Formation and Removal of Oxidation By-Products from drinking water treatment Plant

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ABSTRACT

Every day, millions of people around the world receive clean drinking water from their drinking water treatment plants. The most widely used disinfectants in use today are chlorine, ozone, chlorine dioxide, and chloramines; each generates a unique set of DBPs in drinking water. Oxidation by-products (OBPs) are created when chlorine reacts with organic matter or dissolves organic carbon (DOC) in the water. The oxidants react with the organics to form oxidation by-products (OBPs), which are toxic and harmful to human beings.

The objective of this study is to remove OBPs from drinking water treatment plants using chemical oxidation and coagulation treatment methods to remove oxidation by-products.

The samples were analyzed using Fluorescence's Spectrophotometer Sampling Analyser (EEM) to record the fluorescence spectral of OBPs in the water samples; TOC was analyzed using Shimzu to detect the dissolved organic carbon (DOC) using standard procedure 5310D; UV_{254} nm was used to absorb the DOC spectrum; and Agilent 8890 chromatography (GC) was also used to determine the retention time (RT), responses, and properties of Trihalomethane THMs (EPA 551.1).

Coagulants, such as aluminum chlorohydrate, polymerized ferrous sulfate, and ferric chloride were used, during the experimental condition aluminum chlorohydrate proved to be very effective in removing oxidation by-products, similarly for oxidants sodium hypochlorite and potassium permanganate helped destabilize and aggregating fine particles, including organic matter in the water, and also aiding in removing suspended particles, and oxidation by-product.

The change in the emission spectrum would indicate that the chemical composition of the solution has been successfully changed by the oxidation process. Moreover, standard sample results of Trihalomethanes retention time (Rt), and peak areas are good for removing Trihalomethanes species. The TOC removal efficiency of OBPs is higher which indicates that sodium hypochlorite is effective in removing OBPs from drinking water. origin. These findings highlight the importance of removing and controlling oxidation by-products in drinking water treatment plants that have formed sediments

Keywords: Drinking Water Treatment Plant, Excitation-Emission Matrix, Coagulation, Oxidation By-product OBPs. Trihalomethane.

1. INTRODUCTION

When chlorine combines with organic materials (Liu, 2021) or dissolves organic carbon (DOC) in water (Kumari, 2022; Nikolaou, 2004), oxidation by-products (OBPs) are produced. Additionally, the oxidants and organics may react to create hazardous compounds known as OBPs that are detrimental to human health (Gallard, 2002). To ensure the security of the water supply, OBPs must be controlled and removed from drinking water (Wee, 2023). To make water suitable for human consumption, it must be treated (Khalifa, 2018). The main OBPs that are generated in water are trihalomethanes (THMs) and haloacetic acids (HAAs) (Sinha, 2021). Both conventional coagulation treatment and chemical oxidation treatment techniques are effective in eliminating OBPs (Titchou, 2021)

Significant amounts of known OBPs have been found, however, there are still significant amounts that are unknown (de Castro Medeiros, 2019). Drinking water that has been chlorinated was trihalomethanes (THMs) were initially found (Liu, 2019; Mazhar, 2024). Chlorination produces a variety of OBPS, such as THMs, HAAs, and HBQF (Zhang, 2020). As a result, OBPs in

drinking water systems are getting more and more attention. By maximizing the dose of oxidants, both OBPs and organic matter can be effectively eliminated (Qu, 2010). This would raise the efficacy of treatment and lower the chance of developing OBP. It is noteworthy that oxidation by-product concentrations in drinking water are regulated by water treatment facilities to guarantee that they remain within safe bounds (Giannakis, 2021; Kumar, 2023)

Over the years, the effort has been made to prevent oxidation by-products by using so many techniques and methods. For instance, chlorination, enhanced coagulation, water management practices ozone, ultraviolet, Granular activated carbon (GAC), and Advanced oxidation process (AOPs) to prevent the production of OBPs (Rekhate, 2020; Zainudin, 2018). Disinfectants such as bromide or iodide, Natural Organic Matter, bacteria, chlorine dioxide, chloramine, sodium hypochlorite, and ozone interact with these agents to form distinct classes of OBPs that are highly harmful (Richardson, 2007). Several countries have adopted particular sets of rules to limit some individuals or groups of OBPs or DBPs, because of OBPs carcinogenicity, cytotoxic, and genotoxic effects (Richardson, 2007). China and certain European Nations have imposed extremely strict thresholds for total THMs, HAAs, and HBQs (Giuseppe et al., 2005). The uses of coagulation strategies and other treatment methods like absorption, and membrane filtering are often employed to reduce OBPs in DWTP (A. Bhatnagar, & Sillanpää, M., 2017) However, the above literature only focused on the formation and removal of OBPs from drinking water and not the removal of OBPs from sludge water before discharge.

The chemical compounds used in the treatment process reduce the contaminants from the water treatment plant to be immediately deposited in the community's hydric bodies. Consequently, it is not a good choice since it could lead to the unintended formation of mud deposits and contamination of rainfall and its dispersal in aquatic bodies (Monteiro et al., 2007). However several OBPs, including HBQ, THMs, and HAAs, might be present in the sedimentation tanks, which would be extremely dangerous for both the environment and the discharge system (Padhi, 2019). Numerous chemical compounds found in the residual from the drinking water treatment process are toxic and resistant to remediation (Qrenawi, 2021; Rak, 2009). Suspended particles and naturally occurring iron and aluminum salts are added as chemical coagulants

In addition to the added chemical coagulant, the WT sediment also contains minerals and other elements from the source water (Qrenawi, 2021). Many techniques, such as membrane filtration and biological removal, have been developed recently to remove harmful organic chemicals from drinking water (A. Bhatnagar, & Sillanpää, M., 2017; Bibi, 2017; Cevallos-Mendoza, 2022; Matilainen, 2011). Residual water may contain certain hazardous disinfection by-products, although the majority of research on OBPs concentrates on the drinking water treatment procedure and OBPS prevention rather than the water residue or sediments itself (Cai, 2016; Kozari, 2020; Srivastav, 2020). The sophisticated water treatment method can eliminate some of the OBPs in the effluent, but some may still be present in the sediments, which presents a serious risk to the discharging water system. It is crucial to develop new technologies that can efficiently extract oxidation byproducts from drinking water treatment facilities (Von Gunten, 2018). Large volumes of sludge known as treatment residuals, or water treatment residuals containing both organic and inorganic elements, are produced by water treatment plants (EPA, 2011). Chemical recovery from DWTP can yield benefits from the recoverable compounds themselves, reduce the quantity of produced contaminants, and enhance the sludge treatment process (Anuththara, 2022; Qrenawi, 2021). The quantity and properties of the contaminants dictate the procedures and expenses related to treating, moving, and finally disposing of them (Ahmad, 2016). As a result, creating a comprehensive treatment process for a particular kind of contaminant requires having a solid understanding of the appropriate and accessible processing techniques for that kind of sludge (Qrenawi, 2021). DWTP contaminant's residual management is important because of its composition, amount, and cost and there must be regulatory criteria to adhere to water treatment sludge handling (Nguyen, 2022; Price, 2018).

The application of water treatment technologies is essential to human health and enables people to profit from drinking water and other uses (Li, 2018; Von Gunten, 2018). Strict treatment standards for drinking water are enforcing in addition to OBP law to decrease DBP precursors via coagulation, absorption granular and activated carbon ((NPDWR), 2024; Kroehler, 2014; Pérez-Lucas, 2022; Tsaridou, 2021; Zazouli, 2017). To extract these by-products from drinking water coagulation, flocculation, absorption, and occasionally oxidation can be used (Ahmad & Azam, 2019). Chemical oxidants have several practical advantages in the practice of treating drinking water (Lee et al., 2023). It is ultimately a multi-objective process that helps to raise the overall quality of drinking water and serves a variety of important functions (Duan et al., 2021). Chemical oxidation reactions may significantly reduce the concentration of many of these organic in drinking water, but the chemical products created by the oxidation reactions could also be harmful to the public's health (Titchou et al., 2021a, 2021b). The research on pre-oxidation coagulation could raise the standard of water quality (Ghernaout, 2020). It appears that both organic matter and

OBPs can be successfully removed by optimizing the oxidants dose. this would improve therapy effectiveness and decrease the risk of OBP formation (Han et al., 2022).

Therefore, it makes sense to look into the elimination of OBPs using pre-oxidation coagulation methods (Han et al., 2022). Using Gas Chromatography System (GC), Fluorescence excitation-emission matrix (EEM) spectroscopy Total organic carbon analysis. Therefore, the purpose of this study was to use Chemical pre-oxidation coagulation techniques to remove the Formation of Oxidation By-Products from drinking water treatment process and, examine the formation of Oxidation by-products formation of THMs, and HBQF, other common OBPs in conventional coagulation methods potential for removing pollutants from drinking water treatment plants. It also evaluated the variation of the microbial community structure during the water treatment process under coagulation pre-oxidation recycling practice. Using Sodium hypochlorite (NaOCl) and potassium permanganate (KMnO$_4$) oxidant on NOM, the effect of OBP recovery on microbiological safety was examined. Chemical oxidation has been extensively investigated for the elimination of OBPs, TOC, and micro-pollutants with Pre-oxidation being one of the most efficient and cost-efficient processes—the elimination of OBPS from sediments or water sludge before discharge. The DWT sludge is a blend of solid and liquid that can be disposed of as garbage. Even while it occasionally qualifies as a natural resource, it is frequently an unwelcome strain on the environment and the economy.

2.0 Materials and Methods

Suzhou drinking water treatment plant (DWTP) in Jiangsu province, China, is the main sample source for this experiment. One of the primary drinking water supplies for Shanghai city currently serves roughly 5,000,000 people but can supply up to 10,000,000 m3/d. The following treatment techniques were used: After pre-ozonation, coagulation, sedimentation, sand filtration (SF), post-ozonation, and biological activated carbon (O3-BAC) at Suzhou DWTP, the drinking water quality was further enhanced by the application of nanofiltration technology (Wei, 2022; Chen, 2021). Deionize Milli-Q is also used to perform experimental work and to prepare different coagulant concentrations. Sodium alginate, humic acid, and tannic acid (Aldrich, sodium form) were used for the initial investigations (i.e., TOC, UV, and EEM) (Kaczmarek, 2020). Then, aqueous solutions of organic precursors that reacted as representative structural units of humic compounds or aromatic compounds were used in the experiments. The following model compounds were utilized in these experiments: methanol (e.g., Baker, reagent grade), dichloromethane (CH$_2$Cl$_2$) (Mallinckrodt, 99.8%); Aluminum chlorohydrate (Aldrich, 98%); polyferric chloride (Aldrich, 98%); and polymerized ferrous sulfate (Aldrich, 21%); Methyl tert butyl ether (CH$_3$OC(CH$_3$)$_3$ abbreviated as MTBE baker reagent grade); and Sodium chloride (NaCl): premium grade pure. Ammonium chloride solution (NH$_4$Cl) and sulphuric acid (H$_2$SO$_4$) were used to prepare a standard solution. and chlorine was obtained from sodium hypochlorite (Aldrich, >5% accessible chlorine). The abovementioned commercial products were used to make stock solutions, and the actual concentration of accessible chlorine in the stock solution was determined by TOC and UV-254nm. To eliminate the organic matter, basic sodium hypochlorite (NaOCl) was used for this experiment to remove organic matter (Wang, 2018). TOC was analyzed (Shimizu) to detect the dissolved organic carbon (DOC) per the standard procedure 5310D, and UV254nm was used to absorb the DOC spectrum (Zhang, 2009). The DOM distributed in the WTP with heterogeneous mixtures and complex components is believed to be the primary precursor for the formation of THMs and toxic DBPs in the WTP (Bedner, 2006; Wang, 2011) In the most extensively used water treatment methods, such as coagulation, sedimentation, filtration, and disinfection, the coagulation process is set up so that the coagulant chemicals are removed using sodium hypochlorite concentration (Xie, 2024). The experiments were carried out for concentration, retention time, pH, and coagulant and chlorine dose with the chlorine concentrations of 0.5 mg/L, 1 mg/L, 1.5 mg/L, 2 mg/L, and 2.5 mg/L) (Kumari, 2022). OBPs in drinking water are formed when organic matter (DOM) and natural organic matter (NOM) react with an oxidant or chlorination treatment process in water (Zainudin, 2018a). DOM is a wide range of chemicals, including amino acids, carboxylic acids, humic substances, and tannic acids (Hua, 2007; Thurman, 2012). Several individual (DOM) compounds were tested for OBPs, including hydrophilic and hydrophobic acids, bases, and neutral compounds, using the techniques developed by (Imai et al., 2002; Wei, 2022).

2.1 Sample preparation and reagents used in the test

All chemicals employed in the experiment were of reagent grade and specified differently. The water used in this study has a pH ranging between 6 and 7 and 7.244 μS/cm conductivity control, respectively. A separate mixture of 0.08g of sodium, tannic acid, and humic acids at different concentrations in a beaker filled with 1200 ml of Suzhou water treatment plant (DWTP). The solution was vigorously agitated for 30 minutes at 250 rpm using an MYP13-2S magnetic stirrer to mix properly and dissolve organic compounds. The flocks developed at the bottom of the container, 0.45 μm is poured in PVDF membrane filters to filter

the sample solution, and it is kept at 4°C (Uman, 2020; Yuan, 2021). And 800 ml of the solution was transferred into five distinct, clean bottles. with different sodium hypochlorite concentrations (NaOCl) (i.e., 0.5 mg/L, 1 mg/L, 1.5 mg/L, 2 mg/l, and 2.5 mg/L), were measured using 200 transferred pipettes, and it was chlorinated with sodium hypochlorite. 800 milliliters of these water samples were poured into five clean containers labeled respectively. (Reckhow et al., 1990). The samples were tested for TOC, UV, and EEM concentrations using the Total Organic Analyzer (TOC). See figure 4

2.2 Fluorescence Spectrophotometer

Fluorescence's Spectrophotometer Sampling Analyzer EEM (model F-7100, Hitachi Japan) was used to record the fluorescence spectra of water samples. EEM scans were obtained by scanning at a speed of 12,000 nm/min over excitation (Ex) wavelengths of 200–500 nm and over-emission (Em) wavelengths of 200–550 nm. The intervals for Ex and Em were both fixed at 5 nm. To eliminate Raman scatter peaks, the fluorescence signal of the pure water sample from Suzhou DWTP and Milli-Q water was removed from the EEMs. Raman unit.

Fluorescent dissolved organic matter (FDOM) has been extensively characterized and tracked using fluorescence spectroscopy (EEM). this technique offers a non-destructive nature, high sensitivity, speed, and affordability (Hudson et al, 2007 Systems, 2009; Fellman et al, 2010). Using all of the wavelength-dependent fluorescence intensity data from EEMs quantitatively analyses. See figure 2 and 3.

2.3 Agilent 8890 Chromatography (GC)

Agilent 8890 chromatography (GC) was used to investigate the molecular weight (MW) distribution and properties of DOM fractions (EPA 551.1 Trihalomethanes; EPA 552.2 Halo-acetic Acid) standards for disinfection by-products (Cohen et al., 1990). THMs and HAAs in the samples were determined using USEPA methods 551.1. THMs compounds were extracted using MTBE by liquid-liquid extraction and analyzed by Agilent 8890 chromatography (GC) equipped with an electron capture detector and DB-5 fused silica capillary column (30 m × 0.53 mm, 1.5 mm film thickness). Detailed process and instrument settings can be found in the support information (figure 1). Suzhou DWTP and Milli-Q Pore Water were prepared as stock solutions quenched with sodium sulfates, methanol, and MBTE to examine THMs and HAAs. The samples were then analyzed using an Agilent 8890 GC-ECD apparatus.

2.4 Standard Sample Preparation

The standard sample was prepared and stored to be used for the detection of DBPs, the standard sample containing Trihalomethane compounds.

i)   Sample preparation

The standard materials adopt dichloromethane, monobromodichloromethane, dibromochloromethane as a solute with accurate purity, pure methanol as solvent was prepared by weight volumetric methods in a clean laboratory at room temperature 20°C

ii)   Traceability and valuation methods

Standard values for the concentration of the reference substance, are the prepare values and the quantitative values are checked by the gas phase spectrum (FD), the traceability of the CRM can be guaranteed by using the preparation methods of measurement and the measuring instruments which meet the domain of metrological properties

iii)   Characteristic and extended uncertainty, the extended uncertainty of standard values is mainly composed of the uncertainty of raw materials, purity weighing constant volume, uniformity, and stability

iv)   preparation of a Standard sample to store the standard solution of Trihalomethanes standard. See figure 1

200 µl of Trihalomethanes standard sample, titrated with methanol to 10 ml mark of flask bottle to be used for the detection of DBPs. This prepared sample was used in the different water samples from Suzhou WTP. See Table 1

Table 1. Six standard sample solutions were prepared for the Liquid-liquid extraction to detect OBPs or DBPs from the water samples.

Suzhou WTP samples Standard Solution (SS)	Prepare sample	THMs	MBTE	Volume of water sample
Membrane influent (SS1)	50 μl		2 ml	10 ml
Membrane effluent (SS2)	100 μl		2 ml	10 ml
Production water (SS3)	200 μl		2 ml	10 ml
Concentration water (SS4)	400 μl		2 ml	10 ml
Alkaline wash (SS5)	600 μl		2 ml	10 ml
Acids wash (SS6)	800 μl		2 ml	10 ml

3.0 RESULTS DISCUSSION

3.1 standard sample analysis using Agilent 8890 Chromatography (GC) for the detection of DBPs

THMs and HAAs in the samples were determined using USEPA methods 551.1 and 552.2 respectively. THMs and HAAs were extracted using MTBE by liquid-liquid extraction and analyzed by Agilent 8890 gas chromatography (GC) equipped with an electron capture detector and a fused silica capillary column (30 m × 0.53 mm, 1.5 mm film thickness)—a very sensitive detector for electrophilic compounds such as halogenated organic compounds. A standard sample substance was prepared to store, and be used for the detector of DBPs, a standard sample containing Trihalomethanes, four standard samples of Dichloromethane, Fluorobromomethane, Dibromochloromethane, and Bromoform as solutes with accurate purity, pure methanol as solvent were prepared by weight of volumetric methods in a clean state pollution laboratory at room temperature 20^0C, the standard values for the concentration of the reference substance is prepared to value and the quantitative value is checked by the gas phase spectrum (FD). THM standards were made, and the peak height or peak area for each THM component from the chromatogram was plotted as a function of concentration to provide calibration plots for the GC-ECD method.

The sample result shows that the homogeneity conforms to the rule of the test and the stability test is good, based on the given retention times

  I.　Trichloromethane (chloroform) has a retention time of 2.149
 II.　Fluorobromomethane has a retention time of 3.074
III.　Dibromochloromethane has a retention time of 5.148 and
IV.　Bromoform has a retention time of 9.723.

This retention time indicates the elution order and the relative retention time of the compounds during the gas chromatograph analysis, the elution order is determined by the interaction between the compounds and the stationary phase inside the GC Colum. lower retention time indicates the compound elutes earlier and has a higher volatility on the other hand higher retention time indicates that the compound elutes later and has a lower volatility. Therefore, the results suggest that trichloromethane (chloroform) is the most volatile compound and elutes earliest followed by Fluorobromomethane, dibromochloromethane, and finally bromoform which is the least volatile and elutes the latest

Figure 1. Four Trihalomethane compounds show different retention times and responses. THM standards were made, and the peak height or peak area for each THMs component from the chromatogram was plotted as a function of concentration to provide calibration plots for the GC-ECD method**.** (a) Showing standard curve of retention time and response areas of Trichloromethane (Rt) is 2.149 mins (b) Fluorobromomethane retention time is 3.074 mins (c) Dibromochloromethane retention time is 5.148 mins and (d) Bromoform retention time is 9.723min. The curve obtained from the standard curve can be used to show the relationship between the concentration of trihalomethane compounds and the corresponding signals or responses obtained from the GC chromatography, this curve can be used to quantify the amounts of trihalomethanes in the water samples by comparing the response of the sample with a standard curve, the curve can be used to determine the

concentration of trihalomethanes in the water sample, evaluates the effectiveness of the disinfection process, and assess potential health risks associated with the presence of these compounds in drinking water.
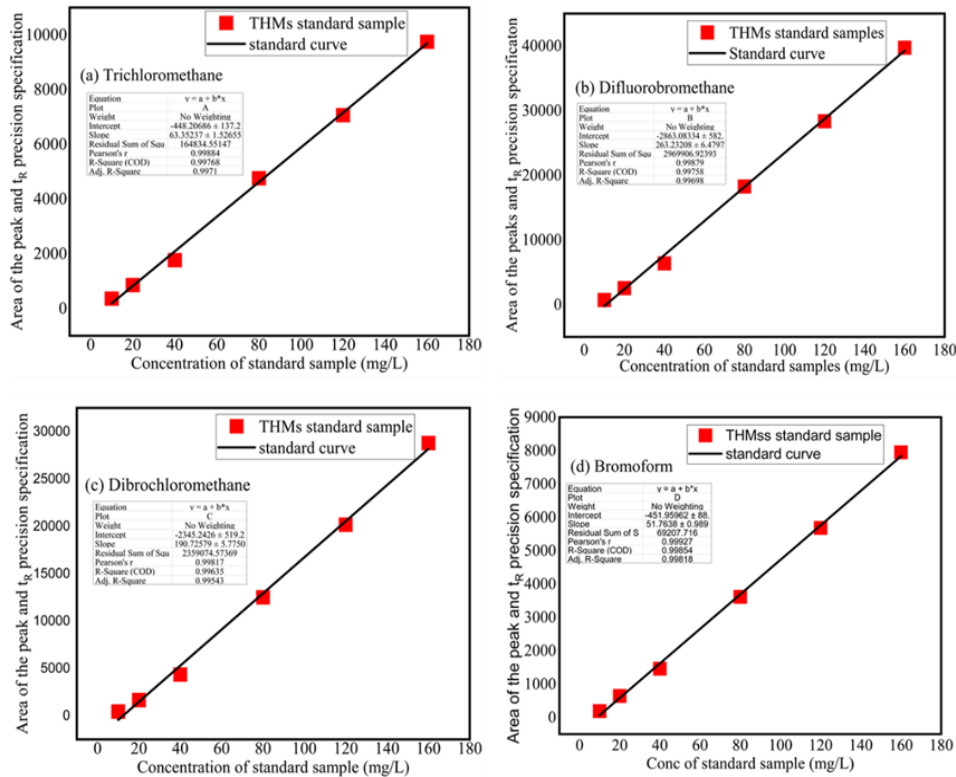

Figure 1 Standard curve of retention and peak area of four trihalomethane species

3.2 fluorescence Spectrophotometer Using Integration method excitation emission matrix-parallel factor analysis (EIFA) Scan analysis of spectral peak of OBPs

The fluorescence spectrophotometer (model F-7100, Hitachi, Japan) records the results of organics (tannic acids, humic acids, and sodium alginate). The removal of disinfectant by-products (DBPs) in the WTP using humic acids, with concentration of sodium hypochlorite, a spectrophotometer was determined comparing the results with blank distilled water to zero, to estimate the concentration of organic compounds and DBPs in the water, the techniques provides estimate not direct measurement of DBPs concentration, as the concentration of NaOCl increases the excitations wavelength peaks spectral decreases, indicates that the organic materials present in the solution which resulted in a decrease in the level of several regulated DBPs see Figure 2. A fluorescence spectrophotometer (model F-7100, Hitachi, Japan) was used to record the fluorescence spectra. By periodically monitoring the emission (Em) spectra in the 200 nm–500 nm range and the excitation wavelengths (Ex) in the same range at 5nm intervals in the excitation domain, six-dimensional spectra were produced. The six spectra have different concentrations of NaOCl starting from 0.5 mg/L, 1.0 mg/L, 1.5 mg/L, 2 mg/L, 2.5 mg/L, and 3 mg/L. The excitation-emission matrix (EEM) data was processed using MatLab or (MathWorks). The ratio of fluorescence intensity at different emissions and excitations. can be used to compute a fluorescence index (FI) based on the EEM data (McKnight et al 2001). Organic matter with an ancestral (microbial) origin is represented by a greater FI (>2.5), while organic matter with an allochthonous (terrestrial) origin is represented by a lower FI (<1.3). Figure 2 Emissions and Excitations matrix of potassium permanganate ($KMnO_4$) oxidant and organic sodium alginate spectral peaks. New peaks are seen as the concentration of $KMnO_4$ oxidants increases, this can be observed from the peaks below.

a. Emission (Ex) 300 nm - Ex 370 nm and Excitation Ex 250 nm – Em 270 nm, related aromatic content of organic pollutants
b. Emission (Ex) 350 nm –Ex 450 nm, and Em 250 nm –Em 340 nm connected to humic compounds.

c. At peak Ex 380 nm – Ex 400 nm and Em 250 nm - 280 nm pollutants started to break down by potassium permanganate acids (KMnO$_4$), the aromatic organic protein

d. At the peak of Ex 350 nm -400 nm and Em 250 nm- 280 nm, the organic pollutants continue to break down, and most of the particles are destroyed as the concentration of potassium permanganate acids (KMnO$_4$) increases.

e. At the peak of Ex 250 nm – 380 nm and Em 250 nm – 275 nm most of the organic pollutants were removed as the concentration of potassium permanganate (KMnO$_4$) increased there are new changes in the peaks.

f. Between 350 nm -370 nm and Em 250 nm - 210 nm, the peak of organic pollutants decreases drastically, no organic pollutants were seen, and they were complexly removed from the solution.
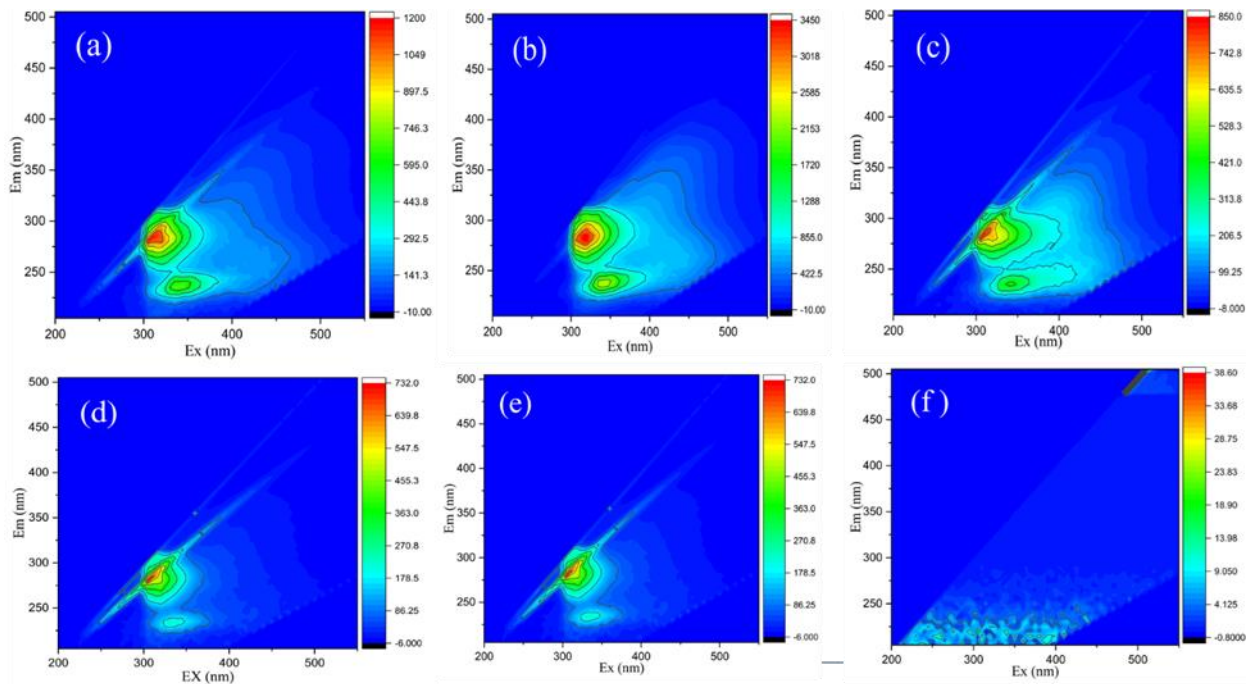
Figure 2 Excitation emission of six (3-D scan) spectral peaks of organic sodium alginate after potassium permanganate (KMnO$_4$) oxidation

In the analysis of organic humic acids and sodium hypochlorite (NaOCl) solution using fluorescent emission excitation for oxidation by-products and other impurities, the emission spectral is observed to see a shift in the peak intensities and emission wavelength and there are new appearance of spectral peaks see Figure 3

a. The peaks Ex 300 nm -400 nm and Em 250 nm -300 nm, the peak was not seen because the sodium hypochlorite (NaOCl) concentration was 0.5 mg/L it was a very low concentration, therefore not effective in breaking the organic materials, oxidation by-products, and other impurities.

b. The peak Ex 300 nm –Em 400 nm and Em 200 nm – 300 nm, the concentration of NaOCl was 1mg/L somehow strong and the peaks started to break certain organic compounds, oxidation by-products, and the organic materials and certain oxidation by-products started disappearance due to strong oxidants concentration.

c. Ex 320 nm -400 nm, and Em 200 nm- 230 nm the peak breakdown completely, the concentration NaOCl concentration applied was 1.5 mg/L and was able to break down most of the organic materials, oxidation by-products, and other impurities disappeared from the water.

d. Ex 300 nm -350 nm, and Em 230 nm-270 nm, 2 mg/L of the concentration of NaOCl applied to the organic, the concentration of the oxidant was high, its breakdown almost all the organic materials present in the water, removal of oxidation by-products, and other impurities continues, as the concentration increases the more effective the oxidants to remove impurities and oxidation by-products from the water.

e. Ex 340 nm – 450 nm, Em 260-450 nm, the concentration of NaOCl was 2.5 mg/L, no organic materials and impurities were seen, clear solution, finally concluded that as the concentration of NaOCl increases the more effective the oxidants reduces or removed oxidation by-products from the water

f. At the peak of Ex 350 nm -400 nm and Em 250 nm- 280 nm, the organic pollutants continue to break down, and most of the particles are destroyed as the concentration of sodium hypochlorite acids increases.

g. At The peak of Ex 250 nm – 380 nm and Em nm 250 nm – 275 nm most of the organic pollutants were removed as the concentration of sodium hypochlorite increased, this can be observed from the peak.

h. Between 350 nm -370 nm and Em 250 nm - 210 nm, the peak of organic pollutants decreases drastically, no organic pollutants were seen, and they were complexly removed from the water. A significant alteration in the emission spectral one would suggest that the oxidation process has been effective in removing the chemical composition of the organic materials and oxidation by-products. See Figure 3.
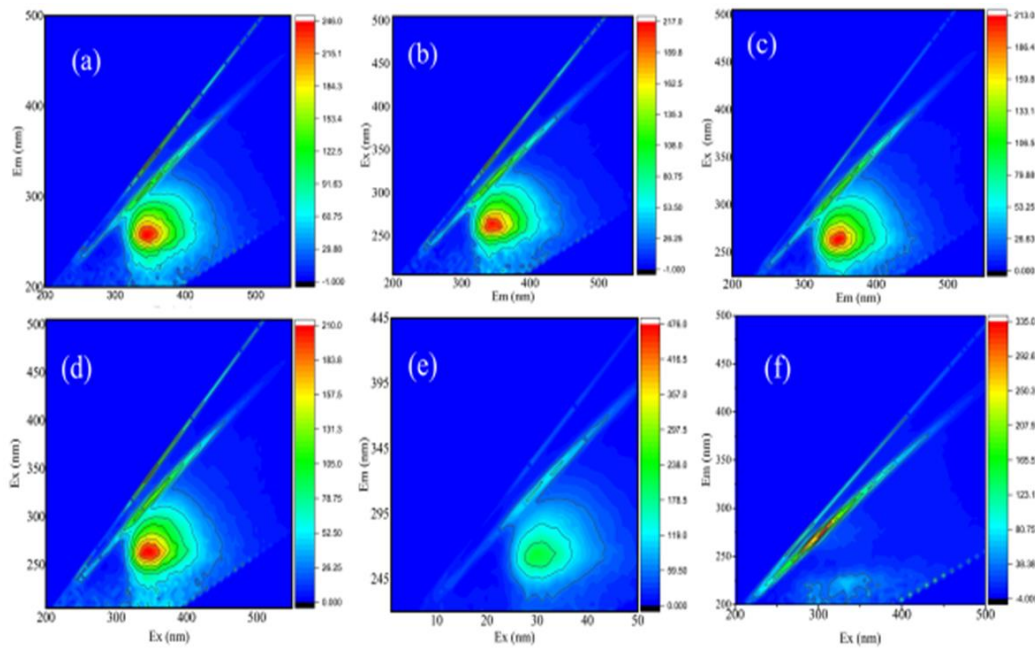

Figure 3 Fluorescence excitation-emission matrices (EEMs) of organics humic acids after sodium hypochlorite (NaOCl) oxidation.

3.3 Organics compounds after coagulation of sodium hypochlorite oxidation to remove total organic matter and oxidation by-products in drinking water treatment plant (WTP).

Total Organic Carbon (TOC) of Tannic Acids, Humic Acids, and Sodium Alginate using sodium hypochlorite as an oxidant to remove oxidation by-products (OBPs). TOC analysis is vital in assessing organic carbon content in diverse samples, aiding in water quality assessment and process control. Organic matter was formed in the water, and sodium hypochlorite oxidized the organic materials. Tannic acids, humic acids, and sodium alginate were used as organic compounds to react with sodium hypochlorite oxidants during the coagulation filtration process. 0.8 g of different organics was placed in 1200 milliliters of water sample, which was stirred in a magnetic stirrer at about 300 rpm for 30 min, for the oxidation to take place, 800 ml of the water sample was prepared using Suzhou water treatment plant and Milli-Q pore-deionized water, different oxidants was added to the water sample, with five different concentration mark 0.5 mg/L, 1 mg/L. 1.5 mg/l. 2 mg/L and 2.5mg/L. 100 milliliters was utilized, filter with 0.45 μm membrane, 10 milliliters of each sample was inserted into the TOC analyzer together with the distilled water sample.

The TOC analyzer measures the concentration of organic content and oxidation by-products in the sample solution. NaOCl concentrations were marked at 0.5 mg/l, 1 mg/L, 1.5 mg/L, 2 mg/L, and 2.5 mg/L for each separate solution. The experiment was performed on three separate sample solutions (i.e., humic acid, tannic acid, and sodium alginate solution). The data for

this experiment is shown in Figure 4. The diagrams clearly show that NaOCl was successful in removing OBPs from the water samples. The graph clearly shows how contaminants were successfully removed as the concentration of NaOCl increased from 0.5 mg/L to 2. 5 mg/L. Organic materials were successfully removed from the water samples provided; see Figures 4
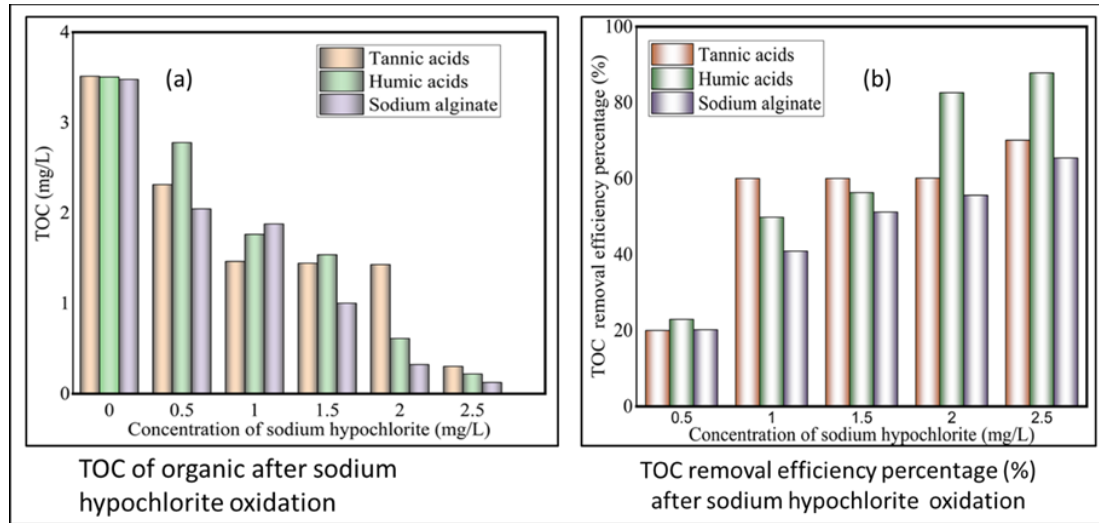

Figure 4. TOC of organic and removal efficiency percentages after sodium hypochlorite oxidation.

Organic compounds (Tannic acids, humic acids, and sodium alginate to determine TOC concentration in the solution, from figure 4 (a) TOC at zero (0) i.e. no NaOCl was added, the TOC was high 3.5 mg/L, the addition of NaOCl concentration to organic solution the TOC started decreasing, from 3.5 mg/L to 0.2 mg/L, indicating that NaOCl can reduce organic TOC and other impurities. Graph (b) removal efficiency from 0.5 mg/L to 2.5 mg/L concentration, that is organic sodium alginate, tannic acids, and humic acids were 20 %, 20 %, and 22 % respectively as the concentration of NaOCl increases, the removal percentages increase from 20 %, 20 %, 22 % to the removal efficiency of 64 %, tannic acids, sodium alginate 68 % and humic acids to 85 % after treatment. these indicate that the concentration of NaOCl is effective in reducing the TOC and increasing the removal efficiency and other oxidation by-products in the water. However, NaOCl's high concentration can also contribute to oxidation by-product formation. care must be taken and regular monitoring of WTP during the coagulation process.

$KMnO_4$ reacting with Humic acids and Sodium alginate solution concentration of $KMnO_4$ are as 0.8g of sample of different organic (tannic acid, humic acids, and sodium alginate) was treated with 0.5 mg/L,1mg/L, 1.5 mg/L, 2 mg/L and 2.5 mg/L in the solution of tannic acids humic acids and sodium alginate respectively with potassium permanganate. During the TOC analysis, $KMnO_4$ oxidizes the organic carbon compounds present in the sample converting them into carbon, after coagulation and nanofiltration processes. TOC was analyzed by a Total Organic Carbon Analyzer (TOC-V CPN) machine autos ampler Shimadzu TOC analyzer. The result is plotted, and the data shows how $KMnO_4$ reduces dissolved organic matter (DOM) in the solution. See Figure 5 (a) and (b).
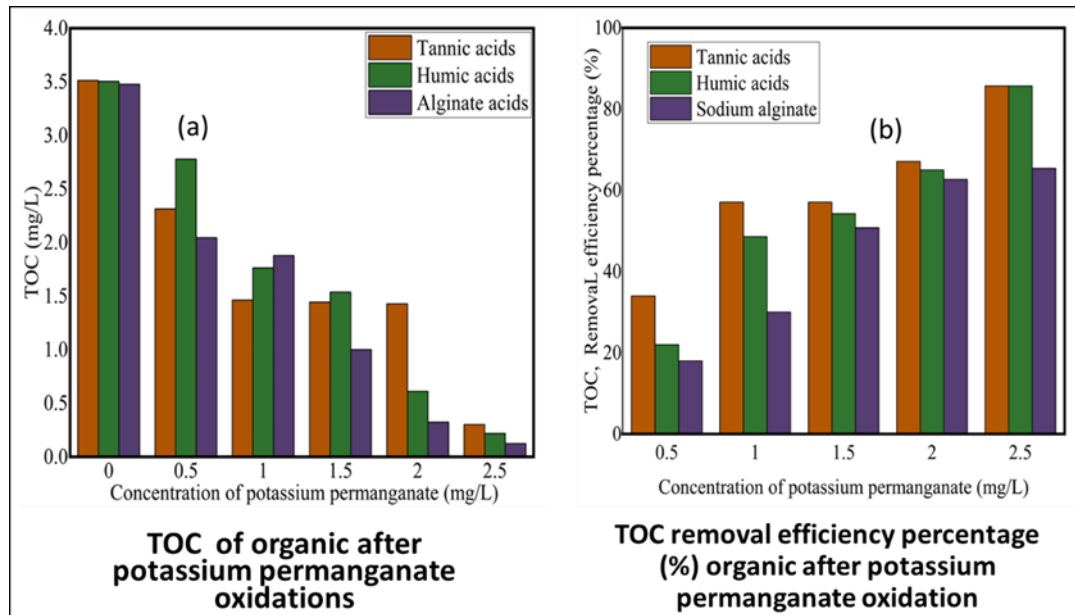
Figure 5. TOC of organic and removal efficiency percentage after potassium permanganates coagulation.

From graph 5(a) above the TOC after potassium permanganates oxidation, the TOC of the different organics results reduces from 0.0 mg/L with TOC of 3.5 mg/L of $KMnO_4$ to the concentration of 2. 5 mg/L with TOC values of 0.001 mg/L, indicating that $KMnO_4$ is effective in removing TOC, and oxidation by-products. Figure 5 (b) shows TOC removal efficiency percentages from the graph the percentage increases from 18 % to 65 % for sodium alginate, 20% to 82% for humic acids, and 36% to 82 % for tannic acids. the concentration of $KMnO_4$ with the lowest percentage being sodium alginate because of its organic composition, and structure, is not very active with $KMnO_4$ Compared to tannic and humic acids which are very active with $KMnO_4$.TOC results can provide the measured amount of organic carbon in the water sample, this information is compared to regulatory standards or used as a baseline for further water treatment, this information can help you understand the presence and behavior of organic compounds in water and the quality of water you have.

3.4 Total organic carbon of organic coagulants after coagulation using sodium hypochlorite

Polymerized ferrous sulfate, polyferric chloride, and aluminum chlorohydrate coagulant using sodium hypochlorite (NaOCl) as oxidant after coagulation to determine TOC, and to remove OBPs in drinking water treatment plants. Coagulants, such as aluminum chlorohydrate, polymerized ferrous sulfate, and ferric chloride used in water treatment destabilize and aggregate fine particles, including organic matter in the water, and also help to remove suspended particles and organic matter they form flocs that settle out by sodium hypochlorite on the other part its oxidizing agents, disinfect the water and kills pathogen and bacteria, this helps sedimentation of filtration for removal. Sodium hypochlorite as an oxidant is used to oxidize and break down organic compounds into smaller more easily treatable forms. It can also help in disinfection by killing microorganisms present in the water.

During the treatment processes using chemical oxidation, by-products are formed as a result of the reaction between the coagulants and the organic matter present in the water. The presence of these oxidation by-products can be assessed using TOC (total organic carbon analysis is a method used to measure the total organic carbon present in the water sample, the TOC analyzer measures the amounts of carbon that is present in organic molecules in the water solution, both the organic and the contaminants and any oxidation by-products that is form during the treatment processes. measuring TOC helps to determine the effectiveness of the coagulants and oxidants in removing organic matter from the water. The experiment performed using TOC analysis led to the reduction of organic carbon concentration, this indicates that the coagulant is effective and oxidant in removing organic matter from the water.

Figure 6 (a-c) below. One can observe from the display graph results that as the dosage of the coagulants and oxidants increase from 10 mg/L to 50 mg/L leads to the reduction of TOC from higher to lower concentration, this can furthermore kill microorganisms with the reaction of NaOCl, Oxidation by-product can also be effectively removed from the water, see figure 6.
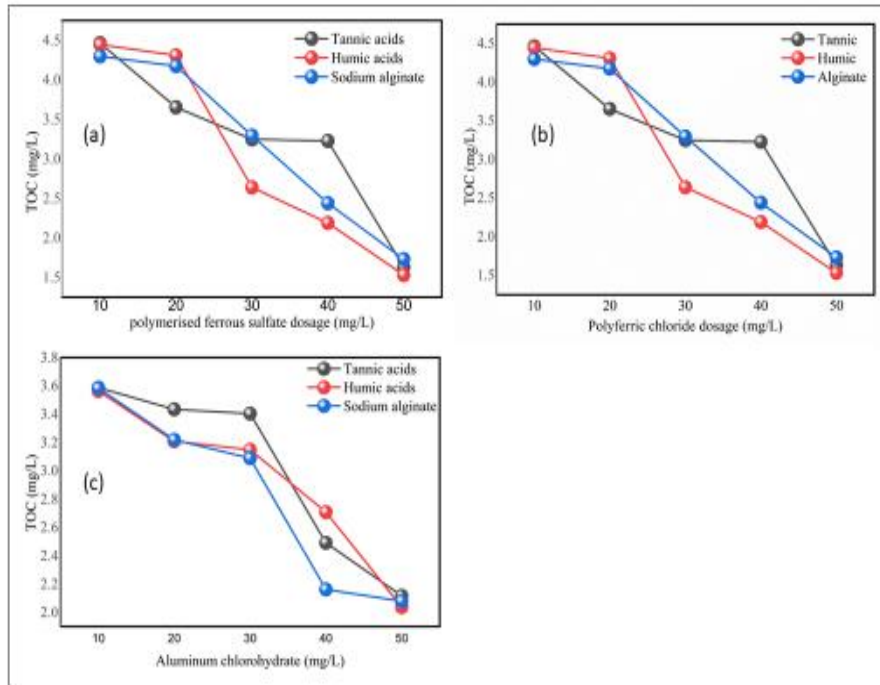

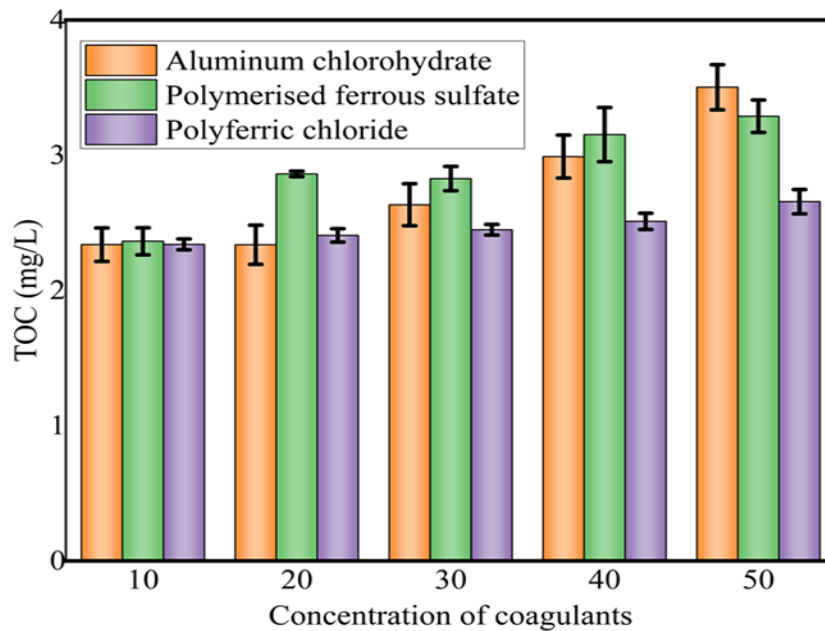**Figure 6** (a-c) Total Organic Carbon coagulants after coagulation process

Figure 7 shows different organic coagulant concentrations after coagulation

Figure 7 the bar chart above depicting the performance of the three organic coagulants aluminum chlorohydrate, polyferric chloride, and polymerized ferrous sulfate coagulant, reveals valuable insights into their effectiveness. Aluminum chlorohydrate has the highest bar indicating that it exhibited the most significant coagulation efficiency in the tested condition of the experiment and polymerized ferrous sulfate shows commendable levels of coagulation performance.
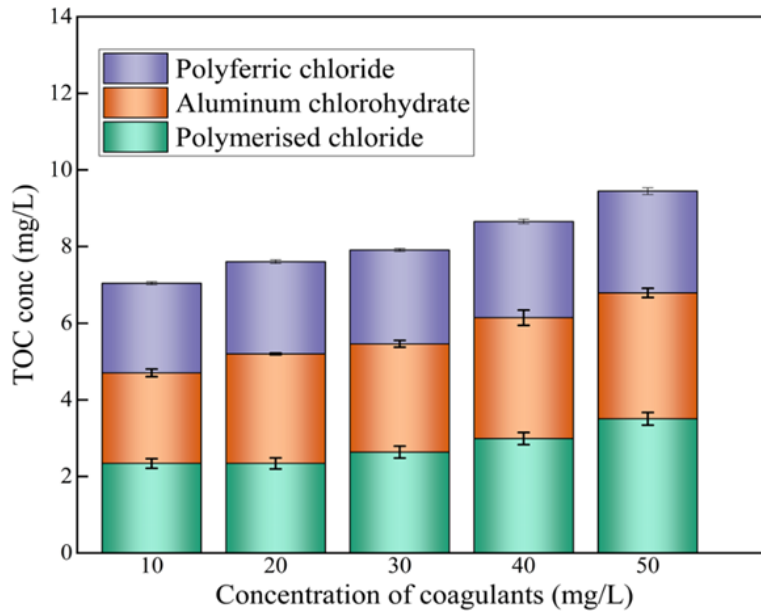

Figure 8 shows coagulant levels at different concentrations of TOCs

Figure 8 shows the three different levels of coagulant concentration; these indicate the trends at which the TOC is been increasing from the concentration of 10 mg/L to 50 mg/L at different TOCs.

3.5 The analytical signal (peak area), retention time, response, and evaluation of four THMs compounds using GC–ECD to detect the concentration of THMs in drinking water

The concentration range under investigation and the corresponding correlation coefficients (r) for calibration curves with every THM species are displayed in Table 2 -4. And figure 8-9. The findings indicate that the concentration ranges typically evaluated in drinking water have generally satisfactory linearity and conformity. The measuring instrument meets with the metrological properties, i.e. concertation, peak areas, retention time, pressure, and temperature, and to study the response, and peak areas and make forecasts to help detect THMs, this graph can be used to quantify the amounts of THMs in the water samples by comparing the samples response area with the concentration, the chart can be used to determine the concentration of trihalomethanes in the water sample, evaluates the effectiveness of the disinfection process, and assess potential health risks associated with the presence of these compounds in drinking water, the four compounds are as follows

1.   Trichloromethane ($CHCl_3$)

2.   Bromodichloromethane ($CHBrCl$)

3.   Dibromochloromethane ($CHClBr_2$) and

4.   Tribromomethane ($CHBr_3$)

Table 4.4 shows the results of retention, peak area, concentration, and responses from the GC ECD test.

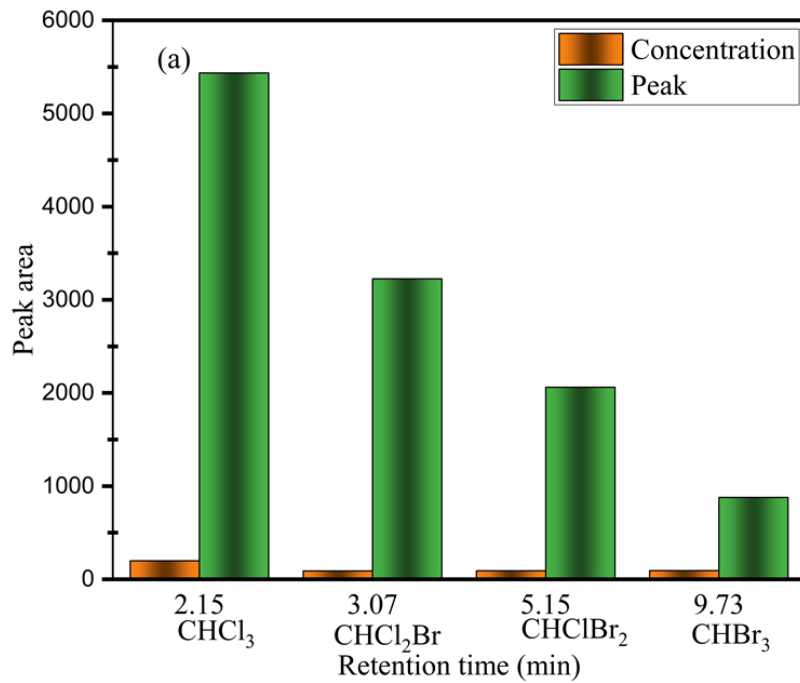| THMs	Retention time	Response factors	Peak	Concentration[ug/L]	
CHCl3	2.15 min	32.269	15660.969	485.321	485.321
CHCl2Br	3.07 min	29.171	1489.015	51.044	51.044
$CHClBr_2$	5.15 min	16.293	925.304	56.793	56.793
CHBr3	9.73 min	8.973	441.485	49.200	49.200

Figure 9 The peak areas and retention time of THMs compounds

Figure 9 displays the results from Table 2 Showing the peak area and concentration of four THMs species in drinking water treatment. From the result display, $CHCl_3$ at the retention of 2.15 mins the concentration of 322 (ug/L) was high and the peak was very high due to a few times reaction as the time increases the concentration of $CHCl_3$ decreased together with the peaks also decreased indicating very good linearity and better removal of the $CHCl_3$, $CHCl_2$, CHC_2Br, and $CHBr_3$ species in the water.
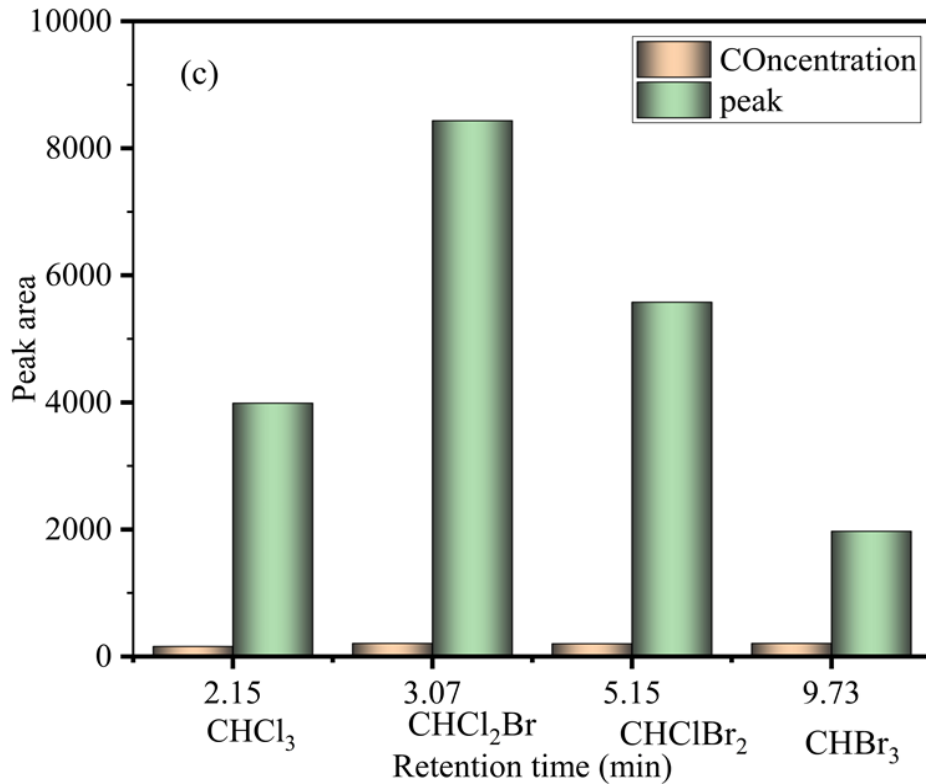
Figure 10. The peak area and retention time of THMs species in water

3.6 WATER QUALITY ANALYSIS

Table 3. Different water parameters and coagulants with Suzhou water treatment samples analysis

Water samples	Alum used	The volume of the water sample (ml)	Concentration (mg/L)	pH	TOP (10ml)	COD (10ml)	Conductivity
Raw water	$AlCl_3.2H_2O$	1200	20	7.07	1.433	0.052	7.355
influent	$FeSO_4$	1200	20	7.16	0.880	0.038	11.51
Effluent	Al_2SO_4	1200	20	7.32	0.121	0.025	63.70
Alkaline Wash	$AlCl_3$	1200	20	7.37	0.324	0.037	11.20
Acids wash	$FeCl_3$	1200	20	7.48	0.542	0.033	14.41

7. Conclusion

THM standards were made, and the peak height or peak area for each THMs component from the chromatogram was plotted as a function of concentration to provide calibration plots for the SCMS-GC-ECD method. For the detection of DBPs, the standard samples containing THMs. The standard curve of the chromatograph shows that the instrument is good for the test and the solute with accurate purity, pure methanol was prepared by weight volumetric methods in a clean laboratory at a room temperature of 20 C. The standard values of the concentration of the reference substance are prepared value and the

quantitative value is checked by the gas phase spectrum for the standard samples, and the measuring instrument meets the domain of the metrological properties.

The concentrations are 10 ppm,20 ppm,40 ppm, 80 ppm and 120 ppm retention time for four THMs standard samples are as follows 2.149,3,074,5.148 and 9.723. the result shows that the homogeneity conforms to the rule of the test and the stability is good. This retention time indicates the elution order and the relative retention time of the compounds during the gas chromatograph analysis, the elution order is determined by the interaction between the compounds and the stationary phase inside the GC Colum. In general, a lower retention time indicates the compound elutes earlier and has a higher volatility on the other hand higher retention time indicates that the compound elutes later and has a lower volatility. Therefore, the results suggest that trichloromethane (chloroform) is the most volatile compound and elutes earliest followed by Fluorobromomethane, dibromochloromethane, and finally bromoform which is the least volatile and elutes the latest

Fluorescent dissolved organic matter (FDOM) has been extensively characterized and tracked using fluorescence spectroscopy (EEM), using all of the wavelength-dependent fluorescence intensity data from EEMs quantitatively analyses, FDOM is one of the benefits of the FRI approach. It effectively captures the heterogeneity found in FDOM. Moreover, in comparison to other fractionation methods that take days to complete

The problem of oxidation by-products in drinking water sludge is a primary concern to everyone, because of the emergence of oxidation by-products pollutants in DWTP. TMMs and HAAs, at present, it is obvious that the chemical composition of the coagulant and organic matter from the source water must be effectively treated before discharge in the community. Treatment facilities must be regularly checked at least twice per month, to know the oxidation by-products level in the DWTP.

Agriculture, as well as domestic activities of the human population. As mentioned in the introduction, wastewater treatment plants have been identified as one of the main sources of organic pollution. Thus, much more effort should be made for the improvement of sludge water, and cleaning processes. The authors involved in the preparation of this Special Issue described the results of examinations, at a laboratory results, of the efficiency of chemical as well as physical processes for the removal or degradation of oxidation by-products and micro-pollutants. However, it should be noted that the extension of the proposed processes for technological scale requires intense additional studies.

Environmental studies, especially those concerning the determination of THMs, HAAs, and HBQF by-products, require effective treatment and concentration.

The reagents used for this purpose meet the requirements of WHO, EPA, and China standards, as well as

The issue seems to be proper for environmental studies as they are effective and environmentally friendly in environmental safety.

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