Covalently Bound Organic Silicate Aluminum Hybrid Coagulants: Preparation, Characterization, and Coagulation Behavior

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Covalently bound organic silicate aluminum hybrid coagulants were synthesized by employing two silane coupling agents [diethoxydimethylsilane (DEDMS), γ-aminopropylmethyldiethoxysilane (APDES)] as silicon sources. An additional coagulant was synthesized using another silane-tetraethylorthosilicate (TEOS) for comparison. Both the coagulant with DEDMS and that with APDES as the silicon source were shown to be covalently bound by infrared (IR) analysis. All three hybrid coagulants were characterized by pH, zeta potential, Al species distribution, and transmission electron microscopy (TEM) analysis. The results indicated that the silicon source played a significant role in aspects of the chemical and physical structure, Al species distribution, and electrochemistry characteristics. Specifically, the coagulant with APDES as the silicon source featured the highest zeta potential value, the highest content of Al\(_{3+}\), and reticulated aggregate. The coagulation behaviors of the three hybrid coagulants were also investigated by treating synthetic water containing humic acid (HA). The hybrid coagulant with APDES as the silicon source exhibited the best coagulation behavior in terms of HA removal and turbidity removal, due to the combination of the zeta potential, Al species distribution, and organic functional groups.

Introduction

Coagulation is an essential process for colloidal particles and dissolved organic matter (DOM) removal in drinking water and wastewater treatment. Since the coagulation efficiency highly depends on the choice of coagulant (1, 2), the preparation of new coagulants and the study of their mechanism are significant.

The studies and applications of inorganic polymer coagulants (3–11), the second generation of metal salt coagulants, have developed rapidly during the past two decades. The prime advantages of these coagulants are their superior coagulation efficiency in comparison to traditional metal salt coagulants as well as their lower cost in comparison to organic polymer coagulants (12). An Al-polysilicate coagulant, a relatively new inorganic polymer coagulant, was developed in the 1990s and has attracted the interest of many researchers in the field (12–20). It not only possesses the advantages of Al-polymer, but also some advantages of the silicate component, including large particle size (12), strong adsorption bridging ability (16), and a wide coagulation pH range (19). Compared with traditional Al-polymer, the Al-polysilicate coagulant performs more efficiently in removing algae, turbidity, oil, chemical oxygen demand (COD), and total phosphate (TP) (19). Unfortunately, the current silicate component of the Al-polysilicate coagulant is mainly activated silicic acid or polysilicic acid, both of which are negatively charged. The charge neutralization function of positively charged Al-polymers will decrease when introducing a negatively charged silicate component into the Al-polymer products (16, 21). In this way, a net positive modification to the silicate component is worthy of study. Meanwhile, the hydroxyls from the added activated silicic acid or polysilicic acid are easily polymerized with Si-hydroxyl or Al-hydroxyl around them to form a netlike, even gel structure (22), resulting in a reduction in the stability of this coagulant (16). In contrast to the polymer with netlike structure, the linear polymer is unlikely to transform into gels in solution and will easily exert the bridging function. Accordingly, the development of the linear polymer is preferred in order to improve the solubility and stability of the Al-polysilicate coagulant.

A Si atom can not only combine with Al or Fe by the −O− bond to form an inorganic polymer (23), but can also connect with a nonmetallic atom (a C atom, for instance), to form organic silicate material by a covalent bond, such as silane coupling agents (24). These agents contain both alkoxyl (−OR) and special organic groups (−R) connected to the Si atom. The alkoxyl (−OR) can be easily transformed into a hydrophilic hydroxyl in solution. The Si-hydroxyl formed can polymerize with other hydroxyls connected to Si or Al atoms (25, 26). Hence, it is reasonable to employ silane coupling agents as silicate components to prepare Al-polysilicate coagulants. Tetraethylorthosilicate (TEOS), a common silane, has been used to synthesize this coagulant, resulting in products with a high degree of polymerization exhibiting excellent coagulation performance (27, 28). However, other silane coupling agents containing special organic groups, which would modify the net charge of the silicate component, form polymers with a linear structure, and enhance the coagulation efficiency, have not yet been used in the preparation of Al-polysilicate coagulants.

Another significant contribution of employing silane coupling agents to prepare Al-polysilicate coagulants is that a covalently bound inorganic and organic hybrid coagulant could be obtained. The organic component is involved in the initial structure of the silane coupling agent, while the inorganic component can be connected to the Si atom by a Si−O−Al bond. Currently, the preparation of inorganic and organic hybrid coagulants is limited to the simple mixing of inorganic and organic components. The two components are only loosely compounded by complexation of electrostatic bonding, which cannot provide enough stability to the inorganic and organic hybrid coagulants. Accordingly, it was reasonable to infer that a covalently bound inorganic and organic hybrid coagulant could exhibit superior coagulation efficiency.
Coagulation performance is closely correlated to the key characteristics of coagulant. Previous studies indicated that the removal of humic substance, for example, was significantly affected by the zeta potential, speciation, and organic functional group of the added coagulant. However, none of these three factors can exclusively determine the coagulation performance. Advances in practical coagulation performance require the combination of all these characteristics.

The principal objective of this work was to prepare covalently bound organic silicate aluminum hybrid coagulants with a reasonable combination of zeta potential, speciation, and organic functional group. Two silane coupling agents—diethoxydimethylsilane (DEDMS) and γ-aminopropylmethyldiethoxysilane (APDES)—were employed for this purpose. None of these three factors can exclusively determine the coagulation performance. Advances in practical coagulation performance require the combination of all these characteristics.

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**Experimental Section**

**Materials.** The three silicon sources—TEOS [Si(OCH3)4; CAS No. 78-10-4], DEDMS [(CH3)2Si(OCH3)2; CAS No. 78-62-6], and APDES [NH2CH2CH2Si(OCH3)2; CAS No. 3179-76-8]—were purchased from Sigma-Aldrich (USA).

**Preparation of Coagulants.** The organic silicate aluminum hybrid coagulants were prepared by a slow alkalinity titration method at room temperature. First, calculated amounts of 1.0 mol/L AlCl3 solution, silane, and deionized water were mixed into a 500 mL flask at the determined Si/Al molar ratio of 0.4. Under rapid stirring, the mixture was titrated by NaOH (0.5 mol/L) to the target B value (OH/Al) of 2.0 within a fixed titration time of 3 h. The final concentration of aluminum (AlT) was 0.2 mol/L. The products with TEOS, DEDMS, and APDES as the silicon sources were abbreviated HC-T, HC-D, and HC-A, respectively. Meanwhile, the polyaluminum chloride (PACl) and polyaluminum silicate chloride (PASiC) were prepared for comparison. Details are presented in the Supporting Information.

**Coagulant Characterization.** IR spectroscopy of the organic silicate aluminum hybrid coagulants was recorded on a Raman950/Magna-IR750 (USA) IR spectrometer, and the results for polysilicic acid and PACl were also obtained for comparison and further analysis. The zeta potentials of HC-T, HC-D, and HC-A were measured using a Malvern, Zetasizer 2000 (U.K.). A jar test was conducted by treating synthetic water containing humic acid (HA) to evaluate the coagulation behavior of these organic silicate aluminum hybrid coagulants.

**TABLE 1. Properties of HC-T, HC-D, and HC-A**

<table>
<thead>
<tr>
<th>sample</th>
<th>silane</th>
<th>AlT (mol/L)</th>
<th>B</th>
<th>Si/Al</th>
<th>pH</th>
<th>zeta potential value (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC-T</td>
<td>TEOS</td>
<td>0.2</td>
<td>2.0</td>
<td>0.40</td>
<td>3.51</td>
<td>24.1</td>
</tr>
<tr>
<td>HC-D</td>
<td>DEDMS</td>
<td>0.2</td>
<td>2.0</td>
<td>0.40</td>
<td>4.05</td>
<td>15.3</td>
</tr>
<tr>
<td>HC-A</td>
<td>APDES</td>
<td>0.2</td>
<td>2.0</td>
<td>0.40</td>
<td>4.38</td>
<td>25.2</td>
</tr>
</tbody>
</table>

**FIGURE 1. IR spectra of (a) polysilicic acid and PACl and (b) HC-T, HC-D, and HC-A.**

**FIGURE 2. Zeta potential of HC-T, HC-D, and HC-A at different pH.**

**TABLE 2. Al Distribution in HC-T, HC-D, and HC-A Obtained Using Al-Ferron Spectrophotometry and 27Al-NMR Spectra**

<table>
<thead>
<tr>
<th>sample</th>
<th>AlT (%)</th>
<th>AlE (%)</th>
<th>AlL (%)</th>
<th>Almon (%)</th>
<th>Al13 (%)</th>
<th>Alun (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC-T</td>
<td>25.8</td>
<td>9.0</td>
<td>65.2</td>
<td>28.5</td>
<td>71.5</td>
<td></td>
</tr>
<tr>
<td>HC-D</td>
<td>19.7</td>
<td>50.7</td>
<td>29.6</td>
<td>21.6</td>
<td>72.2</td>
<td></td>
</tr>
<tr>
<td>HC-A</td>
<td>4.0</td>
<td>74.2</td>
<td>21.8</td>
<td>3.1</td>
<td>72.2</td>
<td></td>
</tr>
</tbody>
</table>

a Undetectable.

**FIGURE 3. 27Al-NMR spectra of HC-T, HC-D, and HC-A.**
methods of IR, zeta potential, and TEM are provided in the Supporting Information. Al-Ferron spectrophotometry was carried out using a Specord 200 spectrophotometer (Germany). Al\textsubscript{mon}, Al\textsubscript{13}, and Al\textsubscript{13}, which represent the monomeric species, medium polymeric species, and high polymers or colloidal species, respectively (33, 34), could be divided artificially according to the kinetic difference of the reaction between the Al species and the Ferron reagent. The 27Al-NMR spectra were measured by a Varian 300 MHz NMR spectrometer (Mercury Plus, USA). The chemical shift (0 ppm) of the 27Al-NMR spectra corresponded to Al\textsubscript{mon} (monomeric species), while the signal near 63 ppm corresponded to Al\textsubscript{13} (a medium polymeric Al species). The concentrations of Al\textsubscript{13} and Al\textsubscript{mon} were determined by the ratio of the integrated intensity of the corresponding peak to that of Al(OH)\textsubscript{4}\textsuperscript{-} at 80 ppm. The amount of the undetectable species (Al\textsubscript{un}) was obtained by subtracting Al\textsubscript{mon} and Al\textsubscript{13} from the known total concentration of aluminum (Al\textsubscript{T}).

Jar Test. Commercially available peat HA (Tianjin, China) was purchased, with a molecular weight in the range of 2000–50,000 Da. The HA was dissolved in a 0.1 mol/L NaOH solution, then filtered through a 0.45 \( \mu \)m membrane filter and stored in a refrigerator. The test water was prepared by adding the HA stock solution to a solution of 50% deionized water and 50% tap water (31). The values were determined to be –13.1 mV for the zeta potential, 10.0 mg/L for dissolved organic carbon (DOC), 11.5 NTU (nephelometric turbidity unit) for turbidity, and 0.95 for UV\textsubscript{254}. Before the jar test, the pH of the test water was adjusted to 6.0 with 0.1 mol/L HCl. 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 for the residual turbidity and UV\textsubscript{254} absorbance measurement (after filtration through a 0.45 \( \mu \)m membrane) to evaluate the coagulation efficiency. Samples were drawn to measure the zeta potential value after 1 min of rapid stirring. The zeta potential, DOC, turbidity, and UV\textsubscript{254} were detected by a potentiometer (Zetasizer 2000, Malvern, U.K.), total organic carbon analyzer (Phoenix 8000, USA), turbitimeter (2100N Turbitimeter, Hash, USA) and UV-vis 8500 spectrophotometer (Shanghai, China), respectively. The coagulation behaviors of the prepared HC-T, HC-D, HC-A, PACl, and PASiC were evaluated by the jar test.

Results and Discussion

IR analysis. The chemical structures of the three hybrid coagulants (HC-T, HC-D, and HC-A), polysilicic acid, and PACl were identified by IR analysis (Figure 1a and b). An absorbance signal around 1640 (1612–1642) cm\textsuperscript{-1} was noted for the above five compounds, which was attributed to the Al-OH or Si-OH peak. From the IR of the known compound PACl, the peaks at 1090 and 984 cm\textsuperscript{-1} were assigned to Al-OAl (stretching or scissoring). From the known polysilicic acid, the peak appearing at 1080 cm\textsuperscript{-1} was assigned to Si-OSi. For HC-T, a strong and broad peak was observed around 974 cm\textsuperscript{-1} and was assigned to the combination of Si-OAl and Al-OSi. For HC-D and HC-A, characteristic peaks were observed for both organic (Si-C) and inorganic components (Si-OAl, Al-OSi). It was therefore concluded that HC-D and HC-A were covalently bound inorganic and organic hybrid coagulants.

Zeta Potential. The properties of the samples are summarized in Table 1. The pH value of HC-A is higher than that of HC-D, while HC-T has the lowest pH value of the three (Table 1).

For HC-A, the APDES employed contained an aminopropyl group. The aminopropyl can bind a proton to become.
positively charged in a weakly acidic environment, which modifies the net charge of the hybrid coagulant to a higher positive charge. Thus the highest zeta potential value is obtained in HC-A, followed by HC-T, and then HC-D. A detailed experiment was carried out to investigate the change of zeta potential with respect to pH (Figure 2). For all three hybrid coagulants, a similar pattern was observed in the change of the zeta potential value over a wide range of pH (Figure 2). With increasing value of pH, beginning at an acidic pH, the zeta potential value increased and reached a maximum in a pH range between 6.0 and 7.0 on the positive side, then decreased monotonically, passed the isoelectric point at a pH range between 9.0 and 11.0, and finally became negative.

Significant differences were noted among the curves. The curve of the zeta potential versus pH for HC-A was higher than that for HC-D, while the curve of HC-T was the lowest of the three. Moreover, the isoelectric point moved toward the alkaliescent side for silicon sources in this order TEOS, DEDMS, and APDES. The positive charge of the coagulants in the pH range 3–9 mainly came from the Al–Si polymeric species. At higher pH of 9–11, the covalently bound structure of HC-D and HC-A could retard the effect of pH, which gave HC-D and HC-A higher zeta potential values than HC-T. Generally, HC-A had a higher zeta potential over a wider pH range, demonstrating that HC-A might possess eminent charge-neutralization ability for water and wastewater treatment practice.

**Distribution of Al species.** It is generally believed that the coagulation performance of Al-based coagulants is closely related to the distribution and transformation of the Al species (9). Al-Ferron complexation timed spectrophotometry and 27Al-NMR measurements, two of the most commonly used methods, were adopted to investigate the Al distribution of the hybrid coagulants.

The timed complexation reaction curves of HC-T, HC-D, and HC-A were measured by Al-Ferron complexation timed spectrophotometry. The contents of Alb, Alb, and Alc were then calculated (Table 2). It was noted that Alb was the dominant species in HC-T, while HC-D and HC-A featured Alb as the dominant species, and the highest content of Alb was obtained in HC-A. The results demonstrated that the type of silicon source exhibited significant influence on the Al species distribution. High-molecular-weight polymers were likely to be formed in HC-T. However, either HC-D or HC-A contained less Alc than HC-T, but with a medium-molecular-weight polymer as the dominant species.

All three silanes contained ethoxy groups, which were easy to hydrolyze into hydroxyls, which then polymerized the Al-hydroxyl to form Si–Al polymers. TEOS contained four ethoxys, more than DEDMS and APDES, and resulted in greater Si–O–Al bond generation (Figure 1b). Polymers with higher molar structure were thus likely formed in HC-T. DEDMS was found to have weaker hydrolysis ability than TEOS. The steric effect of the methyl groups in DEDMS might hinder the hydrolysis of DEDMS and the further polymerization with aqueous-Al or Al-hydroxyl ions. Therefore, in HC-D, it was difficult for Si–Al polymers to be formed and transformed into species with a higher polymerization degree, but with medium Al species as the dominant species. HC-A contained the highest zeta potential among the three hybrid coagulants (Table 1 and Figure 2). 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. Moreover, as an electron-releasing group, the aminopropyl could accelerate the hydroxyl-based condensation reaction rate in the preparation process, forcing part of the monomeric species to be transformed into the medium polymeric species. Thus the highest content of Alb was observed in HC-A.

Compared to the Al-Ferron assay, the 27Al-NMR technique has the characteristic advantage of revealing structural details for Al species such as Almon and Al13. The 27Al-NMR spectra of HC-T, HC-D, and HC-A are shown in Figure 3 and the contents of Al species are listed in Table 2. Each peak of the 27Al-NMR spectra corresponded to a specific species. The Alb signal (~63 ppm) was observed in HC-A and HC-D but not in HC-T. When the silicon source of the hybrid coagulant was in the order TEOS, DEDMS, and APDES, the Alb signal (~63 ppm) became stronger and the Almon signal (0 ppm) became weaker. Correspondingly, the content of Alb increased and that of Almon decreased. It was proved that Alb, regarded sometimes as the Alb species (35), was the most active species responsible for the coagulation performance in Al-based coagulants (2, 36). A high content of Alb was therefore the main aim in the research and production industry of Al-based coagulants. It could be thus conferred that HC-A would exhibit excellent coagulation performance.

**Morphology Analysis.** TEM is an intuitive way to observe the actual morphology of a liquid coagulant. The TEM micrographs of HC-T, HC-D, and HC-A are shown in Figure 4. The aggregate of HC-T was much larger and more compact than that of HC-D and HC-A. The aggregate of HC-A was reticulated while that of HC-D was the smallest of the three hybrid coagulants.

HC-T was likely to form a netlike and compact structure with a high molecular weight (Al was the dominant species as showed in Table 2), and was easily adsorbed onto the surface of particles due to the large amount of hydroxyls. It was thus inferred that HC-T could exhibit excellent adsorption ability and enhance the sweep flocculation when used in water treatment. However, as with HC-D, a linear polymer instead of a netlike one was preferred, resulting from the symmetry structure of DEDMS. HC-A contained mostly the medium-molecular weight polymer, Alb (Table 2). Moreover, as a polar group, the aminopropyl of APDES was easily combined with other polymers. Thus, the aggregate of HC-A appeared in a reticulated style. Accordingly, it was believed that bridging might be the primary coagulation mechanism for HC-A.

Meanwhile, the stability of different coagulants when stored was also observed. It was found that the new covalently bound organic silicate aluminum hybrid coagulants exhibited better stability than PASiC under the same conditions. More detailed information is provided in the Supporting Information.

**Coagulation Behavior.** The removal of HA by HC-T, HC-D, and HC-A as well as PACl and PASiC were examined in the dose range of 2.5 × 10−5 to 40 × 10−5 mol Al/L at the original system pH of 6.0. The pH changes with the addition of different coagulants were investigated, and detailed information is provided in the Supporting Information. As shown in Figure 5, the zeta potential increased from the negative side to the positive side with increased dosage for all the five coagulants. However, the behaviors involving turbidity removal were different. The residual turbidity after coagulation decreased before reaching the optimal dosage (around 5–15 × 10−5 mol Al/L). Then, the turbidity removal deteriorated with further increase of the coagulant dosage due to the restabilization of flocs caused by excessive positive charge, especially for HC-T (Figure 5b). For HC-D, the restabilization was of a limited degree, similar to the coagulation behavior of PACl, but more obvious than that of PASiC. However, for HC-A, there was no obvious restabilization phenomenon throughout the dosage range. In terms of UV254 removal, no obvious deterioration of the removal efficiency was observed with increasing coagulant dosage for any of the five coagulants, including HC-T. At high dosage,
HC-A exhibited the highest UV_{254} removal efficiency among the five coagulants. In the coagulation experiment, the settling performance of the five coagulants were also investigated. Compared with PACI, larger flocs and a more rapid sedimentation rate were observed for the coagulants containing silicon components (HC-T, HC-D, HC-A, and PASiC), especially HC-A. The silicon component and the aminopropyl group of HC-A enhanced the bridge effect, thus improving the settling performance of HC-A.

As previously mentioned, an excellent coagulation performance was based on the combination of the main characteristics of the coagulant used. For the three organic silicate aluminum hybrid coagulants prepared in this study, these key characterizations involved the zeta potential, Al species distribution, and organic functional groups. In a weak acid environment, the humic substances were negatively charged and dissolved in water. Therefore, the charge neutralization was the main coagulation mechanism at lower dosage (21). The zeta potential played the most important role under these conditions. However, excessive positive charge could also lead to the restabilization of the formed flocs once the added coagulant exceeded “the optimum dosage”, resulting in the deterioration of the residual turbidity (Figure 5b). This phenomenon was more obvious in HC-T, which contained the highest amount of Al_{mon} accompanied by the lowest amount of Al_{13}. In contrast, there was no obvious restabilization for HC-A which contained the highest amount of Al_{13} (Table 2). The results are consistent with Shi’s study, where severe restabilization occurred for nonpreformed Al species but no restabilization was observed for Al_{13} at pH 5.5 (31). Due to their larger size and higher positive charge, the association of Al_{13} species with HA is stronger and such interactions might be able to induce the reformation of long HA molecules around the Al_{13} species. Consequently, the positive charges of the Al_{13} species can be greatly shielded, which can be enhanced for the silicon-containing coagulants because of their obvious bridge effect. However, the interactions of the Al_{mon} species with HA can be much weaker and might not be able to induce the reformation of HA molecules. Therefore, the coagulants showed varying degrees of restabilization due to their different AI speciation and bridge effects. Moreover, in terms of HC-A, the aminopropyl of APDES might enhance the adsorption of HC-A to the HA, due to its selective combination with the carboxylic group of HA. As a result, a superior efficiency of UV_{254} removal was observed in HC-A (Figure 5c). In the coagulation experiment, HC-A exhibited the best coagulation performance, because it achieved the combination of optimum zeta potential, Al species distribution, and organic functional groups.

Acknowledgments

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Supporting Information Available

More detailed information about the experimental methods (coagulant preparation, IR, TEM, and zeta potential measurements) and additional results and discussion (stability, pH changes during the coagulation process, cost effectiveness). This information is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited


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