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Study of pretreatment with combined coagulants on sewage from municipal waste transfer stations

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Abstract

This study presents a comprehensive evaluation of twelve inorganic-organic composite coagulants for the pretreatment of complex, high-strength wastewater from municipal solid waste transfer stations. The sewage, characterized by significant variability in turbidity, COD, TN, and NH_3-N, poses considerable treatment challenges. Four inorganic coagulants (PAFC, PFS, PSAF, PAC) were combined with three polyacrylamide-based flocculants (APAM, CPAM, NPAM) and assessed for their removal efficiencies under optimized dosage and pH conditions. Results demonstrated that the PAC-NPAM combination achieved the highest overall performance, with removal rates of 98.4% for turbidity and 86.7% for COD, along with rapid floc settling. The PFS-CPAM system was particularly effective for ammonia nitrogen removal, while PSAF-based coagulants attained high COD reduction but poor decolorization. The findings highlight the synergistic mechanisms of charge neutralization and polymer bridging in composite coagulants, providing a practical and efficient pretreatment strategy to enhance the treatability of variable waste transfer station effluents and alleviate the load on downstream treatment processes.

Keywords: Waste transfer station effluent; Coagulation pretreatment; Inorganic coagulant; Organic coagulant; Combined coagulant.

Subject classification codes: include these here if the journal requires them

1. Introduction

The effective management of municipal solid waste (MSW) critically depends on the operation of transfer stations, which serve as pivotal nodes for waste consolidation and transport. A significant environmental challenge arising from these facilities is the generation of complex, high-strength wastewater, commonly termed refuse transfer station sewage [1]. This effluent stream is typically a composite of three primary sources: (1) refuse leachate, formed through moisture release, rainfall percolation, and mechanical compression during waste handling, which is characterized by elevated concentrations of organic matter, ammonia nitrogen (NH_3-N), heavy metals, and

biorefractory compounds [2]; (2) cleaning wastewater, originating from equipment and vehicle wash-down, contributing suspended solids, fats, oils, grease, and surfactants; and (3) incidental rainwater, which dilutes the stream but simultaneously amplifies hydraulic load and mobilizes pollutants, leading to considerable temporal variability in both quantity and quality . The overall effluent generation is influenced by waste composition, operational practices, and climatic conditions, resulting in a matrix that exhibits high organic strength, poor biodegradability, and fluctuating physicochemical properties. These characteristics necessitate robust, adaptable, and cost-effective treatment solutions.

Conventional management strategies for this wastewater encompass direct recharge (recirculation), which risks long-term salinity and pollutant accumulation; evaporation, an energy-intensive process susceptible to scaling; and comprehensive non-hazardous treatment involving advanced biological-physicochemical trains, which often entail high capital and operational costs [3]. While numerous treatment methods exist [4], many struggle with efficient removal of the specific pollutant profile found in this sewage, and cost-effectiveness remains a concern [5, 6]. Given the prevalent high concentration of poorly biodegradable organics and salinity, physicochemical pretreatment is frequently considered a prerequisite to enhance treatability and protect downstream processes [7].

Among physicochemical options, coagulation presents a particularly promising pretreatment technology due to its operational simplicity, rapid response to variable loads, and proven efficacy in aggregating colloidal particles, precipitating dissolved species, and removing a significant fraction of organic pollutants and color [8]. Notably, coagulation can also improve the biodegradability of recalcitrant streams, such as membrane concentrates from leachate treatment [9]. The process mechanisms, including charge neutralization, adsorption/bridging, and sweep coagulation, allow for the effective reduction of turbidity and organic load, thereby alleviating the burden on subsequent treatment stages. Its advantages of low capital investment, operational stability, and easy integration into existing treatment trains make it highly suitable for application in MSW transfer station sewage management[10]. However, the

performance of coagulation is highly dependent on coagulant selection and operational parameters (e.g., dosage, pH), especially for complex and variable matrices like transfer station sewage. A systematic evaluation and optimization of modern coagulant formulations, particularly inorganic-organic composites, for this specific application remains a knowledge gap in the literature.

To address this gap, this study conducts a comprehensive performance assessment and optimization of twelve distinct inorganic-organic composite coagulants for treating real-world MSW transfer station sewage. The specific objectives are: (1) to characterize the key physicochemical properties and temporal variability of the target wastewater; (2) to evaluate and compare the removal efficiencies of key pollutants (turbidity, COD, TN, and NH_3-N) for each composite coagulant; and (3) to identify the optimal dosage and pH conditions for the most effective coagulant combinations. The findings are expected to provide actionable insights for wastewater treatment engineers and operators, contributing to the development of more efficient, resilient, and sustainable pretreatment strategies for complex waste-derived wastewater streams.

2. Experimental materials and methods

2.1 Experimental samples and analysis

2.1.1 Experimental samples

The experimental sewage samples were collected from the Binjiang Development Zone Sanitation Service Center, located approximately 240 meters west of the intersection of Ningwu Avenue and Zhonghuan Avenue in Jiangning District, Nanjing City, Jiangsu Province. As depicted in Fig 1, the raw wastewater from the municipal waste transfer station exhibits a distinct yellowish-brown appearance, containing substantial amounts of suspended garbage residues. The surface of the wastewater is typically covered with an oily film, foam, and low-density floating debris, accompanied by a pronounced pungent odor. These visual and olfactory characteristics indicate a high level of organic and particulate pollution, which is consistent with the complex composition typical of waste transfer station effluents.



Fig 1. Overview of the sampling site and characteristics of the raw sewage: external view of the Binjiang development zone sanitation service center (a); appearance of the raw sewage collected from the refuse transfer station (b and c), showing its yellowish-brown color, suspended solids, and surface scum.

2.1.2. Analysis of waste transfer station sewage

The study systematically evaluated the performance of different combined coagulants in treating wastewater from municipal solid waste transfer stations through Coagulation experiments. The objectives were to assess the removal efficiency of key pollutants by measuring water quality parameters such as turbidity (Tur), chemical oxygen demand (COD), total nitrogen (TN), and ammonia nitrogen (NH_3-N) after treatment, and thereby determine the optimal coagulant concentration, dosage, pH, and sedimentation time, so as to identify the most effective coagulation pretreatment process for this type of wastewater.

The sewage from waste transfer stations exhibits complex and highly variable characteristics due to its composite origin[11]. To systematically assess its quality, raw water samples were collected daily at 8:00 AM from March 13 to 19, 2024 at a transfer station in Nanjing. Key parameters, including pH, turbidity, COD, TN, and NH_3-N, were analyzed (Table 1).

Data revealed significant fluctuations in all measured parameters. The pH was consistently acidic (4.66-6.81), attributed to anaerobic fermentation of organic waste [12]. Tur (136.2-833.6 NTU) and COD (922-11988 mg/L) varied drastically, influenced by factors such as waste composition, cleaning activities, and rainfall dilution (e.g., notably lower values on March 19). Nitrogen species (TN: 30.0-233.2 mg/L; NH_3-N: 4.80-29.30 mg/L) also showed considerable variation. The non-linear relationship between TN and NH_3-N suggests complex transformations of nitrogenous compounds, affected by waste storage time and local redox conditions . In summary, the sewage is characterized by high and variable concentrations of pollutants, presenting a challenge for stable treatment. This variability underscores the need for a robust and adaptable pretreatment process, such as coagulation, which can effectively handle such fluctuations and improve subsequent treatment stages .

Table 1. Variations of effluent quality from the waste transfer station

Date	Tur (NTU)	COD (mg/L)	TN (mg/L)	NH_3-N (mg/L)	pH
3.13	500	3576	60.2	28.04	4.66
3.14	320.6	4576	73.6	14.72	5.09
3.15	535	5294	53.6	16.58	4.82
3.16	136.2	3346	65	16.12	5.87
3.17	833.6	11988	233.2	27.54	4.93
3.18	657.2	10248	167.8	29.3	5.09
3.19	448.8	922	30	4.8	6.81

2.2 Chemical reagents and instruments

The chemical reagents and instruments, along with their specifications and suppliers, are summarized in Table S1 and Table S2. The study primarily investigated four inorganic coagulants including Polymeric aluminum ferric chloride (PAFC), polymeric ferrous sulfate (PFS), polymeric aluminum silicate ferric (PSAF), and

polymeric aluminum chloride (PAC) and three polyacrylamide-based organic flocculants of anionic polyacrylamide (APAM), cationic polyacrylamide (CPAM, 40% ionicity), and nonionic polyacrylamide (NPAM). These were selected for their widespread use and efficacy in water treatment processes. Standard reagents for water quality analysis, including COD digestion vials and reagent tubes for total nitrogen (TN) and ammonia nitrogen (NH_3-N) determination, were also employed to ensure accurate and comparable measurements. The water used in the experiment was deionized water, while the determination of calcium and magnesium content employed ultrapure water.

2.3 Experimental design

The experimental design was structured to systematically evaluate twelve inorganic-organic composite coagulants, each formed by combining one of four inorganic coagulants (PAFC, PFS, PSAF, PAC) with one of three polyacrylamide-based organic flocculants (APAM, CPAM, NPAM). Coagulation tests were conducted in batch mode using 500 mL of raw wastewater. For each test, a specified dosage of inorganic coagulant was added under rapid mixing (300 r/min, 10 min), followed by pH adjustment (range 6–11) using NaOH. Subsequently, a given volume of organic flocculant was introduced under slow mixing (200 r/min, 30 s). After a defined settling period, the supernatant was collected for analysis of turbidity, COD, TN, and NH_3-N. Key operational parameters, including coagulant/flocculant dosage and pH, were optimized through preliminary jar tests based on floc formation, settling characteristics, and pollutant removal efficiency. All experiments were performed in duplicate, alongside control tests (without coagulant), to ensure reliability and to establish baseline values.

2.4 Analysis methods

Water quality parameters were analyzed using standardized procedures. pH was measured with an electrode method (Raycom PHS-3C pH meter), and turbidity was determined directly using a portable turbidimeter (Hach 2100Q). All plotting and data processing were performed with Origin 2018.

COD was determined by Hash Rapid test method U.S. Environmental Protection Agency (USEPA) colorimetric method with a range of 200~15000 mg/L. The COD

value read should be multiplied by 10 for the corresponding COD value of the original sample at the end. TN was determined using the high range persulfate oxidation method (Test'N TubeTM tube) of the Hash Rapid Test Method, with a selected range of 2 to 150 mg/L. NH_3-N was determined by the high range salicylic acid method (Test'N TubeTM tube) of the Hash rapid test method, with the selected range of 0.4 to 50.0 mg/L. COD, TN and NH_3-N values were read at the end and the results were expressed in mg/L.

The removal efficiency (η, %) for Tur, COD, TN, and NH_3-N were calculated according to the following equation:

$$\eta = \frac{C_1 - C_0}{C_0} \times 100\%$$

Where, C_0 indicates the concentration of Tur, COD, TN, and NH_3-N in in raw emulsified wastewater (NTU, mg/L); C_1 indicates the concentration of turbidity, COD, TN, and NH_3-N in the emulsified wastewater (mg/L) after the addition of the agent; η indicates the rate of pollutant removal.

3. Results and discussion

3.1 Coagulation pretreatment using PAFC in combination with PAM

Coagulation is a cornerstone physicochemical pretreatment strategy for high-strength, complex wastewaters like those from municipal waste transfer stations. Its efficacy stems from the ability to remove colloidal particles, a significant portion of organic matter, and certain nutrients through destabilization and aggregation. Inorganic metal salt coagulants, such as Polymeric aluminum ferric chloride (PAFC), are highly effective in neutralizing the negative surface charges typically borne by contaminants (charge neutralization) and enmeshing particles through hydroxide precipitate formation (sweep flocculation) [13]. However, the flocs formed by inorganic coagulants alone can be small and fragile, leading to slow settling. This is where organic polymeric flocculants, like Polyacrylamide (PAM), play a critical role. By adsorbing onto multiple destabilized particles, these long-chain polymers act as bridges, fostering the formation of larger, stronger, and faster-settling aggregates [14]. This section presents a systematic investigation into the pretreatment performance of PAFC when sequentially combined with three ionic variants of PAM including Anionic (APAM), Cationic (CPAM), and

Nonionic (NPAM) which applied to raw sewage from a waste transfer station, aiming to identify the most effective pairing and its optimal operational conditions.

3.1.1 PAFC and APAM coagulation pretreatment studies

According to the dosage combinations of PAFC and APAM listed in Table S3, the transfer station sewage was treated. The solid-liquid separation performance after treatment is illustrated in Fig. 2a. During the experiment, it was observed that with increasing PAFC dosage, a large number of visible flocs rapidly formed in the wastewater. Initially fine, these flocs quickly coalesced into large, dense "flocs" upon stirring and APAM addition, significantly accelerating the settling rate. A clear mud-water interface formed within 2-3 minutes.

The results show that the effluent Tur was drastically reduced, with removal rates consistently above 97% after combined use of PAFC and APAM (Fig. 3a, Table S4). The optimal dosing group (Group 2: PAFC 7 mL + APAM 3 mL, pH=10) produced the largest and most compact flocs. After settling, the supernatant was transparent and colorless, in stark contrast to the original wastewater's yellowish-brown, turbid state with oily films and foam. The COD removal rate was approximately 74.1%, with TN and NH_3-N removal rates of 37.7% and 28.3%, respectively.

PAFC hydrolyzes in water to generate various high-valency polymeric cations (e.g., hydrolysis products of Fe^{3+}, Al^{3+}), which effectively neutralize the negative surface charge of colloidal particles in the wastewater, compress the double electrical layer, and promote colloidal destabilization [15]. Polymeric aluminum ferric chloride (PAFC), an inorganic polymer coagulant, possesses strong charge neutralization and adsorption-bridging capabilities. When combined with Anionic Polyacrylamide (APAM), it further enhances floc formation and settling performance. APAM, as a long-chain polymer, bridges the destabilized colloids to form larger flocs, accelerating sedimentation. Their synergy not only improved turbidity and COD removal but also contributed to the adsorption and co-precipitation of some nitrogenous pollutants. The higher TN removal compared to NH_3-N may be related to the entrapment and adsorption of organic nitrogen by the flocs.

3.1.2 Coagulation pretreatment using PAFC in combination with CPAM

According to the dosage combinations of PAFC and Cationic Polyacrylamide (CPAM) listed in Table S5, the transfer station sewage was treated. The solid-liquid separation performance after treatment is illustrated in Fig. 2b. Compared to the APAM combination, CPAM addition led to faster floc formation, but the flocs appeared slightly looser. CPAM carries its own positive charge. When combined with PAFC, it can produce a stronger charge neutralization effect. Under optimal conditions (pH=11, PAFC 3 mL + CPAM 1 mL), cloud-like flocs formed rapidly after stirring. The settled supernatant was clear, but the sludge volume at the bottom was somewhat larger. Fig. 3b shows removal rates of 96.9% (Tur), 80.6% (COD), 30.5% (TN), and 15.2% (NH_3-N) for this combination (Table S6). While COD removal was effective, NH_3-N removal was relatively low.

The positive charge characteristic of CPAM further enhances the neutralization and adsorption of negatively charged pollutants (e.g., humic acid, colloidal organic matter). The relatively high COD removal rate (>80%) indicates good removal capability for dissolved organic pollutants. The lower NH_3-N removal rate is likely because ammonia nitrogen exists primarily in ionic form and is not sufficiently adsorbed or precipitated during the coagulation process.

3.1.3 Coagulation pretreatment using PAFC in combination with NPAM

According to the dosage combinations of PAFC and Nonionic Polyacrylamide (NPAM) listed in Table S7, the transfer station sewage was treated. NPAM primarily relies on the amide groups on its molecular chain to adsorb particles via hydrogen bonding, exhibiting strong bridging ability but weak charge neutralization. The coagulation process with this combination was relatively unstable. At low dosages (Groups 1, 2), almost no visible flocs formed, or very little supernatant was produced. Increasing the dosage (Groups 3, 4) resulted in floc formation and supernatant, but the flocs were loose, settled slowly, and the supernatant remained deeply colored (light yellow) with poor transparency (Fig. 3c, Table S8). Measurable samples were only obtained at higher dosages (PAFC 11 mL + NPAM 7 mL, pH=9), with removal rates of 80.4% (turbidity), 72.3% (COD), 38.5% (TN), and 17.2% (NH_3-N).

Under the experimental pH conditions, the hydrolysis degree of amide groups in

NPAM is low, and it mainly functions through long-chain bridging [16]. The moderate TN removal might be due to specific adsorption of certain nitrogenous organics by NPAM. However, the difficulty in floc formation and low separation efficiency indicate poor compatibility of this combination with the specific wastewater matrix, possibly due to interference from the complex ionic composition and pH environment on hydrogen bonding.

3.1.4 Comparative Analysis

Among the three PAFC-organic coagulant combinations, distinct performance profiles emerged, governed by the interplay between charge neutralization and bridging mechanisms. The PAFC-APAM system demonstrated the most balanced performance, achieving high removal rates across all measured parameters (Tur >97%, COD: ~74%, TN: ~38%, NH_3-N: ~28%) while producing a clear, colorless supernatant and dense, fast-settling flocs. This synergy stems from the complementary roles of PAFC's multivalent cations (charge neutralization and destabilization) and APAM's long anionic chains (bridging and aggregation) [17]. The PAFC-CPAM combination showed a pronounced advantage in COD removal (~81%), likely due to enhanced adsorption of negatively charged organic matter by the doubly cationic system (PAFC cations + CPAM). However, its NH_3-N removal was the lowest (~15%) in this series. While floc formation was rapid, the flocs were looser, leading to slightly larger sludge volume. In contrast, the PAFC-NPAM system was the least effective and most unstable. Its performance was highly dosage-dependent and produced poor-quality supernatant with significant residual color. The lack of ionic charge on NPAM resulted in weak initial destabilization, relying solely on hydrogen bonding for bridging , which proved inefficient in this complex wastewater matrix. Therefore, for PAFC-based pretreatment, anionic (APAM) or cationic (CPAM) polyacrylamides are effective co-coagulants, with the choice depending on the target pollutant, Nonionic PAM is not recommended.

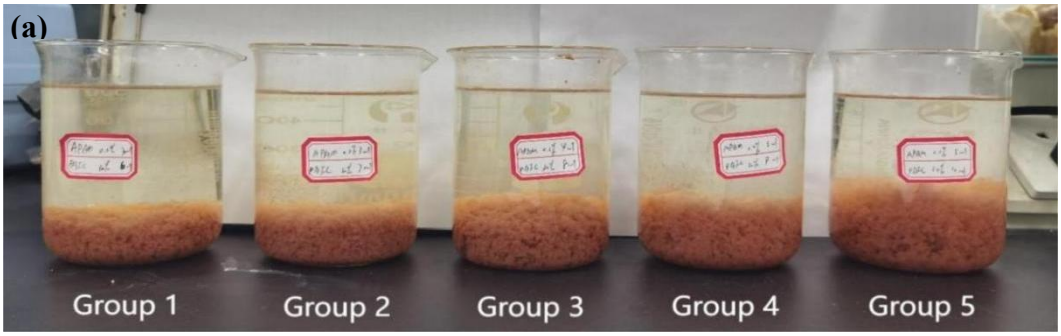


Fig. 2 Coagulation effect of PAFC and APAM composite (a), PAFC and CPAM composite (b), PAFC and NPAM composite (c)

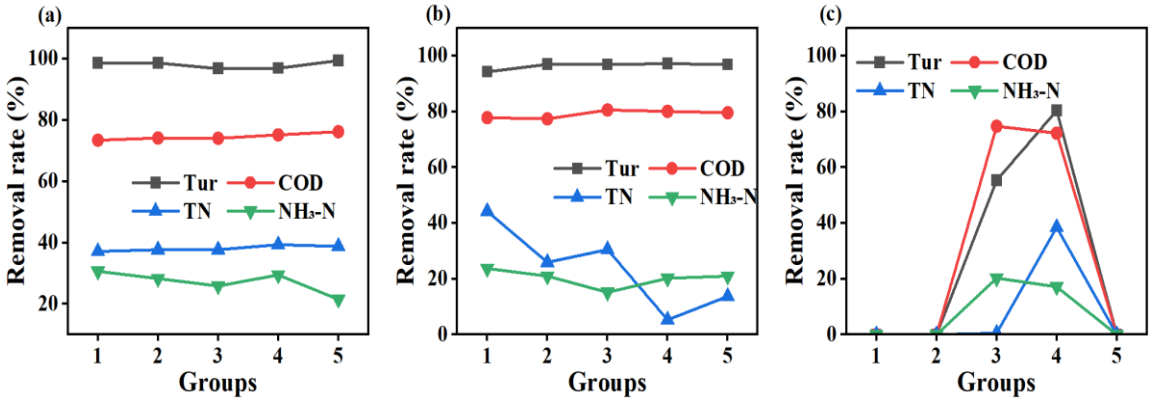


Fig. 3 Removal rates of efluent Tur, COD, TN and NH_3-N after coagulation pretreatment using PAFC and APAM composite (a), PAFC and CPAM composite (b), PAFC and NPAM composite (c).

3.2 Pretreatment study with combined coagulants of PFS and PAM

3.2.1 Coagulation pretreatment study of PFS and APAM

Based on the dosage combinations of Polyferric sulfate (PFS) and Nonionic polyacrylamide (NPAM) specified in Table S9, the transfer station sewage was treated. PFS has strong flocculation capability and a wide applicable pH range. Upon PFS addition, the wastewater color immediately changed from yellowish-brown to reddish-

brown. After adding APAM, dark brown, compact flocs formed, settling rapidly with a clear mud-water interface. The supernatant color was slightly deeper (light yellow) compared to using PAFC but had high transparency (Fig. 4a). Under conditions of pH=8, PFS 9 mL + APAM 6 mL, the removal rates of Tur, COD, TN and NH_3-N were 96.4%, 78.5%, 37.1%, and 23.9%, respectively (Fig. 5a, Table S10). the removal rate of NH_3-N was better than that in the PAFC system.

Hydrolysis products of PFS, such as $Fe(OH)_3$, possess a network structure that effectively adsorbs and encapsulates pollutants [18]. Combined with APAM, floc size increases, accelerating sedimentation. The relatively higher NH_3-N removal may be attributed to ion exchange or complexation between Fe^{3+} hydrolysis products and NH_4^+ [19].

3.2.2 Coagulation pretreatment study of PFS and CPAM

The combined dosage of PFS and cationic polyacrylamide (CPAM) is shown in the Table S11. The flocs generated by the PFS-CPAM combination were reddish-brown in color, with uniform morphology and a compact structure. However, the settled supernatant still exhibited a light reddish tint, indicating the presence of residual iron ions (Fig. 4b). As the dosage increased, the floc volume gradually expanded and the settling performance improved, although the color of the supernatant also deepened correspondingly, suggesting a slight rise in residual iron concentration with higher chemical addition (Fig. 4b).

As presented in Table S12 and Fig. 5b, the optimal treatment efficiency was achieved under the conditions of pH=8, with PFS at 2 mL and CPAM at 1 mL. At this dosage, the removal rates reached 94.9% for turbidity, 75.4% for COD, 32.3% for TN, and 30.6% for NH_3-N. The cationic nature of CPAM acts synergistically with the polynuclear cations formed from PFS hydrolysis, collectively enhancing charge neutralization and sweep flocculation. The further improvement in NH_3-N removal observed in the experiment may be attributed to the electrostatic adsorption of ammonium ions by CPAM. This combined system not only strengthens coagulation but also demonstrates an auxiliary removal effect on dissolved nitrogen pollutants.

3.2.3 Coagulation pretreatment study of PFS and NPAM

The coagulation effect of this combination was extremely poor. Regardless of pH and dosage adjustments, the wastewater failed to form settleable flocs. Only a small amount of very fine suspended matter appeared, and the water remained uniformly turbid even after prolonged settling (Fig. 4c). Therefore, the combination of PFS and NPAM is not suitable for pretreatment of this type of wastewater. NPAM lacks charge neutralization capability, and the positive charge of PFS hydrolysis products within the experimental pH range may be insufficient to fully destabilize the colloids [20]. The two lack an effective synergistic mechanism to achieve destabilization and aggregation of colloidal particles.

3.2.4 Comparative analysis

The iron-based PFS exhibited different synergistic behaviors with PAMs compared to the aluminum-iron-based PAFC. A major advantage of PFS combinations was their consistently higher ammonia nitrogen removal (23-31%) compared to equivalent PAFC systems. This can be attributed to the specific affinity of iron hydrolysis products (e.g., $Fe(OH)_3$) for ammonium ions through mechanisms like adsorption or weak complexation.

The PFS-APAM combination again provided robust and reliable performance with excellent turbidity removal and good settling characteristics. The PFS-CPAM system offered a further boost in NH_3-N removal (~31%) but resulted in a supernatant with a residual reddish tint, indicating potential iron carry-over—a practical consideration for downstream processes. Critically, the PFS-NPAM combination failed completely, producing no settleable flocs. This underscores a fundamental incompatibility, suggesting that the hydrolysis species of PFS in this wastewater cannot effectively collaborate with the non-ionic bridging mechanism of NPAM under the tested conditions. PFS is a potent inorganic coagulant for this application, particularly when ammonia removal is a priority. APAM is the recommended organic co-coagulant for reliable performance. CPAM can be used for enhanced NH_3-N removal but may increase effluent color. NPAM should be avoided with PFS.

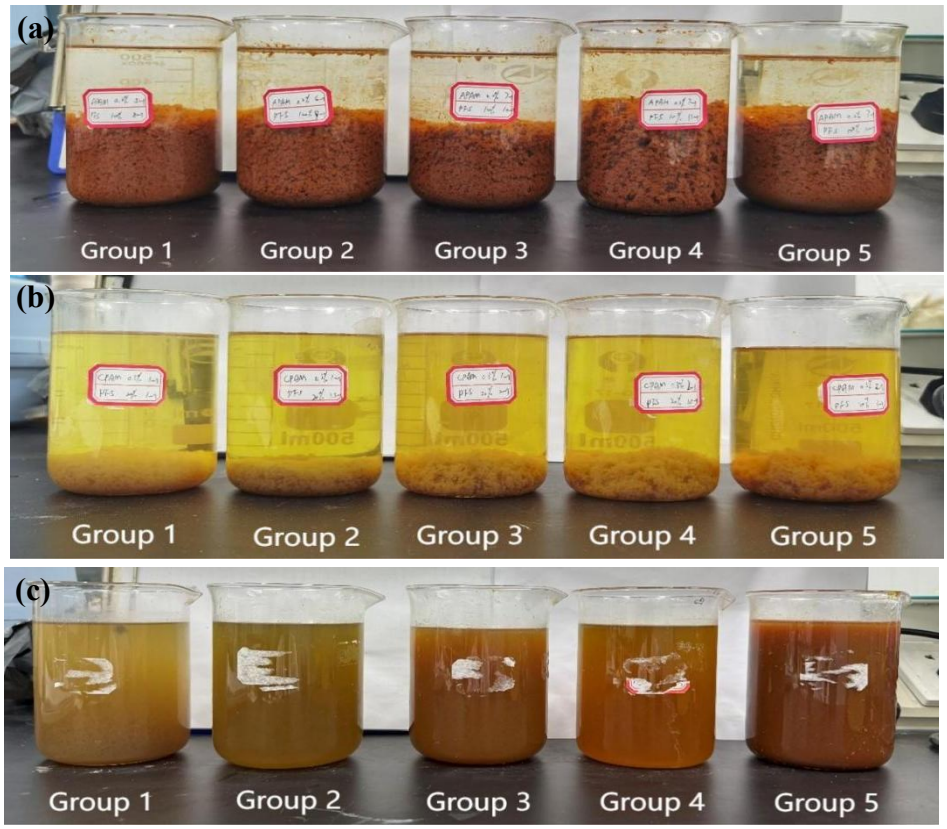


Fig. 4 Coagulation effect of PAFC and APAM composite (a), PAFC and CPAM 40 ionicity composite (b), PAFC and NPAM composite (c)

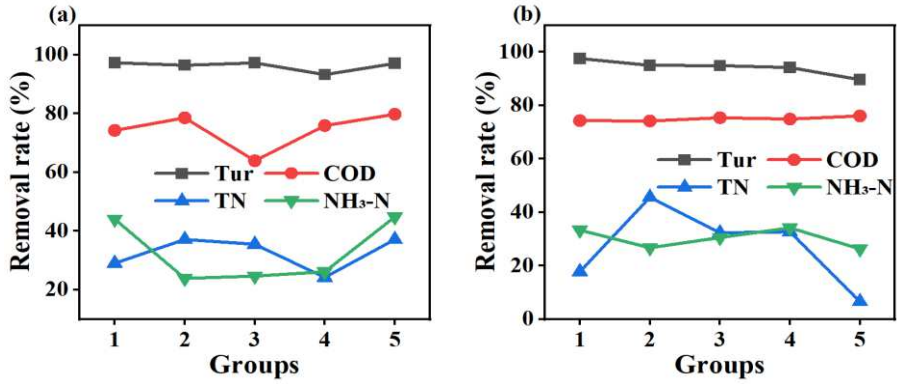


Fig. 5 Removal rates of efluent Tur, COD, TN and NH_3-N after coagulation pretreatment using PFS and APAM composite (a), PFS and CPAM composite (b).

3.3 Pretreatment study with combined coagulants of PSAF and PAM

3.3.1 Coagulation pretreatment study of PSAF and APAM

The specific dosage of the combined addition of polymeric aluminum silicate ferric (PSAF) and anionic polyacrylamide (APAM) is shown in the Table S13. PSAF possesses both adsorption and coagulation functions. After PSAF addition, the

wastewater viscosity slightly increased. Combined with APAM, a flocculent material was generated. These flocs were less compact than those formed by aluminum or iron salt coagulants, appearing loose and cotton-like, with moderate settling speed. A notable phenomenon was the poor color removal. Even under optimal conditions (pH=9, PSAF 12 mL + APAM 8 mL), the supernatant remained distinctly yellowish-brown (Fig. 6a), despite achieving removal rates of 98.6% (turbidity), 85.1% (COD), 36.7% (TN), and 17.2% (NH_3-N) (Table S14, Fig. 7a).

The silicate ions present in PSAF can enhance the network skeleton structure of flocs, improving the entrapment capability for colloids and fine suspended solids [21]. Its high COD removal rate might be related to the specific adsorption of organic matter by the polyaluminosilicate-ferric aggregates. However, its limited ability to remove colored dissolved organic matter (e.g., humic acids) results in high effluent color.

3.3.2 Coagulation pretreatment study of PSAF and CPAM

The combined dosage of PSAF and CPAM is shown in the Table S15. The flocs formed by the PSAF-CPAM combination exhibited superior settling characteristics compared to those generated by the PSAF-APAM system, demonstrating faster sedimentation rates and a more compact structure. Correspondingly, the supernatant clarity showed noticeable improvement, with a significant reduction in color and suspended solids. However, it did not achieve a completely optically clear solution, retaining a slight haze as illustrated in Fig. 6b.

Based on the data presented in Table S16 and Fig. 7b, the optimal treatment performance was attained under alkaline conditions at pH=9, with a dosage of 3 mL PSAF combined with 2 mL CPAM. This configuration yielded high removal efficiencies: 96.2% for Tur, 83.5% for COD, 38.3% for TN, and 18.6% for NH_3-N. The enhanced performance is attributed to the effective synergy between the cationic functional groups of CPAM and the polynuclear hydroxyl cations generated by PSAF hydrolysis. This cooperation strengthens the charge neutralization of colloidal pollutants and promotes the formation of larger, more settleable flocs through bridging and sweep flocculation mechanisms[22]. The notably higher removal rate of TN likely results from the co-precipitation and entrapment of nitrogen-containing organic

compounds within the growing floc matrix during the aggregation process.

3.3.3 Coagulation pretreatment study of PSAF and NPAM

The combined dosage of PSAF and NPAM is shown in the Table S17. This combination could form flocs with moderate settleability, but sludge production was extremely high, with settled sludge volume accounting for about one-third of the original water volume. Although supernatant was present, it was deeply colored with poor transparency (Fig. 6c). As shown in Table S18 and Fig. 7c, at pH=10, PSAF 11 mL + NPAM 6 mL, removal rates were 91.4% (turbidity), 82.3% (COD), 37.0% (TN), and 17.9% (NH_3-N). The bridging effect of NPAM assists PSAF in floc formation, but both have limited ability to remove hydrophobic colored substances. The high sludge production also implies higher operational costs, making this combination less economical.

The combined dosages of PSAF and NPAM evaluated in this study are detailed in Table S17. This reagent combination was capable of forming flocs with moderate settleability. However, a significant drawback was the excessively high sludge production, with the volume of settled sludge accounting for approximately one-third of the original wastewater volume. Although a supernatant layer was formed after settling, it remained deeply colored and exhibited poor transparency, as visually documented in Fig. 6c.

Performance data under optimal conditions, as summarized in Table S18 and Fig. 7c, indicate that at pH=10 with a dosage of 11 mL PSAF and 6 mL NPAM, the removal rates reached 91.4% for turbidity, 82.3% for COD, 37.0% for TN, and 17.9% for NH_3-N. The primary mechanism is attributed to the bridging effect of high-molecular-weight NPAM, which assists the metal hydrolyzates from PSAF in forming larger floc aggregates[23]. Nevertheless, both reagents possess a limited capacity for removing dissolved hydrophobic chromophoric substances, which explains the persistent color in the supernatant. Furthermore, the substantial sludge yield not only poses challenges for subsequent sludge handling but also implies significantly higher operational costs for dewatering and disposal. Consequently, despite its moderate treatment efficiency, this combination is considered less economical and practical for full-scale application.

3.3.4 Comparative analysis

PSAF-based combinations presented a unique profile, characterized by exceptionally high COD removal (82-85%) but persistently poor color removal. The silicate component in PSAF likely forms an extended network that efficiently traps and adsorbs organic molecules, explaining the high COD efficiency [8]. However, this structure seems less effective at removing the specific chromophoric dissolved organic compounds responsible for the yellow-brown color.

Regarding organic polymer choice, PSAF-APAM achieved the highest turbidity and COD removal but the worst supernatant color. PSAF-CPAM slightly improved color and settling but at the cost of a small reduction in COD removal. The PSAF-NPAM system was operationally problematic, generating an excessively large volume of loose sludge, which would pose significant challenges for sludge handling and disposal in a real-world plant, outweighing its decent removal rates. PSAF composites are highly effective for organic pollutant (COD) removal but are not suitable if decolorization is a primary treatment goal. APAM is the best performer for maximizing COD removal with PSAF, but the significant residual color must be considered. The high sludge yield with NPAM makes it an impractical choice.

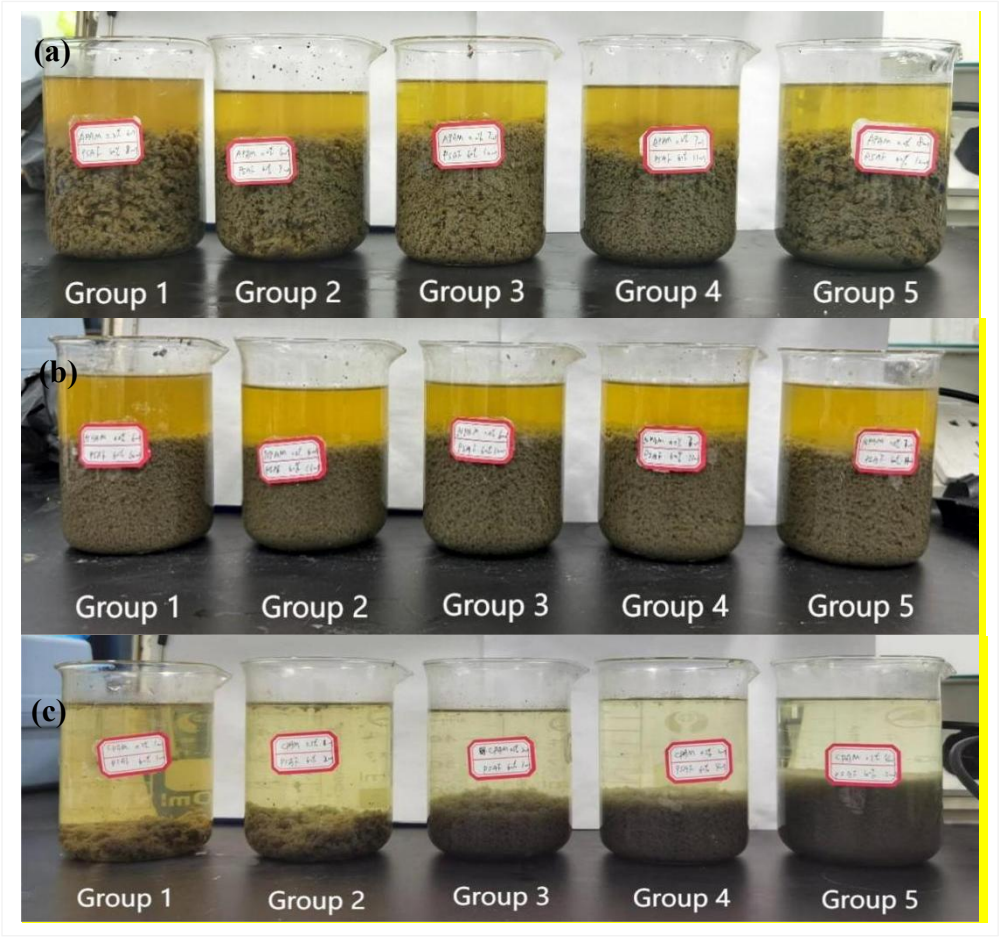


Fig. 6 Coagulation effect of PSFC and APAM composite (a), PSFC and CPAM 40 ionicity composite (b), PSFC and NPAM composite (c)

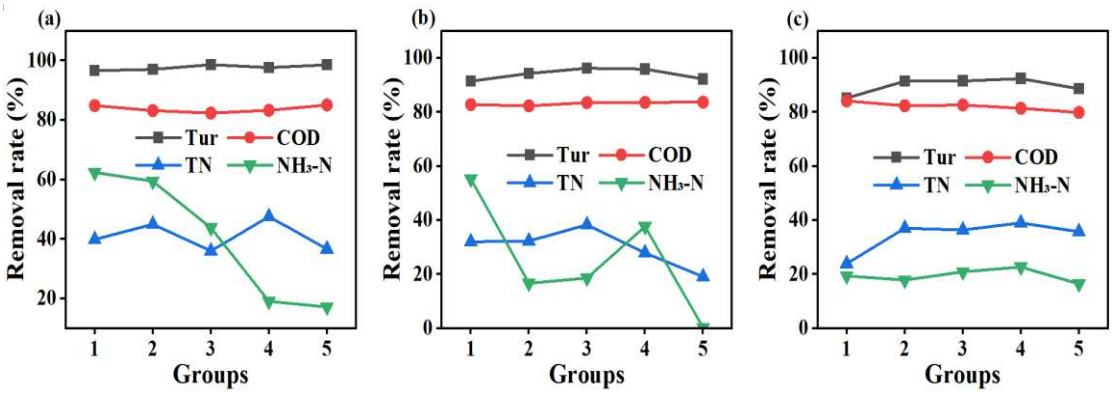


Fig. 7 Removal rates of efluent Tur, COD, TN and NH_3-N after coagulation pretreatment using PSFC and APAM composite (a), PSFC and CPAM 40 ionicity composite (b), PSFC and NPAM composite (c)

3.4 Pretreatment study with combined coagulants of PAC and PAM

3.4.1 Coagulation pretreatment study of PAC and APAM

The dosages of PAC and APAM used in the coagulation experiments are summarized in Table S19. PAC, a widely employed inorganic coagulant in water treatment, rapidly induced the formation of numerous fine floc particles upon addition to the wastewater. Subsequently, the introduction of APAM dramatically promoted floc growth, resulting in the formation of dense, white aggregates. These flocs exhibited excellent settling characteristics, descending swiftly and completely to form a sharp, well-defined mud-water interface. The resultant supernatant was notably clear and transparent, demonstrating superior visual and sensory quality, as shown in Fig. 8a.

Performance data under optimal conditions, extracted from Table S20 and Fig. 9a, indicate that at pH=8 with a dosage of 4 mL PAC and 3 mL APAM, the removal efficiencies reached 90.8% for Tur, 85.7% for COD, 36.4% for TN, and 23.3% for NH_3-N. The effectiveness of this combination stems from a synergistic mechanism: PAC hydrolysis produces highly positively charged polynuclear hydroxyl complexes, such as the potent Al_{13} species, which efficiently destabilize colloids through charge neutralization [24]. The subsequent addition of APAM further strengthens the floc architecture via bridging and patching mechanisms, significantly enhancing both floc robustness and settling velocity. This cooperative action is particularly effective in the removal of COD, likely through the enmeshment and adsorption of organic pollutants within the growing floc matrix. The combination thus represents a highly effective and reliable approach for achieving both high treatment efficiency and excellent effluent clarity.

3.4.2 Coagulation pretreatment study of PAC and CPAM

The dosage combinations of polyaluminum chloride (PAC) and cationic polyacrylamide (CPAM) used in the experiments are presented in Table S21. PAC, as an efficient inorganic coagulant, compresses the double electric layer of colloids through its hydrolysis products, while CPAM, a cationic organic polymer, contributes both charge neutralization and adsorption bridging[25]. The flocs formed by this combination were large in size and exhibited a markedly whiter color compared to those produced by the PAC-APAM system. They settled rapidly, possessed a dense structure,

and yielded a supernatant with clarity comparable to that of the PAC-APAM combination, demonstrating good visual quality (Fig. 8a).

As shown in Table S22 and Fig. 9b, the optimal treatment performance was achieved under the conditions of pH=10, with a dosage of 7 mL PAC and 3 mL CPAM. The removal rates reached 93.6% for turbidity, 84.3% for COD, 37.5% for TN, and 30.4% for NH_3-N. Notably, the NH_3-N removal efficiency of this combination was the highest among all PAC-based formulations tested. This enhanced performance is primarily attributed to the high positive charge density of CPAM, which acts synergistically with polynuclear hydroxyaluminate species generated from PAC hydrolysis. This synergy creates a stronger overall positive charge environment and enhances charge neutralization capacity, leading to more effective adsorption and removal of negatively charged colloidal particles, dissolved organic matter, and cationic pollutants such as NH_4^+ through electrostatic attraction. This "inorganic-organic cationic synergy" mechanism not only improves coagulation efficiency but also enhances the capture capacity for specific dissolved ions, offering a combination of treatment effectiveness and operational stability in practical applications.

3.5.3 Coagulation pretreatment study of PAC and NPAM

The combined dosages of PAC and NPAM evaluated in this study are detailed in Table S23. Remarkably, this specific combination demonstrated the most rapid and complete solid-liquid separation among all the formulations tested. Upon cessation of stirring, the formed flocs settled exceptionally swiftly, typically within tens of seconds, resulting in a supernatant that immediately attained high clarity with virtually no residual suspended matter, as clearly illustrated in Fig.8. Performance data extracted from Table S23, 24, and Fig. 9 indicate that under alkaline conditions at pH=10, with a dosage of 8 mL PAC and 3 mL NPAM, the treatment achieved the optimal removal efficiencies across the entire experimental series: 98.4% for turbidity, 86.7% for COD, 34.3% for TN, and 30.2% for NH_3-N. This combination successfully couples highly effective pollutant removal with superior separation kinetics, highlighting its significant potential for practical engineering applications.

The outstanding performance stems from a well-defined synergistic mechanism.

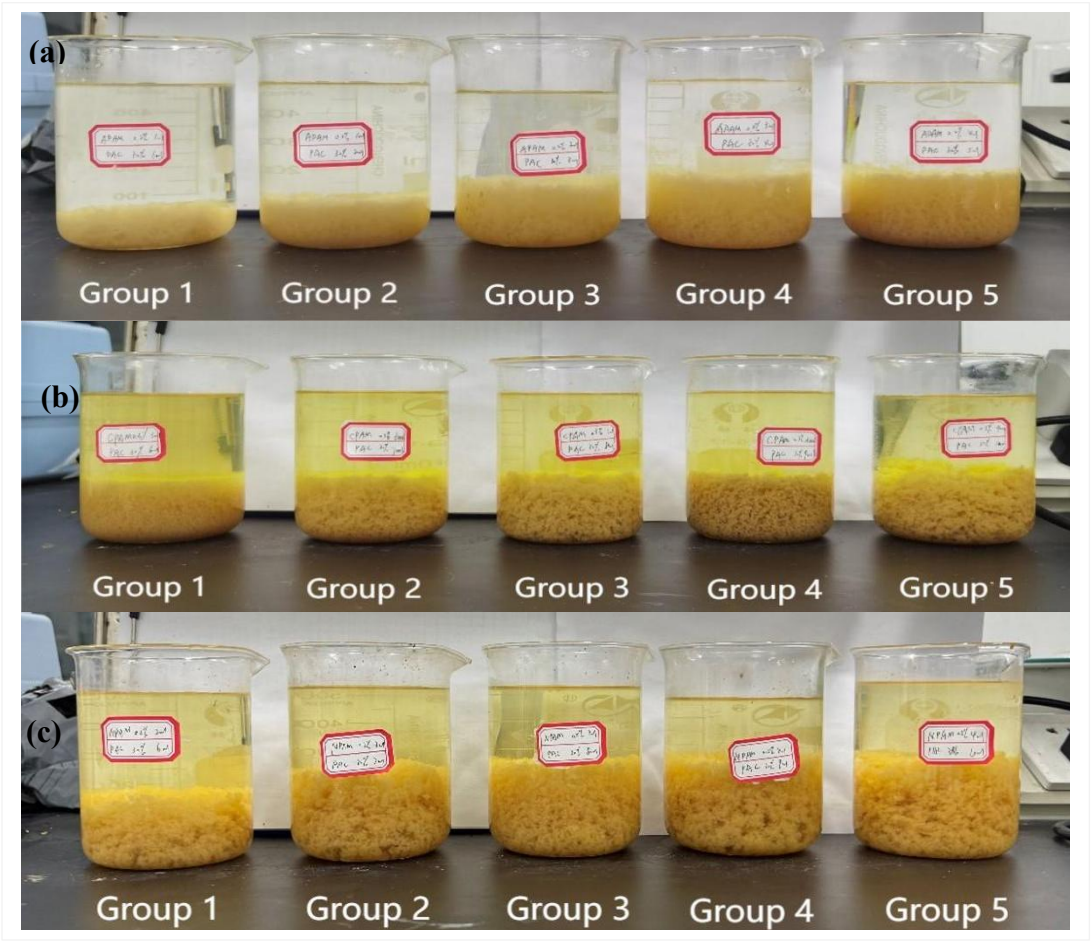
PAC provides potent charge neutralization, destabilizing colloidal particles and creating primary adsorption sites[26]. Simultaneously, NPAM, with its long-chain molecular structure, performs excellent bridging functions. It efficiently connects the destabilized microflocs into large, dense, and compact aggregates. This synergy not only enhances the incorporation of pollutants into the floc matrix but also critically improves the floc density and settling velocity, thereby achieving the observed rapid and effective mud-water separation. The efficiency of this process underscores the practical advantage of reduced settling time and compact sludge volume in potential full-scale operations.

3.5.4 Comparative Analysis

The PAC-based systems overall provided the best water clarity and most aesthetically pleasing supernatant. Among them, the PAC-NPAM combination stood out as the top performer across the study, achieving the highest turbidity removal (98.4%) and excellent COD removal (86.7%) with the most rapid and complete sedimentation. This remarkable synergy occurs because PAC's highly charged Al_{13} species [9] perform near-complete charge neutralization and micro-floc formation, while NPAM's long, uncharged chains excel at bridging these pre-formed micro-flocs into large, dense aggregates without the charge repulsion that can sometimes occur with ionic PAMs.

The PAC-APAM and PAC-CPAM combinations also performed very well. PAC-CPAM offered the highest NH_3-N removal (~30%) within the PAC series, similar to the trend observed with PFS-CPAM, highlighting CPAM's particular affinity for aiding ammonium ion removal. PAC-APAM produced very clear water with balanced removal efficiencies.

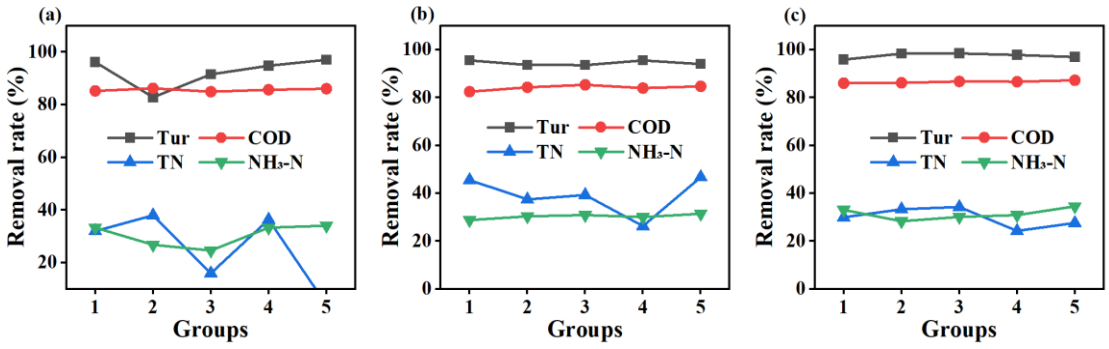
PAC demonstrates excellent compatibility with all three types of PAM, offering flexibility. The PAC-NPAM combination is the most recommendable for overall performance, especially regarding sedimentation speed and effluent clarity. PAC-CPAM is optimal when ammonium removal is a specific target. The widespread availability and lower cost of PAC further enhance the practical appeal of these combinations.



552

553 Fig. 8 Coagulation effect of PAC and APAM composite (a), PAC and CPAM 40 ionicity composite

554 (b), PAC and NPAM composite (c)



555

556 Fig. 9 Removal rates of efluent Tur, COD, TN and NH_3-N after coagulation pretreatment using

557 PAC and APAM composite (a), PAC and CPAM 40 ionicity composite (b), PAC and NPAM

558 composite (c).

559 **4 Conclusion**

560 This study investigated twelve combined coagulants for pretreating complex

sewage from municipal waste transfer stations. Key findings show that the PAC-NPAM combination achieved the highest overall performance, with turbidity and COD removal rates of 98.4% and 86.7%, respectively, and excellent floc settleability. The PFS-CPAM combination was more effective for ammonia nitrogen removal, while PSAF-based coagulants achieved high COD removal but poor color reduction. The research demonstrates that combining inorganic and organic coagulants enhances pretreatment efficacy through synergistic charge neutralization and bridging mechanisms. These results provide a practical and economical technical foundation for optimizing coagulation processes in treating challenging landfill leachate and transfer station wastewater.

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