Humic Acid Removal from Water with PAC-Al$_{30}$: Effect of Calcium and Kaolin and the Action Mechanisms

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ABSTRACT: Polyaluminum chloride with a dominant species of Al$_{30}$ (PAC-Al$_{30}$) was prepared in laboratory and used for humic acid (HA) removal from water. The action properties and mechanisms of PAC-Al$_{30}$, HA, calcium, and kaolin were tested and discussed. The results showed that the existence of calcium or kaolin contributed to the HA removal when the PAC-Al$_{30}$ dosage was sufficient. When the PAC-Al$_{30}$ dosage was 0.01 and 0.02 mmol/L, the HA removal rate was increased by 66.59 and 42.20%, respectively, with a calcium concentration of 2.0 mmol/L, or increased by 53.31 and 40.92%, respectively, with the kaolin particle concentration of 150 mg/L. Calcium could compress the double electrical layers or complex with HA to neutralize a part of the surface negative charge of HA, but could not make the water system reach its isoelectric point. The mechanisms of calcium and kaolin’s promoting coagulation effect were adsorption neutralization and collision aggregation respectively, but these actions were much weaker than that of PAC-Al$_{30}$ with HA. The adsorption neutralization capacity of PAC-Al$_{30}$ was calculated to be nearly 60 times than that of calcium, and the higher $\gamma$ value of calcium modified by the Sips equation may indicate that the adsorption or neutralization sites of calcium on HA were pickier than PAC-Al$_{30}$.

1. INTRODUCTION

Humic acid (HA) is a kind of natural organic matters (NOMs) that are widely found in soil and surface water. Although the HA itself is not toxic, it can play a significant role in the environmental behavior of heavy metals, pesticides, and some other pollutants.\textsuperscript{1,2} Furthermore, HA is well-known to be a precursor of carcinogenic and mutagenic disinfection by-products (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs).\textsuperscript{3,4} Many countries and health organizations have made strict rules to control the NOMs concentration in drinking water, and a lot of scholars have focused on the techniques of HA removal.\textsuperscript{5,6,7} As a cost-effective treatment method, the enhanced coagulation was recommended by the U.S. Environmental Protection Agency (USEPA) for NOM removal in water.\textsuperscript{8}

Polyaluminum chloride (PAC) is a widely used coagulant in enhanced coagulation in which the $[\text{AlO}_x\text{Al}_{12-x}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{3+}$ (Al$_{13}$) and $[\text{Al}_{50}\text{O}_{88}(\text{OH})_{48}(\text{H}_2\text{O})_{24}]^{18+}$ (Al$_{30}$) were considered to be the dominating effective hydrolytic species.\textsuperscript{9,10} Compared to the PAC with a high Al$_{13}$ content (PAC-Al$_{13}$), the PAC with a high Al$_{30}$ content (PAC-Al$_{30}$) showed better coagulation efficiency because of its larger nanoscale molecular size, more positive charges, and higher structure stability.\textsuperscript{11–13} In recent years, the Keggin-type aluminum polyoxocation species, Al$_{30}$, has gradually attracted the attention of scientists not only as a coagulant but also in the other areas. Liu et al.\textsuperscript{14} found that the purity of the Al$_{30}$ could exceed 92% by an organic complexation method. Tahmasebi\textsuperscript{15} investigated the adsorption behavior of phosphate, chromate, and selenate with different activities on Al$_{30}$ species that consolidated on graphene oxide. Zhu\textsuperscript{16} prepared a kind of Keggin-Al$_{30}$-pillared montmorillonite, which would offer exciting opportunities to the preparation of excellent porous materials with superior thermal stability.

PAC-Al$_{30}$ was firstly prepared and applied to reduce turbidity in water by Chen et al.\textsuperscript{17} Then, Zhang et al.\textsuperscript{13} prepared three kinds of PAC-Al$_{30}$ with different degree of Al hydrolysis ratios ($B = [\text{OH}^-]/[\text{Al}^{11+}]$), and investigated the HA removal efficiency under different initial pH and coagulant dosage conditions. The floc development and charge neutralization capacity of PAC-Al$_{30}$ were also studied with the simulated wastewater by Chen et al.\textsuperscript{17} and Zhang et al.\textsuperscript{13} Although some coagulation properties of PAC-Al$_{30}$ have been studied, the interactions among HA, PAC-Al$_{30}$ and some other positively charged ions like calcium or clay particles like kaolin have not been systematically investigated so far, and the quantitative relationship between them also remained unclear.

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The role of calcium in the NOM removal with ferric chloride was conducted and evidenced that calcium could play a significant role in organic aggregation. In coagulation experiments with Dismal Swamp fulvic acid (FA), calcium reduced residual FA and substantially widened the pH range of effective treatment. Yao et al. evaluated the effects of calcium on flocs formed by PAC in HA treatment by a coagulation-ultrafiltration (UF) process and found that calcium could promote the size and strength of flocs formed from PAC. Although so many studies regarding the effect of the calcium ions on the NOM removal were reported, none of those studies referred to the influence of calcium in the coagulation with PAC-Al30 systemically and quantitatively. Thus, it is necessary and meaningful to investigate the HA removal by PAC-Al30 when calcium is present in the system. After all, the coagulation behavior of different metal hydrolytic species is quite different.

In addition to calcium, particles like kaolin are common substances that coexist in natural water. People like to use kaolin to simulate the turbidity of wastewater to study the efficiency of turbidity removal in water. On the other hand, people even added kaolin or other particles to promote coagulation. A novel nucleation-induced pelleting coagulation (NPC) process was proposed to improve the separation efficiency of fluffy flocs during coagulation in which diatomite was used as the nucleation agent. You et al. demonstrated that kaolin suspending in water helped improving the removal efficiency of TiO2 nanoparticles from water with polyaluminum ferric chloride (PAFC) and cationic polyacrylamide (CPAM). Zhao et al. studied a novel dextran-based flocculant on the treatment of dye and found that the improvement of removal efficiency was attributed to the fact that partial Congo red (CR) dye molecules were adsorbed onto kaolin particles before flocculation and were synergistically flocculated accompanied by kaolin particles. Particle-modified coagulation/flocculation has recently received increasing attention in the field of water treatment. However, the coagulation interaction of the PAC-Al30, which has nanoscale Al species itself, with a HA water sample that contained kaolin needs to be verified through experiments.

The objective of this study is to investigate the coagulation properties of PAC-Al30 systemically when calcium or kaolin is present in the HA water system. These findings will not only represent an important advance in understanding how calcium or kaolin could improve coagulation but also in predicting the conditions under which calcium or kaolin may prove beneficial. Based on these findings, the possible mechanisms of Ca−HA−PAC-Al30 and kaolin−HA−PAC-Al30 reactive pathways were discussed.

2. MATERIALS AND METHODS

2.1. Coagulants and Water Samples. All reagents used in the research were analytical grade, except for the HA, which was commercial and with the average molecular weight of about 3000. All solutions were prepared by deionized water except for those pointed out specifically. PAC-Al30 with a total aluminum concentration (Alc) of 0.2 mol/L and a B value of 2.4 was prepared as reported. The prepared PAC-Al30 solution was aged at room temperature for 5 days before detection and coagulation experiments. The working HA water was prepared as in ref 12. A calculated amount of CaCl2 or kaolin was added into the working solution to simulate the bivalent cation and particles in natural water. Unless otherwise specified, the pH of working HA solutions was adjusted to around 7.0 with 0.1 mol/L HCl solution or 0.1 mol/L NaOH solution before the addition of PAC-Al30.

2.2. Experimental and Analytical Methods. Coagulation experiments were carried out at room temperature (about 20 °C) using the jar test on a six-paddle gang stirrer (MY3000-6B, Meiyu Co., China). At first, 500 mL working HA solution was added into the 1000 mL beaker. Then, a measured amount of PAC-Al30 was added into the working HA solution under rapid stirring. The HA solution was stirred rapidly at 200 rpm for 2 min after coagulant dosing, followed by slow stirring at 30 rpm for 20 min and then settled for 30 min. The supernatant was withdrawn and filtered through the common qualitative filter paper for UV−vis and residual aluminum detection (the water sample UV−vis detection result after filtering by the quantitative filter paper and 0.45 μm filter membrane was shown in Figure 1S in the Supporting Information). In order to avoid the effect of filtration on turbidity, the static supernatant was directly taken with a syringe during turbidity measurement.

Fourier transform infrared spectroscopy (FTIR) (Shimadzu Co., Japan) of HA analysis used the KBr tablet method with a detection frequency of 41 cm−1. UV−vis, which represent HA concentration, was measured at 254 nm through a 2550 UV spectrophotometer (Shimadzu Co., Japan). Turbidity was measured with a Turb550 (WTW, Germany), and residual aluminum concentration was measured by spectrophotometry with chorme azurol S at 620 nm through a 721 vis spectrophotometer (Jingke Co., China) according to standard examination methods for drinking water−metal parameters (GB/T 5750.6−2006). The Al−Ferron time-wise complex colorimetric analysis was used to detect the hydrolyzed form of aluminum in PAC-Al30 on a UV−vis spectrometer (2550, Shimadzu Co., Japan). Absorbance values at 370 nm were picked from 1 to 120 min after mixing the sample with ferron reagent. It was operationally divided that the species reacted with ferron reagent in 1 min were regarded as Alw, the species reacted with ferron reagent between 1 to 120 min as Al30, and those species cannot react with ferron reagent after 120 min as Alc. The density of PAC-Al30 solution was detected with a Meip density meter. The zeta potential of the water sample system was measured with a Zetasizer Nano ZS (3000HS, Malvern Co., U.K.). After PAC-Al30 or CaCl2 was added into HA working solution with rapid mixing, the water sample was taken out using a syringe immediately to measure zeta potential.

3. RESULTS AND DISCUSSION

3.1. Characteristics of PAC-Al30. The characteristics of prepared PAC-Al30 were detected, and the hydroxy-Al species distribution, density, and particle size are listed in Table 1. Alc species was the main component of prepared PAC-Al30 which accounted for 40.6% of total aluminum. Studies had shown that Alc in a PAC solution prepared by forced hydrolysis and heating under reflux was basically equivalent to Al30, and the important role of Alc or Al30 in the coagulation process had been reported by previous reports of us and other scientists. The Alc or Al30 with high degree of polymerization may play an excellent role of adsorption neutralization, bridge-aggregation, precipitation, and sweep-flocculation in the coagulation process depending on its high positive charge and nanoscale molecular size. The liquid PAC-Al30 had a density of 16414  https://doi.org/10.1021/acsomega.0c00532
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1.036 g/cm³, which is almost the same as pure water, indicating that it was more inclined to solution than sol.

Originally, the aluminum salt solution was completely dissolved, but because of the hydrolysis products of macromolecules such as Al₁₃ and Al₃₀, or aggregates of them, the nanosized particles could be detected. The size distribution of prepared PAC-Al₃₀ was detected and is shown in Table 1. It can be seen from Table 1 that the PAC-Al₃₀ with a mean size of 3.86 nm after 10 days of aging. The main particle diameters were distributed at 3.62 and 4.19 nm, accounting for 36.3 and 30.2% of the total particle number, respectively.

3.2. Characteristics of HA. The FTIR and zeta potential of the test with HA is shown in Figure 1. HA is a kind of macromolecular mixture with a complex structure. It shows incomplete infrared spectrum according to the origin, extraction method, and environmental conditions. Although HA does not have a standard infrared spectrum like a pure compound, its main structure and main functional groups are basically the same. It can be seen from Figure 1 that the HA had three distinct absorption peaks around 3400, 1600, and 1100 1/cm. The broad peak at 3400 1/cm could be attributed to the stretching vibrations of free –OH and hydrogen-bonded –OH within or between HA molecules. The absorption peaks at 1700, 1600, and 1300 1/cm were generally considered to represent –COOH groups on HA, and the absorption peak around 1100 1/cm was the deformation vibration of the C–H bond on the benzene ring.

From the infrared spectrum analysis of HA, it can be seen that the primary functional groups of the HA used in the experiment include hydroxyl, carboxyl, and aromatic rings, which result was consistent with the typical structure of HA proposed by Schulten and Schnitzer. The polyfunctional structure of HA determined that it had strong chemical activity and was easy to exchange, adsorb, and complex with other ions or substances.

Zeta potential is one of the important indicators for evaluating the charging performance of colloidal particles. As can be seen from Figure 1, the HA aqueous solution (pH = 7.02) exhibited remarkable charged characteristics. There was a narrow and strong potential peak appearing at ~18.0 mV with a half width of 3.65 mV. It was generally considered that the HA macromolecules were negatively charged in water due to the dissociation of hydroxyl and carboxyl groups.

3.3. Influences of Calcium on the PAC-Al₃₀ Coagulation. The PAC-Al₃₀ was proved to be a good coagulant for water and wastewater treatment. The influence of calcium on HA coagulation at different PAC-Al₃₀ dosages was shown in Figure 2. It can be seen from Figure 2 that calcium had an obvious influence on the HA coagulation when the PAC-Al₃₀ dosages was less than or equal to 0.02 mmol/L. As the PAC-Al₃₀ dosage was 0.01 or 0.02 mmol/L, a little calcium significantly decreased the residual UV₂₅₄. As the PAC-Al₃₀ dosage was 0.01 and 0.02 mmol/L, the HA removal rate increased by 66.59 and 42.20%, respectively, with a calcium concentration of 2.0 mmol/L. However, with the increase of the calcium concentration, the residual UV₂₅₄ value did not continue to decrease. After a calcium concentration of more than 2.0 mmol/L, the residual UV₂₅₄ value remained basically unchanged. Furthermore, when the dosage of PAC-Al₃₀ was more than or equal to 0.04 mmol/L, the residual UV₂₅₄ value was also almost unchanged along with the increase of calcium concentration.

It also can be seen from Figure 2 that under the same calcium concentration, the residual UV₂₅₄ value all decreased with the increase of PAC-Al₃₀ dosage, but the extent of this effect decreased with the increase of calcium concentration. Without calcium in the water, the HA removal rate increased

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c00532) FTIR spectroscopy and zeta potential of HA (FTIR detected with HA powder and zeta potential tested with 10 mg/L HA water solution and pH of 7.02).

| hydroxy-Al species distribution (%) | density (g/cm³) | mean size (nm) | size distribution | number (%) |
| Al₁ | Al₃₀ | Al₃₀ | 1.036 | 3.86 | 27.3 | 32.1 | 40.6 | 2.7 | 2.5 |
| 3.12 | 18 | 3.62 | 36.3 | 4.19 | 30.2 | 4.85 | 11.3 | 5.61 | 1.8 |

![Figure 2](https://dx.doi.org/10.1021/acsomega.0c00532) Effect of calcium on HA removal at different dosages of PAC-Al₃₀.
from 20.49 to 89.76% with the increase of PAC-Al$_{30}$ dosage from 0.01 to 0.06 mmol/L. However, when the calcium concentration in water was 2.5 mmol/L, the HA removal efficiency only increased from 72.93 to 87.80% along with the increase of PAC-Al$_{30}$ dosage from 0.01 to 0.06 mmol/L. The presence of calcium in the water could reduce the effect of coagulant dosage on the coagulation effect.

The residue of Al in the use of aluminum salt coagulants has always been a concern of people because studies have shown that excessive aluminum may have a certain harm to human health. The residual Al concentration in the purified water always been a concern of people because studies have shown that excessive aluminum may have a certain harm to human health. The residual Al concentration in the purified water was tested, and the results were shown in Figure 3. As can be seen in Figure 3, first of all, the residual Al concentration in the effluent of all water samples did not exceed 0.2 mg/L as defined in China’s Sanitary Standards for Drinking Water and that the limited standard is consistent with that of the World Health Organization and the European Community organization. Second, the addition of calcium did not change the tendency of the residual Al concentration in water to increase with the increase of the PAC-Al$_{30}$ dosage. However, although not very significant, we can still find in Figure 3 that, under the same PAC-Al$_{30}$ dosage conditions, the added calcium had depressed the residual Al concentration in the water to a certain extent.

3.4. Influences of Kaolin Particles on Coagulation. Kaolin particles in water could increase the particle concentration and then increase the collision efficiency between particles, but they might also have competition with HA for coagulant. The influences of kaolin particles on HA coagulation can be seen from Figure 4. It shows that the collision action was prior to the competition when the coagulant dosage was low. As the PAC-Al$_{30}$ dosage was 0.01 and 0.02 mmol/L, the HA removal was increased by 53.31 and 40.92%, respectively, with a kaolin particle concentration of 150 mg/L but when the coagulant dosage was sufficient (higher than or equal to 0.04 mmol/L), the kaolin had no obvious effect on the HA removal.

The turbidity of water samples after coagulation was also measured in Figure 5. It could be seen from Figure 5 that when the dosage of PAC-Al$_{30}$ was less than or equal to 0.02 mmol/L, the added kaolin particles cannot be effectively removed and result in increased turbidity of the effluents. When the kaolin concentration was 150 mg/L, the turbidity of effluent increased to a maximum of 8.79 NTU. When the dosage of PAC-Al$_{30}$ was increased to 0.04 and 0.06 mmol/L, the kaolin particles were effectively removed and the turbidity of effluent was nearly 0.01 NTU, which was much lower than the 1NTU stipulated in China’s Sanitary Standards for Drinking Water.

The initial pH of the water sample is one of the important factors affecting the coagulation effect. Here, the effect of initial pH on PAC-Al$_{30}$ coagulation (with a PAC-Al$_{30}$ dosage of 0.02 mmol/L) as different amounts of added kaolin were added was examined and is shown in Figure 6. It could be seen from Figure 6 that both residual UV$_{254}$ and turbidity became lower values under acidic conditions. When initial pH was the same, the residual UV$_{254}$ all decreased with the increase of the added kaolin amount, and this promotion effect was more obvious when the pH of the raw water was between 7.0 and 8.0. The turbidity showed a different trend from residual UV$_{254}$. Although some data points showed inconsistencies, the overall trend was that when the initial pH was less than 7.5, the addition of kaolin reduced the turbidity of the effluent; but when the initial pH was greater than 7.5, the addition of kaolin caused an increase of turbidity, and this action was more significant when the addition of kaolin was high. Moreover, it should be noted that the turbidity of effluent were higher than the raw HA water even if no kaolin was added. This might be because the input of PAC-Al$_{30}$ had formed fine flocs in the water sample, but these flocs remained in the water and caused the increase of turbidity in the case of insufficient PAC-Al$_{30}$ dosage.

The effect of kaolin on residual Al concentration in the purified water at different dosages of PAC-Al$_{30}$ was also detected in Figure 7. With the same effect as calcium, the residual Al concentration in the effluent of all water samples.
did not exceed 0.2 mg/L. However, in contrast with calcium, the addition of kaolin is seen to slightly increase the residual Al concentration in the water. This might be related to contained aluminum of the kaolin itself.

3.5. Action Mechanisms of Calcium. Actions between HA and calcium could be explained with the Deryaguin, Landau, Verwey, and Overbeek (DLVO) theory, which was a classical theory on the stability of charged colloidal solution. It was generally considered that the negatively charged HA could disperse in natural water stably and chronically due to the electrostatic repulsion among HA macromolecules. According to the DLVO theory, cations like calcium can compress the double electrical layers or complex with HA to neutralize a part of the surface negative charge. It was found in experiment that the HA working solution was very stable within a few days, but a slight HA precipitation could be observed after one night when calcium was added. The promoting effect of calcium on PAC-Al₃₀ coagulation might be due to the early adsorption or complexation with HA reducing the electrostatic repulsion of HA particles. Abeyasinghe et al. proved that the electrostatic potential of Al₃₀ was positive throughout, and with higher values at the central and lower values at both ends. A possible Ca−HA−PAC-Al₃₀ reaction pathway in the system was shown in Figure 8 in which the Al₃₀ was used as a typical representative of aluminum hydroxyl forms in PAC solution.

The adsorption neutralization capacity of calcium was quantitatively studied. As shown in Figure 9, the absolute value of the zeta potential of the HA water system decreased with the increase of calcium dosage, which indicated a charge neutralization mechanism of calcium. However, the zeta potential never reached the isoelectric point for calcium; when the dosage of calcium was more than 2.0 mmol/L, the zeta potential was kept at a value of −13.7 mV. This trend was generally in agreement with the effect of calcium on the removal of HA in Figure 2. A comparative study on PAC-Al₃₀ was conducted, and the results are also shown in Figure 9. Just a very small amount of PAC-Al₃₀ could cause a rapid increase of zeta potential and reach the isoelectric point quickly at a PAC-Al₃₀ dosage of 0.08 mmol/L. Then, the zeta potential of the HA water system continued to increase until the PAC-Al₃₀ dosage was higher than 0.8 mmol/L, and the zeta potential value was basically stable at 24.9 mV.

The Sips equation was proved can be used to quantitatively describe the adsorption neutralization of aluminum species onto HA by our precious researches. The Sips equation can be seen as a result of introducing a nonuniform parameter $\gamma$ into the Langmuir equation, so it was also called Langmuir

Figure 6. Effect of initial pH on PAC-Al₃₀ coagulation as different kaolins were added (with a PAC-Al₃₀ dosage of 0.02 mmol/L).

Figure 7. Effect of kaolin on the residual Al concentration in the purified water at different dosages of PAC-Al₃₀.

Figure 8. Possible reaction pathway among calcium, HA and PAC-Al₃₀.

Figure 9. Effect of calcium or PAC-Al₃₀ dosage on the zeta potential of the HA water system (HA concentration of 10 mg/L and pH of 7.02).
EXT (extended) equation. The mathematical function of the Sips isotherm was expressed as eq 1,

$$q_e = \frac{q_m \cdot K_S \cdot C_e^\gamma}{1 + K_S \cdot C_e^\gamma}$$

(1)

where $C_e$ is the dosage of coagulants, $q_e$ is the increased value of the zeta potential, and $q_m$ is the maximum increased value of zeta potential when equilibrium reaches. $K_S$ is the Sips constant, and the $\gamma$ is a parameter that represents the surface heterogeneity of the adsorbent.

The fitted results are shown in Figure 10 and Table 2. The experimental data fitted well with the Sips equation, and the correlation coefficients ($R^2$) were 0.990 and 0.986 for PAC-Al$_{30}$ and calcium, respectively. The equilibrium zeta potential could be obtained by adding the $q_m$ value together with $-18.0$ mV (the zeta potential value of raw water), and they were $27.25$ and $-14.19$ mV for PAC-Al$_{30}$ and calcium, which were very similar to the equilibrium zeta potential values estimated from Figure 9. $K_S$ in the Sips equation could be used to express the adsorption neutralization capacity of coagulants. The larger the $K_S$ value, the stronger the adsorption neutralization capacity. Comparing the $K_S$ values of PAC-Al$_{30}$ and calcium in Table 2, it could be seen that the adsorption neutralization capacity of PAC-Al$_{30}$ was nearly 60 times than that of calcium. The $\gamma$ in the Sips equation represented the heterogeneity of adsorbent surface, and the $\gamma$ value being closer to 1 indicated that the adsorbent surface was more homogeneous. The higher $\gamma$ value of calcium might indicate that the adsorption or neutralization sites of calcium on HA were pickier than PAC-Al$_{30}$.

Overall, although calcium had some advantageous effects to neutralize the surface negative charges of HA, we do not need to add calcium to promote coagulation in actual because the charge neutralization degree was much less than that of PAC-Al$_{30}$. However, in the coagulation of high-hardness water that contains higher calcium, the effect of calcium should be considered and the dosage of PAC-Al$_{30}$ can be reduced appropriately than the water without or less calcium.

3.6. Action Mechanisms of Kaolin. Although the influence tendency of kaolin on HA coagulation at different PAC-Al$_{30}$ dosages was similar to that of calcium, the action mechanism might be absolutely different. Unlike calcium, kaolin particles were negatively charged generally. While the action between calcium and HA could be explained by the DLVO theory, the action between kaolin and HA could be interpreted with the collision and adsorption theory. Tambo and Wang$^{34}$ believed that particles in water flocked together through collision, two of them aggregated first to form a duplex particle, and then the duplex particles collided with the prime particle or the other duplex particle to form treble or fourfold particles, and so on, much bigger flocs gradually formed. According to the collision theory, appropriate increase of the particle concentration could increase the collision probability of particles by stirring or Brownian motion. Therefore, although the kaolin was negatively charged, when a small amount of kaolin particles existed in water, the removal of HA was possibly promoted by collision aggregation. This collision aggregation action might occur between any particles like kaolin and HA, kaolin and kaolin, or kaolin and PAC-Al$_{30}$. However, the efficiency of this collision aggregation was not 100%, and much lower than the coagulation effect of PAC-Al$_{30}$. After all, in addition to collisions, adsorption and neutralization also played a vital role in the coagulation process. So, when the amount of kaolin was too high and there was not enough PAC-Al$_{30}$ to produce coagulation, a large amount of kaolin particles would stay in the water and increase the turbidity of the effluent. A possible kaolin—HA—PAC-Al$_{30}$ reaction pathway in the system is shown in Figure 11.

4. CONCLUSIONS

The prepared PAC-Al$_{30}$ possessed more Al$_3$ species and a nanoscale molecular size of 3.7 nm after 10 days aging, which may play an excellent role of adsorption neutralization, bridge aggregation, precipitation, and sweep flocculation in the coagulation process.

The infrared spectrum of the test with HA showed that it contained primary functional groups of hydroxyl, carboxyl, and aromatic rings. The HA working solution was negatively charged with a zeta potential value of $-18.0$ mV.

As the PAC-Al$_{30}$ dosage was $0.01$ and $0.02$ mmol/L, the HA removal rate increased by $66.59$ and $42.20\%$, respectively, with a calcium concentration of $2.0$ mmol/L or increased by $53.31$ and $40.92\%$, respectively, with a kaolin particle concentration of $150$ mg/L. However, these actions were both not significant with a higher dosage of PAC-Al$_{30}$.

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**Table 2. Fitted Parameters of the Sips Equation**

| added substance | $q_m$ (mV) | $K_S$ | $\gamma$ | $R^2$ |
|-----------------|------------|-------|---------|-------|
| PAC-Al$_{30}$   | 45.25      | 67.73 | 1.99    | 0.990 |
| calcium         | 3.81       | 1.13  | 2.83    | 0.986 |

Figure 10. Relationship between the increased zeta potential and PAC-Al$_{30}$ or calcium dosage modified with the Sips equation.

Figure 9. $K_S$ in the Sips equation could be used to express the adsorption neutralization capacity of coagulants. The larger the $K_S$ value, the stronger the adsorption neutralization capacity.
The increased zeta potential of PAC-Al$_{30}$ and calcium fitted well with the Sips equation with equilibrium zeta potentials of 27.25 and $-14.19$ mV for PAC-Al$_{30}$ and calcium, respectively. The adsorption neutralization capacity of PAC-Al$_{30}$ was calculated to be nearly 60 times than that of calcium, and the higher $\gamma$ value of calcium modified by the Sips equation may indicate that the adsorption or neutralization sites of calcium on HA were pickier than PAC-Al$_{30}$.

The initial pH of water sample had an important impact on PAC-Al$_{30}$ coagulation as different amounts of kaolin were added. The residual UV$_{254}$ all decreased with the increase of the added kaolin amount, while the turbidity showed the two sides. When the initial pH was less than 7.5, the addition of kaolin reduced the turbidity of the effluent, but when the initial pH was greater than 7.5, the addition of kaolin might cause an increase of the turbidity.

The added calcium reduced the residual Al concentration in the water to a certain extent, but unlike calcium, the addition of kaolin seen to slightly increase the residual Al concentration in the water.

Calcium could compress the double electrical layers or complex with HA to neutralize a part of the surface negative charge but did not make the water system reach its isoelectric point. The mechanisms of calcium and kaolin promoting the coagulation effect were adsorption neutralization and collision aggregation, respectively. Despite this, we do not need to add calcium or kaolin to promote PAC-Al$_{30}$ coagulation in actual because both the adsorption neutralization and aggregation capacity degree of calcium nor kaolin were much less than the PAC-Al$_{30}$.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00532.

(Figure 1S) UV254 detection result after filtering by a quantitative filter paper and 0.45 µm filter membrane (PDF)

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Notes

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