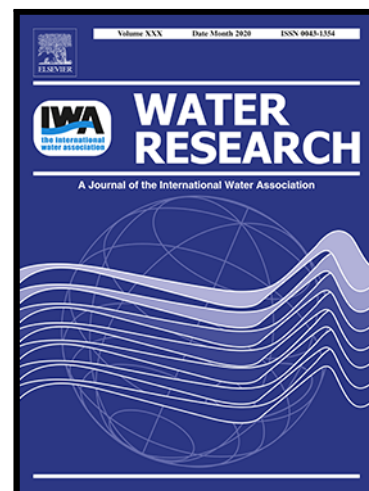


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Highlights

- Saturated and reduced tannins and lignin-like compounds enhance Al coagulation.
- High molecular weight and abundant carboxyl groups of DOM favors Al coagulation.
- Unsaturated and oxidized lipids, protein and carbohydrates inhibit Al coagulation.
- High polarity and low carboxylate content of DOM is unfavorable for Al coagulation.
- Al₁₃ removed molecules in a wider range of molecular weights than Al₀ and Al₃₀.

Unraveling the characteristics of dissolved organic matter removed by aluminum species based on FT-ICR MS analysis

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Abstract

Given the complexity of dissolved organic matter (DOM) and its interactions with coagulant chemicals, the mechanisms of removal by aluminum (Al) coagulants remains a significant unknown. In this study, six test waters containing DOM of different molecular weight (MW, <1 kda, 1-10 kda and >10 kda) and hydrophobicity (hydrophilic, transphilic and hydrophobic) were prepared and coagulated with Al₀, Al₁₃ and Al₃₀ chemicals. The molecular-level characteristics of DOM molecules that were removed or resistant to removal by Al species were analyzed using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The results showed that at the molecular level, saturated and reduced tannins and lignin-like compounds exhibited high coagulation efficiency because of their high molecular weight and abundant carboxyl groups. Unsaturated and oxidized lipids, protein-like, and carbohydrates compounds were relatively resistant to Al coagulation because of their higher polarity and lower content of carboxyl groups. For the test water matrices, transphilic DOM was more resistant to coagulation when compared to the test water containing hydrophilic DOM. Al₁₃ removed molecules across a wider range of molecular weights than Al₀ and Al₃₀, thus the DOC removal efficiency of Al₁₃ was the highest. This study furthers our understanding about the interactions of Al with DOM, and provides scientific insights on the operation of treatment plants to improve control of DOM.

Keywords: dissolved organic matter; Al species; coagulation; FT-ICR MS; PARAFAC

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analysis

1. Introduction

Dissolved organic matter (DOM) is a highly heterogeneous mixture that is ubiquitous in source water (Shi *et al.*, 2020; Wang *et al.*, 2018). It has been shown that DOM has negative impacts on water treatment processes and water quality, such as membrane fouling, taste and odor problems, and the formation of disinfection byproducts (Jiang *et al.*, 2020; Zhang *et al.*, 2003). As an important target substance in water treatment, DOM can be removed by a number of treatment processes, among which the most widely used and economically feasible process is coagulation (Sillanpää *et al.*, 2023). Aluminum (Al) salts have been the most commonly used coagulants in water treatment plants for DOM removal due to their effectiveness and relatively low cost (Berube *et al.*, 2013; Bratby, 2016; Ma *et al.*, 2022).

DOM is a complicated matrix composed of a variety of aliphatic and aromatic compounds. While the mechanism of DOM removal by aluminum-based coagulants has been investigated over many years (Leenheer *et al.*, 2003; Sillanpää *et al.*, 2023), there are still significant gaps in our understanding of coagulant-DOM interactions during the coagulation process. In previous studies, DOM characteristics, such as apparent molecular weight (MW) and hydrophobicity, have been commonly used to understand the effectiveness of Al species in removing DOM (Krzeminski *et al.*, 2019; Mikola *et al.*, 2013). These characteristics also serve as indicators for providing quick understanding about the treatability of the source water (Xiao *et al.*, 2016). The consensus of previous studies is that high molecular weight DOM is more readily removed by aluminum-based coagulants than low molecular weight DOM due to its relatively higher negative charge density (Korshin *et al.*, 2009; Szlachta *et al.*, 2009). In addition, hydrophobic DOM has been found to be more efficiently removed by coagulation than hydrophilic material. This is linked to the increased aromaticity of hydrophobic DOC, it having a higher specific colloidal charge and an increased potential for adsorption onto hydrophobic coagulant precipitates (Sharp *et al.*, 2006; Swietlik *et al.*, 2004). However, the study of Han *et al.* showed that the coagulation

efficiency of Al-based coagulants did not increase with the enhancement of DOM hydrophobicity, and the removal efficiency of hydrophobic base and hydrophobic neutral compounds was much lower than that of hydrophilic DOM (Han *et al.*, 2015). The inconsistent results of these studies suggest that MW and hydrophobicity are not absolute indicators of whether DOM can be removed by coagulation, and other characteristics of DOM besides MW and hydrophobicity affect the complexation of Al with DOM. Exploring the unknown characteristics of DOM that potentially control their removal by coagulation has important implications for the selection of water treatment processes and operational conditions in water plants.

In terms of molecular structure, aromatic compounds have been found to be effectively removed by aluminum-based coagulants, and carboxylic acid and phenolic sites are the two most important functional groups that control the binding of DOM and Al (Beggs *et al.*, 2011; Shi *et al.*, 2016). The difference in how DOM of different MW or hydrophobicity can be coagulated is considered to be related to these specific molecular structures and compositions, predominantly because these ionizable functional groups give charge to the compound (Lapointe *et al.*, 2021; Li *et al.*, 2021b). Various methods have been used in previous studies to try to characterize these aspects of DOM structure. Li *et al.* (2021b) investigated changes in DOM characteristics including Al-binding active sites (carboxyl and phenolic group) caused by pre-oxidation using ultraviolet/visible (UV/vis) spectroscopy (Li *et al.*, 2021a). However, this method is limited for characterizing the structure of molecules such as the type and number of functional groups. Santos *et al.* (2022) studied the molecular composition of DOM reacting with Al in hydromorphic podzols by Fourier Transform Infrared Spectroscopy (FTIR) and pyrolysis-gas chromatography-mass spectroscopy (Py-GC/MS) (Dos Santos *et al.*, 2022). Although these two combined methods can measure more types of functional group and specific molecular structure of DOM compared to UV/vis spectroscopy, pyrolysis product identification is dependent on a mass spectral library. Compounds containing nitrogen, oxygen, and sulfur are not widely characterized in these databases (De Aguiar *et al.*, 2022). In recent years, electrospray ionization coupled with fourier-transform ion cyclotron resonance mass spectrometry

(ESI FT-ICR MS) has been found to be a powerful tool for the determination of more detailed information on molecular characteristics of DOM, including the degree of saturation, as well as oxygen, sulfur and nitrogen content (Riedel *et al.*, 2012). The high resolution and mass resolving power of ESI FT-ICR MS allows for more comprehensive and accurate identification of DOM molecules (De Aguiar *et al.*, 2022).

Aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) and polymeric aluminum chloride (PACl) are widely used aluminum-based coagulants in coagulation processes (Yang *et al.*, 2010b). Al_a (monomeric species), Al_b (medium polymer species) and Al_c (colloidal or solid species) are the important Al species in aluminum-based coagulants (Chen *et al.*, 2018). The overall aim of this study was to therefore elucidate how individual DOM molecule characteristics control the ability of the compound to be removed by coagulation using different Al species. This was achieved using ESI FT-ICR MS, complemented with both three-dimensional excitation-emission matrices (3D-EEM) fluorescence spectroscopy and parallel factor analysis (PARAFAC). Concurrently, the molecular characteristics and removal profiles were aligned with DOM fractionation based on MW and hydrophobicity. This study furthers our understanding on the interactions between Al and DOM, and provides scientific insights on the operation of treatment plants to facilitate improved control of DOM.

2. Materials and methods

2.1. Isolation of DOM of different MW and hydrophobicity

DOM derived from wastewater was used to prepare test solutions containing organic matter of different characteristics. This approach was used because of the difficulty of directly separating different fractions of DOM from real drinking natural water sources at the appropriate concentration to then prepare test solutions. In addition, this allowed the research to explore the impact of wastewater derived DOM on drinking water treatment processes. This is important given that treated wastewater is routinely discharged into natural water that is then used as a source of drinking water. This approach also ensured that the background water quality was similar and enabled

effective comparability of FT-ICR MS test results. Further detailed reasoning for using municipal wastewater DOM are provided in **Section 1** of the **Supporting Information (SI)**. The wastewater was collected following coarse screening from a wastewater treatment plant in Beijing, China, and was filtered using a 0.45 μ m polyethersulfone membrane (PALL, Supor-450) to remove particles. **Table S1** displays the essential information on the primary wastewater quality.

The MW distribution of DOM was determined using Liquid Chromatography - Organic Carbon Detection (LC-OCD, DOC-LABOR, Germany), as shown in **Table S2**. Based on this data, three different test waters were prepared containing organic matter of different MW range: test water 1 (TW 1): <1 kDa, TW 2: 1-10 kDa, TW 3: >10 kDa. Another three test waters composed of DOM of different hydrophobicity were prepared following separation by resins: TW 4: hydrophilic, TW 5: transphilic, and TW 6: hydrophobic. The detailed DOM fractionation procedure is described in **Section 2** of the **SI**, and a schematic diagram is presented in **Fig. S2**. The six test waters were then stored at 4°C. Before coagulation, the dissolved organic carbon (DOC) of each test water sample was diluted to approximately 2.5 mg/L, and the pH was adjusted to 7.50 (± 0.03) using 0.1 M NaOH or HCl. **Table S3** provides information on the dilution factors and water quality indicators of the six test waters.

2.2. Preparation of Al₀, Al₁₃ and Al₃₀

Al₀, Al₁₃ and Al₃₀ represent Al_a (including low-polymeric Al), Al_b (including medium-polymeric Al) and Al_c (including sol or gel Al), respectively (Yan *et al.*, 2007). Al₀ and Al₁₃ are the common components in widely used Al coagulants and Al₃₀ has a great potential for application in coagulation in the future because of its superior performance when compared to Al₁₃ for the removal of arsenic, organic matter and microorganisms (Liu *et al.*, 2022). In order to comprehensively investigate the relationship between the DOM characteristics and the initial Al species, pure Al₀, Al₁₃ and Al₃₀ were prepared as coagulants, respectively. Al₀ was prepared from AlCl₃ (Macklin, China). Al₁₃ was prepared according to previously published methods (Wang *et al.*, 2019). In brief, under rapid stirring at 65°C, saturated NaHCO₃ was added into

0.2 M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ solution, resulting in PACl with an OH-/Al ratio of 2.2. The Al_{13} solution was then purified using Na_2SO_4 and BaCl_2 via precipitation/distillation. The Al_{30} solution was prepared by heating PACl solution with an OH-/Al ratio of 2.2 at 95°C for 48 hours under magnetic stirring, and then purified by precipitation/metathesis method after cooling to room temperature (Liu *et al.*, 2021). The content of Al_a , Al_b , and Al_c in these three solutions (**Table S4**) was determined by the Ferron timed complexometric colorimetric method (Xu *et al.*, 2003). The final total Al concentration for each of these Al_0 , Al_{13} , and Al_{30} solutions was 3.0 g/L.

2.3. Coagulation jar tests

Six test water samples with different fractions of DOM were coagulated with Al_0 , Al_{13} , and Al_{30} , respectively. In order to maintain consistency and simplify the experimental setup to focus on the analysis of DOM molecular structure, the coagulant dosage was set to $3.0 \text{ mg} \cdot \text{L}^{-1}$ (as Al) based on reference to an actual water treatment plant. The coagulation process was divided into three stages, including rapid mixing at 300 rpm for 1.5 minutes, intermediate mixing at 80 rpm for 11 minutes, and slow mixing at 40 rpm for 20 minutes, followed by a settling time of 20 minutes. Each set of experiments was performed in duplicate. The test waters and supernatant samples were filtered by $0.45 \mu\text{m}$ polyethersulfone membrane for DOC (TOC-VCPH, Shimadzu, Japan), 3D-EEM (F-4700, Thermo Fisher, USA) and ESI FT-ICR MS analysis (SolariX, Bruker, Germany).

2.4. ESI FT-ICR MS analysis

Bond Elut PPL solid phase extraction cartridges (1.0 g, 6 mL, Agilent, USA) were used to remove salt in solutions prior to ESI FT-ICR MS measurement (Dittmar *et al.*, 2008; Yuan *et al.*, 2017). The electrospray ionization was in negative ion mode and the test conditions were set as follows: the speed of continuous sampling was $120 \mu\text{L} \cdot \text{h}^{-1}$, capillary inlet voltage was 4.0 kV, ion accumulation time was 0.06 s, mass range was set between 100-800 Da, and data size was set to 4 M words. The signal-to-noise ratio (S/N) and dynamic range were enhanced by superimposing the time domain signal 300

times. The instrument was calibrated with $10 \text{ mmol} \cdot \text{L}^{-1}$ sodium formate before sample detection and the detected quality errors of the assays were less than 1 ppm after calibration. Internal standard calibration was done using a deuterated stearic acid ($\text{C}_{18}\text{D}_{35}\text{H}_1\text{O}_2$, 10^{-5} mol/L). In this study, the majority of peaks contained C, H, O, N, S elements, while compounds with P and Cl were excluded because of their low detection levels ($<0.5\%$). The stoichiometric ranges used to establish the boundaries of the classification and the equations for relevant parameters are described in **Section 3** and **Section 4** of the SI (Geng *et al.*, 2018; Kellerman *et al.*, 2014).

2.5. 3D-EEM and PARAFAC analysis modeling

The excitation (E_x) and emission (E_m) wavelengths were 200-400 nm and 220-550nm, respectively, with wavelength steps of 5nm. The scan slit and speed for E_x and E_m were 5 nm and 60,000 nm/min, respectively. Photomultiplier detector voltage was fixed at 700 V. Before EEM measurement, the UV_{254} values of water samples (UV-6100, MAPADA, Shanghai) were all confirmed to be lower than 0.05 cm^{-1} to avoid any inner filter effect (Maqbool *et al.*, 2022). The EEM of Milli-Q water blank was subtracted from each sample's EEM. The PARAFAC modelling was applied on combined EEMs ($n = 42$) of 6 test waters and 36 supernatant samples. This modelling was performed using the DOMFlour toolbox in Matlab R2018a (Stedmon *et al.*, 2008).

2.6. Statistical analysis

Correlation analysis was applied to study the correlation between DOC, fluorescence intensity and DOM characteristics using IBM SPSS 25.

3. Results and Discussion

3.1. DOC removal rate of different DOMs

The DOC removal of different MW and hydrophobic DOM after coagulation with the three Al salts are shown in **Fig. 1**. According to **Fig. 1(a)**, the removal rate of DOC exhibited an obvious increasing trend with MW. This result is consistent with previous studies, which suggested that organic compounds of higher MW were more easily

removed by adsorption and/or sweep coagulation onto hydroxide precipitates under alkaline pH conditions (Korshin *et al.*, 2009; Siélichi *et al.*, 2008). **Figure 1(b)** demonstrates that the DOC removal rate of hydrophilic DOM was slightly higher than that of hydrophobic DOM, and the removal rate of DOC for transphilic DOM was the lowest. However, this result contradicts previous studies, which indicated that organic compounds of stronger hydrophobicity were more easily removed through Al coagulation due to their enrichment in aromatic carbons, phenolic structures, and conjugated double bonds that contribute to the negative charge of water (Finkbeiner *et al.*, 2020; Mallya *et al.*, 2023). Wang *et al.* (2013) found a high positive correlation between the percentage of hydrophobic and high MW fractions and their removal by coagulation for 13 source waters in China (Wang *et al.*, 2013). However, in this study, there was no correlation between the DOC removal rates and the DOM material that was isolated according to MW and hydrophobicity. Further exploration of DOM molecular structures was therefore carried out to develop a deeper understanding of the interaction and complexation of Al coagulants with DOM. Furthermore, even though Al₁₃ exhibited the highest removal rate (40%) for DOM with MW > 10 kDa, 60% of the molecules remained in solution and were not removed. Investigating the structures of resistant DOM molecules is also essential for optimizing water treatment efficiency.

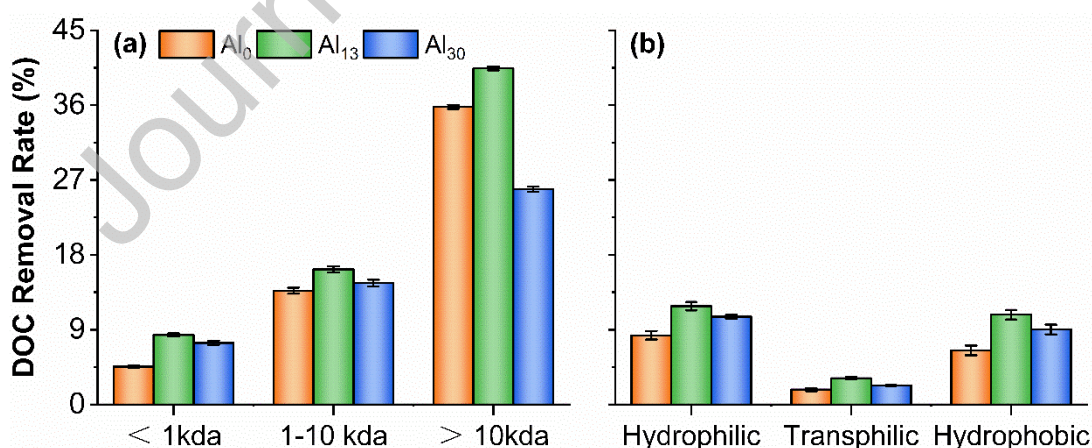


Fig. 1 DOC of six test waters before and after coagulation with Al₀, Al₁₃ and Al₃₀ (a: DOM isolated by MW; b: DOM isolated by hydrophobicity).

3.2. NOSC and (DBE-O)/C distribution of removed DOM molecules

For these six test waters, the DOC removal rates of Al₀, Al₁₃ and Al₃₀ were

significantly positively correlated (**Table S5**), indicating that the organic matter removal trends of three Al species were similar. This result was similar to our published study on the formation mechanism of organically-bound Al, which found a significant negative correlation between DOC removal efficiency and organically-bound Al concentration (He *et al.*, 2024). Consistent with the analytical approach of this published study, in order to investigate the removability of organic molecules during coagulation at the molecular level, the four test waters (TW 1, TW 3, TW 4 and TW 5) with higher and lower DOC removal rates (as shown in **Fig. 1**), and the supernatants after coagulation with Al₀, Al₁₃, and Al₃₀ were selected for FT-ICR MS analysis. Since the coagulation process does not involve the transformation of organic matter, there are no newly generated organic molecules formed during coagulation (Wu *et al.*, 2007). As listed in **Table S6**, organic molecules of different molecular compositions (CHO, CHNO, CHOS, CHNOS) in the four test waters could be partially removed by Al₀, Al₁₃ and Al₃₀.

Double bond equivalents minus oxygen per carbon ((DBE-O)/C) and nominal oxidation state of carbon (NOSC) are commonly used to reflect the degree of unsaturation and redox state of molecules, respectively (Brooker *et al.*, 2018; Phungsai *et al.*, 2018). More detailed information of (DBE-O)/C and NOSC can be found in **Section 4** of the SI. The (DBE-O)/C value can be used to compare the degree of unsaturation provided by the oxygen-containing functional groups and the carbon skeleton. More positive values of (DBE-O)/C indicate a higher degree of unsaturation provided by the carbon skeleton, instead of unsaturation provided by oxygen-containing functional groups. Positive and negative values of NOSC represent oxidized and reduced states, respectively. The molecules are usually classified into four compounds groups based on the (DBE-O)/C and NOSC values: unsaturated and oxidized compounds ((DBE-O)/C>0) and NOSC>0), unsaturated and reduced compounds ((DBE-O)/C>0) and NOSC<0), saturated and reduced compounds ((DBE-O)/C<0) and NOSC<0), and saturated and oxidized compounds ((DBE-O)/C<0) and NOSC>0) (Yu *et al.*, 2022). **Figure 2(a)** depicts the NOSC and (DBE-O)/C diagram of organic molecules with different molecular compositions removed by Al₀, Al₁₃ and Al₃₀, and

the horizontal and vertical curves outside the frame represent changes in the number of molecules. It can be seen that the molecules removed by Al_0 , Al_{13} and Al_{30} exhibited similar characteristics. For removed molecules composed of CHO, CHOS, CHNO and CHNOS elements, they were mainly characterized as being saturated and reduced compounds. In addition, the proportion of the frequency of these removed molecules in different test waters was also different. Statistical analysis showed that for Al_0 , Al_{13} and Al_{30} , the proportion of the removed saturated and reduced compounds composed of CHO, CHOS, CHNO and CHNOS was significantly positively correlated with the DOC removal rate (**Fig. 2(b)**). These results indicate that saturated and reduced compounds were more likely to be removed by Al coagulation.

Negative values of (DBE-O)/C indicate that oxygen-containing functional groups provide more unsaturation than the carbon skeleton (Ma *et al.*, 2022). The carboxyl group is known to be an important functional group for the complexation of organic matter with Al (Provenzano *et al.*, 2004). Song *et al.* (2019) investigated the effect of the number of carboxyl groups on the coagulation efficiency and found that a higher number of carboxyl groups was more beneficial for Al coagulation because more complexes could be formed between the carboxyl groups and hydrolyzed Al (Song *et al.*, 2019). NOSC can also be seen as an indicator of polarity, with low NOSC values representing poor polarity and solubility, which is beneficial to coagulation (Jennings *et al.*, 2022). Yu *et al.* (2022) studied the changing pattern of DOM during Al flocs aging and suggested that Al flocs prefer to absorb reduced and saturated NOM, which was consistent with this study. **Figure S3** shows that the proportion of saturated and reduced compounds in four test waters, with the opposite trend to DOC removal rate. Saturated and reduced compounds contents were highest and lowest in >10kda and transphilic test waters, resulting in highest and lowest DOC removal rate, respectively.

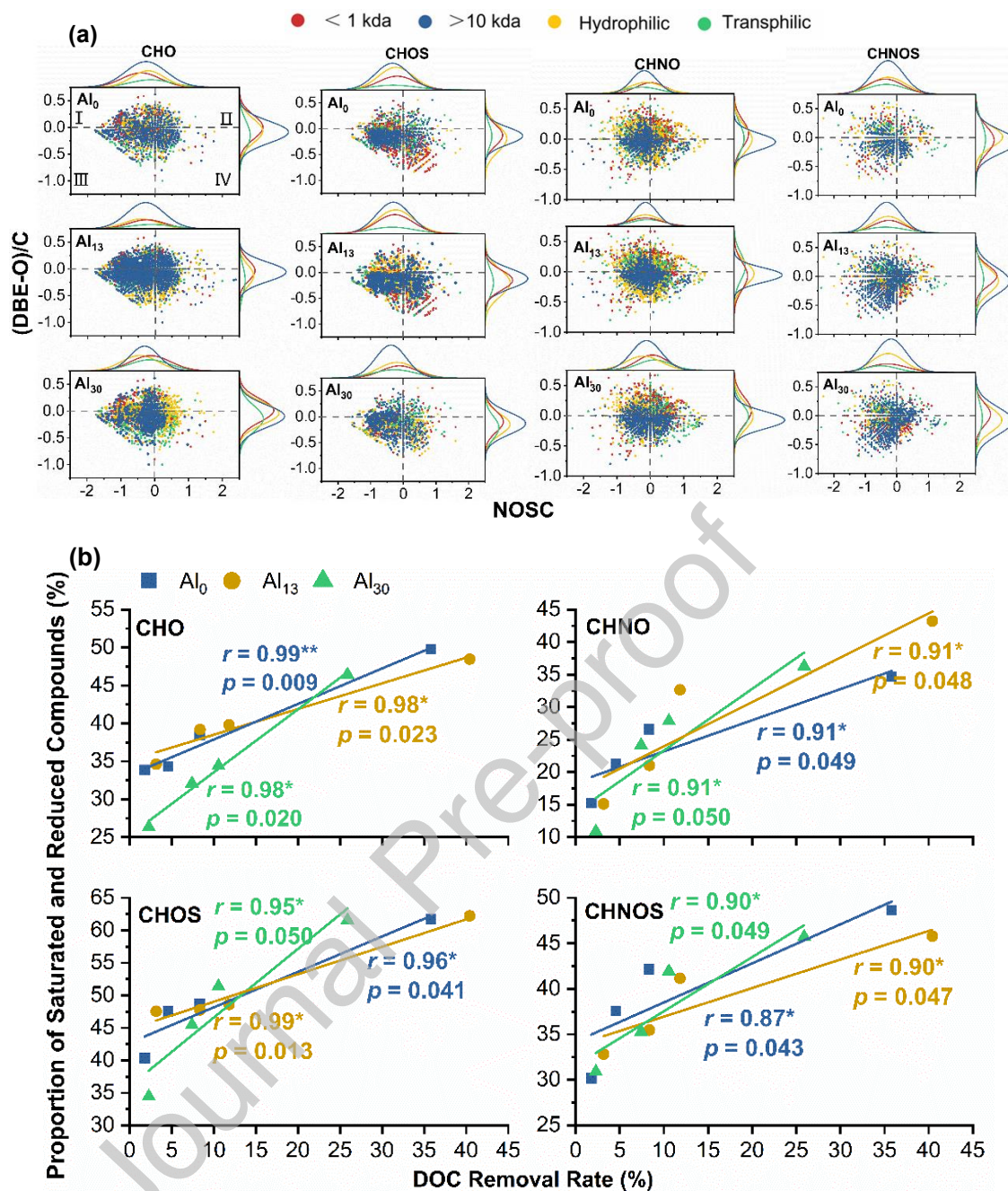


Fig.2 (a) NOSC vs. (DBE-O)/C diagram of removed molecules, and (b) correlation between the proportion of the saturated and reduced compounds and the removal rate of DOC. The four compounds were I: unsaturated and reduced compounds, II: unsaturated and oxidized compounds, III: saturated and reduced compounds, and IV: saturated and oxidized compounds. The curves outside the frame represented changes in the number of molecules. The proportion was calculated by dividing the number of molecules of saturated and reduced compounds by the total number of removed molecules.

3.3. NOSC and (DBE-O)/C distribution of DOM molecules resistant to coagulation

In this study, the DOC removal rates were lower than 50% (**Fig. 1**), indicating that the test water contained a large number of molecules resistant to coagulation by Al_0 , Al_{13} and Al_{30} . Exploring the characteristics of resistant molecules is beneficial for improving the coagulation efficiency of aluminum-based coagulants. **Figure 3(a)** shows the NOSC and (DBE-O)/C distribution of the resistant molecules and they are concentrated in the regions of $\text{NOSC} > 0$ and $(\text{DBE-O})/\text{C} > 0$, which are unsaturated and oxidized compounds. Pearson correlation analysis verified that the proportion of unsaturated and oxidized substances was significantly negatively correlated with the DOC removal rate as depicted in **Fig. 3(b)**. This result indicates that when the test water contains a large amount of unsaturated and oxidized organic compounds, it is difficult to be removed by aluminum-based coagulants. Yu *et al.* (2022) also found that unsaturated and oxidized DOM were released from Al flocs during aging, suggesting that the complexation of Al with unsaturated and oxidized DOM was unstable (Yu *et al.*, 2022). In this study, the transphilic test water contained more unsaturated and oxidized compounds than the hydrophilic test water (**Fig. S4**), resulting in lower DOC removal of transphilic organic matter than was seen for hydrophilic organic matter. These results infer that for the coagulation process, the treatability of organic matter in the source water is better related to the molecular properties of the organic compounds, rather than being predicted by bulk parameters such as the apparent MW or hydrophobicity. Although appropriately increasing the Al salt dosage could increase the floc size and the sweeping flocculation, which may be favorable to increase the potential for removal of DOM, it was expected that the preference for different types of DOMs would remain the same (Fusheng *et al.*, 2008; Li *et al.*, 2003; Sillanpää *et al.*, 2014). Fe-based coagulants have been reported to be more able to remove unsaturated and oxidized DOM, while ozonation can transform unsaturated DOM into saturated species (Pan *et al.*, 2023; Wu *et al.*, 2022). Though pre-ozonation may increase the oxidized DOMs, Al-based coagulants are more efficient at removing saturated and oxidized DOMs than unsaturated and oxidized DOMs. Therefore, utilisation of Al-Fe

composite coagulants or pre-ozonation processes prior to the coagulation process could be used to improve the removal efficiency of unsaturated and oxidized compounds that are resistant to coagulation.

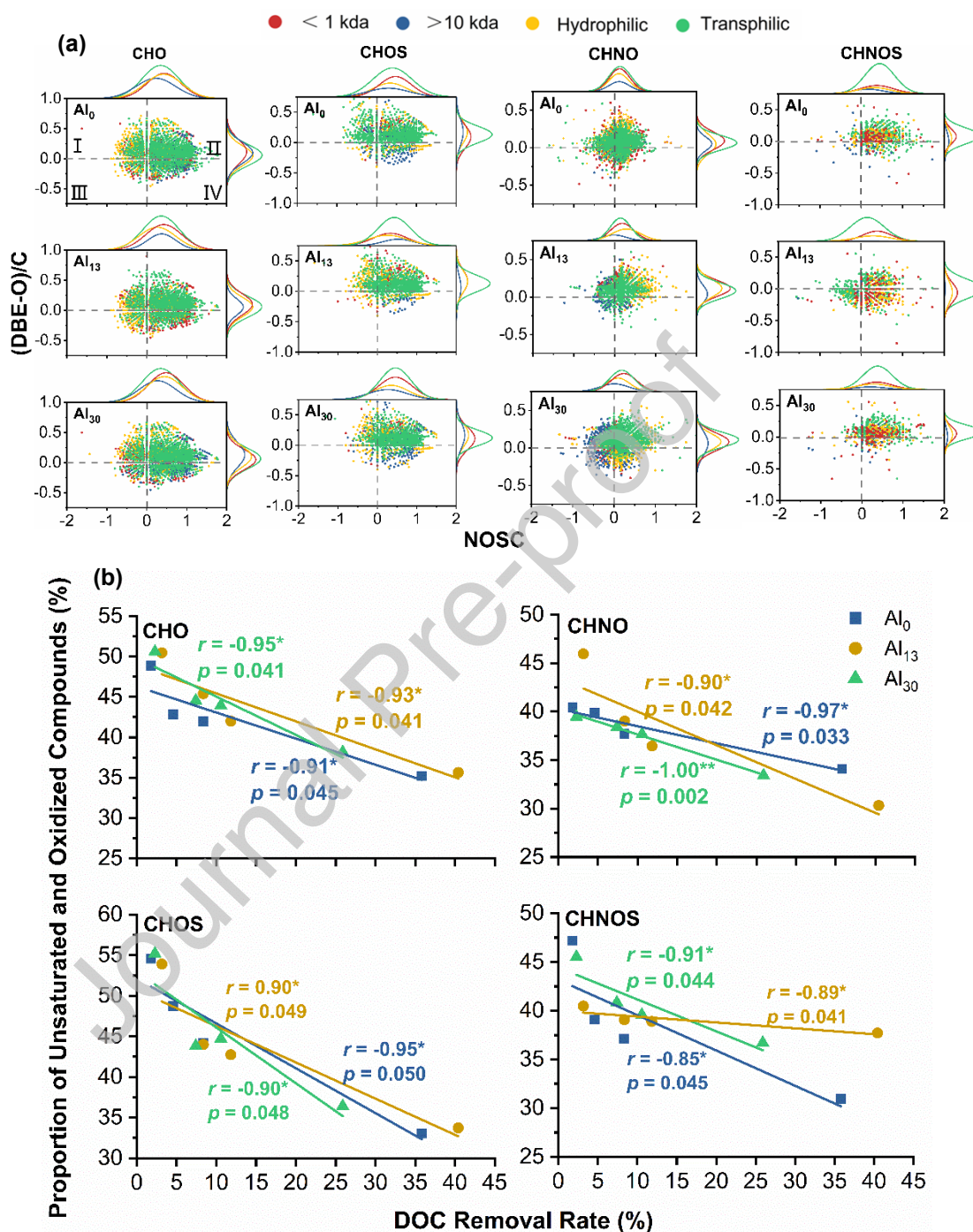


Fig. 3 (a) NOSC vs. (DBE-O)/C diagram of resistant molecules, and (b) correlation between the proportion of the unsaturated and oxidized compounds and the removal rate of DOC.

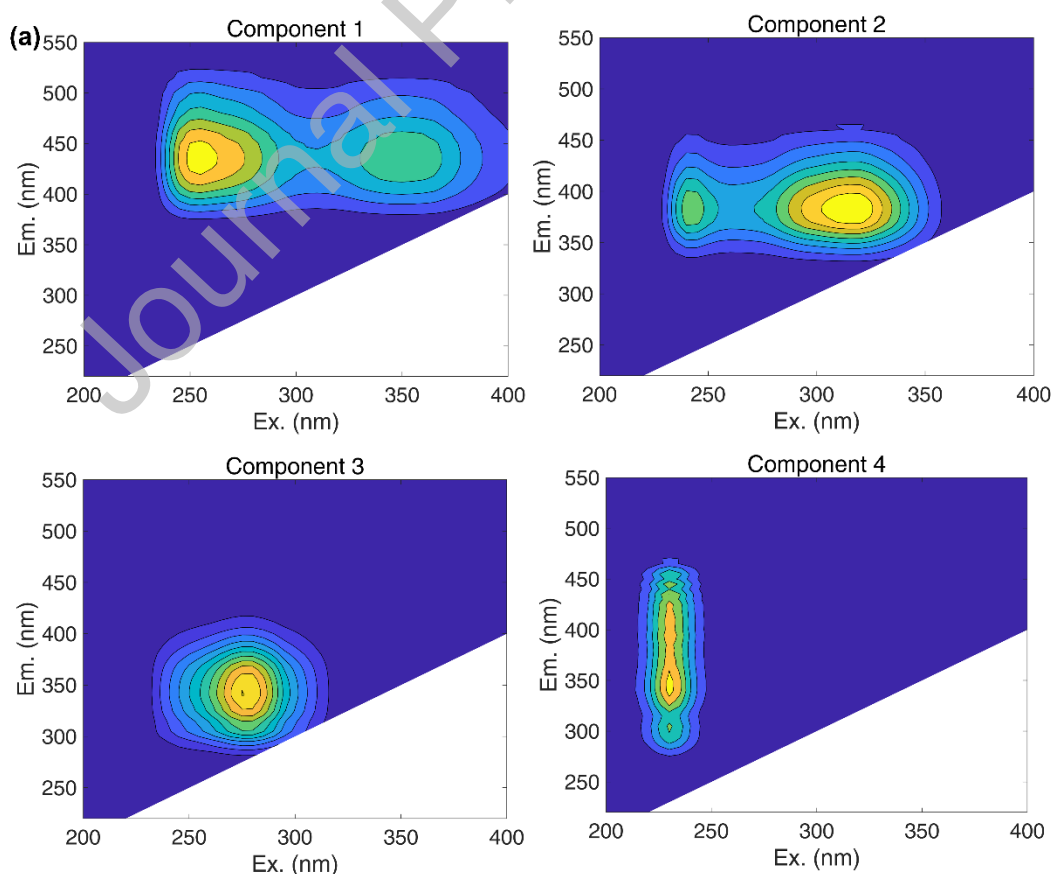
3.4. Comparison of DOM that removable and resistant to coagulation

3D-EEM was combined with PARAFAC to qualitatively analyze the main DOM components contributing to the overall fluorescence of the samples (Henderson *et al.*, 2009; Oloibiri *et al.*, 2017). In this study, four major DOM components were distinguished by PARAFAC analysis. These were C1, C2: humic- and fulvic-like compounds, C3: microbial by-product-like compounds, C4: protein- and fulvic-like compounds (detailed PARAFAC results are shown in **Fig. 4(a)** and **Table S7**). The fluorescence intensities of four components before and after coagulation and their corresponding removal rates are shown in **Fig. S5** and **Fig. S6**. All four components were partially removed by the aluminum-based coagulants, with the humic- and fulvic-like compounds being the most efficiently removed. Pearson correlation analysis (**Fig. 4(b)**) showed that the DOC removal rate of the six test waters after coagulation with Al₀, Al₁₃ and Al₃₀ had a significant positive correlation with the content of humic- or fulvic-like compounds in the test waters, and a non-significant negative correlation with the content of microbial by-product-like and protein-like compounds. This result suggests that humic- or fulvic- like compounds were more favorable to Al coagulation than protein- and microbial by-product-like compounds.

This result was consistent with the FT-ICR MS analysis. It can be clearly seen in **Fig. 5(a)** that removed molecules were mainly lignins and tannins compounds, and resistant compounds were mainly lipids, protein-like and carbohydrates compounds. Lignins compounds have been shown to have similar structures to humic acids (Bao *et al.*, 2018). Many previous studies reported that tyrosine- and tryptophan-like protein compounds were more resistant than humic- and fulvic-like compounds during coagulation because of their higher polarity (Jathan *et al.*, 2023; Wang *et al.*, 2021). Humic acids have relatively high molecular weights and are consisting of abundant phenol, quinone, carboxyl, alcohol and sugar groups (Kleinhempel, 1970). The deprotonated carboxyl group of the HA molecule was considered to be the main bonding site for aluminum species under neutral pH conditions (Tan *et al.*, 2019). The Kendrick mass defect (KMD(COO)) analysis clearly demonstrated the difference in the structure of the molecules that were removed and resistant to coagulation (**Fig. 5(b)**). Compounds that

differ only by a carboxyl group are presented on the same horizontal line. The removed saturated and reduced compounds were mainly distributed in the right side of the KMD plot, indicating that removed molecules had a higher molecular weight and contained more carboxyl groups than the resistant molecules. Therefore, for aluminum-based coagulants, saturated and reduced compounds with high molecular weight and abundant carboxyl groups are the important compounds that affect the coagulation efficiency (being more favourably removed).

It is well known that pH is an important factor affecting the hydrolysis of Al salts and the characteristics of DOM (Sillanpää *et al.*, 2018), but the experimental conditions in this study were pH 7.5. The effect of pH on the structure of removed and resistant DOM molecules of Al-based coagulants needs to be further investigated in the future. In addition, it is still unknown whether higher dosages of Al-based coagulants can remove the resistant unsaturated and oxidized DOMs. Therefore, the effect of dosage of Al-based coagulants on the removal efficiency of resistant DOMs also need to be taken into account in the future.



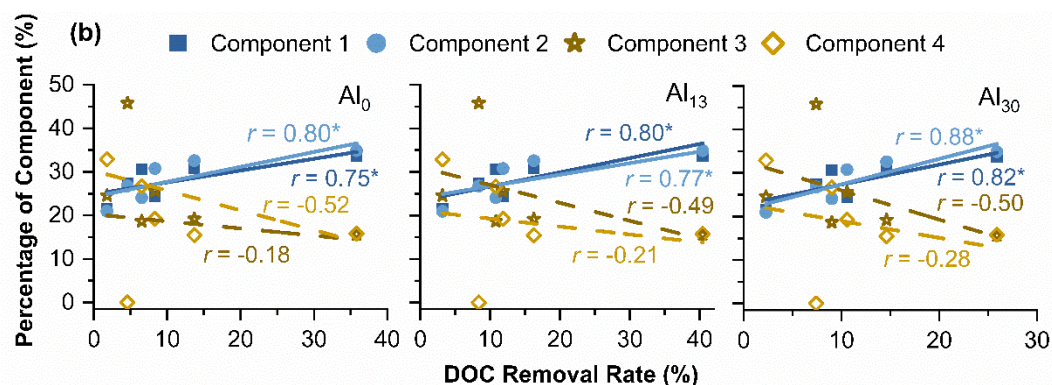


Fig.4 (a) EEMs of four PARAFAC components and (b) correlation between the percentage of four components in six test waters and the DOC removal rate.

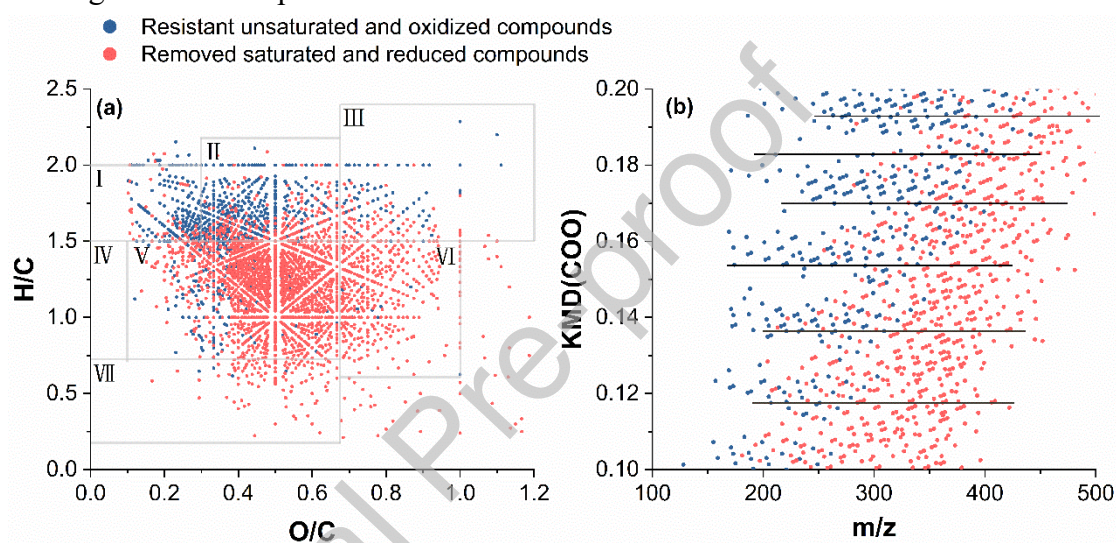


Fig.5 (a) van Krevelen diagrams of DOM molecule distribution in test waters, and (b) Kendrick mass defect (KMD(COO)) analysis of saturated and reduced compounds, and saturated and oxidized compounds. I: lipids, II: protein-like, III: carbohydrates, IV: unsaturated hydrocarbons, V: lignins, VI: tannins and VII: aromatic structures. Molecules at the same horizontal line differ by a number of carboxyl groups.

3.5 Difference in coagulation performance between Al₀, Al₁₃ and Al₃₀

The DOC removal from all six test waters following Al₁₃ coagulation were higher than those of Al₀ and Al₃₀ (**Fig. 1**), showing that Al₁₃ was the most advantageous Al species for the removal of DOM, a result consistent with previous studies (Li *et al.*, 2017; Zhang *et al.*, 2021). Given that the Al₀, Al₁₃ and Al₃₀ showed the greatest difference in removal of >10 kDa DOM, the following analysis focused on the characteristics of the removed molecules in the >10 kDa DOM range. The Kendrick

mass defect (KMD) analysis was applied to compare the differences in the composition of molecules for CHO, CHNO and CHOS removed by Al_0 , Al_{13} and Al_{30} . The KMD(CH_2) and NKM(CH_2) plots show the distribution of CH_2 -homologous molecules that are on the same horizontal line (Lv *et al.*, 2016). For molecules composed of CHO, CHNO and CHOS, Al_0 mainly removed the smaller and larger molecular weight homologues, Al_{30} removed the larger molecular weight homologues, and Al_{13} removed the small, intermediate molecular and large molecular weight homologues (**Fig. 6**). Jiao *et al.* (2015) reported that under neutral conditions and high dosage, the coagulation mechanism of Al_0 was mainly sweep flocculation, entrapment and adsorption, while that of Al_{13} was primarily charge neutralization, and that of Al_{30} was predominantly sweep flocculation (Jiao *et al.*, 2015). DOM with low MW can be removed by phenolic hydroxyl absorption on the surface of colloidal $Al(OH)_3$ formed by *in situ* hydrolysis of Al_0 (Xiong *et al.*, 2018). Sweep flocculation was effective for removal of larger molecules and particles (Yang *et al.*, 2010a). For Al_{13} , its superior performance was attributed to: 1) its high positive charge; 2) its ability to bind strongly within aggregates, and 3) being insensitive to hydrolysis before adsorption to the particle surface (Hu *et al.*, 2006). It is therefore beneficial to increase the content of Al_{13} in aluminum-based coagulants for DOM removal during coagulation processes.

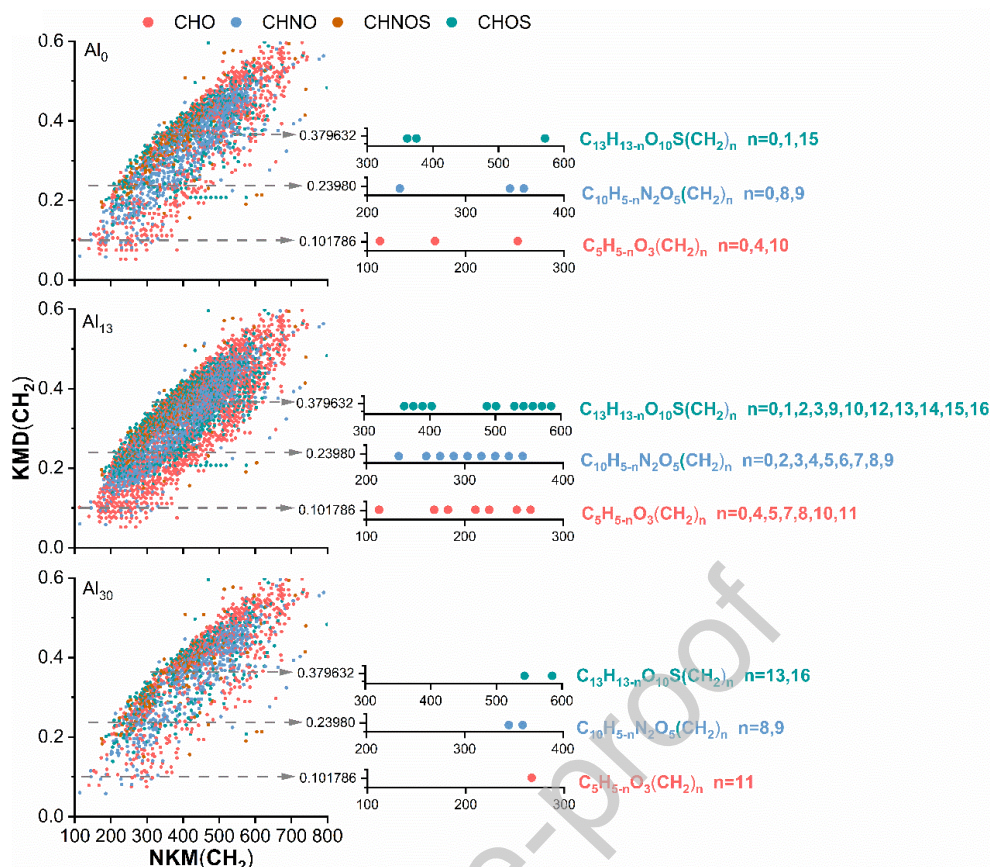


Fig. 6 The Kendrick mass defect (KMD(CH₂)) of molecules removed after coagulation for >10 kDa DOM for Al₀, Al₁₃ and Al₃₀.

4. Conclusions

In this study, we prepared six test waters containing DOM of different MW (<1 kDa, 1-10 kDa and >10 kDa) and hydrophobicity (hydrophilic, transphilic and hydrophobic). Pure Al₀, Al₁₃ and Al₃₀ coagulants were prepared as coagulants to treat the test waters. ESI FT-ICR MS, complemented by 3D-EEM and PARAFAC analysis, was used to investigate the characteristics of DOM molecules which were removable or resistant to Al₀, Al₁₃ and Al₃₀ coagulation to provide information beyond MW and hydrophobicity. The following conclusions were drawn:

- (1) The DOC removal rate of aluminum-based coagulants increased with the increase in MW, however for the organic compounds investigated here, there was no significant relationship with removal and the hydrophobicity of the DOM. For coagulation, hydrophobicity based on separation by resin fractionation was not a reliable index for assessing the treatability of the test water.

- (2) The analysis of molecular characteristics using ESI FT-ICR MS revealed that the DOM removed by aluminum-based coagulants was mainly composed of reduced tannins and lignin-like compounds with high carbon skeleton saturation. The molecules resistant to coagulation were mainly oxidized lipids, as well as protein-like and carbohydrate compounds with high carbon skeleton unsaturation. PARAFAC analysis showed that humic- and fulvic-like compounds, which were structurally similar to lignin-like compounds, were more favorable for coagulation than protein and microbial byproduct-like compounds. The removed molecules had larger molecular weights and contained more carboxyl groups, whereas the resistant molecules had fewer carboxyl sites complexing with the Al species.
- (3) Al₁₃ was significantly more effective than Al₀ and Al₃₀ for the removal of the above-mentioned removable DOM. Al₀ mainly removed the smaller and larger molecular weight homologues, Al₃₀ removed the larger molecular weight homologues, and Al₁₃ could additionally remove some of the intermediate molecular weight homologues.

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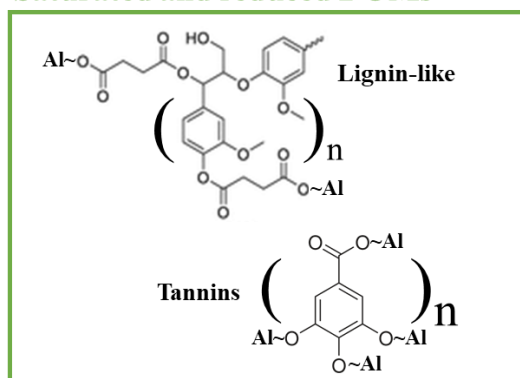
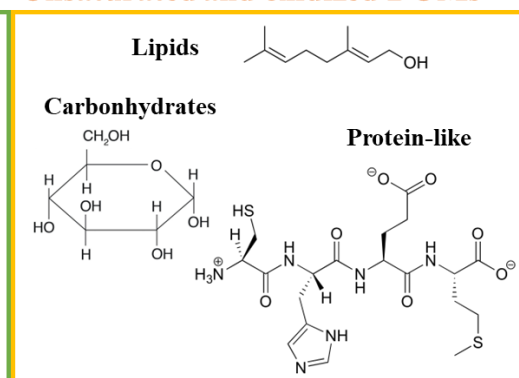
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Graphical abstract

Saturated and reduced DOMs**Removed compounds****Unsaturated and oxidized DOMs****Resistant compounds****Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



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Unraveling the characteristics of dissolved organic matter removed by aluminum species based on FT-ICR MS analysis

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