Synergistic function of bentonite, poly-aluminum chloride, and cationic polyacrylamide to realize highly efficient coagulation–flocculation process for leachate treatment

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ABSTRACT

This work introduces a coagulation–flocculation leachate treatment process using colloidal inorganic bentonite particles. The synergistic effect of the inorganic mineral bentonite, poly-aluminum chloride (PAC), and cationic polyacrylamide (C-PAM) was investigated. The results demonstrate that the traditional combination of PAC and C-PAM had a certain coagulation–flocculation effect on the treatment of leachate. However, most flocs in this treatment floated and were difficult to separate. The colloidal bentonite disrupted the ionic balance of the leachate and led to a synergistic effect with PAC and C-PAM. When 8 g/L, 32 mL/L, and 20 mL/L of bentonite, PAC, and C-PAM were used, the removal efficiency of chemical oxygen demand, turbidity, suspended solids, and total phosphorus in the supernatant reached 72.3%, 97.6%, 93.8%, and 97.5%, respectively. The zeta potential dropped from –40.1 to –2.37 mV with the addition of colloidal bentonite, indicating that through electric neutralization and destabilization, pollutants in the leachate were adsorbed and trapped. Even though the average size of the floc decreased from 1,298 to 1,119 μm, the flocs became tighter and had higher specific gravities, allowing them to precipitate more rapidly and increasing the volume ratio of the supernatant. The floating flocs rapidly settled and the floc volume ratio was only 7.2%. The addition of bentonite effectively promoted the coagulation–flocculation effect. Overall, this work demonstrates that bentonite significantly improves coagulation–flocculation treatment and provides a strong scientific basis for the establishment of subsequent biological treatment processes.

Keywords: Leachate; Bentonite; Enhanced primary treatment; Charge neutralization; Coagulation–flocculation

1. Introduction

An increasing amount of domestic waste is being created in cities and rural areas. Consequently, municipal solid waste (MSW) incineration facilities are being constructed in larger numbers in China. The imperfect MSW classification system in China has led to a high moisture content in waste (50%–60%). MSW incineration naturally dehydrates this waste, but it also produces a significant amount of leachate. Existing MSW incineration power plants and landfill sites produce leachate with complex compositions, high concentrations, chromaticity and strong pungent odors. Furthermore, this leachate contains a variety of toxic and harmful substances such as refractory naphthalene, phenanthrene, and other aromatic compounds [1,2]. Concentrated leachate is wastewater with high concentrations of organic substances and a low biological oxygen demand (BOD_5)/chemical oxygen demand (COD) ratio [3–5].

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There are many techniques for treating the leachate from incineration power plants [6]. Leachate is difficult to treat using conventional biological methods. Currently, leachate treatment methods mainly include physical and chemical treatment [7], advanced oxidation [8], membrane separation [9], and biological treatment [10]. Membrane bioreactors (MBR) using the double membrane method (NF/RO) process, and multi-effect evaporation treatment methods are also increasingly used to treat leachate [11]. However, the shortcomings of MBR treatment processes have become increasingly prominent due to the high concentration of organic matter in leachate, which blocks pipelines and requires the pipes to be continuously cleaned. Furthermore, the required cleaning agents cause secondary pollution and result in excessively high processing costs.

Due to the strengthening of environmental protection requirements, MSW incineration power plants should be able to perform advanced leachate treatment. The coagulation–flocculation precipitation method is a promising option that acts as an effective pretreatment method by adding polyacrylamide (PAM) and either the inorganic polymer coagulant poly-aluminum chloride (PAC) or poly-ferric sulfate (PFS) to the leachate. This treatment method is widely used in wastewater treatment facilities due to its low cost and relatively high efficiency in removing organic pollutants [12]. Although the coagulation–flocculation of leachate has been reported in a wide range of literature, most studies have focused on the removal efficiency of pollutants in the supernatant [13,14]. For practical applications, the floc settling speed, supernatant volume, and floc volume also require attention. Even if the removal efficiency of pollutants is high, practical application in the industry can be difficult due to the small supernatant volumes, the presence of loose flocs, and a slow sedimentation speed. Therefore, a coagulation–flocculation process with a fast sedimentation speed, small floc volume, and easy dehydration would be very promising. Furthermore, to the best of our knowledge, the application of bentonite as a flocculant in landfill leachate treatment has not yet been investigated.

In this study, the use of the inorganic mineral bentonite contained in colloidal particles was used in a coagulation–flocculation process to treat leachate. The synergistic effect of bentonite, PAC, and cationic polyacrylamide (C-PAM) on the flocculation performance was investigated, and the best-operating conditions were obtained to provide reliable experimental data for MSW incineration power plants.

2. Materials and methods

2.1. Leachate characteristics

Leachate was collected from the Shuanggang MSW incineration power plant located in Tianjin, China. This plant has been operated since 2005 and has a total area of 7.1 ha. The daily garbage disposal capacity of this plant is 1,200 t/d and it disposes of 400,000 tons of garbage per year. Leachate samples were collected from a garbage storage tank that collects 300 tons of leachate per day. After collection, the leachate samples were immediately transported to the laboratory in a sealed container. Leachate samples were stored at 4°C to minimize chemical and biological changes.

2.2. Inorganic mineral material bentonite

The inorganic mineral material used in this experiment was bentonite, which has the chemical composition $(Al_2, Mg_3)Si_4O_{10}OH_2 \cdot nH_2O$. Bentonite is a non-metallic mineral with montmorillonite as its main mineral component, which is sandwiched by two silicon-oxygen tetrahedrons. This 2:1 type crystal structure is composed of layered aluminum oxide octahedrons. Due to the layered structure formed by the montmorillonite unit cell, certain cations such as Cu, Mg, Na, and K are present in the bentonite. These cations are compatible with the montmorillonite unit cell, providing bentonite with good ion exchange properties. The bentonite used in this experiment was obtained from Shijiazhuang Hangquan Mineral Products Co., and it had a chemical composition of 50.95% SiO_2, 16.54% Al_2O_3, 0.26% FeO, 2.26% CaO, 4.65% MgO, 0.47% K_2O, and 23.29% H_2O. The bentonite was sieved with a 200-mesh sieve and stored in plastic jars at room temperature prior to use.

2.3. Coagulation–flocculation process

According to the results of a preliminary experiment, the raw leachate was pretreated by dilution to a 1:5 dilution ratio. In this study, a JJ4 six-link synchronous coagulation stirrer (Jiangxi, China) was employed for the coagulation–flocculation processes. The coagulation–flocculation experiments were conducted at room temperature. First, bentonite was mixed with the diluted leachate in a 250 mL beaker and initially stirred at a high speed of 350 rpm for 2 min. PAC (3%) was then added to the beaker, which was stirred for an additional 30 s at 350 rpm followed by 30 s at 250 rpm. Next, C-PAM (0.1%) was added to the beaker, which was stirred for another 30 s at 250 rpm. Finally, the wastewater was stirred at a slow speed of 50 rpm for 30 s and was then left to settle for 5 min. The purpose of the initial high stirring speed was to allow the leachate to fully contact the bentonite, PAC, and C-PAM. The purpose of the low stirring speed was to ensure floc growth. The experimental settings are presented in Table 1. Experiments R1, R2, and R3 were used to investigate the effect of PAC, C-PAM, and bentonite on the coagulation–flocculation process.

At the end of each coagulation–flocculation experiment, liquid samples were obtained using a plastic syringe from a depth of approximately 3 cm below the water surface for analytical determination. The COD, suspended solids (SS), total phosphorus (TP), and turbidity removal efficiencies were calculated using Eq. (1).

$$\text{Removal} (\%) = \frac{C_i - C_f}{C_i} \times 100\% \tag{1}$$

where C_i and C_f are the initial and final pollutant concentrations in the leachate (mg/L).

2.4. Analytical methods

2.4.1. Zeta potential

The liquid samples described in Section 2.3 were used for zeta potential analysis. Zeta potentials were measured

Table 1
Experiments of leachate on coagulation–flocculation

Name	R1	R2	R3
Bentonite (g/L)	8	8	0, 4, 8, 12, 16, 20
3% PAC (mL/L)	12, 16, 20, 24, 28, 32	32	32
0.1% C-PAM (mL/L)	16	8, 12, 16, 20, 24, 28	20

using a Micro Electrophoresis System (JS94H, Shanghai, China).

2.4.2. Floc morphology

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

2.4.3. Chemical analysis

COD, SS, and TP removal efficiencies were analyzed according to the standard methods for the examination of water and wastewater of the American Public Health Association (APHA) [15]. Turbidity was determined by a turbidity meter (WTW Turb550, Germany). The pH was determined by precision acidity meter (WTW pH3210, Germany). The total heavy metal content in the solutions was determined using an inductively coupled plasma-mass spectrometer (ICP-MS) instrument (Dual-view Optima 5300 DV, Beijing, China).

3. Results and discussion

3.1. Leachate characteristics

Table 2 shows the leachate characteristics generated by the incineration power plant after being diluted to a 1:5 dilution ratio. Leachate composition usually depends on the leachate age and the solid waste degree of stabilization [16]. The characteristics of the leachate used for this work demonstrate a young age due to the leachate's acidic pH and high organic load. This leachate was also generally biodegradable, as indicated by its BOD_5/COD ratio of 0.61. The Mn, Cu, Zn, Cd, Cr, Pb, Ni, and Hg concentrations in the leachate were measured to be 0.590, 0.390, 4.800, 0.077, 0.054, 0.074, 0.590, and 0.006 mg/L, respectively. Experiments were carried out at the original pH of 6.0. This neutral acid flocculation environment was more conducive to the flocculation treatment of the leachate, consistent with previous research results [17].

3.2. Coagulation–flocculation effect under different PAC dosages

The influence of PAC dosage on the coagulation–flocculation treatment process was investigated. In these

Table 2
Leachate water quality index after 5 times dilution

Parameter value standard[a]	Value	Standard[a]
pH	6	6~9
COD (mg/L)	21,440	100
BOD_5 (mg/L)	13,000	30
BOD_5/COD ratio	0.61	–
Turbidity (NTU)	432	–
Total phosphorus (mg/L)	69.94	3
Ammoniacal nitrogen (mg/L)	342.6	25
Suspended solids (mg/L)	810	30
Mn (mg/L)	0.590	–
Cu (mg/L)	0.390	–
Zn (mg/L)	4.800	–
Cd (mg/L)	0.077	0.010
Cr (mg/L)	0.054	0.100
Pb (mg/L)	0.074	0.100
Ni (mg/L)	0.590	–
Hg(mg/L)	0.006	0.001
Zeta potential (mV)	–40.1	–

[a]Environmental Quality (Standard for Pollution Control on the Landfill Site of Municipal Solid Waste) Regulations GB 16889-2008.

experiments, the bentonite dosage was 8 g/L, the PAC dosage was 12, 16, 20, 24, 28, or 32 mL/L, and the C-PAM dosage was 16 mL/L, relative to the volume of diluted leachate (1:5 dilution ratio). PAC is a traditional coagulant whose enhanced hydrolysis forms high molecular weight polymers of different sizes. PAC forms flocs by adsorption and sweeping.

PAC dosage can affect the coagulation–flocculation process because an insufficient dosage or overdosage of coagulant results in poor coagulation–flocculation performance. The optimum amount of PAC can prevent the excessive use of coagulant, reducing the cost of wastewater treatment. PAC hydrolyzes in the leachate, and its hydrolyzed alum salt compounds are adsorbed by suspended humus-containing particles in the water during the mixing process. The turbidity, SS, and TP removal efficiencies sharply increased at the beginning of the experiment, but the rate of increase gradually slowed down. Fig. 1a shows that with the addition of PAC, the polymer formed by the PAC through enhanced hydrolysis mainly adsorbed some dissolved organic pollutants, with little effect on the reduction of water quality indicators such as turbidity, SS, and TP. A PAC dosage of 12 mL/L was not high enough for the dissolved organic pollutants to be adsorbed and removed from the wastewater.

For a PAC dosage of 32 mL/L, the final COD, turbidity, SS, and TP concentrations were 7,567 mg/L, 12.6 NTU, 52 mg/L, and 1.97 mg/L, respectively. The corresponding removal efficiencies were 64.71%, 97.08%, 93.58%, and 97.18%, respectively. COD showed a higher removal efficiency with increasing PAC dosage. The COD removal efficiency trend with increasing PAC dosage was initially linear. However, at higher concentrations, the further addition of PAC did not improve the leachate removal efficiencies.
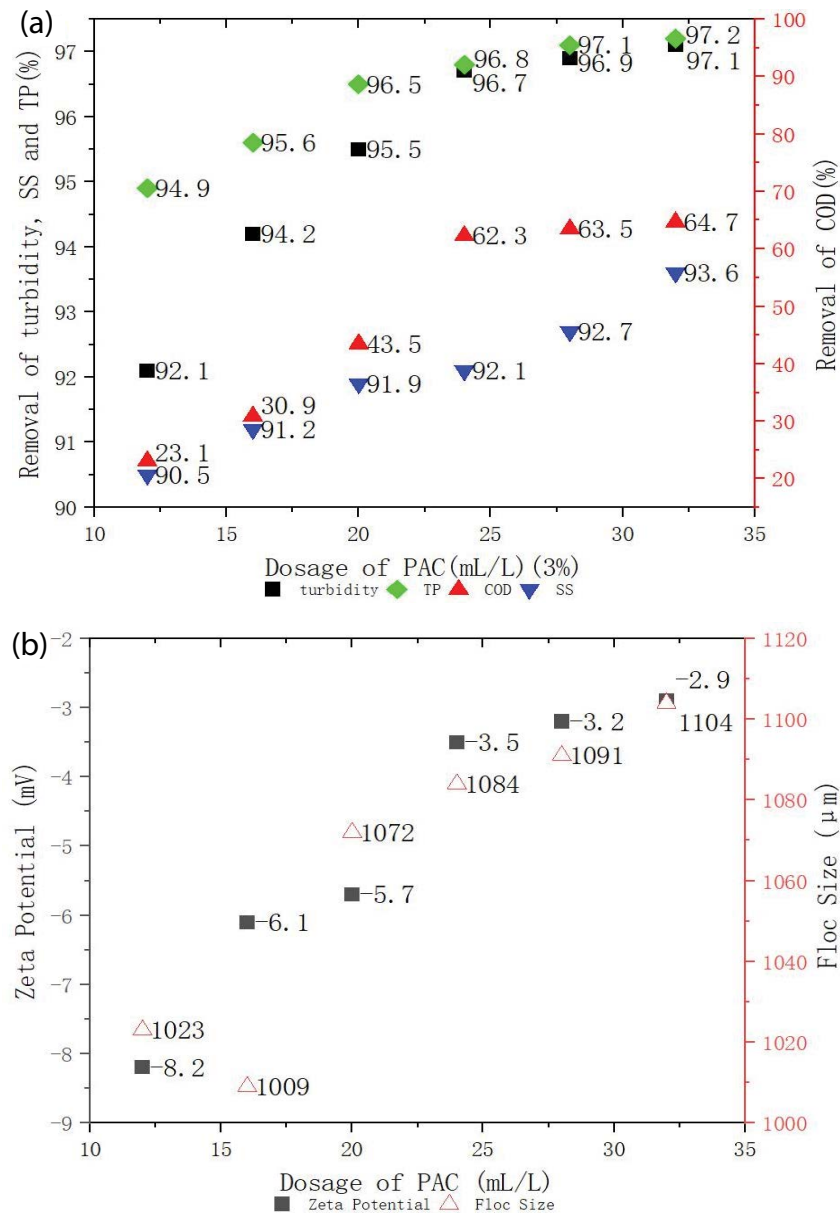
Fig. 1. Effect of PAC dosage on turbidity, COD, SS and TP removal efficiency (a) and zeta potential and floc size (b).

This can be explained by the breakage of flocs due to the excess PAC, which causes an inversion of the charge and disperses the agglomerated particles [18]. The turbidity removal efficiency increased to a maximum value of 97.08% with the addition of PAC. This phenomenon was attributed to the stabilization of colloidal particulates when the coagulant was used at a dosage above the optimum value [19]. Fig. 1a shows that the removal efficiencies of COD, turbidity, SS, and TP in the leachate were acceptable at a PAC dosage of 32 mL/L. From an economic perspective, it is unnecessary to further increase the PAC dosage beyond this.

As shown in Fig. 1b, the zeta potential values of the leachate for PAC dosages of 12, 16, 20, 24, 28, and 32 mL/L were −8.2, −6.1, −5.7, −3.5, −3.2, and −2.9 mV, respectively. When the PAC dosage was 32 mL/L, the zeta potential increased from −40.1 mV (raw leachate) to −2.1 mV (32 mL/L PAC dosage) and the floc size increased from 1,023 μm (12 mL/L) to 1,104 μm (32 mL/L) after coagulation–flocculation. It can be reasonably assumed that PAC is positively charged after hydrolysis. PAC neutralizes the negatively charged colloids in the leachate. As the dosage of PAC increases, hydrolysis is strengthened, leading to the generation of more $Al(OH)_{3(am)}$ and monomers with positive charges, which adsorb surrounding particles and are eventually removed by precipitation [20]. The concentration of negatively charged colloids in the water decreased with the gradually increasing zeta potential. This behavior is supported by the fact that PAC has a strong aluminum charge neutralization ability, high structural stability, and a large nanosized molecular diameter [18,21,22].

3.3. Coagulation–flocculation effect under different C-PAM dosages

To optimize the dosage of C-PAM for coagulation–flocculation, experiments were performed using a bentonite dosage of 8 g/L, a PAC dosage of 32 mL/L (based on the results shown in Section 3.2), and C-PAM dosages of 8, 12, 16, 20, 24, and 28 mL/L. The pollutant removal efficiencies under different C-PAM dosages are presented in Fig. 2.

C-PAM had a significant influence on the water quality index of the supernatant. The COD value initially decreased and then increased with increasing C-PAM dosage. When the C-PAM dosage was increased to 20 mL/L, the COD, turbidity, SS, and TP concentrations were 5,941 mg/L, 10.6 NTU, 50 mg/L, and 1.76 mg/L, respectively, and their corresponding removal efficiencies were 72.3%, 97.6%,

93.8%, and 97.5%, respectively. The TP discharge standard in the leachate was 3 mg/L (Table 2), satisfying Chinese wastewater standards.

C-PAM plays a pivotal role in the flocculation process. C-PAM polymerizes the flocs formed by coagulation through the double interaction of electric neutralization and adsorption bridging. Under the actions of shear force and centrifugal force from the stirring device, the flocs continuously collide and form large particles to realize the separation of mud and water. Because C-PAM is a coagulant aid, the mechanism of its combination with PAC mainly relies on the excellent ductility of the C-PAM macromolecular chain in conjunction with the Al^{3+} of PAC and the –O in PAM to form a stable network structure in which solid particles and other impurities in the leachate can be stably enveloped. This process promotes the removal of turbidity, SS, and TP during the flocculation process.
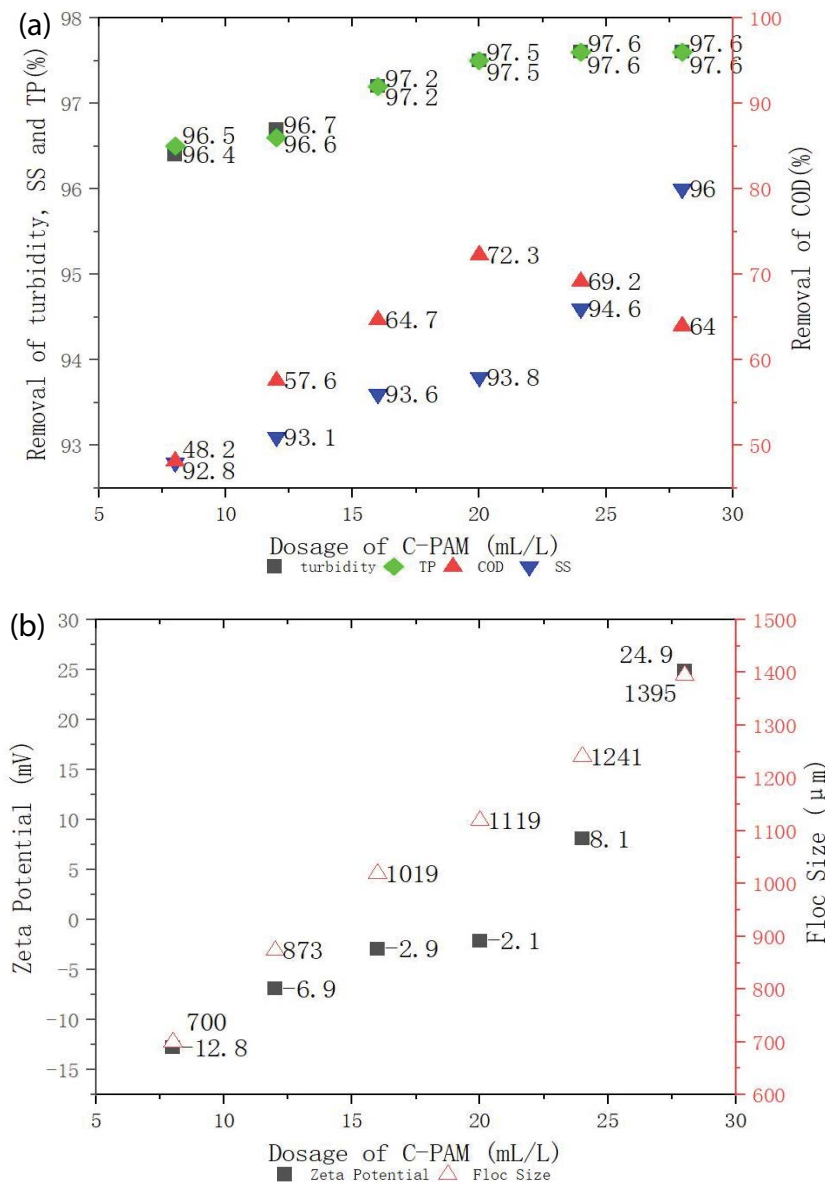

Fig. 2. Effect of C-PAM dosage on turbidity, COD, SS and TP removal efficiency (a) and zeta potential and floc size (b).

However, the removal efficiency of COD showed a decreasing trend at C-PAM dosages above the optimal 20 mL/L (Fig. 2a). When C-PAM cannot effectively combine with flocs to form secondary agglomerates, it remains in the water phase, so an optimal dosage of C-PAM is necessary for leachate treatment.

Fig. 2b shows that with increasing C-PAM dosage from 8 to 28 mL/L, the zeta potential increased from −12.8 to 25.0 mV and the floc size increased from 700 to 1,395 μm. The zeta potential approached 0 mV when the dosage of C-PAM was 20 mL/L due to the positive charge of the cationic C-PAM. This suggests that a stabilization of charges occurred in the leachate solution at this C-PAM dosage. However, the addition of excessive C-PAM adsorbed by colloid particles in the leachate led to a charge reversal of the colloids from negative to positive. These colloids were then restabilized and they repelled each other, resulting in a lower degree of agglomeration. The zeta potential increased from 0 to 24.9 mV with C-PAM dosages above the optimum point, typical behavior in coagulation–flocculation processes controlled by the neutralization of charges. Due to its high molecular weight and high positive charge density, C-PAM helped to bridge and strengthen the fragile flocs. This increased the floc size and corresponding settling rate, resulting in higher clarification efficiency. However, excessively high C-PAM dosages increased the COD of the supernatant.

3.4. Coagulation–flocculation effect under different bentonite dosages

To determine the optimal bentonite dosage for the coagulation–flocculation process, a PAC dosage of 32 mL/L, C-PAM dosage of 20 mL/L, and bentonite dosages of 0, 4, 8, 12, 16, and 20 g/L were used. The experimental results are shown in Fig. 3.

Bentonite dosage significantly affected the COD removal efficiency. Fig. 3a shows that when the bentonite dosage was increased from 4 to 8 g/L, the COD, turbidity, SS, and TP concentrations were significantly reduced from 16,483 mg/L, 28.4 NTU, 72 mg/L, and 2.34 mg/L to 13,568 mg/L, 23.9 NTU, 61 mg/L, and 2.1 mg/L, respectively. These values correspond to COD, turbidity, SS, and TP removal efficiencies of 36.7%, 94.5%, 92.5%, and 96.8% for 4 g/L bentonite and 72.3%, 97.6%, 93.8%, and 97.5% for 8 g/L bentonite. The high COD removal efficiency under 8 g/L bentonite can be attributed to the composition of the biologically treated leachate, which contains a significant fraction of recalcitrant and high molecular weight organic substances [23]. Bentonite has a high specific gravity. The uniform dispersion of bentonite in the flocs therefore forces the flocs to rapidly settle under the action of gravity. Through the combined effect of bentonite, PAC, and C-PAM, dense flocs were formed. These flocs rapidly settled and led to the production of a higher volume of supernatant with a low COD concentration, convenient for separation and biological treatment. With increasing bentonite dosage, the COD removal efficiency significantly increased, but the other water quality indicators did not significantly change.

Fig. 3b shows the zeta potential values and floc sizes of selected bentonite dosages. The zeta potential values for bentonite dosages of 0, 4, 8, 12, 16, and 20 g/L were −9.3, −9.1, −2.1, −7.2, −8.7, and −23.9 mV, respectively. Under 8 g/L bentonite, the zeta potential of the supernatant was −2.1 mV. The zeta potential value for the bentonite dosage of 8 g/L was −8.5 mV when it was added to 1 L water, indicating that bentonite had more negative charges on its surface. These charges are mainly due to the lattice defects on the bentonite surface. Bentonite's surface charge imbalance is caused by isoelectric isomorphic substitution in its solid lattice, interstitial atoms, and vacancies, a process that is not significantly affected by the external environment (e.g., pH value). Although the zeta potential dropped from −2.1 to −23.9 mV under excessive bentonite dosages, the experimental results reported in Fig. 3a show that the concentrations of COD, turbidity, SS, and TP were slightly reduced due to adsorption by bentonite.

As shown in Fig. 3b, the decline in floc size from 1,298 μm without bentonite to 1,119 μm at a dosage of 8 g/L bentonite signified that the flocs became more compact and were able to settle to the bottom of the solution. This demonstrates that both floc formation and its state were significantly changed by the combined treatment of bentonite, PAC, and C-PAM.

Based on this result, the optimum bentonite, PAC, and C-PAM dosages were determined to be 8 g/L, 32 mL/L, and 20 mL/L, respectively. This treatment realizes the synergistic effect of bentonite, PAC, and C-PAM in leachate coagulation–flocculation treatment.

3.5. Function of bentonite in enhancing separation efficiency

Most previously reported studies have focused on the removal of pollutants [24–26]. However, in leachate treatment plants, more attention should be paid to enhancing floc settlement, which allows more supernatant to be obtained and improves the performance of subsequent biological treatment processes. To investigate the effect of bentonite on the floc settling time and the volume of supernatant, two experiments were performed, one with 8 g/L bentonite and one without bentonite.

When bentonite was not added, a leachate coagulation–flocculation effect was still observed. When the coagulation–flocculation treatment was stopped, loose flocs were formed by the enhanced PAC hydrolysis. Fig. 4a shows that 90% of the flocs floated to the surface and 10% of the flocs settled to the bottom of the beaker. Fig. 5a shows that flocs produced without bentonite were fluffy, with a particle size of 1,298 μm. These flocs were large and loose, so they floated on the liquid surface after stirring. After 15 min, more than 80% of the flocs were still floating on the water surface, not conducive for subsequent solid-liquid separation. In contrast, under the optimal dosages of bentonite, PAC, and C-PAM, the flocs almost completely precipitated within 1 min. The turbidity in this experiment was 10.6 NTU and a large volume of transparent supernatant (92.8%) was obtained. The greatest differences between these two experiments were the removal efficiency of COD, the denser precipitated flocs, and the larger volume of supernatant. Therefore, the use of bentonite achieves the purpose of first-level enhanced coagulation–flocculation leachate treatment.
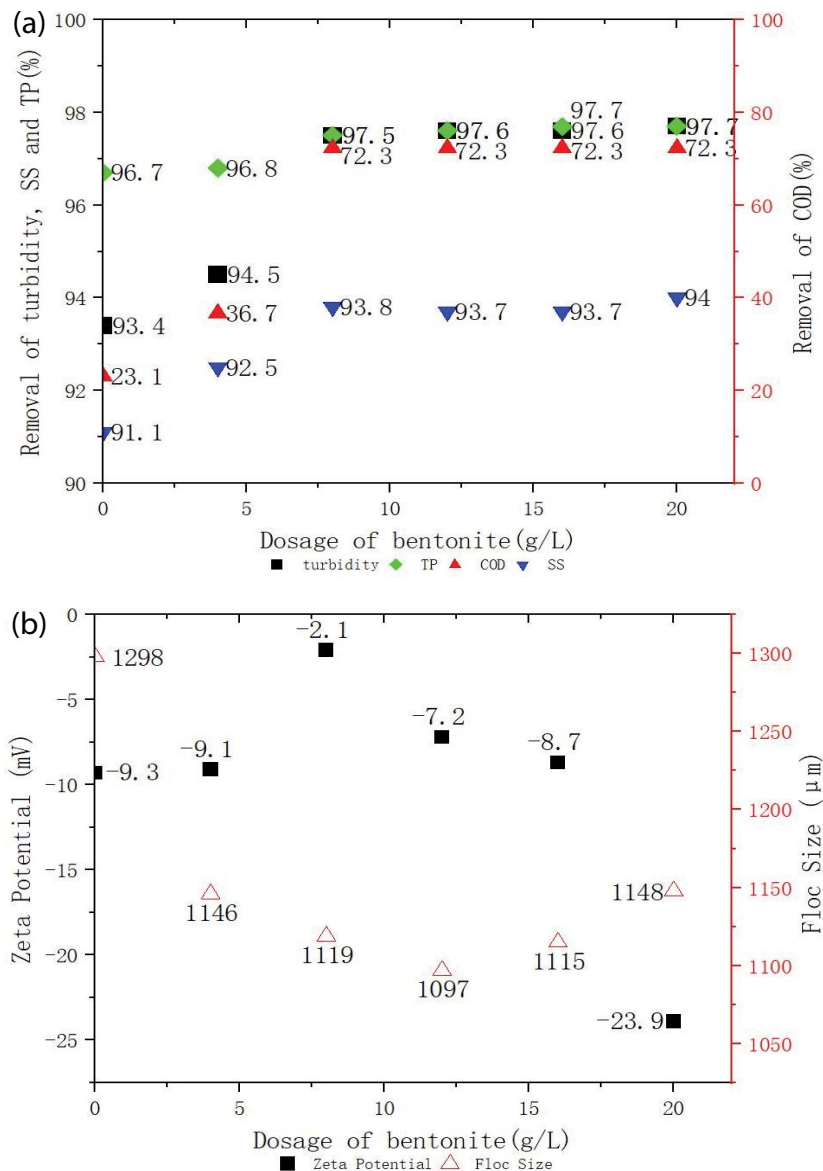
Fig. 3. Effect of bentonite dosage on turbidity, COD, SS and TP removal efficiency (a) and zeta potential and floc size (b).

Fig. 6 shows digital photographs of the leachate after coagulation–flocculation. Fig. 6a shows that after flocculation, the supernatant was very turbid under an insufficient PAC dosage, indicating the presence of a higher pollutant concentration in the supernatant. When the PAC dosage was 32 mL/L, the supernatant was very clear and transparent, and the final experimental results also showed that the treatment effect under this dosage was satisfactory. Fig. 6b shows that increasing the C-PAM dosage enhanced the agglomeration of the settled flocs and gradually clarified the supernatant to facilitate subsequent separation. However, the addition of C-PAM also potentially increased the COD concentration, which might undermine the water quality. Fig. 6c clearly shows a higher floc settlement rate with the addition of bentonite. Because bentonite has a certain adsorption capacity, the COD, turbidity, SS, and TP concentrations were also significantly decreased in the presence of

bentonite. Notably, weak fluctuations did not affect the settlement state of the flocs at the bottom of the beaker.

Overall, the addition of the inorganic mineral bentonite was extremely beneficial for the sedimentation and rapid separation of flocs. This behavior can be explained by the following process: the addition of bentonite leads to the formation of colloids due to the effect of the bentonite microparticles. Bentonite particles are uniformly dispersed in the leachate as colloidal particles by rapid stirring for 2 min in the early treatment stage. Under the action of PAC, electric neutralization and destabilization occur, leading to coagulation and the adsorption and net capture of pollutants in the leachate [27]. At the same time, the organic polymer C-PAM has an affinity for the organic pollutants in the leachate. C-PAM absorbs or sweeps these pollutants and forms small secondary agglomeration flocs [28]. Furthermore, the high specific gravity of bentonite, which is dispersed in
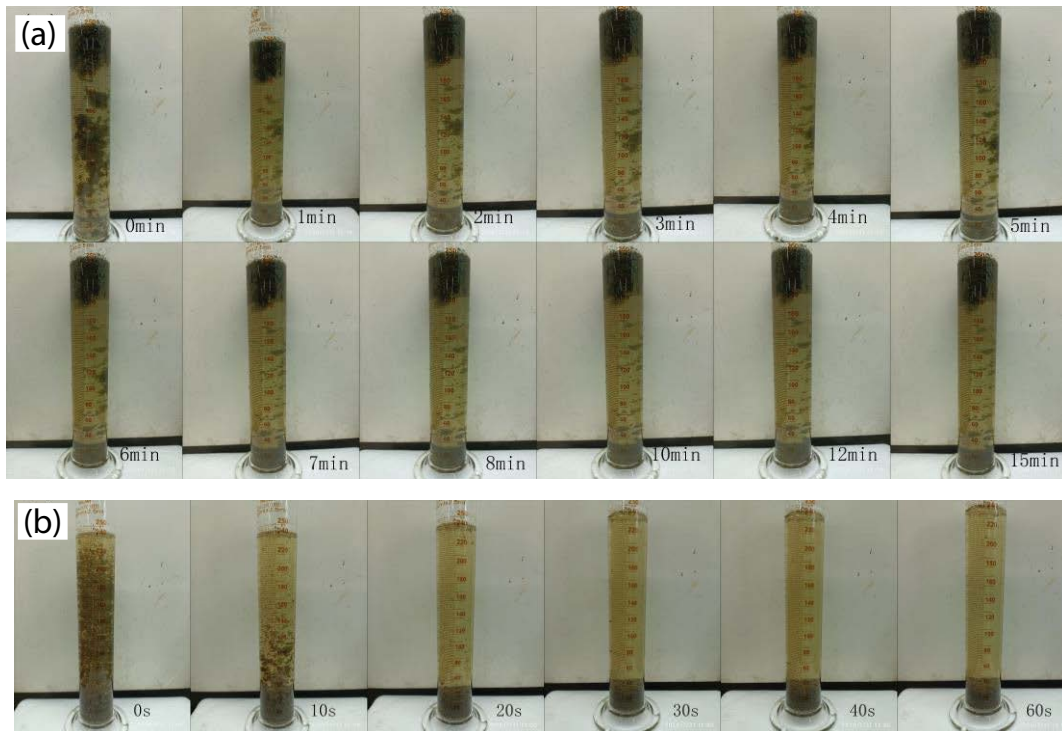
Fig. 4. Settling time and supernatant volume under 32 mL/L PAC, 20 mL/L C-PAM (a) and 8 g/L PRT, 32 mL/L PAC, 20 mL/L C-PAM (b).
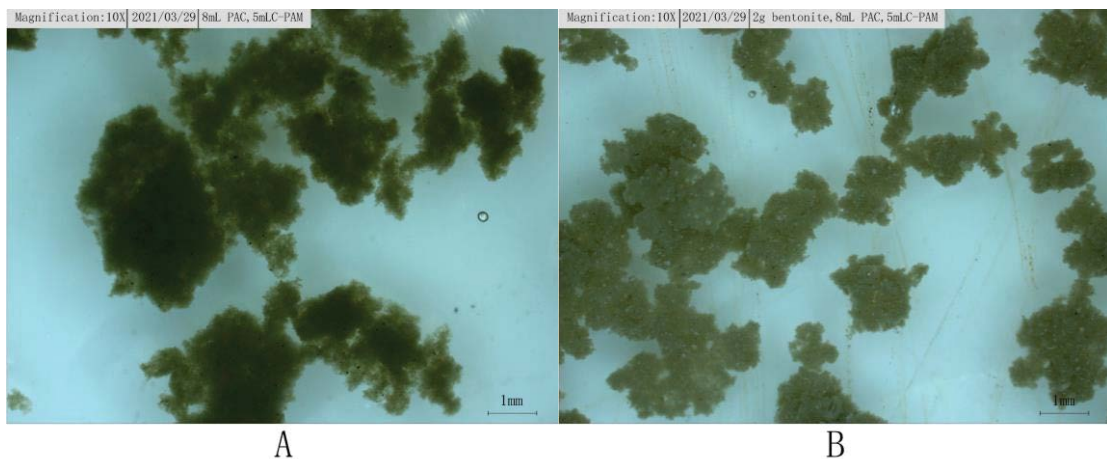

Fig. 5. Images of particles and flocs at 10x magnification for flocculant with 32 mL/L PAC, 20 mL/L C-PAM (A) and 8 g/L PRT, 32 mL/L PAC, 20 mL/L C-PAM (B).

the flocs, forces the flocs to quickly settle under the action of gravity.

Consequently, through the synergistic effect of bentonite, PAC, and C-PAM, dense flocs are formed and quickly settled. The low concentration supernatant can be used for subsequent biological treatment with a lower organic loading. The less compact sludge obtained by this process with a smaller volume means that a smaller sludge thickening tank could be used, reducing the capital costs of leachate treatment plants.

3.6. Removal of heavy metals by coagulation–flocculation

The typical content of heavy metals in leachate also far exceeds wastewater discharge regulations. Heavy metals have a negative environmental impact because they can inhibit the metabolic activity of microorganisms and inactivate microbial enzymes. In addition, heavy metal ions are difficult to degrade in the environment.

Table 3 shows the heavy metal content of raw leachate, the coagulation–flocculation product with 8 g/L bentonite,
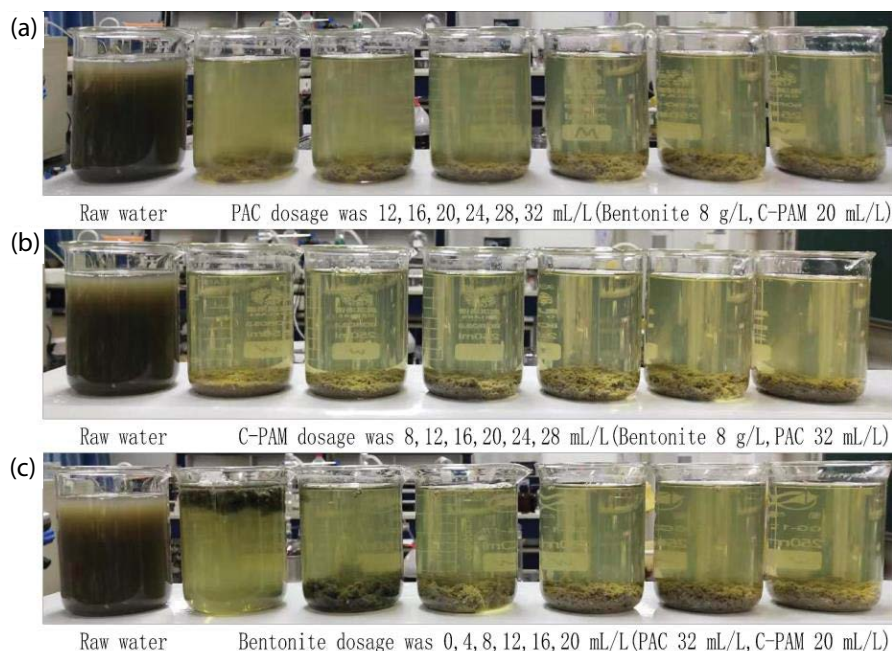
Fig. 6. Flocculation effect under different dosages of PAC (a), C-PAM (b) and bentonite (c).

Table 3
Heavy metals of raw water (5 times dilution), mixed 8 g/L and without bentonite in R3 after coagulation–flocculation

Name	Raw water	With bentonite	Without bentonite
Mn (mg/L)	0.590	0.340	0.380
Cu (mg/L)	0.390	0.030	0.100
Zn (mg/L)	4.800	0.420	1.180
Cd (mg/L)	0.077	0.061	0.073
Cr (mg/L)	0.054	0.036	0.040
Pb (mg/L)	0.074	0.053	0.062
Ni (mg/L)	0.590	0.410	0.480
Hg (mg/L)	0.006	0.002	0.004

and the coagulation–flocculation product without bentonite. Under the effect of PAC and C-PAM, the content of heavy metals such as Mn, Cu, Zn, Cd, Cr, Pb, Ni, and Hg in the raw leachate decreased from 0.590, 0.390, 4.800, 0.077, 0.054, 0.074, 0.590, and 0.006 mg/L to 0.380, 0.100, 1.180, 0.073, 0.040, 0.062, 0.480, and 0.004 mg/L, respectively. This can be attributed to the hydrolyzed PAC forming a large three-dimensional network structure in the water. This structure agglomerated the destabilized heavy metal ions in the leachate, and the resulting flocs became larger under the bridging action of the organic polymer C-PAM. The larger flocs were separated from the aqueous phase and precipitated under the action of gravity, removing the heavy metals from the wastewater. However, the bentonite-free flocs floated on the top of the treated wastewater, not conducive to subsequent separation treatment processes.

The addition of bentonite both promoted the rapid settlement of flocs and led to enhanced heavy metal absorption from the leachate. Under the synergistic effect of bentonite,

PAC, and C-PAM, the removal rate of the heavy metals Mn, Cu, Zn, Cd, Cr, Pb, Ni, and Hg was reduced to 0.340, 0.030, 0.420, 0.061, 0.036, 0.053, 0.410, and 0.002 mg/L, respectively. This represents removal efficiencies of 42.4%, 92.3%, 91.3%, 20.8%, 33.3%, 28.4%, 30.5%, and 62.5%, respectively.

3.7. Mechanism discussion

Four theories have been proposed to describe the mechanism of flocculation: the compression of the double electric layer, charge neutralization, and bridging and sweeping precipitation. The network structure of the PAC-based coagulants physically captures small, suspended particles through agitation and precipitation, as shown in Fig. 7a. The sweeping effect always plays a dominant role in turbidity abatement. However, the formed flocs in typical flocculation processes are usually large and spongy, making them vulnerable to minor disturbances. If these settled flocs are vigorously stirred, achieving flocculation again is very difficult.

Fig. 7b shows the synergistic effect of bentonite, PAC, and C-PAM. The PAC is hydrolyzed into many small flocs to effectively neutralize the negatively charged colloids. The presence of bentonite helps these small flocs grow into larger conglomerations by Van der Waals forces between the destabilized particles. The use of bentonite leads to a more rapid settling velocity, which can be explained by the high specific gravity of bentonite particles. Bentonite has a relatively high density and a particle size of 74 μm. The bentonite dissolved in the leachate leads to the neutralization of electric charges and destabilization under the action of PAC, upsetting the ion balance of the leachate and adsorbing and trapping the pollutants in the leachate. Under the action of the C-PAM flocculant, the small flocs form secondary agglomerations and larger flocs. The high
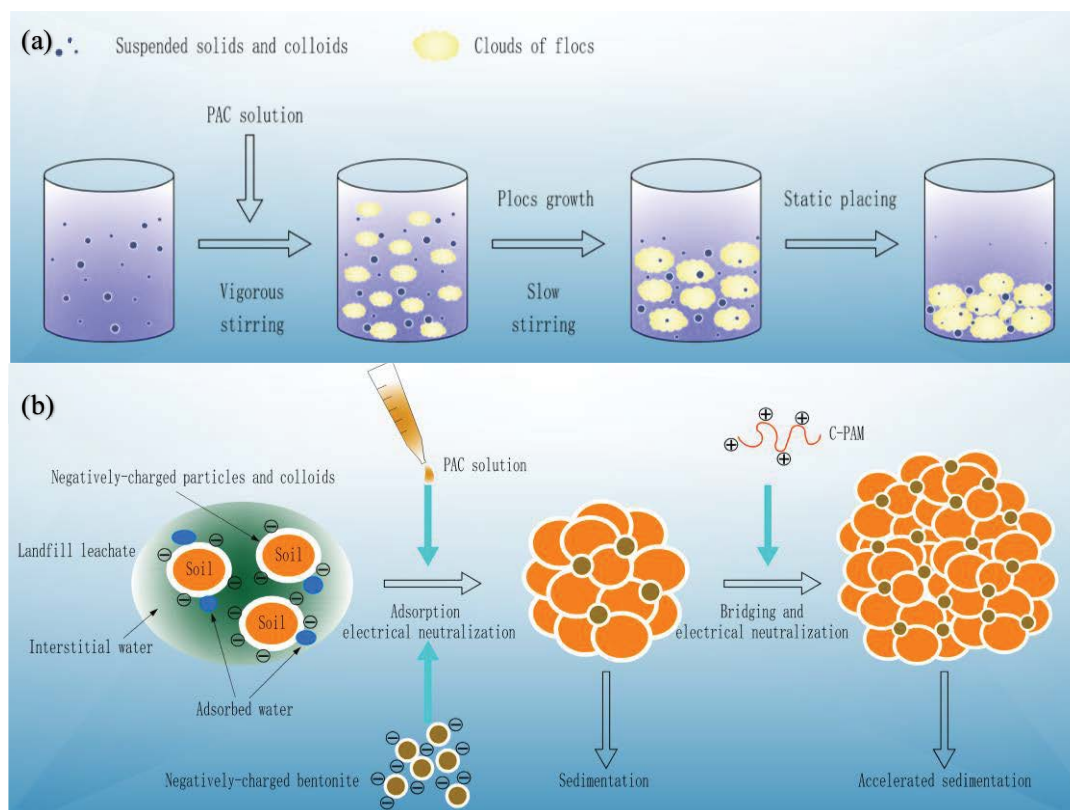
Fig. 7. Schematic of coagulation–flocculation by PAC (a) and bentonite, PAC and C-PAM (b).

specific gravity of bentonite accelerates the settling speed of the flocs. These flocculated aggregates are compact in structure and do not easily float.

4. Conclusions

A primary enhanced coagulation–flocculation method with bentonite was developed herein for the treatment of leachate. When the dosages of bentonite, PAC, and C-PAM were 8 g/L, 32 mL/L, and 20 mL/L, the removal efficiencies of COD, turbidity, SS, and TP were 72.3%, 97.6%, 93.8%, and 97.5%, respectively. The synergistic effect of bentonite, PAC, and C-PAM improved the coagulation–flocculation effect, led to a rapid settling time of less than 1 min, and resulted in a large volume of supernatant (92.8% of the total volume). These effects are conducive for subsequent solid-liquid separation. This combined coagulation–flocculation treatment process is expected to significantly reduce the cost of leachate treatment.

Acknowledgements

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