NOM removal and residual Al minimization by enhanced coagulation: roles of sequence dosing with PACl–FeCl₃
Ming-Han Tsai, Lap-Cuong Hua, Kochin Huang and Chihpin Huang

ABSTRACT
To remove higher proportions of natural organic matter (NOM) in water treatment plants, over dosing of Al-based coagulant is frequently applied. However, this leads to the risk of an excess of coagulant residue in the clean water. In this study, sequential coagulation with polyaluminum chloride (PACl) and FeCl₃ was proposed to improve the removal of NOM as well as to minimize residual Al. Single dosing with either PACl or FeCl₃ in particular was compared with sequential coagulation, with different dosing sequences of PACl–FeCl₃ (P–F) or FeCl₃–PACl (F–P). At optimum dosage, sequential coagulation P–F showed twice as much dissolved organic carbon (DOC) removal from water containing algogenic organic matter, compared to single dosing of PACl and sequential coagulation F–P. However, sequential coagulation F–P was the most effective approach for humic substance removal that improved DOC removal up to >70% compared to other dosing approaches (<60%). Practical treatment with real water also showed the advantages of sequential coagulation with P–F in improving the removal of low SUVA NOM by 18% compared to the traditional single dosing of PACl. As expected, the Al residues found in both sequential coagulation (0.07 mg/L) were significantly reduced compared to single dosing with PACl (0.15 mg/L), indicating the promising application of sequential coagulation for future safe water treatment.

Key words | coagulation, FeCl₃, NOM, PACl, residual Al

HIGHLIGHTS
● Coagulation behavior was firstly clarified for sequential coagulation.
● PACl–FeCl₃ dosing improved the removal of algogenic organic matter.
● Effective removal of humic acid was observed by FeCl₃–PACl dosing.
● Residual soluble Al was minimized significantly with sequential coagulation.
● Reservoir water confirmed PACl–FeCl₃ in having higher organics removal than PACl.

INTRODUCTION
Humic substances (HS) and algogenic organic matter (AOM) are commonly occurring natural organic matter (NOM) in the aquatic environment. Seasonal occurrence of algal blooms and the release of high concentration of AOM often occur as a result of excess nutrients in natural water (Henderson et al. 2008). Generally, AOM comprises large amounts of nitrogenous organics and hydrophilic (HPI) substances, including free amino acids, peptides and proteins with low specific ultraviolet absorbance (SUVA) value (<2 L/mg C m) (Pivokonsky et al. 2016). By contrast, HS, typically humic acid (HA), either released by soil or produced by the biodegradation of dead plants contains hydrophobic organics with relatively high aromaticity (SUVA value >2 L/mg C m) (Edzwald 1993). Both AOM

doi: 10.2166/aqua.2020.010
and HA are always associated with unacceptable taste and odor in the treated water (Henderson et al. 2008; Ma et al. 2012a, 2012b). In fact, NOM has been proved to bring severe problems in water treatment plants, regardless of their origins, such as increasing coagulant demand (Bernhardt et al. 1985) and resulting in membrane fouling (Campinas & Rosa 2010). Moreover, NOM serving as an important precursor of disinfection byproducts (DBPs) could adversely affect human health (Fang et al. 2010). Therefore, more attention should be paid to ensure the safety and quality of treated drinking water where NOM exists.

Coagulation-flocculation followed by separation process is an indispensable process for particle removal from a water body. PACl has been widely applied as a coagulant because of its low cost and wider working pH range (Matilainen et al. 2010). Although PACl performs well in particle destabilization, it is ineffective in interacting with dissolved organic matter (DOM) (Ghernaout et al. 2014). The formation of DOM-Al complexes during coagulation (Ma et al. 2012a, 2012b) frequently failed to form precipitates at low dosage, which resulted in low DOM removal by sedimentation (Yang et al. 2010). Previous studies have demonstrated that such suspended complexes could be removed by surface adsorption and sweep flocculation only when the dosage was further increased (Pivokonsky et al. 2014). Unfortunately, increasing an Al-coagulant dosage poses the threat of unintentional overdosing, which increases the risk of excessive Al residues in the finished water (Jiao et al. 2015; Pivokonsky et al. 2016). The acceptable level of residual Al in finished water is regulated at <0.2 mg/L as Al in the U.S. and <0.16 mg/L in Taiwan. Therefore, residual Al must be controlled to meet the standards for safe drinking water.

In general, content of residual Al varies according to pH levels (Yang et al. 2010) and the applied dosage of Al-based coagulant (Lin & Ika (2019b)). The lowest Al residue has been found at low water pH (e.g. 6.5) for Al-based coagulant (Jiao et al. 2015). However, in practice the control of pH is difficult because high fluctuation of turbidity in raw water always needs the application of a relatively higher dosage of PACl coagulants. This can cause high risk of residual aluminum, especially for high alkaline water (pH > 8), which is usually associated with algal activity. Under such conditions, high amounts of Al still exists in the form of soluble Al(OH)₄⁻ (Duan & Gregory 2005), indicating that the control of the Al dosage may be a more feasible strategy for this issue, rather than pH control. In this context, adjusting dosage of Al or replacing Al-based coagulants by others has been recommended as a simple and feasible way to deal with the problem of excessive residual Al.

Furthermore, both Al- and Fe-based coagulant are commonly used for low turbidity and NOM water treatment. Compared to Al-based, Fe-based coagulant is more effective in reducing the concentration of NOM in natural water (Zhao et al. 2011), because its binding capacity is high and induces strong Fe-NOM interaction (Pivokonsky et al. 2012). Lin & Ika (2019a) reported that active Fe(OH)₃ contains a large number of binding sites which enabled a more efficient particle aggregation than PACl. Greater removal of NOM was also achieved by Cheng et al. (2003) with the application of FeCl₃ (39%) compared to PACl and alum (14.2 and 25.3%) for reservoir water. For algae-containing water, Fe coagulant is also believed to perform not only in destabilizing algal cells, but also in adsorbing the AOM (Pivokonsky et al. 2016). Pivokonsky et al. (2009) showed that Fe has a high affinity for AOM with DOC, resulting in the removal of 50% at acidic pH. Moreover, high removal (70–78%) of protein from AOM was obtained by Fe coagulation, especially at pH 4–6 (Pivokonsky et al. 2016). Although Fe performs much better in NOM destabilization than Al, including HA and AOM, it is rarely applied in practice because of its corrosive nature, high cost and its inability to deal with high turbid water resulting from sudden rainfall.

In this study, the combined use of Al and Fe coagulant is hypothesized to be an effectively alternative approach in enhancing the destabilization performance of NOM and particles, and eliminating the problem of Al residue. Although the coagulation of particles by the combination of Al- and Fe-based coagulants has been reported elsewhere (Cheng et al. 2003; Lin & Ika (2019b)), research targeting the removal of NOM is limited, and the dosing sequence by Al/Fe coagulation has rarely been compared. We suggest that the dosing sequence could induce different coagulation behaviors and result in higher purification performance compared to traditional single-coagulant dosing.
This study investigates the feasibility of Al/Fe sequential coagulation on the improvement of NOMs and particle removal, and the minimization of residual soluble Al ([Al] residual). To reduce the [Al] residual after treatment and simultaneously improve the NOMs and particle removal, Al was replaced by Fe coagulant in a half dosage (molar ratio of Al:Fe ¼ 1:1). Furthermore, the destabilization behavior of NOM, including AOM and HA, with different dosing sequence (PACl–FeCl3 and FeCl3–PACl) are discussed. For synthetic water experiments, AOM from a green alga *Chlorella* sp. and Aldrich HA solution were mixed with kaolin particles to simulate eutrophic and a humic-rich aquatic systems. *Chlorella* sp. was selected because it is a commonly encountered alga in shadow, fresh water (Ndlela et al. 2016). The experiment was also conducted for water collected from a local reservoir to verify the feasibility of the sequential coagulation in real application.

**MATERIALS AND METHODS**

**Materials**

*Chlorella* sp. was collected in a local reservoir. The protocols of *Chlorella* sp. isolation and cultivation as well as AOM extraction followed those of our previous study, with a minor modification (Hua et al. 2019). These were: after isolation, the alga was cultivated in a 10 L photo-bioreactor at room temperature of 25 °C with intermittent illumination (16:8 light–dark cycle) by TL 4 lamps (35 μmol photons/m²/s). The aeration (5% CO₂ + 95% air) rate was set at 500 mL/min to provide carbon source for algae growth, and the algae suspension was collected from the photo-bioreactor at stationary phase by centrifugation. AOM was extracted via a lyophilizing-grinding-filtering method (Supplementary material). HA (Sigma-Aldrich) was prepared by dissolving the powder in the deionized water. The characteristics of the obtained AOM and HA are listed in Supplementary material, Table S1. NaClO₄, NaHCO₃ and kaolin particles were purchased from JT Baker, USA. The commercial PACl (Chung Hwa Chemical, Taiwan) and FeCl₃ (Jongmaw Chemical, Taiwan) were used in this study for either single dosing (as a control group) or sequential coagulation. The fraction of Al and Fe species analyzed by Ferron method (Lin et al. 2009) for both coagulants is listed in Supplementary material, Table S2.

**Preparation of synthetic and reservoir water**

The synthetic water was prepared by mixing kaolin particles (12–15 NTU) with AOM and HA solutions (DOC of 3–3.5 mg/L) in deionized water (DI). 0.01 M of NaClO₄ and 100 mg/L as CaCO₃ of NaHCO₃ were also added to provide ionic strength and alkalinity. The pH was adjusted using 0.1 M HCl and NaOH to 7.8–7.9 to simulate high alkaline water. In this study, algae-containing water was collected from a local reservoir (Mingde, Taiwan) and pre-stirred at 30 rpm before jar test experiments. The water quality data for both synthetic water AOM + kaolin (SW–A), HA + kaolin (SW–H) and for reservoir water (RW) are given in Table 1.

**Jar test procedure**

Jar test was performed with a jar test apparatus (Phipps & Birds, PB-700, USA), at room temperature of 27 °C. Various dosages from 0.08 to 0.17 mM were applied. For the sequential coagulation, P–F and a reversed sequence F–P were designed. The first dose was added at the beginning of the rapid mixing, while the second dose was injected 30 s after the first dose. The dosage in mM of PACl and FeCl₃ in

<table>
<thead>
<tr>
<th>DOC (mg/L)</th>
<th>Turbidity (NTU)</th>
<th>SUVA (L/mg C m)</th>
<th>pH</th>
<th>Zeta potential (mV)</th>
<th>Alkalinity (mg/L as CaCO₃)</th>
<th>Chlorophyll a (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW–A 3.0–3.2</td>
<td>12–15</td>
<td>0.12–0.44</td>
<td>7.8–8.0</td>
<td>-37</td>
<td>100</td>
<td>N.A. a</td>
</tr>
<tr>
<td>SW–H 3.3–3.8</td>
<td>12–15</td>
<td>5–6</td>
<td>7.8–8.0</td>
<td>-58</td>
<td>100</td>
<td>N.A. a</td>
</tr>
<tr>
<td>RW 2.9–3.5</td>
<td>8–12</td>
<td>0.83–1.14</td>
<td>7.8–7.9</td>
<td>-14</td>
<td>100–120</td>
<td>18–20</td>
</tr>
</tbody>
</table>

aN.A.: Not analyzed.
sequential coagulation was halved (PACl:FeCl₃ = 1:1) of the designed dosage. Rapid mixing was carried out at 240 G for 1 min, followed by slow mixing at 25 G for 15 min, and the mixture was then allowed to settle for another 15 min. During rapid mixing pH was measured at 10, 25, 35 and 60 s. Samples were collected through the outlet of the jar at 30 s (before the second dose) and 60 s (before rapid mixing ended) to verify the destabilization mechanism, by measuring the zeta potential of the particles. The zeta potential was measured by Zetasizer (Zetasizer nano ZS, Malvern).

Ultrafiltration fractionation of synthetic and reservoir water

To clarify the characteristics of NOM in the water matrix of SW–A, SW–H, and RW, water samples were fractionated into four different molecular weight cut-off sizes (>100 kDa, 100–30 kDa, 10–30 kDa and <10 kDa) by a centrifugal device with membrane support (Macrosep Advance Centrifugal Device, Pall, USA). The fractionation conditions followed our previous study (Hua et al. 2019). The fractionated samples were stored at −20 °C before use.

Supernatant analysis

To evaluate the destabilization performance of AOM and HA, dissolved organic carbon (DOC) was analyzed by a TOC analyzer (Shimadzu, TOC-5000A, Japan), with operating pressure maintained at 200 ± 10 psi. Samples had to be at least 30 ml and filtered through 0.45 μm membrane, followed by adding 2 to 3 drops of 1:1 HCl before measurement. In addition, the treated water after sedimentation was collected directly for turbidity measurement. The [Al] residual in the treated water was analyzed by ICP-OES (Agilent, Inductively Coupled Plasma Optical Emission Spectrometry 710 Series ICP-OES, USA), after filtration through 0.45 μm membrane.

Floc formation observation by FlocCAM

In this study, FlocCAM (Jar FlocCAM®, Durasens), a camera used to monitor floc properties, was installed on the jar during fast and slow mixing. White light (wavelength 420–750 nm) produced by LEDs was used as the light source. The physical characteristics of the floc, including floc size, fractal dimension and its number, was obtained by receiving the fraction of the reflected/scattered light from the floc and suspended particles in the monitored region. The detection limit for the particle size ranged from 30 to 15,000 μm. The advantage of this technique was that the floc could be monitored directly through the glass of the jar without altering its structure.

RESULTS AND DISCUSSION

Effect of dosage on destabilization performance

Figure 1 shows the effect of dosage on the destabilization performance by the sequential coagulation. The removal of DOC for both SW–A (low SUVA, 0.12–0.44 L/mg C m) and SW–H (high SUVA, 5–6 L/mg C m) is shown in Figure 1(a) and 1(b). For SW–A, the removal of DOC by traditional PACl increased with the increase of dosages, and achieved the highest (12%) at 0.17 mM. Unexpectedly, the increase of dosage had little effect on DOC removal when FeCl₃ was applied. However, higher DOC removal (18–20%) was observed at lower dosages (below 0.14 mM) for FeCl₃, compared to PACl (3–9%), indicating that FeCl₃ possessed great potential in elevating the removal of AOM.

Interestingly, the sequential coagulation improved the DOC removal from 12.2 to 24.5% at optimal dosage (0.17 mM) only when PACl was introduced prior to FeCl₃ (P–F). However, when PACl was added after FeCl₃ (F–P), it showed no improvement in the removal of DOC compared to the traditional PACl.

On the other hand, the removal of DOC for SW–H was generally higher (over 50%) than for SW–A. However, the performance of DOC removal by either single dosing or the sequential coagulation revealed an opposite trend (Figure 1(b)). The traditional PACl showed a slightly higher DOC (59%) removal than FeCl₃ (55%) at optimal dosage (0.11 mM). The sequential coagulation F–P successfully elevated the DOC removal about 10% (up to 70%), while sequential coagulation P–F showed no improvement to the removal of DOC (55%), compared to the traditional single dosing at 0.11 mM. The sequential
coagulation performance in this study strongly depended on the characteristics of the water, typically its SUVA value. Sequential coagulation P–F showed higher capability to treat SW–A (low SUVA value), while sequential coagulation F–P was more suitable in dealing water with high SUVA value.

Although sequential coagulation P–F was demonstrated to improve the AOM destabilization performance, the highest DOC removal was still restricted to approximately 25%. Therefore, it is important to better understand the characteristic of AOM. Table S3 gives the DOC contribution and SUVA values of different MW fractions for AOM. The result confirmed that 10–30 kDa was the main contribution of the total DOC (75%). In addition, the lowest SUVA value of 0.05 L/mg C m revealed its high hydrophilicity that could make it very difficult to interact with either particles or the precipitates produced by the coagulants in the water. The coagulation of fractionated AOM (10–30 kDa) with kaolin particles also showed that these substances were barely destabilized (Figure S2). Such low DOC removal can then be explained by the existence of massive AOM at 10–30 kDa. As for HA (Table S4), the SUVA value was high (4.2–7.9 L/mg C m). More than 50% of the total DOC was contributed by the substances with MW 30–100 kDa (16.7%) and >100 kDa (35.2%), which gave rise to a relatively higher DOC removal than that of AOM.

The effects of the dosage on the turbidity removal by the sequential coagulation are illustrated in Figure S1a and S1b. At sufficient dosages (0.14–0.17 mM), the turbidity removal for SW–A by the sequential coagulation P–F and single dosing of FeCl₃ showed a slightly higher removal (93.4–95%) than the traditional PACl and sequential coagulation F–P (88.5–93.2%). A similar result was also obtained for SW–H when the sequential coagulation P–F effectively improved the turbidity removal of 5–10% compared to the traditional PACl (Figure S1b). Therefore, it could be concluded that the sequential coagulation P–F was superior to single dosing of PACl in term of particle removal regardless of water characteristics.

More attention should also be focused on the [Al] residual in the finished water. Figure 2 shows the concentrations of [Al] residual at various dosages by sequential coagulation for both waters. Our result show that the concentrations of [Al] residual were effectively minimized when sequential coagulation was applied under various dosages. Comparing the concentration of [Al] residual at 0.08 mM for PACl, the amount of [Al] residual at 0.17 mM for sequential coagulation remained more than two times lower, even with the addition of a similar dosage (0.08 and 0.085 mM) of PACl. Furthermore, the dosing sequence revealed a different trend, in that the concentration could be further reduced by P–F, while F–P remained higher for both types of waters. The results in this study are similar to those demonstrated by Cheng et al. (2005), in which the [Al] residual could be minimized more effectively when Al-based coagulant was dosed first. These astonishing results

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**Figure 1** Effect of dosage on DOC removal (a) SW–A (b) SW–H by Al/Fe sequential coagulation (DOC: 3.0–3.9 mg/L, turbidity: 12.5–16.3 NTU, pH: 7.8–7.9, alkalinity: 100 mg/L as CaCO₃). Error bars represent the standard deviation of experimental replication.
achieved by sequential coagulation confirmed its considerable potential for application to future on-site water purification applications.

Coagulation behavior of sequential coagulation

Enhancement of NOM destabilization

NOM destabilization refers to the participation of metal coagulant that can neutralize the negative charge of NOM, facilitating its aggregation and the complexation with the coagulant. The removal of NOM for SW–A and SW–H was improved by the application of the sequential coagulation with P–F and F–P, respectively. The coagulation behavior might become complicated as NOM, kaolin particles and two coagulants existed in the system at the same time. Thus, the interaction between single coagulant and NOM should then be first clarified. Figure 3 shows the interaction between different coagulants (PACl/FeCl3) and different NOMs (AOM/HA) in terms of DOC removal at optimal dosages (SW–A: 0.17 mM; SW–H: 0.11 mM). The results clearly demonstrated that the interaction between FeCl3 and AOM was stronger compared to PACl–AOM interaction. These results confirmed those of Pivokonsky et al. (2012) who showed that the protein/peptides AOM had high tendency to adsorb onto Fe-oxide-hydroxide at neutral pH (6–8). As for HA, PACl revealed a slightly higher binding ability than FeCl3. The result indicates the advantage of FeCl3 in destabilizing AOM and of PACl in destabilizing HA.

It is known that zeta potential is a crucial indicator in determining destabilization performance as well as coagulation behavior. The different characteristics of various coagulants, including Al-based and Fe-based, could also follow different coagulation pathways, even when sequence dosing is carried out. Furthermore, lower pH conditions are always favorable for higher organic matter removal (Yang et al. 2010). To gain better insight into the destabilization performance during sequential coagulation, the change of zeta potential during the rapid mixing period was monitored...
(Figure 4(a) and 4(b)). For SW–A by sequential coagulation P–F, the first dose of PACl did not react with the AOM efficiently (Figure 3). It rather altered the charge on the particles to a more neutral condition of a zeta potential from $-37.5$ to $-18$ mV. When FeCl$_3$ was introduced, AOM formed complexes with Fe ions effectively as a result of the in-situ rapid reduction of pH (Figure 4(c)) and the strong interaction between Fe and AOM. As a result, fewer Fe ions were absorbed onto the kaolin-Al particles, raising the charge from $-18$ to $-9$ mV. Under such circumstances, the surface of the floc became partially covered by Fe, which implied that there was a high possibility for AOM to be adsorbed onto the floc during the slow mixing process (Figure 1(a)).

For sequential coagulation F–P, the first dose of FeCl$_3$ could absorb AOM during the first-staged rapid mixing. The Fe ions preferred to react with AOM, and thus the charge was only slightly altered from $-37.5$ to $-33$ mV. However, this Fe–AOM interaction did not proceed as intended when the second dose of PACl was applied. The highly positive-charged Al ions barely reacted with AOM but accumulated on/adhered to the surface of kaolin-Fe particles. This phenomenon was verified by the dramatic increase of zeta potential from $-35$ to $+0.25$ mV, after the addition of PACl. Although the same amount of Fe was injected by sequential coagulation for both sequences, the reaction pH (7.9–7.2) and the charge condition ($-37$ mV) for Fe by F–P was not as suitable as what had occurred in the system by P–F. The improved level of DOC removal by sequential coagulation P–F was thus confirmed (Figure 1(a)).

The coagulation behavior of SW–H by sequential coagulation was slightly different from that of SW–A. Sequential coagulation P–F showed no improvement in the removal of DOC. When PACl was dosed first, a large number of Al ions preferred to react with HA (were consumed by HA).
As a result, only small amounts of Al ions were absorbed on the particles, which was confirmed by a slightly neutralized charge (−57 to −42 mV) (Figure 4(b)). In other extra coagulation experiments, the first dose of PACl showed significantly elevated zeta potential from −50 to +15 mV in the system with only kaolin (and without HA). This confirmed that Al ions were largely consumed by HA instead of kaolin particles when HA were present. However, a pH of 7.9–7.6 during the PACl reaction period was too high for efficient destabilization (Figure 4(d)), and only small amounts of HA were captured. As FeCl₃ participated in the system, the Fe ions largely adhered to particle surfaces and decreased the chance for Al to react with HA (Figure 1(b)).

The application of sequential coagulation F–P effectively upgraded its ability to remove DOC for SW–H. The change of zeta potential during rapid mixing showed a similar trend to SW–A. The first dose of FeCl₃ induced the in-situ reduction of pH, which not only destabilized the amount of HA, but also gave rise to a lower pH condition for the second dose of PACl. When this was added, the pH condition of 7.35–7.1 was favorable for efficient HA destabilization. Sequential coagulation F–P demonstrated the importance of a dosing sequence and thus showed greater promise for achieving higher DOC removal from water with HA (Figure 1(b)).

Floc formation

The size of floc formed is a useful indicator for predicting the effectiveness of turbidity removal. Generally, the larger the size of floc, the higher rate of turbidity removal. The effect of sequential coagulation on floc formation by different NOMs is shown in Figure 5. As expected, the size of the floc showed a positive correlation with turbidity removal for SW–A and SW–H for all dosing strategies. The floc size formed by traditional PACl for SW–A was 250 μm. With the addition of FeCl₃, sequential coagulation P–F resulted in significant aggregation of the floc to approximately 400 μm, while the floc formed by F–P was slightly

Figure 5 | Effect of sequential coagulation on floc formation (a) SW–A (b) Kaolin at 0.17 mM and (c) SW–H (d) Kaolin at 0.11 mM (DOC: 3.0–3.9 mg/L, pH: 7.8–7.9, alkalinity: 100 mg/L as CaCO₃).
smaller (350 μm) (Figure 5(a)). Lee et al. (2008) reported similar results additionally, in that the dosing of Fe in Al coagulation enlarged the size of the floc from 50 μm (PACl) to 60–76 μm (FeCl₃ + PACl). The study presented by Lin & Ika (2019a) also revealed an increase of floc size when PACl was supported by FeCl₃ (400 μm) in comparison with single PACl (320 μm). This is because Fe-based coagulants generally form larger floc than Al-based coagulants (Lin & Ika 2019a). Therefore, Fe-based coagulants can always serve as promising coagulant aid for coagulation performance improvement.

A control group with only kaolin particles in the water was implemented at 0.17 mM of dosage to examine the effect of AOM on floc formation. Results showed that the size of the floc increased slightly with the addition of AOM for all dosing strategies (Figure 5(b)). AOM contained small amounts of large MW biopolymer (10% in terms of DOC) (Table S3), which had been reported by Wang et al. (2013), and this large MW biopolymer (>100 kDa) could easily interact with PACl and assist in coagulation (aggregation of particles). We then also observed an increased floc size for SW–A.

For SW–H, the effect of sequential coagulation showed a similar trend with effect on floc formation. Sequential coagulation P–F certainly enlarged the size of the floc to 290–300 μm, while F–P resulted in a similar floc size of 220–250 μm compared to traditional PACl (Figure 5(c)). A controlled experiment was also carried out at 0.11 mM of dosage to determine the effect of HA on floc formation (Figure 5(d)). Our results show that the size of the floc decreased dramatically for all dosing strategies when HA was present in the water. For a system containing only kaolin particles, metal ions, whether Fe or Al, adsorbed on the particles, aggregating to form larger floc. However, the existence of HA in the water competed with the kaolin particles, forcing metal ions to react with HA directly. Fewer remaining free metal ions then would absorb onto the kaolin particles, and this was the main reason for the significant decrease of floc size. Besides, a longer lag time in floc size evolution in SW–H compared to SW–A was due to the relatively lower applied dosages (SW–A: 0.17 mM, SW–H: 0.11 mM). Although the growing of floc size was delayed significantly for single dosing of Fe, an apparent increase of floc size can be seen once it started to aggregate.

**Final pH affects the [Al] residual minimization**

pH is one of the most important factors which affects the hydrolysis of Al compounds, thus determining the amount of soluble Al in the water. At higher pH, soluble Al(OH)₄⁻ is dominant, but as the pH decreases, Al(OH)₄⁻ transformed to solid-phase Al(OH)₃ which decreased the amount of soluble Al in the solution (Duan & Gregory 2005). Our study demonstrated that the sequential coagulation could effectively minimize the [Al] residual (Figure 6), and determined that the final pH of the traditional PACl was

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**Figure 6 |** Effect of the sequential coagulation on final pH for (a) SW–A (b) SW–H at various dosages (DOC: 3.0–3.9 mg/L, pH: 7.8–7.9, alkalinity: 100 mg/L as CaCO₃). Error bars represent the standard deviation of experimental replication.
higher than sequential coagulation F–P followed by P–F at various dosages. The decrease in pH obtained for both sequential coagulation was a result of the $H^+$ released during in-situ PACI and FeCl$_3$ hydrolysis. It should be noted that FeCl$_3$ played a major role in reducing the solution’s pH because it can produced more $H^+$ during the hydrolysis compared to pre-hydrolyzed coagulant PACI (Duan & Gregory 2005). Based on this concept, it was better to add FeCl$_3$ as the second dose to provide complete FeCl$_3$ hydrolysis in order to achieve lower pH. Sequential coagulation P–F thus resulted in a slightly lower pH with less [Al] residual remaining than sequential coagulation F–P. The results of this study (Figure 2) could also be confirmed by Cheng et al. (2005) that lower [Al] residual remained when Al-based coagulant was dosed followed by Fe-based coagulant due to lower final pH compared with the opposite dosing sequence.

Despite the effect of dosing strategies on pH, the existence of different NOMs also impacted on the hydrolysis of coagulants. With the same dosages, the final pH of SW–A was slightly higher than that of SW–H, which indicated that the hydrolysis of coagulant was influenced more by AOM than by HA.

**Practical application of sequential coagulation**

In this study, the sequential coagulation demonstrated to be very promising in improving the coagulation performance and minimizing [Al] residual. Whereas P–F was recommended for low SUVA water (SW–A), F–P was showed as advantageous in treating high SUVA water (SW–H). To better understand its feasibility and potential capacity in a real water matrix, the coagulation experiments with sequential coagulation were conducted for raw water collected from Mingde reservoir. Figure 7(a) shows the purification performance resulting from the application of the sequential coagulation for RW treatment. The optimal dosage of

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**Figure 7** Effect of sequential coagulation on (a) DOC, turbidity removal, (b) floc formation, (c) change of zeta potential and (d) residual soluble Al (DOC: 2.95–3.54 mg/L, SUVA: 0.95 L/mg C m, turbidity: 8–12 NTU, pH: 7.8–7.9, alkalinity: 100–120 mg/L as CaCO$_3$, dosage: 0.11 mM). Error bars represent the standard deviation of experimental replication.
0.11 mM of sequential coagulation was also determined by the maximum DOC removal for RW. We noted that RW had low SUVA values (0.83–1.14 L/mg C m) (Table S5), one of the characteristics of SW–A water. Therefore, we hypothesized that the coagulation behavior for RW will be similar to that of SW–A water.

As illustrated in Figure 7(a), DOC removal was enhanced significantly from 15–17%, and up to up to 33%, with the application of sequential coagulation P–F, while either single dosing of PACl or sequential coagulation F–P had less impact on DOC removal. Although the enhancement of turbidity removal was insignificant, the sequential coagulation P–F removed the greatest amount of turbid particles. In addition, the performance of turbidity removal can be correlated to the evolution of floc size where sequential coagulation P–F formed the largest size of the floc (Figure 7(b)). Similar trend can be seen from the change of zeta potential for RW (Figure 7(c)) compared to SW–A water experiment (Figure 4(a)). When sequential coagulation P–F was applied, the first dose of PACl neutralized the particles (−15 to −7 mV) instead of effectively reacting with organic matter. When the second dose of FeCl3 was introduced, the low SUVA organic matter was captured and a reactive Fe-NOM floc was formed. The zeta potential remained nearly unchanged. As for sequential coagulation F–P, the high positively charged Al ions absorbed onto the Fe-NOM floc leading to a significant increase of zeta potential (−13 to 0 mV) which inhibited further adsorption reaction between the Fe-NOM floc and the free NOM. Therefore, insufficient removal of NOM was observed compared to sequential coagulation P–F.

On the other hand, the amount of [Al] residual was effectively minimized to below 0.05 mg/L by the application of sequential coagulation for RW (Figure 7(d)). Furthermore, the least Al was detected when P–F was applied. The results obtained from the RW experiment further confirmed the stability of sequential coagulation P–F for low SUVA water treatment.

Proposed coagulation behavior for sequential coagulation

In view of the result presented above, possible coagulation behavior for NOM/particle destabilization by sequential coagulation is shown in Figure 8. For low SUVA water (SW–A and RW) with sequential coagulation P–F, the first dose of PACl acted as a destabilizer which neutralized the charge of either kaolin particles or AOM. The second dose of FeCl3 coated the surface of the particles and showed a higher tendency to adsorb AOM. The final size of the floc was also enlarged by the formation of Fe(OH)3 after the addition of FeCl3. For sequential coagulation F–P, the second dose of PACl interfered with the reaction of Fe on AOM. The Al ions adhered on the surface of the particles which reduced the opportunity for AOM to react with Fe. Furthermore, the size of the floc was limited as a result of the interference on Fe(OH)3 formation by PACl.

When high SUVA water (SW–H) was tested by sequential coagulation P–F, the pH was still too high for effective Al–HA interaction after PACl addition. The second dose of FeCl3 even interrupted the Al–HA reaction (Fe ions covering the surface of the floc), which weakened the destabilization performance of HA. On the other hand, the first
A dose of FeCl₃ resulted in lower pH conditions, which benefited the later injection of PACl to cover the particle’s surface and achieving higher HA adsorption. However, the small size of the floc observed was a result of the addition of PACl after FeCl₃.

CONCLUSIONS

This study investigated the destabilization performance of NOM (AOM and HA) and kaolin particles, and the minimization of [Al] residual by the application of sequential coagulation. Our results show that sequential coagulation P–F can be used to improve NOM destabilization for SW–A, while sequential coagulation F–P was more promising in treating SW–H. In this study, FeCl₃ resulted in a greater ability to destabilize AOM, while PACl was more effective in reacting with HA. PACl, the first dose of sequential coagulation P–F, efficiently neutralized the charge condition in most of the water, which facilitated the subsequent addition of Fe to absorb AOM. For SW–H, by contrast, the first dose of Fe significantly reduced the solution’s pH, allowing an efficient Al–HA interaction, and that significantly enhanced HA removal. Moreover, most particles were destabilized effectively by only the sequential coagulation dosed with P–F sequence. This sequence also showed substantial reduction of [Al] residual in the treated water. The result for RW, a low SUVA water, applying sequential coagulation thus confirmed the applicability of P–F sequence for achieving higher DOC removal associated with lesser amount of [Al] residual compared to the traditional single-dose PACl. The contribution of this study was that the sequential coagulation can be implemented in different dosing sequences to achieve optimal performance for NOM, depending on the characteristics of the water, and specifically its SUVA value.

ACKNOWLEDGEMENTS

We are grateful for financial support from the Ministry of Science and Technology of Taiwan with this project MOST 108-2221-E-009-075-MY3.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES


Lin Jr, L. & Ika, A. R. 2019b Effect of Al speciation on residual turbidity and Al minimization by coagulation with single and


Zhao, Y. X., Gao, B. Y., Shon, H. K., Cao, B. C. & Kim, J. H. 2011 Coagulation characteristics of titanium (Ti) salt coagulant compared with aluminum (Al) and iron (Fe) salts. *Journal of Hazardous Materials* **185** (2–3), 1536–1542.

First received 14 January 2020; accepted in revised form 20 July 2020. Available online 4 August 2020