Article

Impact of Conditioning Agent Addition Sequence on Dewatering Performance of Advanced Anaerobic Digested Sludge

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Abstract: The advanced anaerobic digestion process enhances sludge resource utilization. However, thermal hydrolysis pretreatment of anaerobically digested sludge reduces dewatering efficiency due to excessive organic matter decomposition. This necessitates significant time and effort for sludge conditioning in wastewater treatment plants. Using conditioning agents can achieve high dewatering efficiency. This study investigates how the order of adding coagulants and flocculants impacts the dewatering performance of digested sludge. The results indicate that, compared to the flocculation–coagulation process with the same dosage, the coagulation–flocculation process leads to a 15–20% increase in the average particle size of digested sludge. The content of polysaccharides and proteins in S-EPS decreases by 28.8–30.8% and 10.1–11.3%, respectively. The filter cake solids content increases by 8.5%, and there is an increase in surface water channels within the flocs. This is because initially adding coagulants efficiently adsorbs small particles, forming larger aggregates that settle effectively. This promotes the breakdown of extracellular polymeric substances, releasing more bound water. Adding flocculants later bridges the aggregates, further enhancing settling and filtration performance, thereby improving sludge dewatering efficiency. These research findings contribute to a better understanding of the mechanisms of coagulant and flocculant co-conditioning for digested sludge and provide recommendations for optimizing sludge conditioning steps.

Keywords: sludge dewatering; advanced anaerobic digestion; addition sequence; coagulation; flocculation

1. Introduction

Activated sludge technology, as a core technology in the field of wastewater treatment, plays a crucial role in modern wastewater treatment plants. Consequently, the widespread use of activated sludge technology is accompanied by a significant increase in sludge production. Sludge, as a byproduct of wastewater treatment, accumulates heavy metals, refractory organic compounds, persistent organic pollutants, microplastics, and other pollutants from wastewater. Improper disposal and landfills of sludge poses significant risks to ecosystems such as water, soil, and the atmosphere as well as human health [1–3]. It is estimated that approximately 50% of the operating costs of wastewater treatment plants are related to the treatment and management of sewage sludge [4]. Common methods for sludge disposal include agricultural and forestry utilization, sanitary landfilling, incineration, and the production of construction materials. Compared to these methods, anaerobic digestion not only removes odors and pathogens but also decomposes some of the organic matter in sludge to produce biogas, which can supplement the energy consumption of anaerobic digestion, indirectly reducing carbon emissions [5]. To overcome the challenges encountered during the anaerobic digestion hydrolysis process, researchers are exploring various physical, mechanical, chemical, thermal, and biological methods to pretreat sludge.
to accelerate solubilization, increase the hydrolysis of refractory organic matter, and enhance energy recovery during anaerobic digestion [6]. Among these methods, thermal hydrolysis processes use high-temperature and high-pressure conditions to efficiently induce sludge thermal and dissolution reactions. This not only promotes sludge dewatering and volume reduction but also contributes to greenhouse gas reduction, making it one of the most prominent commercial technologies today.

However, subjecting sludge to anaerobic digestion after thermal hydrolysis can lead to excessive decomposition of organic matter within the sludge flocs. This results in an increase in the apparent viscosity of the sludge and a decrease in its filtration performance, thereby negating the advantages brought by thermal hydrolysis to sludge dewatering performance [7]. Wu and Jiang’s [8] research related to dewatering of sludge with a moisture content of 98.8% and anaerobic digestion of sludge with a moisture content of 96.9% found that the anaerobic digestion process disrupts cell walls, causing a significant transfer of extracellular polymeric substances (EPSs) from the solid phase to the liquid phase. This leads to the degradation of large molecules such as proteins and polysaccharides into smaller molecules, resulting in a significant reduction in sludge particle size. The number of sub-colloidal particles increases significantly, thereby increasing the specific surface area of sludge flocs. This enhances the sludge particles’ adsorption capacity for water, causing a substantial reduction in the dewatering rate of anaerobic digestion sludge compared to residual sludge. This situation requires wastewater treatment plants to spend a considerable amount of time on adjustment parameters (dosage, stirring speed, mixing time, addition order), significantly reducing production efficiency.

Dewatering is a critical step in the treatment and disposal of sludge. Achieving high dewaterability not only reduces sludge production and its associated transportation and management costs but can also reduce the leachate production in sludge landfills [9]. However, due to the highly hydrated colloid structure of microbial aggregates, small sludge particles form stable suspensions in water, making them difficult to separate directly [10]. Therefore, to enhance sludge dewatering performance, sludge conditioning is necessary before mechanical dewatering. Currently, various processes, including chemical, physical, biological, and mixed conditioning, have been developed to improve sludge dewatering. Wastewater treatment plants primarily use three methods for sludge dewatering: chemical pretreatment, high-pressure filtration, and electromechanical dewatering [11,12]. These pretreatment methods aim to enhance the settling and filtration performance of sludge, thus increasing the release of bound water within sludge flocs and further altering the dewatering capacity and rheological properties of sludge [13]. One of the most commonly used and effective methods in wastewater treatment plants to improve sludge dewaterability is adding coagulants and flocculants individually or in combination [14]. A substantial amount of research indicates that, compared to other conditioning methods, the combined use of coagulants and flocculants in sludge conditioning can convert the bound water within the sludge into free water through agglomeration, leading to improved filtration performance and higher solid content. Additionally, this approach can maintain sludge properties and organic matter content without increasing the sludge volume. Please refer to Table 1 for details [7,12,14]. It is generally believed that coagulants should be added before flocculants [15,16]. However, it is currently unclear whether the addition sequence of coagulants and flocculants will affect the dewatering performance of sludge and other conditioning conditions during advanced anaerobic digestion of sludge, leading to the need for wastewater treatment plants to expend a considerable amount of time and effort on tuning processes.

Therefore, to address the knowledge gaps in the coagulant–flocculant co-conditioning of anaerobic digestion sludge and optimize the coagulation–flocculation combined conditioning process to further enhance the dewatering efficiency of advanced anaerobic digestion sludge in wastewater treatment plants, this study first determined the optimal conditioning conditions for each conditioning agent. Based on this, the dewatering performance and rheological properties of anaerobic digestion sludge were studied for three
groups: no pretreatment, coagulation–floculation process, and floculation–coagulation process. This study primarily focused on investigating the impact of the order of coagulant and floculant addition on the dewatering performance of anaerobic digestion sludge and the changing trends in rheological properties and analyzed the mechanisms leading to differences in their dewatering performance.

Table 1. Comparison of different conditioning methods.

<table>
<thead>
<tr>
<th>Pre-Treatment Methods for Sludge Dewatering</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition of porous materials</td>
<td>Changes the floc structure to enhance floculation</td>
<td>Increases the final volume of dewatered sludge, leading to higher treatment costs.</td>
</tr>
<tr>
<td>Ultrasonic</td>
<td>Enhances the decomposition of floculants.</td>
<td>Generates additional water-binding surfaces, resulting in a lower dewatering rate.</td>
</tr>
<tr>
<td>Alkaline treatment</td>
<td>Alters the floc structure of sludge to become more hydrophobic.</td>
<td>Increases the volume of sludge, leading to corrosion effects.</td>
</tr>
<tr>
<td>Heat treatment</td>
<td>Enhances hydrolysis capability to hydrolyze sludge floes.</td>
<td>The existence of the Maillard reaction can lead to the generation of wastewater rich in complex nitrogen-containing compounds that are difficult to treat.</td>
</tr>
<tr>
<td>Electrochemical treatment</td>
<td>Utilizing osmotic pressure and electrolysis to degrade EPS can improve the efficiency of removing free water and bound water.</td>
<td>High energy consumption, corrosion of electrodes, and expensive maintenance costs.</td>
</tr>
<tr>
<td>Conditioning agent</td>
<td>Economical, good dewatering effect, without additional increase in sludge mass and external water-binding surfaces.</td>
<td>The impact of filtrate recycling.</td>
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</table>

2. Materials and Methods

2.1. Sludge Samples and Chemicals

The original sludge (RS) samples were obtained from the effluent of an advanced anaerobic digestion process at a wastewater treatment plant in Beijing, China. The pre-treatment process involved high-temperature hydrolysis at 165 °C. The sludge ammonia nitrogen content of 2300 mg/L, an alkalinity of 8980 mg/L, a total solids (TS) range of 6% to 7%, a pH range of 8.4 to 8.5, and a soluble chemical oxygen demand (SCOD) content of approximately 51,810 mg/L. To ensure accurate and reliable experimental results, the digested sludge was sealed and stored in a refrigerator at 4 °C before the experiments. Each batch of comparative experiments was completed within one week. The main conditioning agents used were cationic polyacrylamide (PAM) particles with an average molecular weight of approximately 150,000, poly aluminum chloride (PAC) powder with a concentration of approximately 28–30% of aluminum chloride, and the poly ferric sulfate (PFS) powder with a concentration of approximately 20–21% of iron sulfate (Chengdu Aikeda Chemical Technology Co., Ltd., Chengdu, China).

2.2. Digested Sludge Conditioning and Dewatering

PAM was utilized as a floculant, while PAC and PFS were employed as inorganic coagulants. In the experiment, 250 mL of sludge was placed in a 500 mL beaker. A 2‰ mass fraction solution of PAM and a 5‰ mass fraction solution of PAC and PFS were prepared. The sludge was pre-stirred at 200 rpm for 1 min before the addition of the conditioning agent. Subsequently, the mixture was stirred at 300 rpm for 5 min after the addition of the conditioning agent. PAM was dosed at 0‰, 1‰, 2‰, 3‰, 4‰, 5‰, and 6‰; PAC at 0%, 2%, 4%, 6%, 7%, 8%, and 9%; and PFS at 0%, 4%, 6%, 8%, 10%, 11%, 12%, to investigate the effect of the conditioning dose on the solids content of the filter cake and to determine the optimum dose of coagulant and floculant. The optimum dosage of coagulant and floculant was determined. Four dosing sequences were then tested at the optimum dose: PAC-PAM, PAM-PAC, PFS-PAM, and PAM-PFS. Finally, samples were taken after conditioning to determine the solids content of the vacuum-filtered sludge cake, the rheological characteristics of the sludge, and its physicochemical indexes, and to analyze the dewatering performance and related mechanical changes.
Particle size distribution is generally considered another key factor affecting sludge dewaterability, as the surface charge of sludge particles and the microstructure of sludge flocs can also be improved by adjusting the particle size distribution [12]. Therefore, particle size and filter cake solids content were used to evaluate sludge dewaterability. Particle size was measured using a laser particle size analyzer (Mastersizer 2000, Malvern, Worcestershire, UK), and vacuum filtration (XZ-1, Jinan Aoxin, Jinan, China) was performed under a vacuum pressure of 0.08 MPa for 15 min. The filtered sludge cake was then dried at 105 °C for 24 h, and different durations (10 min, 20 min) of testing under a vacuum pressure of 0.08 MPa were conducted to evaluate the moisture content. All tests were conducted in triplicate.

2.3. Physicochemical Properties of Sludge

2.3.1. Extracellular Polymeric Substance (EPS) Extraction and Analysis

Soluble extracellular polymer substance (S-EPS) was extracted from EPS in sludge by separating the sludge samples in 50 mL centrifuge tubes at 4000 rpm for 5 min and then filtering the supernatant using 0.45 μm organic microporous filter membranes. Loosely bound extracellular polymers (LBEPS) were obtained by resuspending the remaining sludge from the previous step to 50 mL in a 0.05% NaCl solution preheated to 70 °C and mixed thoroughly, then sonicated for 10 min, followed by centrifugation at 6000 rpm for 10 min and filtration of the supernatant. The remaining sludge particles left in the centrifuge tube were again mixed with NaCl solution (0.05 wt%) preheated to 70 °C to 50 mL and placed in a water bath at 60 °C for 30 min. The sludge mixture was finally separated by centrifugation at 8000 rpm for 15 min and the supernatant was filtered [17]. The EPS was analyzed for protein (soluble proteins, SPr), polysaccharides (SPs), and soluble chemical oxygen demand (SCOD) concentrations. Soluble protein (SPr) and soluble polysaccharides (SPs) were determined using the Komas Brilliant Blue method and the Sulphuric Acid-Phenol method, respectively, in conjunction with a HACH DR6000 UV spectrophotometer (HACH, Loveland, Colorado, USA).

2.3.2. Basic Characteristics of the Sludge

The pH value of the sludge was determined using a Swiss Mettler-Toledo 210 pH meter. The solids content of the sludge cake (TS) was determined by the weight method. The samples were dried in a constant-temperature oven at 105 °C for 24 h and the TS was calculated based on the mass before and after drying, using the formula in Equation (1).

\[
TS = \frac{M_3 - M_1}{M_2 - M_1}
\]

where TS is the solids content of the mud cake (%); \(M_1\) is the mass of the evaporation dish (g); \(M_2\) and \(M_3\) represent the total mass of sludge and evaporation dish before and after drying treatment (g), respectively.

2.3.3. Morphological Analysis

To investigate the morphological changes of digested sludge samples, the floc structures of the sludge were analyzed using two different measurement scales. Firstly, the floc structures of the sludge were measured using an image analysis system of a fluorescence microscope (Axio A1, Zeiss, Oberkochen, Germany). Secondly, the surface structures of the sludge samples were analyzed using a scanning electron microscope (ZEISS GeminiSEM 300, Germany).

2.3.4. Rheological Experiments

Rheological testing was conducted using a rotational viscometer (HAAKE Viscotester 550, Thermo Fisher Scientific, Waltham, MA, USA) equipped with a low-temperature thermostat heating system (DCY-0506, Shanghai Shunyu Hengping Instrument, Shanghai, China) capable of heating the sludge sample to \((20 \pm 0.1) ^\circ C\). The following pre-settings [18]
were applied for each experiment: low-speed stirring until the desired experimental temperature was reached, pre-shear at a shear rate of 1000 s\(^{-1}\) for 5 min, followed by a 1 min rest period at 0 s\(^{-1}\) to establish equilibrium. To minimize errors caused by large particles, the sludge was sieved using a 0.6 mm mesh sieve before each experiment. For each rheological experiment, 10 mL of sludge sample was introduced into the measuring cup.

The HAAKE RheoWin JobManager (550) software collected and analyzed the rheological data. The sludge flow curves were obtained by applying incrementally increasing shear rates from 0 to 1000 s\(^{-1}\) over 180 s, with 30 data points set throughout the shear process. The yield stress was determined according to the method reported by Farno et al. [16] and finally fitted using the Herschel–Bulkley model (2).

\[
\tau = \tau_0 + k \cdot \gamma^n
\]

where \(\tau\) and \(\tau_0\) are the shear stress and yield stress of sludge (Pa), respectively; \(k\) is the consistency coefficient (Pa \cdot s\(^n\)); \(\gamma\) represents the shear rate of sludge (s\(^{-1}\)); and \(n\) is the flow behavior index (dimensionless).

Thixotropy refers to the difference in the rate of internal structure breakdown and reconstruction, leading to changes in the internal network structure over time at a given shear rate. It is typically used to describe the recoverability of the structure after being disrupted. The internal structure of sludge flocs inevitably disintegrates under shear. If the shear forces applied to the sludge do not exceed the deformation limit of the flocs, the floc structure may recover to its original state when the shear forces are removed [19]. The K-value can be used to quantify the thixotropic behavior of sludge, where a higher K-value indicates lower thixotropy.

Thixotropic testing was also performed using the HAAKE Viscotester 550 rotational viscometer (Thermo Fisher Scientific China Ltd., Shanghai, China). The sludge was pre-sheared for 5 min at a shear rate of 5 s\(^{-1}\), followed by a 10 min operation at a shear rate of 600 s\(^{-1}\). In this study, the thixotropic behavior of the sludge was quantified using the thixotropic kinetic coefficient method. Under a constant shear rate, the temporal changes in sludge viscosity were normalized (using the dimensionless form) and can be represented as follows:

\[
\frac{\eta - \eta_e}{\eta_0 - \eta_e} = e^{-Kt}
\]

where \(K\) is the thixotropic kinetic coefficient and \(\eta, \eta_0,\) and \(\eta_e\) represent the shear viscosity (Pa \cdot s) at the moment \(t\), at the initial moment, and when the steady state is reached, respectively. The value of \(K\) can be obtained by fitting a time-normalized viscosity scatter plot to it and using it as a basis for evaluating thixotropy; the smaller the thixotropic kinetic coefficient \(K\), the greater the thixotropy.

3. Results and Discussion

3.1. Determination of the Optimal Conditioning Agent Conditioning Conditions

Optimal conditioning conditions for individual coagulants and flocculants were determined based on the filter cake solids content, as depicted in Figure 1. From Figure 1a, it can be observed that the cake solids content first increased and then decreased with an increase in PAM dosage. When the dosage was 3‰, the cake’s solids content reached its maximum value of 34.81%. Initially, PAM promoted the aggregation of sludge colloidal particles through charge neutralization and adsorption bridging mechanisms and converted hydrophilic colloids into hydrophobic colloids through hydration, thereby improving the dewatering performance of sludge [20]. However, when excessive PAM was added, the excess polymer network structure wrapped around the already-formed destabilized particles, causing electrostatic repulsion due to positive charges to re-stabilize the destabilized particles’ solids content. In addition, the excess long-chain PAM enhanced the adsorption bridging effect between the sludge flocs, forming a more compact floc structure that encapsulated some water, making it difficult to release [21]. The solids content of the sludge cake increases and then slowly decreases with increasing PAC dosage. When the dosage
was 6%, the cake’s solids content reached a peak (33.89%). PAC is mainly hydrolyzed to produce polymeric cations of different degrees of aggregation. The polar active groups on the surface of PAC reacted with the colloidal particles in the sludge to achieve high charge neutralization, accelerated the release of bound water in sludge particles, and adsorbed and bridged to reduce the formed gel layer, thereby promoting sludge particle destabilization and settling [22]. However, when excessive PAC was added, the metal ion complexes covering the sludge particles caused repulsion between the particles, weakening the charge neutralization. Moreover, these polymers adsorbed free water, making it difficult for water to flow out, resulting in a decrease in solids content. However, due to the presence of a large number of aluminum hydroxyl binding sites in PAC itself for adsorbing sludge particles, the cake solids content was still maintained above 30% [23]. Compared to PAC, PFS had stronger cost-effectiveness and applicability. With the increase in PFS dosage, the cake solids content of conditioned sludge first increased and then tended to stabilize. When the dosage was 10‰, the cake’s solids content reached its maximum value of 33.83%. PFS hydrolyzed to produce substances such as polymeric multi-nuclear complexes, which interacted with the sludge colloidal particles through processes such as charge neutralization, adsorption bridging, and net capture and entanglement. This promoted the flocculation of colloidal particles and the release of adsorbed water, thereby improving the cake’s solids content [24]. When the PFS dosage further increased, the size of the sludge flocs reached a stable state, and the flocs provided colloid protection during the stable period, resulting in minimal changes in the cake solids content even at high dosages.

![Graphs showing effects of conditioning conditions on solids content](image-url)

**Figure 1.** Effect of various conditioning conditions on the solids content of digested sludge: (a) conditioning agent dosage, (b) stirring speed, (c) agitation time.

During the sludge conditioning process, the stirring speed has a significant impact on the dewatering performance indicators of the sludge. Appropriate stirring speed facilitates the collision and aggregation of sludge flocs, promoting thorough mixing of sludge particles with conditioning agents, thus accelerating floc formation and achieving adsorption aggregation of destabilized particles [25]. In the experiments, all groups were
controlled with a 5 min stirring time, using the optimal dosages of conditioning agents and operating at varying stirring speeds. The results, as shown in Figure 1b, indicate that as the stirring speed increases, the filter cake solids content of each group initially rises, followed by a rapid decline. For the sludge conditioned with PAM, PAC, and PFS, the optimal stirring speeds were 450 rpm, 450 rpm, and 600 rpm, resulting in filter cake solids contents of 35.69%, 33.64%, and 35.01%, respectively. At lower speeds, the conditioning agent first in contact with the sludge combines with the upper-layer sludge to form flocs that float on the surface. This prevents subsequently added conditioning agents from penetrating the sludge and results in a top-thick, bottom-thin appearance after stirring. At higher speeds, the initially formed sludge flocs are disrupted, and adsorbed chains are mechanically damaged, reducing the bridging ability of the conditioning agents and causing floc degradation [26].

Sludge mixing systems need to achieve significant particle aggregation in a relatively short time, where mixing action influences the stretching, dispersion, and active collision of conditioning agent chains throughout the system [27]. Adequate mixing time ensures thorough mixing of sludge particles with conditioning agents. In the experiments, each group used the optimal conditioning agent dosage and stirring speed and conducted tests with varying mixing times. The results, as shown in Figure 1c, reveal that with increasing mixing time, the filter cake solids content of sludge conditioned with PAM, PAC, and PFS initially rises and then rapidly declines. The optimal mixing times for these sludges were 11 min, 8 min, and 8 min, respectively, resulting in filter cake solids contents of 30.84%, 33.46%, and 32.42%. When the mixing time is too short, the conditioning agents fail to react sufficiently with the sludge, leading to poorer dewatering performance. Conversely, when the mixing time is too long, the ongoing shear strength disrupts the settled large flocs, causing them to return to the sludge surface, reducing sedimentation efficiency, and subsequently affecting the sludge’s dewatering performance [28].

3.2. Effect of Pretreatment on Sludge Dewatering Performance Based on Particle Size and Solids Content

The particle size distribution of sludge flocs is commonly considered a key factor influencing sludge dewatering performance [29]. According to the study by Zhou et al. [30], smaller sludge particles increase sludge viscosity and easily block water passage in the cake and filter cloth, thus increasing sludge filtration resistance. It has also been found that a high proportion of smaller particles in sludge flocs reduces their strength, leading to the collapse of water channels during shear processes and weakening the dewatering efficiency [13]. Therefore, the impact of the conditioning agent dosing sequence on sludge filtration capacity according to particle size evaluation is shown in Figure 2. After conditioning, the particle size of the sludge was further increased, thereby enhancing its dewatering performance compared to the original sludge particle size. For example, the median particle sizes of sludge with PAC-PAM and PFS-PAM dosing sequences reached 78.87 µm and 78.09 µm, respectively. It is worth noting that the dewatering results shown in Figure 3 were consistent with this, demonstrating that the effect of dosing the coagulant (PAC, PFS) before the flocculant (PAM) was better than dosing the flocculant before the coagulant (PAM-PAC/PFS). This indicated that the dosing sequence of conditioning agents had a significant impact on sludge filtration performance, with a preference for better dewatering performance in the coagulation–flocculation process compared to the flocculation–coagulation process. This was because adding the coagulant first released a large number of polar groups and charged colloids, which neutralized the negative charge on the surface of sludge particles through diffusion and electrostatic attraction and inhibited the hydrolysis and ionization of carboxyl and phosphate groups in the sludge, thereby reducing the content of negative ions in sludge flocs [31]. Meanwhile, under the effects of compressed double layers and net capture and entanglement, the van der Waals forces between sludge flocs were reduced, resulting in the destabilization of a larger number of sludge flocs. At this stage, adding the flocculant allowed it to act as a medium, forming a network to aggregate these flocs through adsorption bridging, electrostatic reactions, and
hydrogen bonding forces, further promoting the formation of larger and stronger secondary flocs, thereby enhancing the sedimentation performance of sludge flocs [32].

![Figure 2](image1.png)

**Figure 2.** Effect of conditioning agent dosing sequence on sludge particle size.

![Figure 3](image2.png)

**Figure 3.** Effect of different conditioning dosing sequences on the solids content (%) of the cake after 10 min, 15 min, and 20 min of sludge filtration under vacuum at 0.08 MPa.

The experiment investigated the effect of the conditioning agent addition sequence on sludge dewatering efficiency by measuring the cake solids content. After 15 min of filtration at 0.08 MPa, the cake solids content of the conditioned sludge is shown in Figure 3. Under the PAC-PAM and PFS-PAM sequences, the cake solids content reached 34.98 ± 0.21% and 35.49 ± 0.2%, respectively. In contrast, the cake solids content was lower under the PAM-PAC and PAM-PFS sequences, measuring 32.24 ± 0.22% and 32.65 ± 0.33%, respectively. These results were consistent with Figure 3. At filtration times of 10 min and 20 min, the cake solids content of the sludge conditioned under the PAC-PAM and PFS-PAM sequences was higher than that conditioned under the PAM-PAC and PAM-PFS sequences, although...
the difference was not significant. At a filtration time of 10 min, the PAC-PAM and PFS-PAM sequences achieved cake solids contents of 33.68 ± 0.31% and 34.94 ± 0.26%, respectively, which were 6.53% and 2.48% lower than the dewatering rates under this sequence at 20 min. This indicated that combined conditioning could improve the sludge dewatering efficiency. Furthermore, under the conditioning sequence of coagulant–flocculant, there was a significant enhancement in the degree of floc disruption in the digested sludge, resulting in the release of more bound water as free water, and consequently, extending the filtration time further enhanced the dewatering efficiency of digested sludge [8]. The results also showed that the conditioned sludge had lower moisture content under the coagulant–flocculant sequence than the flocculant–coagulant sequence, indicating higher cake solids content under the former sequence. These results revealed that the co-treatment of coagulant and flocculant significantly enhanced the dewatering performance of digested sludge, and the digested sludge with the coagulant–flocculant process demonstrated better dewatering performance than that with the flocculant–coagulant process.

3.3. Composition of EPS

Mikkelsen and Keiding [33] discovered that the chemical composition of sludge flocs is a key influencing factor in sludge dewatering, with EPS playing the most significant role. Subsequently, Houghton et al. [34] found that the optimal dewatering performance of different sludges corresponded to specific EPS content. Yuan et al. [35] indicated that the hydrophilicity and hydrophobicity of sludge flocs, as well as the surface charge, zeta potential, and stability of sludge floc structure, depend on the ratio of polysaccharides to proteins in EPS, which aligns with the theoretical proposition by Chen et al. [36] that the protein-to-polysaccharide ratio in EPS may affect sludge dewatering performance. The components of EPS (SEPS, LBEPS, and TBEPS) and the changes in polysaccharides and proteins within them were determined after pretreatment of different sludges.

Figure 4a shows that SEPS had the highest content among the different EPS layers. After combined conditioning, the EPS content in the conditioned sludge decreased significantly compared to sludge conditioned with a single conditioning agent, with a noticeable decrease in the SEPS layer. Compared to the original sludge, the concentration of SEPS in the conditioned sludge decreased by 48.32%, 52.48%, 47.43%, and 51.49%, respectively. The sludge conditioned under the PAC-PAM and PFS-PAM sequences showed a greater reduction in SEPS concentration, indicating better dewatering performance associated with the SEPS layer. The LBEPS and TBEPS layers also exhibited some reduction after combined conditioning, although the decrease was not significant. Some studies have collectively referred to LBEPS and SEPS as mucous EPS, which accounted for 18–40% of the total EPS content, and the removal of mucous EPS could lead to a 40% decrease in sludge resistance to filtration [37]. It was widely recognized that changes in mucous EPS significantly affected sludge filtration performance, and the content of mucous EPS was consistently related to sludge dewatering performance. The concentration of each EPS component in the sludge subjected to combined conditioning was lower than that in the sludge treated with a single conditioning agent, indicating that combined conditioning could disrupt and adsorb as much EPS as possible from the sludge, retaining it in the sediment. The performance of organic matter removal was significantly better than that of single-conditioning agent treatment, consistent with the research findings by [23]. According to the extended DLVO theory [38], the energy barrier between high-concentration SEPS and sludge colloids was related. When a high concentration of SEPS existed, the dispersed sludge needed sufficient energy to overcome this barrier for flocculation. The hydrolysis products of inorganic coagulants first interacted with soluble organic matter before reacting with sludge particles and combining with LBEPS. Studies showed [39,40] that when the LBEPS concentration was too high, the loosely structured flocs composed of LBEPS could reduce the density difference between the solid and liquid phases, leading to weakened binding strength between cells and resulting in poorer flocculation and dewatering efficiency. Therefore, reducing the concentrations of SEPS and LBEPS was crucial for improving sludge dewatering performance,
and the reduction in SEPS concentration was a prerequisite for more efficient reactions with LBEPS by the conditioning agent. Under the conditioning sequence of coagulation–floculation, the total content of SEPS and LBEPS in the sludge significantly decreased compared to the original sludge, resulting in good dewatering performance. Anaerobic storage of activated sludge was commonly employed in wastewater treatment, but it could lead to sludge decomposition and the release of SEPS. Some studies [23] suggested that shortening the anaerobic storage time could potentially avoid sludge decomposition and maintain dewaterability. In addition, the sludge concentration process could also remove SEPS and increase the solids concentration.

![Figure 4](image.png)

**Figure 4.** Effect of different conditioning conditions on (a) the concentration of EPS in each layer; (b) the protein (PN) and polysaccharide (PS) content of SEPS, LBEPS, and TBEPS.

Figure 4b illustrates the changes in soluble polysaccharides (SPs) and soluble proteins (SPr) in different EPS layers after combined conditioning. It could be observed that the main components in each EPS layer were proteinaceous substances, followed by polysaccharides. This was consistent with the findings of [41], indicating that the protein in EPS was primarily composed of hydrophilic substances in the sludge, thus having a much greater impact on dewatering performance compared to polysaccharides and humic substances. For the combined conditioning group, the concentration order of SPr in each layer was PAM-PFS > PAM-PAC > PFS-PAM > PAC-PAM, indicating a strong positive correlation between the decrease in SPr concentration and the improvement in sludge dewatering performance. These results suggested that the coagulation–floculation process had a superior disruptive effect on sludge EPS compared to the flocculation–coagulation process. Furthermore, previous studies have confirmed that reducing the pH of the sludge, creating an acidic environment, could lead to a decrease in EPS and intracellular substances [16,42]. In this study, the decrease in solution
pH due to the dosage of inorganic coagulants’ hydrolysis might have been another factor contributing to the reduction in EPS and intracellular substances.

3.4. Zeta Potential and Particle Size

Elakneswaran et al. [31] showed that the aggregation and settling performance of sludge flocs are influenced by the zeta potential. A higher negative charge on the sludge leads to a more stable floc structure and lower dewatering efficiency. Additionally, adjusting the particle size distribution can improve the surface charge of sludge particles and the microstructure of sludge flocs [43]. Therefore, the changes in zeta potential and particle size were measured as shown in Figure 5. Compared to the original sludge with a zeta potential of −29.2 mV, all conditioning agents imparted a positive charge to the sludge. Furthermore, the coagulation–flocculation process exhibited better charge neutralization performance than the flocculation–coagulation process. As shown in Figure 5a, the sludge conditioned with PAC-PAM and PFS-PAM increased the zeta potential to −11.6 mV and −10 mV, while the sludge conditioned with PAM-PAC and PAM-PFS only increased to −15.1 mV and −14.5 mV. Considering that the finer anaerobic digested sludge particles were less likely to settle, the addition of coagulants first allowed the hydrolyzed cations from the coagulants to attach more fully to the colloidal particles for charge neutralization while coordinating with EPS to promote the compression of EPS gel structure and enhance the compressibility of sludge flocs. This provided more water pathways for water to escape from the sludge, and subsequently, the addition of flocculants with their strong bridging capabilities could achieve more efficient dewatering. On the other hand, if flocculants were added first, larger and denser aggregates were formed with the sludge particles during the initial reaction, which hindered the subsequent reaction with coagulants, greatly reducing the efficiency of combined conditioning. Therefore, after coagulation–flocculation conditioning, larger and more destabilized colloidal particle aggregates could be formed, leading to the release of a greater amount of bound water into the sludge, resulting in improved dewatering performance.

![Figure 5](image)

**Figure 5.** Effect of different conditioning methods on (a) sludge zeta potential and (b) particle size distribution (T = 25 °C).

As the absolute value of the zeta potential decreased, the electrostatic repulsion effect weakened, leading to an improvement in the aggregation of unstable colloidal particles [44]. Therefore, a similar trend was also observed in terms of particle size variation. As shown in Figure 5b, the particle volume distribution of these samples was as follows: PAC-PAM > PFS-PAM > PAM-PFS > PAM-PAC. These results indicated that the coagulation capability of the coagulation–flocculation process was superior to that of the flocculation–coagulation process.

3.5. Morphological Characteristics of Flocs

Figure 6 displays the typical structural morphology of sludge flocs after different pretreatments. Under the combined action of coagulants and flocculants, the irregular sludge
particles aggregated and formed dense sludge flocs. This phenomenon was consistent with the aforementioned physicochemical characteristics. Furthermore, significant differences were observed among different sequential conditioning processes. The flocs formed by PAC-PAM and PFS-PAM were noticeably denser than those formed by PAM-PAC and PAM-PFS. These differences are also demonstrated in Figure 7. Compared to the rough and loose original floc structure, the coagulant mainly promoted the formation of more compact agglomerates in the sludge, while the flocculant further facilitated the fragmentation of the sludge flocs. After conditioning through the coagulation–flocculation process, the number and size of permeable channels and the degree of fragmentation of the sludge flocs were significantly improved, thereby exhibiting good filterability and dewaterability. However, the sludge treated under the flocculation–coagulation process showed no significant changes. On the other hand, the sludge conditioned through the flocculation–coagulation process did not show noticeable changes. This might have been attributed to the higher proportion of smaller particles in the anaerobically digested sludge. When flocculants were added first, active collisions occurred between the flocculant chains and particles due to Brownian diffusion, fluid motion, and settling rate, leading to excessive bending of floc channels and subsequently deteriorating the dewatering performance of sludge flocs. Therefore, sludge treated via the coagulation–flocculation process exhibited significantly improved dewatering performance in filter cakes.

Figure 6. Microscopic morphology of sludge flocs under different conditioning sequences.
3.6. Sludge Rheology Curves

The viscosity ($\mu_a$) is the ratio between the shear stress ($\tau$) and the shear rate ($\gamma$) of sludge, which can be evaluated through sludge flow curves. It is a fundamental parameter for describing the liquid characteristics of sludge. As sludge is a pseudo-plastic non-Newtonian fluid, its viscosity varies with the applied shear stress (or shear rate). Therefore, apparent viscosity is introduced to describe its characteristics. The yield stress ($\tau_0$) refers to the minimum applied force required for the fluid–structure and network strength to weaken, initiating the flow of the fluid [19]. The yield stress is commonly used to characterize non-Newtonian fluids as it represents the structural resistance generated due to shear rate or stress. Researchers can gain insights into the material’s grid strength and structure using yield stress, which can be used to characterize sludge dewatering and flow behavior in pipelines. The consistency index ($k$) is a measure of viscosity but is not equal to the viscosity value. The higher the viscosity, the larger the consistency index. The flow behavior index ($n$) is a dimensionless coefficient. When $n > 1$, the fluid is yield-thickening and thickens with increasing shear; when $n < 1$, the fluid is yield-thinning and thins with increasing shear.

The variation in the viscosity and rheological properties of conditioned sludge with the

**Figure 7.** Scanning electron microscope images of raw sludge and sludge under different conditioning conditions.
shear rate was studied under different conditioning agent dosage sequences to verify the changes in sludge morphology. The viscosity of conditioned sludge at various shear rates and its rheological properties were studied to verify the changes in sludge morphology under different conditioning agent addition sequences. As shown in Figure 8a, both the original sludge and conditioned sludge exhibited a sharp decrease in viscosity at low shear rates, followed by a gradual decrease, finally reaching a shear-thinning characteristic and pseudo-plastic behavior. Additionally, it can be observed from Figure 8b that the shear stress under the sequence of PAC-PAM and PFS-PAM was lower than that under the sequence of PAM-PAC and PAM-PFS, indicating a lower strength of the network formed during the coagulation–flocculation process [45]. This suggested that the flocs treated with the coagulation–flocculation process might have had a better ability to reduce the sludge network strength and improve dewatering efficiency. Furthermore, the rheological data from different conditioning agent addition sequences were fitted to describe and predict the sludge characteristics more efficiently through rheological properties. Table 2 showed that the yield stress of the coagulant–flocculant sequence group was higher than that of the reverse sequence group. The yield stress of the sludge conditioned with PFS and PAM together was higher than that of the PAC and PAM group, and the PFS-PAM sequence had a higher yield stress compared to the reverse sequence group, making it the highest among all batches. This is due to the higher ability of trivalent iron ions in PFS to form complex ions, which can hydrolyze the sludge flocs to release their internal free water and bound water to the greatest extent through electrostatic neutralization and bridging effects. Therefore, this group also exhibits the best dewatering performance. From the consistency coefficient \( k \) and flow behavior index \( n \), it could be observed that the two groups conditioned with PFS and PAM had lower consistency and flow behavior indices close to 1, indicating that their viscosity and flowability were much better than those of the PAC and PAM conditioned groups.

According to the research [46], below the critical shear stress, the forces between colloids in sludge tended to reconstruct the solid structure, while the shearing forces tended to disrupt the solid structure. Once the critical shear strength is reached, the solid structure completely collapses, and the fluid begins to flow. In practical production, if the shear stress at the pipe wall is not sufficient to maintain uniform flow, the thixotropic effect can cause pipeline transport to be affected by blockages. Therefore, the variation in sludge flow characteristics over time must be considered in the design of pipelines and pumping systems. As the shear stress generated during continuous flow is a power function of TS, this phenomenon worsens with an increase in sludge solid concentration. Additionally, thixotropic behavior can cause sludge to accumulate and remain for a long time in mixing tanks or reactors, forming dead zones if improper shearing occurs, which is undesirable in engineering. Therefore, a good understanding of thixotropy is crucial for developing efficient stirring and mixing mechanisms to optimize the treatment process at the lowest cost.

To quantify the thixotropy of sludge under different conditioning agent dosage sequences, the structural model proposed by [47] was used to assess the thixotropy of sludge. The thixotropic kinetic coefficient \( K \) and normalized viscosity changes are shown in Table 3 and Figure 8c. The goodness of fit \( (R^2) \) for all batches of conditioned sludge thixotropy was greater than 0.9, indicating a good fit of the model. Furthermore, it could be observed that the values of \( K \) for the two groups of the coagulation–flocculation combined conditioning process were lower than those of the two groups of flocculation–coagulation combined conditioning process. This indicated that the thixotropy of sludge was higher with the coagulation–flocculation combined conditioning and the ability of conditioned sludge to rebuild a floculent network structure deteriorated after shearing, along with a decrease in viscosity. This suggested that the network structure strength of conditioned sludge was low and more prone to flow, leading to a better release of moisture held within the floc, thus indicating better dewaterability.
Table 2. Results of fitting the Herschel–Bulkley model to the conditioned sludge for different conditioning agent dosing sequences.

<table>
<thead>
<tr>
<th>Sludge Samples</th>
<th>( \tau_0 ) (Pa)</th>
<th>( K ) (Pa s(^n))</th>
<th>( n )</th>
<th>( R^2 )</th>
<th>Ultimate Viscosity (Pa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS</td>
<td>2.60838</td>
<td>0.03241</td>
<td>0.75443</td>
<td>0.96694</td>
<td>0.02260</td>
</tr>
<tr>
<td>PAM-PAC</td>
<td>1.66037</td>
<td>0.13096</td>
<td>0.71736</td>
<td>0.98317</td>
<td>0.02181</td>
</tr>
<tr>
<td>PAC-PAM</td>
<td>1.67007</td>
<td>0.11747</td>
<td>0.73172</td>
<td>0.99141</td>
<td>0.02113</td>
</tr>
<tr>
<td>PAM-PFS</td>
<td>2.54025</td>
<td>0.01733</td>
<td>0.99315</td>
<td>0.97910</td>
<td>0.02045</td>
</tr>
<tr>
<td>PFS-PAM</td>
<td>2.58787</td>
<td>0.01668</td>
<td>0.99379</td>
<td>0.96656</td>
<td>0.02002</td>
</tr>
</tbody>
</table>

Table 3. Thixotropic kinetic coefficients of the conditioned sludge for different conditioning agent dosing sequences.

<table>
<thead>
<tr>
<th></th>
<th>RS</th>
<th>PAM-PAC</th>
<th>PAC-PAM</th>
<th>PAM-PFS</th>
<th>PFS-PAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thixotropic kinetic coefficients K</td>
<td>0.00708</td>
<td>0.00480</td>
<td>0.00462</td>
<td>0.00459</td>
<td>0.00442</td>
</tr>
<tr>
<td>Goodness of fit (R(^2))</td>
<td>0.91405</td>
<td>0.98392</td>
<td>0.97889</td>
<td>0.97516</td>
<td>0.96637</td>
</tr>
</tbody>
</table>

3.7. Mechanistic Analysis of Dehydration Performance

Based on the above experimental results and analysis, a mechanistic analysis was proposed about the influence of the coagulation–flocculation conditioning sequence and flocculation–coagulation conditioning sequence on the dewatering performance of advanced anaerobically digested sludge. Under the coagulation–flocculation process, the
hydrolysis action of the coagulant could be fully utilized to release more water. The thermal hydrolysis anaerobic digestion of sludge promoted the transfer of a large amount of EPS from the solid phase to the liquid phase, resulting in a sudden increase in the soluble EPS content and an increase in the apparent viscosity of the sludge, thereby reducing its filtration performance (Figure 8a) [8]. Following the advanced anaerobic digestion process, the internal floc structure of the sludge ruptured, resulting in the release of a portion of bound water, which became free water. During the coagulation–flocculation process, when the coagulant was initially mixed with the floc particles, the coagulant reacted fully with the particles, accelerating the floc breakdown. The subsequently added flocculant could then efficiently bridge the destabilized particles. However, if the flocculant was added first, larger and denser aggregates could form with the sludge particles initially, which prevented the subsequent coagulant from functioning effectively. Therefore, after coagulation–flocculation conditioning, larger destabilized colloidal particle aggregates could be formed, allowing more bound water to be released into the sludge, resulting in improved dewaterability. These observations were consistent with previous studies, which had shown that the bound water content in the sludge system was a key factor affecting dewatering performance [16]. Consequently, the digestion sludge treated by the coagulation–flocculation process achieved significant improvements in both the filterability and dewatering performance of the sludge cake.

4. Conclusions

The influence of the coagulant–flocculant conditioning sequence on the dewatering performance of advanced anaerobically digested sludge was investigated. The main research findings are as follows:

The order of coagulant and flocculant addition has a significant impact on the dewatering performance of advanced anaerobically digested sludge, including its filtration performance, organic matter content, rheological properties, and filter cake moisture content. In the coagulation–flocculation process, the solid content in the filter cake increased by approximately 9% compared to the reverse order. Therefore, the coagulant should be added before the flocculant.

Compared with the flocculation–coagulation process, in the coagulation–flocculation process, the average particle size of digested sludge increased by approximately 13%. Moreover, the contents of polysaccharides and proteins in S-EPS decreased by approximately 31% and 11.2%, respectively. The surface porosity of sludge flocs increased, while the curvature decreased, leading to a significant improvement in filtration efficiency. Additionally, the solid content in the filter cake at 20 min was 6% higher than that at 10 min, indicating that appropriately extending the filtration time can further enhance the dewatering performance of sludge.

Digestive sludge processed through the coagulation–flocculation sequence exhibits improved flowability. During the dewatering process of sewage plant digesting sludge, the dewatering process can be adjusted based on the sludge’s flowability parameters.

The mechanism of the influence of the coagulation–flocculation sequence on the dewatering performance of digestion sludge was analyzed.

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