
Enhancing floc growth by oxidative and reductive modification of organic matter structure

Baofeng Zhu ^{a,b,1}, Mengjie Liu ^{b,*}, Kai Zhang ^b, Nigel Graham ^c, Wenzheng Yu ^{a,b,*}

^a School of Water Conservancy and Environment, University of Jinan, Jinan 250022, China

^b Key Laboratory of Drinking Water Science and Technology, Research Centre for Eco-Environmental Sciences (RCEES), Chinese Academy of Sciences, Beijing 100085, China
(wzyu@rcees.ac.cn)

^c Department of Civil and Environmental Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom

¹ This work is finished at RCEES, Chinese Academy of Sciences

Abstract: Coagulation is a critical process in drinking water treatment for removing contaminants, but its efficiency is challenged by complex natural organic matter (NOM) and emerging micropollutants. Conventional strategies (e.g., enhanced coagulation and novel coagulants) overlook the role of NOM characteristics in floc formation. Existing studies lack systematic evaluation of how chemical preconditioning (oxidation/reduction) modifies NOM functional groups and influences floc dynamics, particularly regarding molecular-scale mechanisms and water matrix effects. This study comparatively evaluates hypochlorite (NaClO), hydrogen peroxide (H₂O₂), and sodium borohydride (NaBH₄) pretreatments for NOM modification and their impacts on floc growth during coagulation. It was found that while NaClO (0.2–4 mg/L) reduced molecular weight and increased hydrophilicity, it consistently enhanced floc size (up to 44%) by hydroxylating aromatic NOM. H₂O₂ exhibited a biphasic effect, and floc size improved at low doses (1 mg/L) but declined at high doses (>4 mg/L) due to excessive carboxyl group formation, inducing electrostatic repulsion. NaBH₄ (50–100 mg/L) promoted floc growth by reducing carbonyl to hydroxyl groups, though high doses (>100 mg/L) reduced efficacy due to borate interference. This work establishes molecular-level mechanisms for NOM-coagulant interactions, highlights the essential role of hydroxyl groups on floc formation, and provides a scientific basis for optimizing pretreatment-coagulation sequences tailored to specific water quality.

Keywords: Coagulation; Organic matter; Oxidation; Reduction; Functional groups

1 Introduction

Coagulation remains one of the most critical and widely adopted processes in drinking water treatment plants (DWTPs), serving as the primary barrier for removing suspended colloids, natural organic matter (NOM), and microbial pathogens (Cai et al., 2022; Deng et al., 2024; Peydayesh et al., 2021; Shirakawa et al., 2022; Zhang et al., 2021). Therefore, its efficiency directly determines the performance of subsequent processes such as sedimentation, filtration, and disinfection (Deng et al., 2019; Müller et al., 2019; Yu et al., 2016). Contemporary coagulation practices predominantly employ trivalent metal salts (e.g., aluminum and iron-based coagulants) (Guo et al., 2022; Lin et al., 2014; Yang et al., 2023; Yang et al., 2025), which hydrolysis in water and generate precipitates to absorb the impurities in water, and then aggregate to form large flocs that are separated from water in the following sedimentation process (Zhang et al., 2021). Hence, the dynamic processes of floc formation, including aggregation, breakage, and re-growth, are critical determinants of coagulation performance (Gonzalez-Torres et al., 2014; Song et al., 2023), as larger, denser flocs not only enhance organic matter entrapment but also improve settleability, reducing sludge volumes and operational burdens (Vahedi and Gorczyca, 2014).

The efficacy of conventional coagulation faces great challenges due to the increasing complexity of water sources, driven by climate change impacts and escalating anthropogenic pollution (Kim et al., 2025; Xiao et al., 2013). Particularly problematic is the limited removal efficiency (typically 10-30%) for dissolved NOM as well as the poorly settleable flocs (Cheng et al., 2025). To address these challenges, two principal strategies have been proposed. The first

one is to enhance coagulation through operational optimization (e.g., pH adjustment and coagulant dosing), as advocated by the U.S. EPA (Edzwald and Tobiasson, 1999; Ho and Newcombe, 2005); The second one is to develop novel coagulant with enhanced NOM affinity (Jarvis et al., 2012; Wang et al., 2016; Yang et al., 2025).

While these approaches have yielded significant improvements (Jarvis et al., 2012; Xia et al., 2024; Zhao et al., 2016), a critical component in the coagulation process, the NOM itself, has been overlooked in past studies. Emerging evidence suggests that the functional group composition (e.g., carboxyl, hydroxyl, and aromatic moieties), hydrophobicity, and molecular weight distribution of organic matter fundamentally govern its interactions with metal coagulants (Liu et al., 2024a; Zhang et al., 2021). This molecular-scale understanding challenges traditional macroscopic coagulation paradigms and raises important questions about whether intentional NOM modification through pretreatment could optimize subsequent coagulation. Although some studies have explored pretreatment-coagulation synergies (Qi et al., 2016b; Zhou et al., 2024), systematic investigations remain scarce, particularly regarding the comparative evaluation of different chemical pathways on NOM modification and their cascading effects on floc dynamics.

Among various chemical pathways, pre-oxidation is currently the most common method for enhancing coagulation, as it requires no changes to existing treatment processes in DWTPs. A variety of oxidants are employed in DWTPs to oxidize organic compounds, including ozone, chlorine dioxide (ClO_2), hydrogen peroxide (H_2O_2), sodium hypochlorite (NaClO), potassium permanganate (KMnO_4), and ferric chloride (FeCl_3) (Lin et al., 2021). Ozone is a widely used

oxidant in water treatment (Xu et al., 2025); however, recent studies suggest that it primarily increases the saturation degree rather than the oxidative degree of molecules (Liu et al., 2022), which may adversely affect coagulation efficiency, as the coagulation process preferentially, removes aromatic components. KMnO_4 offers a dual function of oxidation and coagulation in removing dissolved organic matter (DOM) (Lin et al., 2021), but the color of the treated water may be affected by residual manganese ions. NaClO , which is recognized for its strong oxidative properties, is extensively applied in DWTPs (Cao et al., 2023). H_2O_2 , a versatile and environmentally friendly oxidant, decomposes into water and oxygen without causing secondary pollution (Chen et al., 2025), and is widely used in environmental, chemical, and other industries. These oxidants exhibit selective reactivity toward electron-rich moieties in NOM, such as phenolic, amino, and olefin groups, and can alter the physical/chemical properties of NOM, or even mineralize it.

Beyond oxidative pretreatment, advanced reduction processes (ARPs) have drawn widespread interest for their remarkable efficiency and high selectivity in reducing various oxidized inorganic and halogenated organic compounds over the past decade (Anh Phan et al., 2024; Ji et al., 2025). Among versatile reductants, sodium borohydride (NaBH_4) is widely used in laboratory analyses (Akin and Şahin, 2025; Ozdemir and Unlu, 2025), and has gained increasing attention in practice due to its strong reduction potential and high efficiency. Nevertheless, research on whether reductants can enhance coagulation, and specifically on the mechanisms that explain how reductants affect coagulation, has not yet been thoroughly conducted.

Based on the above discussion, this study adopted three pre-treatment processes, including one strong oxidation process using NaClO, one moderate oxidation process using H₂O₂, and a reduction process using NaBH₄, to evaluate comparatively their impacts on floc formation dynamics during the coagulation of representative surface water and standard humic acid solution. Using advanced analytical techniques (FTIR, XPS, HPSEC, contact angle measurement) coupled with real-time floc monitoring (PDA), we elucidate how each pretreatment modifies NOM characteristics and subsequently influences floc development. The result of this study provides novel insights into the molecular-level mechanisms governing NOM-coagulant interactions and establishes a scientific foundation for optimizing pretreatment-coagulation sequences. The findings have important practical implications for developing targeted pretreatment strategies tailored to specific water quality characteristics. Furthermore, the systematic comparison of different pathways advances our fundamental understanding of structure-activity relationships in aquatic organic matter, with potential applications beyond coagulation processes.

2 Materials and Methods

2.1 Source water and materials

The source water used for drinking water treatment was collected from the Jingmi River in Beijing, China. This river serves as a water source for industrial production, agricultural irrigation, and domestic use. In addition, to verify the generalizability of the experimental results, a standard humic acid (HA) solution was prepared by adding commercial humic acid powder (Aldrich, Germany) to deionized (DI) water. The HA solution was diluted to the same dissolved organic carbon (DOC) value as JM water, and 5 mM sodium bicarbonate (NaHCO_3 , analytical reagent) was added as a buffer system. The physical and chemical properties of the two water samples are presented in the Supporting Information (SI, **Table S1**). Prior to the coagulation experiment, the pH of the HA solution was adjusted to 8 using hydrochloric acid (HCl , guaranteed reagent) and sodium hydroxide (NaOH , analytical reagent). NaHCO_3 , HCl and NaOH were all obtained from Sinopharm (China).

The pretreatments for conditioning the NOM include two oxidation processes and one reduction process. Here, Hydrogen peroxide (30% H_2O_2 , guaranteed reagent) and sodium hypochlorite (NaClO , Chemical pure) from Sinopharm (China) are used in the oxidation process, while the sodium borohydride (NaBH_4 , analytical reagent) from Sinopharm (China) is used in the reduction process.

2.2 Pretreatments and coagulation treatment

For pre-oxidation process, NaClO (with an applied concentration of 0.2 mg/L to 0.4 mg/L, SI, **Table S3**) and H_2O_2 (with an applied concentration of 1 mg/L to 8 mg/L, SI, **Table S4**) were

dosed to the raw water. The stock solution of H_2O_2 and NaClO was prepared using DI water, and their applied concentration was determined by titanium sulfate-spectrophotometric method and DPD (N, N-diethyl-p-phenylenediamine)-spectrophotometric method, respectively. The details of the protocols are shown in the supporting information (SI, **Text S1-S2**). The pre-oxidation process was conducted in a glass beaker at room temperature ($25 \pm 1^\circ\text{C}$), and mixed with a rotator at a speed of 200 rpm for 20 min. After oxidation for 20 min, quenching was carried out with 0.1 M sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) (Qi et al., 2016a). For the pre-reduction process, NaBH_4 powder with specific weights was added to JM water to achieve applied concentrations of 20 mg/L to 200 mg/L. The pre-reduction process was conducted in a glass beaker at room temperature ($25 \pm 1^\circ\text{C}$) and mixed at 200 rpm using a rotator until the cessation of gas release. The three pretreatments were termed **CI** (pre-oxidation by NaClO), **HP** (pre-oxidation by H_2O_2), and **BH** (pre-reduction by NaBH_4). During the pretreatment process, the addition of oxidants/reductants caused changes in the pH of the solution (SI, **Table S2**). Before the coagulation treatment, HCl and NaOH were used to adjust the pH to the same value of the raw water.

For coagulation treatment, aluminum sulfate ('alum') hydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$; analytical reagent), obtained from Sinopharm (China), was utilized as the coagulant. A stock solution of alum was prepared at a concentration of 0.1 M using DI water. The coagulation tests were carried out using a Flocculator ZR4-2 (Shenzhen Zhongrun, China) apparatus, which allowed for pre-setting of mixing speeds and durations. A volume of 500 mL feedwater was placed into a 1 L beaker, and the alum stock solution was added to achieve an Al^{3+} concentration

of 0.2 mM (determined by a preliminary experiment, **Figure S1**, SI). Simultaneously, the jar test stirring was initiated with a stirring speed set at 200 rpm (184 s^{-1}) for 1 min of rapid mixing (coagulation), followed by 50 rpm (23 s^{-1}) for 15 min of slow mixing (flocculation). After coagulation/flocculation, the water was filtered through a $0.22\text{ }\mu\text{m}$ membrane (ANPEL, China) using filtration equipment (Jinteng, China) to separate the flocs and water. The flocs on the membrane and the filtration were collected separately for characterization.

2.3 Water quality analysis

The dissolved organic carbon (DOC) concentration was determined using a total organic carbon analyzer (TOC-Vwp, Shimadzu, Japan). The molecular weight (MW) distribution was obtained using size exclusion chromatography (HPLC, Alliance 2695, Waters Corp., USA). The hydrophilicity of water samples was determined using the octanol-water partition coefficient method (SI, **Text S3**). The pH value was measured by a pH meter (Mettler Toledo, Switzerland) and the UV-visible absorbance spectra of the water samples was determined by a UV-vis absorbance spectrometer (UV-2600, Shimadzu, Japan).

Three-dimensional excitation-emission matrix fluorescence spectroscopy (EEM, F-4600, Hitachi, Japan) was employed to identify the fluorescent components (tryptophan-like, tyrosine-like, fulvic acid-like, soluble microbial by-product-like and humic acid-like substances) within NOM. A quantitative analysis method, named fluorescence regional integration (FRI), was applied to quantify the proportion of each fluorescent component in the EEM spectrum. Zeta potential is the electrostatic surface charge potential on colloidal particles and is considered an important parameter for coagulation as it indicates the degree of

electrostatic repulsion between adjacent, similarly charged particles in a dispersion (Liu et al., 2024b). The zeta potential was measured by a laser zeta analyzer (Zetasizer Nano ZS90, Malvern, UK). All measurements were replicated three times for each test.

In addition, water samples after different pre-treatments were freeze-dried and subjected to Fourier transform infrared spectroscopy (FTIR, Spectrum 400, PerkinElmer) to reveal the variation of functional groups. The FT-IR spectrum was normalized using the peak at 1410 cm^{-1} (representing -COOH) as a reference.

2.4 Floc growth monitoring and characterization

Floc growth during coagulation was monitored using a photometric dispersion analyzer (PDA-3000, Rank Brothers, UK), which detects particle fluctuations in water through transmitted light measurements. The system recorded both the average transmitted light intensity (DC value) and root-mean-square (RMS) value of the flocculating component at 1-second intervals via continuous recirculation. The flocculation index (FI), calculated as the RMS/DC ratio, served as a quantitative indicator of particle size (Liu et al., 2024a).

For detailed characterization, formed flocs were collected on 0.45 μm membranes (ANPEL, China) and processed through freeze-drying. The dried samples underwent simultaneous analysis by: Fourier-transform infrared spectroscopy (FTIR, Spectrum 400, PerkinElmer) and X-ray photoelectron spectroscopy (XPS, PHI Quantera II, ULVAC-PHI, Japan) using monochromatic Al K α radiation (150 W). Hydrophilicity assessment of flocs was performed by dynamic contact angle measurements (OCA15EC, DataPhysics, Germany) using the sessile drop method. Freeze-dried flocs were compressed into tablets (FW-5A,

181 Botianshengda, China) before testing. Each measurement employed 2 μ L deionized water as
182 the probe liquid with an 80-second recording window. To ensure statistical reliability, a
183 minimum of six distinct areas were analyzed per sample.

3 Results and Discussion

3.1 Effect of hypochlorite pretreatment (NaClO) pretreatment on coagulation

Chlorination is widely employed as a pretreatment in drinking water treatment plants (DWTPs) due to its dual role in disinfection and organic matter modification. In this study, sodium hypochlorite (NaClO) was applied at concentrations ranging from 0.2 to 4 mg/L (as Cl_2) to evaluate its impact on coagulation efficiency. The flocculation index (FI) and the plateau FI value are two key parameters associated with floc growth. FI is an indicator of floc size, with higher value representing larger floc size. The plateau FI represents the steady-state maximum floc size. Larger floc sizes exhibit a greater rate of settlement, and this favors the separation of impurities in water (Liu et al., 2024a). **Figure 1A** illustrates the floc growth dynamics with and without chlorination pretreatment, revealing a notable enhancement in floc growth. Even at the lowest NaClO dosage (0.2 mg/L), the plateau floc size increased significantly from 8.6 ± 0.2 to 12.3 ± 0.4 μm (a 44% improvement, **Figure 1B**). Interestingly, further increases in NaClO concentration did not substantially alter floc size, suggesting that the oxidative modification of NOM reaches a saturation point at relatively low chlorine doses.

The observed improvement in floc growth can be attributed to structural changes in NOM induced by hypochlorite oxidation. FT-IR analysis (**Figure 1C**) identified characteristic functional groups in NOM (**Table 1**). The peak at 1650 cm^{-1} was assigned to C=O stretching in amides or quinones. A major band at 1410 cm^{-1} corresponded to C-O stretching in phenolic -OH or symmetric COO^- vibrations. The peaks at 1130 and 1030 cm^{-1} are indicative of C-OH and C-O-C stretching, respectively (Chen et al., 2015; Wang et al., 2018; Zhang et al., 2019).

Notably, NaClO pretreatment led to a progressive increase in the 1030 and 1130 cm⁻¹ bands, suggesting an enrichment of the hydroxyl group in NOM.

It is known that sodium hypochlorite (NaClO) is hydrolyzed in water to form hypochlorous acid (HOCl), which acts as an electrophilic reagent and reacts with structures such as aromatic rings, olefins, amino groups, and β -diketones in NOM. Through electrophilic acid substitution to form chlorophenols, electrophilic addition to form chlorohydric alcohols or chloramines, oxidative bond breaking leading to ring opening of the aromatic ring and generation of small molecule carboxylic acids, and ultimately decarboxylation to disinfection by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Ge et al., 2023; Jiang et al., 2020; Lee et al., 2023). At the low NaClO doses (<1mg/L) used in this study, the dominant effect appears to be hydroxylation rather than extensive mineralization. The minimal impact of low-dose NaClO pre-oxidation (<1 mg/L) on UV₂₅₄ (data not shown) further corroborates this observation (**Figure S2**, SI). The newly formed hydroxyl groups enhance flocculation by providing additional coordination sites for trivalent metal coagulants (e.g., Al³⁺/Fe³⁺ hydrolysis products) (Liu et al., 2024a).

XPS analysis further corroborated these findings. High-resolution C 1s scans (**Figure 1D**) revealed that untreated flocs consisted of 62% C-C (aliphatic/aromatic carbon), 21% C-O (hydroxyl/ether groups), 11% C=O (carbonyl groups), 6% COOH (carboxyl groups). After 1 mg/L NaClO pretreatment, the C-C content decreased sharply to 42%, while oxygen-rich functional groups increased (C-O: 32%, C=O: 17%, COOH: 9%). In addition, the O 1s peak (**Figure S3**, SI) also indicated that the oxygen content of the DOM (binding energy of 532~533

eV) showed an upward trend (DOM O: 53%→68%), suggesting more oxygen-containing groups were adsorbed onto flocs. This chemical shift was accompanied by increased hydrophilicity in both water samples (**Figure 1E**) and floc surface (**Figure 1F**). For water samples, the hydrophilicity/hydrophobicity was determined by the octanol-water partition coefficient (log P). A log P < 0 indicates strong hydrophilicity, and a lower value corresponds to greater hydrophilicity. As for flocs, the enhancement of floc surface hydrophilicity was evidenced by a decrease in the contact angle. The images demonstrate a gradual reduction in the contact angle with increasing NaClO dosage (**Figure S4**, SI). Therefore, it can be concluded that NaClO pretreatment oxidized hydrophobic NOM moieties (e.g., aromatics) and generated hydrophilic hydroxyl/carbonyl groups, which enhanced metal-NOM complexation during coagulation and thus promoted larger floc formation. A similar trend was also observed when using a standard HA solution as raw water (**Figure S5**, SI), where the FI value increased from 11.9 ± 0.3 to 16.2 ± 0.5 μm at 0.2 mg/L NaClO. However, it observed a slight decrease in FI values at higher NaClO doses, implying that excess NaClO can have a detrimental effect by breaking chains, leading to a decrease in molecular weight and an increase in hydrophilicity.

Figure 1

Table 1

3.2 Effect of hydrogen peroxide (H₂O₂) pretreatment on coagulation

The influence of hydrogen peroxide (H₂O₂) pretreatment on coagulation exhibited distinct concentration-dependent behavior (**Figure 2A** and **Figure S6**, SI). In contrast to NaClO

pretreatment, which produced a positive impact across all applied concentrations, H₂O₂ demonstrated a biphasic effect: the plateau floc size initially increased from 8.6 ± 0.2 μm to 12.7 ± 0.4 μm at 1 mg/L H₂O₂, but subsequently declined to 7.0 ± 0.2 μm at 8 mg/L H₂O₂ (**Figure 2B**). The C-OH peak (at a wavenumber of 1130 cm^{-1}) in the FT-IR spectrum showed a similar trend, the intensity of which first increased and then decreased with increasing H₂O₂ dosage (**Figure 2C**). XPS analysis of flocs formed under optimal H₂O₂ concentration (1 mg/L) confirmed an increase in oxygen-containing functional groups (C-O: 24%, C=O: 18%, COOH: 9%) compared to untreated samples, suggesting that hydroxyl group enrichment contributed to improved floc growth at lower oxidant levels (**Figure 2D**). Furthermore, the oxygen content of the DOM (**Figure S7, SI**) shows an upward trend (DOM O: 53%→62%), which also indicates an increase in oxygen-containing functional groups. However, the deterioration in floc size at higher H₂O₂ concentrations (> 6 mg/L), where performance fell below baseline levels, cannot be explained solely by hydroxyl group depletion. This implies alternative mechanisms, possibly involving excessive oxidation or changes in organic matter charge characteristics.

Figure 2E demonstrated that the hydrophilicity variation of water samples after H₂O₂ treatment followed a similar biphasic pattern, which first showed a slight increase and then decreased to baseline levels (i.e., similar level to with raw JM water). As for the contact angle of flocs, the contact angle dramatically decreased from 36.3 ± 0.8 mV to 29.5 ± 0.5 mV at 1 mg/L H₂O₂, and then gradually increased to 34.5 ± 0.7 mV at 8 mg/L H₂O₂ (**Figure 2F and Figure S8, SI**). These findings underscored fundamental differences between H₂O₂ and NaClO pretreatment mechanisms. While NaClO universally promotes floc growth through persistent

hydroxylation, H₂O₂ exhibits concentration-dependent effects. This is, it is beneficial at low doses but detrimental at higher concentrations, which will be discussed in detail in the following sections.

Figure 2

3.3 Mechanistic differences in organic matter modification by two processes

To elucidate the fundamental differences between NaClO and H₂O₂ pre-oxidation processes, we systematically examined changes in molecular weight (MW) distribution and zeta potential across different oxidant concentrations. **Figure 3A** reveals a striking contrast: while H₂O₂ treatment induced minimal alterations in MW distribution, NaClO caused a significant reduction in MW, particularly for high-MW organic fractions. This divergence strongly suggests that these two oxidants follow fundamentally different reaction pathways when interacting with NOM.

The powerful oxidative capacity of NaClO primarily stems from hypochlorous acid (HOCl), which acts as a potent electrophile capable of non-selectively attacking electron-rich moieties in organic molecules, including aromatic rings, carbon-carbon double bonds, and heteroatom-containing functional groups (**Figures 3C and 3D**). This aggressive oxidation mechanism, often involving free radical intermediates, leads to systematic cleavage of C-C and C=C bonds within the organic skeleton. Consequently, the oxidation process simultaneously introduces oxygen-containing functional groups (hydroxyl, carboxyl) while progressively fragmenting macromolecules into smaller carboxylic acids (e.g., formic acid, acetic acid). This

comprehensive degradation pathway explains the observed substantial reduction in molecular weight with increasing NaClO concentration. Consequently, these reactions directly disrupt the core fluorophores and conjugated systems responsible for fluorescence, resulting in a more pronounced decrease in fluorescence (**Figure S9**, SI).

In contrast, the oxidizing power of hydrogen peroxide alone is weak, and its action relies primarily on the modification of specific functional groups (e.g., aldehyde groups, olefins) by nucleophilic hydroperoxylate ions (HOO^-) or limited oxidation triggered by the slow generation of a small number of hydroxyl radicals ($\cdot\text{OH}$) (Zhang et al., 2025b). The reaction of H_2O_2 is usually confined to the conversion of functional groups (e.g., olefin epoxidation, oxidation of aldehydes to carboxylic acids) and rarely breaks stable C-C bonds or aromatic ring structures (Naranov et al., 2024; Zhu et al., 2025) so that molecular weight changes are insignificant and the products are mostly polar derivatives of the original molecule rather than fragmented small molecules (**Figure 3E**). Therefore, the decrease in fluorescence intensity after H_2O_2 treatment was relatively modest (**Figure S10**, SI) compared to that of NaClO-treated samples (**Figure S9**, SI), which is primarily attributed to the generation of carboxyl groups that act as fluorescence quenchers (Chen and Knutson, 1988).

The zeta potential measurements (**Figure 3B**) provide further mechanistic insights into how these oxidation processes differentially affect coagulation performance. Notably, H_2O_2 treatment caused a continuous increase in zeta potential (reaching > -20 mV at higher concentrations), while NaClO maintained relatively stable surface charges across all tested doses. This observation suggests that H_2O_2 oxidation leads to progressive accumulation of

carboxyl groups on NOM surfaces. Although both hydroxyl and carboxyl groups can theoretically serve as coordination sites for metal coagulants, the ionization behavior of carboxyl groups under typical coagulation conditions (pH ~7.8) is difficult to complex with hydrolysis precipitates. Meanwhile, it introduces significant electrostatic repulsion between flocs (Liu et al., 2024). This effect likely explains the deterioration in floc formation observed at elevated H₂O₂ concentrations.

Figure 3

3.4 Effect of organic matter modification on floc growth dynamics

To summarize, the divergent impacts of sodium hypochlorite (NaClO) and hydrogen peroxide (H₂O₂) oxidation on floc development stem from their distinct modification pathways for the architecture of natural organic matter (NOM), as illustrated in **Figures 3C-3E**. Zhang et al. employed Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to demonstrate that after NaClO pre-treatment, the relative abundance of lignin-like and tannin-like compounds decreased significantly, accompanied by an increase in signal intensities of aliphatic and highly oxidized compounds (Zhang et al., 2025a). This finding aligns well with the characterization results obtained in this study. NaClO functions as a strong electrophilic oxidant that preferentially attacks electron-rich aromatic domains (particularly phenolic moieties), inducing ring cleavage and carbon chain scission (**Figure 3D**). This partial fragmentation converts macromolecular NOM into low-molecular-weight (LMW) aliphatic derivatives (**Figure 3A**), while simultaneously introducing abundant hydroxyl groups through

epoxidation/hydrolysis reactions alongside minor carboxyl group formation (**Figures 1C and 1D**). These structural modifications collectively enhance the hydrophilicity of treated water (**Figure 1E**) while crucially reducing steric hindrance and exposing latent binding sites. During subsequent coagulation, Al^{3+} hydrolysis products form stable complexes with hydroxyl-rich LMW fragments, further increasing floc hydrophilicity as evidenced by reduced contact angles (**Figure 1F**). This ligand-promoted bridging effect, combined with accelerated diffusion kinetics of smaller organic molecules toward metal hydrolysis precipitates, overcomes the potential disadvantages of increased hydrophilicity and ultimately yields larger, more stable flocs (**Figures 1A and 1B**).

In contrast, H_2O_2 exhibits more moderate oxidative capabilities when applied alone. At lower concentrations, it selectively hydroxylates aromatic rings and aliphatic chains without significant depolymerization (**Figure 3A**). This targeted oxidation increases hydroxyl group density while moderately elevating carboxyl group content (**Figures 2C and 2D**). The study by Zhang et al. also confirmed this observation. After H_2O_2 pre-treatment, the overall molecular composition shifted toward higher O/C ratios with minimal change in H/C, indicating the predominance of oxygenation reactions without significant dehydrogenation or cleavage (Zhang et al., 2025b). The preservation of macromolecular frameworks results in smaller hydrophilicity increases compared to NaClO treatment (**Figure 2E**), though flocs still exhibit significantly reduced contact angles due to the preferential complexation between Al^{3+} hydrolysis products and hydroxyl groups. However, at elevated H_2O_2 concentrations (>4 mg/L), progressive oxidation converts hydroxyl groups to carboxyl functionalities, as indicated by

decreased C-OH peak intensities in FT-IR spectra (**Figure 2C**). This transformation not only depletes metal-binding sites but also introduces substantial electrostatic repulsion (**Figure 3A**) that impedes floc aggregation (**Figures 2A and 2B**).

Moreover, the detrimental effects of carboxyl enrichment extend beyond charge repulsion. Ionized carboxyl groups (-COO^-) create strong hydrophilic domains that promote directional water molecule arrangement through electrostatic interactions. When charged particles approach during aggregation, they must overcome significant energy barriers to displace these structured hydration layers. The unexpected increase in the contact angle of flocs at high H_2O_2 concentrations (**Figure 2F**) can be attributed to a complex interfacial phenomenon. Although freeze-drying removes bulk water, carboxyl-bound water molecules may persist under vacuum conditions, forming nanoscale hydrophilic films. More critically, surface ionization creates negatively charged floc interfaces where electrostatic forces distort surface topography. During contact angle measurement, these charged surfaces attract H^+ ions from water droplets, effectively forming electrical double layers that function as ‘spring bases’ to restrict droplet spreading. Consequently, the specialized wetting behavior of charged surfaces paradoxically increases contact angles despite enhanced hydrophilicity. This explains the apparent contradiction to classical wetting theory while highlighting the unique interfacial properties of carboxyl-rich flocs. These mechanistic insights reveal that optimal oxidative pretreatment requires careful balancing of functional group modification. While hydroxyl group enrichment generally promotes coagulation through improved complexation, excessive carboxyl group generation introduces multiple aggregation barriers (Zhang et al., 2021), including charge

repulsion, hydration layer expansion, and interfacial charge effects.

Due to the distinct mechanisms by which the two oxidants modify NOM, they exhibit different practical applications in water treatment. NaClO demonstrates relatively broad dose versatility, effectively altering NOM over a wide dose range, thereby providing greater flexibility and stability for water sources with fluctuating NOM levels. In contrast, H₂O₂ exhibits a narrower dose versatility and is highly concentration-dependent, requiring precise control.

3.5 Effect of pre-reduction process on floc dynamics

While previous research has predominantly focused on peroxidation processes for modifying NOM properties to enhance treatment performance, this study presented novel insights into the effects of pre-reduction on floc growth dynamics. Our investigation revealed a distinctive concentration-dependent triphasic response to sodium borohydride (NaBH₄) pretreatment (**Figure 4A**). At low concentrations (20 mg/L), the FI value slightly increased from 8.6 ± 0.2 to 9.5 ± 0.3 . Moderate concentrations (50–100 mg/L) induced remarkable floc enlargement (50 mg/L: 12.2 ± 0.3 ; 100 mg/L: 14.2 ± 0.4), demonstrating the potential of controlled reduction to enhance coagulation. Interestingly, higher doses (>100 mg/L) caused a slight decrease in floc size, though performance still exceeded baseline levels (200 mg/L: 11.2 ± 0.5) (**Figure 4B**), suggesting complex secondary effects at elevated reductant concentrations.

Detailed mechanistic analyses elucidated critical functional group transformations underlying these observations. XPS revealed a decrease in carbonyl (C=O) content (11% → 6% at 200 mg/L) accompanied by increased hydroxyl (C-O) groups (21% → 24%) (**Figure**

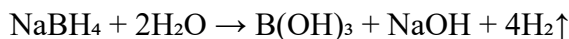
4D). These findings were corroborated by FT-IR results, which showed attenuated carbonyl peaks (1650 cm^{-1}) and enhanced hydroxyl signals (1130 cm^{-1}) (**Figure 4C**). These data confirm the reductive conversion of carbonyl to hydroxyl groups ($\text{C=O} \rightarrow \text{C-OH}$), generating additional coordination sites for metal coagulants and thereby improving floc formation (**Figure 4E**).

Interestingly, the EEM fluorescence intensity of JM water exhibited a gradual increase upon the addition of NaBH_4 (**Figure S11**, SI). In comparison with the addition of 100 mg/L NaBH_4 to DI water (**Figure S12**, SI), it can be concluded that the observed fluorescence enhancement is not attributable to the intrinsic fluorescence of NaBH_4 itself, but rather results from its reaction with NOM in JM water. Fluorescence regional integration (FRI) analysis revealed that the enhancement occurred predominantly in the fulvic acid-like and humic acid-like regions (**Figure S13**, SI). NOM in JM water contains fluorescent functional groups such as aromatic rings, carbonyl groups, and quinone groups. Among these, quinone groups act as fluorescence quenchers, whereas their reduced form, hydroquinone, serves as a fluorescence enhancer. As a strong reducing agent, NaBH_4 reduces functional groups including carbonyl and quinone moieties within fluorescent NOM components (e.g., humic and fulvic acids) to hydroxyl or alkyl groups, thereby increasing fluorescence efficiency. Furthermore, the reduction of quinone groups to hydroquinone eliminates quenching effects. Collectively, these mechanisms account for the enhanced fluorescence observed in NaBH_4 -treated JM water.

Figure 4

However, the diminished performance at higher NaBH_4 concentrations can be attributed

to competing chemical processes. Excessive NaBH₄ undergoes hydrolysis in aqueous solutions according to the reaction:



This reaction leads to two significant consequences: (1) a substantial pH increase due to NaOH generation (**Table S2**, SI), and (2) the formation of boric acid (B(OH)₃), which further dissociates to produce borate anions (B(OH)₄⁻). These borate species compete with NOM for active sites on aluminum hydrolysis products, forming stable complexes that interfere with optimal floc formation (Xu and Peak, 2007). This competition mechanism was further corroborated by the contrasting behaviors observed between commercial humic acid (HA) solutions and natural surface water (JM water). Although the HA solution exhibited a similar trend to JM water in terms of how HP and Cl pretreatment affected floc growth during coagulation (**Figures S3 and S4**, SI), its response to BH differed significantly (**Figure 5D-5E**). Notably, high NaBH₄ concentrations completely suppressed floc formation in HA solutions, suggesting near-total consumption of Al precipitates by borate species (**Figure 5A-5B**). In contrast, the decline in the coagulation performance of JM water was less pronounced, likely due to the buffering effects from background cations such as Ca²⁺ (**Figure 5C**), which mitigate borate interference (Uchikawa et al., 2015). This explanation is further supported by the sharp decrease in free Ca²⁺ concentration at high NaBH₄ doses (>100 mg/L), indicating significant cation-borate interactions (**Figure 5F**).

The demonstrated efficacy of pre-reduction in promoting floc growth highlighted the crucial role of hydroxyl groups in facilitating floc formation during coagulation. Compared to

pre-oxidation, the primary advantage of pre-reduction lies in its distinct mechanism, which specifically targets recalcitrant NOM fractions that are insensitive to oxidative treatment and provides a unique pathway for enhancing subsequent coagulation. Thus, in specific scenarios where pre-oxidation proves ineffective, pre-reduction offers a novel and unique advantage for enhancing the performance of water treatment processes. This study introduces a new perspective by suggesting that pre-reduction should not be viewed as a direct replacement for pre-oxidation, but rather as a complementary and targeted strategy. These findings provide valuable conceptual advances for future NOM modification strategies. Specifically, it suggested that targeted chemical reduction of specific functional groups could represent a promising way for optimizing coagulation processes.

Moreover, the observed disparities between laboratory HA solutions and natural surface water (i.e., JM water) highlight the critical influence of background water chemistry in real-world treatment scenarios (Liu et al., 2024b). These differences serve as an important reminder that idealized laboratory conditions may not fully capture the complex interactions occurring in actual water matrices, emphasizing the need for pilot-scale validation of novel treatment approaches. Future research should explore synergistic effects between reduction pretreatment and conventional coagulation processes, as well as investigate alternative, more practical reducing agents that could achieve similar benefits without the drawbacks associated with NaBH_4 . Additionally, the pH-dependent behavior of borate species suggests that pH control strategies might help mitigate performance limitations at higher reductant doses, potentially expanding the operational window for this innovative pretreatment approach.

Figure 5

Conclusion

This study systematically investigated the molecular-scale mechanisms by which chemical preconditioning (oxidation/reduction) modulated NOM functionality to enhance floc growth during coagulation. The key insights reveal that hydroxyl group (-OH) enrichment serves as a universal driver for improved floc formation across all pretreatment strategies, as it facilitates stronger coordination with trivalent metal coagulants (e.g., Al^{3+} hydrolysis products). However, the efficacy of each method is critically dose-dependent, governed by distinct reaction pathways.

(1) NaClO oxidation hydroxylates aromatic NOM at low doses (0.2 mg/L), enhancing floc size by up to 44%. Yet, its aggressive fragmentation of high-MW organics and increased hydrophilicity may compromise floc stability at elevated concentrations.

(2) H_2O_2 oxidation exhibits a biphasic effect, where low doses (1 mg/L) promote -OH formation, but excess (>4 mg/L) generates carboxyl groups (-COO^-), inducing electrostatic repulsion and hydration-layer barriers that impede aggregation.

(3) NaBH_4 reduction selectively converts carbonyls to hydroxyls (50–100 mg/L), boosting floc growth; however, overdosing (>100 mg/L) releases borate anions (B(OH)_4^-) that compete with NOM for Al^{3+} sites, and thus offsetting its benefits.

This study establishes the molecular-level framework linking the NOM functional group to the floc growth dynamic, challenging conventional paradigms focused mostly on coagulant optimization. By demonstrating that targeted -OH enrichment, rather than indiscriminate oxidation, optimizes coagulation, we provide a mechanistic basis for tailoring pretreatment to

specific NOM characteristics (e.g., aromaticity, MW distribution).

This study has proposed for the first time a reductive pretreatment technique for organic matter modification, systematically elucidating its unique advantages over pre-oxidation in terms of mechanism and treatment efficacy. However, future research should further evaluate the application costs of reducing agents, considering the feasibility of scaling up from laboratory to pilot-scale testing. In-depth investigations are also needed to explore the mechanistic differences among various reductants and to determine whether the response to pretreatment varies with the characteristics of the source water. The results of this study have provided a new pathway for enhanced coagulation, by modifying NOM structure via well-controlled pre-treatments, to achieve sustainable water purification.

Acknowledgments

This study was financially supported by the National Postdoctoral Fellowship Program of China (Grant No. BX20240404), the National Natural Science Foundation of China (Grant No. 52370184), the International Partnership Program of Chinese Academy of Sciences (Grant No. 032GJHZ2023063MI, No.309GJHZ2023003MI), National Key Research and Development Program of China (Grant No.2022YFC3204205-3), and the Beijing Natural Science Fund for Distinguished Young Scholars (Grant No. JQ21032).

Author Contributions Statement

Baofeng Zhu: Investigation, Data curation, Visualization, Writing - original draft. Mengjie Liu: Supervision, Writing - review & editing. Kai Zhang: Formal analysis, Writing - review &

editing. Nigel Graham: Supervision, Writing - review & editing. Wenzheng Yu: Supervision,
Writing - review & editing.

Additional information

Competing financial interests: The authors declare no competing financial interests

Appendix A. Supplementary data

The Supplementary Information contains 3 Texts, 4 Tables and 13 Figures as follows:

Determination of H₂O₂ concentration (**Text S1**);

Determination of NaClO concentration (**Text S2**);

Determination of Octanol-Water Partition Coefficient (logP) (**Text S3**);

Physical and chemical properties of feedwater (**Table S1**);

pH value of water samples after different pretreatments (**Table S2**);

The specific applied concentration in mg Cl₂ per mg DOC (**Table S3**);

The specific applied concentration in mg H₂O₂ per mg DOC (**Table S4**);

Variations in DOC under different coagulant doses (**Figure S1**);

Effect of hypochlorite pretreatment (NaClO) on UV in JM water (**Figure S2**);

High-resolution scans (O 1s) of X-ray photoelectron spectroscopy of flocs formed with and
without pretreatment by 1 mg/L NaClO (**Figure S3**);

Contact angle images of flocs formed on JM with and without pretreatment by different
concentrations of NaClO (**Figure S4**);

Effect of NaClO pretreatment on coagulation for HA solution (**Figure S5**);
Effect of hydrogen peroxide (H₂O₂) pretreatment on coagulation for HA solution (**Figure S6**);
High-resolution scans (O 1s) of X-ray photoelectron spectroscopy of flocs formed with and
without pretreatment by 1 mg/L H₂O₂ (**Figure S7**);
Contact angle images of flocs formed on JM with and without pretreatment by different
concentrations of H₂O₂ (**Figure S8**);
EEM fluorescence spectra after NaClO pretreatment (**Figure S9**);
EEM fluorescence spectra after H₂O₂ pretreatment (**Figure S10**);
EEM fluorescence spectra after sodium borohydride pretreatment (NaBH₄) (**Figure S11**);
EEM fluorescence spectra detected after adding 100mg/L of NaBH₄ to pure water (**Figure S12**);
Fluorescence spectral region integration of EEM (III and V) after NaBH₄ pretreatment (**Figure S13**).

References:

- Akın, M.B. and Şahin, Ö. 2025. Hydrogen production via methanolysis of sodium borohydride using acetic acid as a catalyst. *Renewable Energy* 240, 122247.
- Anh Phan, K., Lohwacharin, J., Oguma, K. and Sharma, V.K. 2024. Bromate in drinking water: Occurrence and removal by ultraviolet/sulfite advanced reduction processes. *Chemical Engineering Journal* 490, 151759.
- Cai, G., Liu, T., Zhang, J., Song, H., Jiang, Q. and Zhou, C. 2022. Control for chlorine resistant spore forming bacteria by the coupling of pre-oxidation and coagulation sedimentation, and UV-AOPs enhanced inactivation in drinking water treatment. *Water Research* 219, 118540.
- Cao, L., Wang, J., Wang, Z., Cheng, Y., Dai, J., Ma, J., Chen, Y., Liu, Z. and Xie, P.

2023. Comparison of peracetic acid and sodium hypochlorite enhanced Fe(II) coagulation on algae-laden water treatment. *Journal of Hazardous Materials* 445, 130571.

Chen, H., Lin, T., Wang, Y., Lu, F., Shi, Y. and Yin, J. 2025. Advanced oxidation process with hydrogen peroxide and sulfite for superfast degradation of micro-contaminants in drinking water. *Journal of Hazardous Materials* 490, 137790.

Chen, R.F. and Knutson, J.R. 1988. Mechanism of fluorescence concentration quenching of carboxyfluorescein in liposomes: Energy transfer to nonfluorescent dimers. *Analytical Biochemistry* 172(1), 61–77.

Chen, W., Habibul, N., Liu, X.-Y., Sheng, G.-P. and Yu, H.-Q. 2015. FTIR and Synchronous Fluorescence Heterospectral Two-Dimensional Correlation Analyses on the Binding Characteristics of Copper onto Dissolved Organic Matter. *Environmental Science & Technology* 49(4), 2052–2058.

Cheng, Z., Lin, Z., Chen, X., Zhang, X. and Zhang, H. 2025. Unraveling the mechanisms underlying AOM-induced deterioration of the settling performance of algal floc. *Water Research* 274, 123115.

Deng, L., Ngo, H.-H., Guo, W. and Zhang, H. 2019. Pre-coagulation coupled with sponge-membrane filtration for organic matter removal and membrane fouling control during drinking water treatment. *Water Research* 157, 155–166.

Deng, Z., Xu, A., Wei, X., Zhang, X. and Pan, B. 2024. Formation of Aluminum–Fluoride Complexes Compromises Defluoridation Efficiency of Aluminum-Based Coagulation. *Environmental Science & Technology* 58(33), 14918–14928.

Edzwald, J.K. and Tobiason, J.E. 1999. Enhanced coagulation: US requirements and a broader view. *Water Science and Technology* 40(9), 63–70.

Ge, X., Gao, Y., Yang, Y., Chen, G., Ma, S., Hu, B., Yu, Y. and An, T. 2023. Mixed bromine/chlorine transformation products of tetrabromobisphenol A formed in the combustion of printed circuit boards: Emission characteristics and transformation pathways. *Science of The Total Environment* 859, 160104.

Gonzalez-Torres, A., Putnam, J., Jefferson, B., Stuetz, R.M. and Henderson, R.K. 2014. Examination of the physical properties of *Microcystis aeruginosa* flocs produced on coagulation with metal salts. *Water Research* 60, 197–209.

Guo, K., Wang, Z., Pan, J., Liu, B., Wang, Y., Yue, Q., Gao, Y. and Gao, B. 2022. Highly efficient Al-Ti gel as a coagulant for surface water treatment: Insights into the hydrolysis transformation and coagulation mechanism. *Water Research* 221, 118826.

Ho, L. and Newcombe, G. 2005. Effect of NOM, turbidity and floc size on the PAC adsorption of MIB during alum coagulation. *Water Research* 39(15), 3668–3674.

Jarvis, P., Sharp, E., Pidou, M., Molinder, R., Parsons, S.A. and Jefferson, B. 2012. Comparison of coagulation performance and floc properties using a novel zirconium coagulant against traditional ferric and alum coagulants. *Water Research* 46(13), 4179–4187.

Ji, X., Hou, L.-a., Yu, S., Xu, Y., Gao, M., Zhang, W. and Xiao, Q. 2025. Fast complete reduction of chlorite to chloride from drinking water in Al(III)/sulfite system: Kinetics, mechanisms, and applications. *Chemical Engineering Journal* 504, 158898.

Jiang, J., Han, J. and Zhang, X. 2020. Nonhalogenated Aromatic DBPs in Drinking Water Chlorination: A Gap between NOM and Halogenated Aromatic DBPs. *Environmental Science & Technology* 54(3), 1646–1656.

Kim, C., Debusmann, P., Abdighahroudi, M.S., Schumacher, J. and Lutze, H.V. 2025. Fenton–coagulation process for simultaneous abatement of micropollutants and dissolved organic carbon in treated wastewater. *Water Research* 281, 123583.

Lee, J., Eom, S., Sohn, S., Kim, T. and Zoh, K.-D. 2023. Degradation of bisphenol A, bisphenol S, and bisphenol AF in the UV-LED/chlorine reaction: Effect of pH on the kinetics, transformation products, and degradation pathway. *Chemical Engineering Journal* 470, 144041.

Lin, J.-L., Huang, C., Dempsey, B. and Hu, J.-Y. 2014. Fate of hydrolyzed Al species in humic acid coagulation. *Water Research* 56, 314–324.

Lin, Y., Lou, Y., Li, A., Wei, Y., Li, H., Zhou, M. and Li, Y. 2021. Effects of pre-oxidation by ozone, permanganate and ferrate on generation and toxicities of disinfection byproducts. *International Journal of Environmental Science and Technology* 19(7), 5969–5984.

Liu, M., Graham, N., Gregory, J., Elimelech, M. and Yu, W. 2024a. Towards a molecular-scale theory for the removal of natural organic matter by coagulation with trivalent metals. *Nature Water* 2(3), 285–294.

Liu, M., Liu, X., Graham, N.J.D. and Yu, W. 2024b. Uncovering the neglected role of anions in trivalent cation-based coagulation processes. *Water Research* 254, 121352.

Liu, M., Siddique, M.S., Graham, N.J.D. and Yu, W. 2022. Removal of Small-Molecular-Weight Organic Matter by Coagulation, Adsorption, and Oxidation: Molecular Transformation and Disinfection Byproduct Formation Potential. *ACS ES&T Engineering* 2(5), 886–894.

Müller, J., Levai, S., Titzschkau, L., Popović, N., Carevic, D., Drewes, J.E. and Hübner, U. 2019. Role of reduced empty bed contact times and pre-treatment by coagulation with Fe(III) salts on the removal of trace organic compounds during sequential biofiltration. *Science of The Total Environment* 685, 220–228.

Naranov, E., Ramazanov, D., Agliullin, M., Sinyashin, O. and Maximov, A. 2024. Recent Advances in Aromatic Hydroxylation to Phenol and Hydroquinone Using H₂O₂. *Catalysts* 14(12), 930.

Ozdemir, R. and Unlu, D. 2025. Investigation of the efficiency of hydrogen production from sodium borohydride hydrolysis with a novel biobased catalyst “Bio-MOF”. *International Journal of Hydrogen Energy* 142, 875–885.

Peydayesh, M., Suta, T., Usuelli, M., Handschin, S., Canelli, G., Bagnani, M. and Mezzenga, R. 2021. Sustainable Removal of Microplastics and Natural Organic Matter from Water by Coagulation–Flocculation with Protein Amyloid Fibrils. *Environmental Science & Technology* 55(13), 8848–8858.

Qi, J., Lan, H., Liu, H., Liu, R., Miao, S. and Qu, J. 2016a. Simultaneous surface-adsorbed organic matter desorption and cell integrity maintenance by moderate

prechlorination to enhance *Microcystis aeruginosa* removal in $\text{KMnO}_4\text{--Fe(II)}$ process. *Water Research* 105, 551–558.

Qi, J., Lan, H., Miao, S., Xu, Q., Liu, R., Liu, H. and Qu, J. 2016b. $\text{KMnO}_4\text{--Fe(II)}$ pretreatment to enhance *Microcystis aeruginosa* removal by aluminum coagulation: Does it work after long distance transportation? *Water Research* 88, 127–134.

Shirakawa, D., Shirasaki, N., Matsushita, T., Matsui, Y., Yamashita, R., Matsumura, T. and Koriki, S. 2022. Evaluation of reduction efficiencies of pepper mild mottle virus and human enteric viruses in full-scale drinking water treatment plants employing coagulation–sedimentation–rapid sand filtration or coagulation–microfiltration. *Water Research* 213, 118160.

Song, Q., Yang, B., Liu, M., Song, S., Graham, N. and Yu, W. 2023. Floc aging: Crystallization and improving low molecular weight organic removal in re-coagulation. *Water Research* 243, 120328.

Uchikawa, J., Penman, D.E., Zachos, J.C. and Zeebe, R.E. 2015. Experimental evidence for kinetic effects on B/Ca in synthetic calcite: Implications for potential B(OH)_4^- and B(OH)_3 incorporation. *Geochimica et Cosmochimica Acta* 150, 171–191.

Vahedi, A. and Gorczyca, B. 2014. Settling velocities of multifractal flocs formed in chemical coagulation process. *Water Research* 53, 322–328.

Wang, B.-B., Liu, X.-T., Chen, J.-M., Peng, D.-C. and He, F. 2018. Composition and functional group characterization of extracellular polymeric substances (EPS) in activated sludge: the impacts of polymerization degree of proteinaceous substrates. *Water Research* 129, 133–142.

Wang, X., Li, M., Song, X., Chen, Z., Wu, B. and Zhang, S. 2016. Preparation and Evaluation of Titanium-Based Xerogel as a Promising Coagulant for Water/Wastewater Treatment. *Environmental Science & Technology* 50(17), 9619–9626.

Xia, R., Liu, W., Nghiem, L.D., Cao, D., Li, Y., Li, G. and Luo, W. 2024. A novel chitosan and polyferric sulfate composite coagulant for biogas slurry pretreatment by simultaneous flocculation and floatation: Performance and underlying mechanisms. *Water Research* 258, 121781.

Xiao, F., Simcik, M.F. and Gulliver, J.S. 2013. Mechanisms for removal of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from drinking water by conventional and enhanced coagulation. *Water Research* 47(1), 49–56.

Xu, D. and Peak, D. 2007. Adsorption of Boric Acid on Pure and Humic Acid Coated am- Al(OH)_3 : A Boron K-Edge XANES Study. *Environmental Science & Technology* 41(3), 903–908.

Xu, X., Wan, J., Wang, G., Huang, Z., Li, Q., Chen, Y., Zhou, J., Li, W., Sun, J., Wu, J. and Sun, Q. 2025. Enhanced flocculation air-flotation process with moderate pre-oxidation of sodium hypochlorite and ozone for the treatment of high algal water: Performance, process optimization and mechanism. *Journal of Water Process Engineering* 72, 107554.

Yang, B., Graham, N., Liu, P., Liu, M., Gregory, J. and Yu, W. 2023. Atomic-Level Structural Differences between Fe(III) Coprecipitates Generated by the Addition of Fe(III)

Coagulants and by the Oxidation of Fe(II) Coagulants Determine Their Coagulation Behavior in Phosphate and DOM Removal. *Environmental Science & Technology* 57(33), 12489–12500.

Yang, B., Zhou, P., Tian, L., Graham, N., Li, G., Su, Z. and Yu, W. 2025. The nanoscale explanation of metal cations differences in enhancing the Fe(III) coagulation performance. *Water Research* 280, 123524.

Yu, W., Graham, N.J.D. and Fowler, G.D. 2016. Coagulation and oxidation for controlling ultrafiltration membrane fouling in drinking water treatment: Application of ozone at low dose in submerged membrane tank. *Water Research* 95, 1–10.

Zhang, B., Wang, Q., Zhou, L., Li, X., Tong, F., Wang, X., Wang, Y., Xu, C., Shi, X. and Tang, B. 2025a. Effective control disinfection byproducts in municipal wastewater by UV-based advanced oxidation/reduction pre-treatments: Insights from FT-ICR-MS analysis. *Journal of Hazardous Materials* 499, 140202.

Zhang, X., Graham, N., Xu, L., Yu, W. and Gregory, J. 2021. The Influence of Small Organic Molecules on Coagulation from the Perspective of Hydrolysis Competition and Crystallization. *Environmental Science & Technology* 55(11), 7456–7465.

Zhang, X., Yang, C.-W., Li, J., Yuan, L. and Sheng, G.-P. 2019. Spectroscopic insights into photochemical transformation of effluent organic matter from biological wastewater treatment plants. *Science of The Total Environment* 649, 1260–1268.

Zhang, Y., Sun, W. and Yin, W. 2025b. Precise regulation of UV/H₂O₂ processes: – OH generation/reaction and DOM transformation as the main free radical scavenger. *Water Research* 277, 123282.

Zhao, H., Wang, L., Hanigan, D., Westerhoff, P. and Ni, J. 2016. Novel Ion-Exchange Coagulants Remove More Low Molecular Weight Organics than Traditional Coagulants. *Environmental Science & Technology* 50(7), 3897–3904.

Zhou, Z., Sun, T., Li, X., Ren, J., Lu, Z., Liu, Y., Li, K. and Qu, F. 2024. Reliable assessment and prediction of moderate preoxidation of sodium hypochlorite for algae-laden water treatment. *Water Research* 266, 122398.

Zhu, J., Graham, N., Li, G., Gregory, J. and Yu, W. 2025. Benzene Ring-Driven Metal Hydrolysis and Floc Formation in Coagulation: Mechanistic Insights from Organic Structural Units. *Environmental Science & Technology*, 5c11429.

Figure Captions

Figure 1. Effect of sodium hypochlorite pretreatment (NaClO) on coagulation. (A) Floc growth curve with/without pretreatment. (B) Plateau floc size (evaluated by FI) under different concentrations of NaClO. Error bars represent the standard deviation of triplicate measurements. (C) FT-IR spectrum of JM water treated by different concentrations of NaClO. (D) High-resolution scans (C 1s) of X-ray photoelectron spectroscopy of flocs formed with and without pretreatment by 1 mg/L NaClO (measured as Cl₂). (E) The hydrophilicity of JM water treated with different concentrations of NaClO. The Y-axis (log P) represents the log index of the partition coefficient of the organic matter in the aqueous phase and the organic phase (octanol), the smaller the value the more hydrophilic the organic matter is. Error bars represent the standard deviation of triplicate measurements (n = 3). (F) Box plot showing the contact angle of flocs formed with JM with and without pretreatment by different concentrations of NaClO (n=6).

Figure 2. Effect of hydrogen peroxide (H₂O₂) pretreatment on coagulation. (A) Floc growth curve with/without pretreatment. (B) Plateau floc size (evaluated by FI) under different concentrations of H₂O₂. Error bars represent the standard deviation of triplicate measurements. (C) FT-IR spectrum of JM water treated by different concentrations of H₂O₂. (D) High-resolution scans (C 1s) of X-ray photoelectron spectroscopy of flocs formed with and without pretreatment by 1 mg/L H₂O₂. (E) The hydrophilicity of JM water treated with different concentrations of H₂O₂. The Y-axis (log P) represents the log index of the partition coefficient of the organic matter in the aqueous phase and the organic phase (octanol), the smaller the value the more hydrophilic the organic matter is. Error bars represent the standard deviation of triplicate measurements (n = 3). (F) Box plot showing the contact angle of flocs formed with JM with and without pretreatment by different concentrations of H₂O₂ (n=6).

Figure 3. Comparison of the two pre-oxidation processes. (A) The molecular weight

distribution of water treated by different concentrations of NaClO (Cl, top) and H₂O₂ (HP, bottom). **(B)** Zeta potential of water treated by different concentrations of NaClO (Cl, top) and H₂O₂ (HP, bottom). Error bars represent the standard deviation of triplicate measurements (n = 3). **(C-E)** Schematic diagram showing the structure of pristine natural organic matter (NOM, C), Chlorinated NOM **(D)**, and H₂O₂-treated NOM **(E)**.

698

Figure 4. Effect of sodium borohydride (NaBH₄) pretreatment on coagulation. **(A)** Floc growth curve for JM water with/without pretreatment. **(B)** Plateau floc size (evaluated by FI) under different concentrations of NaBH₄. Error bars represent the standard deviation of triplicate measurements. **(C)** FT-IR spectrum of JM water treated by different concentrations of NaBH₄. **(D)** High-resolution scans (C 1s) of X-ray photoelectron spectroscopy of flocs formed with and without pretreatment by 200 mg/L NaBH₄. **(E)** Schematic diagram showing the structure of pristine natural organic matter (NOM, left), and Low NaBH₄-treated NOM (right).

699

Figure 5. The differences in the mechanism of sodium borohydride (NaBH₄) in JM water and HA solution. **(A-C)** Diagrams of the different action mechanisms of nature organic matter (NOM) with coagulant interactions in the two solutions, NOM-coagulant interactions **(A)**, High NaBH₄-treated NOM-coagulant in HA solution **(B)**, and High NaBH₄-treated NOM-coagulant in JM water **(C)**. **(D)** Floc growth curve for HA solution with/without pretreatment. **(E)** Plateau floc size (evaluated by FI) under different concentrations of NaBH₄ in HA solution. **(F)** The concentration of free Ca²⁺ in JM water with different doses of NaBH₄. Error bars represent the standard deviation of triplicate measurements (n = 3).

700

Table 1: Wavenumber and corresponding functional groups in the FT-IR spectrum

Wavenumber (cm ⁻¹)	Functional group
1650	C=O stretching (amide I or quinone)
1410	C-O stretching (phenolic -OH) or COO ⁻ symmetric stretching
1130	C-O stretching (alcohol/phenol)
1030	C-O-C stretching (ether, e.g., polysaccharides)

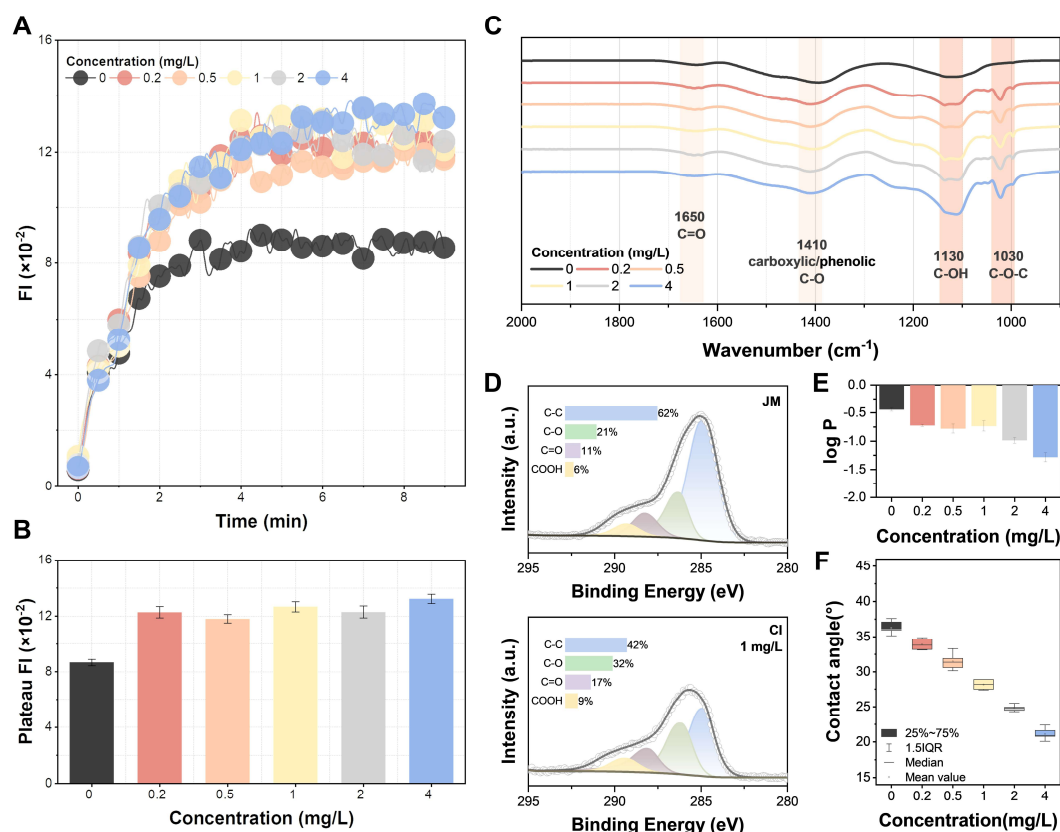


Figure 1. Effect of sodium hypochlorite pretreatment (NaClO) on coagulation. (A) Floc growth curve with/without pretreatment. **(B)** Plateau floc size (evaluated by FI) under different concentrations of NaClO. Error bars represent the standard deviation of triplicate measurements. **(C)** FT-IR spectrum of JM water treated by different concentrations of NaClO. **(D)** High-resolution scans (C 1s) of X-ray photoelectron spectroscopy of flocs formed with and without pretreatment by 1 mg/L NaClO (measured as Cl_2). **(E)** The hydrophilicity of JM water treated with different concentrations of NaClO. The Y-axis ($\log P$) represents the log index of the partition coefficient of the organic matter in the aqueous phase and the organic phase (octanol), the smaller the value the more hydrophilic the organic matter is. Error bars represent the standard deviation of triplicate measurements ($n = 3$). **(F)** Box plot showing the contact angle of flocs formed with JM with and without pretreatment by different concentrations of NaClO ($n=6$).

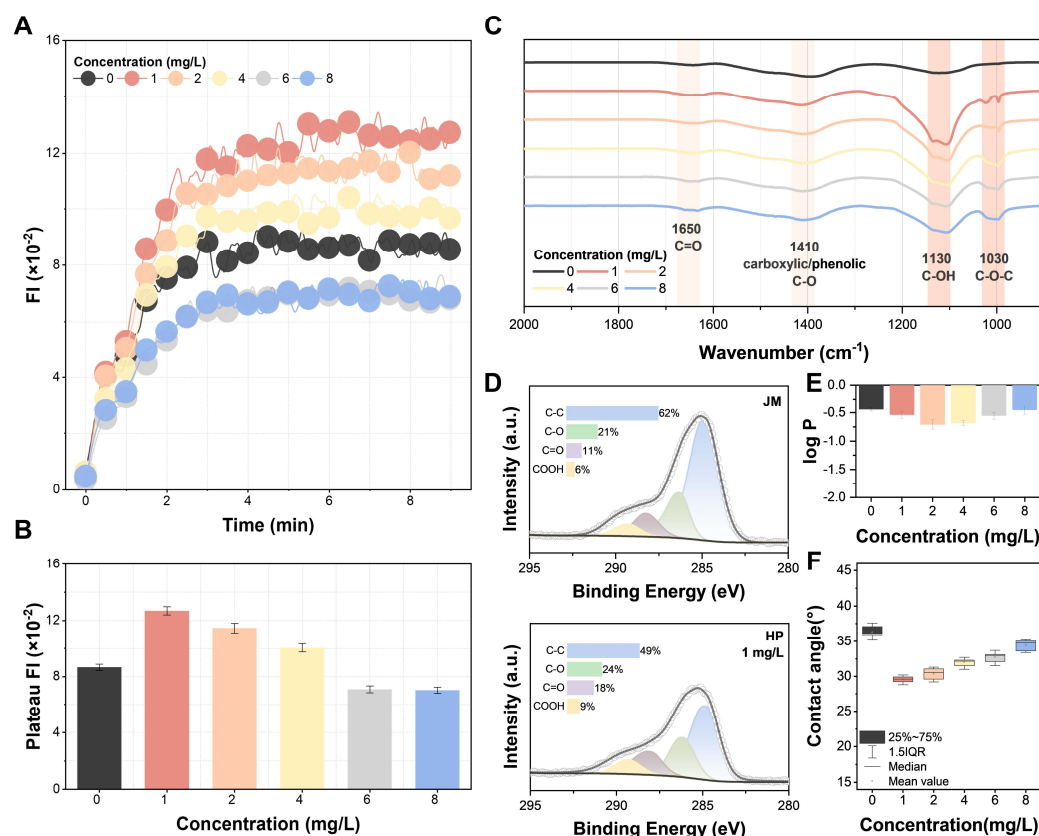


Figure 2. Effect of hydrogen peroxide (H_2O_2) pretreatment on coagulation. (A) Floc growth curve with/without pretreatment. (B) Plateau floc size (evaluated by FI) under different concentrations of H_2O_2 . Error bars represent the standard deviation of triplicate measurements. (C) FT-IR spectrum of JM water treated by different concentrations of H_2O_2 . (D) High-resolution scans (C 1s) of X-ray photoelectron spectroscopy of flocs formed with and without pretreatment by 1 mg/L H_2O_2 . (E) The hydrophilicity of JM water treated with different concentrations of H_2O_2 . The Y-axis (log P) represents the log index of the partition coefficient of the organic matter in the aqueous phase and the organic phase (octanol), the smaller the value the more hydrophilic the organic matter is. Error bars represent the standard deviation of triplicate measurements (n = 3). (F) Box plot showing the contact angle of flocs formed with JM with and without pretreatment by different concentrations of H_2O_2 (n=6).

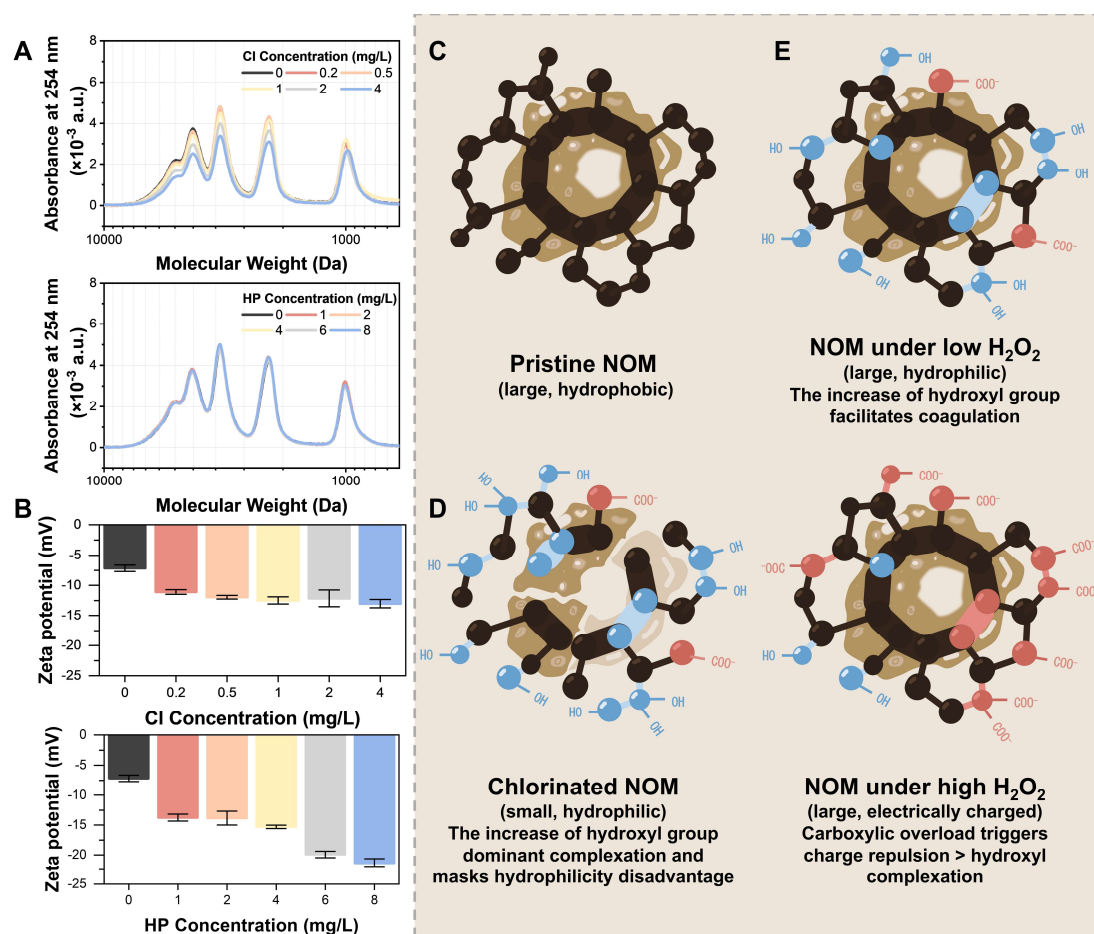


Figure 3. Comparison of the two pre-oxidation processes. (A) The molecular weight distribution of water treated by different concentrations of NaClO (Cl, top) and H_2O_2 (HP, bottom). (B) Zeta potential of water treated by different concentrations of NaClO (Cl, top) and H_2O_2 (HP, bottom). Error bars represent the standard deviation of triplicate measurements ($n = 3$). (C-E) Schematic diagram showing the structure of pristine natural organic matter (NOM, C), Chlorinated NOM (D), and H_2O_2 -treated NOM (E).

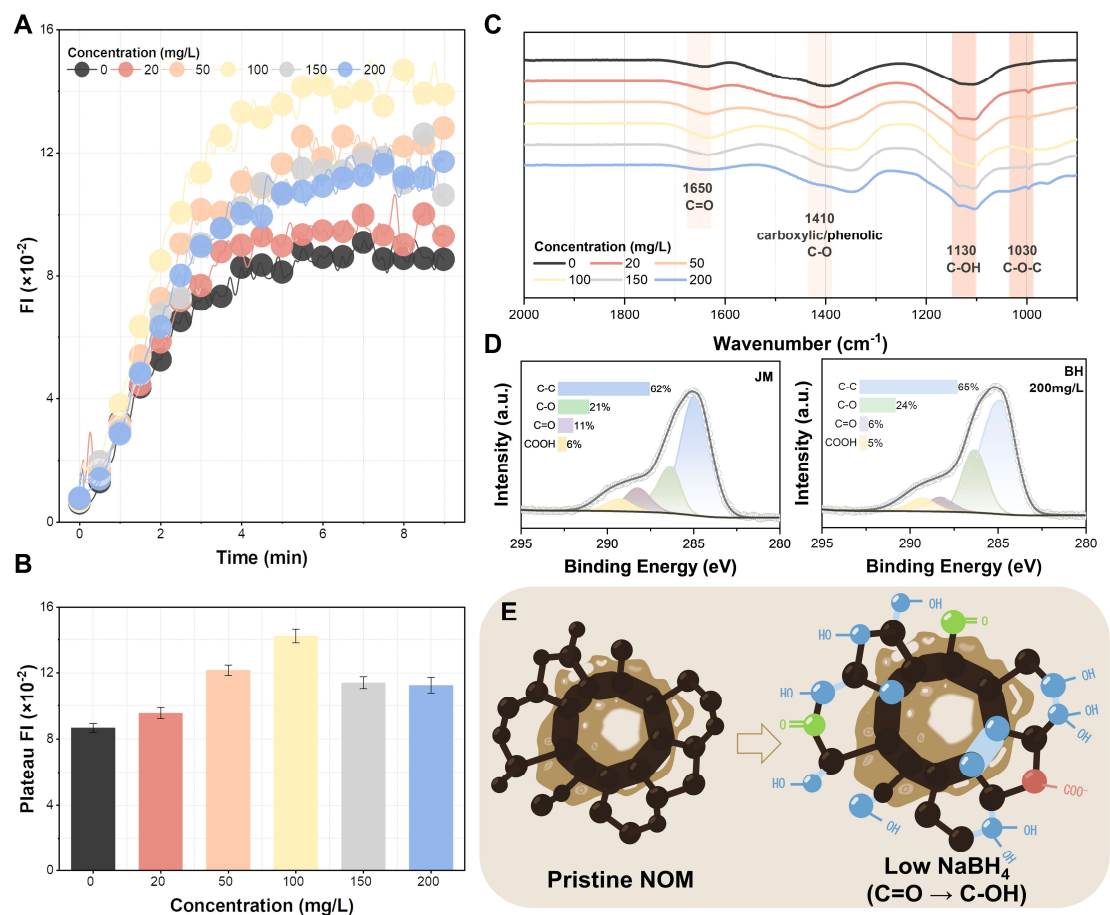


Figure 4. Effect of sodium borohydride (NaBH₄) pretreatment on coagulation. (A) Floc growth curve for JM water with/without pretreatment. **(B)** Plateau floc size (evaluated by FI) under different concentrations of NaBH₄. Error bars represent the standard deviation of triplicate measurements. **(C)** FT-IR spectrum of JM water treated by different concentrations of NaBH₄. **(D)** High-resolution scans (C 1s) of X-ray photoelectron spectroscopy of flocs formed with and without pretreatment by 200 mg/L NaBH₄. **(E)** Schematic diagram showing the structure of pristine natural organic matter (NOM, left), and Low NaBH₄-treated NOM (right).

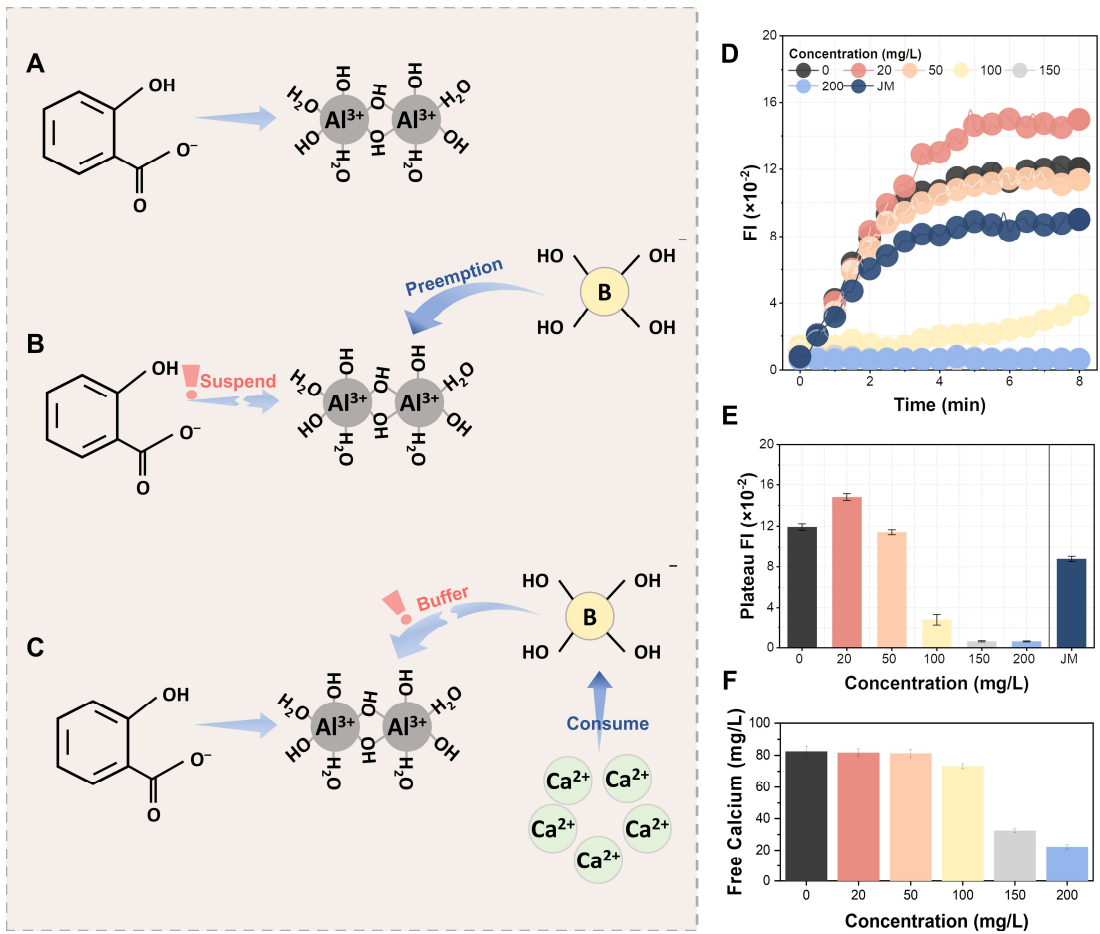


Figure 5. The differences in the mechanism of sodium borohydride (NaBH_4) in JM water and HA solution. (A-C) Diagrams of the different action mechanisms of nature organic matter (NOM) with coagulant interactions in the two solutions, NOM-coagulant interactions (A), High NaBH_4 -treated NOM-coagulant in HA solution (B), and High NaBH_4 -treated NOM-coagulant in JM water (C). **(D)** Floc growth curve for HA solution with/without pretreatment. **(E)** Plateau floc size (evaluated by FI) under different concentrations of NaBH_4 in HA solution. **(F)** The concentration of free Ca^{2+} in JM water with different doses of NaBH_4 . Error bars represent the standard deviation of triplicate measurements ($n = 3$).