Optimized coagulation pretreatment alleviates ultrafiltration membrane fouling: The role of floc properties and slow-mixing speed on mechanisms of chitosan-assisted coagulation

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ABSTRACT

To alleviate ultrafiltration (UF) membrane fouling, the pre-coagulation of poly-aluminum chloride (PACl) with the aid of chitosan (CTS) was conducted for synthetic humic acid–kaolin water treatment. Pre-coagulation of three molecular weights (MW) CTSs (50–190 kDa (CTSL), 190–310 kDa (CTSM) and 310–375 kDa (CTSH)) was optimized with slow-mixing speeds of 30, 60 and 90 r/min, respectively. The removal efficiency and floc properties as well as membrane fouling were analyzed, and were compared to results obtained by conventional coagulation with PACl. Results showed that variations in floc properties could be ascribed to the coagulation mechanisms of CTSL/CTSM/CTSH at different slow-mixing speeds, resulting in reduced UF membrane fouling. Specifically, at the low speed of 30 r/min, all three CTS types produced flocs with similar properties, while CTSL resulted in the lowest removal efficiency and aggravated irreversible fouling. At the appropriate speed of 60 r/min, CTSM generated the most compact flocs with the combined effects of bridging and path mechanisms. The compact cake layer formed could alleviate irreversible fouling, which was beneficial for prolonging the operation of the UF membrane. At the high speed of 90 r/min, CTSH formed fragile flocs and aggravated irreversible membrane fouling. We considered membrane fouling to be affected by floc properties and the resultant removal efficiency, which was governed by the MW of the CTS used and the slow-mixing speed applied as well.

Introduction

Ultrafiltration (UF) technology has increasingly been applied in drinking water treatment, owing to its excellent purification properties under variable feed-water characteristics (Li et al., 2016). Membrane fouling is the main limitation impeding its wide application (Ma et al., 2014). To alleviate membrane fouling, the coagulation process is considered one of the most promising pretreatments. The combined process of coagulation pretreatment and ultrafiltration (C-UF) has widely been used in water treatment (Liu et al., 2017; Shen et al., 2017). In the process of C-UF, flocs accumulate on the UF membrane surface to
produce a cake layer, which can potentially cause membrane fouling as a result of concentration polarization and pore plugging. Different floc properties lead to the different degrees of membrane fouling (Feng et al., 2015; Ma et al., 2018). Previous studies have demonstrated that the floc properties are governed by the type of coagulant or coagulation aid and mixing conditions used, with different coagulation mechanisms including charge neutralization, sweep flocculation and bridging effects (Dubey et al., 2018; Ly et al., 2018; Sun et al., 2015).

As a conventional aluminum-based coagulant, polyaluminum chloride (PACl) has two main drawbacks, including the high cost of sludge disposal and the health risks of aluminum contamination of the environment (it has been related to the onset of Alzheimer’s disease) (Cortini et al., 2018; Kushwaha et al., 2010). Using synthetic polymers as an alternative can reduce the sludge volume, but they also suffer from risks of secondary pollution. As a consequence, environmentally friendly natural polymers have been the focus of attention. Among these, chitosan (CTS), obtained from deacetylation of chitin, is one of the most promising candidates (Ding et al., 2018). Although CTS can be highly effective as a coagulant, it is still not commercially available because of the high production costs. So far, CTS is usually used as coagulant aid to reduce the production costs and to improve the coagulation efficiency (Lessoued et al., 2017; Xu et al., 2014).

As reported, the aiding effect of CTS is dependent on its structural factors, i.e., molecular weight (MW) and degree of deacetylation (DD) (Guibal et al., 2006; Loganathan et al., 2018). Li et al. (2013) demonstrated that MW was more pivotal than DD, and they also showed that CTS with MW in the range of 168–232 kDa adsorbed kaolin particles by charge neutralization, with bridging effect as well as path mechanisms, while CTS with 21–74.5 kDa MW was active in flocculation predominantly by charge neutralization. Meraz et al. (2016) confirmed that CTS with lower MW performed better for pollutant removal and required a lower dosage during the treatment of water containing nejayote (an industrial water pollutant). Miranda et al. (2016) focused on the effect of CTS MW on floc properties during the treatment of wastewater from paper production, and found that CTS with 297 kDa MW produced flocs with the largest mean size, while CTS with 444 kDa MW formed the strongest flocs.

Mixing conditions during coagulation are another important factor affecting the floc properties. It has been found that slow-mixing speed is related to floc characteristics: as the mixing speed increases, floc size declines, while the floc strength, recoverability and floc dimension improve (Ayoub et al., 2014; Yu et al., 2011). Lin et al. (2013) observed that mixing speed influenced the floc properties, which was correlated to the coagulation mechanism involved. Additionally, many efforts have been made to verify that mixing speed should be properly matched with the type of coagulant or coagulant aid and the coagulation mechanisms. Nan et al. (2016a) illustrated that when stirred at different mixing speeds, the coagulation performance and floc characteristics were slightly influenced when PACl was used as the coagulant. Onen et al. (2018) pointed out that the synthetic polymers required lower mixing speeds than conventional coagulants. These findings demonstrated that the floc properties were influenced by the effect of the coagulant type and slow-mixing speed.

In the process of C-UF, the individual effects of the type of coagulant or coagulant aid and mixing conditions on membrane fouling have been studied. Feng et al. (2015) and Wang et al. (2016) stated that different types of conventional coagulants resulted in different fouling mechanisms influenced by floc properties. Wang et al. (2017c) testified that the total fouling resistance was reduced by addition of CTS, as compared with the conventional aluminum-based coagulants alone. Nan et al. (2016b) declared that increased mixing speed led to more severe cake fouling. Accordingly, the effect of different MW-CTS at distinct slow-mixing speeds on floc properties during C-UF treatment merits systematic study.

The effect of CTSs’ MW and slow-mixing speeds on removal efficiency and floc properties have been poorly studied so far with regard to their resulting effects on UF membrane fouling during the treatment of micro-polluted surface water. The major aims of this work were: (1) to explore the influence of MW-CTS and slow-mixing speeds during the flocculation phase on coagulation efficiency and floc properties in humic acid (HA)–kaolin polluted water; (2) to investigate the effect of these two factors on UF membrane fouling mechanisms; and (3) to compare and reveal the relationship between floc properties and UF membrane fouling. Based on conventional jar tests, the coagulation efficiency was comparatively evaluated by measuring the decrease of UV254 and removal of CODmMn, as well as by determining turbidity removal after coagulation. Furthermore, the parameters of strength factor, recovery factor, floc size and fractal dimension of flocs were characterized. The normalized permeate fluxes and membrane fouling resistances were investigated to better understand the membrane fouling mechanism.

1. Materials and methods

1.1. Synthetic surface water

HA and kaolin clay were used in combination as pollutants to represent natural organic matter and turbidity-causing matter, respectively. HA stock solution was prepared by dissolving 10.0 g humic acid sodium salt (Aladdin Chemical Corporation, Shanghai, China) into 1.0 L Milli-Q deionized (DI) water. The pH was adjusted to 7.50 ± 0.05 by adding 0.1 mol/L NaOH. Kaolin (Fuchen Chemical Reagent Factory, Tianjin, China) stock solution was prepared by dispersing 200 g kaolin into 500 mL of DI water by high-speed stirring with the pH raised to 7.50 by adding 0.1 mol/L NaOH. After blending for 2 hr, the clay suspension was diluted to 1.0 L and allowed to stand for 17 hr in a measuring cylinder. The top 700 mL was decanted and retained.

The synthetic surface water was prepared by diluting 5.0 mL of the HA stock solution into 10.0 L tap water, and adding the kaolin solution to adjust the initial turbidity to 70.0 ± 4.5 NTU. The other characteristics of the synthetic surface water used were as follows: UV254 = 0.155 ± 0.010 cm−1, CODMn = 4.5 ± 0.2 mg/L, temperature = 20 ± 1°C, pH = 7.42 ± 0.05.
1.2. Coagulant and coagulant aids

PACI (Fuchen Chemical Reagent Factory, Tianjin, China) was selected as the coagulant and CTS (Sigma–Aldrich, Beijing, China) with various MWs was used as the coagulant aid: low MW CTSL (50–190 kDa), medium MW CTSM (190–310 kDa) and high MW CTSH (310–375 kDa). All CTS used had the same DD range (75%–85%). A PACI stock solution of 0.2 mol/L Al was prepared using DI water. The CTS solutions were prepared by dissolving 0.5 g CTS into 500 mL acetic acid (A.R, 1.0% (W/W)), and stirred at 300 r/min overnight.

1.3. Jar test

Coagulation experiments were conducted in 1.0 L beakers using a programmable six-paddle blender (ZR4–6, Zhongrun Water Industry Technology Development Co. Ltd., China) at 25°C. The experimental procedure was as follows: initial mixing at 300 r/min (G = 367 sec⁻¹) for 0.5 min to obtain homogeneity; mixing at 300 r/min for 1 min while the PACI was added and towards the end when the CST was added; slow-mixing at 30/60/90 r/min (G = 17/42/73 sec⁻¹), respectively for 15 min with a settling phase of 15 min. After final settling (15 min) the supernatant was collected and used to measure residual turbidity, UV254 absorbance and CODMn concentration. All experiments combined PACI with one of the three MW CTSs, denoted as PACI-CTSL, PACI-CTSM and PACI-CTSH, respectively. Turbidity was monitored using a 2100 N turbidimeter (Hach, USA). The supernatant was filtered through a 0.45 μm acetate fiber membrane prior to UV254 determination using a UV/Vis spectrophotometer (UV2600, China). CODMn was measured using a COD-60A Measuring Unit (Hach, USA).

1.4. Ultrafiltration process

The UF experiments were conducted using a magnetically stirred batch cell (Amicon 8400, Millipore, USA) with a capacity of 400 mL and an effective area of 45 cm². The experiments were performed in dead-end mode with a constant pressure of 0.08 MPa, which was controlled by a pressure gauge. During the experiments, the permeate flux was recorded using an electronic balance connected to a computer. For each UF experiment, UF membranes (PALL, USA) with an MW cut-off of 100 kDa were used. The membrane was placed inside the cell and the feed water was drawn from the coagulation process without sedimentation. After flocculation at slow-mixing phase of 30/60/90 r/min, the feed water sample was added directly from the top of the cell into the magnetically stirred batch cell.

Before the filtration test, the DI water flux of the UF membrane was determined by filtration of 300 mL DI water. Subsequently, 300 mL of water sample was injected into the system with the permeate flux automatically recorded as described above. After the filtration, the fouled membrane was removed from the cell and gently cleaned with a sponge to remove the cake layer, and then 300 mL DI water was filtered to determine the flux after physical cleaning. All filtration tests were performed in duplicate for each sample.

1.5. Floc characteristics

1.5.1. Floc formation, breakage and regrowth measurements

Experiments on the kinetics of formation, breakage and regrowth of flocs were performed using an intelligent particle dispersion analyzer (iPDA-100, EcoNovel Company Ltd. Seoul, Korea). The average transmitted light intensity (dc value) through the flowing sample and the root-mean-square value (rms) of the fluctuating component were monitored. Their ratio rms/dc provides a sensitive measure of particle aggregation and is also described as FI. This ratio strongly correlates with the respective floc size and increases as flocs grow larger. The coagulation procedures of floc formation, breakage and regrowth was carried out as follows: after a rapid-mixing phase of 300 r/min for 1 min and slow-mixing phase of 30/60/90 r/min for 15 min, flocs were remixed at 300 r/min for 1 min followed by a floc regrowth period at 30/60/90 r/min for 15 min. FI was recorded automatically by a PC data acquisition system (Pico ADC-11, Pico Technology, UK) at 1 sec intervals.

The floc strength factor $S_f$ and recovery factor $R_f$ describe flocs’ strength and recovery ability, and are calculated according to Eqs. (1) and (2) (Yukselen and Gregory, 2004), respectively, where $d_1$ is the maximum FI value before floc breakage; $d_2$ is the FI value when the flocs are broken after intensive stirring at 300 r/min; $d_3$ is the maximum FI value for regrowth of flocs after intensive stirring. Here, $S_f$ is a measure of the resistance of the formed flocs to shear force, while $R_f$ is a measure of the sensitivity of the aggregates of ruptured flocs after breakage. The larger $S_f$ is, the less sensitive the flocs are to breakage from increased mixing speed, so that they are considered to be stronger. Likewise, flocs with larger $R_f$ values show better recoverability after high shear forces, that is, they are more recoverable after breakage.

\[
S_f = \frac{d_2}{d_1} \times 100
\]

\[
R_f = \frac{d_3 - d_2}{d_1 - d_2} \times 100
\]

1.5.2. Fractal dimension and floc size

As flocs have the characteristics of fractals, fractal theory can describe irregular floc structures as follows (Wang et al., 2017a), where $A$ is the projected area, $F$ is the characteristic measure of perimeter, and $D_{pf}$ is the two-dimensional fractal dimension. Generally, smaller $D_{pf}$ values indicate flocs with highly branched and porous structures, while flocs with more a compact structure produce higher $D_{pf}$ values.

\[
A \propto F^{D_{pf}}
\]

Floc size $d$ was calculated by Eq. (4) (Logan and Kilps, 1995):

\[
d = \left( \frac{4A}{\pi} \right)^{\frac{1}{2}}
\]

1.6. Membrane fouling resistance analyses

The resistance-in-series model was used to analyze the membrane fouling resistance (Choo and Lee, 1996). The total
resistance ($R_t$) included intrinsic membrane resistance ($R_m$),
cake fouling resistance ($R_c$) and pore blocking resistance ($R_p$).

\[ R_t = R_m + R_c + R_p \]  \hspace{1cm} (5)

\[ R_m = \frac{\Delta P}{\mu J_1} \]  \hspace{1cm} (6)

\[ R_t = \frac{\Delta P}{\mu J_2} \]  \hspace{1cm} (7)

\[ R_p = \frac{\Delta P}{\mu J_3} - R_m \]  \hspace{1cm} (8)

where $\mu$ (Pa·sec) is the fluid viscosity, $J$ (m$^3$/m$^2$·sec) is the permeate flux, $J_1$ (m$^3$/m$^2$·sec) is the flux of the filtration of DI water with a new membrane, $J_2$ (m$^3$/m$^2$·sec) is the flux at the end of the feed water sample, and $J_3$ (m$^3$/m$^2$·sec) is the flux of the filtration of DI water after physical cleaning with a sponge.

2. Results and discussion

Initially, applying a slow-mixing speed of 60 r/min to PACl dosages of 0.04, 0.06 and 0.08 mmol/L, the UV$_{254}$, COD$_{Mn}$ and turbidity removal efficiencies with different CTS$_M$ dosages ranging from 0 to 1.0 mg/L were investigated. The results for CTS$_M$ are displayed in Fig. 1. These pilot experiments revealed that for the tested PACl concentrations, there were only marginal differences in UV$_{254}$, COD$_{Mn}$ and turbidity removal as the CTS dosage varied. The increase of UV$_{254}$, COD$_{Mn}$ and turbidity removal was apparent at the lower dosage of CTS$_M$ and was only inapparent at the higher dosage. The pollutant removal was optimized at 0.3 mg/L, as at higher concentrations the removal efficiency started to decline. These findings were consistent with the results reported by Wang et al. (2017b), who reported that CTS combined with PACl could generate Al-NH$_2$ by charge neutralization to enhance coagulation efficiency, while electrostatic repulsion could occur when CTS was added in excess. CTS$_H$ and CTS$_I$ displayed a pollutant removal performance similar to that of CTS$_M$ when applying 60 r/min and 0.04, 0.06 and 0.08 mmol/L PACl (Appendix A Fig. 1S). Therefore, 0.3 mg/L of CTS$_I$/CTS$_M$/CTS$_H$ were chosen for further experiments.

2.1. Effect of chitosan molecular weight and mixing speed on removal efficiency

The effect of different CTS-MW and of variable slow-mixing speeds on removal efficiency was determined next. The dosage of the tested CTS types was kept constant at 0.3 mg/L, while the PACl was varied from 0 to 0.12 mmol/L. The slow-mixing speed was set as 30/60/90 r/min, respectively.

As seen in Fig. 2, for the conventional coagulation with PACl alone, the removal efficiency of UV$_{254}$, COD$_{Mn}$, and turbidity noticeably improved when the PACl dosage varied from 0 to 0.06 mmol/L, while the growth trend was inconspicuous at PACl dosed above 0.06 mmol/L. All of the three CTS types could significantly improve UV$_{254}$, COD$_{Mn}$, and turbidity removal, as compared to the conventional coagulation by PACl alone, which was consistent with a previous study (Wang et al., 2017c).

As observed in Fig. 2a and b, when the slow-mixing speed was set as 30 r/min, it was found that CTS$_I$ gave the highest removal of UV$_{254}$, COD$_{Mn}$, and turbidity for PACl under 0.06 mmol/L, and the differences of the three CTS types became less distinct beyond that PACl concentration. The better coagulation performance of higher MW CTS under 0.06 mmol/L PACl may indicate that it contains higher polymeric surface area that can absorb more particles (Strand et al., 2003). However, Fig. 2c and d show that PACl-CTS$_M$ produced the best removal efficiency at 60 r/min, followed by CTS$_H$ and CTS$_I$, when PACl was dosed below 0.04 mmol/L. As shown in Fig. 2e and f, the effect of different CTS types on removal efficiency was found to vary in the order of PACI-CTS$_I$ > PACI-CTS$_H$ > PACI-CTS$_M$ for PACI under 0.04 mmol/L. These results showed that higher MW of CTS was not directly responsible for the better removal efficiency, which could be explained by two aspects: (1) it was reported that coagulation mechanisms are dependent on the biopolymer chain length and electrostatic interactions of CTS. Therefore, different mechanisms would take place in the experiments with different CTS types (Miranda et al., 2016; Renault et al., 2009); (2) these different mechanisms would produce flocs with different characteristics, which would in
turn affect the coagulation efficiency. The best removal efficiencies of CTSd and CTSi occurred at 60 and 90 r/min, respectively, which indicates that they possibly produced the largest or the most compact flocs, and we further discuss this in Section 2.2.

Interestingly, for the same MW of CTS, the removal efficiency was somewhat influenced by the speed of slow-mixing. Comparing results obtained with the speeds of 30, 60 and 90 r/min shown in Fig. 2, it could be observed that when the PACl dose was under 0.04 mM, all removals at 30 r/min.
were much lower than at 60/90 r/min. For example, when PACl was dosed at 0.04 mmol/L, the average removal of UV254 for the three MW CTSs at 30, 60 and 90 r/min was 56.3%, 81.7% and 77.7%, respectively. The removal differences were marginal for PACl dosed beyond 0.04 mmol/L. This was because low mixing speed impeded the collision frequency of particles and coagulants, which impaired the coagulation efficiency (Xiao et al., 2010). A higher concentration of PACl compensated for the effects of low mixing speed to improve collision efficiency (Yu et al., 2011), whereas the similarly efficient removals at 60/90 r/min reflected that the collision frequency was adequately high in such cases. As reported, the improved slow-mixing speed caused increased suspension stability, leading to reducing the floc size and improving the fractal dimension (Onen et al., 2018; Wang et al., 2018b). Therefore, although the removal efficiencies at 60 and 90 r/min were similar, they formed flocs with distinct properties, which are discussed in the following Section 2.2.

2.2. Floc characteristics

2.2.1. Kinetics of floc formation, breakage and regrowth

Based on the above-mentioned results, the coagulation performance of the different CTS types as determined by UV254, CODMn, and turbidity removal was the most different at 0.04 mmol/L PACl. Therefore, in the next set of experiments the dosage of CTS and PACl was kept constant at 0.3 mg/L and 0.04 mmol/L, respectively, and FI was determined during formation, breakage and regrowth when the three MW CTS types were exposed to slow-mixing speeds of 30/60/90 r/min.

Fig. 3 shows that the FI of the three CTS types followed similar trends at slow-mixing speeds set at 30/60/90 r/min, with a gradual increase during the first state before breakage, followed by a sharp decline at the breakage point, after which the FI was again elevated until reaching a second state plateau. Interestingly, the different CTS-MW resulted in different FI plateaus at the same speed. These plateaus were similar before or after the breakage point occurring at 30 r/min were attributed to the slow speed causing low collision frequency, which impeded the formation of new flocs. The different plateaus of the three CTSs and the shortest balance point occurring at 30 r/min showed that high collision frequency formed flocs with different properties. As reported, CTS with a higher MW resulted in more electrostatic interactions, which could attribute to the bridging effect and result in an improved floc size (Li et al., 2013). Therefore, the highest MW CTS obtained the highest plateau, which could be explained by its effect of higher than that for PACl-CTSM (Fig. 3c). In addition, the mixing speed played a critical role in the floc formation, breakage and regrowth. There was no appreciable variation in the onset or rate of the increase in FI value, but the balance point of floc formation and breakage at 30 r/min was shorter than that at 60 or 90 r/min. Besides, the FI plateau both before and after breakage declined with the increased mixing speed, which verified that flocs with different floc size were formed.

Fig. 3 reflects the fact that the variation of FI is influenced by the MW of CTS as well as by the speed of slow-mixing. It was reported that large flocs under high collision frequency were easily broken up into micro-flocs, which could combine with CTS to produce new flocs (Xu et al., 2015). Therefore, the similar plateaus of the three CTSs and the shortest balance point occurring at 30 r/min were attributed to the slow speed causing low collision frequency, which impeded the formation of new flocs. The different plateaus of the three CTSs at 60 and 90 r/min showed that high collision frequency formed flocs with different properties. As reported, CTS with a higher MW resulted in more electrostatic interactions, which could attribute to the bridging effect and result in an improved floc size (Li et al., 2013). Therefore, the highest MW CTS obtained the highest plateau, which could be explained by its effect of

### Table 1 – Strength factor and recovery factor of flocs at three slow-mixing speeds.

<table>
<thead>
<tr>
<th>Coagulants</th>
<th>Slow-mixing speed (r/min)</th>
<th>30</th>
<th>60</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>PACI</td>
<td>21.06 ± 0.43</td>
<td>32.24 ± 0.35</td>
<td>35.87 ± 0.78</td>
<td></td>
</tr>
<tr>
<td>PACI-CTSL</td>
<td>30.58 ± 0.52</td>
<td>34.47 ± 0.43</td>
<td>44.34 ± 0.27</td>
<td></td>
</tr>
<tr>
<td>PACI-CTSM</td>
<td>31.23 ± 0.11</td>
<td>36.36 ± 0.15</td>
<td>42.97 ± 0.42</td>
<td></td>
</tr>
<tr>
<td>PACI-CTSH</td>
<td>31.96 ± 0.19</td>
<td>38.78 ± 0.25</td>
<td>39.59 ± 0.46</td>
<td></td>
</tr>
<tr>
<td>PACI</td>
<td>70.01 ± 0.36</td>
<td>56.32 ± 0.92</td>
<td>47.63 ± 0.45</td>
<td></td>
</tr>
<tr>
<td>PACI-CTSL</td>
<td>129.65 ± 0.28</td>
<td>98.68 ± 0.43</td>
<td>80.52 ± 0.37</td>
<td></td>
</tr>
<tr>
<td>PACI-CTSM</td>
<td>130.14 ± 0.43</td>
<td>104.41 ± 0.74</td>
<td>78.07 ± 0.56</td>
<td></td>
</tr>
<tr>
<td>PACI-CTSH</td>
<td>130.67 ± 0.32</td>
<td>93.70 ± 0.15</td>
<td>80.43 ± 0.62</td>
<td></td>
</tr>
</tbody>
</table>

*Sf*: Strength factor; *Rf*: Recovery factor.
bridging. However, the cases of PACI-CTSM at 60 r/min (path mechanism) and PACI-CTS at 90 r/min (bridging effects) reflected that not only the CTS-MW but also the mixing speed could affect the involved mechanisms, which affected the FI value (Miranda et al., 2016).

2.2.2. Floc strength and recovery ability

To investigate floc variations, the $S_f$ and $R_f$ of flocs were used to interpret the floc strength and recovery ability. As seen in Table 1, all of the three CTSs at 30/60/90 r/min clearly improved the $S_f$ compared with the CTS-free control, already indicating that stronger flocs were produced in the presence of CTS. Additionally, similar $S_f$ values were found for the three MW CTSs at 30 r/min. At 60 r/min, the $S_f$ increased as with the MW of CTS, resulting in stronger flocs with PACI-CTSM than with PACI-CTS. This may be due to an improved bridging effect of PACI-CTSM, while PACI-CTS may have resulted in more charge neutralization. However, the $S_f$ of PACI-CTSM was lower than that of PACI-CTS at 90 r/min, which reflected that weaker flocs were generated under this condition. This partially verified that the lower removal efficiency of PACI-CTSM at 90 r/min was due to their weaker floc strength. For the same MW CTS, the $S_f$ improved with higher speed, which was in accordance with a previous study (Yu et al., 2011).

Table 1 further illustrates that, compared to the conventional coagulation, all of the three CTSs at 30/60/90 r/min significantly improved the $R_f$ which was due to electrostatic interactions (van der Waals forces and hydrogen bonds) (Meraz et al., 2016). Besides, the $R_f$ of the three MW CTSs were similar at 30 and 90 r/min, while for PACI-CTSM the highest $R_f$ was obtained at 60 r/min. Moreover, it was clear that the $R_f$ at 90 r/min were the lowest among three mixing speeds in all cases, which indicated that in this case the broken flocs were more irreversible.

2.2.3. Fractal dimension and floc size

The fractal dimension ($D_{pf}$) and size of flocs before breakage were calculated to characterize the floc structure (Fig. 4). As shown in Fig. 4a, all three CTS types at 30/60/90 r/min...
improved the $D_{pf}$ compared to the CTS-free control, indicating that the flocs became more compact than with conventional coagulation. At 30 r/min, a similar $D_{pf}$ was obtained for all three MW CTSs, which reflected that flocs were produced with similar compactness. With a speed of 60 r/min, of the three MW CTS types CTS$_{l}$ produced the lowest $D_{pf}$. When synthetic polymers are used as coagulant aids, flocs flocculated by the bridging effect had larger $D_{pf}$ values than flocs produced by charge neutralization (Wang et al., 2017a). Based on this, we ascribe the larger $D_{pf}$ of PACl-CTSM/CTSH to the contribution of the bridging effect. With a speed of 90 r/min, the fact that PACl-CTS$_{l}$ had the highest $D_{pf}$ also confirmed this effect. Comparisons between conditions within a single CTS type showed that the $D_{pf}$ increased with higher mixing speed, which corroborated previous observations (Nan et al., 2016a). As shown in Fig. 4b, the tendency was observed that floc sizes were similar at the plateau of the FI value before breakage (cf. Fig. 3).

When we consider the floc characteristics in terms of $S_{f}$ and $D_{pf}$ as well as floc size, it could be found that the three CTSs formed flocs with similar characteristics at the low mixing speed of 30 r/min. At the appropriate speed of 60 r/min, PACl-CTS$_{l}$ may exhibit more charge neutralization, while CTS with higher MW may show the bridging effect and form more compact and larger flocs. Specially, a high $S_{f}$ and the highest $D_{pf}$ of flocs was observed for PACl-CTSM, which reflected the formation of flexible flocs. This was because the path mechanism applied here. At the high speed of 90 r/min, the high $S_{f}$ and the highest $D_{pf}$ of flocs for PACl-CTS$_{l}$ reflected a combined result of charge neutralization and bridging, which was similar to PACl-CTSM/CTSH. However, PACl-CTSH reached low $S_{f}$ and $D_{pf}$ values but produced the largest floc size. This suggested that in this case fragile flocs were formed that are easily broken and quickly re-coagulate to produce flocs with a porous structure.

### 2.3. UF membrane filtration

The feed water suspensions were filtered through UF membranes (100 kDa) at a constant pressure as described in the Methods section. The impact of different MW-CTS and slow-mixing speeds on the permeate flux ($J/J_{0}$) is presented in Fig. 5. The presence of three MW CTSs increased the membrane flux when compared with the CTS-free control, which alleviated the UF membrane fouling, as had been described before (Wang et al., 2017a).

Interestingly, of the three CTS types, CTS$_{l}$ obtained the lowest flux decline ($J/J_{0} = 0.39$) and thus caused the highest membrane fouling at 30 r/min, while the $J/J_{0}$ of CTS$_{m}$ and CTS$_{h}$ were similar. Bu et al. (2016) reported that both $D_{pf}$ and flocs size could influence the degree of membrane fouling. In general, flocs with denser $D_{pf}$ but smaller sizes could cause more severe membrane fouling. However, in our experiments CTS$_{h}$ reached a similar $S_{f}$ and $D_{pf}$ values but produced the largest floc size. This suggested that in this case fragile flocs were formed that are easily broken and quickly re-coagulate to produce flocs with a porous structure.

![Fig. 6 – Membrane fouling resistances a different slow-mixing speeds. (a) 30 r/min, (b) 60 r/min and (c) 90 r/min.](image-url)
2.4. Resistance analysis

In order to further investigate the mechanism behind membrane fouling, resistance analysis tests were conducted (Fig. 6). When compared with conventional coagulation, all CTS types at 30/60/90 r/min could obviously reduce the $R_t$, which was mainly ascribed to the reduction of $R_c$ and $R_p$. As compared to the average membrane pore size (30 nm, manufacturer provided), the larger size flocs (see Section 2.2) could be completely rejected by the UF membrane, and caused cake fouling. By contrast, the size of similar HA–kaolin particles was close to the diameter of the membrane pores, causing pore fouling (Ma et al., 2014). This result was correlated with the findings from Wang et al. (2017c), who claimed that CTS could generate larger flocs and alleviated cake fouling; moreover, it improved the removal of HA–kaolin particles as a result of alleviating pore fouling.

Additionally, PACl-CTSM achieved similar $R_t$ but the highest $R_p$ at 30 r/min, which led to the highest $R_c$. This explained why of the three CTS types, CTS$_L$ caused the most severe UF membrane fouling. This showed that the total membrane fouling was influenced by two factors, including floc properties and removal efficiency. Furthermore, PACl-CTSM and PACl-CTSH obtained the highest $R_l$ at 60 and 90 r/min, respectively, both of which caused high $R_c$ but low $R_p$. As reported, the value of $R_c$ reflected the reversible fouling that could be reduced by backwashing, while $R_p$ reflected the irreversible fouling, which was difficult to remove by periodic cleaning (Bu et al., 2016; Wang et al., 2018a). Therefore, although these cases (PACl-CTSM at 60 r/min and PACl-CTSH at 90 r/min) produced compact cake layers, the irreversible fouling was alleviated. This was beneficial for prolonging the operation of the UF membrane.

What’s more, for the same MW CTS, the slow-mixing speed further affected total membrane fouling. As compared to the speed of 60 r/min, the $R_t$ of 30 and 90 r/min was slightly higher. Given the removal efficiency and floc properties (see Sections 2.1 and 2.2), at 30 r/min, the higher $R_t$ was related to higher pore fouling, which was due to the lower removal efficiency. When the speed increased to 90 r/min, the increased mixing speed resulted in an improved $D_{pf}$ and a reduced floc size, resulted in aggravating the cake fouling. Therefore, the higher $R_t$ was ascribed to the higher $R_c$. This phenomenon demonstrated that the degree of membrane fouling should consider the balance of floc properties and removal efficiency, when varying the MW of CTS and the mixing speed.

Above all, we concluded that the CTS types and mixing speeds produced flocs with different properties and distinct resultant removal efficiencies, which led to different degrees of membrane fouling. Fig. 7 depicts the mechanisms we considered to play a role. At the low speed of 30 r/min, PACl-CTS, formed flocs with similar characteristics as PACl-CTSM/CTSH. However, CTS$_L$ achieved the lowest removal efficiency,
which aggravated the irreversible membrane fouling. At the appropriate speed of 60 r/min, as compared to PACl-CTS_{L}, PACl-CTS_{M}/CTS_{H} formed more compact flocs, which alleviated the irreversible fouling. Additionally, PACl-CTS_{M} produced flexible flocs, which aggravated reversible fouling but caused the lightest irreversible fouling. At the high speed of 90 r/min, compared with PACl-CTS_{M}/CTS_{H}, PACl-CTS_{L} formed more compact flocs, which alleviated the irreversible fouling.

### 3. Conclusions

In this study we optimized coagulation pretreatment including CTS of three MWs combined with slow-mixing speeds of 30, 60 and 90 r/min, respectively, to alleviate UF membrane fouling for synthetic HA-kaolin water treatment. Removal efficiency, floc properties and membrane fouling were determined. The experimental observations resulted to the following conclusions: (1) The UF membrane fouling was affected by floc properties and removal efficiency, which varied with the MW of CTS and the speed of slow-mixing. With the involvement of CTS at different slow-mixing speeds, the total membrane fouling could be reduced. Specifically, in the case of PACl-CTS_{M} at 60 r/min and PACl-CTS_{L} at 90 r/min, a compact cake layer was formed. This alleviated the irreversible membrane fouling, which was beneficial for prolonging the operation of the UF membrane. (2) Floc properties were affected by the MW of CTS and the slow-mixing speed. The three CTSs formed flocs with similar characteristics at low mixing speed (30 r/min) because of low collision frequency. When the speed improved to 60 r/min, the three CTS types CTS_{M} formed flexible flocs by a combined mechanism of charge neutralization, bridging effect as well as the path mechanism. At the high speed of 90 r/min, CTS_{L} could also show the bridging effect and this formed compact flocs, while CTS_{H} formed fragile flocs. (3) Pollutant removal efficiency should be well matched with the type of CTS and slow-mixing condition. At the low speed of 30 r/min, the highest MW of CTS obtained the best removal because it had the largest polymeric surface area. At the appropriate speed of 60 r/min, CTS_{M} achieved the highest removal because of the roles played by the bridging and path mechanisms. At the high speed of 90 r/min, CTS_{M}/CTS_{H} performed worse, while CTS_{L} reached the highest removal efficiency.

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### Appendix A. Supplementary data

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### References


