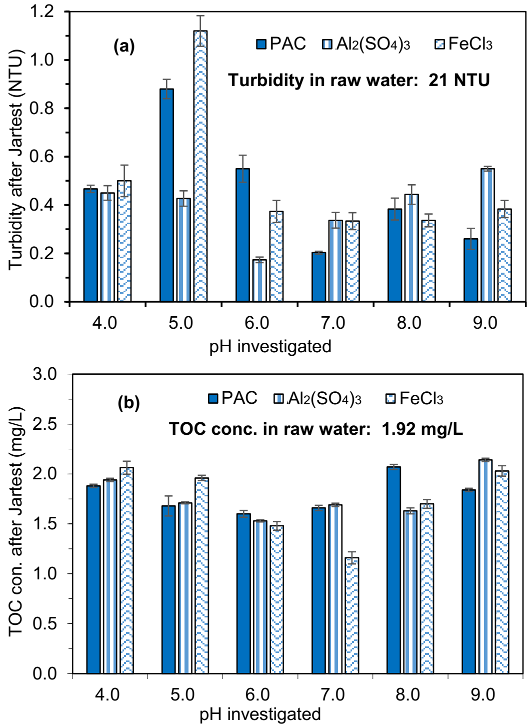


Fig. 4. Effects of initial pH adjustment on (a) turbidity and (b) TOC removal.

The effects of initial pH adjustment on TOC removal were also considered. Fig. 4b presents the changes in TOC concentrations of the water samples collected after the Jar-test along with variations in pH. In the case of PAC as a coagulant, pH of 5.0 - 7.0 was found suitable for TOC removal since there was not much difference in TOC concentration (i.e., it just slightly changed within a range of 1.60 - 1.68 mg/L). For $Al_2(SO_4)_3$ as the coagulant, a pH value of 6.0 was determined as the optimal value since TOC concentration dropped sharply to 1.53 mg/L. Similarly, a pH value of 7.0 was the most effective for TOC removal in the case of $FeCl_3$ as a coagulant due to the very low concentration of TOC (1.16 mg/L).

A study on the removal of turbidity and NOM using coagulation with PAC and $Al_2(SO_4)_3$ was conducted on water from the Yellow River in China [21]. The results showed that an initial pH of 6.0 was efficient to remove turbidity, DOC, and UV-254 with removal efficiencies of 86%, 45%, and 55%, respectively. With a pH < 6.0, PAC dissolves well in water and changes form to a monomer and the cationic polymers $Al_{13}O_4(OH)_{24}^{7+}$, Al^{3+}, and $AlOH^{2+}$. For studies conducted with $FeCl_3$ as the coagulant, it was reported that when the pH is < 8.0, $FeCl_3$ will change to a cationic monomers like Fe^{3+}, $FeOH^{2+}$, and $Fe(OH)_2^+$ [6, 23]. Under these conditions, NOM has a high density of negative ions (anion) and coagulants in cation form, which enhance neutralization and precipitation.

Therefore, in this study, when the removal of turbidity and TOC were integrated, the optimal initial pH for each case of coagulant was determined as the following: pH of 7.0 for PAC, pH of 6.0 for $Al_2(SO4)_3$, and pH of 7.0 for $FeCl_3$. The properties of raw water were also considered in this step. Since the pH of raw water was in the neutral range of 6.85 - 7.14 (Table 2), the above optimal pH values will help to reduce the operational costs and complexity arising from pH adjustment.

3.2.3 Optimal dosage of PAM as flocculant

The PAM polymer was used to enhance the adhesion of floc and accordingly improve the performance of flocculation. In this experiment, the dosage of PAM was varied in a range of 0.05-0.30 mg/L. The optimal dosage of coagulants obtained from Experiment 1 (PAC of 20 mg/L, $Al_2(SO_4)_3$ of 10 mg/L, and $FeCl_3$ of 20 mg/L) and the corresponding optimal pH values (7.0, 6.0, and 7.0) obtained from Experiment 2, were kept similar in all 6 beakers.

Results showed that variations in PAM dosage strongly affected the turbidity removal of PAC and $FeCl_3$ as coagulants, but only slightly impacted these values in the case of $Al_2(SO_4)_3$ (Fig. 5a). High turbidity removal efficiency (>95%) was still obtained in all the cases with different levels of PAM dosage.

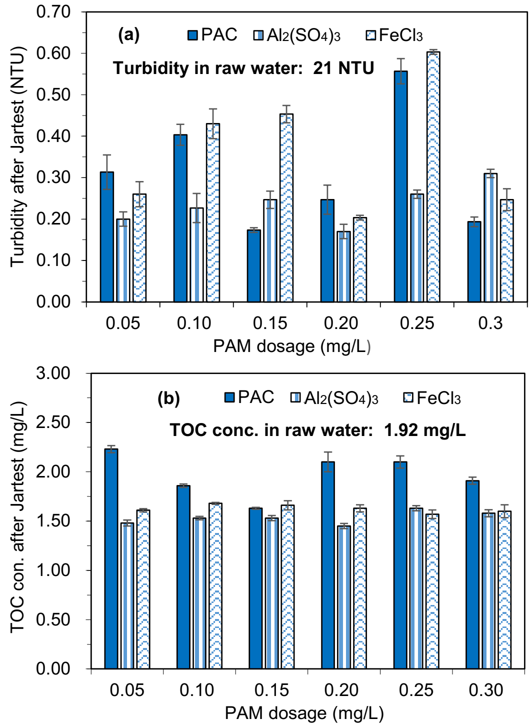


Fig. 5. Effects of PAM dosage on (a) turbidity and (b) TOC removal.

PAM variations had little effect on TOC removal in the case of $Al_2(SO_4)_3$ and $FeCl_3$ as the TOC concentration after the Jar-test in both cases was around 1.5-1.6 mg/L. In the case of PAC, the TOC concentration was still high (>1.6 mg/L) and it also fluctuated along with the increase in PAM dosage. Overall, TOC removal did not improve much in any of the cases as the initial TOC concentration was 1.92 mg/L (Fig. 5b). With some specific PAM levels (i.e., 0.20; and 0.25 mg/L), the TOC concentration after the Jar-test was higher than the initial value, which may be due to the effect of PAM degradation and the excessive amount used in the experiment. Moreover, a very small amount of 0.05 mg/L PAM did not help to remove TOC since the concentration was still higher than the initial value (i.e., 1.92 mg/L).

In all cases, the TTHMs trace concentration was not detected due to the limits of detection (LOD < 5 µg/L).

Thus, based on the results presented in Figs. 5a-5b, the optimal PAM dosages for each coagulant were found to be 0.15 mg/L (PAC), 0.05 mg/L (Al_2SO_4), and 0.05 mg/L ($FeCl_3$). This determination also considers the economic aspect since an excessive amount of PAM does not significantly improve the treatment's efficacy. However, the results of optimal PAM dosage obtained in this study (i.e., 0.05-0.15 mg/L) was not in line with the range typically applied at some water treatment plant (i.e., mostly < 0.01 mg/L), which may be due to several differences between the laboratory and plant conditions, such as the volume of water investigated, the effects of actual mixing and water temperature. Therefore, lower dosages of PAM (i.e., < 0.05 mg/L) are suggested to be considered in the further examination to verify the optimal values obtained in this study and to possibly find out more effective dosages for flocculation.

3.3. Determination of the appropriate coagulants

In order to determine the appropriate coagulant and corresponding operational conditions during the coagulation - flocculation process, a comparison of treatment efficiency obtained in the Jar-test experiments was carried out. Treatment efficiency was determined based on the removal of turbidity, TOC, and the formation potential of DBPs characterized by the trace concentration of TTHMs. Table 3 summarizes all of results obtained with each coagulant operated under optimal conditions.

For turbidity, the results showed that very high removal efficiency (i.e., ≥ 99%) was achieved, indicating the important role of coagulants and PAM polymer as a flocculant in removing all suspended solid and colloids existing in raw water. In the context of the national technical regulation on drinking water quality (Standard No. QCVN 01-1:2018/MOH [3]), the turbidity after the Jar-test in all the cases satisfied the standard (i.e., 2 NTU).

Table 3. Treatment efficiency of different coagulants in comparison with the current operation conditions at the TDWTP.

Source of water sample	**Type of coagulant and flocculant**	**Optimal operational conditions**	**Cost [(1)]** (USD/ m^3)	**Turbidity (NTU)** Raw water: 21 (NTU)		**TOC conc.(mg/L)** Raw water: 1.92 (mg/L)		**TTHMs** (µg/L) Raw water: ND [(2)]
				After Jar-test	***RE***	***After Jar-test***	***RE***	
Raw water sample collected from water intake after Jar-test experiments	PAC	PAC of 20 mg/L pH of 7.0, and PAM of 0.15 mg/L	0.0084	0.17	> 99%	1.63	15.1 %	ND [(2)] in all experimental batches (LOD = 5)
	$Al_2(SO_4)_3$	$Al_2(SO_4)_3$ of 10 mg/L pH of 6.0, and PAM of 0.05 mg/L	0.0088	0.17	> 99%	1.41	26.6 %	
	$FeCl_3$	$FeCl_3$ of 20 mg/L pH of 7.0, and PAM of 0.05 mg/L	0.0219	0.20	99%	1.87	2.6%	
	PAM	PAM of 0.05 mg/L	0.055 x10^{-3}	-	-	-	-	
Clean water sample collected from TDWTP	PAC	PAC of 30 mg/L[(3)] pH of 6.8 with 2 times of pH adjustment No addition of flocculant	0,0125	***Clean water***	***RE***	***Clean water***	***RE***	
				0.21	99%	1.64	14.6 %	

Note: [(1)] The cost is calculated based on the local market prices of coagulant (i.e., 10.44 USD/ pack of 25 kg PAC, 21.97 USD/ pack of 25 kg $Al_2(SO_4)_3$, 27.47 USD/ pack of 25 kg $FeCl_3$, and 64.72 USD/ pack of 25 kg PAM

[(2)] ND = Not detected due to the detection limit of the analysis method

[(3)] Current operational conditions, as informed by the TDWTP

But in the case of a practical application, the performance may decrease due to many factors including the composition of raw water. In this study, the raw water was collected during the dry season, which indicates that the initial turbidity was still low (i.e., 21 NTU). This could be the reason for the good performance of the experiments in turbidity removal. Further research is required to study samples collected in the rainy season, and then investigate the treatment's efficiency and provide a more complete database.

In terms of removal of organic matter to prevent the formation potential of DBPs, positive results were obtained during the Jar-test experiments. Specifically, under optimal operational conditions, the TOC removal percentages were 15.1%, 26.6%, and 2.6% with PAC, $Al_2(SO_4)_3$, and $FeCl_3$, as coagulant. This indicates that $Al_2(SO_4)_3$ resulted in higher TOC removal efficiency as compared to the others. The costs of the coagulants were also considered to evaluate and determine the appropriate coagulant for practical application. The optimal dosage and the cost of $Al_2(SO_4)_3$ coagulant (shown in Table 3) demonstrates that $Al_2(SO_4)_3$ was the most effective and appropriate for turbidity and NOM removal from raw water. It has been reported that the Chinamo Water Treatment Plant, the biggest water supply source of Vientiane capital (the Capital city of Laos), also uses $Al_2(SO_4)_3$ as the main coagulant during the treatment process due to its effectiveness [33]. In this study, although the optimal dosage of $Al_2(SO_4)_3$ (10 mg/L) was lower than the other coagulants, the drawback of Al-based coagulants is the residual aluminum speciation. Studies have reported that residual aluminum may be deposited in distribution systems and potentially release back into cleaned water and affect overall water quality [21, 34]. Similar effects in the case of $FeCl_3$ coagulant were found with a high $Fe(OH)_3$ precipitation tendency and obvious increase in turbidity. The iron instability due to iron release from corrosion scale of the pipe would result in red water phenomenon [35]. Therefore, further investigation needs to be carried out to clarify this issue.

Overall, the TOC removal efficiency obtained in this study was relatively low. The characteristics of NOM in the raw water samples may be one of the reasons. It has been reported that NOM with high molecular weight (MW) and low solubility can be removed easily by coagulation, while NOM with low MW and high solubility results in low removal efficiency due to their good hydrophilicity leading to low adsorption with the coagulant hydrolysate [4, 22]. A previous study has also pointed out that a very low NOM removal percentage (10 - 50%) occurs in water treatment processes using conventional technologies (e.g., coagulation - flocculation) [36]. However, the biggest advantage of coagulation - flocculation is that it can remove NOM based on the existing treatment system without high investment, as compared to other advanced technologies. Therefore, in the case of large-capacity water treatment plants, like the TDWTP, it is important not to interfere too much with the existing process since it may require costly changes of the treatment facility and interrupt the clean water supply.

3.4. Comparison of experimental efficiency with actual performance at the TDWTP

The treatment efficiency obtained in this study was also compared with the treated water currently produced in the TDWTP. Treated water samples were collected from the TDWTP to analyze their turbidity, TOC, and TTHMs concentration. In the plant, the same type of coagulant as PAC is used. The results obtained in this study (i.e., optimal PAC dosage of 20 mg/L at initial pH of 7.0, and PAM of 0.15 mg/L) were comparable with the values of the samples obtained at the TDWTP (i.e., PAC dosage of 30 mg/L, pH of 6.8 with 2 times of pH adjustment and without flocculant) (Table 3). When operational cost is taken into consideration, the use of PAC at optimum conditions reported by this study consumed an average of 0.0084 USD/m^3 water, which is lower than that currently found in TDWTP (i.e., 0,0125 USD/m^3 water). This indicates the optimum dosage of PAC with PAM as flocculant as suggested in this study can help to reduce the operational cost.

The optimal PAC dosage found during the Jar-test is lower than that currently used at the plant. On the other hand, when $Al_2(SO_4)_3$ was used as the coagulant in the experiment, the optimal dosage of $Al_2(SO_4)_3$ was just 10 mg/L (Table 3), but it helps to reduce the amount of coagulant and thus can reduce the operational cost. The usage of Al-based coagulant in the form of either PAC or $Al_2(SO_4)_3$ in the long run may cause deposition of residual Al speciation. Therefore, the lesser the amount of Al-based coagulant used, the lower is the risk of Al deposition. Accordingly, it is suggested that $Al_2(SO_4)_3$ at the optimal dosage of 10 mg/L replaces PAC at 30 mg/L, which is currently being deployed at the TDWTP. This can improve water quality in terms of both turbidity and organic matters and mitigate the formation of aluminum residuals in the distribution pipelines.

Furthermore, at the TDWTP, the pH needs to be adjusted 2 times (before and after coagulation), which may be due to the complicated and large capacity system as compared to lab-scale Jar-test experiments. Currently, the flocculant PAM is not used in the real treatment system, thus affecting the floc formation and resulting in low efficiency of the sedimentation basin. During the site-survey at the TDWTP, a large number of small flocs were observed in the outlet of sedimentation basin, which cause more load for the filtration step thereafter. Therefore, based on the results obtained in this study, utilization of PAM at 0.05 mg/L should be investigated further and applied at the TDWTP.

It must be noted that TTHMs were not detected in any of the experimental batches in this study nor in the clean water sample from the TDWTP, indicating the high safety and quality of the drinking water plant supplies to the customer. The raw water quality at the Hoa An water intakes and pumping station and the current coagulation - flocculation treatment process provide a good quality of water output. Nevertheless, the removal of NOM in surface raw water during the treatment process and forecasting the risk of TTHMs formation are always essential. This may need more detailed and frequent monitoring in the future at the plant. At present, the TDWTP does not have specific steps in this direction. Therefore, it is suggested that the NOM parameter measured by either TOC or DOC and TTHMs concentration should be added to the periodic monitoring plan at the TDWTP to ensure the sustainability of the water's quality.

4. Conclusions

In this study, the optimal operational conditions of the coagulation and flocculation process to remove turbidity and NOM from surface water at the TDWTP were determined. The results showed that the optimal dosage of PAC, $Al_2(SO_4)_3$, and $FeCl_3$ was 20, 10, and 20 mg/L, respectively. Increase in coagulant dosage did not improve the removal efficiency of turbidity and NOM much; rather it caused negative effects in some cases. The optimal initial pH values for the coagulation and flocculation process with PAC, $Al_2(SO_4)_3$, and $FeCl_3$ was 7.0, 6.0, and 7.0 respectively, indicating that not much in terms of chemicals is required for the pH adjustment. The addition of the anion polymer PAM significantly affected the removal efficiency of turbidity, but little effect was found in the case of TOC. The optimal PAM dosages when using PAC, $Al_2(SO_4)_3$, and $FeCl_3$ coagulants were found to be 0.15, 0.05, and 0.05 mg/L, respectively. Under optimal conditions, the turbidity removal was very high (≥99%) but TOC removal efficiency was low in all cases. The highest TOC removal (of 26.6%) was obtained with the $Al_2(SO_4)_3$ coagulant with the initial TOC value of 1.92 mg/L. This study also indicates that the coagulation and flocculation treatment resulted in a positive response in terms of TTHMs removal. TTHMs concentration measured under the experimental conditions and the actual water treatment system at the TDWTP, was under the detection limit (LOD = 5 μg/L). It is suggested that during the water treatment process of that TDWTP, $Al_2(SO_4)_3$ coagulant of 10 mg/L should be used with the addition of PAM flocculant of 0.05 mg/L at the optimal pH of 6.0 to maximize the treatment efficiency and reduce operation cost.

Recommendations

- Frequent monitoring of NOM and TTHMs should also be carried out at the TDWTP to assure the continuing good water quality.
- Also, the characterization of raw water quality should consider UV-254 absorbance, SUVA-value, and water alkalinity to understand the correlation between the NOM and coagulation.
- In addition, seasonal effects on raw water quality should be considered in the future work since the pH, turbidity, TOC will vary throughout the year, which accordingly affects the coagulation efficiency.
- The experimental determination of chlorination after coagulation should be tested to determine the THM formation potential of coagulated water. This helps to confirm the performance of coagulation for removal of NOM and predict the possibility of DBPs formation.

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