The influence of various additives on coagulation process at different dosing point: From a perspective of structure properties

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ABSTRACT

Structure properties of flocs (size, fractal dimension (D_f), etc.) have a high impact on coagulation efficiency. In this work, the influences of three different additives (ferric salt (Fe), phosphate (P), and citric acid (CA)) on coagulation process/efficiency were investigated. Results showed that a small amount of extra Fe can facilitate the growth of Al flocs by providing more 'active sites'. Although zeta potential and D_f showed a limited change, the average floc size increased apparently and the increment was more obvious when Fe was added after the formation of the flocs. In contrast, P addition during the rapid mixing period will decrease the final average floc size, while the influence is less significant when P was added after the growth of the flocs. In terms of CA, a more striking negative effect on the growth ability of the flocs was observed compared to P. The strong complexing/coordination interactions between CA and aluminum hydroxide is the main reason behind the influence. CA also significantly decreased the D_f value of the flocs compared to P, and D_f showed a comparatively higher decrease when P or CA was added during the rapid mixing stage compared to the addition after the flocs formation. These results indicated that the addition of CA or P during the rapid mixing stage 'inactivated' or occupied more 'active sites' on the preliminarily formed Al NPs during the hydrolysis process, and therefore presented stronger impact on the morphology/size of the formed flocs.

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Introduction

Coagulation is still one of the most efficient and economical processes utilized in water/wastewater treatment (Pliego et al., 2012; Teh et al., 2016; Zagklis et al., 2012; Zheng et al., 2015). Meanwhile, considering its numerous merits, lots of emerging integrated purification technologies also adopt it as the pre-treatment process to alleviate membrane fouling. For instance, coagulation-ultrafiltration technology (CUF) (Barbot et al., 2008; Haberkamp et al., 2007; Tabatabai et al., 2014; Yu et al., 2014) and coagulation-nanofiltration technology (CNF) (Listiarini et al., 2010; Pal et al., 2014; Riera-Torres et al., 2010). Wildly application of coagulation means the target water needs to be treated can be various. Therefore, to understand the influences of the surrounding substances on the coagulation process and then manually control the coagulation efficiency is necessary.

Recently, some research works focused on the influence of additional dosage of coagulant and its dosing strategy on the coagulation process, through which the efficiency of coagulation can be enhanced (Yu et al., 2010a) or the membrane fouling can be alleviated (Liu et al., 2011). Yu did lots of work in this field (Yu et al., 2015, 2010b, 2011; Yu et al., 2016) and claimed that the additional dosage of coagulant will introduce the fresh precipitant, which can improve the binding ability (via the 'active point') of the flocs formed during coagulation (Wu et al., 2019; Yu et al., 2018). However, no comparison has been done between the additional coagulant or additives added at the beginning and steady period of the coagulation process. Since at the rapid mixing stage, the primary NPs have larger amount of *in-situ* formed 'active sites', which contribute to the connection among the NPs to form the flocs. In contrast, during the steady period, the number of remaining 'active sites' will gradually decrease due to the dynamic equilibrium between 'detachment' and 'attachment' of the flocs. Therefore, based on our previously proposed theory, the time for the dosage of the additives could exert different impacts on the floc growth, which will be further confirmed in this study.

As one of the main pollutants in natural water, natural organic matter (NOM) can be partly removed via coagulation. Considering this, some research works studied the impact of NOM on flocs formed during coagulation. Jarvis et al. gave us a clear description about the influence of NOM on floc structure using ferric sulfate as coagulant (Jarvis et al., 2005). After that, by using NEXAFS spectroscopy, Christl and Kretzschmar pointed out the surface interactions between NOM and the functional groups on the surface of the flocs formed during the coagulation process (Christl and Kretzschmar, 2007). In addition, Masion et al. found that the polynuclear Al species formed during the coagulation can be depolymerized by the organic ligands of NOM along with the reaction time (Masion et al., 2000). All these works revealed that NOM has a great influence on the coagulation process. Since most of the NOM contains carboxyl and hydroxyl groups, which can coordinate/complex with metal ions. Therefore in this study, for simplicity, we choose citric acid (CA) (contains both carboxyl and hydroxyl groups) as the model organic to investigate its influence on Al flocculation.

Similarly, coagulation was also utilized to treat detrimental eutrophication water sources (Tran et al., 2012; Zhang et al., 2014). Therefore, it is important to understand the influence of phosphate (P) on coagulation as well. In view of the past works, there were lots of debates on whether the removal of P through coagulation is mainly electrostatic adsorption or via chemical reactions or both. Peak et al. showed that the interaction between P and amorphous $Al(OH)_3$ is adsorption rather than the formation of aluminum phosphate precipitation (Peak et al., 2002). However, lots of papers also reported that monodentate or bidentate complexes will be formed during the interaction between P and $Al(OH)_3$ (Guan et al., 2005; Li et al., 2013). However, no work gave information about the influence of P on floc growth and the structural properties of the flocs formed during coagulation.

Herein, ferric salts (Fe), P, and CA were chosen as the additives to investigate their influences on flocs formation during the coagulation process. Specifically, different dosing points, i.e. at the rapid mixing stage or during the steady period, were

applied to explore the impacts on floc growth and further verify our previously proposed 'active sites' theory. Through the analysis of the presented phenomenon, the results obtained in this study could lead to a better understanding of the coagulation mechanism. Especially, by interpreting the reasons behind the influences of different additives on floc formation, it can provide the basis to optimize the coagulation process, which could favor, for example, the subsequent membrane filtration process.

1. Materials and methods

1.1. Materials

Aluminum sulfate hydrate (alum) was used as coagulant in this study, and the stock solution was prepared at a concentration of 0.05 mol/L (0.1 mol/L Al^{3+}). Iron sulfate hydrate, disodium phosphate (Na_2HPO_4) and citric acid were prepared at a concentration of 0.05 mol/L, 0.1 mol/L and 0.01 mol/L, respectively. $NaHCO_3$ was used as the buffering salt here and was prepared at a concentration of 0.1 mol/L in DI water, all the referred reagents were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd., China.

1.2. Jar test

In this study, a flocculator (ZR4-2, Zhongrun, China) which allows stirring speeds and times to be pre-set was used to simulate the flocculation process. Each test was conducted in synthetic natural water (5 mg humic acid sodium salt (Sigma-Aldrich) in 1 L of DI water) that contains 5 mmol/L $NaHCO_3$. During the jar test, the pH of the working solution was kept at 7.0 by the addition of 0.1 mol/L HCl or NaOH at the start stage. The temperature was maintained at 25±1 °C.

The procedure of the coagulation test was similar to that of previous research (Yu et al., 2010a). Alum was added into 1 L solution to give a concentration of 0.1 mmol/L with stirring at 200 r/min. This rapid mixing speed was maintained for 1 min and the stirrer speed was then reduced to 50 r/min, to allow the growth of flocs. In order to investigate the influence of different additives on the growth of flocs during coagulation process, different dosages of Fe, P or CA were added at the end of rapid mixing (1 min) or at the 6 min, respectively, which corresponded to the moment before and after the flocs formed.

1.3. Zeta potential

Floc samples were taken for zeta potential measurement after the dosing of each additive using a Zetasizer instrument (Zetasizer Nano ZS90, Malvern, UK). Each sample was measured immediately and the value was determined from three respective measurements.

1.4. Floc structural analysis

The monitor of flocs' characteristics including its size and the coagulation process was synchronized by connecting the flocculator to a laser diffraction instrument (Malvern Mastersizer

2000, Malvern, UK), the water sample was circulated between the optical unit of the Mastersizer and the flocculator through a peristaltic pump at a speed of 20 mL/min, relevant data were recorded on PC at an interval of 30 sec.

Based on the description of Bushell and Amal (2000), the relationship between mass (M) and mass fractal dimension (D_f) of mass fractals meet: $M \propto L^{D_f}$. In terms of the principle of the laser diffraction, it meets the equation as follow (Li and Ganczarczyk, 1988):

$$Q = \frac{4\pi n \sin(\delta/2)}{\gamma}$$

Where Q is the Scattering momentum which reveals the differences between the incident and scattered beam, θ is the scattering angle, λ is the wavelength of the radiation in a vacuum and n is the refractive index of the surrounding medium.

For independently scattering aggregates, based on Rayleigh–Gans–Debye (RGD) scattering theory, we can obtain the following relationship among I, Q and D_f (Li and Ganczarczyk, 1988): $I \propto Q^{D_f}$.

From the equation above, we can easily get the value of D_f by simply plot I against Q on a log-log scale, but reliable results were obtained only on the condition of (Schmidt and Avnir, 1989):

$$(1/R_{aggregate}) << Q << (1/R_{particle})$$

Where $R_{aggregate}$ and $R_{particle}$ are the primary particle size and the size of the aggregate, respectively.

1.5. Microscopic observation and FT-IR measurement

The procedure for microscopic observation of the flocs formed during coagulation was the same as our previous study (Yu et al., 2010c). Briefly, during the slow mixing period, samples of flocs were taken from below the surface of the suspension with a hollow glass tube with an inner diameter of 5 mm. One end of the tube was inserted 3.0 cm below the surface and the other end was covered by a finger, and then the samples were withdrawn carefully. After transferring the sample onto a flat microscope slide, the image of flocs in the sample was captured by an optical microscope with a CCD camera (GE-5, Aigo, China). For FT-IR measurement, the flocs formed after the coagulation were collected via filtration using mixed cellulose esters (MEC) membrane with pore size of 0.2 μm. Thereafter, the collected flocs on the membrane surface were washed with 100 mL DI water to remove the residual salts and then vacuum-dried before measurement.

2. Results and discussion

2.1. Effect of Fe on the coagulation process

To understand the influence of Fe on Al flocs formation during coagulation, different dosages of Fe were added at the initial stage (1 min, Fig. 1a) or 6 min (Fig. 1b) after alum was added. The difference between the two dosing strategies can be well recognized and the results implied that the dosing time of Fe is a vital factor determining the growth kinetic of the flocs.
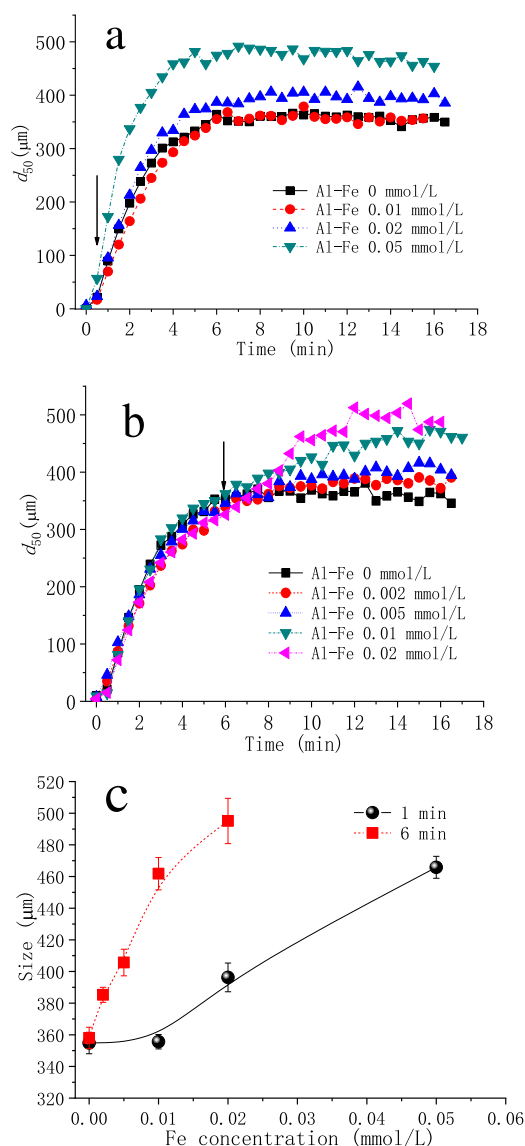

Fig. 1 – The addition of FeCl$_3$ on alum coagulation efficiency (0.1 mmol/L Al^{3+}) at pH 7: (a) added just after rapid mixing and (b) added 5 min after rapid mixing, and (c) their balanced size.

Specifically, when Fe was added at the end of fast stirring point (1 min) (Fig. 1a), it can be seen that Fe can enhance the growth ability of the primary particles and this kind of influence was more evident at a higher dosage. However, for all dosages, similar time was spent to reach the dynamic balance of the floc size (d_{50}), but with different growth rates. The result suggested that the addition of Fe might not change the collision efficiency or the surface properties of the primary particles but provided more active binding sites. This kind of change on one way enabling the particles more prone to connect with each other, giving a higher growth velocity; on another way, letting particles have the possibility to own more connection sites per unit area, enabling the flocs grew to a larger size under the same applied shear. Similar effect was also revealed in our previous work, which showed that the

continuous dosing mode during coagulation will lead to larger flocs finally (Yu et al., 2012).

In comparison with the dosage at 6 min, it also showed us that the additional dosage of Fe can significantly improve the growth ability of the flocs. The apparent difference is that under this circumstance the flocs are more sensitive to the added Fe. With just 0.01 mmol/L dosage, the flocs grew to a comparably size as the addition of 0.05 mmol/L Fe at the initial stage (1 min). It should be noted that before the addition of the Fe under this strategy, the flocs almost grew to a steady size to a plateau. Therefore, it can be understood that the additional Fe dosage in this situation plays a role like the 'bridge connection'. This kind of action can directly improve the connection efficiency between the already formed flocs via the 'active sites' provided by the hydrolysis of the added Fe, resulting in higher growth ability. The mechanism is similar to our previous work, which claimed that the additional dosage of coagulant shortly before the end of the breakage, which can bring the fresh hydroxide precipitate, could help to cement aggregating particles together (Yu et al., 2010b), and the binding sites on the surface of the flocs were regarded as the 'active areas' (Yu et al., 2011).

2.2. Effect of P on the coagulation process

The effect of P on the formation of the floc was also explored by adding different amounts of P at different time stages during the coagulation process. From the results shown in Fig. 2, it can be observed that P gave a negative effect on the growth ability of the flocs compared to Fe, especially when the dosage was given at 1 min.

When P was added just after the rapid mixing, regardless of the different dosages, the growth rate of the flocs showed no change, but the latterly corresponded plateau value of the floc size negatively correlated to the amount of the dosage (Fig. 2a). It can be assumed that the addition of P might not severely impact the connection efficiency of the polynuclear Al species formed at the beginning stage of coagulation since no change of growth rate was observed. However, the reduced plateau value of the floc size indicated that the adsorption of P on the surface of the primary formed Al nanoparticles can reduce the growth ability of the flocs. The reason should be mainly ascribed to the occupation of parts of the 'active sites' on the primary formed nanoparticles via surface complexation between P and aluminum hydroxide (Guan et al., 2005). In contrast, it can be seen that the addition of P at 6 min after the rapid mixing had no significant influence on the final floc size (Fig. 2b). Under this circumstance, since the flocs already grew to a steady-state and it was assumed that the outside surface of the flocs which exposed to the surroundings will adsorb P very fast once the P added. Therefore, the role of P to occupy the 'active sites' of the flocs is much weaker compared to the addition of P at 1 min (after the rapid mixing) and the floc size was less influenced by the addition of P.

2.3. Effect of CA on the coagulation process

Results from the influence of CA on the coagulation process at different dosing time with different dosages were shown in
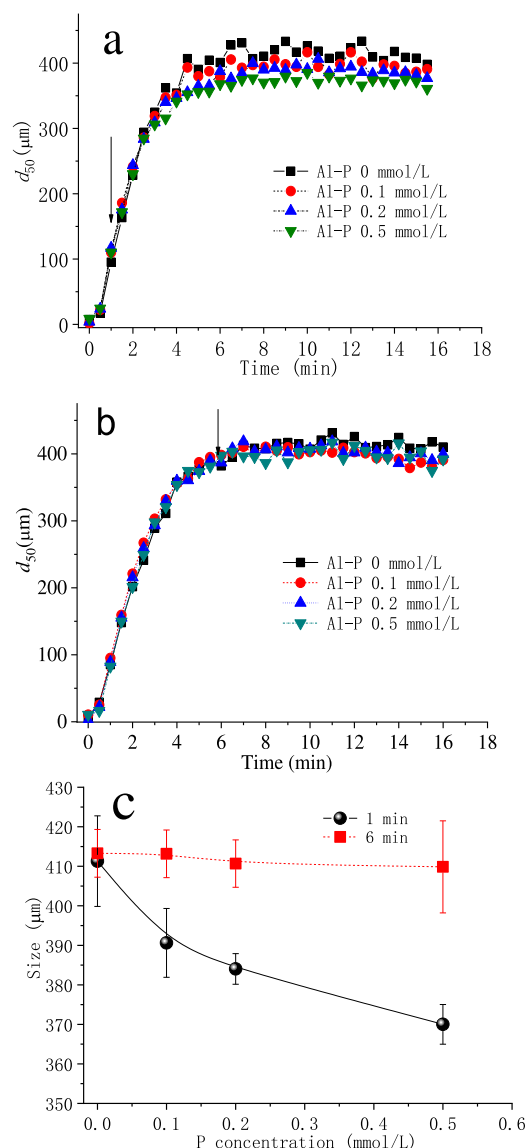

Fig. 2 – The influence of phosphate on the coagulation process at pH 7: (a) added just after rapid mixing and (b) added 5 min after rapid mixing, and (c) their balanced size.

Fig. 3. Evidently, CA showed a considerably negative effect on flocs growth.

With the addition of CA at the beginning of the coagulation stage, both the growth velocity and final size of the flocs significantly decreased, and the final size of the flocs seems inversely proportioned to the dosage of CA: with the dosage of CA increased from 0 to 0.005 mmol/L, the size of the flocs sharply decreased from approximately 380 to around 240 μm. This result revealed the connection point or the 'active sites' on the surface of the primarily formed Al nanoparticles reduced after CA addition. When CA was added right after the primary Al nanoparticles formation, the polycation species of Al could possibly be protected by the interaction with CA and inhibit the further interaction between the nanoparticles; in addition, CA can also inhibit the formation of the seed
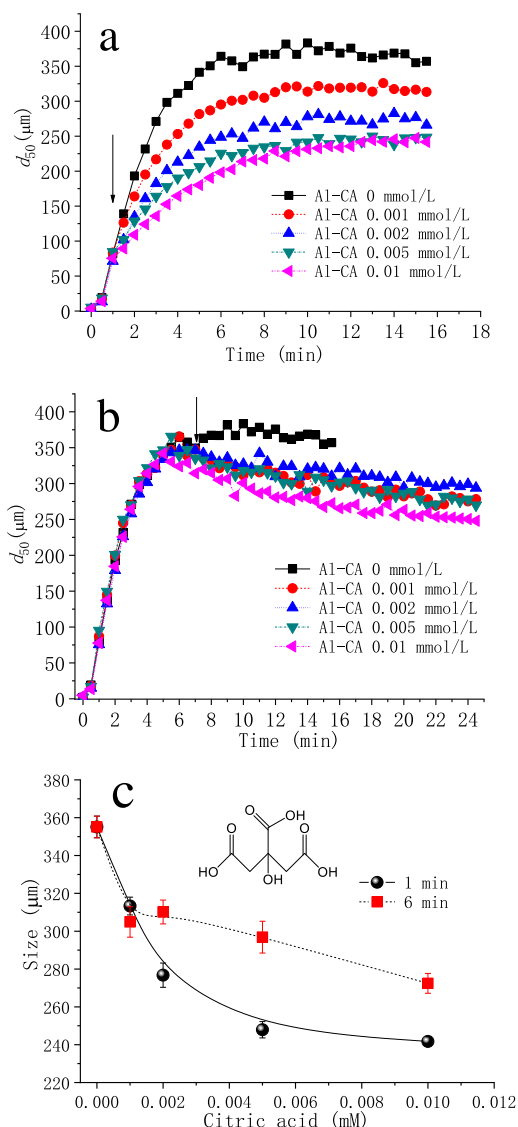
Fig. 3 – The influence of citric acid dosing time on coagulation process at pH 7: (a) added just after rapid mixing and (b) added 5 min after rapid mixing and c) their balanced size.

Fig. 4 – Influence of different concentrations of the additives on zeta potential of the flocs under different dosing modes.

2.4. Influence of additives on zeta potential of the flocs

The floc stability and size at steady state during coagulation can be revealed by the value of its zeta potential (Sharp et al., 2006a), which closely related to coagulation efficiency. As indicated by Sharp et al., the optimal zeta potential rang for coagulation is between −10 to +3 mV (based on the water from a waterworks in England) (Sharp et al., 2006b). Furthermore, Schrader et al. (2005) revealed that high zeta potential is imperative in order to minimum the membrane resistance when adopting nanofiltration technology followed by the coagulation process. In this work, zeta potentials of the flocs formed under different dosing modes with different dosages were investigated (Fig. 4) and the results showed different influences caused by different additives. Fe had the least effect on zeta potential of flocs while CA greatly reduced its values, and the influence given by P is between them. This result indicated the different interaction modes between the different additives and Al flocs. For Fe, its hydrolysis products are similar to Al, and thus the zeta potential was not sensitive to the addition of Fe. While for P, the surface adsorption of negatively charged P can evidently decrease the zeta potential of Al flocs. It can also be observed that the zeta potential values of the flocs with P addition at 1 min were lower than these with P addition at 6 min, which mainly because the primarily formed flocs were small and therefore the adsorption of P on per unit area of the flocs will be higher compared to the larger flocs formed at 6 min. In terms of CA, the values of zeta potential decreased more sharply compared to the situation of P, and the zeta potential gap between the addition of CA at 1 min and 6 min is larger than that presented in the addition of P as well, revealing a stronger and quicker interaction between CA and the Al flocs. Based on these results, it can be understood that with the additives of either P or CA, the coagulation efficiency will decrease due to the decreased zeta potential. While with the addition of Fe, none significant change of the zeta potential was observed, referring less influenced growth ability during coagulation, which is inconsistent with the growth curves of the flocs discussed above, indicating that the introducing of 'active sites' via fresh hydroxide precipitate (hydrolysis products of Fe) can promote the growth ability of the flocs via reaction, for example, $\equiv$Al–OH$^{(-1/2)}$ + $\equiv$Fe–OH$_2$$^{(+1/2)}$ → $\equiv$Al–OH–Fe$\equiv$ + H$_2$O.

polycation species of Al due to the complexation, which is unfavorable for the floc growth (Dabbs et al., 2005). As such, the addition of CA at 1 min will not only retard the growth rate of the flocs but also inhibit the connection between these transient nanoparticles, reducing the final size of the flocs.

A different changing mode of the floc size was observed when CA was added at 6 min (Fig. 3b). Once after the addition of CA, the floc size gradually decreased along with the reaction time, and the higher CA dosage, the smaller the final flocs will be. Under this circumstance, it can be suggested that CA acted as a strong complexing agent, inducing a strong complexation between the polynuclear species of Al and CA (Dabbs et al., 2005), eventually leading to the dissociation of the Al flocs and therefore the gradually reduced floc size.
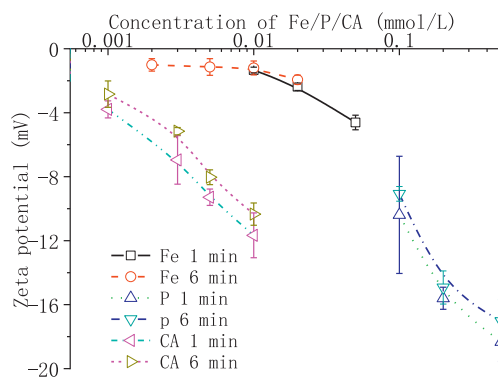
2.5. D_f of the flocs formed at different conditions

D_f is an important parameter of flocs and it can directly influence the separation process since the higher D_f represents compact and high-density flocs which are more desirable in water treatment (Gregory, 1998). The positive correlation between floc strength and floc dimension was also demonstrated by Li et al. (2007) through the analysis of 2-dimension pictures observed by microscopy. In terms of the D_f of the flocs formed in this study, different additives presented significantly different influences (Fig. 5). For Fe, the addition of Fe only slightly decreased the D_f of the flocs and the highest change happened with the addition of 20 μmol/L Fe at 6 min (around 0.03 decrement). However, based on the above results, the size of the flocs after Fe addition showed a marked increase in both situations though the extent was different. Normally, the increased floc size will give a lower D_f (Chakraborti et al., 2003), therefore, the size is not the only factor influencing D_f. With the addition of Fe at pH 7, the fresh precipitate will be formed once Fe was added and the results revealed that the fresh precipitant can react with Al flocs either on the primary stage or steady stage, enhancing the floc growth. The difference between the two dosing time is that when Fe was added at 1 min, the flocs have not grown completely and the hydrolysis species of Fe work somewhat the same role as Al, providing more 'active sites' to let the flocs grow up; while for the dosage of Fe at 6 min, the flocs almost grew to a steady-state and under this circumstance, the newly formed precipitate works as the linkers to connect Al flocs together. Considering the higher surface area of the larger flocs formed at 6 min, the flocs will more sensitive to the Fe addition at this moment than the dosage at 1 min. Due to the similarity between Al and Fe, it worth to believe that the additional of Fe won't give much change to the surface chemical properties of the flocs, and therefore less influence on D_f as well.

For the addition of P, it showed a slightly different changing mode of D_f between two dosing strategies. When P was added at 1 min, it can be understood that the 'layer by layer adsorption' of P on the primary nanoparticles will result into a slightly looser structure compared to the one without P addition and the impact will be stronger at a higher dosage of P. For the addition of P at 6 min, the flocs almost grew to a steady-state and therefore the adsorption of P on the surface of the already formed flocs won't have much influence on the structure or D_f.

In comparison with Fe and P, CA showed a significant influence on D_f and the influence was different between the two dosing strategies as well. When CA was added right after the rapid mixing stage, the preliminarily formed polynuclear Al species will immediately coordinate or complex with CA and cause the inactivation of the 'active sites' on the NPs, for example, via surface reaction: $\equiv Al-OH_2^{(+1/2)} + H_2L^- \rightarrow \equiv Al-LH_2^{(-1/2)} + H_2O$, in which L denotes the hydro-carboxylic acid (CA). This will result in the lower density of the bonding sites among the NPs, and therefore lead to a looser floc structure (lower D_f) and smaller floc size. In comparison, when CA was added after the formation of the floc, since the flocs were already formed via 'active sites' connection, CA will therefore react with these remaining or newly exposed 'active
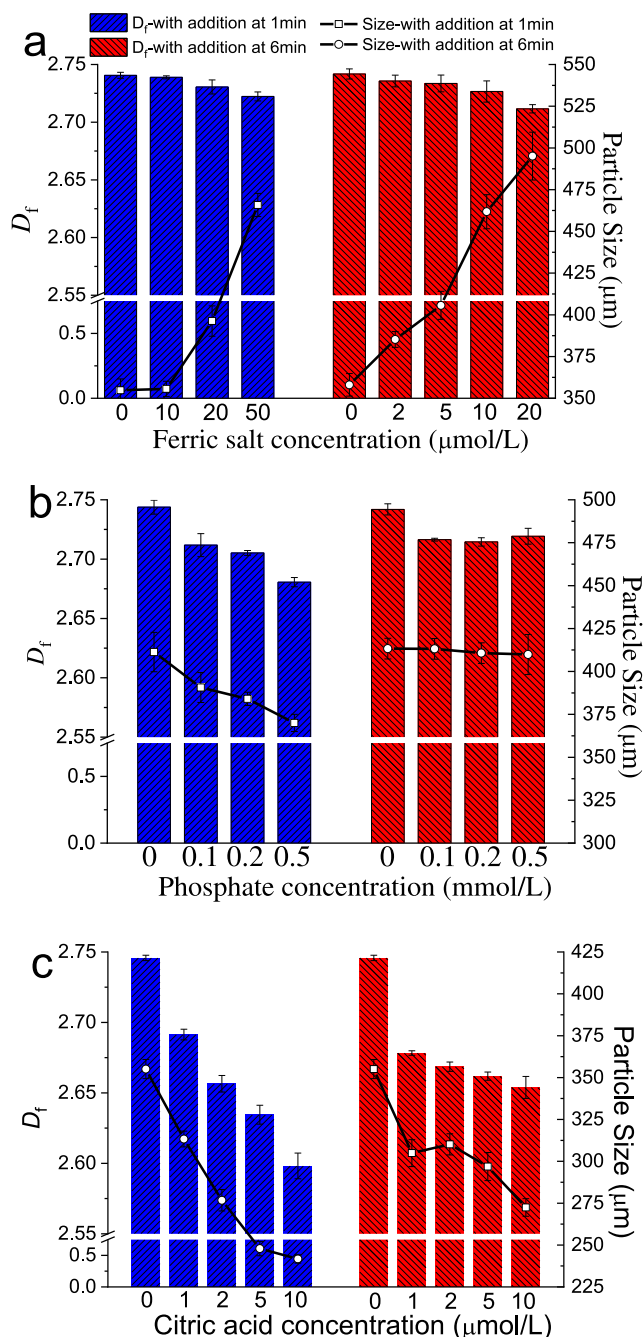

Fig. 5 – Influence of different additives (ferric salt (a), phosphate (b) and citric acid (c)) and dosing points (left: added just after rapid mixing and right: added 5 min after rapid mixing) on fractal dimension and size of flocs.

sites', for instance, via reaction $\equiv Al-OH-Al\equiv + H_2O \rightarrow \equiv Al-OH^{(-1/2)} + \equiv Al-OH_2^{(+1/2)}$, during the dynamic equilibrium between 'detachment' and 'attachment' of the flocs. This kind of chelating or complexing effect between CA and Al will gradually lead to the dissociation of the Al flocs, which is a time-dependent process, and this could also be the reason for the less sensitivity of the floc size and D_f to the dosage of CA compared to the addition of CA at 1 min.
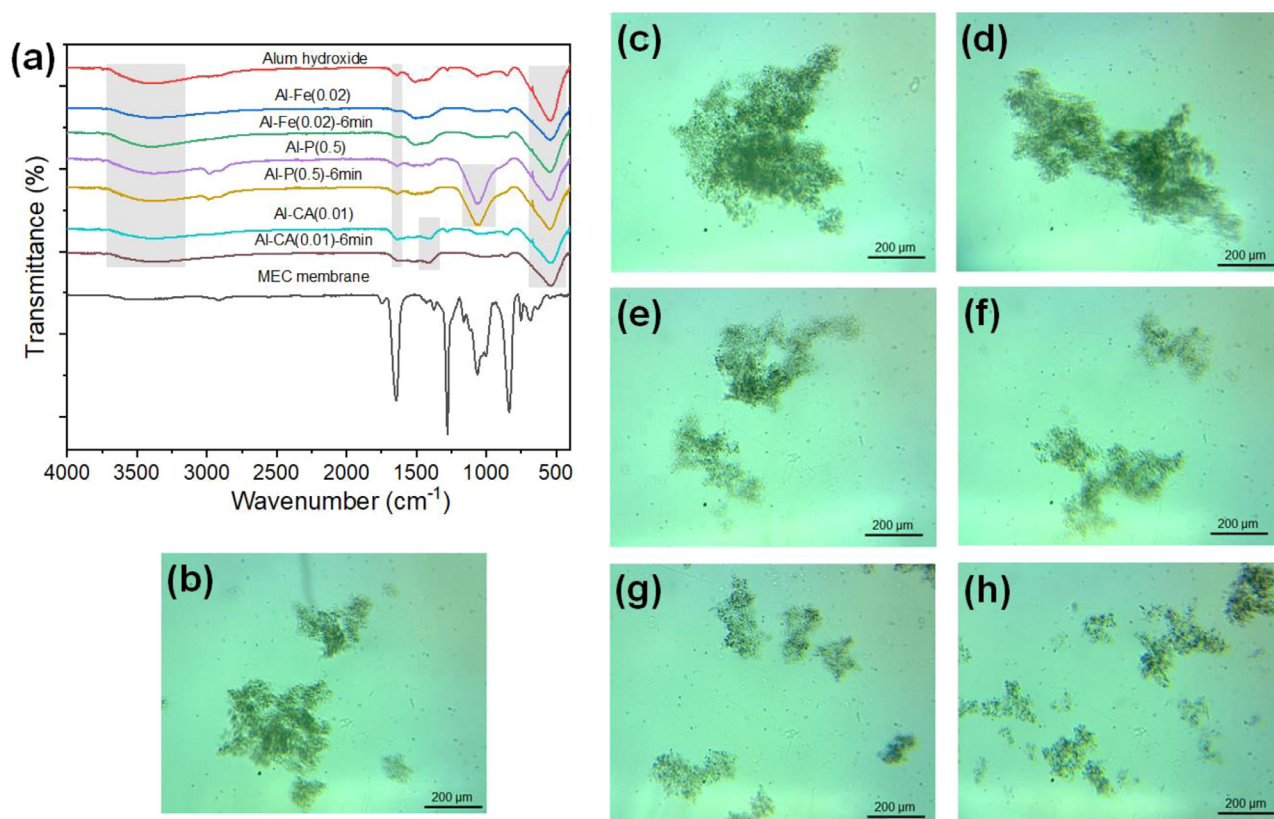
Fig. 6 – ATR-FTIR spectra of the Al flocs formed with different additives at different dosing time (a) and the representative microscopic images of Al flocs formed with different dosages at different dosing time (alum hydroxide (b), with the addition of Fe at 1 min (c) and 6 min (d), with the addition of P at 1 min (e) and 6 min (f), with the addition of CA at 1 min (g) and 6 min (h)).

2.6.   ATR-FTIR and microscopy analysis of the flocs

The infrared spectrum of the Al flocs formed at different conditions is shown in Fig. 6a. For all samples, a broad band between 2800 and 3800 cm^{-1} can be observed, representing the stretching vibration of hydroxyl groups. Additionally, the band around 1640 cm^{-1} can be assigned to bending vibration of H$_2$O and another band between 500 and 800 cm^{-1} is from the Al–O vibrations of aluminum in octahedral coordination (Serna et al., 1977). Since the ferric hydroxide has similar surface functional groups as aluminum hydroxide (the band of Fe–O vibration is also at around 500 cm^{-1}), no significant difference was observed between the alum flocs and flocs with the addition of Fe, either at dosage point of 1 min or 6 min. In terms of flocs formed with P addition, a broad band between 800 and 1250 cm^{-1} appeared, representing the inner-sphere complexes formation between P species and aluminum hydroxide (Guan et al., 2005). As to the situation of CA addition, a band around 1400 cm^{-1} showed up, which could be ascribed to the γ(COO$^-$) stretching vibration of coordinated carboxylate groups with Al (Liu et al., 2006). Carboxylate anions have been shown strong tendency to coordinate with aluminum atoms (Liu et al., 2006; Vaudry et al., 1996) via surface reaction like: $\equiv$Al–OH$_2^{(+1/2)}$ + H$_2$L$^-$ → $\equiv$Al–LH$_2^{(-1/2)}$ + H$_2$O. The strong coordination interactions between CA and aluminum hydroxide can thus 'inactive' the bonding sites (on the surface of the pri-

mary Al NPs or newly formed during the floc breakage), resulting the reduction of the flocs size.

Microscopic observations further revealed the difference among the flocs formed with different additives at different dosage times. With the addition of Fe at 1 min, the flocs grew to be larger and compact (Fig. 6c), indicating that the hydrolysis of Fe took participate in the formation of the primary floc and play a similar role as Al species. Compared to the dosage of Fe at 6 min, it can be seen from Fig. 1 that Al flocs already grew to be stable before the addition of Fe. Therefore, the further growth of Al flocs should be ascribed to the connection between the already formed flocs via the freshly formed ferric hydroxide (Yu et al., 2011), as also shown in Fig. 6d. In terms of P addition, it seems that the inner-sphere complexes formation between P and aluminum hydroxide had no significant influence on the macroscopic morphology of the formed flocs (Fig. 6e and 6f). With the addition of CA, different morphologies between the flocs formed at the dosage time at 1 min and 6 min can be identified (Fig. 6g and 6h). When dosing at 1 min, the final formed flocs were small and loose, revealing that the addition of CA weakened the growth ability of Al flocs, mainly because of the complexation between CA and the primary formed Al nanoparticles. As such, the 'active sites' on the Al flocs during the primary growth were occupied by CA (Yu et al., 2011), leading to lower growth ability of Al flocs. For the situation of CA addition at 6 min, it should be noted that

Al flocs almost grew to be stable at this moment. Further addition of CA at this point could result in the dissociation of the flocs via chelating or complexing, which can also be indirectly revealed by the uneven size distribution of the flocs and existence of the small fragments as shown in Fig. 6h.

2.7.　Significance and future perspectives

Coagulation is wildly adopted as the main technique for drinking water treatment worldwide. The flocculation process plays vital role in flocs formation and therefore the overall treatment efficiency of the coagulation process. Understanding the growth mechanism of the flocs could help to control or adjust the flocculation process at different situations. P and CA are prevalent in natural ecosystem, which can easily access in aquatic system and then the drinking water treatment plants. This study provided the evidence that both P and CA have negative influence on flocculation process, leading to the formation of smaller and looser flocs. In contrast, a small amount of extra Fe addition during or after the flocs formation can contribute to the formation of larger flocs with insignificant influence on the D_f. The results obtained can contribute to a better understanding of the coagulation mechanism and give a solid basis to guide the practical operation of the flocculation unit of the drinking water treatment plant. Furthermore, coagulation is also increasingly utilizing and gaining popularity as the pretreatment for membrane filtration. The size of the flocs formed during coagulation can directly influence the formation of cake layer on the membrane surface and therefore the membrane fouling development along with the long-term filtration. Lowering the influence of P or CA on the formation of flocs can thus favor the membrane filtration process. Future works, especially from the perspective of surface reactions between the chemicals and ligands on the surface of the primarily formed NPs, will be conducted to further understand the mechanism of the floc growth during coagulation and then guide the practical application.

3.　Conclusion

According to the results and analysis given above, the main conclusions of this work are:

1. Additional Fe dosage at either 1 min or 6 min can significantly contribute to the growth of flocs and the contribution was more obvious when dosing after the formation of the flocs. However, zeta potential and D_f of the flocs were not significantly influenced by Fe.
2. Adsorption of P on the primarily formed Al nanoparticles negatively influenced the growth ability of the flocs. However, it showed a limited impact on the flocs when added after the formation of the flocs.
3. CA can strongly influence the formation and stability of the Al flocs due to the complexation or chelating effect between CA and Al, resulting in a decrease in both flocs size and D_f.
4. The dosing time of additives is an important factor influencing the properties of the flocs.
5. The 'active sites' on the surface of flocs own the ability to connect particles together decided the floc size and D_f.

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