Aggregation of nano-sized alum–humic primary particles

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ABSTRACT

In order to understand the mechanism of floc formation and growth in coagulation process, effect of zeta potential and surface characteristic of nano sized primary particles on coagulation efficiency were investigated by coagulation of humic acid with alum in this study. It was demonstrated that only 1 min rapid mixing was enough for adsorption of humic acid onto the precipitates of alum, and 15 min flocculation (slow mixing) only induced the formation and growth of flocs. The primary particle size of alum–humic flocs was near 50 nm and spherical. Mathematical model deduced from Derjaguin–Landau–Verwey–Overbeek (DLVO) theory showed that the formation of micro-flocs (or lag time) was determined by the square value of zeta potential of nano-sized primary particles and intensity of Brownian motion, which is closely related to water temperature. There was an absolute critical zeta potential, i.e. 13.5 mV in this study, determining whether two nano-sized particles could overcome the energy barrier consisted of Van der Waals force and electrical double layer repulsion force to allow floc formation to occur at a certain temperature. The Brownian motion determined whether the nano-sized primary particles (aluminum hydroxide precipitates with humic acid) had the opportunity to overcome the repulsive force and cement with each other. Low coagulation efficiency at high latitude area in winter is caused by low collision frequency, which is mainly attributed to the low intensity of Brownian motion at a low temperature. Furthermore, it was demonstrated that aggregation of micro-flocs or their clusters significantly depended on activated sites on the primary particles rather than the zeta potential of primary particles when sweep flocculation dominated the coagulation mechanism if the size of flocs was larger than some value.

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1. Introduction

Coagulation/flocculation is the most common process to remove particles and other contaminants from water, although the coagulation mechanism has been explored for a long period. The characteristics of flocs formed in the coagulation are influenced by coagulant type and dosage, mixing condition and raw water quality; while the efficiency of solid/liquid separation processes is influenced by characteristics of flocs including floc size and structure.

Dempsey et al. [1,2] and Edwards and Amirtharajah [3] reported that coagulant demand was strongly dependent on humic concentration. For removal of humic substances by hydrolyzing coagulants such as aluminum and ferric salts, two main mechanisms

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have been proposed [4,5]: (a) Binding of cationic metal species to anionic sites of the humic material, thus neutralizing charge of humic material at low pH around 5 or less (charge neutralization). (b) At higher pH, precipitates of amorphous metal hydroxide adsorb the dissolved organic substances (sweep coagulation). All experiments were conducted in this study at pH much higher than 5 where the second mechanism was dominated. Actually, it is usually not easy to distinguish between the mechanisms of precipitation and adsorption. The results of some study [6] showed that it was mainly determined by pH and coagulant dosage. Kim et al. [7] found that flocs formed under sweep coagulation were larger and more compact than those formed under charge neutralization. Although the removal of pollutants by coagulation/flocculation has been studied for many years, knowledge of the floc growth mechanism remains limited. Especially, the actual cause of connection between two micro-flocs, especially chemical bonds is still not fully understood.

The collision frequency and growth of aggregates depend on chemical surface of micro-flocs (primary particles) with different dosage and species of coagulant, local shear forces and the suspending

electrolyte. Chemical surface of micro-flocs may be influenced by temperature, especially at low temperature. Hanson and Cleasby [8] found that the effect of both energy input parameters and flow field characteristics on coagulation performance were insignificant at low temperature. Moreover, Xiao et al. [9] found that low temperature caused slow coagulation rate at early stage, though the zeta potential of flocs formed at low and normal temperature was almost the same. In this study mathematical model was founded to describe the coagulation process and explain the involved mechanisms.

Mathematical model deduced by Dentel [10] was applied to illustrate the coagulation of humic substances by considering them as small colloids with a substantial contribution to surface area in the system, and zeta potential of flocs was average of humic acid and coagulant. Some developed coagulation models differed somewhat from the two mechanisms (charge neutralization and sweep coagulation) in means of explaining destabilization phenomena [11,12]. They postulated that, under many conditions, the neutralization and reversal of colloid charge were caused by precipitation of positively charged metal hydroxide. Snodgrass et al. [13] concluded that the rate of complexation of fulvic acid with monomers or small polymers of aluminum was faster than homogeneous growth of aluminum hydroxide nuclei due to the high zeta potential of aluminum hydroxide nuclei. Logan and his students have developed collision theories for fractal objects in 1990s by using latex particles (1.48 or 2.84 μm) as the primary particles charged by NaCl [14,15].

In this study, humic acid was considered as dissolved substance which just changed the charge of alum precipitate. The aim of this study is to better understand the adsorption process of humic acid to alum precipitate and to explore what mainly determines or influences the formation and growth of micro-flocs. The size of primary particles was uniform and near 50 nm. Mathematical model deduced from DLVO theory was utilized to investigate the effect of Brownian motion and zeta potential on the collision of two primary particles, and then on the formation of micro-flocs, where little related publication can be found until now. In addition, the surface activation and quantity of $\eta_2\text{-OH}_2$ and $\eta_2\text{-OH}$ on surface of micro-flocs were discussed to explore the mechanism of micro-floc growth.

2. Materials and methods

2.1. Stock humic acid solution and coagulant

Four grams of humic acid (Jufeng, Shanghai, China), was dissolved in deionized (DI) water, with pH adjusted to 7.0, and mixed by a magnetic stirrer for 24 h. Then the suspension was filtered by 0.45 μm acetate fiber membrane. The solution was diluted to 500 mL in a measuring flask and was stored in the dark. Humic acid used here was the same as the one used by Xu et al. [16], and it had been analyzed by them.

Aluminum sulfate hydrate (analytical pure) “alum” was used. Stock alum solution was prepared at a concentration of 0.1 M Al in DI water.

2.2. Jar test

For the flocculation tests, the stock humic acid (HA) was diluted in 1000 mL tap water (Harbin, China), in a 1.2 L beaker, to give the test solution with a HA concentration of 4 mg/L. Tap water was left for 1 day to release the residual chlorine. During the jar test, the initial pH of solution was near 7.0. Total organic carbon (TOC) of the test water was 4.34 mg/L [17]. The temperature was maintained at $25 \pm 1^\circ\text{C}$.

The equipment used in this study was a Flocculator (ZR4-2, Shenzhen Zhongrun, China), which enables mixing speed and time to be preset. The solution was stirred at 50 rpm for 1 min to mix uniformly. After that a certain dosage of alum was added with a simultaneous increase of stirring speed to 200 rpm. The rapid mixing speed of 200 rpm was maintained for 1 min, and then reduced to 50 rpm for 20 min or more to allow floc growth to occur.

2.3. Other methods

Samples were taken immediately after dosing coagulant and 1 min rapid mixing, and zeta potentials were determined by a zeta sizer (Nano ZS90; Malvern Inc., UK). UV_{254} (0.45 μm) was measured after 1 min rapid mixing or another 15 min flocculation by an ultraviolet/visible spectrophotometer (U-3010, Hitachi High Technologies Co., Japan). Dissolved organic carbon (DOC) was determined with a total organic carbon (TOC) analyzer (TOC-VCPH, Shimadzu, Japan). The residual Al concentration (0.45 μm) was measured by ICP-OES (Perkin–Elmer, USA).

During the slow mixing period, a sample of flocs was taken from below the surface of the solution by a glass tube with an inner diameter of 0.5 cm. The tube was open at both ends; one end of the tube was inserted gently about 25 mm into the coagulated solution to avoid contacting the stirrer [9]. The flocs in the tube were withdrawn carefully by covering the other end of the tube with a finger. After transferring the sample to a flat mental slide, samples were then air-dried and gold-coated by a sputter and observed under scanning electron microscopy (SEM; JSM7401F, JEDL, Japan).

2.4. Floc monitoring

During the coagulation process, sample was siphoned from the stirred jar at 20 mL/min through a 3 mm transparent plastic tube and continuously monitored by a PDA 2000 (Rank Brothers, UK) based on the “turbidity fluctuation” technique [18]. After passing through the monitor, sample was returned to the stirred jar by a peristaltic pump. The experimental procedure was similar to that of Yukselen and Gregory [19]. The average transmitted light intensity (dc value) through the flowing sample and the root-mean-square value (rms) of the fluctuating component are monitored. The ratio (rms/dc) provides a sensitive measure of particle aggregation and it is often called *Flocculation Index* (FI). The FI value is strongly correlated with floc size and always increases as flocs grow larger. So the FI value provides a sensitive measure of particle aggregation [18]. In this study, after the FI value reached an initial steady value, coagulant was added into the suspension and the FI value was recorded by a PC data acquisition system at 1 s intervals.

3. Results

3.1. Zeta potential and UV_{254} removal

The results in Fig. 1 show the residual UV_{254} after 1 min rapid mixing and 15 min flocculation (slow mixing), and zeta potential of micro-flocs after 1 min rapid mixing at different alum dosages at initial pH near 7.0. The pH decreased as the dosage of alum increased, while UV_{254} decreased from 0.158 cm^{-1} to 0.154 cm^{-1} as the pH decreased from 7.03 to 5.72 (DOC from 4.355 mg/L to 4.232 mg/L). Therefore, the effect of pH itself on the variation of dissolved NOM could be ignored here. Results in Fig. 1 show that the alum–humic flocs are negatively charged at low alum dosage and that charge reversal occurs at around 0.04 mM Al. The zeta potential increased dramatically increased until 0.08 mM Al, and at

Fig. 1. Residual UV_{254} , zeta potential and pH at different alum dosages.

higher dosages it increases only slightly and stayed at around 16 mV.

There was an appreciable reduction in UV_{254} at 0.015 mM Al when zeta potential changed from -15 mV to -13 mV, and then it was gradually increased at higher dosages. It is clear that there was no significant difference of UV_{254} removal between the case of after 1 min rapid mixing and that of after 15 min flocculation, as shown in Fig. 1. The results indicated that if the removal of humic substances was achieved by adsorption on precipitated aluminum hydroxide, it could be finished within 1 min or even shorter time after precipitation occurred. The result was confirmed by different waters in different areas of China. It suggested that the flocculation process only improved the size of destabilized particles (flocs), and the mechanism of which will be discussed later.

3.2. Flocculation index

In view of coagulant cost and sludge volume in sedimentation tank, the optimal coagulant dosage corresponding to the best coagulation performance is of great importance. Results from continuous monitoring of humic acid coagulation with different alum dosages are shown in Fig. 2. At a very low dosage of 0.01 mM Al (-15 mV), no change of FI value was observed (data were not shown), which was the same as that formed at a very high dosage of 0.1 mM Al (15 mV). At a slightly higher dosage of 0.012 mM the FI value began to rise slowly after a long lag time of about 1300 s. However, at the dosages of 0.015–0.08 mM Al, a rapid rise in FI occurred soon after no more than 500 s. In these cases, the FI reached a plateau value after a few minutes. Comparing these

Fig. 2. Effect of alum dosage (mM Al) on the growth of flocs, as measured by the Flocculation Index.

results with the data of zeta potential in Fig. 1, it could be seen that the onset of coagulation was correlated with coagulant dosages, indicating that the absolute value of zeta potential corresponding to a certain dosage should be lower than 13 mV to ensure coagulation process could occur. At the dosage of 0.04 mM Al, the zeta potential was about 0.9 mV, which was closed to zero. When the alum dosage was higher than 0.1 mM Al, FI value did not increase and maintained at low value. Moreover, it was also found that the plateau FI values were nearly the same when the dosage changed from 0.012 mM to 0.08 mM Al in this study.

3.3. Lag time and coagulation rate

Flocculation process is very important because the floc properties influence the separation/purification process. There is a variable lag time, depending on coagulant dosage, during which the precipitate particles are ready to aggregate to form flocs, but the aggregates are not yet large enough to give a measurable increase in FI value.

As shown in Fig. 3, when the alum dosage was lower than 0.01 mM Al, the lag time was relatively long, much longer than 1500 s. At a dosage of 0.012 mM Al, the FI value began to rise after a lag time of about 1300 s; while the lag time was less than 500 s at higher dosages of 0.015–0.08 mM Al, especially at a moderate dosage. However, for a dosage of 0.1 mM Al, the lag time was more than 1500 s, which implied that precipitates of alum were difficult to connect with each other.

From the FI curves in Fig. 2, the coagulation rate (defined by Xiao et al. [9]) as a function of coagulant dosage is shown in Fig. 3. Coagulation rate was found to vary with coagulant dosage. It increased when the dosage of alum was higher than 0.012 mM Al, and then became plateau when the dosages were in the range of 0.02–0.07 mM Al, even though the zeta potentials corresponding to these alum dosages were different from each other. The results showed that the coagulation rate was determined not only by the zeta potential of micro-flocs, but also by some characteristics of the floc surface, and the result was very similar with the finding of Fe (III) coagulation by Xiao et al. [20].

3.4. Relationship between zeta potential and lag time

What actually cause different lag time of the coagulation process, zeta potential of flocs, surface characteristic of flocs, or others? In order to explain the involved mechanism, absolute values of zeta potential and lag time at different alum dosage were compared with each other. As shown in Fig. 4, with the increasing of alum dosage from 0.01 to 0.10 mM Al, the lag time gradually

Fig. 3. Effect of alum dosage on the lag time of FI value and coagulation rate.

Fig. 4. Relationship between lag time and absolute value of zeta potential.

decreased at first, and the absolute value of zeta potential of flocs also decreased; then both the lag time and the absolute value of zeta potential increased in the later stage. If the absolute value of zeta potential of the flocs was higher than 13.5 mV, lag time would increase to infinite time, i.e. stabilization or re-stabilization, whether zeta potential was negative or positive. Thus it can be concluded that there must be a relationship between zeta potential and lag time, which is of great significance in coagulation/flocculation process. Fig. 4 showed that the optimum coagulant dosage was at a zeta potential somewhat offset from zero. Many researchers [11,21,22] also found that the optimum dosage of coagulant was not the dosage when the zeta potential was 0 mV but near 0 mV, which may be due to other factors such as solvation and floc volume effects or chemical bonds.

3.5. Discussion

In general, perikinetic (diffusion-induced) and orthokinetic (shear-induced) collisions are the two important mechanisms involved in particle transportation. Xiao et al. [9] pointed out that perikinetic collision induced by Brownian diffusion mainly dominates dynamics of particles smaller than 1 μm ; whereas the orthokinetic collision induced by hydrodynamic shear gradients primarily controls the coagulation rate of particles larger than 1 μm . Therefore, before the FI value increases, the coagulation efficiency is determined by collision frequency;

Humic substances may be considered as either soluble macromolecules or small colloids [10]. In this study, humic substances were assumed as the former, such that the coagulation of them may be modeled by accounting for their substantial contribution to charge on small precipitate particles of alum in the system. The flocs formed by alum and humic acid were consist of thousands of nano-sized primary particles (near 50 nm), as shown in Fig 5a. Therefore, the chemical characteristic and reaction dynamics of primary particles was explored here.

When pH is low, there is little OH^- in the solution, and most of existing mode of Al^{3+} is $[\text{Al}(\text{OH})_2]^{3+}$ and a small part of Al^{3+} changed into $[\text{Al}(\text{OH})_2(\text{OH})]^{2+}$. As the pH increases or Al^{3+} is added into the raw water, some $[\text{Al}(\text{OH})_2]^{3+}$ will deprotonate and change into $[\text{Al}(\text{OH})_{2-n}(\text{OH})_n]^{(3-n)+}$. Then $[\text{Al}(\text{OH})_{2-n}(\text{OH})_n]^{(3-n)+}$ react with humic acid or another $[\text{Al}(\text{OH})_{2-n}(\text{OH})_n]^{(3-n)+}$ to form nano-sized primary particles. After that, Brownian motion will be the force which causes a quick connection between two nano-sized primary particles, by changing $\eta_2\text{-OH}_2$ and $\eta_2\text{-OH}$ into $\mu_2\text{-OH}$ and H_2O . The rapid formation of alum flocs can be also explained by the same mechanism. When the hydroxide precipitates with humic acid formed, DLVO theory is considered to be suitable to illustrate the

Fig. 5. SEM of alum-humic flocs (a) and schematic diagram of variation of free energy with particle separation according to DLVO theory (b).

process of particle connection, especially between two nano-sized primary particles.

The net energy is given by the sum of double layer repulsive force and Van der Waals attractive force that the particles experience as they approach one another. DLVO theory suggests that the stability of a particle in solution is dependent upon its total potential energy function V_T . If the ionic strength is low, such as drinking water, there is no secondary minimum, as shown in Fig 5b. This theory recognizes that V_T is the balance of several competing contributions [23]:

$$V_T = V_A + V_R + V_S \quad (1)$$

where V_S is the potential energy due to the solvent, it usually only makes a marginal contribution to the total potential energy over the last few nanometers of separation. V_A is Van der Waals force, and V_R is electrical double layer repulsive force. The balance between V_A and V_R is very important, since they make the attractive and repulsive contributions respectively.

This theory proposes that an energy barrier resulting from the repulsive force prevents two nano-sized particles approaching one another and adhering together (Fig. 5). If the particles with sufficient energy (Brownian motion) can overcome that barrier, the attractive force will pull them into contact and then adhere together strongly and irreversibly, where coagulation/flocculation eventually occurs. In this case, the distance between two particles must be shorter than h_a , as shown in Fig 5b. Therefore, if the nano-sized particles have a repulsive force which is strong enough, the dispersion will give a resistant effect on flocculation and the colloidal system will be stable.

For the interaction between two spherical particles, and here is nano-sized spherical particles, V_A is relatively simple as below:

$$V_A = -\frac{Aa}{12h} \quad (2)$$

where A is the Hamaker constant, and it is equal to 10.6 kT for water at 25 °C; a is radius of particles and h is the particle separation. The repulsive potential V_R is a far more complex function. As the size of primary particles was around 50 nm, V_R can be calculated as follow:

$$V_R = \frac{4\pi\epsilon a^2}{h+2a} \left(\frac{kT}{ze}\right)^2 \xi^2 \exp(-\kappa h) \quad (3)$$

where ξ is the zeta potential, κ is a function of the ionic composition, k is Boltzmann constant, T is absolute temperature, z is the valence of counterions, e is the elementary electric charge. $\epsilon = \epsilon_r \epsilon_0$, where ϵ_0 is the vacuum permittivity and ϵ_r the relative dielectric constant of the solvent.

$$V_T = -\frac{Aa}{12h} + \frac{4\pi\epsilon a^2}{h+2a} \left(\frac{kT}{ze}\right)^2 \xi^2 \exp(-\kappa h) \quad (4)$$

The stability of an aqueous dispersion is influenced by three main parameters: surface potential, nature and ionic strength of electrolyte solution, and Hamaker constant. According to our previous research [24] and the result of Xiao et al. [9], zeta potential (or electrophoretic mobility) of flocs will not change as coagulation process continues, even after the flocs are broken, which shows that zeta potential is determined by coagulant dosage and pH of solution. In addition, ionic strength changed little as the alum dosage increased below a certain value. Hamaker constant is considered constant for a specific system. Thus total attractive force F can be expressed as follows:

$$F = -V_T = \frac{Aa}{12h} - \frac{4\pi\epsilon a^2}{h+2a} \left(\frac{kT}{ze}\right)^2 \xi^2 \exp(-\kappa h) = mG \\ = 4/3\pi a^3 \rho G \quad (5)$$

where ρ is the density of particles, G is the acceleration of particles. The distance between two particles can be calculated as follows:

$$H - h(t) = \int_0^{t_F} v(t)dt = \int_0^{t_F} \left(v_0 + \int_0^t G(t)dt \right) dt \quad (6)$$

where H is the distance between two particles, and v_0 is the statistical highest velocity of particles by Brownian motion and other force at fixed condition. The higher temperature, the higher v_0 of particles. $v(t)$ is the velocity of primary particles moved towards to other primary particles as function of time. t_F is the time needed for the two primary particles to adhere with each other.

$$O \text{ is substituted for } \frac{Aa/12}{4/3\pi a^3 \rho} \text{ and } P \text{ for } \frac{4\pi\epsilon\epsilon_a a^2}{4/3\pi a^3 \rho} \left(\frac{kT}{ze}\right)^2.$$

From formula (5) and (6), it can be calculated that:

$$H - h_a = v_0 t_F + \int_0^{t_F} \left(\int_0^t \left(\frac{O}{h(t)} - \frac{P \xi^2 \exp(-\kappa h(t))}{h(t) + 2a} \right) dt \right) dt \quad (7)$$

where H is the distance between two particles and h_a is the distance of adhered particles as shown in Fig. 5b.

Here it is proposed that there is an average value $\bar{h}$, when the distance of particles $h(t)$ changes from H to h_a .

$$\left(\frac{O}{\bar{h}} - \frac{P \xi^2 \exp(-\kappa \bar{h})}{\bar{h} + 2a} \right) t_F^2 + 2v_0 t_F - 2(H - h_a) = 0 \quad (8)$$

Also M is submitted for $\frac{O}{2h} = \frac{Aa/12}{4/3\pi a^3 \rho h}$, and N for

$$\frac{P \xi^2 \exp(-\kappa \bar{h})}{2(\bar{h} + 2a)} = \frac{4\pi\epsilon\epsilon_a a^2}{4/3\pi a^3 \rho} \left(\frac{kT}{ze}\right)^2 \xi^2 \exp(-\kappa \bar{h})$$

So formula (8) can be changed into

$$(M - N \xi^2) t_F^2 + v_0 t_F - (H - h_a) = 0 \quad (9)$$

The size of flocs measured by Mastersizer 2000 was very similar with photometric dispersion analyzer (PDA), which is determined by the number concentration of particles (flocs) and their extinction (or scattering) cross sections [24]. The size of flocs here was determined by the number of nano-sized particles, and the effect of fractal dimension of flocs was ignored here. Therefore, lag time here could be linear correlated with t_F .

$$\text{If } \bar{V}_A > \bar{V}_R, \text{ i.e. } M > N \xi^2, \text{ lag time } \sim t_F \\ = \frac{-v_0 + \sqrt{v_0^2 + 4(M - N \xi^2)(H - h_a)}}{2(M - N \xi^2)} \quad (10)$$

$$\text{If } \bar{V}_A < \bar{V}_R, \text{ i.e. } M < N \xi^2, \text{ lag time } \sim t_F \\ = \frac{v_0 - \sqrt{v_0^2 - 4(N \xi^2 - M)(H - h_a)}}{2(N \xi^2 - M)} \quad (11)$$

$$\text{If } \bar{V}_A = \bar{V}_R, \text{ i.e. } M = N \xi^2, \text{ lag time } \sim t_F = (H - h_a)/v_0 \quad (12)$$

$$\text{where } v_0^2 - 4(N \xi^2 - M)(H - h_a) > 0 \quad (13)$$

If absolute $\xi > \left(\frac{v_0^2 + 4M(H - h_a)}{4N(H - h_a)} \right)^{0.5}$, it is impossible for the particles to adhere with each other, and the lag time will be infinity (∞). Here the critical zeta potential is near 13.5 mV. The higher temperature is, the higher v_0 and the broader range of ξ become. This result can well explain the phenomenon found by Xiao et al. [9], who observed that it was more difficult for particles to coagulate at low temperature while it was easier to coagulate at high temperature.

At moderate coagulant dosages, the variation of particle surface charge is certainly more important than the increase of floc volume fraction [10]. So when sweep coagulation dominates the coagulation mechanism, volume of alum precipitates will not change the characteristic of floc surface.

When the size of micro-floc exceeds a certain value, it is easy for the floc to overcome the potential energy V_T , because its kinetic energy which is determined by orthokinetic collision (hydrodynamic shear gradients) can be higher than V_T . At this time, applied shear and characteristic of floc surface determine the coagulation efficiency.

As reported by Xiao et al. [9], there was no significant difference of coagulation rate between low and high temperatures. As shown in Fig. 3, when the alum dosage was in a certain range, coagulation rate showed little change, and here the characteristic of floc surface will be the dominant reason. Therefore, the zeta potential of flocs should not be the key factor when micro-flocs achieve a certain size.

In order to know whether residual dissolved aluminum will change during coagulation process, which may change the surface of micro-flocs and improve their connection, concentration of residual dissolved aluminum after adding 0.1 mM alum (2.7 mg/L) was measured at pH 7.0, as shown in Table 1. It can be seen that the concentration changed little during flocculation, which indicated that the connection of micro-flocs must be mainly dependent on some materials on the surface of micro-flocs.

The study of Phillips et al. [25] demonstrated that most Al-(hydr)oxide phases, such as bayerite, contain edge-linked Al octahedra with surfaces that also contain terminal water (and/or hydroxyls) and paired bridging hydroxyls which interact with the solvent. It is speculated that there are a quantity of η_2 -OH₂ on the surface of newly formed hydroxide precipitates, and it can react with η_2 -

Table 1
Concentration of residual dissolved aluminum at different time at pH 7.0.

Time (min)	1	2	3	5	11	16
Residual Al (mg/L)	0.0283	0.0292	0.0311	0.0330	0.0311	0.0339

Fig. 6. Relationship between zeta potential and lag time.

OH, which change into μ_2 -OH and H_2O as pH increases. In this case, there are a lot of η_2 -OH₂ and η_2 -OH in moderate pH, while higher pH will cause lower quantity of η_2 -OH₂ and higher quantity of η_2 -OH, and lower pH will cause higher quantity of η_2 -OH₂ and lower quantity of η_2 -OH, respectively. As a result, the coagulation rate is relatively higher at moderate dosage and moderate pH, as shown in Fig 3. This mechanism is of great significance to explain many phenomena in coagulation process and to further explore the coagulation mechanisms (see Fig. 6).

4. Conclusion

The main conclusions of this work are:

1. It was demonstrated that only 1 min rapid mixing was enough for adsorption of humic acid onto the precipitates of alum, and 15 min flocculation (slow mixing) only induced the formation and growth of flocs.
2. The primary particles size of alum–humic flocs was near 50 nm. The formation of micro-flocs was determined by the square value of zeta potential and intensity of nano-sized primary particles (around 50 nm) by Brownian motion, which is closely related with temperature. The higher temperature is, the broader range of zeta potential meeting high coagulation efficiency.
3. There must be a relationship between absolute zeta potential and lag time, and optimum coagulant dosage was at a zeta potential somewhat offset from zero.
4. The coagulation rate was determined by the surface activation of flocs rather than zeta potential of floc, after micro-flocs formed.

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