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Characterization and coagulation performance of covalently bound organic silicate aluminum hybrid coagulants: effects of Si/Al, *B* value and pH

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ABSTRACT

Covalently bound inorganic–organic hybrid coagulants are believed to be the goal of coagulant development for water treatment. In this study, covalently bound organic silicate aluminum hybrid coagulants were synthesized by employing γ-aminopropylmethyldiethoxy silane (APDES) as silicon source with different Si/Al molar ratios (Si/Al = 0.1, 0.2, 0.3, and 0.4) and basicity values ($B = 0.5$, 1.0, 1.5, and 2.0). The APDES–Al hybrid coagulants (HC-As) were characterized by the measurement and analysis of pH, zeta potential, Al species distribution, and morphology. The results indicated that Si/Al and *B* played important roles in aspects of the physical structure, the Al species distribution, and the electrochemistry characteristics. Specifically, the HC-A with Si/Al = 0.4 and $B = 2.0$ featured the highest content of Al_{13}, the reticulated aggregate and the largest pH range for high zeta potential. The coagulation performances of HC-As were also investigated by treating synthetic water. At a low dosage, the HC-A with Si/Al = 0.4 and $B = 2.0$ exhibited the best coagulation behavior in terms of humic acid removal and turbidity removal. Besides Si/Al and *B*, the effect of pH on the coagulation performance of HC-A was also studied using an additional hybrid coagulant with tetraethoxysilane as the Si source for comparison. The results showed that HC-A has a larger pH range for simultaneous humic acid and turbidity removal.

Keywords: Hybrid coagulants; Covalently bound; γ-aminopropylmethyldiethoxysilane; Organic silicate aluminum

1. Introduction

Coagulation is a classic water treatment process to remove particle and colloid from water. These pollutants are usually removed through compressing double electric layers, counterion adsorption, charge neutralizing, polymer bridging, or sweep flocculation [1–3]. The coagulation performance varies greatly with different coagulants. Various kinds of coagulants have been developed in the past several decades, including inorganic coagulants, organic coagulants, and composite inorganic–organic coagulants [4,5]. Among them, Al-polysilicate coagulant, as a kind of relatively new inorganic coagulants presents not only the Al-polymer

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properties but also the advantages of the silicate component [6,7]. However, the current silicate component of this kind of coagulant is mainly negatively charged silicic acid or polysilicic acid, which restrains the charge neutralization function.

In order to save the advantages of the silicate component and the good charge neutralization function of the Al-coagulants, silane coupling agents [8], whose alkoxyl group can be easily transformed into a hydrophilic hydroxyl in solution, were polymerized with hydroxy-aluminum through Si–O–Al bound to obtain covalently bound hybrid coagulants. One commonly used silane is tetraethylorthosilicate (TEOS), which has been used to synthesize this kind of coagulant, resulting in products with coagulation performance. Another kind of silane—aminopropylmethyldiethoxysilanes (APDES)—is also used for the formation of hybrid materials and interpenetrated networks [9]. What is more, it has been found that APDES can only give linear macromolecules by silanol condensation [10], which would also lead to a linear structure in hybrid coagulants and enhance the coagulation efficiency.

In the previous investigation, three kinds of covalently bound organic silicate aluminum hybrid coagulants have been prepared and their characterizations and coagulation behavior were also studied by Zhao and Peng et al. [11,12]. In those studies, γ-APDES and aluminum hybrid coagulant (HC-A) was first prepared and has been approved to be the best in terms of humic acid removal and turbidity removal, due to the combination of the zeta potential, Al species distribution, and organic functional groups. However, the effects of Si/Al molar ratio (Si/Al), basicity (*B*), and pH on the characterization and the coagulation performance of HC-A coagulants are still lacking.

The main objective of this study is to investigate how some factors, including Si/Al, *B* value and pH influence on the performance of HC-A. HC-As with different Si/Al and *B* values were characterized by zeta potential measurement, ^{27}Al-NMR spectroscopy, and transmission electron microscope (TEM). The coagulation performance of these HC-As was investigated by treating synthetic turbid water and humic acid-containing water, respectively. The effect of pH on the coagulation performance of HC-A was also studied, with TEOS and aluminum hybrid coagulants (HC-T) and polyaluminum chloride (PACl) for comparison.

2. Materials and methods

2.1. Chemicals and materials

Commercially available peat humic acid (Tianjin, China) was purchased, with a molecular weight in the range of 2,000–50,000 Da. The humic acid was dissolved in a 0.1 mol/L NaOH solution, then filtered through a 0.45 μm membrane filter and stored in a refrigerator. TEOS [$Si(OC_2H_5)_4$; CAS No. 78-10-4] and APDES [$NH_2C_3H_6CH_3Si(OC_2H_5)_2$; CAS No. 3179-76-8] were purchased from Sigma Aldrich (USA). PACl ($B = 2.0$) was self-prepared according to Zhao et al. [11]. All other reagents used in this study were of analytical grade. Deionized water was used to prepare all solutions and rinse all glass ware.

2.2. Preparation and identification of coagulants

Coagulants with different *B* values and Si/Al were prepared using alkalinity titration method at room temperature [12]. A calculated amount of 1.0 mol/L $AlCl_3$ solution, APDES and deionized water were transferred into a 500 mL triflask according to the designated Si/Al (0.1, 0.2, 0.3, and 0.4).The purpose of adding deionized water was to obtain products with the same total Al concentration (Al_T). With rapid stirring, the solution in the triflask was titrated using a certain amount of NaOH solution according to the targeted *B* values (0.5, 1.0, 1.5, and 2.0). A measured volume of NaOH solution with the concentration of 0.5 mol/L was taken in a peristaltic pump and introduced into the triflask within a fixed titration time of 3 h. The hybrid coagulants with APDES as Si source were conveniently labeled HC-A1–HC-A7 according to their Si/Al and *B* value (Table 1). Meanwhile, the hybrid coagulants with TEOS as Si source (HC-T), whose Si/Al and *B* value were 0.4 and 2.0 respectively, were prepared for coagulation performance comparison.

2.3. Jar test

The effect of Si/Al and *B* value on the coagulation performance of HC-A was investigated by treating synthetic turbid water and humic acid-containing water, respectively. The synthetic turbid water was prepared by adding kaolin to deionized water and its turbidity was measured to be 91 NTU. The synthetic humic acid-containing water was prepared by adding the humic acid stock solution to a solution of 50% deionized water and 50% tap water and its UV254 was measured to be 0.24. Before the jar test, the pH of both kinds of test water was adjusted to 7.5 with 0.1 mol/L NaOH.

The effect of pH on the coagulation performance of HC-A, HC-T, and PACl was investigated by treating the synthetic humic acid-containing water mentioned above. The values were determined to be 13.1 mV for

Table 1
Physicochemical characteristics of HC-As with different Si/Al and *B* value

Sample	*B*	Si/Al	pH	Zeta potential (mV)	Al species distribution (%)		
					Al_{mon}	Al_{13}	Al_{un}
HC-A1	2.0	0.1	4.03	28.7	15.6	39.3	45.1
HC-A2	2.0	0.2	4.21	27.7	6.3	55.8	37.9
HC-A3	2.0	0.3	4.26	26.6	5.5	71.6	22.8
HC-A4	2.0	0.4	4.38	25.2	3.1	72.2	24.7
HC-A5	1.5	0.4	3.91	22.7	25.3	21.1	53.6
HC-A6	1.0	0.4	3.78	19.7	43.8	6.7	49.4
HC-A7	0.5	0.4	3.68	11.9	71.7	1.9	26.4

the zeta potential, 10.0 mg/L for dissolved organic carbon (DOC), 11.5 NTU for turbidity, and 0.95 for UV254. Before the jar test, the pH of the test water was adjusted to certain values (3.0, 4.0, 5.0, 6.0, 7.0, and 8.0) with 0.1 mol/L NaOH and 0.1 mol/L HCl. Coagulant dosage was set to be 30×10^{-5} mol Al/L.

The coagulation experiments were performed using a program-controlled TA6-1 jar test apparatus with six paddles. The procedure consisted of 2.0 min of rapid stirring (250 rpm), 15 min of slow stirring (50 rpm), and 30 min of settling. Then, samples were drawn from 2 cm under the surface to evaluate the coagulation efficiency to measure the zeta potential value after 1 min of rapid stirring. All of the coagulation experiments were conducted in three replicates, and the average values are reported here.

2.4. Analysis

The zeta potentials of HC-A with different *B* values and Si/Al were measured using a Malvern, Zetasizer2000 (UK). For the measurement of the zeta potential of the coagulant at different pH, the test sample was first diluted to a concentration of 5 mM Al/L, and then adjusted to different pH values (3, 4, 5, 6, 7, 8, 9, 10, and 11). The zeta potential was measured half an hour after the pH adjustment.

Al species distribution was measured by a Varian 300 MHz NMR spectrometer (Mercury Plus, USA). The chemical shift (0 ppm) of the ^{27}Al-NMR spectra corresponded to Al_{mon} (monomeric species), while the signal near 63 ppm corresponded to Al_{13} (a medium polymeric Al species). The concentrations of Al_{13} and Al_{mon} were determined by the ratio of the integrated intensity of the corresponding peak to that of $Al(OH)_4$ at 80 ppm. The amount of the undetectable species (Al_{un}) was obtained by subtracting Al_{mon} and Al_{13} from the known Al_T.

Samples of three different HC-As (HC-A1 with Si/Al = 0.1 and *B* = 2, HC-A4 with Si/Al = 0.4 and *B* = 2, HC-A6 with Si/Al = 0.4, *B* = 1) and 10-time diluted HC-A4 were chosen to be observed and imaged by a JEM-200CX (Japan) TEM at an accelerating voltage of 200 kV, a guaranteed lattice resolution of 0.20 nm and point resolution of 0.45 nm.

The DOC and turbidity were detected by a total organic carbon analyzer (Phoenix 8000, USA) and a turbidimeter (2100N Turbitimeter, Hash, USA), respectively. The removal of humic acid was monitored by the reduction in UV254 absorbance after the jar test using a UV–vis 8500 spectrophotometer (Shanghai, China).

3. Results and discussion

3.1. Physicochemical characteristics

As summarized in Table 1, HC-A1–HC-A4 had the same *B* value and increased Si/Al ranging from 0.1 to 0.4. With their Si/Al increasing, the pH of the HC-A coagulants increased but their zeta potential slightly decreased. The aminopropyl group in APDES can bind a proton to slightly increase the pH of the system and the positive charge of the coagulants. The reason why zeta potential did not increase with Si/Al could be attributed to the exposed Si-hydroxyl on APDES. Despite this, the zeta potential was still rather high for HC-A4 in comparison with other covalently bound organic silicate aluminum hybrid coagulants, like HC-T and diethoxydimethylsilane and aluminum hybrid coagulant (HC-D) [11]. Meanwhile, the Al_{13} content increased with Si/Al. It has been proved that Al_{13} is the most active species in Al-based coagulants and that the coagulation performance of polymeric aluminum coagulants is closely related to the content of Al_{13} species [13,14]. It could be thus speculated that HC-A4 with higher Si/Al value would exhibit better coagulation performance than HC-A1–HC-A3.

HC-A4–HC-A7 had the same Si/Al and decreasing *B* value from 0.5 to 2. Their pH is decreased with *B* value since less base was added to the system during the preparation process. With *B* value decreasing, the

Al_{un} and the Al_{13} content decreased and the Al_{mon} content increased. As a result, the Al_{13}content in HC-A coagulants is closely related to the *B* value, which is consistent with the investigations of PACl [15,16]. With the same Si/Al, increasing *B* value led to larger particle size and more positive charge. Consequently, the zeta potential was increased from 11.9 to 25.2, when *B* was increased from 0.5 to 2.0. High zeta potential and high Al_{13} content generally resulted in good charge neutralization and polymer bridging function. Thus, HC-A4 with higher *B* value would exhibit better coagulation performance than HC-A5–HC-A7.

3.2. Morphology

As shown in the TEM micrographs of different HC-As, the aggregate of HC-A1 (Si/Al = 0.1, *B* = 2.0) (Fig. 1(A)) was more compact and bigger than that of HC-A4 (Si/Al = 0.4, *B* = 2.0) (Fig. 1(B)). It could be clearly observed that the aggregate of HC-A with higher Si/Al tended to be reticulated. This can be owed to the hydrolysis reaction of oxyethyl group on APDEAS and the steric effect of the aminopropyl and methyl on APDES. The reticulated structure is favorable of polymer bridging function.

HC-A6 (Si/Al = 0.4, *B* = 1.0) got the smallest aggregates (Fig. 1(C)) because of its low *B* value. This result is in consistent with the measured distribution of Al species. It proved that *B* value increasing would result in stronger aggregates. Aggregates with bigger size are helpful to sweep flocculation.

3.3. Electrical characteristic

Destabilization of colloid can be achieved by an increase in ionic strength or specific adsorption of counterions [1]. In this case, the electrical characteristic of coagulants is significant for the destabilization process. As shown in Fig. 2, HC-A1 (Si/Al = 0.1 and *B* = 2.0) and HC-A6 (Si/Al = 0.4, *B* = 1.0) got the highest zeta potential at pH 8 and pH 5, respectively. The zeta potential of HC-A6 then decreased when pH is increased from 5 to 9 and became negative when pH >7. In contrast, the zeta potential of HC-A1 rose from −24 to −8 mV when pH changed from 9 to 10, indicating more hydrogen ions were adsorbed on the particle surface, which could be caused by the lower dipole moment or the condensation [17] of the aggregates with their further hydrolysis polymerization. HC-A4 (Si/Al = 0.4 and *B* = 2.0) got the highest zeta potential when pH was around 6–7 and did not become negative until the pH was approaching 11. The zeta potential of HC-A4 was much higher than that of HC-A1 under acid conditions and also higher than that of HC-A6 under alkaline condition. It can be concluded that HC-A4 has the widest suitable pH range for coagulation.

3.4. Coagulation performance

3.4.1. Effects of Si/Al

Using HC-A coagulants with different Si/Al ranging from 0.1 to 0.4, the turbidity and humic acid removal were investigated under neutral pH condition (7.5). Fig. 3 shows the variation of residual turbidity and humic acid as a function of the coagulant dosage, respectively. All the four HC-A coagulants had good performance on removing turbidity and humic acid under high Al dosage. But there are apparent differences among them at low Al dosage (2×10^{-5} mol/L). With Si/Al ratio increasing, both the residual turbidity and UV254 were decreased. In this case, the slightly decreased zeta potential with higher Si/Al (Table 1) did not have significantly bad influence on the performance of HC-coagulants. This can be attributed to the silicon component of HC-As, especially the aminopropyl groups. First, aminopropyl, as an

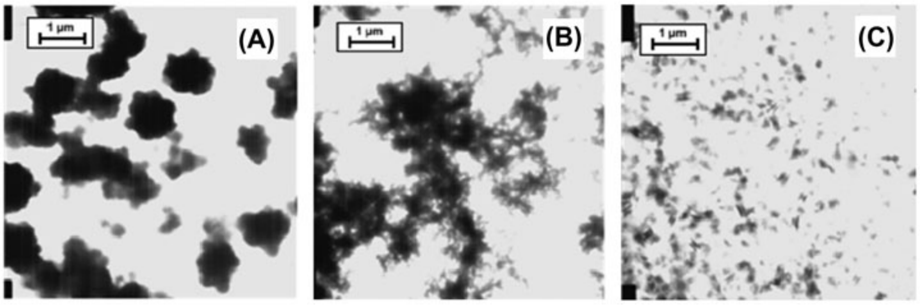

Fig. 1. TEM micrographs of (A) HC-A1 (Si/Al = 0.1, *B* = 2.0), (B) HC-A4 (Si/Al = 0.4, *B* = 2.0), and (C) HC-A6 (Si/Al = 0.4, *B* = 1.0).

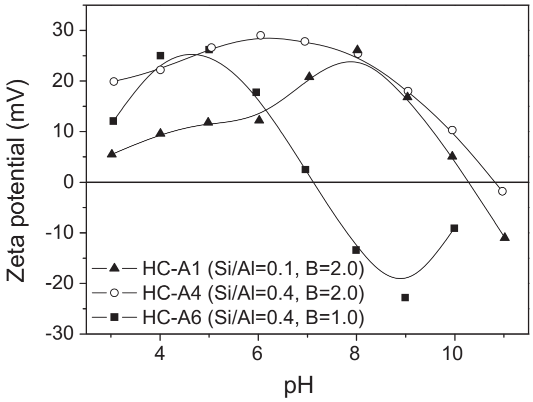

Fig. 2. Zeta potential of HC-A1 (Si/Al = 0.1, *B* = 2.0), HC-A4 (Si/Al = 0.4, *B* = 2.0), and HC-A6 (Si/Al = 0.4, *B* = 1.0) at different pHs.

electron-releasing group, could accelerate the polycondensation reaction between Al-hydroxyl and Si-hydroxyl, forcing Al_{mon} to be transformed into Al polymer [12]. Second, its steric hindrance and electrostatic repulsion effect hindered the medium polymeric Al species (Al_{13}) from being transformed into the higher polymeric species, and as a result, the reticulated structure was formed. Al_{13} and the reticulated structure were favorable for adsorption bridging ability of coagulants. Therefore, HC-A4 with Si/Al = 0.4 had better performance than those HC-As with lower Si/Al.

3.4.2. Effects of *B* value

The turbidity and humic acid removal were also investigated under neutral pH condition (7.5) using HC-As with different *B* value as coagulants. As shown in Fig. 4, all HC-As had good performance on removing turbidity and humic acid under high Al dosage. Under low Al dosage (2×10^{-5} mol/L), HC-A with higher *B* value had better turbidity and humic acid removal ability in the following order: HC-A4 > HC-A5 > HC-A6 > HC-A7, that is, the coagulation performance is increased with *B* value increasing. This can be explained from three aspects. First, as the most active species, Al_{13} was increased with *B* value. Second, the zeta potential also significantly increased with *B* value, resulting in strong charge neutralizing function. Third, HC-As with higher *B* value had larger particle size, and even the reticulated structure formed together with high Si/Al ratio (0.4), which is helpful to the functions of sweep flocculation and adsorption bridging. Therefore, *B* value of 2 is the optimal value in this study. HC-A4 still had better performance compared with those HC-As with lower *B* value.

3.4.3. Coagulation pH range

HC-A4 had the best coagulation performance under neutral pH condition. It is necessary to investigate its coagulation pH range. HC-T and PACl were used for comparison as another covalently bound Si-Al hybrid coagulant and a conventional coagulant, respectively.

As shown in Fig. 5(A), HC-T became a source of turbidity pollution instead of treating it with the final turbidity ranging from 15 NTU to 19 NTU under acidic conditions (pH 3–6) with initial turbidity of 11.5 NTU. PACl had poor turbidity removal performance under weak acidic conditions (pH 6). Al-based coagulants generally had bad coagulation performance under acidic pH, because the hydrolysis and polymerization of Al^{3+} was inhibited to a certain extent [18]. However, HC-A behaved good turbidity removal in the pH range from 3 to 9. The protonated amino groups in HC-A under acidic condition would increase the numbers of the positive charges and then enhance the charge neutralization function of the hybrid coagulant.

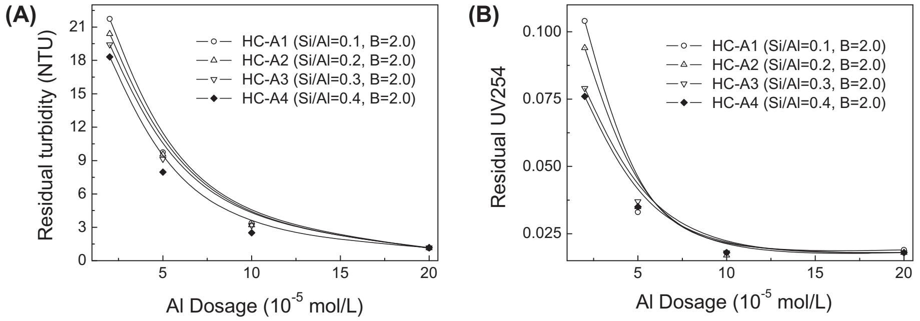

Fig. 3. Turbidity removal with initial turbidity of 91 NTU (A) and humic acid removal with initial UV254 of 0.24 (B) by HC-As with different Si/Al.

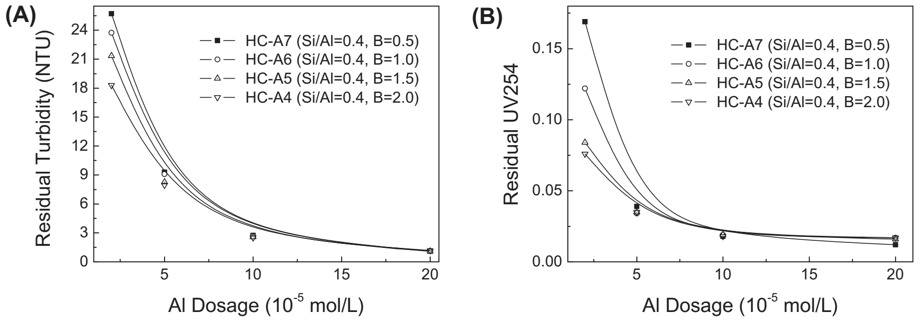

Fig. 4. Turbidity removal initial turbidity of 91 NTU (A) and humic acid removal (B) by HC-As with different *B* value initial UV254 of 0.24.

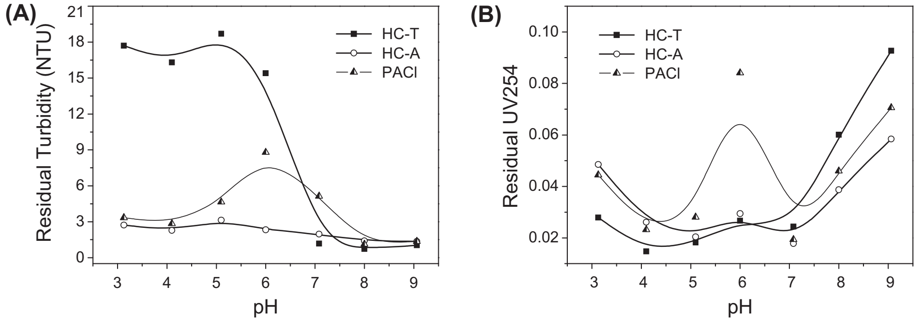

Fig. 5. Turbidity (A) and humic acid (B) removal by HC-A4, HC-T, and PACl at different pH with initial turbidity of 11.5 NTU and UV254 of 0.95.

HC-T and HC-A had similar and satisfactory UV254 removal performances, while PACl got a relatively bad one under pH 6. Among the three, the UV254 removal performance of HC-T was best at pH 4 but badly influenced by alkaline condition (Fig. 5(B)), and HC-A got the best UV254 removal performance under alkaline condition. Coagulants generally tended to form hydroxide precipitates at high pH. Consequently, sweep coagulation became the dominated mechanism for the organic matter removal [19], which is why all the three coagulants performed worse in terms of UV254 removal with pH over 7. As for HC-A, charge repulsion existed between the positively charged aminopropyl and aqueous-Al ions or Al-hydroxyl ions. The charge repulsion as well as the steric effect of the methyl groups hindered the medium Al species from being transformed into the higher species. For one thing, there was less hydroxide precipitates in HC-A under high pH. For the other, the high molecule weight polymer tended to form reticulated structure and enhanced polymer bridging function of HC-A. Thus, HC-A was less influenced by pH change compared with HC-T.

4. Conclusions

Covalently bound APDES and aluminum hybrid coagulants with different Si/Al and *B* values have been synthesized and studied. Si/Al and *B* played important roles in aspects of the Al species distribution, the morphology, the electrical characteristic, and the coagulation performance of the coagulants. Among the HC-A coagulants, the HC-A4 (Si/Al = 0.4, $B = 2.0$) featured the highest content of Al_{13}, the reticulated aggregate and the largest pH range for high zeta potential. The coagulation experiments showed that HC-A4 also exhibited the best coagulation behavior in terms of humic acid removal and turbidity removal at low Al dosage and HC-A4 had a broad suitable pH range from 3 to 9 for coagulation.

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