

## Removal effect of trihalomethanes (THMs) and halogenated acetic acids (HAAs) precursors in reclaimed water by polyaluminum chloride (PACl) coagulation

Juncheng Wang<sup>a</sup>, Wen Yue<sup>a</sup>, Zhenghao Wang<sup>b</sup>, Yu Bai<sup>c</sup> and Jina Song<sup>a,\*</sup>

<sup>a</sup> College of Energy and Environmental Engineering, Hebei University of Engineering, No. 19 Taiji Road, Handan City, Hebei Province 056038, China

<sup>b</sup> College of Environment, Hohai University, Nanjing City, Jiangsu Province 210024, China

<sup>c</sup> Handan Municipal Engineering Company, Handan City, Hebei Province 056001, China

\*Corresponding author. E-mail: songjina@126.com

### ABSTRACT

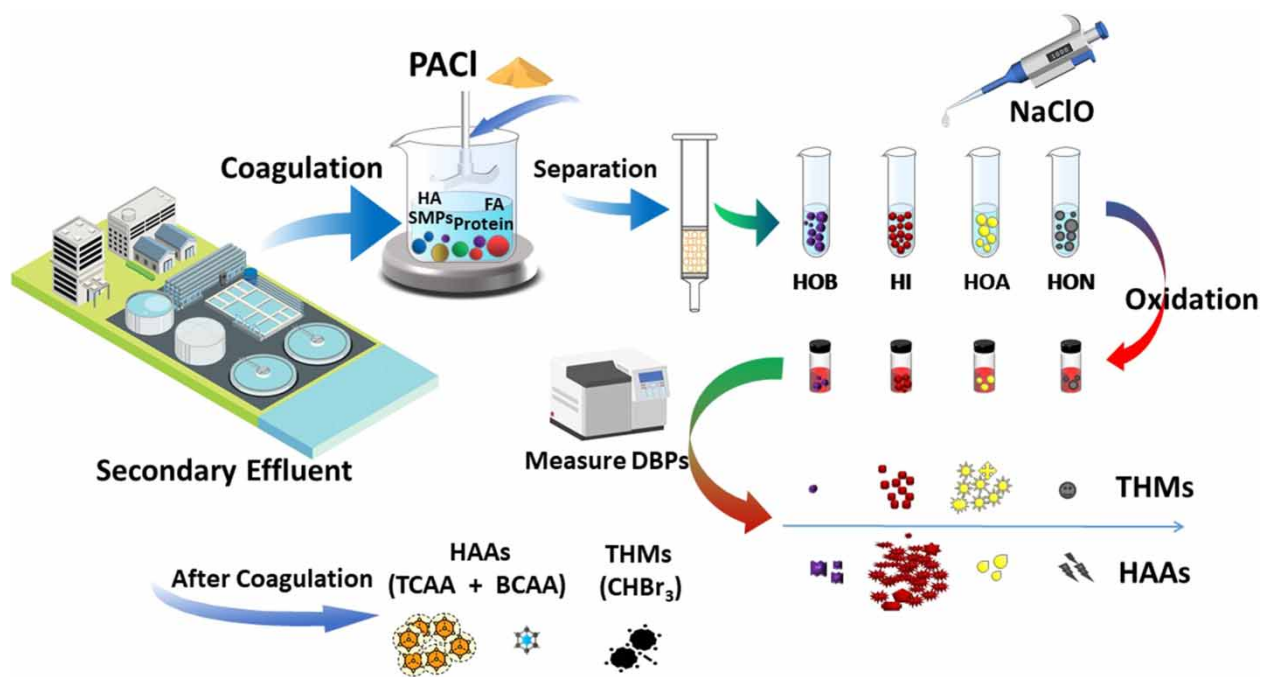
This study analyzed the removal effect of various doses of polyaluminum chloride (PACl) on wastewater treatment plants at pH 7. The sewage plant's secondary effluent organic matter (EfOM) separates into four components: hydrophobic base (HOB), hydrophilic (HI), hydrophobic acid (HOA), and hydrophobic neutral (HON). The removal effect for various forms of organic waste is optimum at 16 mg/L and that halogenated acetic acids (HAAs) and trihalomethanes (THMs) are formed simultaneously. After PACl treatment, hydrophobic organic compounds were converted to humic acid (HA), fulvic acid (FA), soluble microbial products (SMPs), and other HI organic compounds, increasing the amount of HAAs produced by HI fractions. Removal rate of hydrophobic organic compounds, particularly HON, is 92.8% when using PAC. Moreover, after EfOM coagulation, most HAAs are trichloroacetic acid (TCAA), followed by bromochloroacetic acid (BCAA) and bromodichloroacetic acid (BDCAA). Only HOB can produce monochloroacetic acid (MCAA), whereas HA and SMPs with HOA are primary components of dichloroacetic acid (DCAA). The toughest removable byproduct of THMs is  $\text{CHBr}_3$ , and after condensation of each THM component, only HOA and HON produce  $\text{CHBr}_3$ , while HI produces only a minimal quantity of  $\text{CHBrCl}_2$  and  $\text{CHCl}_3$ . This finding is critical for understanding how disinfection byproducts are produced after chlorinating EfOM.

**Key words:** coagulation, component separation, disinfection byproducts, effluent organic matter, polyaluminum chloride

### HIGHLIGHTS

- Industrial grade PAC for coagulation.
- Secondary effluent dissolved organic components are separated (HOB, HI, HOA, HON).
- DOC, EEM, SFS analysis of coagulation effects.
- Five-day disinfection byproduct generation amount (HAAs and THMs).
- Each element correlates to the by-coagulation product's removal impact.

## GRAPHICAL ABSTRACT



## 1. INTRODUCTION

The conflict between the lack of water resources and the deterioration of the water environment has gotten worse once more with the improvement of water quality and quantity needed for urban and industrial production, and the search for unconventional water sources is still one of the key ways to resolve this conflict (Wang *et al.* 2016). As a sewage plant, which is an 'Essential Device' for the smooth functioning of the city, the enhanced treatment of secondary effluent might temporarily ease the shortage of available water resources to some extent, and it is produced daily in a sizable amount, and the quality is generally steady (Krzeminski *et al.* 2019). One of the most efficient ways to address the issue of water resources is to choose advanced treatment of secondary effluent as reuse water (Chhipi-Shrestha *et al.* 2019). As the so-called good water does not ask the source, the wise use of reclaimed water is significant to society (Haldar *et al.* 2022). The advanced direct treatment of secondary effluent in a sewage plant has a much higher water resources reuse efficiency than discharging secondary effluent into a natural water body for natural degradation and then advanced treatment (Lyu *et al.* 2016). It can avoid secondary pollution of water sources in natural water bodies (Numberger *et al.* 2022). However, the difficulty of the water treatment process in such an operation will be somewhat challenging (Oscar *et al.* 2017).

However, disinfection of secondary effluent organic matter (EfOM) may produce large amounts of disinfection byproducts (DBPs) and cancer cells, with trihalomethanes (THMs) and halogenated acetic acid (HAAs) serving as the main DBPs (Hong *et al.* 2013a). THMs and HAAs are significant DBPs toxic to humans due to their cytotoxicity, mutagenicity, teratogenicity, and carcinogenicity (Srivastav *et al.* 2020). As a result, countries around the world have enacted relevant laws and regulations to protect human health, and conducted many experimental studies on how to control and mitigate their harm to the human body (Padhi *et al.* 2019). HAAs include monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), and chlorodibromoacetic acid (CDBAA) (Mompremier *et al.* 2019). Zhang *et al.* (2013) realized that  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBr}_3$  were the main chlorination byproducts in reclaimed water, accounting for roughly 80% of total THMs. Tubić *et al.* (2013) noticed that the hydrophilic material structure contributed more to the formation of THMs; the humic acid structure is closely related to the formation of HAAs.

Due to the obvious significant harm caused by DBPs, researchers (Zheng *et al.* 2015) began investigating methods to reduce DBPs. Many people (Sillanpää *et al.* 2018) prefer to use coagulation disinfection byproduct precursors as much as possible before disinfection to remove DBPs. As one of the advanced wastewater treatment processes, the coagulation process has

numerous advantages (Dotto *et al.* 2019), including a broad application range, sufficient experience, high economy, and a low transformation cost of the water plant on an original basis. Lin's (Lin & Ika 2020) study revealed that PAC destabilizes the carbon disinfection byproduct (C-DBP) precursor, resulting in lower C-DBP production and better removal. Zhao *et al.* (2013) discovered that the hydrophilic component increases after coagulation, and the physicochemical properties change. The main precursors of HAAs are hydrophobic neutral substances, but the majority of organic matter is hydrophobic acidic substances. The scientists (Dayarathne *et al.* 2020) found that PAC polymer hydrolysate has a higher positive charge than monomer hydrolysate, and the high charge density is likely to interact with the negative charge to change the NOM, enabling the NOM to be removed very efficiently.

While many researchers study the formation of DBP utilizing lake water, rivers, and laboratory-made water sources, secondary effluents from sewage plants are rarely used as research objects. Investigate the degree of removal of various kinds of EfOM in sewage facilities' secondary effluent and their potential to create byproducts. To investigate the causes of the formation of HAAs and THMs in the sewage plant's secondary effluent after chlorination, the EfOM was separated based on its hydrophilic qualities into four components by large pore-size adsorption resin (Wang *et al.* 2013), namely hydrophobic base (HOB), hydrophilic (HI), hydrophobic acid (HOA), and hydrophobic neutral (HON). The removal of each component and the formation of DBPs before and after coagulation were explored using the common coagulant PAC. Determination of unsaturated content and proportion of each component of organic matter by dissolved organic carbon (DOC) and the molecular weight (MW) were determined by liquid chromatography size exclusion chromatography (LC SEC), the excitation–emission matrix (EEM) and synchronous fluorescence spectrum (SFS) were determined to determine the type of organic matter in EfOM; gas chromatography (GC) was used to determine the amount and potential of THMs and HAAs formation after chlorination for 5 days. The relationship between the physicochemical parameters of each EfOM component and the creation of HAAs was investigated, as well as the selection of relevant water treatment materials and methods for further treatment. The findings are critical for further research on PAC coagulation's elimination of EfOM disinfection byproduct precursors.

## 2. EXPERIMENTAL METHOD AND ANALYSIS

### 2.1. Experimental procedure

#### 2.1.1. Experimental water samples

The water sample was taken from the secondary effluent of a three-tank oxidation ditch process at Handan City's sewage treatment plant. After passing through a 0.45 µm filter membrane, the water samples were stored at 5 °C in the dark.

#### 2.1.2. Coagulation conditions

Use PAC (industrial grade, with an Al content of around 26%), 1 g dissolved in 100 ml of high-purity water, and a beaker to hold 500 ml of the water sample. The concentration measured by re-titration is approximately 1 mg/L. Under a pH of 7, coagulation was performed using a gradient of 12, 14, 16, 18, 20, and 22 mg/L, coagulation by six blenders, quick stirring for 1 min at a speed of 200 rpm/min, slow stirring for 30 min at a speed of 20 rpm/min, and precipitation for 60 min.

#### 2.1.3. EfOM resin adsorption separation

Before separating the organic matter, the resin is activated with methanol; after the activation is complete, the values are cleaned with pure water. When the effluent is neutral after elution, carry out the following steps: (1) The chromatography column with an inner diameter of 2 cm was filled to a height of around 10 cm with XAD-8 resin, and the water sample was raised to a height of about 30 cm to bring down the outflow liquid, and 500 ml of water was sampled and filtered through a 0.45 µm cellulose acetate membrane. Wash the resin column with a 500 ml solution of HCl (0.1 mol/L). The effluent is HOB, and the resin adsorbs HON components. (2) After the effluent passing through the resin column is adjusted to an acidic pH = 2 with concentrated HCl, the effluent is passed through the chromatography column, and the effluent is HI, and the resin adsorbs HOA components at the same time. (3) Elute the resin column with 0.1 mol/L NaOH, and the effluent is HOA. (4) Methanol was used to perform a Soxhlet extraction on a resin column for 24 h. Methanol dissolved in HON was then placed in a beaker, fully volatilized at 50 °C, and then dissolved with 500 ml of pure water to obtain HON. After completing all steps, the four component solutions are adjusted to pH 7 and stored for later use.

#### 2.1.4. Dosage of sodium hypochlorite

As a chlorine oxidant, sodium hypochlorite was utilized, with a density of 1.17 g/cm<sup>3</sup> and an effective rate of roughly 10%. Since each elution solution had a varied effect on the pH of each component organic solution after separation, the pH of each component solution was adjusted to pH 7 by adding a tiny quantity of sodium acetate solution (0.1 mol/L).

The chlorine concentration in the water sample should be guaranteed to be 0.05 mg/L; DBPs formation formulas were tested by gradient chlorination. The results show that when the dosage of 200 ml of a water sample is 80 µl, the total yield of THMs and HAAs does not increase, so the optimal dose for 5 days to form potential is 80 µl.

#### 2.1.5. Determination of THMs production

The extraction of disinfection byproducts is carried out by referring to relevant standard methods (Wang *et al.* 2013). The headspace bottle was filled with 3 g of NaCl (GR) and 10 ml of the water sample to be examined. The sample was quickly sealed with the headspace bottle top, shaken vigorously, and dissolved the sodium chloride. For 20 min, the sample was immersed in a 50 °C water bath. After heating, the gas in the upper section of the container can be removed for determination using the injection needle.

Only seven HAAs were investigated in the experiment since the experimental study discovered that two HAAs (CDBAA and TBAA) are also formed in pure water. The detection limit is 2 µg/L, and the recovery percentage of substitutes spiked in the sample range is 91.2–100%.

The used headspace bottles and injection bottles are first soaked in potassium dichromate for 24 h before being washed three times with deionized water under ultrasonic conditions, cleaned once with methanol, dried, and reused, and the headspace bottle caps are single-use.

#### 2.1.6. Determination of HAAs production

After 5 days, add 1 ml sodium thiosulfate to terminate the reaction; the water sample (40 ml) was placed in a separating funnel, added with 2 ml sulfuric acid, then quickly added with 8 g sodium chloride to dissolve until no white particles, added 6 ml methyl tertiary-butyl ether (MTBE), extracted for 3 min, stood for 3 min; collect the lower water phase. 3.0 ml of the extract was accurately transferred to a 15 ml colorimetric tube, 30 µl of HAAs standard solution was added, and 3 ml of the locally prepared sulfuric acid-methanol solution was added for mixing (MEP Standard No. HJ 758-201, 2015).

The colorimetric tube was removed from the 50 °C hot water bath where it had been derivatized for 120 min, allowed to cool to room temperature, then filled with 7 ml of sodium chloride solution. The cap was then tightened, and the container was shaken vigorously before the lower aqueous phase was extracted with a 10 ml scale pipette. One milliliter of saturated sodium bicarbonate solution should be added gradually. The bottle cap should then be tightened to prevent leaks. The 1.0 ml upper extract was transferred to a 2 ml brown injection container to determine the results.

### 2.2. Experimental examination

#### 2.2.1. Determination of DOC, EEM, and SFS

The amount of dissolved organic matter in water samples is represented by DOC, and its TOC (DOC) value is determined by combustion. The TOC-L total organic carbon analyzer produced by Shimadzu (Japan) was used for determination. Excitation–emission matrix (EEM) and synchronous fluorescence spectrum (SFS) were analyzed by a fluorescence spectrometer (Hitachi F7100, Japan). The relative molecular weight was determined by the volume exclusion method. High-performance liquid chromatography (HPLC-2030, Shimadzu, Japan) was used. The absorbance at 254 nm is commonly used to calculate HA content (Korshin *et al.* 2009), and HA is a crucial component of DOC (Siddique *et al.* 2022). Moreover, the absorbance at 220 nm is related to carboxylic acids and aromatic groups that are prone to substitution reactions to form chlorination byproducts, which is related to the ability of the substance to produce DBPs (Korshin *et al.* 2009). The chromatographic column was Zenix SEC-100, and the detection wavelength was 220 and 254 nm.

#### 2.2.2. Determination of THMs and HAAs

The correlation coefficient ( $R^2$ ) of the standard curve of CDBAA and TBAA was less than 0.6. Only seven HAAs were reported in the experiment since subsequent research revealed that related byproducts could also be recovered from pure water. Analysis was performed using a gas chromatograph (Agilent6890N, USA). The injection conditions of THMs were as follows: gasification chamber temperature: 220 °C; heating program: initial temperature 40 °C for 5 min, at 8 °C/min to 100 °C, and then at 6 °C/min to 200 °C for 1 min; detector temperature: 320 °C; carrier gas: nitrogen; carrier gas flow rate:

1.0 ml/min, tail gas flow rate: 30 ml/min; split ratio: 20:1; injection volume: 50.0  $\mu$ l. HAAs compounds were analyzed and determined on a quartz capillary column with a length of 30 m, an inner diameter of 0.32 mm, a film thickness of 0.25  $\mu$ m, and a stationary phase of 5% phenyl/95% dimethyl polysiloxane (MEP Standard No. HJ 620-2011, 2011). The remaining parameters were set according to MEP Standard No. HJ 758-2015 (2015).

### 3. RESULTS AND DISCUSSION

#### 3.1. Dissolved organic carbon

Figure 1 displays the removal rate of HOB, HOA, and HON of the three components of PAC for EfOM showed a trend of increasing first and then decreasing with the increase of the amount of input, among which the removal rate of DOC reached a maximum of 64.2% when HOB was a dose of 14 mg/L, and the removal rate of HOA and HON reached the highest removal rate of 33.68 and 92.8% when a dose of 16 mg/L, respectively; Nearly, all components are proportionately eliminated by sweep coagulation at pH7 (Jin *et al.* 2018a). PAC has a weak removal impact on the HI component owing to its hydrophilicity; the highest removal rate is 5%. The removal effect of the HI component is the poorest when the removal rates of HOB, HI, and HOA are at their highest; on the whole, a dose of 16 mg/L is the optimal dosage. Han's study (Han *et al.* 2015) came to a similar conclusion, with HI components increasing after coagulation treatment.

PAC is a pre-hydrolyzed form of  $AlCl_3$  that is intermediate between  $Al^{3+}$  and  $Al(OH)_2$ . Aluminum hydroxide can be formed when only a small amount of alkalinity is consumed in the water sample, and organic pollutants in the water can be removed using net capture-scanning. The removal effect of PAC on each component demonstrates that polyaluminum has a good removal effect on hydrophobic substances but a poor removal effect on hydrophilic substances. Organic matter's carboxyl and aliphatic hydroxyl groups will participate in the formation of amorphous  $Al(OH)_3$ , and the removal of DOC will be accomplished through complexation (Jin *et al.* 2018b).

Figure 2 shows the statistical diagram of the proportion of each component after PAC coagulation. It is evident that as the PAC dosage increases, the HI component grows initially before decreasing and peaking at a level of 16 mg/L, accounting for 58%.

In line with this, the proportion of the remaining three components, HOB, HOA, and HON, which account for 5, 39, and 2%, respectively, practically achieves the lowest value at the same moment. Coagulation could indeed easily eliminate hydrophobic DOM components (Zhou *et al.* 2020). Accordingly, when PAC is added to water, the intricacy of the reaction transforms hydrophobic compounds into hydrophilic compounds (Hong *et al.* 2013b). According to Liu's simulation of the model (Liu *et al.* 2009), the molecular weight dropped following coagulation plus disinfectant oxidation, yet a significant amount of hydrophobic chemicals were changed into hydrophilic ones. Small molecular organic matter was present in higher concentrations as a result of the secondary oxidation of hydroxyl groups and the oxidation of disinfectants. This behavior is in line with the DOC elimination effect mentioned above.

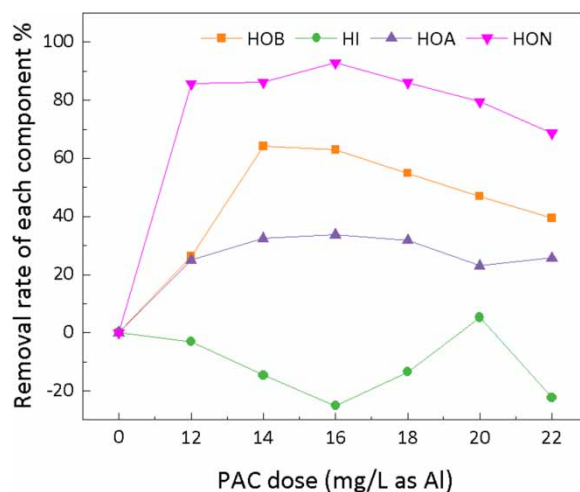
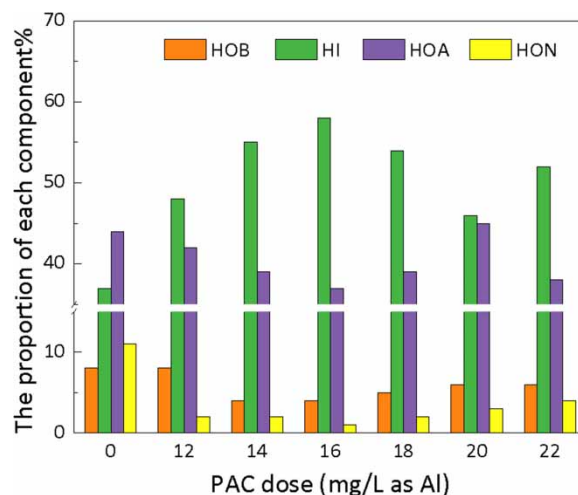


Figure 1 | DOC removal rate of EfOM components after coagulation with different dosages of PAC.



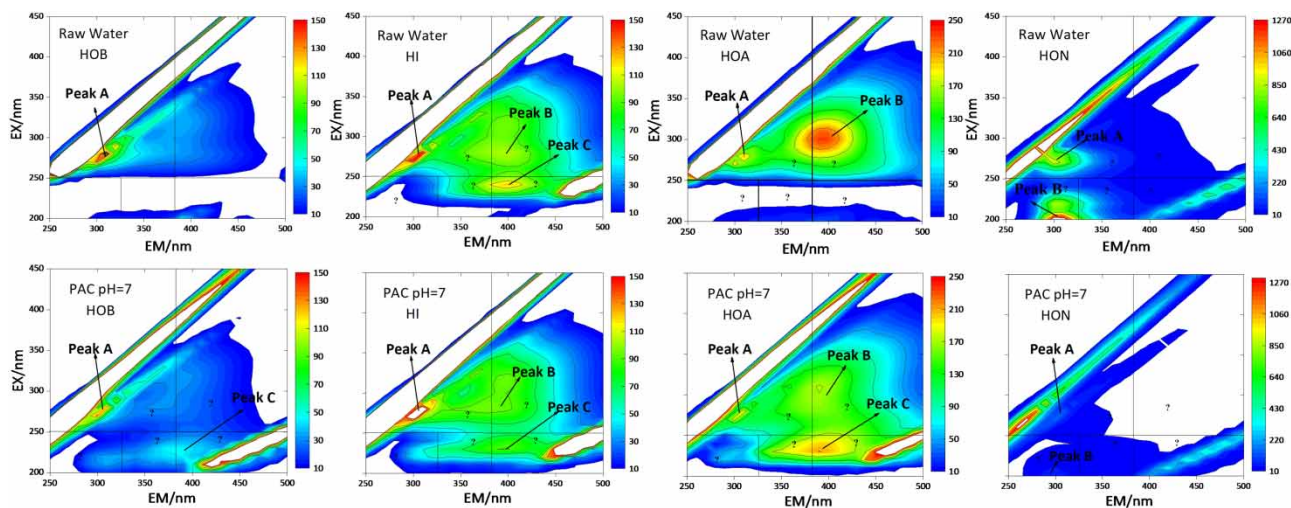
**Figure 2** | The proportion of EfOM components after coagulation with different dosages of PAC.

### 3.2. Excitation–emission matrix

The Fuzzy Rule Interpolation (FRI) method (Yu *et al.* 2019) divides EfOM into five regions which correspond to several categories of substances. It employs different chemicals to emit different fluorescence in particular locations to determine the category of organic matter. The specific substance classes and excitation and emission wavelengths are aromatic protein I (Ex/Em 200–250 nm, 250–330 nm), aromatic protein II (Ex/Em 200–250 nm, 330–380 nm), FA (Ex/Em 200–250 nm, 380–550 nm), SMPs (Ex/Em 250–330 nm, 280–380 nm), and HA (Ex/Em 250–400 nm, 380–550 nm). To make clarify the discussion, use the abbreviation of the four components in conjunction with the marked peaks in the EEM (e.g., peak HOB-A).

The EEM is shown in Figure 3 before and after coagulation using the recommended dosage of PAC (16 mg/L). The representative substances of each EfOM component differ. As a result, this affects the degree of the corresponding fluorescence response. HON has a substantially higher display level than the other three. The representative HON compounds, SMPs (HON-A) and aromatic protein I (HON-B), have a greatly diminished and essentially eliminated fluorescence response degree after coagulation.

PAC has a weak removal effect on SMPs (HON-A), the representative substance of the HOB component; The display level of SMPs (HI-A) in HI components after coagulation was higher, indicating that SMPs carried more fluorescent groups than



**Figure 3** | EEM of EfOM components after coagulation with different dosages of PAC.

before coagulation, whereas HA (HI-B) and FA (HI-C) had almost no removal effect, similar to the DOC coagulation change of HI components mentioned above. Ma's study (Ma *et al.* 2014) results were similar, with the hydrophilic component consisting of FA, SMPs, and HA, with FA making up a higher percentage than the other two. The removal effect of the representative substance SMPs (HOA-A) in the HOA component was obvious, and the removal effect of HA (HOA-B) was almost non-existent, but the response peak of FA (HOA-C) appeared.

### 3.3. Synchronous fluorescence spectrum

SFS is classified into three groups based on where the distinctive peak is located (Xiong *et al.* 2021; Figure 4). The wavelength ranges from 250 to 300 nm for fluorescent proteins, 300 to 380 nm for fluorescent fulvic acid (FA), and 380 to 550 nm for fluorescent humic acid (HA) (Wei *et al.* 2014).

Protein-like fluorescent substances in region I and FA fluorescent substances in region II were among the four components of EfOM. The HON component has a much higher fluorescence response than the other three components, but after PAC coagulation, the fluorescence response is greatly reduced, and the removal effect is obvious. After PAC coagulation, the protein-like fluorescent substances and FA fluorescent substances in HOB, HI, and HOA have almost no removal effect, and the response degree of protein-like and FA fluorescent substances in HOA components has increased slightly.

### 3.4. Molecular weight

The absorbance at 254 nm is commonly used to calculate HA content, and HA is a key component of DOC. We are measuring the molecular weight before and after coagulation is extremely useful for detecting disinfection byproduct precursors.

Figure 5 reveals that the majority of HOB's molecules have a molecular weight between  $5 \times 10^3$ – $1 \times 10^4$  kDa and  $5 \times 10^4$ – $1 \times 10^5$  kDa. HI, HOA, and HON components have mostly molecular weights between  $1 \times 10^3$  and  $1 \times 10^4$  kDa. Additionally, there are only a few molecules between 100 and 200 kDa in size. The medium molecular weight HA of the HOB and HOA components is still present in some amount after the net capture-scrolling effect of PAC. It is important to note that the medium molecular weight substances are essentially removed by PAC, which has a better removal impact on HOA components; Similar results were reported in Lin's investigation (Lin & Ika 2020), which determined that PAC performed admirably in the removal of hydrophobic and hydrophilic organic materials with a molecular weight of roughly 1 kDa. The HI component's medium molecular weight HA molecules were still present, but the big and small molecular weight HA chemicals had been eliminated. The HON component's medium molecular weight HA was eliminated.

### 3.5. Generation potential and amount of THMs and HAAs

#### 3.5.1. Trihalomethanes

Figure 6 illustrates that the four components of the EfOM produce the greatest variety of THMs, with the HI component producing the greatest quantity of THMs. According to the synthesis volume, HI forms four different types of THMs:  $\text{CHBrCl}_2$ ,  $\text{CHBr}_3$ ,  $\text{CHBr}_2\text{Cl}$ , and  $\text{CHCl}_3$ . According to the peak of EEM, the SMPs of the HI component increased, which could explain

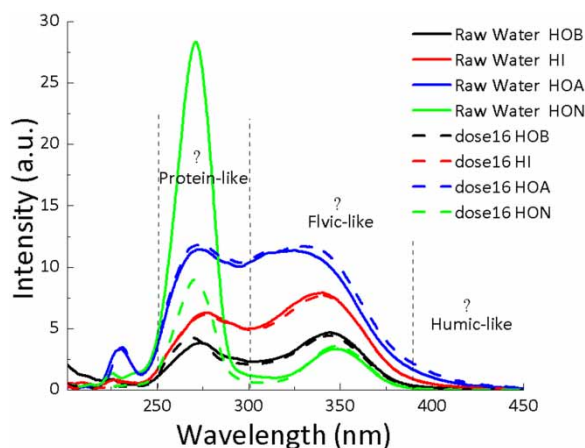
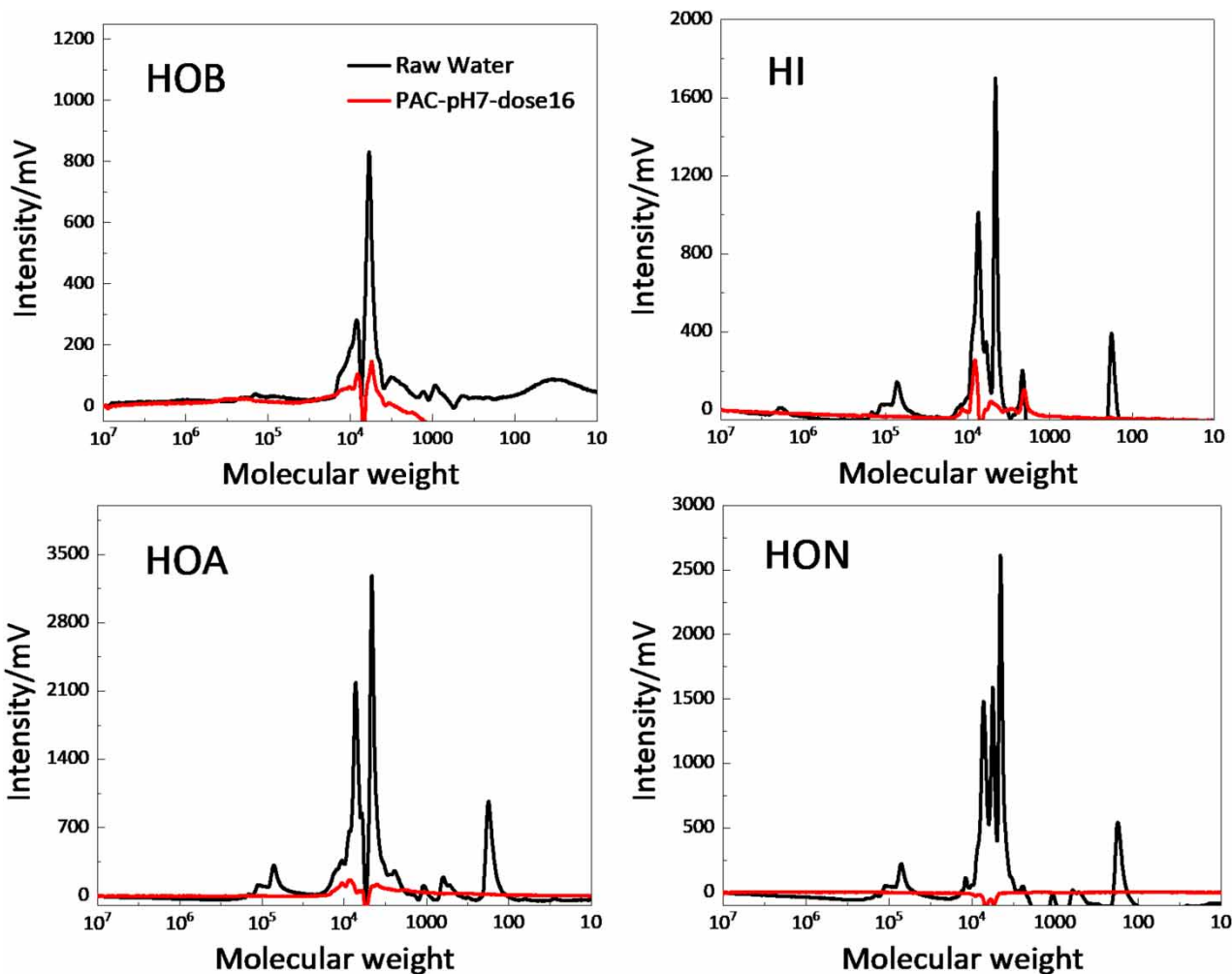


Figure 4 | SFS changes of EfOM components after coagulation with the best dosage of PAC.



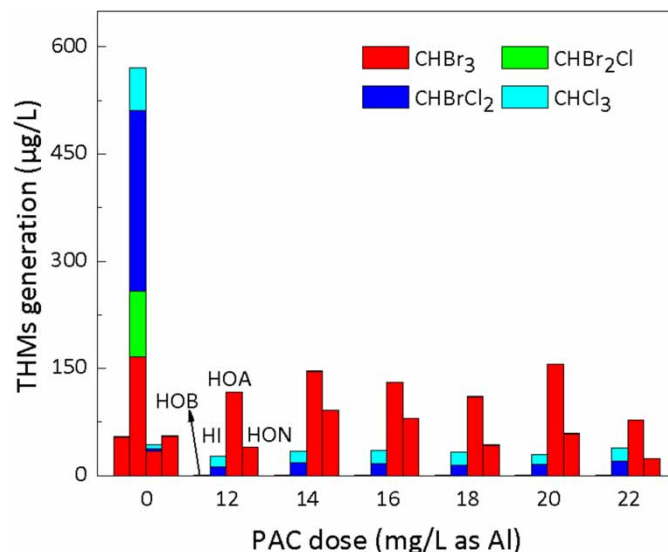
**Figure 5** | MW changes of EfOM components after coagulation with the best dosage of PAC.

why  $\text{CHBr}_3$  was removed entirely while  $\text{CHBr}_2\text{Cl}$  and  $\text{CHCl}_3$  still had partial residues. According to the peak intensities of SFS and MW, the removal effect of PAC coagulation on the small molecular weight FA of HOA and HON components is negligible, and the residual FA still produces some  $\text{CHBr}_3$ . As a result, the primary precursor of  $\text{CHBr}_3$  is hydrophobic acidic and neutral small molecule FA.

The only product of the HOB and HON components is  $\text{CHBr}_3$ , and the DOC removal rates of HOB and HON after PAC coagulation are as high as 64.2 and 92.8%, respectively, consistent with Ramavandi's finding (Ramavandi *et al.* 2015) that DOC and water temperature have the greatest impact on total THM formation potential in river water. Besides that, he discovered that chloroform concentration increased as bromide ion concentration increased. HOB did not produce  $\text{CHBr}_3$  after coagulation, whereas HON did, and there was no significant correlation with PAC dosage. HOA generated tiny amounts of  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHCl}_3$ , and  $\text{CHBr}_3$ . Hong *et al.* (2013b) found that hydrophobic acidic substances were the main precursors of  $\text{CHCl}_3$ . Following the PAC reaction,  $\text{CHBr}_2\text{Cl}$  and  $\text{CHCl}_3$  production almost completely stopped, whereas  $\text{CHBr}_3$  production greatly increased. It may be assumed that the reaction of HA and chlorine produce  $\text{CHBr}_2\text{Cl}$  and  $\text{CHCl}_3$  and that the rise in  $\text{CHBr}_3$  creation was caused by the significant quantity of FA generation when combined with the alterations of the preceding EEM characteristic peaks.

PAC coagulation has not been effective in removing small molecule organic matter and hydrophilic substances, and the residual difficult-to-remove substances are the primary precursors of disinfection byproducts. Additionally, EfOM tends to



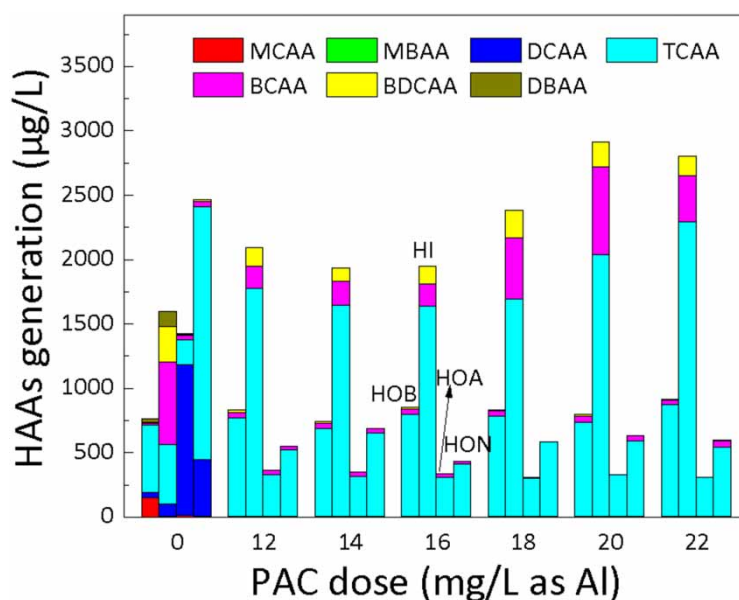


**Figure 6** | THMs production of EfOM components after coagulation with different dosages of PAC.

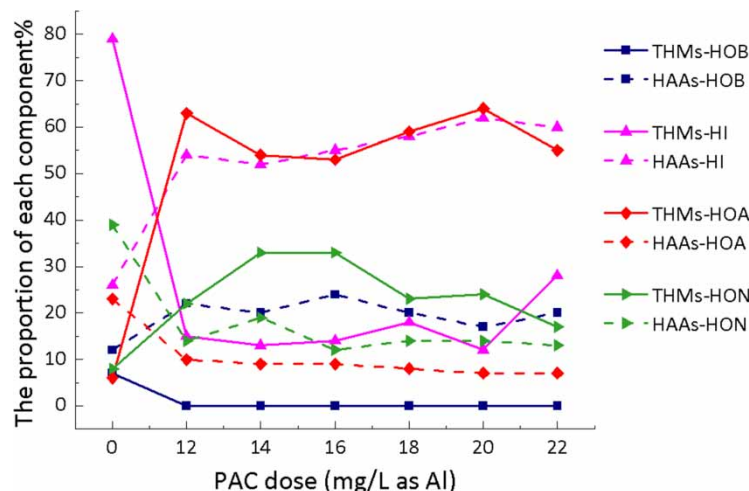
carry more functional groups that can be readily substituted during coagulation, which raises the probability that EfOM will bind to bromide ions and create bromide.

### 3.5.2. Halogenated acetic acids

Figure 7 reveals that before EfOM was treated without PAC, all four components produced DCAA, with the HOA component producing the most, followed by the HON, HI, and HOB components. The major constituents of HAA are TCAA, DCAA, and BDCAA, and the study's findings are consistent with Zhao's experimental findings (Zhao *et al.* 2013). However, after coagulation, DCAA generation almost completely stopped, independent of the dosage of PAC. It is important to note that only the HOB component produces MCAA, and only the HI component produces BDCAA. However, MCAA is no



**Figure 7** | The amount of HAAs produced by EfOM components after coagulation with different dosages of PAC.



**Figure 8** | EfOM fractions' THM and HAA production curves about PAC dosage.

longer formed after coagulation, whereas BDCAA is still present. DBAA is a typical byproduct of HOB and HI components, although it can be eliminated by PAC coagulation.

It is evident that HAAs primarily generate TCAAs as a byproduct, and Zhao's research (Zhao *et al.* 2013) reveals that HONs constitute 62% of the total formation of HAAs before PAC treatment. The predominant byproduct of the HI component changed from BCAA to TCAA with the addition of PAC. The trend in the production of TCAA and PAC doses was initially a quick increase, followed by a period of stability and a gradual rise. The four components formed by PAC coagulation had a less-than-perfect removal efficiency of TCAA, and the components HOB, HI, and HOA even exhibited an increasing tendency after coagulation. The main components of HAA, according to Liu's research (Liu *et al.* 2016), are DCAA and TCAA, and aluminum salts have the lowest total amount of HAAs when the coagulation conditions are close to neutral, as in the experimental conclusion part. The hydrophobic components have more phenolic hydroxyl groups and conjugated double bonds, which react with chlorine to form DBP, particularly TCAA; the relative hydrophilic components may have more amino, carboxy, and alkyl hydroxyl groups and have a high potential for forming DCAA and Br-DBP during chlorination (Li *et al.* 2014).

The fluctuation curve of the proportion of each HAA and THM component in the overall amount with an increase in PAC dosage is shown in Figure 8. The overall number of HAAs and the change in DOC had a clear correlation. The lowest DOC value and the lowest levels of total HAAs and THMs generation were achieved when the dosage of PAC was 16 mg/L.

THMs can be eliminated with the addition of PAC, although HAAs exhibited an increased tendency. When the dosage was higher than 16 mg/L, the HAAs generation of the HOB component stayed largely constant. The proportion of THMs produced by HI components to the total generation continued to decline with an increase in PAC dosage, but HAAs exhibited the reverse trend. With a rise in PAC dosage, the percentage of HAAs produced by HOA components to the total production rose. In contrast, THMs showed the reverse trend and remained mostly consistent, making up roughly 7% of the production. About 14% of the HAAs generated by HON components stabilized. Overall, the quantity of DBPs produced can be significantly decreased by using PAC for coagulation, and chlorination disinfection will yield the greatest byproducts but has very low toxicity (Duan *et al.* 2020).

#### 4. CONCLUSION

- (1) The maximum removal rate for several categories was attained at 16 mg/L of PAC, and hydrophobic material removal was effective. As much as 92.8% of the hydrophobic neutral organic matter was removed, 64.2% of the hydrophobic alkalinity was removed, and 33.6% of the hydrophobic acid was removed. The proportion of each component in organic matter showed that many hydrophobic neutral compounds were changed into hydrophilic substances because the removal rate of hydrophilic substances was negative.

(2) EEM, SFS, and MW revealed that the majority of the organic matter in EfOM was medium molecular weight organic matter  $5 \times 10^3$ – $1 \times 10^4$  kDa, with a slight amount of small molecular weight organic matter in HI, HOA, and HON. Since the environmental diversity of SMPs, each component displayed fluorescence characteristic peaks, but the HON component contained significantly more than the other three.

The SMPs observed in HOB, and HI components were largely removed after PAC coagulation, while HOA had almost no effect. In addition to SMPs, HI has many HA, FA, and HA in the HOA section that are difficult to remove. When the fluorescence map and molecular weight are combined, it is clear that HA has been completely removed, but FA will be produced after coagulation, implying that PAC converts HA with a medium molecular weight of  $5 \times 10^3$ – $1 \times 10^4$  kDa into some small molecular weight FA; SFS shows that PAC has a poor removal effect on protein fluorescent substances and FA, but a significant removal effect on hydrophobic neutral protein substances (SMPs).

(3) The four EfOM components all produce  $\text{CHBr}_3$ , but the difference is that HOB and HI can be completely removed after PAC coagulation treatment, whereas HOA and HON have little removal effect. Even if FA appears, chlorination will increase the production of HOA components; after chlorination of the four components, various HAA byproducts are produced. Four components can produce DCAA, but HA in the HOA component produces the most DCAA after chlorination.

However, after the coagulation of PACl, most kinds of byproducts are effectively removed. Moreover, some residual DBPs are still very harmful to the human body and difficult to remove. Most of the THMs and HAAs are removed, and only two more harmful, difficult-to-remove DBPs remain in HAA, with TCAA accounting for the vast majority and BCAA and BDCAA accounting for only a tiny part. When the optimal dosage is 16 mg/L, the total amount of HAAs is the least, and the HI component still contains a variety of HAAs after coagulation, accounting for 55% of the total, with TCAA accounting for 84%. THMs only produce  $\text{CHBr}_3$ , a problematic disinfection byproduct to remove.

## ACKNOWLEDGEMENTS

The research was financially supported by the National Natural Science Foundation of China (51908177), the Natural Science Foundation of Hebei Province (E2021402015), and the Science and Technology Research Project of Higher Education Institutions of Hebei Province (ZD2021022).

## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## CONFLICT OF INTEREST

The authors declare there is no conflict.

## REFERENCES

- Chhipi-Shrestha, G., Rodriguez, M. & Sadiq, R. 2019 Selection of sustainable municipal water reuse applications by multi-stakeholders using game theory. *Science of The Total Environment* **650** (2), 2512–2526.
- Dayarathne, H. N. P., Angove, M. J., Aryal, R., Abuel-Naga, H. & Mainali, B. 2020 Removal of natural organic matter from source water: review on coagulants, dual coagulation, alternative coagulants, and mechanisms. *Journal of Water Process Engineering* **40**, 101820.
- Dotto, J., Fagundes-Klen, M. R. & Veit, M. T. 2019 Performance of different coagulants in the coagulation/flocculation process of textile wastewater. *Journal of Cleaner Production* **208**, 656–665.
- Duan, X., Liao, X., Chen, J., Xie, S., Qi, H., Li, F. & Yuan, B. 2020 THMs, HAAs and NAs production from culturable microorganisms in pipeline network by ozonation, chlorination, chloramination, and joint disinfection strategies. *Science of The Total Environment* **744**, 140833.
- Haldar, K., Katarzyna, K. R. & Tapos, K. A. 2022 Urban water as an alternative freshwater resource for matching irrigation demand in the Bengal delta. *Science of The Total Environment* **835**, 155475.
- Han, Q., Yan, H., Zhang, F., Xue, N., Wang, Y., Chu, Y. & Gao, B. 2015 Trihalomethanes (THMs) precursor fractions removal by coagulation and adsorption for bio-treated municipal wastewater: molecular weight, hydrophobicity/hydrophilicity and fluorescence. *Journal of Hazardous Materials* **297**, 119–126.
- Hong, H., Xiong, Y. & Ruan, M. 2013a Factors affecting THMs, HAAs and HNMs formation of Jin Lan Reservoir water exposed to chlorine and monochloramine. *Science of The Total Environment* **444**, 196–204.

- Hong, H. C., Huang, F. Q., Wang, F. Y., Ding, L. X., Lin, H. J. & Liang, Y. 2013b Properties of sediment NOM collected from a drinking water reservoir in South China, and its association with THMs and HAAs formation. *Journal of Hydrology* **476**, 274–279.
- Jin, P., Song, J., Yang, L., Jin, X. & Wang, X. C. 2018a Selective binding behavior of humic acid removal by aluminum coagulation. *Environmental Pollution* **233** (2), 290–298.
- Jin, P., Song, J., Wang, X. C. & Jin, X. 2018b Two-dimensional correlation spectroscopic analysis on the interaction between humic acids and aluminum coagulant. *Journal of Environmental Sciences* **64** (2), 181–189.
- Korshin, G., Chow, C. W. K., Fabris, R. & Drikas, M. 2009 Absorbance spectroscopy-based examination of effects of coagulation on the reactivity of fractions of natural organic matter with varying apparent molecular weights. *Water Research* **43** (6), 1541–1548.
- Krzeminski, P., Tomei, M. C., Karaolia, P., Langenhoff, A., Almeida, C. M. R., Felis, E., Gritten, F., Andersen, H. R., Fernandes, T., Manaia, C. M., Rizzo, L. & Fatta-Kassinos, D. 2019 Performance of secondary wastewater treatment methods for the removal of contaminants of emerging concern implicated in crop uptake and antibiotic resistance spread: a review. *Science of The Total Environment* **648**, 1052–1081.
- Li, A., Zhao, X., Mao, R., Liu, H. & Qu, J. 2014 Characterization of dissolved organic matter from surface waters with low to high dissolved organic carbon and the related disinfection byproduct formation potential. *Journal of Hazardous Materials* **271**, 228–235.
- Lin, J.-L. & Ika, A. R. 2020 Minimization of halogenated DBP precursors by enhanced PACl coagulation: the impact of organic molecule fraction changes on DBP precursors destabilization with Al hydrates. *Science of the Total Environment* **703**, 134936.
- Liu, H., Cheng, F. & Wang, D. 2009 Interaction of ozone and organic matter in coagulation with inorganic polymer flocculant-PACl: role of organic components. *Desalination* **249**, 596–601.
- Liu, Y., Duan, J., Li, W., Beecham, S. & Dennis Mulcahy, D. 2016 Effects of organic matter removal from a wastewater secondary effluent by aluminum sulfate coagulation on haloacetic acids formation. *Environmental Engineering Science* **33** 484–493.
- Lyu, S., Chen, W. & Zhang, W. 2016 Wastewater reclamation and reuse in China: opportunities and challenges. *Journal of Environmental Sciences* **39**, 86–96.
- Ma, D., Gao, B., Xia, C., Wang, Y., Yue, Q. & Li, Q. 2014 Effects of sludge retention times on reactivity of effluent dissolved organic matter for trihalomethane formation in hybrid powdered activated carbon membrane bioreactors. *Bioresource Technology* **166**, 381–388.
- MEP Standard No. HJ 620-2011. Water quality – Determination of volatile halogenated organic compounds – Headspace gas chromatography, 2011.
- MEP Standard No. HJ 758-2015. Determination of haloacetic acids. – Gas chromatography, 2015.
- Mompremier, R., Mariles, Ó. A. F. & Bravo, J. E. B. 2019 Study of the variation of haloacetic acids in a simulated water distribution network. *Water Supply* **19** (1), 88–96.
- Numberger, D., Zoccarato, L. & Woodhouse, J. 2022 Urbanization promotes specific bacteria in freshwater microbiomes including potential pathogens. *Science of The Total Environment* **845**, 157321.
- Oscar, M. R. N., Juan, M. P. H. & Ashantha, G. 2017 Treatment technologies for emerging contaminants in water: a review. *Chemical Engineering Journal* **323**, 361–380.
- Padhi, R. K., Subramanian, S. & Satpathy, K. K. 2019 Formation, distribution, and speciation of DBPs (THMs, HAAs,  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$ ) during treatment of different source water with chlorine and chlorine dioxide. *Chemosphere* **218**, 540–550.
- Ramavandi, B., Farjadfard, S., Ardjmand, M. & Dobaradaran, S. 2015 Effect of water quality and operational parameters on trihalomethane formation potential in Dez River water, Iran. *Water Resources and Industry* **11**, 1–12.
- Siddique, M. S., Xiong, X., Yang, H., Maqbool, T., Graham, N. & Yu, W. 2022 Dynamic variations in DOM and DBPs formation potential during surface water treatment by ozonation-nanofiltration: using spectroscopic indices approach. *Chemical Engineering Journal* **427**, 132010.
- Sillanpää, M., Ncibi, M. C., Matilainen, A. & Vepsäläinen, M. 2018 Removal of natural organic matter in drinking water treatment by coagulation: a comprehensive review. *Chemosphere* **190**, 54–71.
- Srivastav, A. L., Patel, N. & Chaudhary, V. K. 2020 Disinfection by-products in drinking water: occurrence, toxicity and abatement. *Environmental Pollution* **267**, 115474.
- Tubić, A., Agbaba, J., Dalmacija, B., Molnar, J., Maletić, S., Watson, M. & Perović, S. U. 2013 Insight into changes during coagulation in NOM reactivity for trihalomethanes and haloacetic acids formation. *Journal of Environmental Management* **118**, 153–160.
- Wang, D. S., Zhao, Y. M. & Yan, M. Q. 2013 Removal of DBP precursors in micro-polluted source waters: a comparative study on the enhanced coagulation behavior. *Separation and Purification Technology* **118**, 271–278.
- Wang, W., Tang, D., Pilgrim M. & Liu J. 2016 Water resources compound systems: a macro approach to analysing water resource issues under changing situations. *Water* **8**, 2.
- Wei, Z., Zhao, X., Zhu, C., Xi, B., Zhao, Y. & Yu, X. 2014 Assessment of humification degree of dissolved organic matter from different composts using fluorescence spectroscopy technology. *Chemosphere* **59**, 261–267.
- Xiong, J., Wei, Y., Xu, J., Hou, J., Liu, Z., Wang, M. & Tan, W. 2021 Influence of reduction on the fluorescent units and proton binding of humic acids: synchronous fluorescence spectrum and NICA-Donnan modeling. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **626**, 127000.
- Yu, H., Wu, Z., Zhang, X., Qu, F., Wang, P. & Liang, H. 2019 Characterization of fluorescence foulants on ultrafiltration membrane using front-face excitation-emission matrix (FF-EEM) spectroscopy: fouling evolution and mechanism analysis. *Water Research* **148**, 546–555.

- Zhang, F., Wang, Y., Chu, Y., Gao, B., Yue, Q., Yang, Z. & Li, Q. 2013 Reduction of organic matter and trihalomethane formation potential in reclaimed water from treated municipal wastewater by coagulation and adsorption. *Chemical Engineering Journal* **223**, 696–703.
- Zhao, Y., Xiao, F., Wang, D., Yan, M. & Bi, Z. 2013 Disinfection byproduct precursor removal by enhanced coagulation and their distribution in chemical fractions. *Journal of Environmental Sciences* **25** (11), 2207–2213.
- Zheng, D., Andrews, R. C. & Andrews, S. A. 2015 Effects of coagulation on the removal of natural organic matter, genotoxicity, and precursors to halogenated furanones. *Water Research* **70**, 118–129.
- Zhou, Y., Xie, Y., Wang, M., Zou, F., Zhang, C., Guan, Z. & Yan, M. 2020 In-situ characterization of dissolved organic matter removal by coagulation using differential UV-Visible absorbance spectroscopy. *Chemosphere* **242**, 125062.

First received 11 October 2022; accepted in revised form 20 January 2023. Available online 2 February 2023