

Article

Enhanced Coagulation for Algae Removal Using Composite Al-Based Coagulants: Collaborative Optimization Mechanism of Aluminum Morphology

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Abstract: The main purpose of this paper was to reveal the effect of aluminum (Al)-based coagulants on enhanced coagulation for the removal of algae and the synergistic optimization mechanism among different Al species. The formation, breakage, and regrowth processes of algal coagulation flocs formed by a series of monomeric Al-based coagulants ($\text{Al}_2(\text{SO}_4)_3$, Al_{13} , and Al_{30}), $\text{Al}_{13}/\text{Al}_{30}$ composite coagulant and poly(diallyldimethylammonium chloride)/ Al_{13} (PDADMAC/ Al_{13}) composite coagulant were studied. Results indicated that Al_{13} mainly employed a charge neutralization mechanism, which was conducive to the destabilization of algae and the regeneration of flocs, while Al_{30} mainly employed a sweep flocculation mechanism, which was conducive to the formation of algae and the strength of flocs. Meanwhile, the charge neutralization was the main mechanism during the algae coagulation process because it could effectively remove the soluble microbial products (SMP) component in the extracellular organic matter (EOM). Therefore, Al_{13} could achieve a higher coagulation performance than other monomeric Al-based coagulants. The $\text{Al}_{13}/\text{Al}_{30}$ composite coagulant could make up for the deficiency of the sweep flocculation mechanism in Al_{13} and charge neutralization mechanism in Al_{30} , and achieve the best synergistic optimization performance at $\text{Al}_{13}:\text{Al}_{30}=7:3$. Additionally, PDADMAC, as a polymer, could further enhance the charge neutralization ability of Al_{13} at low dosages and the sweep flocculation ability of Al_{13} at high dosages, respectively. However, an excessive dosage would lead to charge reversal and thus reduce the coagulation effect. Therefore, controlling the dosage was key when using Al-composite coagulants. The findings of our research could offer a certain theoretical foundation for the development of inorganic polymer flocculants.

Keywords: coagulation; algae-laden water; composite al-coagulant; EOM; collaborative optimization



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1. Introduction

Algae become ubiquitous in lakes and reservoirs and affect the drinking water treatment performances [1–3], causing issues such as a rising coagulant demand, membrane fouling, and higher formation potentials of disinfection byproducts (DBPs) [4–6]. These problems provoked the reform of the traditional water treatment process, and investigating how to improve the removal efficiency for algae was important to ensure the water quality and quantity. A variety of water treatment chemicals such as pre-chlorination

and pre-oxidation may be used [7,8], but the resultant cell breakage may cause the release of extra- and intra-cellular organic matter (EOM and IOM), which are even greater health hazards [9,10]. In contrast, coagulation, which is regarded as an economical and efficient treatment method, has been widely used in drinking water treatment [11,12]. Furthermore, as the core of the coagulation process, chemical coagulants directly affect the coagulation performances.

Varieties of chemicals have been trialed to coagulate algal particles, including metal coagulants and inorganic polymers [13,14]. Polyaluminum chloride (PAC) is widely used in water treatment plants throughout the world [15,16], and the coagulation performances using PAC have been investigated well. In the coagulation process, some mechanisms (charge neutralization and sweep flocculation) have been established to explain the coagulation performances [17,18]. However, the presence of EOM made the coagulation mechanism complex [19]. Studies have shown that EOM can inhibit the coagulation and algae removal processes by forming complexes with coagulants and adhering to the surface of flocs, but there was also a claim that EOM can enhance the coagulation effect at low doses. The key to this phenomenon was the different concentrations of EOM [20]. Up to now, what was clear was that the different organic compositions and concentrations would impact the coagulant dosage by affecting the surface charges of the algal particles, complexing the metal coagulant, or sterically interfering with Al-based coagulants [21]. Therefore, the removal efficiency for algal particles may not be high enough in some conditions. As described before, how to improve the removal efficiency without causing other problems was important to the health security of drinking water.

Generally, reducing the content of EOM in advance or using new composite coagulants was an effective way to solve these problems. For example, Liu et al. used a moderate oxidant, peroxyacetic acid (PAA), with EOM secreted by algal cells and achieved efficient removal of algal cells under the conditions of 10 mg/L PAA and 12 mg/L polyaluminum chloride [11]. Qi et al. [22] utilized Zn-doped Fe_3O_4 particles in the photocatalytic treatment of algae-laden water and verified that this process was capable of removing algae without causing their destruction, with the algae removal rate reaching up to 96%. However, the increase in process units will inevitably lead to cost increases. Composite coagulants have attracted more and more attention in the water treatment process due to the larger removal efficiency for turbidity and the formation of larger flocs [23]. Wang et al. [24] investigated the removal efficacy of the hydrophobic modified chitosan flocculant (HC) + alum on various drug compounds in different water bodies. The findings indicated that HC was a promising flocculant for eliminating trace drug compounds in surface water. Zhao et al. [25] indicated that the use of anionic and non-ionic polymers could improve the removal of algae or dissolve extracellular organic matter (DEOM). During the coagulation process of Al-based coagulants, it was already known that the coagulation mechanism of a single coagulant was greatly affected by the dosage [26]. For example, with PAC, when the dosage was small (the negative charges were not neutralized), charge neutralization might be the main mechanism. At a high dosage, it would transform from charge neutralization to sweep flocculation. Unfortunately, the concentration of residual aluminum may increase with the increased coagulant dosage. So how to ensure the coagulation performances under a small coagulant dosage was important in the water treatment process [27]. If a composite coagulant that possessed outstanding charge neutralization and sweep flocculation capabilities at a low dosage could have been synthesized, this problem could have been solved. But the prerequisite was to have a sufficient clear understanding of the various mechanisms it employed during the coagulation process, including the formation, breakage, and regeneration of flocs, as well as their synergy mechanism. Meanwhile, the latest literature [28] reported that PDADMAC, a cationic polymer with high charge and high molecular weight, seemed to be an ideal material for solving this problem, and some scholars had prepared it as a composite coagulant to remove algae. However, its application in aluminum-based coagulants and the research on the synergy and optimization mechanism have been relatively small in number. Combining different aluminum forms or

combining them with organic polymers could have combined their respective advantages to deal with various pollutants and different water quality conditions. By studying them, the synergy and optimization effect between aluminum forms and the reaction mechanism with pollutants could have been deeply understood, providing a theoretical basis for the development of new coagulants.

Therefore, this paper takes the individual coagulation processes of highly polymerized Al_{13} and Al_{30} as a reference and uses the coagulation processes of different composite polymeric coagulants (including composite coagulants with different proportions of aluminum species and composite coagulants with the addition of organic polymer coagulant aid PDADMAC) to study the specific roles of different aluminum species in the processes of floc formation, fragmentation, and regeneration, as well as their synergetic optimization principles.

2. Materials and Methods

2.1. Preparation of Water Samples

Microcystis aeruginosa (*M. aeruginosa*), one of the dominant cyanobacteria, which occurs frequently in most eutrophic water bodies in China, was supplied by Wuhan Institute of Hydrobiology of the Chinese Academy of Sciences and used in the present experiments. *M. aeruginosa* was cultured in a 5000 mL narrow-mouth bottle containing 4500 mL BG11 medium (pH = 7.0) under the illumination of a lamp (2000 lx) with a cycle of 12 h light and 12 h dark at 25 °C under continuous aeration [4]. The water samples were prepared by diluting the culture solution of *M. aeruginosa* with deionized water, and 5.0 mmol/L of NaNO_3 and 4.0 mmol/L of NaHCO_3 were added to provide ionic strength and alkalinity. The algae solution was harvested for experiments in the early stationary phase. Generally, the density of algae cells showed a good linear relationship with the suspension at 680 UV absorbance value [29]. Thus, this study chose UV_{680} as a measure of algae cell density and the initial cell density (calculated as UV_{680}) used in the experiments was controlled at 0.118. The solution pH value was adjusted to 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, and 9.0 by 0.1 M of HCl or NaOH solution to investigate the effects of solution pH value on the coagulation performances.

2.2. Preparation of the Used Coagulants

$\text{Al}_2(\text{SO}_4)_3$ (AS): 17.1 g of AS solid is fully dissolved in 500 mL of water, and the final concentration of AS coagulant was 0.1 mol/L.

$\text{PAC}_{2.2}$: $\text{PAC}_{2.2}$ was prepared by the slow alkali drip method. Under the condition of rapid magnetic stirring, 110 mL of 0.1 mol/L of NaOH solution was slowly dropped into 100 mL of 0.5 mol/L of AlCl_3 solution using a peristaltic pump. After the dripping was completed, the $\text{PAC}_{2.2}$ solution could be obtained. It should be noted that the 2.2 in the subscript represents the basicity degree of PAC, that is, $[\text{OH}^-]/[\text{Al}^{3+}] = 2.2$. The concentrations and volumes of NaOH and AlCl_3 can be adjusted, but no precipitation should be generated throughout the preparation process.

Al_{13} : Al_{13} polycation ($[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$), which is composed of a $\text{Al}(\text{O})_4$ tetrahedron surrounded by 12 octahedrally coordinated Al sharing edges (i.e., ϵ -Keggin structure) [17,27], was carried out by sulfate precipitation from $\text{PAC}_{2.2}$ [30]. Specifically, take a certain volume of the prepared $\text{PAC}_{2.2}$ solution, and then add the corresponding Na_2SO_4 solid according to the ratio of $[\text{SO}_4^{2-}]/[\text{Al}^{3+}] = 0.33:1$ (molar ratio). After the reaction is completed, filter the mixed solution to obtain precipitate $\text{Al}_b\text{-SO}_4$. Then, use a $\text{Ba}(\text{NO}_3)_2$ or BaCl_2 solution to replace SO_4^{2-} and filter to obtain a clear solution of the Al_{13} coagulant.

Al_{30} : Al_{30} polycation is another polycation with Keggin structure in hydrolysis poly-aluminum solutions, and it is composed of two Al_{13} molecules connected by four Al monomers [31]. It was prepared by the high temperature-precipitation method [32]. Specifically, the prepared $\text{PAC}_{2.2}$ solution was heated in a water bath at 95 °C for 48 h, and then the steps for preparing Al_{13} to obtain Al_{30} were repeated.

The characters of the prepared coagulants were measured by the Al-Ferron complexation timed spectrophotometry method [33], and relevant results are summarized in Table S1.

PDADMAC/Al₁₃ composite coagulant: the PDADMAC with molecular weights ranging from 400 kDa to 500 kDa was used to prepare the composite coagulants. Different amounts of PDADMAC molecules were added to the Al₁₃ solution according to the mass ratio of PDADMAC/Al = 2.0%, 5.0%, and 10.0% under magnetic stirring until it was homogeneous and clear to prepare the composite PDADMAC-Al₁₃ coagulant. The composite coagulants were allowed to age for 24 h at room temperature, and the dosage was calculated as Al in these experiments.

Al₁₃/Al₃₀ composite coagulant: the research team investigated whether a synergistic effect occurs between different Al-species coagulants, which could improve coagulation performances at a relatively low dosage compared to using Al₁₃ and Al₃₀ alone. Al₃₀ (the main mechanism was bridging effects or sweep flocculation), which had a larger amount of colloidal or gel Al species (Al_c), was chosen to be compared, and some new coagulants were prepared by adding some amount of Al₃₀ solution to Al₁₃ solution.

2.3. Jar Test Experiments and the Analysis of Characteristics of Flocs

A jar test apparatus equipped with six beakers was used to conduct coagulation experiments, and coagulants were added and mixed into each water sample for 1.5 min at 200 rpm to uniformly disperse the coagulant. The rapid mixing was followed by slow mixing for 10 min at 40 rpm to allow floc growth to occur. After it had set for 30 min, the supernatant obtained from a point of 2.0 cm below the liquor surface was analyzed. The coagulation process was measured by Mastersizer 2000 (Malvern Co., Malvern, UK). In order to investigate the breakage and regrowth processes, the flocs after the slow mixing period were exposed to 200 rpm for breakage for 5.0 min. After the breakage period, the stirring rate was decreased to 40 rpm for 10.0 min for the regrowth of flocs. The size measurements were taken every 30 s for the duration of the jar test and the 50-percentile floc size ($d_{0.5}$) was used to denote the floc size in this study. The relative breakage and regrowth of flocs have been previously evaluated by employment of floc strength factors (S_f) and recovery factors (R_f), which may be calculated as follows [4,17]:

$$S_f = \frac{d_2}{d_1} \quad (1)$$

$$R_f = \frac{d_3 - d_2}{d_1 - d_2} \quad (2)$$

where, d_1 , d_2 , and d_3 are the average sizes of flocs in the steady phase before breakage, after the breakage, and after regrowth to another steady phase, respectively. Former studies had shown that S_f indicates the ability of flocs to resist rupture by a certain velocity gradient [34]. Consequently, a larger S_f implies that flocs that are better able to withstand shear and should be considered stronger than those with lower S_f . Likewise, the flocs that larger R_f exhibit better regrowth abilities after breakage than those with lower R_f .

2.4. Scanning Electron Microscope (SEM) Analysis for Flocs

The flocs formed in the coagulation process using different coagulants under optimum dosage were observed with a high-resolution SEM (S-4700 HITACHI, Tokyo, Japan). 10 mL of the algae flocs was concentrated by a centrifuge at 8000 rpm for 10 min. After discarding the supernatant, the sample was fixed and dehydrated. Then the sample was gold-coated and examined under the SEM.

2.5. EOM Analysis

The dissolved organic carbon (DOC, mg/L) of EOM were indicated by a Total Organic Carbon (TOC) analyzer (Shimadzu, Kyoto, Japan), and 3D Fluorescence Excitation-

Emission Matrix (3D-EEM) of EOM was measured on a Varian Eclipse fluorescence spectrophotometer (Hitachi F7000, Tokyo, Japan) in scan mode. Specifically, the excitation wavelength (EX) ranged from 200 to 400 nm, the emission wavelength (EM) ranged from 280 to 550 nm, and the slit widths were both 5 nm, the scanning speed of the spectrum was 12,000 nm/min. Before DOC and 3D-EEM measurements, the samples were filtered using a 0.45 μm mixed cellulose filter.

According to the study of Chen et al. [35], the 3D fluorescence region formed by the EX and EM could be divided into five parts, representing five different types of organic substances, namely: aromatic protein substances I, aromatic protein substances II, fulvic acid substances III, soluble microbial metabolites IV, and humic acid substances V, shown in Figure S3. Meanwhile, through the fluorescence regional integration (FRI) method [35], the integral volume (Φ_i) of a specific fluorescence region, that was, the cumulative fluorescence intensity of organic substances with similar properties, was summed. Finally, Φ_i was standardized by the unit concentration of DOC to obtain the integral standard volume of a specific fluorescence region ($\Phi_{i,n}$), thereby reflecting the relative content of the specific structured organic substances in this region and achieving the quantification function of 3D fluorescence spectroscopy.

3. Results and Discussion

3.1. Characteristics of Raw Water

The 3D-EEM spectrum, microscopic picture and other basic properties of the experimental water sample are shown in Figures S1 and S2 and Table 1, respectively. The turbidity, zeta potential, and DOC of raw water samples were 6.77 NTU, -27.1 mV and 0.571 mg/L, respectively. Furthermore, according to the FRI theory, the relative proportions of protein-like, Humic acid (HA)-like and soluble microbial products (SMP) are 17.08%, 36.92% and 46.00%, respectively.

Table 1. Basic parameters of the experimental water samples.

Indicator	Turbidity (NTU)	UV ₆₈₀	DOC (mg/L)	Zeta Potential (mV)	Protein (%)	HA (%)	SMP (%)
value	6.77	0.118	0.571	-27.1	17.08	36.92	46.00

3.2. Coagulation Performance

3.2.1. Effect of Coagulant Dosage

Coagulant dosage had significant effects on the coagulation performances, and the dosage was adjusted from 0.005 mmol/L to 0.12 mmol/L (calculated as Al). The solution pH was adjusted to 8.5. The residual UV value at 680 nm (UV₆₈₀) was measured for the removal efficiency of algal cells, and the relevant results are summarized in Figure 1.

The results in Figure 1A,B show that the removal efficiency for turbidity and algae cells increased with the increase of the coagulant dosage, and then approached a plateau. Different Al species had different effects on the coagulation performances, and the coagulant dosage was largest when AS was used as a coagulant. The optimum dosages for these coagulants are summarized in Table S2. All these results indicate that when the coagulant dosage was larger than 0.08 mmol/L, the removal efficiency for algae and turbidity could reach greater than 90% no matter what coagulant was used. Moreover, from the perspective of cost, the preparation cost of highly polymerized Al₁₃ and Al₃₀ was approximately 1.5 times that of AS (according to the conversion rate), but the dosage consumed when achieving the best coagulation effect was less than half, especially for Al₁₃. Therefore, it could be concluded that highly polymerized Al₁₃ and Al₃₀ were also more cost-effective. Zeta potentials (ZPs) under different coagulant dosages were measured and the results are shown in Figure 1C. It was observed that zeta potentials increased with increasing coagulant dosages. Compared with AS, additional Al₁₃ and Al₃₀ at the same dose contributed to obviously larger zeta potentials, which might be attributed to the larger positive charges of

Al_{13} and Al_{30} relative to the AS coagulant. When the dosage was small (<0.04 mmol/L), Al_{13} and Al_{30} could utilize electrostatic patch effects effectively, producing the largest removal efficiency for turbidity and algae cells. Although the removal efficiency for turbidity or algae was small when the AS coagulant dosage was small, as the concentration of Al increased, the removal efficiency for algae improved significantly as a result of the sweeping and enmeshment effects [17]. Furthermore, when the coagulant dosage was less than 0.02 mmol/L, the removal rate for turbidity or algae when using Al_{13} as a coagulant was larger than with Al_{30} ; this phenomenon could be well-explained by the zeta potential. For Al_{13} , the ZPs were -15.8 , -11.5 , and -9.21 mV when the coagulant dosage was 0.005, 0.01, and 0.015 mmol/L, while those for Al_{30} were -22.9 , -22.8 , and -20.8 mV, respectively. The absence of charge neutralization in Al_{30} relative to Al_{13} made it need a higher dosage to destabilize the algal cells. Thus, the electrostatic patch effect or charge neutralization was important in the algae removal process.

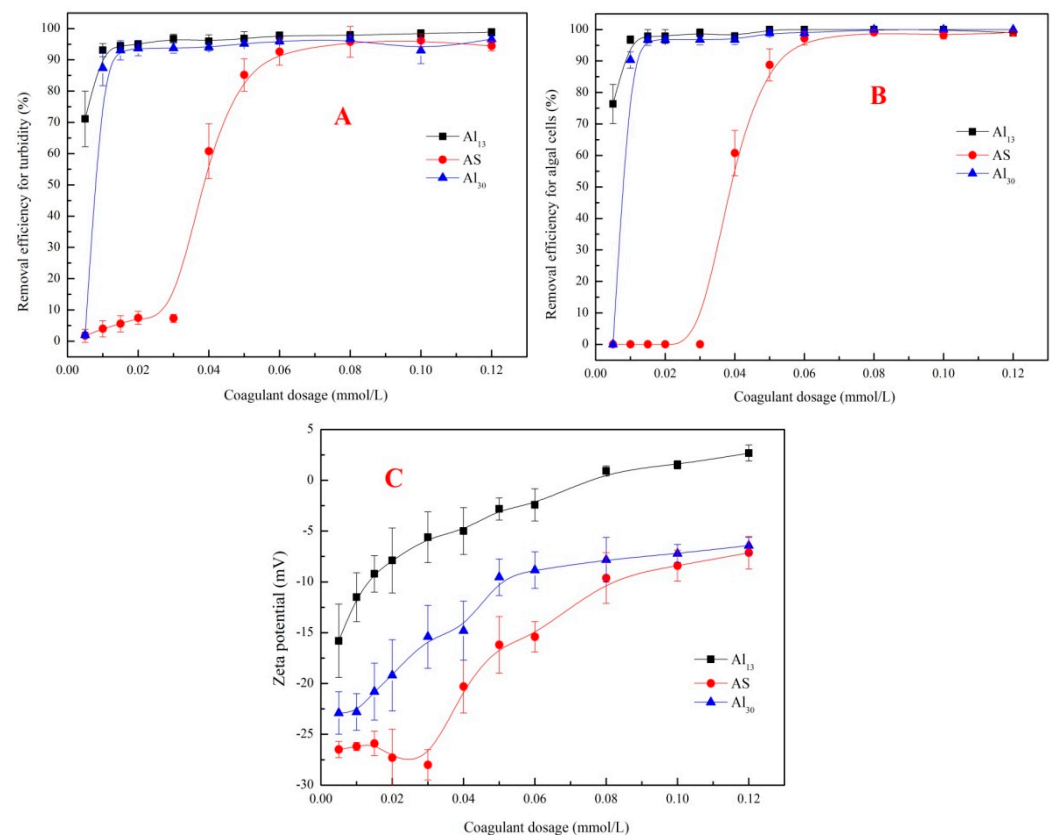


Figure 1. Effects of coagulant dosage on the coagulation performances. (A) Removal efficiency for turbidity; (B) Removal efficiency for algal cells; (C) The variation of zeta potential with the coagulant dosage.

3.2.2. Effect of Solution pH

The coagulant dosage for these three coagulants was adjusted to the optimum dosage according to the results of Table S2, and the effects of solution's pH on the coagulation performance are shown in Figure 2.

Figure 2A,B indicate that the solution's pH had significant effects on the removal efficiency for turbidity and algae cells, and the variations in zeta potentials against the solution pH for three Al-species coagulants are shown in Figure 2C. It was found that zeta potentials decreased with solution pH no matter what coagulants were used. This might be explained by the Al species in the solution, which relies significantly on the solution pH and Al concentration according to the pH aluminum-species diagram [32]. When the Al-based coagulants are added to the water samples, positively charged precipitates can

be formed [27]. Therefore, the negatively charged algae cells would be easily adsorbed onto the positively charged precipitates, which facilitated the removal of algae through subsequent sedimentation or flotation. In alkaline conditions, the aluminum hydroxide precipitates had a larger amount of negative charge [17], and consequently reduced the adsorption capacity of negatively charged algal cells. The Al species distribution in the Al_{13} and Al_{30} solution did not change remarkably at different solution pHs, so the removal efficiency for algal cells or turbidity could remain larger in alkaline conditions [34]. When the solution pH was adjusted to 6.0, the removal efficiency using Al_{13} and Al_{30} was smaller than when using AS as a coagulant. The Al_{13} and Al_{30} solutions had larger amounts of Al_b or Al_c (Table S1), resulting in larger positive charges, so when the solution pH was adjusted to 6.0, charge reversal could happen (ZPs were 3.2 mV for Al_{13} and 1.7 mV for Al_{30}).

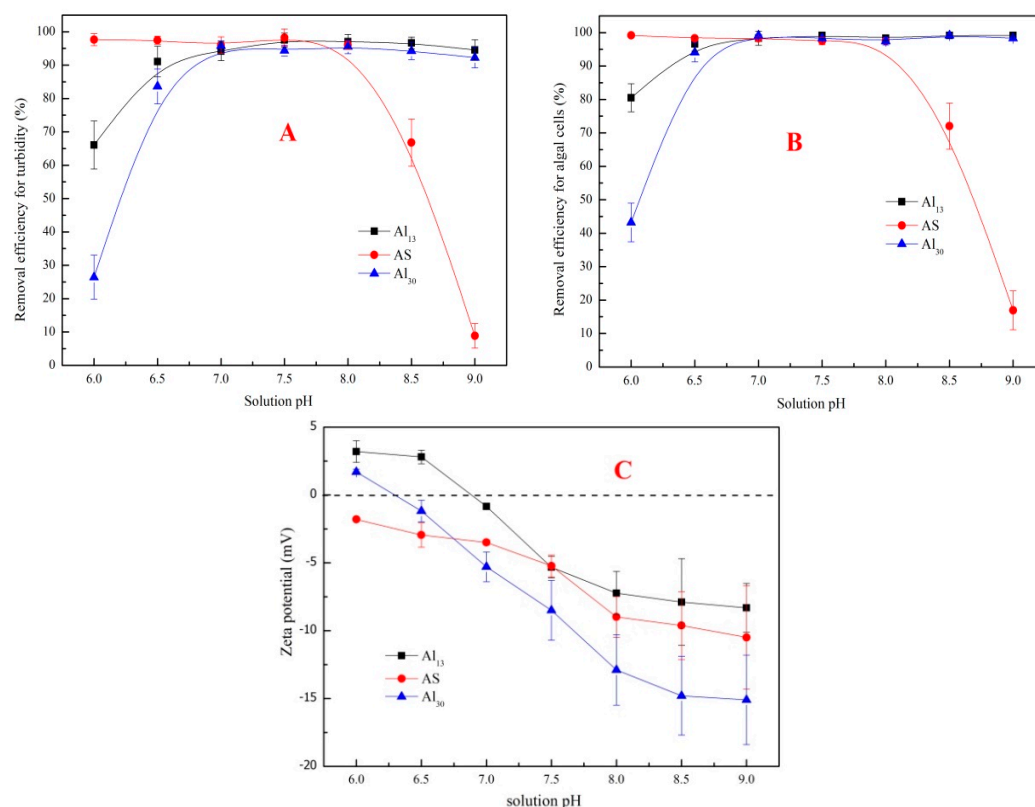


Figure 2. Effects of solution pH on the coagulation performances. (A) Removal efficiency for turbidity; (B) Removal efficiency for algal cells; (C) The variation of zeta potential with the solution pH.

The 3D-EEM spectra of EOM after the coagulation process under different pH conditions are summarized in Figures S4–S6.

Figure S4 shows that the removal efficiency for SMP was significantly dependent on the solution pH value when using AS as the coagulant. However, Figures S5 and S6 show that the removal efficiency of SMP was almost independent of the solution pH. The removal of EOM in the coagulation process was mainly aimed at the SMP and was confirmed in our previous study [4]; it was confirmed again in this study. In order to better understand the removal efficiency for SMP, the removal rate was calculated according to the fluorescence value before and after the coagulation process, and the results are summarized in Table S3. It was found that the SMP removal rate decreased with the increase in pH value when using AS as a coagulant (from 43.43% in pH 6 to 6.29% in pH 9). Al_b concentration decreases with an increase in the pH value, according to the study of Wang et al. [32], which also results in the zeta potentials (Figure 2C) decreasing with the increase in pH when using AS as the coagulant. Al_b was important in the removal of SMP, thus, these results indicated that the main mechanism for the removal of SMP may be charge neutralization. Figure S5

and Table S3 indicate that the Al_{13} had stable removal efficiency for organic matter in the algal suspension, and the removal efficiency for SMP was larger than AS, especially when the solution pH was 9.0. When Al_{30} is used as a coagulant (Figure S6), the bridging effects and sweep flocculation may be the main mechanism. The Al species of Al_{30} did not change remarkably at different pHs, and it had a slightly lower charge neutralization capacity than that of the Al_{13} species under medium and high pH conditions [33]. Thus, the removal efficiency for SMP was smaller than when using Al_{13} as a coagulant. Al_a , as the main species of AS, was the most unstable species [36]. Most Al_a would hydrolyze immediately after dosing and then algal cells and EOM would be removed through sweep flocculation, entrapment, and the adsorption effect.

3.3. Characterization of Flocs

3.3.1. Properties of Flocs Formed by Al_{13} , AS, Al_{30} , and PAC

The properties of flocs were investigated using Al_{13} , AS, Al_{30} , and PAC at the dosages of 0.02, 0.04, 0.08, and 0.12 mmol/L, and S_f and R_f were investigated during the fragmentation and regeneration processes of flocs. The experimental results are shown in Figure 3 and Table 2. The results in Figure 3A show that when the coagulant dosage was 0.02 mmol/L and 0.04 mmol/L, there were no flocs formed. As described in Section 3.2, Al_a had a smaller charge neutralization ability, so when the coagulant dosage was small, there would be no flocs formed. However, there were flocs formed in the regrowth period when the coagulant dosage was 0.04 mmol/L. In the coagulation process, flocs were formed through the collision of particles and coagulants [36]. When the coagulant dosage was 0.04 mmol/L, the coagulant would neutralize the negative charges and the stability of the algal particles was decreased. But the collision was not efficient, so more time would be needed to cause the coagulation performances. With increasing coagulant dosage (0.08 and 0.12 mmol/L), the flocs would form in the formation period through sweep flocculation, entrapment, and adsorption effects. Although the floc size after the growth period was almost the same, the floc growth rate was larger when using a larger coagulant dosage (0.12 mmol/L). When PAC was used as the coagulant (Figure 3B), the flocs would be formed when the coagulant dosage was 0.04 mmol/L due to a larger amount of Al_b species [17]. The maximum floc size (0.12 mmol/L) was about 1000 μm , which was smaller than when using AS as the coagulant. These results may be caused by the bridging effects that existed in the AS solution, especially when the solution pH was near 9.0. When Al_{13} was used as the coagulant (Figure 3C), the flocs would be formed when the coagulant dosage was 0.02 mmol/L, and the floc size in the regrowth period was larger than that in the slow mixing period. When Al_{13} was used as the coagulant, the maximum floc size was near 800 μm (0.04 mmol/L) which was smaller than when using AS or PAC as the coagulant. When the coagulant dosage was increased to 0.08 and 0.12 mmol/L, the floc size decreased due to charge reversal (Zeta potential is 0.92 mV and 2.68 mV in Figure 1C). These results show that the mechanism when using Al_{13} was charge neutralization [27], and this mechanism could effectively destabilize the particles when the coagulant dosage was small. But the absence of sweep flocculation or bridging effects decreased the floc size, and the coagulation performances when Al_{30} was used as the coagulant are summarized in Figure 3D. The results indicate that the flocs would not be formed when the coagulant dosage was 0.02 mmol/L, and these results are different from the flocs formed when using Al_{13} as the coagulant. It is interesting that the floc size after the regrowth period was larger when the coagulant dosage was 0.04 mmol/L using Al_{30} as the coagulant. When the coagulant dosage was smaller, the electric patch effects may be the most important mechanism in the formation of flocs. The electric patch effects could produce larger flocs under a small coagulant dosage, and the positive positions could attract other negative positions to produce larger flocs in the regrowth period. When the coagulant dosage was larger than 0.04 mmol/L, sweep flocculation may be the main mechanism, so the recovery factor was decreased. The results in Table 2 show that the recovery factor decreased with increasing coagulant dosage, and these results may be caused by two mechanisms. One

was the effects of coagulants, and the other was the effects of EOM in the suspension. When the coagulant dosage was small, the charge neutralization or electric patch effects were the main mechanism, so the recovery factor was larger. The EOM molecules also had significant effects on the coagulation performances, and the concentration of EOM decreased with increasing coagulant dosage [37]. Thus, the recovery factor decreased with increasing coagulant dosage. All these results indicate that in the formation of flocs, especially when the coagulant dosage was smaller than 0.04 mmol/L, the charge neutralization ability was important to decrease the repulsive force between algal particles that had negative charges.

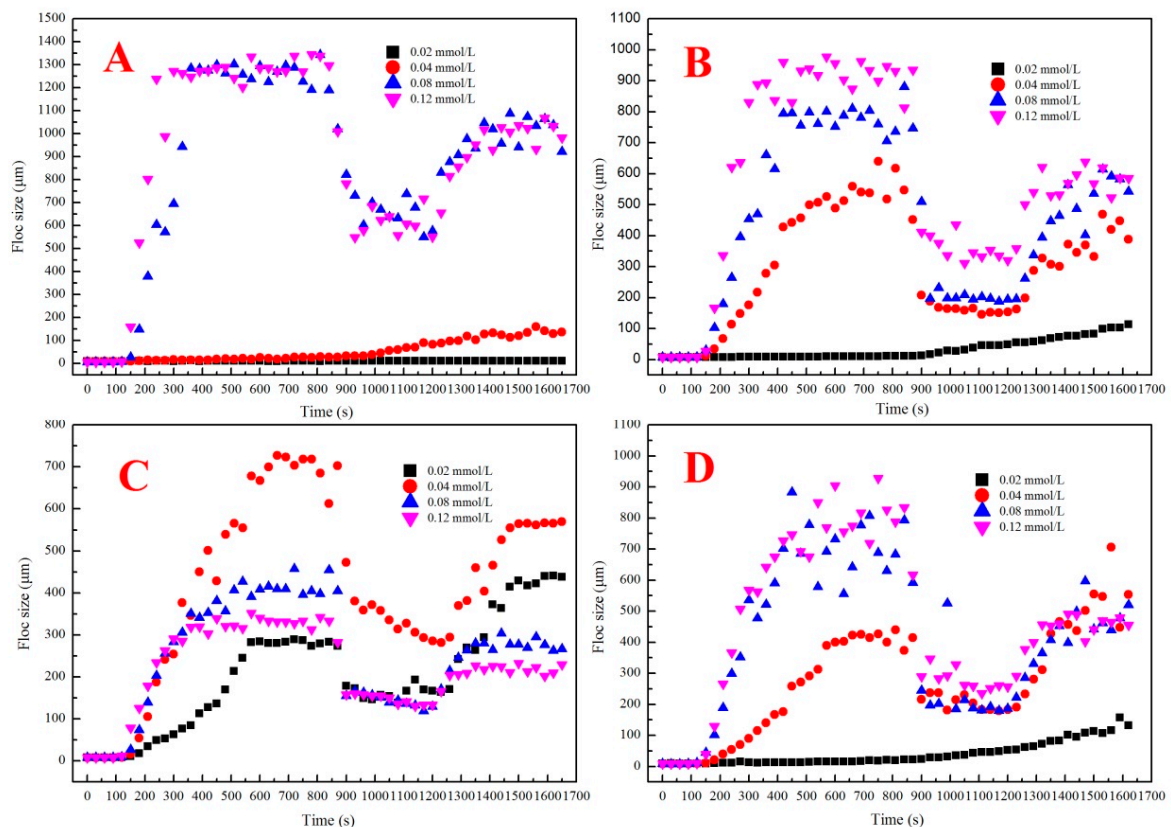


Figure 3. Floc size in the coagulation process under different coagulants ((A): AS; (B): PAC; (C): Al_{13} (D): Al_{30}).

Table 2. Characteristics of flocs formed in this study using AS, PAC, Al_{13} , and Al_{30} .

Coagulants	Coagulant Dosage (mmol/L)	Before Breakage (μm)	After Breakage (μm)	After Regrowth (μm)	S_f (%)	R_f (%)
AS	0.08	1194	578	1014	52.61	60.58
	0.12	1317	540	1003	48.59	53.62
PAC	0.04	580	152	447	26.21	68.92
	0.08	770	192	572	24.93	65.74
	0.12	897	336	564	37.46	40.64
Al_{13}	0.02	282	131	435	58.86	201.324
	0.04	687	310	566	45.12	67.90
	0.08	422	132	275	31.27	49.31
	0.12	329	134	216	40.73	42.05
Al_{30}	0.04	411	187	563	45.49	171.69
	0.08	667	184	460	28.58	51.49
	0.12	819	251	463	30.65	37.32

3.3.2. Properties of Flocs Formed by $\text{Al}_{13}/\text{Al}_{30}$ Composite Coagulants

The results in Figure 3 show that different Al species had different coagulation mechanisms in the coagulation process, and the absence of one mechanism would cause the flocs to not be formed efficiently. Al_{13} could effectively destabilize the particles, and Al_{30} had significant effects on the formation of flocs. Thus, some amount of Al_{30} solution was added to the Al_{13} solution to prepare the new coagulants, and these new composite coagulants with different aluminum species were used to investigate the effects of Al species on the coagulation performances. The results are summarized in Figure 4.

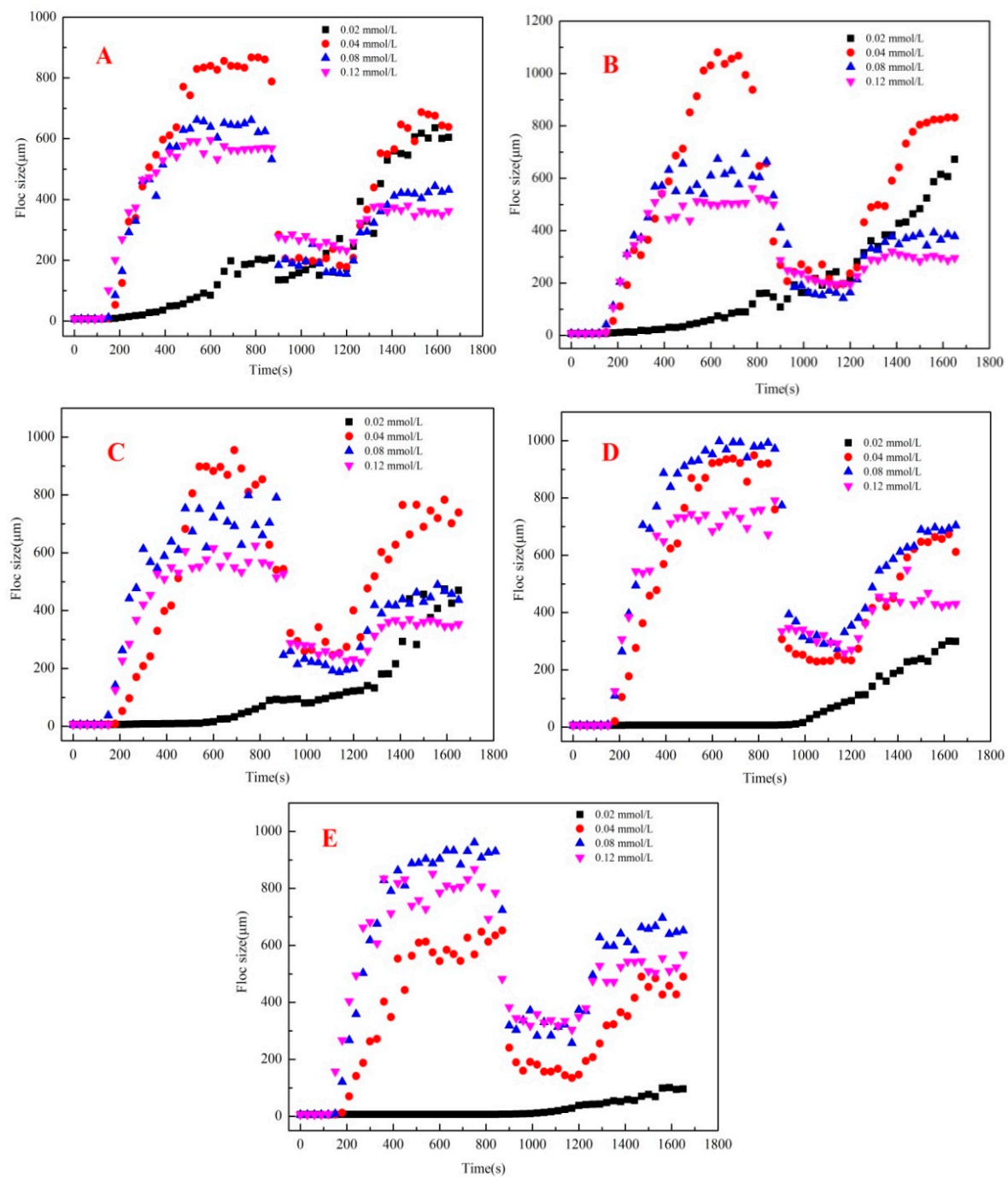


Figure 4. Floc size in the coagulation process ((A): $\text{Al}_{13}:\text{Al}_{30} = 9:1$; (B): $\text{Al}_{13}:\text{Al}_{30} = 7:3$; (C): $\text{Al}_{13}:\text{Al}_{30} = 5:5$; (D): $\text{Al}_{13}:\text{Al}_{30} = 3:7$; (E): $\text{Al}_{13}:\text{Al}_{30} = 1:9$).

Figure 4A shows that once Al_{30} was added to the Al_{13} solution, the floc growth rate was decreased due to the decrease in charge neutralization ability (Zeta potential decreased in Table S4) when the coagulant dosage was small (0.02 mmol/L). When Al_{13} was used as the coagulant, charge reversal may have happened when the coagulant dosage was larger than 0.08 mmol/L, but these results did not exist when Al_{30} was added to the solution. With increasing concentrations of Al_{30} (Figure 4B, $Al_{13}:Al_{30} = 7:3$), the maximum floc size would increase to larger than 1000 μm (0.04 mmol/L), and the floc size after a slow mixing period under the other two coagulant dosages (0.08 mmol/L and 0.12 mmol/L) was also larger than when using Al_{13} as the coagulant. These results may be caused by two mechanisms: the bridging effects increase the floc size in the floc formation period when the coagulant dosage is small; and the decrease in the repulsive force would also increase the floc size when the coagulant dosage is large. With increasing concentrations of Al_{30} , the regrowth ability under 0.02 mmol/L decreased, and the floc size after regrowth decreased to about 150 μm (Figure 4E, $Al_{13}:Al_{30} = 1:9$). As described before, when the coagulant dosage was 0.02 mmol/L, the flocs would not be significantly formed because the number of particles and Al-based coagulants were not enough in these conditions. The charge neutralization would be the main mechanism, so with increasing concentrations of Al_{30} , the charge neutralization ability decreased (Table S4). When the optimum concentration of Al_{30} was added to the solution of Al_{13} , synergistic effects could occur, and the flocs would be significantly formed.

The S_f and R_f of flocs in Table 3 indicate that with an increase in coagulant dosage, the S_f of flocs gradually increased, while the R_f gradually decreased. As analyzed in Table 4, with the increase in coagulant dosage, the mechanism of the coagulant changes from electrostatic cluster/electrostatic neutralization to sweep flocculation. The decrease in electrostatic neutralization leads to a decrease in the recovery factor of flocs, while the decrease in sweep flocculation leads to a decrease in the strength factor of flocs. According to the analysis above, the R_f of flocs was mainly controlled by the effect of electric neutralization, while the S_f of flocs was the result of the combined action of net trapping and organic matter.

Table 3. Characteristics of flocs formed in this study using different composite coagulants (Al_{13} solution composited with Al_{30}).

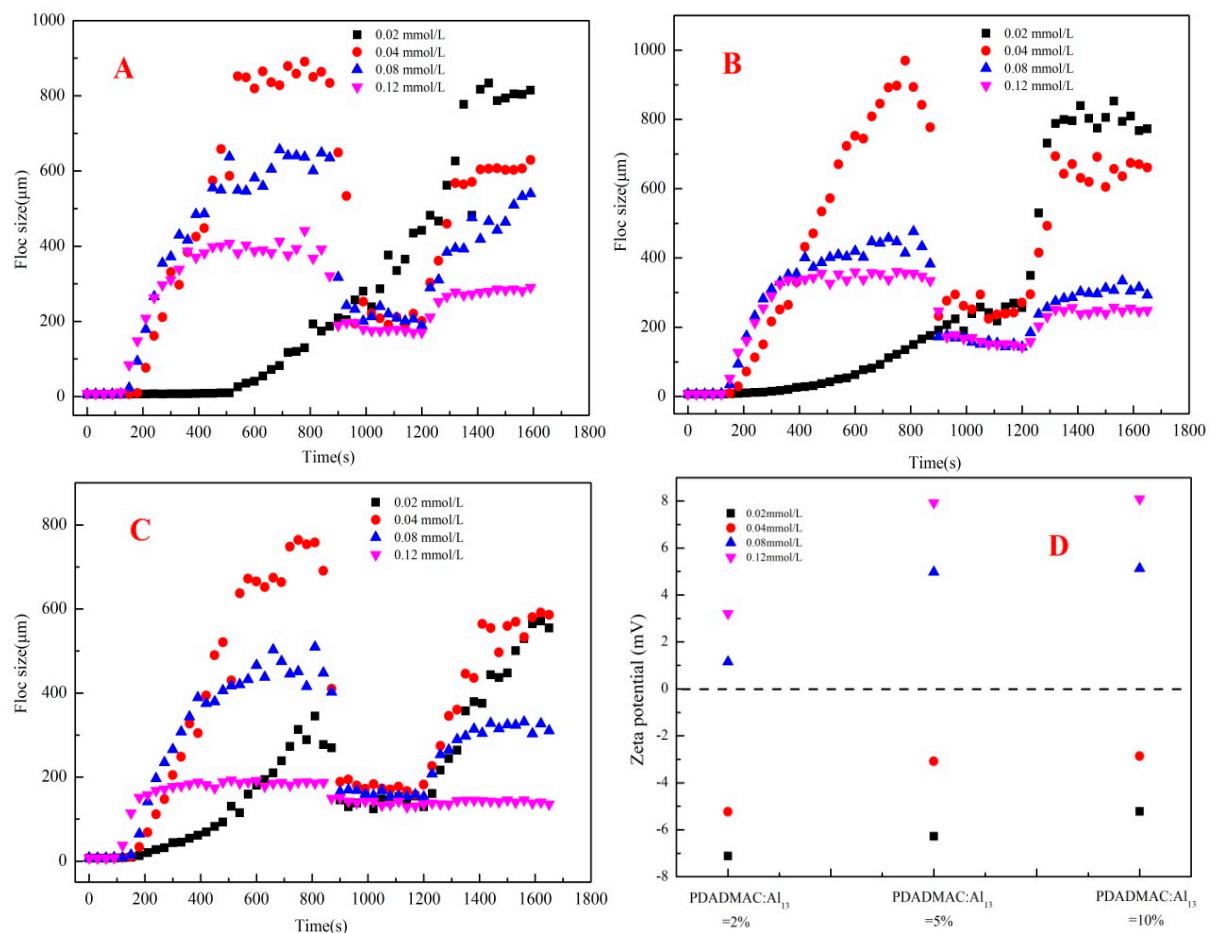
Coagulants	Coagulant Dosage (mmol/L)	Before Breakage (μm)	After Breakage (μm)	After Regrowth (μm)	S_f (%)	R_f (%)
$Al_{13}:Al_{30} = 9:1$	0.04	853	177	659	20.75	71.31
	0.08	640	154	431	24.06	56.99
	0.12	569	232	356	40.74	36.79
$Al_{13}:Al_{30} = 7:3$	0.04	1038	196	829	18.88	75.17
	0.08	628	142	376	22.61	51.54
	0.12	500	195	293	32.13	30.28
$Al_{13}:Al_{30} = 5:5$	0.04	803	400	737	29.11	83.62
	0.08	697	199	465	28.55	53.41
	0.12	570	231	354	40.52	36.28
$Al_{13}:Al_{30} = 3:7$	0.04	911	232	651	25.46	61.70
	0.08	973	354	694	36.33	54.92
	0.12	720	270	427	37.5	34.88
$Al_{13}:Al_{30} = 1:9$	0.04	632	134	449	21.20	63.25
	0.08	921	257	662	27.90	60.99
	0.12	761	304	523	39.94	47.92

Table 4. Characteristics of flocs formed in this study using different composite coagulants (Al_{13} solution composited with PDADMAC).

Coagulants	Coagulant Dosage (mmol/L)	Before Breakage (μm)	After Breakage (μm)	After Regrowth (μm)	S_f (%)	R_f (%)
PDADMAC: Al_{13} = 2.0%	0.04	865	190	604	21.96	61.33
	0.08	631	201	448	31.85	57.44
	0.12	398	174	290	43.72	51.78
PDADMAC: Al_{13} = 5.0%	0.04	913	242	668	26.51	63.48
	0.08	448	143	304	31.92	52.78
	0.12	352	143	250	40.63	51.19
PDADMAC: Al_{13} = 10.0%	0.04	755	158	585	20.93	71.52
	0.08	455	158	313	34.72	52.18
	0.12	185	130	138	70.27	14.54

3.3.3. Properties of Flocs Formed by PDADMAC/ Al_{13} Composite Coagulants

The results in Figure 4 show that the Al_{30} species had significant effects on the reformation of flocs, and the flocculants that had larger bridging effects would also increase the floc size. Because the flocculants had larger positive charges, the floc size increased when the coagulant dosage was small. Three new coagulants (with different concentrations of PDADMAC) are used in this study, and the coagulation performances are summarized in Figure 5 and Table 4.

**Figure 5.** Floc size in the coagulation process ((A): PDADMAC: Al_{13} = 2.0%; (B): PDADMAC: Al_{13} = 5.0%; (C): PDADMAC: Al_{13} = 10.0%; (D): Zeta potentials).

As described before, the flocs would be formed after the breakage period when the coagulant dosage was 0.02 mmol/L. However, with increasing concentrations of PDADMAC, the floc size after the reformation period (0.02 mmol/L) decreased. The results in Figure 5D show that the ZP increased with the addition of PDADMAC, changing from -7.12 mV to -5.22 mV when the dosage was 0.02 mmol/L. This was because the addition of PDADMAC introduced many positive charges into the systems. As described before, the flocs were formed by charge neutralization ability, and the existence of PDADMAC molecules could significantly increase the charge neutralization ability under a small coagulant dosage. When the ratio of PDADMAC/Al was large enough (10%), flocs with a larger floc size formed in the floc formation period. The PDADMAC molecules could significantly increase the bridging effect or sweep flocculation ability under a large coagulant dosage, but the recovery factor decreased in these conditions (Table 4). These results show that the role of the organic coagulant aid in correlation with the dosage and the charge neutralization was dominant under a small dosage, while the sweep flocculation was dominant under a large dosage. Compared to Al_{13} , the existence of PDADMAC could increase the floc size when the coagulant dosage was 0.04 mmol/L (Figure 5A,B), and the floc size decreased when the coagulant dosage was larger (0.08 mmol/L or 0.12 mmol/L) due to charge reversal (Figure 5D). When the coagulant dosage for composite coagulants was large, the existence of PDADMAC would have two significant effects: (1) the positive charge would cause the particles to repel each other; and (2) the adsorption of PDADMAC molecules on particles would cause steric hindrance.

3.3.4. SEM Image for the Flocs under the Optimum Dosage

SEM images for flocs formed by different coagulants are summarized in Figure 6. The results clearly show that there were different mechanisms in the formation of flocs, and the surface of flocs formed by Al_{13} exhibited the largest holes and roughness than that formed by other coagulants. With increasing concentrations of PDADMAC, sweep flocs contained more and more amorphous matters. Because the PDADMAC with a larger molecular weight conducted mostly enmeshment, the algal particles could then be aggregated as sweep flocs. Contrary to Al_{13} , the PDADMAC under optimum dosage (2%) covered the surface of particles, which caused the formation of larger sweep flocs. With increasing concentrations of PDADMAC (5% or 10%), the PDADMAC molecules would adsorb on the surface of particles, and the repulsive force decreased the floc size. When Al_{13} was used as the coagulant, the diffusion-limited aggregation (DLA) induced by charge neutralization predominately governed the coagulation performance. As the particles attach permanently to other particles at first contact, the flocs formed by Al_{13} were possibly formed by cluster-cluster aggregation.

3.4. Mechanism of Collaborative Optimization Process

In summary, the main mechanism of the Al-based composite coagulant in the algae coagulation process can be illustrated by Figure 7. Al_{13} and Al_{30} each employed their corresponding main mechanisms in the algae coagulation process. For the floc formation stage, Al_{13} mainly exerts the electrical neutralization capacity. Its electrostatic cluster effect at a low dosage and the electrical neutralization effect at a high dosage were conducive to the destabilization of algae, but the absence of its sweep flocculation mechanism was not conducive to the growth of flocs. Al_{30} mainly exerted the sweep flocculation capacity, which was conducive to the formation of larger-sized flocs, but the absence of its electrical neutralization capacity made it require a higher dosage to destabilize the flocs. It should be noted here that the “absence” mentioned here was only relative, and each coagulant could employ the above-mentioned mechanism. In the floc breakage and regeneration stage, the electrical neutralization mechanism had an important influence on the regeneration ability of flocs, and the sweep flocculation mechanism had an important influence on the strength of flocs. When using the Al_{13}/Al_{30} composite coagulant, by controlling the ratio, the electrical neutralization capacity, and the sweep flocculation of the composite

coagulant can be coordinated. In this study, when $Al_{13}:Al_{30} = 7:3$, the composite coagulant could maintain a good destabilization performance of flocs while also ensuring a good floc size, and the required dosage of the coagulant was also the lowest. Therefore, the synergistic optimization effect occurs. The effect of PDADMAC on coagulation was mainly related to the dosage. At a low dosage, it could further enhance the electrical neutralization capacity of Al_{13} , and at a high dosage, it could enhance the sweep flocculation ability of Al_{13} ; however, at the same time, it also lead to a decrease in floc size due to the charge reversal phenomenon. In addition to the factors of the above-mentioned coagulants in the algae coagulation process, the EOM secreted by algae also had an important influence on the coagulation process. Since the electrical neutralization effect was more conducive to the removal of algae EOM, the higher proportion of Al_{13} in this study was more conducive to the coagulation process, and Al_{13} only needed a lower dosage to achieve a better coagulation effect than that of Al_{30} .

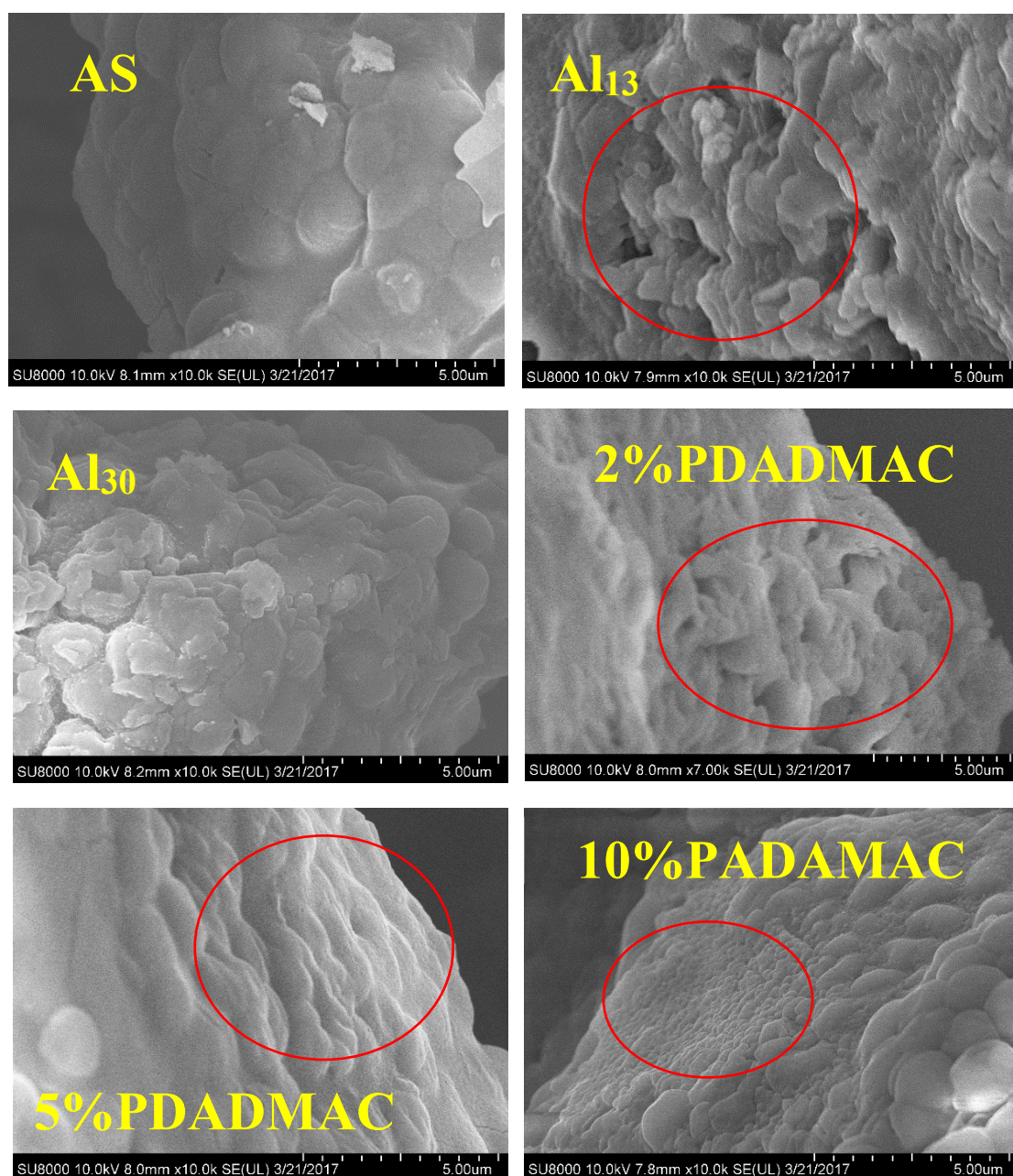


Figure 6. SEM images for flocs formed by different coagulants.

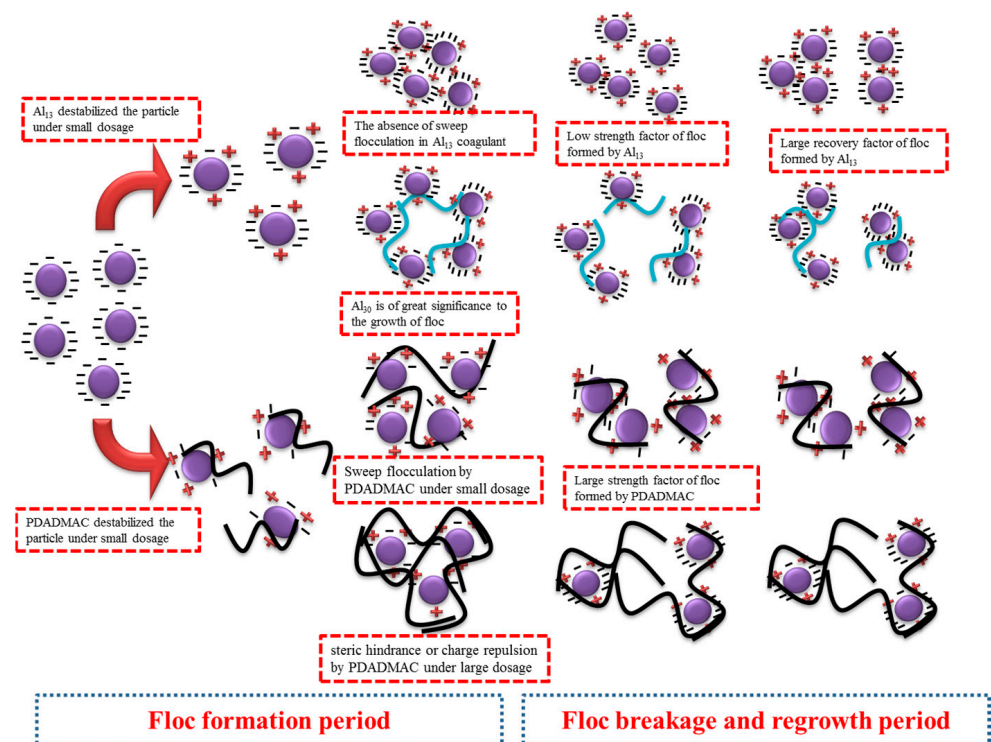


Figure 7. Schematic diagram of the effect of different Al-based coagulants on the formation, breakage, and regrowth mechanisms of algal flocs during the coagulation process.

3.5. Coagulation Performance in the Second Addition

In order to better understand the coagulation mechanism, the effects of the second addition of coagulants on the coagulation performances are summarized in Figure 8. In these experiments, AS was used to coagulate the algae-laden water, and the dosage was adjusted to 0.12 mmol/L. The second addition of coagulant was conducted after the flocs were broken for 1.0 min or 3.0 min. The dosage for the second addition was adjusted to 0.01 mmol/L.

The results in Figure 8 show that when AS was added as the second addition, the floc size after regrowth was significantly larger than with no addition of coagulant, and the flocs (when the second addition was 1.0 min after the breakage) was larger. These results may be caused by the collision between coagulants and particles. The charge neutralization ability for AS was smaller, so in the regrowth period, the flocs would need more time to be formed. When Al_{13} was used as coagulant, the flocs would be significantly reformed once the Al_{13} was added, but the flocs (when the second addition was 1.0 min after the breakage) were smaller. These results indicated that the Al_{13} could form flocs more quickly when the coagulant dosage was 0.01 mmol/L, but the flocs would be more easily broken in the breakage period. When Al_{30} was added in the second addition, the flocs would be formed in the breakage period, but the floc size after the regrowth period had no significant differences. These results could be explained well from the aspect of the coagulation mechanism. After the formation of flocs when using AS as the coagulant, there were some positive charges in the system. The Al_{13} coagulant would combine in the negative charge position formed in the floc breakage period, and then play the role of electric patch effects. These positive charge positions would attract the negative charge positions formed in the floc breakage period. The mechanism when using Al_{30} was bridging effects and sweep flocculation, and the positive position on the surfaces of flocs would decrease the absorption of Al_{30} molecules (the bridging effects and sweep flocculation decrease). Thus, the regrowth of flocs could be affected due to the decrease in bridging effects.

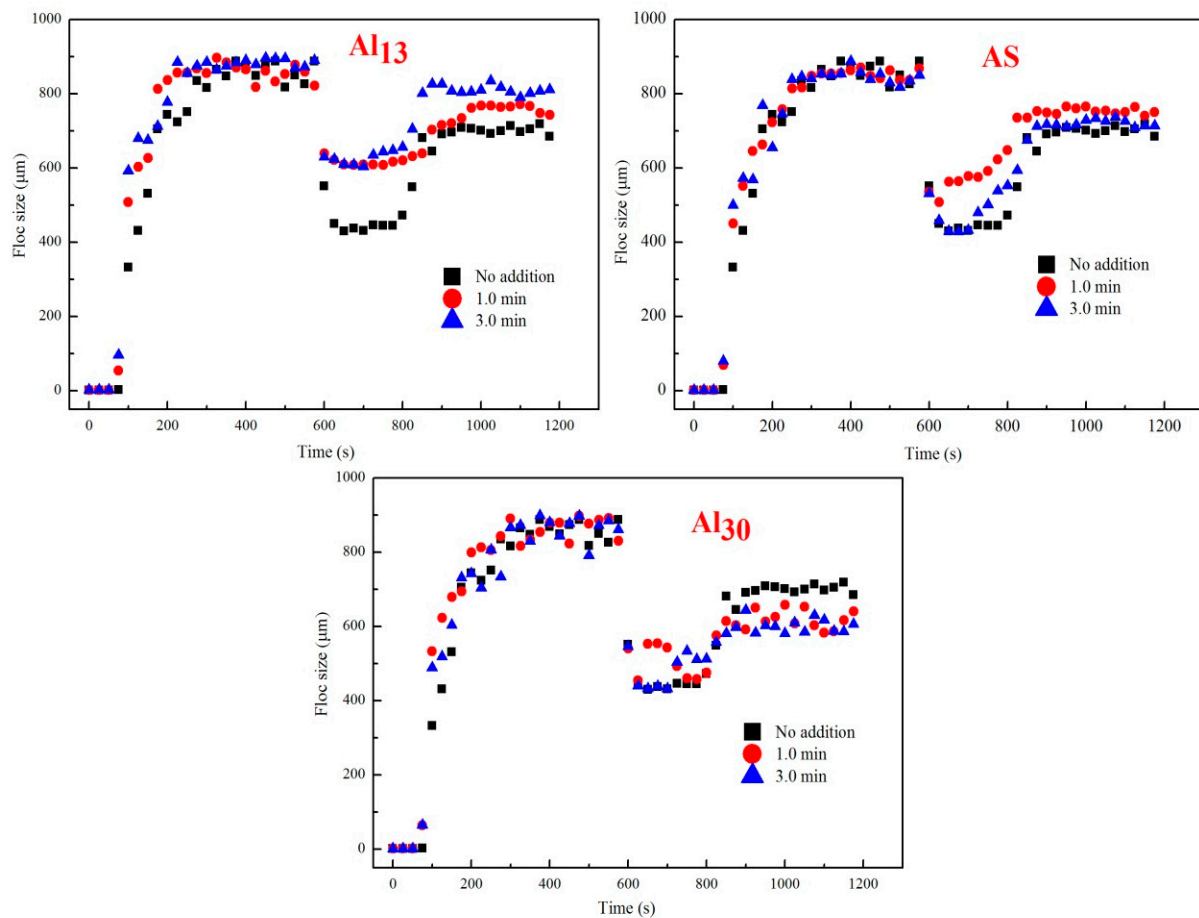


Figure 8. Coagulation performances in the second addition.

4. Conclusions

1. Coagulation mainly removed the SMP component in the EOM of *M. aeruginosa*, and the SMP was mainly removed by the action of electrical neutralization.
2. Al₁₃ played an important role in the destabilization and regeneration of algal flocs. A high content of Al₁₃ could make the flocs destabilize rapidly, and the generated flocs have a relatively high recovery factor. Al₃₀ played an important role in the growth and strength of flocs, and the formed flocs had a larger particle size and strength factor. The two coagulants achieved the optimal effect when the ratio of Al₁₃:Al₃₀ = 7:3, and the speed and strength of the formed flocs were both the largest.
3. The strength factor of flocs was the result of the combined action of organic matter and coagulant. When the dosage of coagulant increased, on the one hand, the coagulation mechanism transitioned from the action of electrical neutralization to the action of entrapment and sweeping, and on the other hand, it led to a decrease in the content of EOM in algae. Thus, the strength factor of flocs increased.
4. The role of PDADMAC coagulant aid in the coagulation process was affected by the dosage. Under the condition of low dosage, its high positive charge and large molecular weight could effectively enhance the electrical neutralization ability and entrapment and sweeping ability of the coagulant. When the dosage was high, the charge reversal phenomenon caused by the excessive positive charge in the system and the steric hindrance phenomenon of large molecules also caused the coagulation efficiency to decrease.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings14070857/s1>, Table S1. Al species distribution in coagulants used in this study. Table S2. Optimum dosage for coagulants used in this study. Table S3. The removal rate for SMP in the coagulation process as a function of pH. Table S4. Zeta potentials in the coagulation process under different coagulants. Figure S1. 3D-EEM spectra of raw solution. Figure S2. Microscopic pictures of the algae solution (*M. aeruginosa*, obtained from The Freshwater Algae Culture Collection at the Institute of Hydrobiology, FACHB). Figure S3. The determination of main fluorescent group in 3D-EEM (published in Chen et al. [35]). Figure S4. 3D-EEM spectra of EOM under different pH conditions when using AS as a coagulant. Figure S5. 3D-EEM spectra of EOM under different pH conditions when using Al₁₃ as a coagulant. Figure S6. 3D-EEM spectra of EOM under different pH conditions when using Al₃₀ as a coagulant.

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