1. Introduction

Surface water (mainly river water) in coastal areas has considered a great source of water supply instead of using groundwater, however, this source has a high concentration of suspended sediments and high organic matters, i.e., from 2.0 - 10.0 mg/L and even some places, the organic matter was higher depending on the regions [1]. Additionally, this water source is sometimes subject to seasonal salt intrusion due to its direct connection to the sea. The salinity increased up to 20 g/L and the intrusion went up to 100 km, affecting many rivers in coastal areas in Vietnam [2]. It led to higher cost for surface water treatment in this area.

In order to treat the organic matter in coastal surface water, traditional technologies such as coagulation-sedimentation-filtration; oxidizing using chlorine, KMnO₄, ozone, etc., have been applied [3–5] and in some developed countries, more advanced technologies can be used including coagulation-adsorption or coagulation-membrane filtration [6–9]. In Vietnam, the common practice has been applying preliminary chlorination to control organic matter, then coagulation and sand filtration [10]. In addition, there are some places that use biological filter tanks [11]. When there is salt intrusion, the water treatment plants often stop taking raw water for a few hours until low tide or they switch completely to another water resource if the salt intrusion process takes several days. In this case, they have to deal with double issues i.e., organic matters and salinity. Normally, organic
matters itself is already a difficult issue and costly for water treatment in developing countries. The problem is that if organic matter content has not been completely controlled, it can react with disinfectants (for instance, Chlorine, a common and cost-effective disinfectant applied in water treatment plants in developing countries) to create unwanted by-products, and then affect users' health. In the early 1970s, some researchers noticed that chlorine or chloramine could react with natural organic substances to produce carcinogenic by-products (DBPs) such as trihalomethanes (THMs), haloacetic acid (HAAs), phenol, N-chloramine, halofuranone, bromohydrin [12]. Chloramine can form the product N-nitrosodimethylamine (NDMA), which is also one of the potential carcinogens, and other substances such as iodoacetic acid if iodine is present in the water [13].

In the US and Europe, regulations are quite strict about the permissible concentrations for these potentially carcinogenic substances. In Vietnam, there are also some specified indicators (see Table 1). The criteria for these by-products in Vietnam are quite close to the standard figures of other countries, except for the higher bromate index and the lower chlorite criterion.

Table 1. Accepted values for THMs in some countries

<table>
<thead>
<tr>
<th>Substance</th>
<th>US EPA [14], µg/L</th>
<th>ECE [15], µg/L</th>
<th>WHO [16], µg/L</th>
<th>Vietnam standard [17], µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromate</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>Chlorite</td>
<td>1000</td>
<td>-</td>
<td>700</td>
<td>200</td>
</tr>
<tr>
<td>Bromodichloromethane</td>
<td>80</td>
<td>100</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>Bromoform</td>
<td>80</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Chloroform</td>
<td>80</td>
<td>100</td>
<td>300</td>
<td>200</td>
</tr>
<tr>
<td>Dibromochloromethane</td>
<td>80</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

A review of several studies on THMs found that the types and concentrations of THMs depended on a number of factors, but most specifically the type and amount of disinfectant used, contact time, concentration of organic and inorganic matters, temperature and pH [18, 19]. Research by Xiao et al. [20] showed that THMs by-products can be partially decomposed under the influence of UV/H₂O₂ process, with higher efficiency than if using only UV light. Another study showed that THM and Haloacetic acids (HAA) concentrations increased with increasing chlorine dosage and that trichloromethane was the major product of the four THMs [21]. A review by Kim et al. [22] indicated that the formation of THMs in seawater was difficult to determine. In recent year, Parveen and Goel [19] studied the effect of saline intrusion on the formation of chlorinated and brominated THM in coastal groundwater, and found that there was an influence of salinity on the formation of THMs and contact time. The increase in total THM formation was proportional to salinity intrusion up to 0.5% for real source water and 1% for artificial water. At higher salinity intrusion, there was no increase in THMs concentration. In the absence of saline intrusion, only chlorinated THMs (TCMs) were formed and no brominated THMs (TBM) were formed, since there was no bromide in coastal groundwater [3]. Meanwhile, studies on the formation of by-products in surface water containing organic matters after chlorination are very limited in Vietnam [23]. A survey of in 6 districts of Ho Chi Minh City showed that the average concentration of THMs in the domestic water sample was 31.40 ± 29.23 µg/L (20 - 110 µg/L), in which, chloroform accounted for most of the THMs residue in the water supply [24]. The study found that the concentration of THMs in water at all survey sites did not exceed the national technical regulation on drinking water quality (QCVN 01-1:2018/BYT), however, there were a few locations, the chloroform residues were higher than the allowable standards of US.EPA (80 µg/L).
Although there have been hundreds of studies on THMs formation during feed water disinfection [22, 25, 26], very few studies have evaluated the effect of salinity (due to saline intrusion to surface water) on THMs formation. This study was to evaluate the formation of THMs (specifically, Chloroform, Bromoform, Dibromochloromethane, and Bromodichloromethane) after the disinfection of treated coastal river water at pilot scale. Effect of salinity and disinfectant concentrations shall be evaluated and considered as the highlight of this study.

2. Materials and Methods

2.1. Raw water

Raw water for this study was taken from the Can River (often also called Hoat River for the section running through Thanh Hoa, a coastal province of Vietnam), from July to September 2022. The water quality during the testing period was recorded as following: pH = 8.11 ± 0.14, total dissolved solids TDS = 790.00 ± 143.05 mg/L, COD\textsubscript{KMnO}\textsubscript{4} (representing for organic matter) = 3 - 9 mg/L; turbidity = 101.63 ± 31.41 mg/L, NH\textsubscript{4}+ – N = 0.23 ± 0.10 mg/L, conductivity = 1118 ± 139 µS/cm. The river has high pH due to the impact of limestone rocks. It is strongly influenced by tides, so the salinity has changed significantly from 0.02% to 0.15% (or 200 to 1500 mg/L in terms of TDS). Similarly, the Br\textsuperscript{–} concentration varied from 0.5 mg/L (when TDS was low) to about 10 - 13 mg/L (when TDS was high). It should be noted that the Br\textsuperscript{–} concentration is normally less than 1 mg/L in fresh water and increases up 80 mg/l in the seawater [16]. So, the raw water in this study occasionally became brackish water (Br\textsuperscript{–} concentration from 1 - 20 mg/L) when there was salinity intrusion. It can be seen on Fig. 1 that Can river (or Hoat river) connects quite closely with the East Sea (only about 10 km from the East Sea).

![Figure 1. Pilot location](image)

2.2. Experimental process

Raw water from Hoat river was pumped by a water pump (SIP 125BE Model, Shinil company) to the mixing tank in which it was mixed with PAC 30% (Viet Tri Chemical Company) with a concentration of 30 mg/L. On the pipeline to the mixing tank, there is an online mixing device (Series 70169,
Set Sunsolar Energy Technologies) for pre-chlorination of organic matter. The chlorine concentration is given so that the residual chlorine is about 0.5 - 1.0 mg/L.

After passing through the mixing tank and Lamen settling tank, it was pumped to sand filter columns, using quartz sand with diameter D = 1.0 - 1.2 mm. In reality, sand filter can be used sometimes before membrane unit for better pre-treatment, depending on the raw water quality. After sand filtration, the treated water was taken to the ultrafiltration (UF) membrane filter tank. UF and microfiltration (MF) membranes are often selected for drinking water treatment at large scale [3], however, UF membrane was chosen in this study as it produced more permeate and controlled better the organic matters than microfiltration (MF) membrane. Even though it is not effective for salt removal. The characteristics of ultrafiltration membranes are shown in Table 2. The permeate was sucked from UF membrane using a specialized pump (DH2-60 series, LIUP pro pump, Italy). The transmembrane pressure was measured in-line with a vacuum gauge (0 to 760 mmHg, Technology of Taiwan). Flow was measured by in-line flow meter (Code: TnF-T3-1-2-H, China). Specifically, the permeability of the membrane was in the range of 20-30 L/m²/h, the transmembrane pressure was about 0.2 ± 0.07 bar. The system was operated for 8 hours/day, and the UF membrane and sand filter were backwashed with clean water at the end of the day for 10 and 15 minutes, respectively. The system was occasionally stopped when there was severe salt intrusion, normally for several hours.

![Experimental diagram](image)

**Table 2. Characteristic of testing UF membrane**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>REGREEN RG020</td>
</tr>
<tr>
<td>Dimension L × W × H (mm)</td>
<td>508 × 480 × 25</td>
</tr>
<tr>
<td>Surface area (m²/sheet)</td>
<td>2</td>
</tr>
<tr>
<td>Outer/Inner diameter (mm)</td>
<td>2.0/1.0</td>
</tr>
<tr>
<td>Pore dimension (µm)</td>
<td>0.03</td>
</tr>
<tr>
<td>Flux (L/m²/h)</td>
<td>6-40</td>
</tr>
<tr>
<td>Material</td>
<td>PVDF</td>
</tr>
</tbody>
</table>

To evaluate the THMs formation, the NaOCl 1M solution (CAS 7681-52-9, Xilong Scientific, China) was mixed with treated water after UF membrane and after sand filtration at a dose such that the measured residual chlorine was in the range of 0.2 - 0.8 mg/L. This range of value was chosen based on the national regulation on residual chlorine in Vietnam (i.e., 0.2 - 1.0 mg/L). The selected THMs for analysis were Chloroform, Dibromochloromethane, Bromodichloromethane and Bromoform because they are often monitored by water plants in Vietnam. The contact time was
24 hours. The THMs sampling were conducted in duplicate. Two conditions of salinity level were evaluated: low salinity of 0.026% \(\pm\) 0.002\%, with Br\(^{-}\) concentration of less than 1 mg/L and high salinity of 0.148\% \(\pm\) 0.015\% with Br\(^{-}\) concentration of around 10 - 13 mg/L. For the test at high salinity, sometimes the salinity in the river was not high enough, thus, NaCl solution (CAS 7647-14-5, Xilong Scientific, China) was added in the mixer tank so that the salinity was maintained around 0.15\%.

2.3. Sampling and analysis

The organic matters in raw water were analyzed in terms of total organic carbon (TOC), ultraviolet at 254-mm wavelength (UV\(_{254}\)), and fractionation. Total organic carbon (TOC) of the sample was measured using a TOC analyzer (VCPH, Shimadzu, Japan) and UV\(_{254}\) nm was determined using a Spectrophotometer (UH5300, Hitachi High Technologies, Japan). The organic fractions from the raw water were isolated using nonionic macroporous sorbents XAD7 and XAD4 (Merck, US). The fractionation method was described in detail elsewhere [27]. The residual chlorine was measured using a pocket colorimeter (DR300, Hach, CO, USA). The salinity parameter was analyzed by salinity meter device (AR8011, Smartsensor, China).

For THMs analysis, the water samples after UF membrane and sand filter were taken into 1000-mL brown glass bottles to minimize the influence of light and the adhesion of substances on the bottle walls. Then they were sent to a certified lab at the Institute of Occupational Health, Ministry of Health. The four specific substances including Chloroform, Dibromochloromethane, Bromodichloromethane, and Bromoform were defined using gas chromatograph and mass spectrometer (Model Trace 1300 series, Thermo Scientific, Waltham, MA, USA) following analytical method proposed by Andersson et al. [28] and EPA 524.2.

3. Results and discussion

3.1. Organic matters and salinity in the raw and treated water

Table 3 presents the organic matters in the raw and treated water. The raw water sample has a rather high organic matter content (TOC = 6.98 \(\pm\) 0.53 mg/L and UV\(_{254}\) = 0.22 \(\pm\) 0.05 (cm\(^{-1}\)).

<table>
<thead>
<tr>
<th></th>
<th>Raw water</th>
<th>After sand filter</th>
<th>After UF membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC (mg/L)</td>
<td>6.98 (\pm) 0.53</td>
<td>3.00 (\pm) 0.97</td>
<td>1.66 (\pm) 0.91</td>
</tr>
<tr>
<td>UV(_{254}) (cm(^{-1}))</td>
<td>0.22 (\pm) 0.05</td>
<td>0.14 (\pm) 0.06</td>
<td>0.10 (\pm) 0.03</td>
</tr>
</tbody>
</table>

The proportions of hydrophobic, hydrophilic and intermediate components were 84\%, 9\% and 7\%, respectively (Fig. 3). This result is quite similar to previous studies, which concluded that the hydrophobic composition of natural organic matter (NOM) is between 60 - 90\% [27]. It should be noted that the hydrophobic fractions are generally composed of the higher molecular weight NOM with activated aromatic rings, phenolic hydroxyl groups, and conjugated double bonds, while the hydrophilic fractions are typically composed of the lower molecular weight NOM with aliphatic ketones and alcohols. The hydrophobic fractions of NOM tend to be more reactive with chlorine than bromine [29].

Moreover, the high organic matters would lead to increasing level of THMs precursors which increases THMs formation and requires more chlorine dosage for maintaining proper chlorine residual in the distribution system [1]. Therefore, it is critical to control the organic matter to accepted values before the disinfection step during the treatment process.
It is clearly seen in Fig. 4 that during the testing period (for example, in July-September 2022), the salinity in the raw water varied as well. The salinity fluctuated with no pattern. It should be noted that the salinity in fact varied by hours during the day. However, the research team could only take samples every morning, so there was only one data per day. Even though, it did not describe exactly the salinity concentration per hour, it could reflect the trend of salinity fluctuation overall.

![Figure 4. Salinity fluctuation](image)

Normally the river has salinity of about 0.02% or TDS in a range of 200 - 300 mg/L. Nevertheless, it could go up to 0.15% (salinity) or 1500 mg/L (TDS) when there was salt intrusion. It should be noted that TDS concentration can also be an indicator of saline water [30] as it closely correlated with dissolved salts such as Cl\(^-\), Br\(^-\), etc. in the water. The Hoat river water normally has the quality of fresh water (salinity < 0.05%). Nevertheless, it occasionally became brackish water (i.e., salinity in a range of 0.05% - 3.0%). As discussed above, the East Sea was only about 10km away from the pilot location, so the intrusion was reasonably possible due to the climate change impact. The impact can also be seen in Br\(^-\) concentration. During testing period (July 2023), the Br\(^-\) concentration in the raw water was occasionally 11.35 ± 1.62 mg/L which was much higher than normal river water, (i.e., from 0.5 - 1.0 mg/L) [16, 31] and lower than in the seawater, i.e., from 65 mg/l to well over 80 mg/l [16]. With the impact of climate change, the salt intrusion has been more and more severe not only in Vietnam, but also at global scale.
3.2. Effect of disinfection concentrations

According to the described experiment above, the concentration of NaOCl solution was added into the UF membrane-treated water so that the residual chlorine concentrations were in order of 0.2, 0.4, 0.6, 0.8 mg/L. In addition, the samples after sand filtration were also mixed with NaOCl solution to achieve a residual chlorine of 0.2 mg/L and sent for THMs analysis, to compare the effectiveness of UF membrane and sand filtration.

Figure 5. Effect of residual chlorine concentration on the formation of THMs (Note: UF-0.2, UF-0.4, UF-0.6, UF-0.8: UF treated water mixed with NaOCl solution to obtain residual chlorine concentration of 0.2 mg/L, 0.4 mg/L, 0.6 mg/L vs 0.8 mg/L; SF: sand filter with 0.2 mg/L residual chlorine concentration)

It can be seen in Fig. 5 the formation of THMs was influenced by the residual chlorine concentration in the water. Most concentrations of THMs increased with increasing concentration of NaOCl disinfectant such that the residual chlorine increased from 0.2 - 0.8 mg/L. According to this result, Chloroform at all concentrations of NaOCl disinfectant was low (below 200 µg/L according to Vietnam National technical regulation QCVN 01-1:2018/BYT or even strict value of 80 µg/L according to US EPA, 2012). Similarly, Bromoform at all concentrations of NaOCl disinfectant was also lower than 100 µg/L according to QCVN 01-1:2018/BYT standard (purple line). However, Bromodichloromethane and Dibromochloromethane were both found and at concentrations higher than the standard in some cases. For example, when the residual chlorine concentration was greater than 0.4 mg/L, it combined with Br\(^-\) ions in the water to form Bromodichloromethane with a concentration greater than the allowed standard (blue line). In addition, when the residual chlorine concentration was greater than 0.8 mg/L, it produced Bromodichloromethane and Dibromochloromethane with a concentration greater than the allowed standard (purple line). The impact of THMs formation on chlorine dose was discussed previously [21, 32, 33]. They found that higher chlorine dose linearly favored a higher overall THM concentration [32], in particular, the formation of brominated-trihalomethanes (Br-THMs) in chlorinated seawater depended on applied chlorine dose. Specifically, their formation
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favored by high chlorine dose, which was similar to the finding in this study. One should be noted that previous study also revealed Dibromochloromethane formed relatively more quickly and at higher concentration than Bromodichloromethane [33]. This can be noticed in Fig. 5. Dibromochloromethane formation was slightly higher than Bromodichloromethane at all chlorine doses.

It should be noted that Br\textsuperscript{−} is usually abundant in seawater with concentration from 65 mg/l to well over 80 mg/l [16]. Due to the influence of occasional salt intrusion, there was the presence of Br\textsuperscript{−} with concentration of 11.35 ± 1.62 mg/l in the testing water. In the dry season, the concentration of Br\textsuperscript{−} ions is certainly greater as salt intrusion is often more severe in the dry season [34]. As a result, it is highly recommended to treat the organic matter well before disinfecting with chlorine-containing solutions once using coastal rivers as a source of water supply.

Fig. 5 also confirmed that the application of coagulation - UF membrane was more effective than coagulation - sand filtration in limiting the formation of THMs by-products. According to Fig. 5, with the same residual chlorine concentration of 0.2 mg/L, the sample after sand filtration has a much higher concentration of THMs than the sample after UF membrane filtration. While the samples passed through the UF membrane all met the standard with a residual chlorine concentration of 0.2 mg/L, the sample after sand filtration had a concentration of Bromodichloromethane that was higher than the allowed standard (> 60 µg/L - blue line). This confirms the superiority of ultrafiltration membranes compared to conventional sand filters in controlling organic matters, a precursor of THMs.

3.3. Effect of water salinity on THMs formation

It should be noted that the assessment of effect of water salinity on THMs formation was conducted in two salinity levels: at low salinity of 0.026% ± 0.002% and high salinity of 0.148% ± 0.015%. With the same residual chlorine concentration of 0.8 mg/L, the formation of THMs is quite different (see Fig. 6).

![Figure 6. Effect of salinity on the formation of THMs substances](image)

According to Fig. 6, there was noticeably the influence of salinity on the formation of THMs. At low salinity range, Bromodichloromethane, Dibromochloromethane and Chloroform all formed at low concentrations, much lower than the allowable values in the regulation for domestic water supply (i.e., 100 µg/L). Nevertheless, at high salinity, both Bromodichloromethane and Dibromochloromethane were present higher than the standard. The result of high THMs formation at high salinity was consistent with the previous studies [33, 35, 36]. In the study of effect of bromide concentration on THMs, Chowdhury et al. [35] rendered that a threefold increase of bromide content (from 40 to 120 mg/L)
caused an increase in total THMs of 30% and about a threefold increase in Bromodichloromethane content. Total THM concentration increased from 12.64 \( \mu g/L \) to 105.34 \( \mu g/L \) after 24 hours and to 115.8 \( \mu g/L \) after 48 hours when salinity increased from 0% to 3% for artificial water. Meanwhile, total THM increased to 119.2 \( \mu g/L \) and 126.4 \( \mu g/L \) after 24 hours and 48 hours, when salinity increased from 0% to 3% for real source water [19]. Additionally, in the presence of bromides, brominated THMs are formed preferentially, and chloroform concentrations decrease proportionally [36]. The reason was explained via the reaction of hypochlorous acid (HOCl) and \( Br^- \) in the water [37]:

\[
\text{NaOCl} + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{NaOH} \tag{1}
\]

\[
\text{HOCl} + \text{Br}^- \rightleftharpoons \text{HOBr} + \text{Cl}^- \tag{2}
\]

The conversion from HOCl to HOBr, when there is the presence of \( Br^- \), is very fast. Due to the predominance of HOBr, the reaction of HOBr with organic matters shall form mostly brominated THMs such as Bromodichloromethane and Dibromochloromethane [36, 38].

4. Conclusions

This paper evaluated the THMs formation during the treatment of surface water at pilot scale in a coastal area of Vietnam, using different coastal disinfection dose and at different salinity levels. The initial results revealed that Chloroform and Bromoform at concentrations were all met the standard for domestic water supply, however, Bromodichloromethane and Dibromochloromethane complexes were all found at concentrations higher than the accepted values when the residual chlorine concentration was greater than 0.4 and 0.8 mg/L, respectively. In addition, the higher salinity, the higher values of THMs were obtained. With the impact of salt intrusion, the presence of \( Br^- \) was more available in the river which increased the chances of forming brominated THMs compounds. As a result, it is recommended to control completely organic matters in the treated water before using chlorine for disinfection when using surface water in coastal areas as the water supply source. Since ultrafiltration (UF) membrane was better than sand filter in control of some THMs compounds in the effluent, it is very promising of using UF in replacement of sand filter for safer water use.

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References


