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Flocculation performance and mechanism of the vermiculite flocculant in the primary enhanced pretreatment of swine wastewater

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ABSTRACT

Owing to the high concentration of swine wastewater produced via dry-wet separation, the current volume of discharge is difficult to process with biochemical treatments. Therefore, the primary enhanced flocculation pretreatments were conducted using both vermiculite and cationic polyacrylamide (C-PAM). After adding 4 g/L vermiculite flocculant and 24 mg/L C-PAM, the turbidity, chemical oxygen demand, suspended substances, total phosphorus and NH_4–N of the swine wastewater were 19.2 NTU, 454.5 mg/L, 34.0 mg/L, 5.5 mg/L, and 267.1 mg/L, respectively, with removal efficiencies of 95%, 66%, 87%, 86% and 10%. Under these conditions, the heavy metals in the flocculated supernatant and sediment met discharge standards. The vermiculite flocculant depended on the action of the dissolved substances in the vermiculite flocculant and the particulate substances. The dissolved species were dominated by electrical neutralization, forcing the colloids to destabilize. The destabilized colloids rely on van der Waals forces and the mass forces between the particulate part of the vermiculite flocculant and destabilized colloids to form flocs of different sizes. Therefore, the vermiculite flocculant exhibited a good sedimentation performance during flocculation. C-PAM swept and adsorbed flocs and organic pollutants to form larger secondary agglomerates, making them easier to settle and separate under particle gravity conditions. The elucidation of the synergistic effect of the vermiculite flocculant and C-PAM provides a strong scientific basis for the primary enhanced pretreatment of swine wastewater.

Keywords: Flocculation mechanism; Swine wastewater; Vermiculite flocculant; Primary enhanced pretreatment

1. Introduction

Over the past two decades, global annual meat consumption per capita has almost doubled [1,2], and China's meat production has ranked first in the world [3]. The main source of pollutants in livestock and poultry farms is intensive animal feed. Livestock and poultry manure can be used as fertilizers in small-scale crop cultivation areas [4]. However, for large areas of crop planting, if swine wastewater is sprayed directly into fields and dry bushes through pumps, it pollutes the water bodies [5]. The discharge of swine wastewater is considered to be one of the main sources of global water system pollution, such as surface water eutrophication and groundwater nitration concentration [6]. Improper discharge leads to serious pollution of surface water, groundwater, farmland ecosystems and air [7–9]. Owing to the high concentration of pollutants in swine wastewater, difficulty in reaching the standard discharge treatment technology, high cost and inadequate maintenance of facilities, it is particularly important to develop ecological, low-cost, and easy-to-control integration technologies from harmless to resource-based [10–12].

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Currently, wastewater treatment in large-scale swine farms mainly adopts three methods: returning to the field, natural treatment mode [13,14] and industrial treatment mode [15]. With the development of large-scale and intensive swine-raising modes, industrialized treatment modes are becoming increasingly important, and biochemical treatment methods remain the mainstream. Among them, the up-flow anaerobic sludge bed/blanket (UASB) can not only generate biogas but also reduce the subsequent biochemical treatment load. However, it is difficult to popularize and apply because of its thermal insulation, complicated operation and large investment [16]. Currently, the swine breeding mode of dry and wet separation has been widely promoted and applied and has greatly reduced the original swine wastewater concentration. However, because urine and wastewater after washing the pigsty still contain many organic pollutants, nitrogen and phosphorus, if all wastewater is treated by direct biochemical methods to meet the discharge standards, the cost is still very high.

Therefore, most colloids, macromolecular organic pollutants and phosphorus in wastewater are suppressed for removal by physical and chemical methods, such as flocculation from the source of the swine wastewater, to reduce the load of subsequent biochemical treatment. The separated sediment can also be used as raw material for composting together with swine manure, turning waste into treasure. Because the currently used pretreatment flocculants are mainly poly aluminum chloride (PAC) or poly ferric chloride (PFS), they are biologically toxic, making it difficult to recycle large amounts of sediment from flocculation [17]. Some studies have shown that PAC is not conducive to the mass transfer of dissolved oxygen in activated sludge, destroying the normal extracellular polymeric substances (EPS) secretion system of activated sludge microorganisms and reducing the protein content, which in turn leads to the inactivation of activated sludge microorganisms. The accumulation of PAC in the system increases biological toxicity [18–21], which affects subsequent biochemical treatment. However, traditional PAC and PFS flocculants have not been popularized and applied. This team developed a non-toxic inorganic mineral flocculant with a good flocculation effect [22].

Ecological non-bio toxic vermiculite inorganic mineral flocculants and conventional cationic polyacrylamide (C-PAM) were used for the first-level enhanced pretreatment of swine wastewater in this study. The synergistic effects of vermiculite flocculant and the combination of vermiculite flocculant and coagulant C-PAM on the pretreatment of swine wastewater were investigated. The pollutant removal ratio, sedimentation performance of flocs, and distribution of heavy metals in the supernatant and sediment were measured. Finally, the flocculation mechanism is provided to give an insight into the novel flocculant.

2. Materials and methods

2.1. Characteristics of swine wastewater

Swine wastewater used in the experiment was obtained from a swine farm in Ning he District, Tianjin, which is a dry and wet separation swine farm. The turbidity, conductivity, salinity and pH of swine wastewater were 405 NTU, 4.03 mS/cm, 2.1 mg/L and 7.43, respectively. The concentrations of chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended substances (SS), total phosphorus (TP) and ammonia nitrogen (NH_4–N) were 1,340; 650; 260; 38 and 296 mg/L, respectively.

2.2. Preparation of the vermiculite flocculant

The specific method and characterization of the inorganic mineral vermiculite for preparing flocculants can be found in the literature [23]. The raw vermiculite was pulverized, passed through a 200-mesh sieve to obtain a powder smaller than 74 μm, then acid-modified with 25% sulfuric acid, and finally dried in an oven at 105°C for 12 h until constant weight. Finally, the dried solid flocculant was placed in a grinder and ground into powder to prepare the powder flocculant.

The two components of the vermiculite flocculant were separated using the following method: 30 g vermiculite flocculant was placed in 1 L of ultrapure water and stirred using a magnetic stirrer at 300 rpm for 30 min to completely dissolve the soluble salt in vermiculite flocculant. Then, the mixed liquid was separated from solid and liquid using a Buchner funnel, and the separation liquid was placed in a beaker and dried in an oven at 105°C until it had a constant weight for use. The separated particulate portion of the vermiculite flocculant was repeatedly washed with ultrapure water to completely separate soluble matter from the particulate portion of the vermiculite flocculant. The separated particulate portion of the vermiculite flocculant was placed on a watch glass and dried in an oven at 105°C until constant weight. Soluble substances in vermiculite flocculants accounted for 30%, whereas the particulate part of the vermiculite flocculant accounted for 70% [24].

2.3. Experimental method

For the flocculation process with only vermiculite flocculant, the vermiculite flocculant was first mixed with 250 mL swine wastewater in beakers, which were initially stirred at a high speed of 350 rpm for 2 min. The speed was then changed to 250 rpm for 1 min. Finally, the wastewater was stirred at a slow speed of 50 rpm for 30 s and left to settle for 5 min. For the flocculation process with the vermiculite flocculant and C-PAM. After adding vermiculite flocculant, fast stirring was carried out, and the pre-mixed 0.1% C-PAM was added. The wastewater was then stirred at a slow speed of 50 rpm for 30 s and left to settle for 5 min. At the end of the flocculation experiment, liquid samples were obtained using a plastic syringe approximately 3 cm below the water surface for analytical determination.

The experimental settings are listed in Table 1. Experiments R1 and R2 were used to investigate the effects of vermiculite flocculant and C-PAM, respectively. The R3 experiment was used to investigate the flocculation effects of the vermiculite raw material, soluble state, particulate part of the vermiculite flocculant and vermiculite flocculant on swine wastewater. The R4 experiment was used to compare C-PAM and anionic polyacrylamide (A-PAM).

Table 1
Design of flocculation experiment of swine wastewater

Name	Beaker 1	Beaker 2	Beaker 3	Beaker 4	Beaker 5
R1	2 g/L flocculant	4 g/L flocculant	6 g/L flocculant	8 g/L flocculant	10 g/L flocculant
R2	4 g/L flocculant + 12 mg/L C-PAM	4 g/L flocculant + 20 mg/L C-PAM	4 g/L flocculant + 24 mg/L C-PAM	4 g/L flocculant + 28 mg/L C-PAM	4 g/L flocculant + 32 mg/L C-PAM
R3		8 g/L vermiculite	2.4 g/L dissolved part of flocculant	5.6 g/L particulate part of flocculant	8 g/L flocculant
R4		4 g/L flocculant	4 g/L flocculant + 24 mg/L C-PAM	4 g/L flocculant + 24 mg/L A-PAM	_

2.4. Zeta potential

For zeta potential analysis, liquid samples were obtained using a plastic syringe approximately 3 cm below the water surface. Zeta potential was measured using a Micro Electrophoresis System (JS94H, Shanghai, China).

2.5. Floc morphology

The liquid flocs at the bottom of the beaker were transferred to a test tube for morphological observation. The floc morphology was evaluated using a biological microscope (Olympus SZ61, Tokyo, Japan). Images of the flocs were processed using a camera (Mshot MD50-B, Guangzhou, China).

2.6. Chemical analysis

The concentrations of COD, SS, TP and NH_4–N were analyzed according to the standard methods for GB 18596-2001 [25]. The turbidity was determined using a turbidity meter (WTW Turb550, Germany). pH was determined by a precision acidity meter (WTW pH3210, Germany). The total heavy metals in the solutions were determined using an inductively coupled plasma mass spectrometer (Dual-view Optima 5300 DV, Beijing, China).

3. Results and discussion

3.1. Flocculation performance of the vermiculite flocculant

3.1.1. Pollutant removal

Fig. 1 shows the effect of different dosages of vermiculite flocculants on the removal of pollutants from swine wastewater. The optimum dosage of the vermiculite flocculant was 8 g/L, where the turbidity, COD, SS, TP and NH_4–N of the swine wastewater were reduced from 405 NTU, 1,340 mg/L, 260 mg/L, 38 mg/L and 296 mg/L to 73 NTU, 612 mg/L, 60 mg/L, 3 mg/L and 284 mg/L, respectively. Their removal ratios in wastewater reached 82%, 54%, 77%, 93% and 4%, respectively.

As shown in Fig. 1a, as the dosage of vermiculite flocculant increased, the turbidity decreased rapidly, then slowly. When the dosage was 8 g/L, turbidity reached the lowest level of 73 NTU. It can be observed from the change in zeta potential that when the dosage exceeded 8 g/L, the zeta potential decreased. This shows that the concentration of vermiculite flocculant was not as high as possible, but there was an optimal dosage. After electrical neutralization was balanced, adding too much flocculant would not only increase the turbidity of the supernatant but also affect the zeta potential in a system with high salinity. As shown in Fig. 1b, with the increase of vermiculite dosage, the SS in the supernatant shows the same characteristics as turbidity. When the dosage of vermiculite was 8 g/L, it reached the lowest level, decreased from 260 mg/L in raw wastewater to 60 mg/L and then increased, which was caused by the excessive dosage of the vermiculite flocculant. With an increase in vermiculite dosage, the COD concentration of the supernatant decreased rapidly at first and then gradually decreased slowly.

Similarly, Fig. 1c shows that both TP and NH_4–N decreased with increasing vermiculite dosages. In contrast, TP decreased significantly, whereas NH_4–N decreased slightly. This was because the modified vermiculite flocculant contains approximately 30 wt.% soluble metal ions such as Fe, Al and Ca and so on, which could easily combine with phosphorus compounds to form insoluble salts and other substances [26,27]. It was difficult on NH_4–N to form insoluble salts and other substances with acid-modified sulfate ions, which was also the reason why the flocculation treatment process had a poor removal effect of NH_4–N, and it was also a general rule of flocculants [28].

The SS and TP of the supernatant had reached the standard, and the COD was also close to the emission standard (GB 18596-2001). The removed SS and COD pollutants were particles, colloids and macromolecular organic pollutants that are relatively difficult to biochemically degrade. Considering practical applications, reducing processing costs was extremely important. Although there was an optimal dosage of the vermiculite flocculant alone, it could be seen from Fig. 1 that the dosage of 4 g/L of vermiculite also had a good flocculation effect, and SS and TP were close to the emission standards.

3.1.2. Separation effect of supernatant and flocs

To investigate the flocculation effect of each flocculant component in the flocculation process, experiments were conducted on vermiculite, vermiculite flocculants, and the soluble and particulate parts of vermiculite flocculant components in swine wastewater under the same conditions. Fig. 2 shows the effects of these four substances on the flocculation of swine wastewater. It was found that a

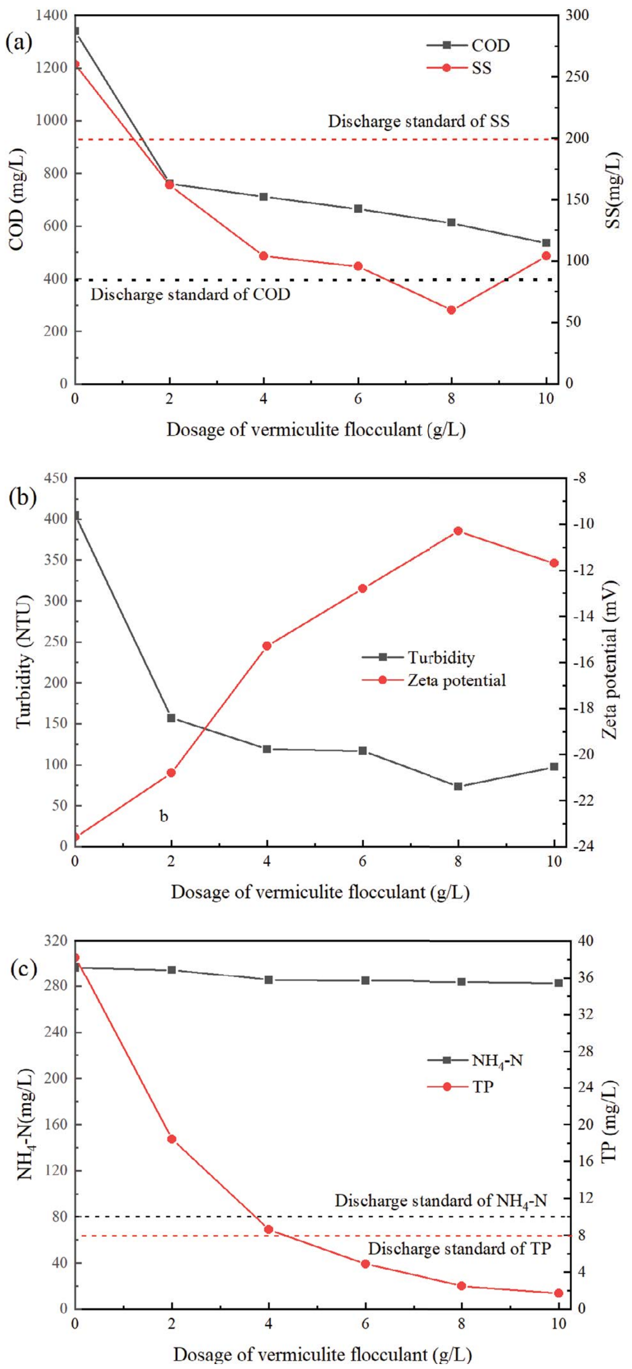


Fig. 1. Effect of different vermiculite flocculant dosages on the removal of pollutants in swine wastewater: (a) COD and SS, (b) turbidity and zeta potential, and (c) NH_4–N and TP.

large number of flocs of different sizes were produced in the solution at the end of flocculation after adding dissolved substances of the vermiculite flocculant and modifying the vermiculite flocculant. After 20 s, the unmodified vermiculite and the modified particulate part of the vermiculite flocculant had almost no flocculation effect on swine wastewater. However, both the modified dissolved substances in the vermiculite flocculant and the modified vermiculite flocculant produced flocculation effects, and the flocs exhibited different degrees of settlement. The modified vermiculite flocculant exhibited an evident flocculation effect. After 10 min, even though there was some particle sediment at the bottom of the beaker, the turbidity was in basic common with that of the raw water. Both the flocculation effect and settling performance of dissolved substances of the vermiculite flocculant and the vermiculite flocculants can result in a large amount of supernatant and less sediment. In contrast, the modified dissolved substances contained more sediment, which was looser and more difficult to compress, and their volume was 5 times that of the modified vermiculite flocculant. According to a study by Wang et al., after treating water samples with PAC, a lot of sludge is produced and the water content is very high, and the treated water samples usually contain a lot of aluminum ions, which makes the treated water samples unsuitable for human consumption and poses a health risk [29]. But the vermiculite flocculant is certified by CMA, non-toxic and harmless, and the sediment after flocculation is small in volume, high in density and small in water content. Yang et al. also concluded that natural polymer flocculants are of interest because of their biodegradability, non-toxicity, ability to undergo different chemical modifications, and wide range of sources [30].

Fig. 3 shows the microscopic photograph of sediment after the flocculation of dissolved substance in the vermiculite flocculant and the vermiculite flocculant. The flocs of the two sediments had obvious differences. The flocs produced by the flocculation of dissolved substance in the vermiculite flocculant were small and particularly loose, while the flocs produced by the flocculation of the vermiculite flocculants were much larger and denser. The particulate part of the vermiculite flocculant can accelerate flocculation, increase flocculation settling speed, and reduce sediment volume. Therefore, it also shows that the particles had no flocculation effect when it was used alone. However, it was used together with the dissolved substance in the vermiculite flocculant.

3.2. Flocculation performance of the vermiculite flocculant with C-PAM

3.2.1. Pollutant removal

In practical applications, the cost of the flocculants must be considered. Comparing the effect of flocculation with the discharge standard of the effluent at a dosage of 4 g/L, the phosphorus content in the supernatant was 9 mg/L, which is very close to the discharge standard of 8 mg/L. Other water quality indicators could also quickly decrease to their expected values. Even when the flocculant dosage was increased, pollutant removal changed slowly. Therefore, the next experiment was carried out with the help of the synergistic effect of vermiculite flocculant and C-PAM.

Fig. 4 shows the effect of different dosages of C-PAM on the removal of pollutants from swine wastewater when the dosage of the vermiculite flocculant was 4 g/L. As shown in Fig. 4a, with an increase in the dosage of C-PAM, the turbidity of the supernatant decreased sharply from 119 NTU after flocculation with only the vermiculite

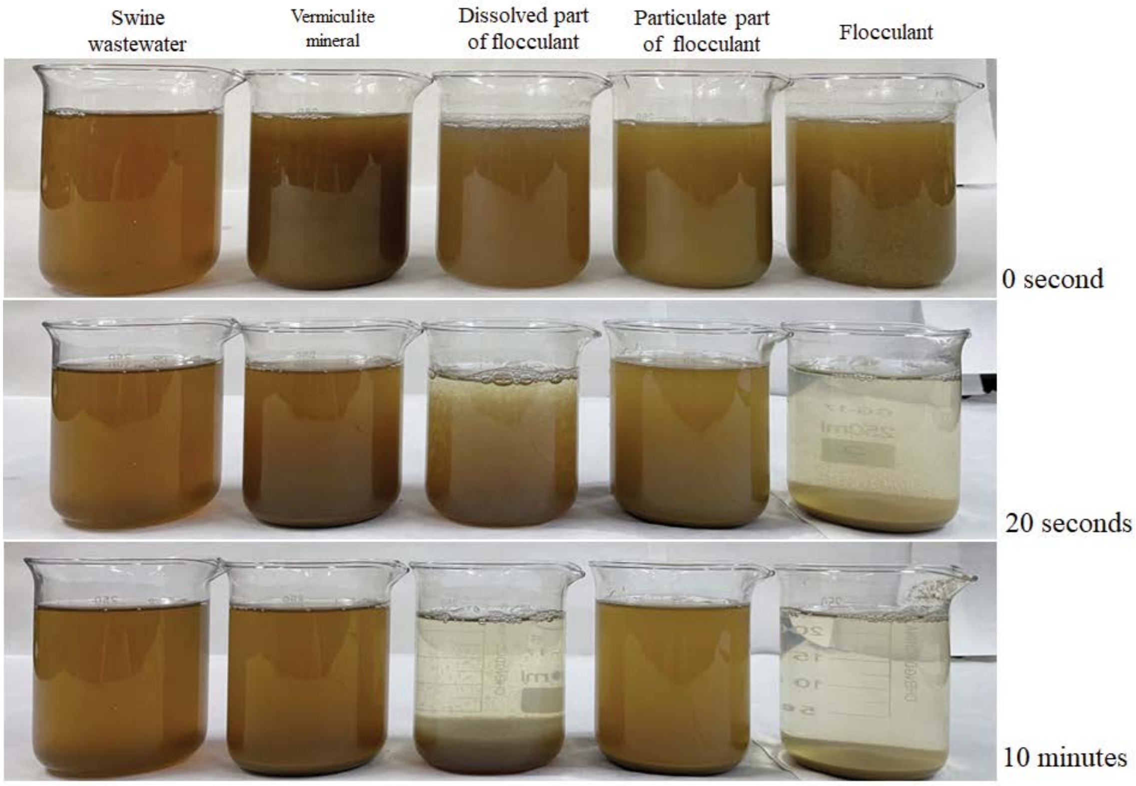


Fig. 2. Separation effect of solid–liquid at different times.

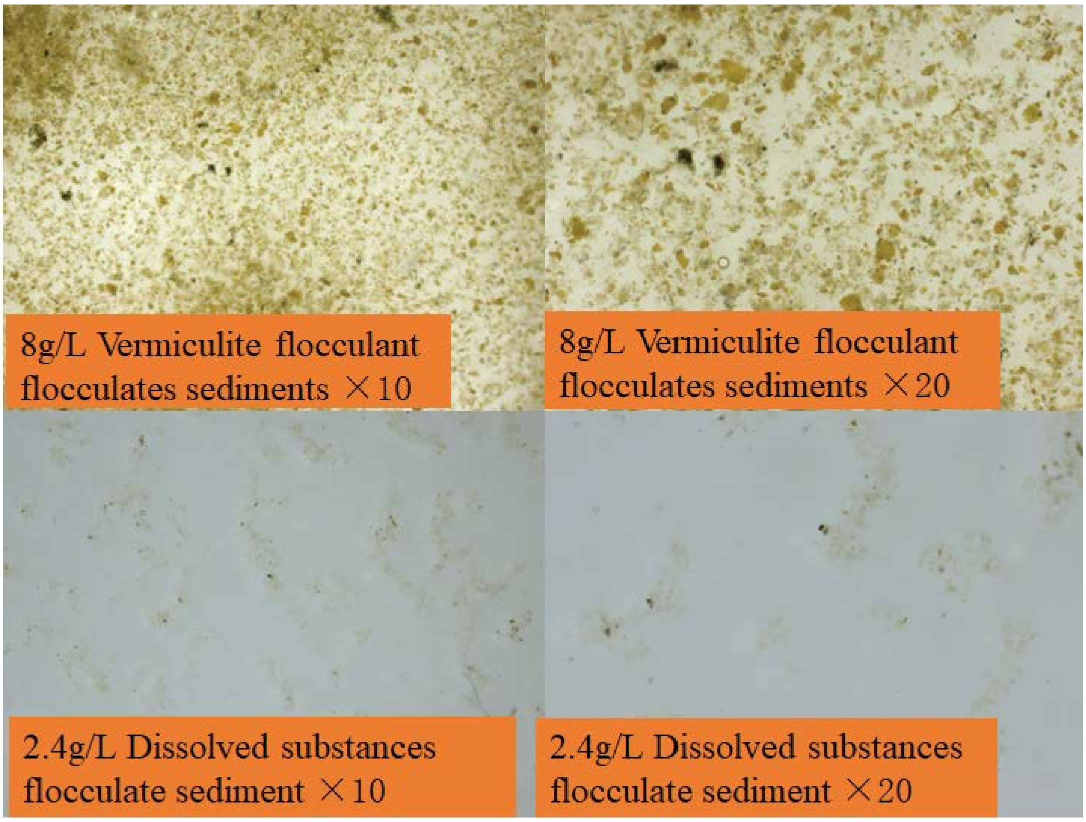


Fig. 3. Microscopic photograph of sediment after flocculation of dissolved substances and vermiculite flocculant.

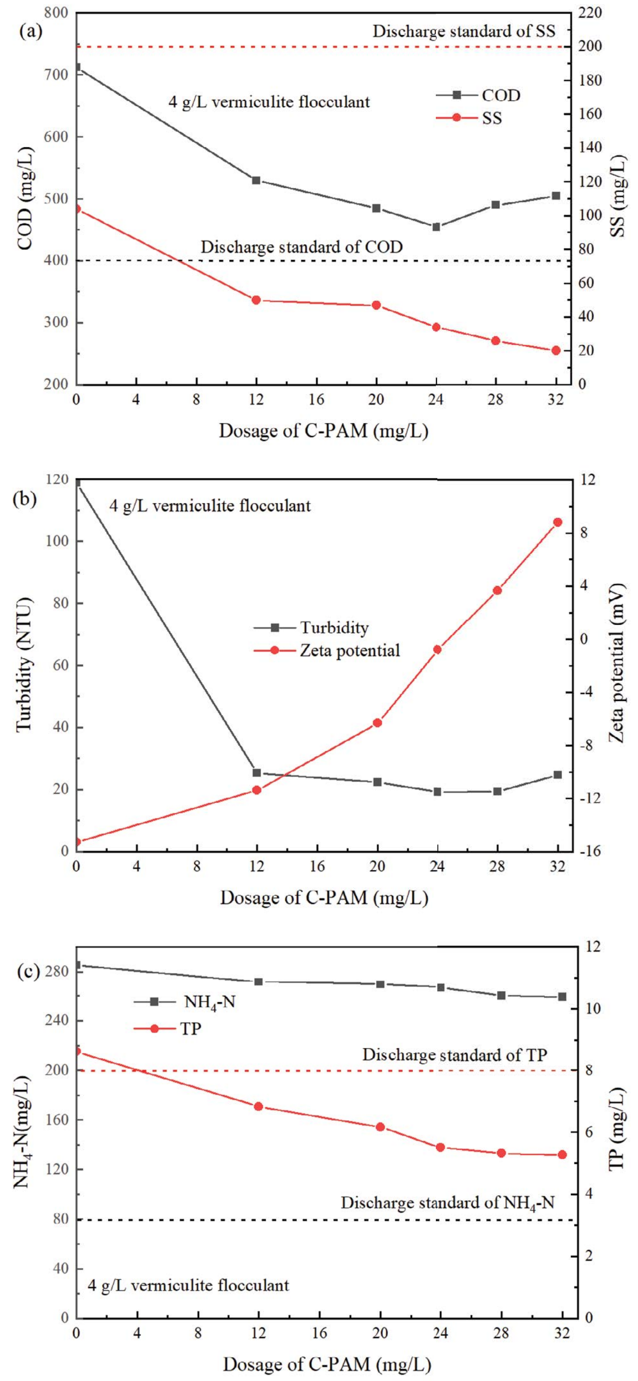


Fig. 4. Removal of pollutants in swine wastewater different dosages of C-PAM at vermiculite flocculant of 4 g/L: (a) COD and SS; (b) turbidity and zeta potential; (c) NH_4–N and TP.

flocculant and then gradually leveled off. When the C-PAM dosage was 24 mg/L, the turbidity of the supernatant reached 19 NTU. From the zeta potential change of the supernatant, it was found that due to the addition of C-PAM, macromolecular pollutants and the particulate part of the vermiculite flocculant in the supernatant, especially colloids, were effectively removed. When the dosage of C-PAM increased again, the turbidity of the supernatant increased, indicating that excess C-PAM that did not participate in secondary agglomeration was dissolved in the supernatant, therefore, an increasing trend came out in turbidity.

As shown in Fig. 4b, the COD and SS of the supernatant decreased with an increase in the C-PAM dosage. When the C-PAM dosage was 24 mg/L, COD and SS decreased to 455 and 34 mg/L, respectively. However, as C-PAM increased again, SS decreased, but COD increased. This may be because the dissolved C-PAM led to an increase in the COD. This also showed that the dosage of C-PAM was not the more the better, but the optimal dosage. As shown in Fig. 4c, TP and NH_4–N in the supernatant also decreased, TP decreased significantly, whereas NH_4–N decreased only limitedly. When the dosage of C-PAM was 24 mg/L, TP decreased to 6 mg/L. Under the action of the vermiculite flocculant and C-PAM, phosphorus in the wastewater was removed. However, the removal ratio of NH_4–N in the flocculation process was low, which was a common problem in the flocculation process and an important topic for future research.

3.2.2. Separation effect of supernatant and flocs

When vermiculite flocculant was added, the size of these flocs that could be observed under the microscope was very limited, and the dosage of vermiculite flocculant was relatively large (Fig. 3). In practical applications, organic polymer coagulants are often added to reduce the dosage of vermiculite flocculants and improve flocculation and agglomeration.

Fig. 5 shows the flocculation effects of raw water, vermiculite flocculant, vermiculite flocculant plus C-PAM and vermiculite flocculant plus A-PAM. It could be seen that when C-PAM was added in the slow stirring stage, larger flocculation aggregates appeared. Once it was stopped, these flocculated aggregates settled rapidly, and the effect of the coagulant was particularly obvious. Compared to C-PAM, the flocs formed by the synergistic effect of A-PAM and vermiculite flocculants were small and relatively loose. Therefore, the flocculation effect of A-PAM was not as good as that of C-PAM.

The microscopy photograph of the vermiculite flocculant with C-PAM and A-PAM after flocculation is shown in Fig. 6. The above analysis results were further confirmed. On the basis of the flocculation effect of the vermiculite flocculant, A-PAM also promoted the agglomeration of the flocs, and the flocs become larger. In contrast, the synergistic effect of C-PAM and the vermiculite flocculant was more obvious, and the flocculation group was larger, which was convenient for floc agglomeration and separation. The synergistic effect of vermiculite flocculant and C-PAM can both reduce the amount of vermiculite flocculant added and reduce the cost of treatment, and also make the floc settle fast and easy to dewater. The study of Liao et al. [31] showed that the combined PAM with flocculant, as long as using the right method, the effect is obvious, and the volume of the floc formed is large, fast settling speed, easy dewatering of the sediment, and the dosage is only 1/300 to 1/30 of the inorganic flocculant.

3.3. Heavy metals in supernatant and sediment

Table 2 shows a comparison of heavy metal content in the supernatant and sediment after flocculation with 4 g/L vermiculite flocculant and 24 mg/L C-PAM with DB12/356-2018 and NY/T525-2021, respectively. In addition to Fe and Mg, heavy metals in the supernatant were not detected as As, Cd, Pd, Cr, Ni and Hg, whereas Fe and Mg were not required in the standard. This shows that the secondary use of the supernatant in this study did not cause heavy metal pollution in the environment. As shown in Table 2, there were no heavy metals such as As and Hg in the sediment. But it contained heavy metals Cd, Pd and Cr, whose concentrations were 0.2, 12.9 and 11.7 mg/kg, respectively, which were far lower than the standard. This shows that the synergistic effect of the non-toxic vermiculite flocculant and C-PAM not only effectively reduces the load of subsequent biochemical treatment but also allows the sediment to be reused as a raw material for composting, realizing resource utilization.

3.4. Flocculation mechanism

3.4.1. Mechanism of the vermiculite flocculant

To investigate the flocculation mechanism in more detail, the turbidity, COD, TP and zeta potential of the supernatant after sedimentation were analyzed (Fig. 7). It can be seen that the COD and TP in the swine wastewater

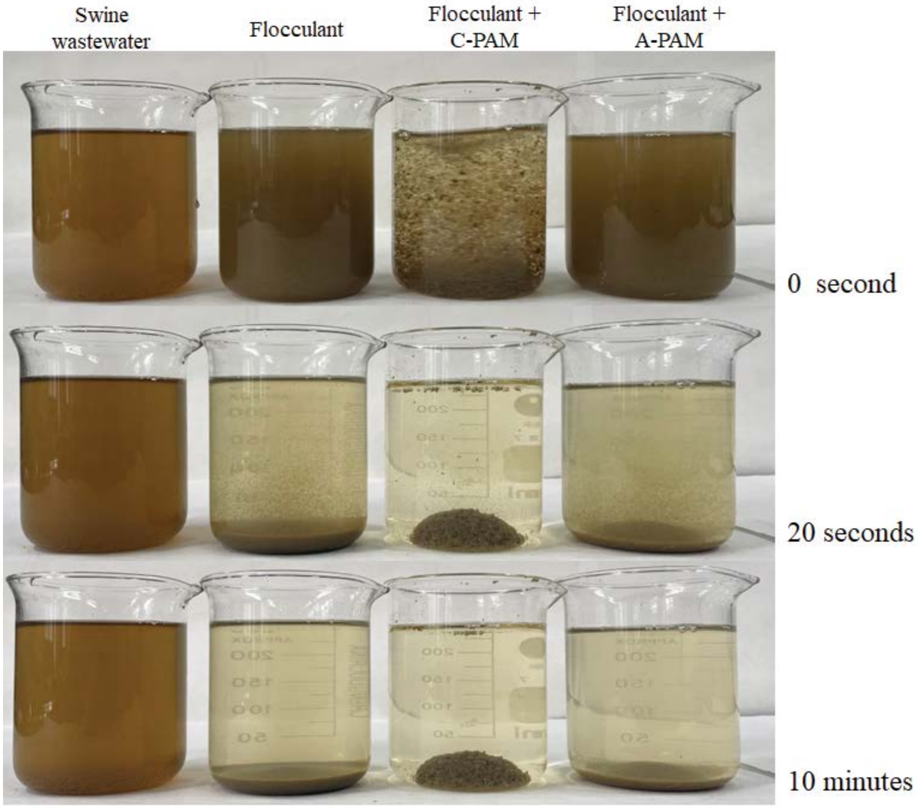


Fig. 5. Separation effect of solid–liquid at different times.

Table 2
Heavy metal content in supernatant (mg/L) and sediment (mg/kg) after flocculation with 4 g/L vermiculite flocculant and 24 mg/L C-PAM

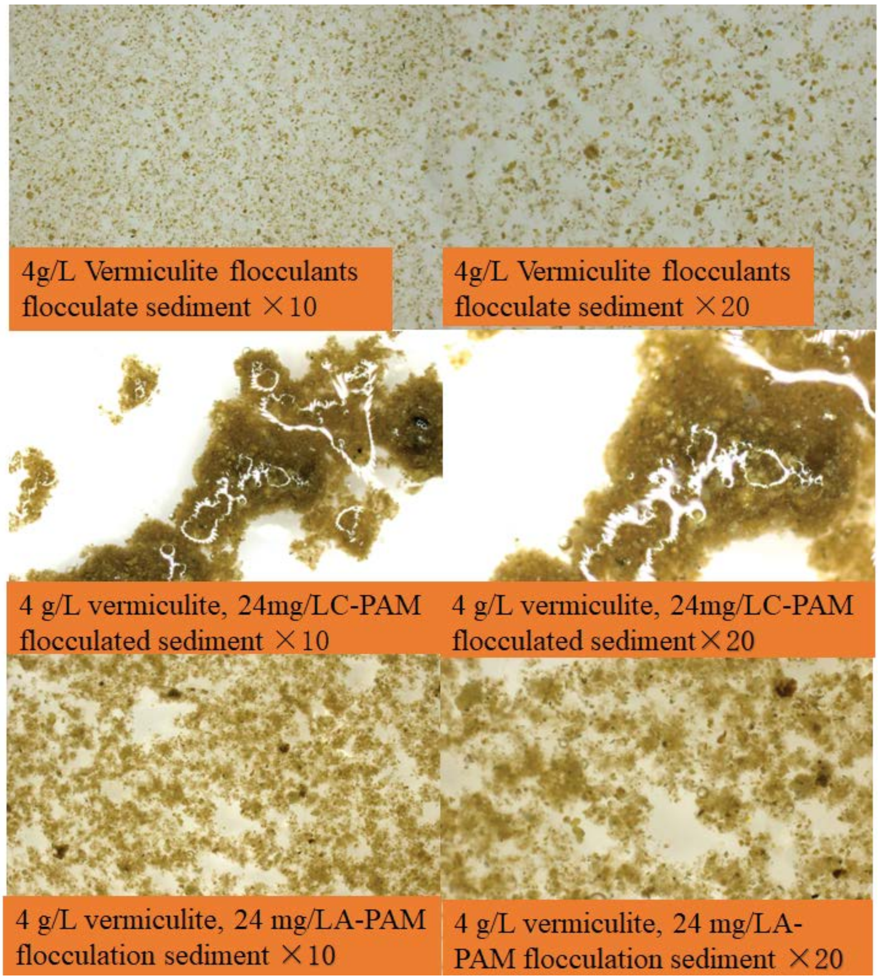
Element	As	Cd	Pd	Cr	Ni	Hg	Mg	Fe
Supernatant[a]	–	–	–	–	–	–	0.250	0.190
Standard[b]	0.100	0.005	0.050	1.500	1.000	0.001	n.s.	n.s.
Sediment[a]	–	0.2	12.9	11.7	–	–	–	–
Standard[c]	15.0	3.0	50.0	150.0	–	2	–	–

[a] Average value of three independent experiments;
[b] Integrated Wastewater Discharge Standard in China (DB12/356-2018);
[c] Organic Fertilizer Limit Index in China (NY/T525-2021).

with unmodified vermiculite and particulate part of the vermiculite flocculant decreased slightly. Owing to the large specific surface areas of the two substances, they adsorbed trace pollutants in swine wastewater to reduce the concentrations of COD and TP. When the dosage of vermiculite raw materials and particulate part of the vermiculite flocculant were 8 and 5.6 g/L, more fine suspensions appeared in the wastewater, and the turbidity increased from 405 to 506 and 494 NTU, respectively. The zeta potential of both supernatants increased from –23.6 to –21.5 mV and –20.6 mV. Owing to the action of hydration ions, the vermiculite raw material had an impact on the colloids in the aquaculture sewage, causing the zeta potential of the solution to increase slightly. It was further explained that the unmodified vermiculite raw material itself did not have a flocculation effect.

The dissolved substances in the vermiculite flocculant produced a good flocculation effect (Fig. 7a). When the dosage of dissolved substance in the vermiculite flocculant was 2.4 g/L, the turbidity, COD, and TP of the swine wastewater were reduced from 405 NTU, 1,340 mg/L and 38 mg/L to 96 NTU, 793 mg/L, 60 mg/L and 3 mg/L, respectively. The zeta potential of the supernatant increased from –23.6 to –16.8 mV, indicating that the dissolved metal ions neutralized the colloids in the wastewater and destabilized a large number of negatively charged colloids [32]. The mass force between the destabilized colloids was greater than the repulsive force of the original negative charges, and under the action of stirring and collision, they attracted each other and gradually formed flocs. However, because the destabilized colloids were organic pollutants, the formed flocs were relatively loose because the negative charges were not completely eliminated. Even if they settled, it was difficult to form dense sediment.

Because a water layer with hydration ions was formed around the particulate part of the vermiculite flocculant, it not only affected the negative charge of the colloid but also the huge mass force attracted the particles destabilized by the dissolved matter more effectively, and the dual effect made the floc larger. In addition, the specific gravity of the mineral particulate part of the vermiculite flocculant was 2.5, which was far greater than that of the destabilized colloid and water. The flocs formed by flocculation settled rapidly under the influence of gravity on the particulate part of the vermiculite flocculant. The sediment volume of vermiculite flocculant was much smaller than that of the flocs of the dissolved material and more supernatant was obtained. Because the sediment contained a large amount of particulate vermiculite flocculant, dewatering performance increased.


4g/L Vermiculite flocculants flocculate sediment ×10

4g/L Vermiculite flocculants flocculate sediment ×20

4 g/L vermiculite, 24mg/LC-PAM flocculated sediment ×10

4 g/L vermiculite, 24mg/LC-PAM flocculated sediment×20

4 g/L vermiculite, 24 mg/LA-PAM flocculation sediment ×10

4 g/L vermiculite, 24 mg/LA-PAM flocculation sediment ×20

Fig. 6. Microscopy photograph of vermiculite flocculant with C-PAM and A-PAM after flocculation.

The modified vermiculite flocculant was composed of dissolved substances in the vermiculite flocculant and particulate substances. Under the same conditions, the flocculation effect of the vermiculite flocculant was better, the settling speed was accelerated, and sediment volume was reduced. When the dosage of the vermiculite flocculant alone was 8 g/L, the turbidity, COD, SS, and TP of the swine wastewater were reduced to 73 NTU, 611 mg/L and 3 mg/L, respectively (Fig. 7a). This shows that the combination of the two forms a good synergistic effect, and the particulate parts of the vermiculite flocculant have a coagulation aid effect. The soluble matter and particulate components of the vermiculite flocculant form a carrier-coagulant effect.

3.4.2. Mechanism of vermiculite flocculant and C-PAM

Fig. 7b shows the turbidity, COD, TP and zeta potential of the raw water and the treated supernatant. In the case of adding 4 g/L of the vermiculite flocculant and 24 mg/L A-PAM, the turbidity, COD and TP of the supernatant were 42 NTU, 636 mg/L and 6 mg/L, respectively. Compared with only adding 8 g/L of the vermiculite flocculant supernatant, the water quality index had significantly reduced. The zeta potential of the supernatant with only the vermiculite flocculant was still negative, and the addition of C-PAM was more conducive to the improvement of the flocculation effect and the zeta potential of the supernatant. The coagulant aid had lipophilicity and could adsorb and sweep some molecular organic pollutants in the water, effectively reducing the COD, turbidity and TP of the supernatant.

After the primary pretreatment with 4 g/L vermiculite flocculant and 24 g/L C-PAM. The synergistic effect was studied, and the turbidity, COD, and TP in swine wastewater were reduced from 119 NTU, 712 mg/L and 9 mg/L to 19 NTU, 455 mg/L and 6 mg/L, respectively. And the zeta potential also increased from –15.30 to –0.97 mV (Fig. 7b). This showed that C-PAM had a good synergistic effect with vermiculite flocculant, which not only reduced the usage of vermiculite flocculant but also improved the flocculation effect and increased the removal effect of pollutants. A-PAM was significantly affected by the negative charge of the zeta potential, and its coagulation-aiding effect was relatively poor. They also showed that the anionic coagulant was not suitable for the coagulation of wastewater with a low negative zeta potential.

According to the above in-depth discussion, the flocculation mechanism of swine wastewater is shown in Fig. 8. The dissolved substance in the vermiculite flocculant had an electric neutralization effect on the colloids in the wastewater [33]. At the same time, the particulate part of the vermiculite flocculant also formed more hydrated ions under the action of the dissolved matter. These hydrated ions

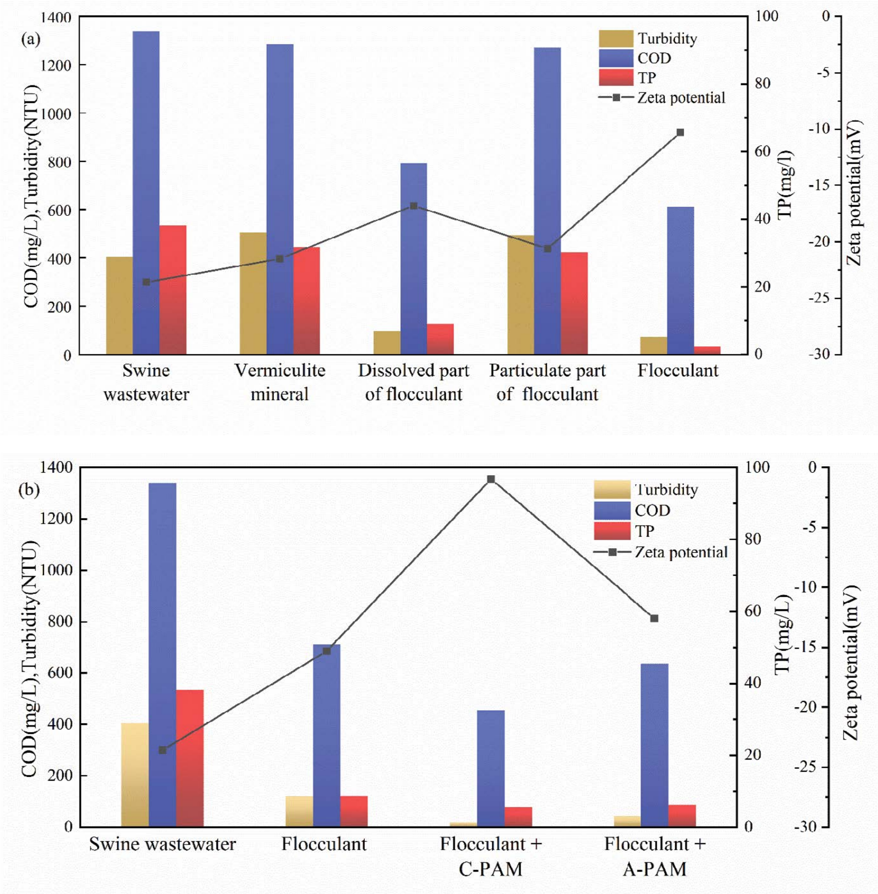


Fig. 7. Water quality of the supernatant after flocculation without C-PAM and A-PAM (a) and with C-PAM and A-PAM (b).

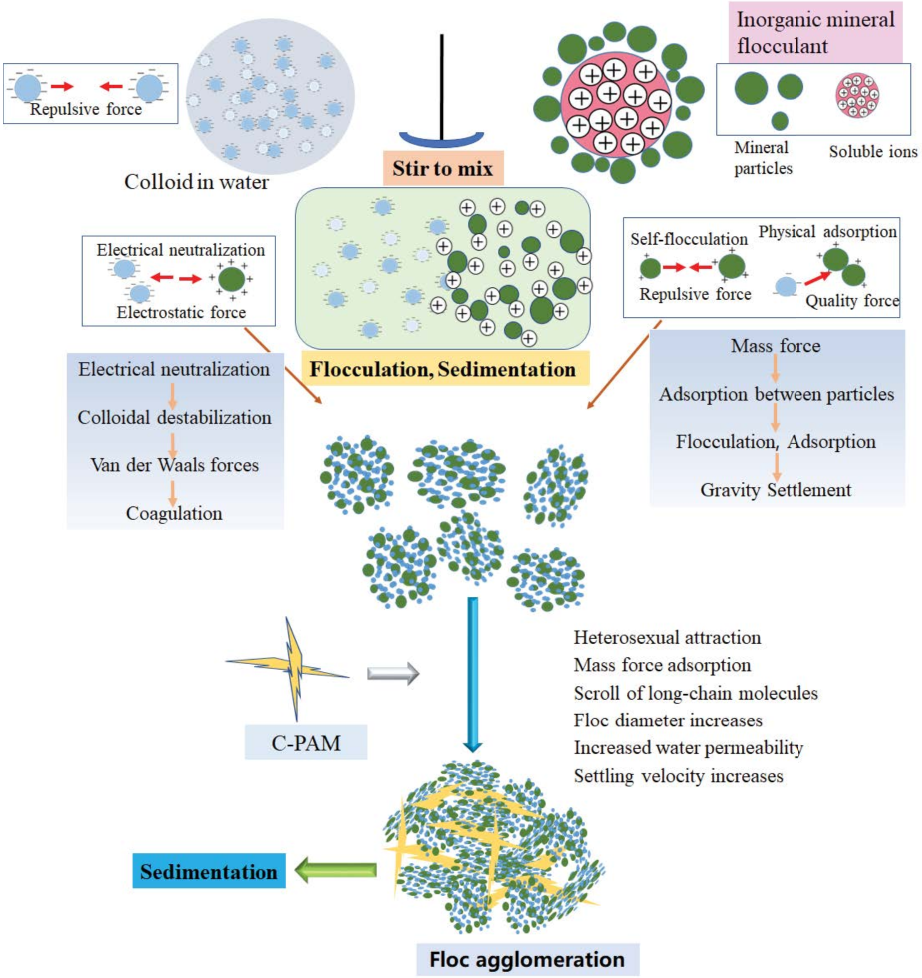


Fig. 8. Flocculation mechanism diagram with vermiculite flocculant and C-PAM.

destabilized the colloid. The destabilized colloids formed aggregates under the action of van der Waals forces [34]. What's more important was that these particulate substances can effectively attract these particles and small flocs to form larger flocs by relying on their huge mass force in the face of destabilized particles. Under the action of slow stirring, these flocs re-aggregate with each other to form larger agglomerations, which settled rapidly by gravity. This process was completely in line with the traditional flocculation mechanism.

When C-PAM was quickly added, C-PAM and the already formed flocs underwent adsorption, sweeping and entrainment again to form larger agglomerates. Because of the lipophilic long-chain group of C-PAM, it was easy to adsorb these low-molecular organic pollutants, resulting in more effective agglomeration [35]. The diameter of the agglomerated flocs increased, and they were easy to settle and separate. Because the inorganic mineral vermiculite flocculant had no biological toxicity, after the sediment was separated, it could be effectively used as a raw material for composting, thereby realizing resource utilization. Simultaneously, the load of subsequent biochemical treatment of the supernatant was greatly reduced.

4. Conclusions

Vermiculite exhibited a good flocculation effect in the primary enhanced pretreatment of swine wastewater. After primary pretreatment with 4 g/L vermiculite flocculant and 24 mg/L C-PAM, turbidity, COD, SS, TP and NH_4–N removal efficiencies in swine wastewater reached 95%, 66%, 87%, 86% and 10%, respectively. The mechanism of vermiculite flocculant formation depends on the flocculation of dissolved substances in the vermiculite flocculant and particulate substances. Dissolved substances in vermiculite flocculants and colloids produce electrical neutralizations to destabilize the colloids. The destabilized colloids rely on van der Waals forces and mass force between the particulate part of the vermiculite flocculant and destabilized colloids to form flocs of different sizes. C-PAM scrolled and adsorbed flocs and organic pollutants to form larger secondary agglomerates, which were easier to settle and separate under the action of particle gravity. The synergistic mechanism of the primary enhanced pretreatment of the vermiculite flocculant and C-PAM explains this process and provides a new process for the rapid separation of swine wastewater.

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Supporting information

As can be seen from Fig. S1, the flocculation experiments were carried out on the hexagonal flocculation stirring device under the operating conditions set for the flocculation experiments, and after the tests, the samples were then stirred uniformly at 75 rpm for 6 s, and then the respective samples were poured into the pre-prepared 250 mL measuring cylinders, and the timing was started, and the pictures were taken separately at the pre-set times. From the pictures, it can be seen that the vermiculite flocculant flocculates and settles fast, and the volume of sediment is very little, which can obtain more supernatant and facilitate solid–liquid separation. This is all thanks to the granules of inorganic mineral flocculants, which have the high mass force and high specific gravity and are easy to flocculate and settle. Compared with the traditional poly aluminum chloride (PAC), vermiculite flocculant, flocculation and sedimentation are much faster than the traditional PAC. 2 min after resting, the sedimentation is basically over, while the PAC only settles 1/3 at this time, even after stabilization of sedimentation, the volume of PAC sediment is still much larger than vermiculite flocculant, which is due to the PAC in the enhanced hydrolysis of a large number of flocs, the specific gravity of light, very loose.

Fig. S2 shows the X-ray diffraction patterns of vermiculite raw material and vermiculite flocculant. From Fig. S2, it can be seen that the main diffraction peaks of vermiculite are accompanied by other impurity peaks before modification, and the 001 diffraction peaks of vermiculite raw material and vermiculite flocculant are obvious, and the peak intensities of both do not change significantly, which indicates that the vermiculite layer spacing does not change significantly before and after modification. In addition, compared with the vermiculite raw material, the acid modification has a certain effect on the surface properties of vermiculite flocculant, and the internal elements of vermiculite have been changed with the dissolution of ions. There are a certain amount of quartz, sodium silica-aluminate, sodium chlorite and sodium feldspar several peaks in vermiculite raw material. Other peaks are not specified because of the complexity and low crystallinity of vermiculite. Most of the amorphous phases of vermiculite particles were dissolved after modification by H_2SO_4, a phenomenon confirmed by the disappearance of the diffuse halo of vermiculite flocculant in Fig. S2 and

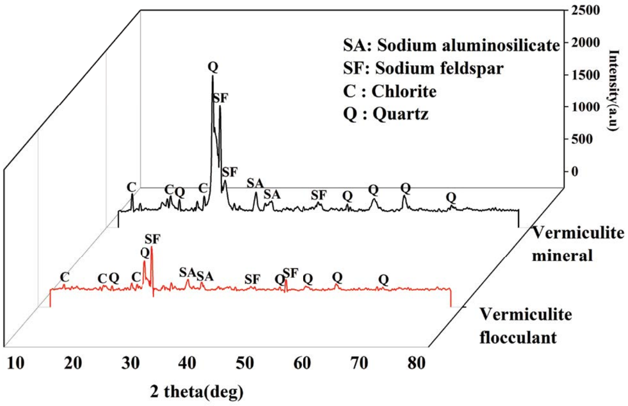

Fig. S2. X-ray diffraction patterns of vermiculite mineral (black line) and vermiculite flocculant (red line).

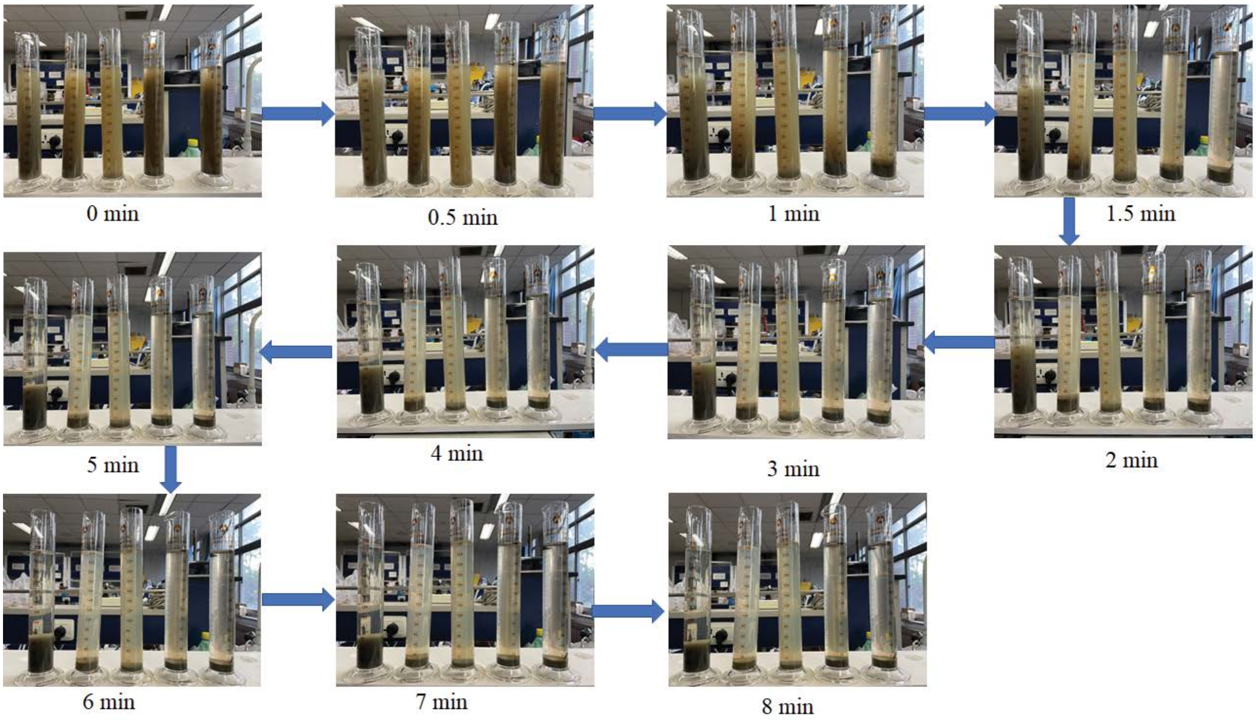
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Fig. S1. Floc sedimentation rate after flocculation of different samples the generation of new sodium feldspar phases after H_2SO_4 modification. This suggests that when the vermiculite raw material is modified with acid, the possible dissolution in vermiculite leads to a slight decrease in reflection intensity.

From Fig. S3, it can be seen that: (a) the vermiculite raw material has the characteristics of the lamellar structure, large particle size, large specific surface area, and particle dispersion; (b) the morphology of acid-modified vermiculite flocculant in the figure changes obviously from lamellar structure to agglomerated structure, and some of the wafers break, which may be due to the reaction between acid modifier and vermiculite, due to the weak intermolecular force, resulting in the acid being adsorbed by vermiculite into the middle layer, making the structure appear smaller of lamellar crystals. At the same time, on the surface of the lamellar structure, a small part of the particle attachment was formed, mainly because the acid replaced aluminum, iron and silicon in the vermiculite, and excess poly aluminium iron silica crystals were formed on the vermiculite surface. The obtained polyaluminoferrosilicon is partly inserted between the layers of the vermiculite structure and partly attached to the surface to form a porous surface. And the dissolved ions form an equilibrium with the compounds on the surface. At the same time, the surface of the particles will form hydrates under the action of water molecules and the positively charged ions will be released in the aqueous solution. These ions play the role of electric neutralization in the flocculation process and also form a certain bridge or mesh structure, which is thus the key role of vermiculite flocculant for flocculation to occur.

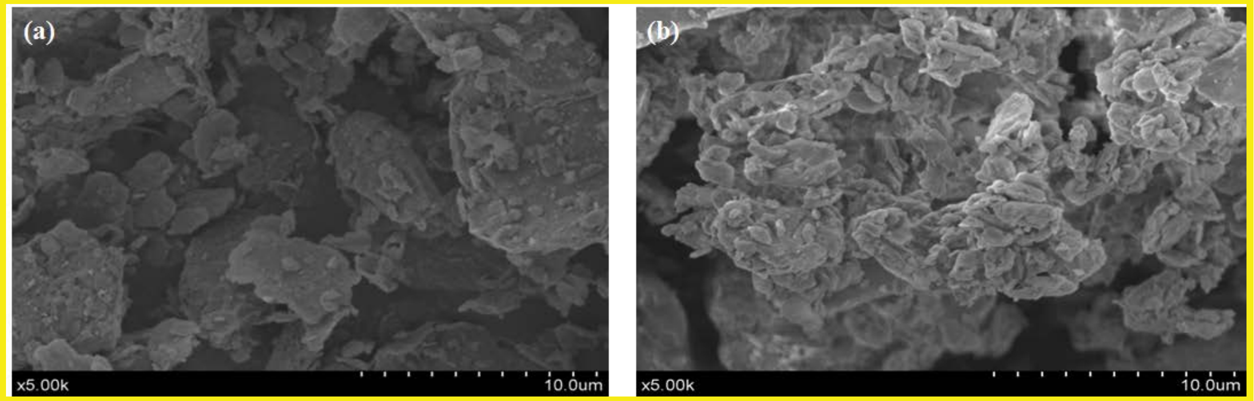

Fig. S3. Scanning electron microscopy images of vermiculite mineral (a) and vermiculite flocculant (b).