Effect of chitosan based Al species on coagulation performance and ultrafiltration characteristics under different pH conditions

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Coagulation is one of the most important processes used for the removal of fine particles and natural organic matter (NOM) in drinking water treatment.

**Shortages of coagulation:**
- Low dissolved organic matters removals
- High chemical consumption in eutrophic water treatment
- Low fatal microorganisms removals

**Ultrafiltration (UF) has been known to be effective for the removal of:**
- Not effective in dissolved organic matter removal
- Membrane foulings

**Shortages of ultrafiltration:**
- High NOM removal efficiency
- Prevent membrane foulings
As aluminum salts dosed into water, there would be a series of hydrolysis reactions and different aluminum species generated: $\text{Al}_a$, $\text{Al}_b$ and $\text{Al}_c$.

Monomeric ($\text{Al}_a$), $\text{Al}^{3+}$, $\text{Al(OH)}^2^+$, $\text{Al(OH)}_2^+$

Tridecamer ($\text{Al}_b$), $\text{AlO}_4\text{Al}_{12}\text{(OH)}_{24}(\text{H}_2\text{O})_{12}^{7+}$

Larger polynuclears ($\text{Al}_c$), $\text{(AlO}_4^2\text{Al}_{28}\text{(OH)}_{56}(\text{H}_2\text{O})_{26}^{18+}$

Chitosan (CS) was the second most abundant biopolymer after cellulose in the world which produced by the deacetylation of chitin.

- Macromolecular polymers
- Positive bridging effect role
- Low cost and non-toxic

CS after acid protonation
Coagulation process

Ultrafiltration process

**Coagulation process**

**Rapid mixing**
- 1.5 min

**Slow mixing**
- 15 min

**Sedimentation**
- 30 min

**Collected water samples**
- Turbidity, UV$_{254}$, DOC, Zeta potential

**Humic acid-Kaolin sample**

**Alb** (ethanol/acetone solution)

**Alc** (methanol/acetone solution)

**AlCl$_3$·6H$_2$O + NaOH**

**Water bath**

**Air drying**

**Purification**

**Aluminum salts coagulants**

**Ultrafiltration**

**UF membrane**

**Balance**

**PC**
**Floc characteristic**

- Floc size \((d_{50})\)
- Strength factor \((S_f)\)
- Recovery factor \((R_f)\)
- Fractal dimension \((D_f)\)

![Graph showing floc characteristic](image)

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

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

- Scattered light intensity \((I)\)
- Scattering vector \((Q)\)

- When pre-formed flocs \((d_1)\) are subjected to an increased shear rate, floc breakage occurred.

- The breakage flocs \((d_2)\) could regrow when the shear force disappeared, which achieved a balance \((d_3)\).
Membrane resistances

Total hydraulic resistance ($R_t$)

External fouling ($R_{ef}$)
- Loosely-attached resistance ($R_{ef-l}$)
- Strongly-attached resistance ($R_{ef-s}$)

Internal fouling ($R_{if}$)
- Reversible resistance ($R_{if-r}$)
- Physically irreversible fouling resistance ($R_{irr}$)

\[ R_t = \frac{\text{TMP}}{\mu J} = R_m + R_{ef} + R_{if} \]
\[ R_{ef-l} = \frac{\text{TMP}}{\mu J_1} - \frac{\text{TMP}}{\mu J_2} \]
\[ R_{ef-s} = \frac{\text{TMP}}{\mu J_2} - \frac{\text{TMP}}{\mu J_3} \]
\[ R_m = \frac{\text{TMP}}{\mu J_0} \]
\[ R_{irr} = \frac{\text{TMP}}{\mu J_4} - \frac{\text{TMP}}{\mu J_0} \]
\[ R_{if-r} = \frac{\text{TMP}}{\mu J_3} - \frac{\text{TMP}}{\mu J_4} \]

$R_m =$ clean membrane resistance ($\text{m}^{-1}$)
$\mu =$ dynamic viscosity of the feed water ($\text{Pa} \cdot \text{s}$)
$\text{TMP} =$ trans-membrane pressure ($\text{Pa}$)
$J/J_0/J_1/J_2/J_3/J_4 =$ permeate flux
The aluminum dosage of 4 milligrams per liter and chitosan dosage of 1 milligram per liter was selected to be the optimal dosages. (Wang W, Yue Q, et al. Purification, characterization and application of dual coagulants containing chitosan and different Al species in coagulation and ultrafiltration process. Journal of Environmental Sciences, 2016)

Coagulation efficiency of Al\textsubscript{a}/Al\textsubscript{b}/Al\textsubscript{c}-CS presented a similar trend as Al species coagulants, and adding adequate CS could enhance the coagulation efficiency within the pH ranges.
Floc sizes

- Floc size achieved maximum value at pH 6 by Al species individually, and the floc sizes were smallest at pH 9 except for Alₐ.
- Floc size in steady-state was apparently increased due to the addition of CS.
- CS as coagulant aid was less affected by pH in water treatment, which indicated that combined Al with CS have a wide pH ranges.
### Floc breakage and re-growth

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Coagulant</th>
<th>pH</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>S&lt;sub&gt;f&lt;/sub&gt;</td>
<td>Al&lt;sub&gt;a&lt;/sub&gt;</td>
<td>25.14 ± 0.22</td>
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<tr>
<td></td>
<td>Al&lt;sub&gt;a&lt;/sub&gt;-CS</td>
<td>30.41 ± 0.27</td>
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<td>Al&lt;sub&gt;b&lt;/sub&gt;</td>
<td>32.70 ± 0.31</td>
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<tr>
<td></td>
<td>Al&lt;sub&gt;b&lt;/sub&gt;-CS</td>
<td>29.48 ± 0.29</td>
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<tr>
<td></td>
<td>Al&lt;sub&gt;c&lt;/sub&gt;</td>
<td>30.01 ± 0.33</td>
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<tr>
<td></td>
<td>Al&lt;sub&gt;c&lt;/sub&gt;-CS</td>
<td>28.10 ± 0.18</td>
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<td>R&lt;sub&gt;f&lt;/sub&gt;</td>
<td>Al&lt;sub&gt;a&lt;/sub&gt;</td>
<td>70.33 ± 0.51</td>
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<tr>
<td></td>
<td>Al&lt;sub&gt;a&lt;/sub&gt;-CS</td>
<td>55.71 ± 0.47</td>
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<td></td>
<td>Al&lt;sub&gt;b&lt;/sub&gt;</td>
<td>67.75 ± 0.54</td>
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<td>50.21 ± 0.42</td>
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<td></td>
<td>Al&lt;sub&gt;c&lt;/sub&gt;</td>
<td>48.89 ± 0.39</td>
</tr>
<tr>
<td></td>
<td>Al&lt;sub&gt;c&lt;/sub&gt;-CS</td>
<td>57.26 ± 0.48</td>
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</tbody>
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- The S<sub>f</sub> and R<sub>f</sub> values of floc increased due to the CS addition.
- Maximum S<sub>f</sub> and R<sub>f</sub> were mainly acquired at pH 6 due to the strongest charge neutralization effect.
$D_f$ was in a stable state at growth period and regrowth period, but a rapidly increasing was found during the breakage period.

$D_f$ showed a reduction when CS as coagulation aid added.
The most serious membrane resistances was observed when no coagulant was used.

The reduction of $R_t$ was due to the larger floc sizes and looser structure when CS was added at the same pH.

In the same system, the smallest total resistances occurred at pH 6, but the maximum value of total resistances achieved at pH 9.
CONCLUSIONS

- HA removal efficiency was the highest at pH 6, and Al\textsubscript{a}/Al\textsubscript{b}/Al\textsubscript{c}-CS increased the removal ratios compared with Al\textsubscript{a}/Al\textsubscript{b}/Al\textsubscript{c}.

- Flocs under acidic conditions were smaller than these under alkaline conditions except for Al\textsubscript{c}. Moreover, larger and looser flocs were formed when CS dosed.

- Membrane resistances were related to membrane fouling which impact on floc size and structure.
Thank you!