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Flocculation property of composite flocculants PAC/CPAM for polluted landscape water pretreatment

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ABSTRACT

In this paper, we investigate the flocculation performance of composite coagulants polyaluminium chloride (PAC) and cationic polyacrylamide (CPAM) for landscape water treatment. The flocculant CPAM was synthesized through low-pressure UV initiation in our laboratory. This method was an environment-friendly and efficient approach. The flocculation mechanism of the combined flocculant was further analyzed by Fourier-transform infrared spectroscopy, three-dimensional fluorescence analysis, zeta potential and microscopic observation. Results indicated that turbidity, UV_{254}, phosphorus, and algae were effectively removed using PAC/CPAM flocculants. Humus and protein were easily removed from landscape water through flocculation. Moreover, electrical neutralization of PAC and the adsorption bridging effect of CPAM were found to be dominant in flocculation. The flocs from using PAC/CPAM were more compacted and stabilized than those from using PAC or CPAM alone. In addition, the appropriate divided addition of PAC was favorable for flocculation.

Keywords: Landscape water; Flocculation; Polyaluminium chloride; Cationic polyacrylamide; Low-pressure ultraviolet

1. Introduction

Freshwater is a limited natural resource, and several parts of the world are facing increasing pressure on their freshwater resources [1]. With the gradual advancement of people's living standard, people are concerned with the city environment, thus, the planning and designing of the landscape water are receiving much attention, and the living areas with a water scene has become popular and welcome [2]. Landscape water plays an important role in the construction of the city and the natural landscape, because of the continuous progress and rapid development of the society. Previous studies showed that pollution of landscape water is a dire concern in many countries and regions of the world because of population growth and accelerated industrialization and urbanization [3]. Many urban lakes, rivers, and other landscape waters were subject to varying degrees of pollution because of various types of sewage and surface runoff inflow [4,5]. For instance, the Taihu Lake, Chaohu Lake, and Dian Lake, the three major lakes in China, have experienced algal blooms [6]. Pollutants brought by urban

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storm water runoff are another reason for causing landscape water pollution. Moreover, due to the poor mobility of landscape water bodies, the long-term accumulation of sediments in water will cause pollution [7]. Landscape water is rich in nitrogen, phosphorus, and other nutrients, leading to algae bloom outbreak at high temperature. Abnormal propagation of algae will damage the ecological balance of the environment, and the lake shows significant dark green color, leading the chrominance of water to increase. The turbidity generally reaches dozens of nephelometric turbidity units (NTU) or even hundreds of NTU, sometimes accompanied by a strong fishy smell. Occasionally, these conditions may turn to black and odorous water body, seriously affecting the esthetics of the landscape water.

In recent years, to address the problem of landscape water pollution, wide ranges of research were launched at home and abroad. To date, the landscape water pollution can be settled using various techniques, such as water diversion and renewal, coagulation–sedimentation, air floatation, and biological contact oxidation. Chen et al. [8] carried out a series of research about the use of reclaimed wastewater for replenishing urban landscape ponds that would largely settle the concern about water shortages. An environmentally friendly chitosan-based graft flocculant was successfully prepared for treating low-algal-turbidity water from Jing Lake. Compared with these methods, flocculation is an important ecofriendly treatment technology with low processing cost requirements [9]. Coagulation is a process of combining small particles into large aggregates (flocs) and for adsorbing dissolved organic matter (DOM) onto particulate aggregates so that these impurities can be removed in subsequent solid/liquid separation processes [10]. Despite its numerous advantages, the research of flocculation in landscape water treatment has not yet been thoroughly investigated. In water treatment, coagulation is an essential process for the removal of fine particulate matters [11]. Coagulation–flocculation is widely used for wastewater treatment because it is efficient and easy to operate [12]. Coagulation–flocculation is welcomed as a pretreatment process for the removal of wastewater turbidity, organic matter, color, and microorganism. The performance of flocculation generally depends on the type and properties of flocculants [13].

The application of combined coagulants/flocculants has recently become a research focus. Aguilar et al. [14] used ferric sulfate as coagulant to treat a slaughterhouse liquid effluent, polyacrylamide (PAM), polyvinyl alcohol, and polyacrylic acid as coagulant aids to improve its coagulation efficiency. Zahrim et al. [15] found that ferric chloride-anionic PAM shows better performance than ferric chloride-polyDADMAC in terms of color removal, and the addition of polymers reduced phytotoxicity of generated sludge [15]. Sudfloc 3850 and algaefloc 19s were considered to be used instead of alum, and they required 10 times lesser dosages than alum. According to the above analysis, to obtain desired flocculation efficiency for landscape water, adsorption and charge neutralization capacity should be enhanced simultaneously. Thus, polyaluminium chloride (PAC) was chosen as coagulant, and cationic polyacrylamide (CPAM) flocculant was prepared through low-pressure UV initiation as flocculation aids in this work. Low-pressure UV initiation was recently used to prepare PAM flocculants. UV initiation can speed up the breakage of double bonds, shorten the reaction time, and improve the degree of polymerization of flocculants. Moreover, compared with high-pressure ultraviolet light, low-pressure ultraviolet light has the advantages of low energy consumption, simple installation, and environmental protection, and is in line with the trend of low carbon and energy saving.

In this work, PAC and CPAM have been combined for treating polluted landscape water. Ammonia concentration (NH_3-N), chemical oxygen demand (COD), total phosphorus (TP), turbidity, and UV_{254} were measured for evaluating flocculation performance. Fourier-transform infrared spectroscopy (FTIR), three-dimensional excitation emission matrix (EEM), zeta potential, and microscopy were employed to analyze the chemical and morphology structures of flocs or supernatant. The flocculation optimum condition and mechanism were discussed for comprehensive understanding of combined coagulation/flocculation.

2. Materials and methods

2.1. Materials

CPAM used in flocculation was sourced from copolymerization of AM and DMDAAC under low-pressure ultraviolet initiation in our previous work [16], and the FTIR spectrum of CPAM is illustrated in Fig. S1. The intrinsic viscosity and mass fraction of CAPM were 882 mg/L and 36.16%, respectively. Commercial flocculant of PAM (MW of 2,000–14,000 kDa) was provided by Aladdin Industrial Corporation (Shanghai, China) for the comparing experiments. The inorganic reagent PAC (>95 wt%) used in this study was provided by East Sewage Treatment Plant (Maanshan, Anhui province, China). Sodium hydroxide (NaOH, 96 wt%), hydrochloric acid (HCl, 1.179 g/cm^3), and sodium chloride (NaCl, 2.165 g/cm^3) without exception were derived from Sinopharm Chemical Reagent Co., Ltd. The pH of original landscape water was adjusted with 0.5 mol/L NaOH or HCl. Distilled water was used to prepare all the solutions through dissolution or dilution. All reagents used in this study were of analytical grade and used directly without any further purification.

2.2. Raw water

The raw water samples were collected from Cihu River (Maanshan, Anhui province, China), which is considered as polluted landscape water in the middle reaches of the Yangtze River in China. This river is landscape water near the business district, showing an eutrophication state, and containing a high concentration of dissolved organic carbon, particularly humic substances.

The seasons have a significant effect on the pollution of closed landscape water bodies apparently. The apparent pollution is serious and the variation of water quality is frequent, especially in high temperature season [17,18]. Moreover, due to the impact of land runoff, the water turbidity would be greatly increased. The water quality indicators, such as ammonia concentration, COD, TP, turbidity, and UV_{254} will also increase substantially. Water samples were collected in March and April of 2017. The water qualities were as follows:

temperature of 10°C–20°C, pH of 7.5–8.5, turbidity of 10–70 NTU, UV_{254} of 0.15–0.65 cm^{-1}, COD of 150–200 mg/L, TP of 15–25 mg/L, ammonia concentration of 30–40 mg/L, and the number of algae of 10–12 × 10^6 L^{-1}. The partial characteristics of the collected raw surface water are listed in Table 1.

2.3. Flocculation performance

Based on the characteristics of water quality of polluted landscape water, this paper has carried out intensive coagulation research, and PAC was selected as coagulant and CPAM as auxiliary flocculant. A series of flocculation experiments were conducted on a ZR4-6 program-controlled jar test apparatus (Zhongrun Company, China). 6 L of raw water was evenly added into six beakers, and the beakers were transferred to the jar test apparatus for mixing. A predetermined dosage of coagulant PAC was added into the sample water before rapid stirring at 300 rpm for 3 min. Then, a certain amount of flocculant CPAM or PAM was added, followed by slow stirring at 50 rpm for 15 min, and free settled for 30 min. Subsequently, supernatant at the depth 1–2 cm below the liquid surface was extracted for further measurement. The UV_{254} of the supernatant was measured by a UV-visible spectrophotometer (T6 Pgeneral Co., Ltd, China) at a wavelength of 254 nm, and the turbidity was determined by a 2100Q turbidimeter (HACH, USA). All the experiments were conducted and measured in triplicate, and the results presented in this paper were the average of the three runs [19].

2.4. Flocculation mechanism

The FTIR spectra of the samples were measured through a Bruker TENSOR27 FTIR (Bruker Company, Germany), and the infrared spectrum was measured in the range of 400–4,000 cm^{-1}. Three-dimensional EEM spectra were measured by an FM-4P-TCSPC fluorescence spectrophotometer (Horiba Jobin Yvon, France) in a 1-cm quartz cuvette. The range of the fluorescent wavelength analysis was 220–550 (E_m) nm and 220–400 (E_x) nm at 3 nm sampling increments [20]. The emission and excitation slit bandwidths were set at 10 nm, and the scanning speed was kept as 1,200 nm·min^{-1}. For the low-level light detection, the voltage of photomultiplier tube was kept at 750 mV, and ambient temperature was about 18°C. All the samples were filtered through the 0.45-μm membrane filter before measuring of EEM spectroscopy. The contour plots between E_m and E_x were drawn through Origin 8.5 software [21–23]. The treated supernatant was measured for the zeta potential on a Malvern nano ZS 90 potentiometer (Malvern company, UK). 25 μL of floc samples were placed on a slide with a pipette and covered with a 24 mm × 24 mm cover slip, and the sample was transferred to an Olympus BX53 microscope (Olympus, Japan) afterwards. The microscope was connected to an Mshot DC30 digital camera (Mingmei, China), and microscopic image acquisition was carried out using the accompanying MShot Digital Imaging System software (Mingmei, China). The cover slip was divided into three areas and observed at a magnification of ×100.

3. Results and discussion

3.1. Flocculation efficiency

3.1.1. Comparison of flocculants

The coagulation efficiency can be improved using the proper coagulants and optimization of the process parameters. In thia research, the flocculation efficiency was compared using PAC, PAM, and CPAM. To select the optimized flocculant combination for the next experiment, the following flocculants were compared: PAC, combined coagulant/flocculant of PAC/PAM, and combined coagulant/flocculant of PAC/CPAM. PAM was sourced from the market for comparison, and CPAM was synthesized in our laboratory. The PAC concentration was prepared at 2 mg/mL, and the PAC dosage of 20–100 mg/L was investigated as the PAM and CPAM dosage set at 0.5 mg/L. The experimental results are presented in Fig. 1.

Turbidity and UV_{254} removal efficiency by using different flocculants all presented a similar variation tendency with the increase of PAC dosage. Turbidity and UV_{254} removal efficiency rapidly increased with the increase of PAC dosage before 60 mg/L, and slowly increased with the further increase of PAC dosage. Under low PAC dosage, collision between pollutant particles and flocculants was inadequate, and to break the stability between pollutant particles was difficult, thereby resulting in low removal efficiency [16]. The collision was quickly promoted with numerous flocculants added into flocculation, continuously forming a large number of fine agglomerates and flocs. However, excess dosage of PAC would cause "cage effect," preventing the growth of flocs and reducing the settling efficiency.

Table 1
Water quality of raw polluted landscape water

Parameters	Average values	Test instruments or method
pH	7.5–8.5	PHS-3C pH meter (Leichi company, China)
Temperature (°C)	10–25	Water thermometer
Turbidity (NTU)	10–70	2100Q turbidity meter (HACH, USA)
UV (abs/254)	0.15–0.65	UV spectrophotometry (T6 Pgeneral Co., Ltd, China)
CODcr (mg/L)	150–200	Potassium bichromate
Ammonia (mg/L)	30–40	Nessler's reagent spectrophotometric
TP (mg/L)	15–25	Molybdenum antimony anti-spectrophotometer
Algae (10^6/L)	10–12	Olympus BX53 microscope (Olympus, Japan)

PAC used alone might cause unsatisfactory result of the removal efficiency. This condition could get relatively small and loose floc formation and minor sedimentation rate. PAC has a low relative molecular weight and a single active hydroxyl group, causing less adsorption and bridging. The PAC/CPAM combination showed the supreme removal effect. As a result, as PAC was added into raw water, charge neutralization initially occurs and promotes formation of particles/flocs. In addition, CPAM or PAM was added into the mixture of raw water and PAC as coagulant aids, and bridging action may be involved in co-precipitation and sorption onto flocs. Finally, the pollutant particles were removed. CPAM can demonstrate excellent performance of adsorption bridging because it is a novel organic cationic flocculant with high cationic degree [24]. Therefore, the following experiments mainly optimize the flocculation performance of PAC/CPAM.

3.1.2. Effect of CPAM dosage

Flocculation efficiency not only depends on the type of flocculants, but also the dosage of a certain flocculant. The effect of flocculant dosage on the removal efficiencies of turbidity and UV_{254} was evaluated using PAC/CPAM. The experiment was examined with the CPAM dosage varied in the range of 0.1–1.2 mg/L at pH 7.0, and PAC dosage was kept constant at 60 mg/L. The experimental results are shown in Fig. 2(a).

Fig. 2(a) presents that with the increase of CPAM dosage, a significant increase was observed in the removal efficiencies of turbidity and UV_{254}, but the increase in tendency could not continue with the further increase in the flocculant dosage. As CPAM dosage increased to 0.4 mg/L, the adsorption capacity of the flocculant increases. This condition is favorable for the neutralization and adsorption of the bridge. The growth rate of removal efficiency was reduced with further increase of CPAM dosage. On the contrary, the removal rate of the turbidity and UV_{254} slightly decreased with the increased CPAM dosage at 0.4–0.6 mg/L. CPAM overdose results in a decrease in the adsorption-bridging capability of the polymer [25]. The number of particles that can be adsorbed is limited, and the effect of adsorption bridging is weakened. This phenomenon results in low removal efficiency. With the increase of CPAM dosage from 0.6–1.2 mg/L, the excessive dosing leads to decreased removal efficiency. Excessive dosage would stabilize the colloidal particles, whereas small dosage might not produce enough charge neutralization and bridging capacity.

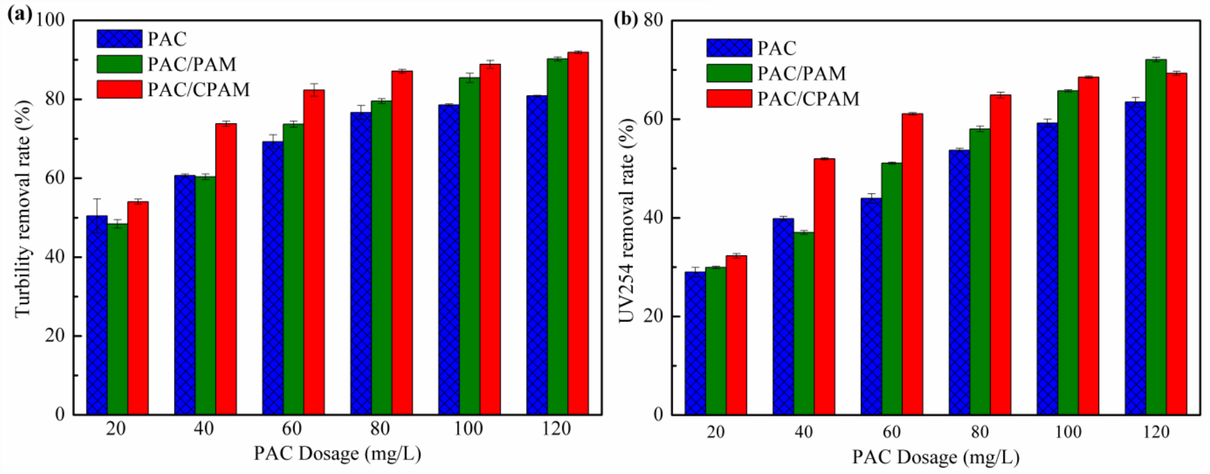

Fig. 1. The effect of flocculants on (a) turbidity removal rate and (b) UV_{254} removal rate.

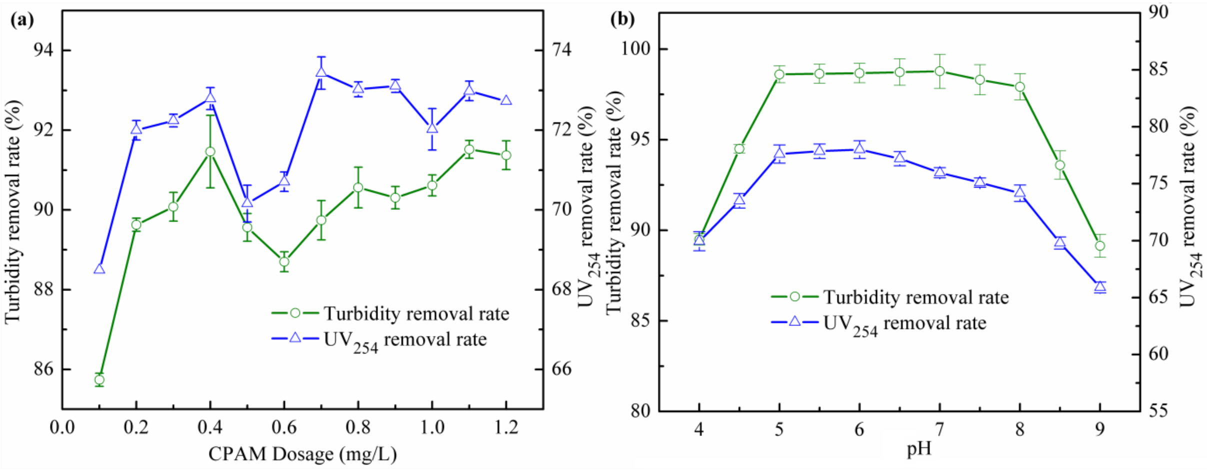

Fig. 2. The effect of (a) CPAM dosage and (b) pH on turbidity removal rate and UV_{254} removal rate.

Therefore, an optimum flocculant dosage for good flocculation was required. Briefly, as the dosage of CPAM is inadequate, the number of adsorption sites of adsorbed particles is less, leading to the weakening of adsorption bridging and the low removal rate. As the dosage is excessive, the surface of the particle adsorbs the excess flocculant, leading to the opposite charge on its surface. In addition, the repulsion between particles is enhanced and back to the state of re-stability, causing the reduction of the removal rate. Consequently, the CPAM dosage was chosen to be 0.4 mg/L based on the consideration of the effect of treatment and economic costs.

3.1.3. Effect of pH value

Aggregation of fine colloidal particles to large particles is a common practice involved in solid/liquid separation by flocculation [26]. As these particles aggregate, the generated flocs may settle depending on their size. Flocculation processes are highly dependent on the process conditions, such as pH and solid concentration [27]. The effect of pH on the flocculation effect is multifaceted. To study the effect of pH on the flocculation, the pH value of the landscape raw water was adjusted by HCl (0.5 mol/L) and NaOH (0.5 mol/L). In this section, 60 mL PAC solution with concentration of 2 mg/mL and 0.8 mL CPAM solution with concentration of 0.5 mg/mL were added into the flocculation, and the results are illustrated in Fig. 2(b).

As shown in Fig. 2(b), PAC/CPAM exhibited high flocculation efficiency in landscape suspensions at pH 5–7, and charge neutralization was dominant in this situation. The removal rate of turbidity and UV_{254} increased rapidly as the pH value increased from 4 to 5. In addition, the turbidity removal rate reached 98.6% at pH = 5, and the turbidity decreased from 62 to 0.8 NTU after flocculation. Under low pH, a large number of H^+ and Al^{3+} shielded CPAM polymer chain, causing the polymer chain curl and the reduced adsorption bridging action. This condition results in decreased flocculation efficiency. The pH value can also affect the hydrolysis and ionization of aluminum ions in the flocculant. Thus, its binding probability with organic pollutants is affected [28]. With the increase of pH value, the positive charge of the CPAM polymer chain was accrued, and the molecular chain stretched, resulting in an increase of neutralization and adsorption bridging effect. Meanwhile, Al^{3+} had changed from simple metal ions to polyhydroxy complexes, generating aluminum hydroxide polymer with excellent flocculation capacity. The main monomer forms of Al(III) in PAC solution are $Al(OH)^{2+}$ and $Al(OH)_2^+$ [29,30]. As the pH value further increased after 7, OH^- ions would appear and Al^+ in the surface water becomes $Al\ (OH)_3$ precipitated particles. OH^- has a great effect on the cationic groups in the CPAM. Then, the positive charge of the high-molecular flocculant CPAM is reduced and the flocculation removal efficiency worsened. Accordingly, the pH range was considered as 5–7.

3.1.4. Effect of stirring speed

During flocculation, rapid stirring was used firstly to make flocculants uniformly distributed in water, whereas slow stirring was employed to promote the contact and collision of flocculants and kaolin particles. This experiment investigated the effects of rapid stirring speed. The stirring procedure was set up and stirred for three parts: rapid stirring (300 rpm) 3 min, slow stirring (50 rpm) 15 min, and free precipitation 30 min. Then, coagulant/flocculant PAC/CPAM was added after adjusting the pH value to 7. Flocculation and sedimentation experiments were conducted, and the results are presented in Fig. 3(a).

As exhibited in Fig. 3(a), the removal efficiency of turbidity and UV_{254} increased significantly with the increase of fast stirring speed from 220 to 300 rpm, and the removal rate reached the maximum at 300 rpm. The reason maybe that under low stirring speed, the flocculants did not adequately contact and collide with pollutant-colloidal particles, and the growth rate of flocs was very slow, resulting in low settling performance [31]. Subsequently, the removal efficiency of turbidity and UV_{254} had a minor increase at the range of 320 and 340 rpm. The cause of this phenomenon maybe that floc breakage combined with particle collision in water forms floc precipitation again. However, with the further stirring, excess increase of the stirring speed would break the generated flocs under hydraulic shear, resulting in decrease of

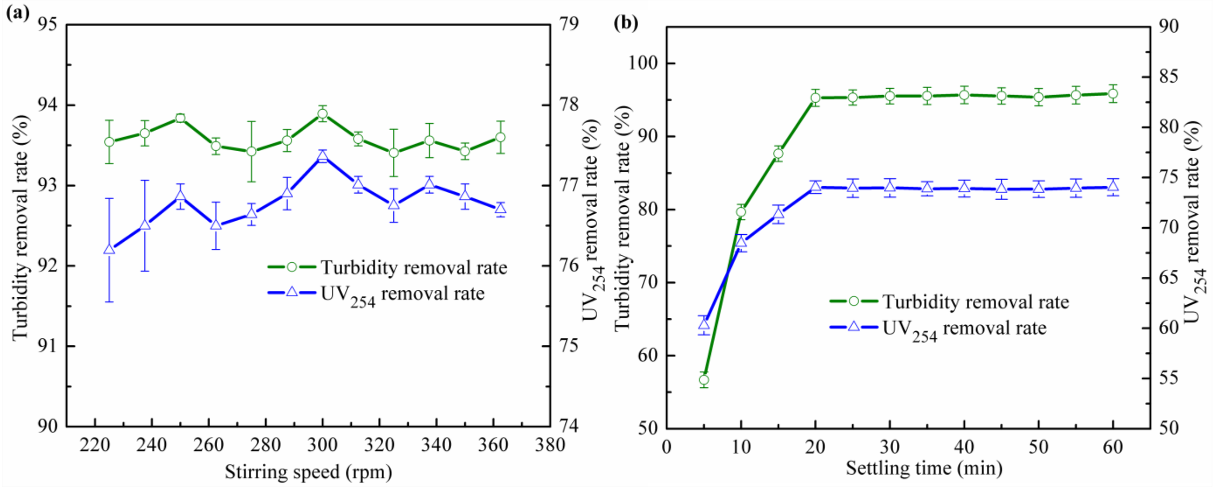

Fig. 3. The effect of (a) stirring speed and (b) settling time on turbidity removal rate and UV_{254} removal rate.

removal efficiency [32]. Therefore, the rapid stirring speed of 300 rpm is satisfactory in this research.

3.1.5. Effect of settling time

Settlement time is an important parameter affecting the separation of solid and liquid to determine the design and investment of sedimentation tank. Sedimentation time was studied to estimate the settling property of flocs. In this section, the agitator program was set as follows: rapid mixing (300 rpm) for 3 min and slow stirring (50 rpm) for 15 min. The effect of settling time was compared at 5–60 min and the results are shown in Fig. 3(b).

As exhibited in Fig. 3(b), the removal rate of turbidity and UV_{254} was gradually increased within 56.7%–95.3% and 60.1%–74.8% with the increase of sedimentation time from 5 to 20 min. The results suggested that the sedimentation of most flocs was completed in a short time, and the particle size and compaction degrees of the generated flocs exceeded the necessary conditions for gravity settling [33]. The removal efficiency did not evidently vary and simply have slight fluctuation with the further increase of sedimentation time to 60 min. In addition, the imperceptible fluctuation was ascribed to the slow growth and settlement of small particle flocs. Consequently, 30 min was considered the optimal settling time.

3.1.6. Effect of addition mode

The inorganic and organic composite flocculants can be added by different addition modes with various stages. This factor influences the bridging effect from CAPM and particle destabilization from inorganic coagulant PAC. Thus, the effect of addition mode was investigated in this research, and the results are shown in Fig. 4(a). According to the analysis results above, 60 mL PAC with concentration of 2 mg/mL and 0.8 mL CPAM with concentration of 0.5 mg/mL were used in this section. Flocculation was set as follows: rapid stirring at 300 rpm for 3 min, followed by slow stirring at 50 rpm for 15 min. Six different addition modes toward dosage and stirring time were illustrated in Fig. S2.

As shown in Fig. 4(a), the turbidity and UV_{254} removal efficiencies of addition mode II (20 + 20 + 20 + 0.8) and mode V (30 + 30 + 0.4 + 0.4) are higher than those of the others. Moreover, the lowest turbidity and UV_{254} removal efficiencies were found by using addition mode VI, which was the traditional addition method. The results suggested that appropriate divided addition of PAC was favorable for flocculation. In comparison, PAC has a high positive charge density, exerting charge neutralization during coagulation process. CPAM has high molecular weight with active functional groups, which can exhibit excellent adsorption and bridging capacity during flocculation. At rapid mixing stage, the divided addition of PAC caused the quick and uniform mixing between PAC and colloidal particles, resulting in efficient destabilization of colloidal particles. However, divided or not divided addition of CPAM has no obvious effect on turbidity and UV_{254} removal. Therefore, adding PAC twice for rapid stirring is encouraged in flocculation.

3.1.7. General water quality

The removal of several general water quality parameters was investigated after flocculation because of the complicated quality of the landscape raw water. The results are shown in Fig. 4(b), illustrating the removal efficiency of turbidity, UV_{254}, ammonia nitrogen, COD, TP, and algae removal at different pH conditions [34,35]. Overall, turbidity removal efficiency could be achieved over 90%, and the maximum one reaches 98.7% at pH values 4–9. In addition, the removal rate of the others was analyzed as follows: UV_{254} of 65.9%–78.0%, ammonia nitrogen of 9.1%–17%, TP of 77.0%–91.9%, COD of 59.6%–75.8%, and the removal rate of algae of 82.3%–99.2%. These results indicated that, except for turbidity and UV_{254}, phosphorus and algae can be effectively removed through flocculants of PAC/CPAM. However, PAC/CAPM used in combination may substantially alleviate consumption of the coagulant/flocculant, improving the water purification efficiency drastically and significantly save economic costs [36].

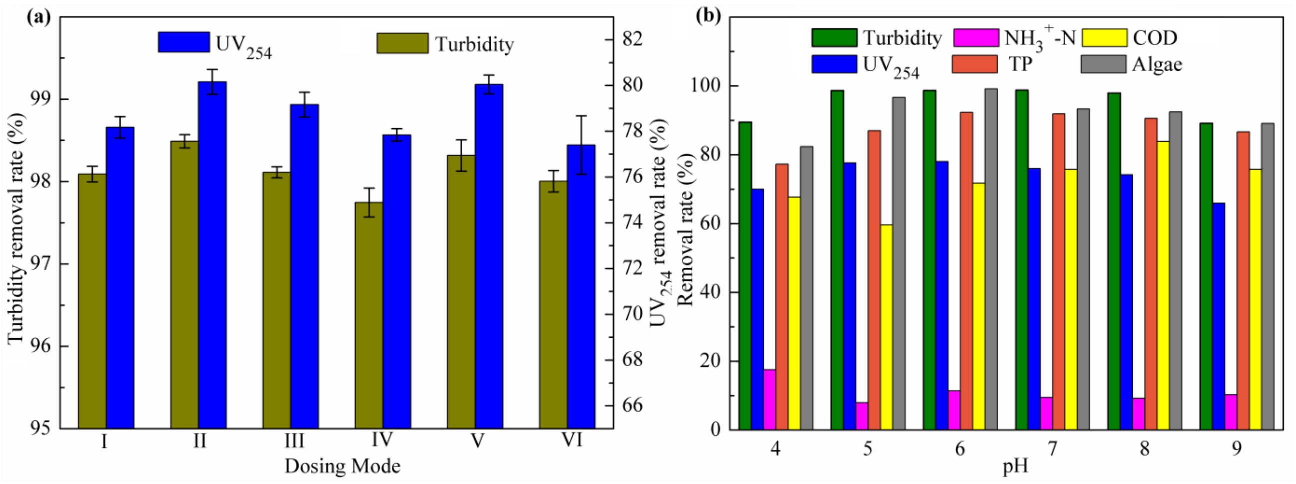

Fig. 4. The effect of (a) dosing mode on turbidity removal rate and UV_{254} removal rate and (b) removal rate of various water quality parameters.

3.2. Mechanism of flocculation

3.2.1. FTIR spectra analysis

The supernatant treated with different flocculants was compared with the raw water by FTIR analysis, and their corresponding spectra are presented in Fig. 5(a). Moreover, the infrared spectra by using PAC/CPAM at different pH values (pH = 4, 7, and 9) are presented in Fig. 5(b). The results showed the presence of a strong broad band at approximately 3,449 cm^{-1}, corresponding to the –OH stretching mode [37]. As exhibited in Figs. 5(a) and (b), adsorption peak at 2,080 cm^{-1} was derived from the characteristic stretching vibration of associating –NH, and peak at 1,637 cm^{-1} was ascribed to C=O stretching vibration of the organic contaminant [38]. In addition, the peaks by using PAC, CPAM, and PAC/CPAM were observed at 3,448, 2,080, 1,637, 561 cm^{-1}, indicating that the chemical structure of pollutants was not changed during flocculation. Combined with Fig. 1, these results illustrated that flocculants can reduce the content of contaminants in water but do not completely remove a certain contaminant.

The infrared spectra of the flocs are presented in Fig. 6. The results show that the peaks appeared mostly derived from pollutants and flocculants. As exhibited in Figs. 6(a) and (b), the characteristic absorption peak at 3,442 cm^{-1} corresponds to the stretching vibration of –OH. The C=O bond-symmetrical stretching vibration characteristic absorption peak at 1,655 cm^{-1} may be sourced from organic pollutants or the amide carbonyl –CO–NH_2 stretching vibration [39]. The results also confirmed that the characteristic absorption peaks at 3,442, 1,655, and 600 cm^{-1} ascribed to –OH, C=O, and benzene ring substituent in the infrared characterization originated from humic acids and protein-like organic pollutants.

3.2.2. Determination of fluorescence EEMs

The information of fluorescent compounds and relative content could be obtained from EEM spectra of supernatant before and after flocculation over a range of excitation wavelengths. We assumed that the rapid filtration treatment would be performed after the coagulation–sedimentation treatment. Three-dimensional EEM fluorescence spectra were measured by fluorometric analysis.

In the aquatic environment, DOM is a mixture of compounds with different structures and a wide range of

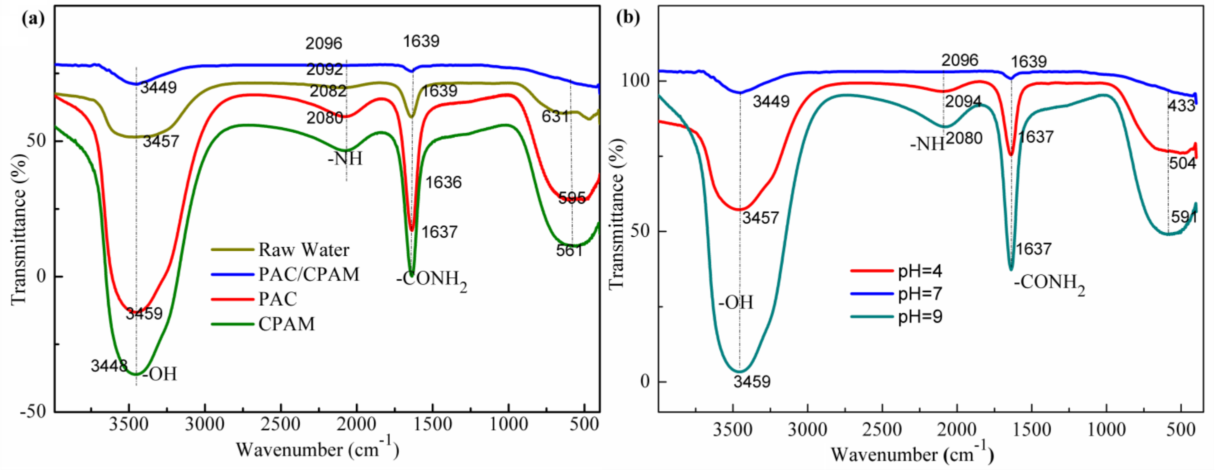

Fig. 5. The effect of (a) flocculants and (b) pH on FTIR spectra of supernatant.

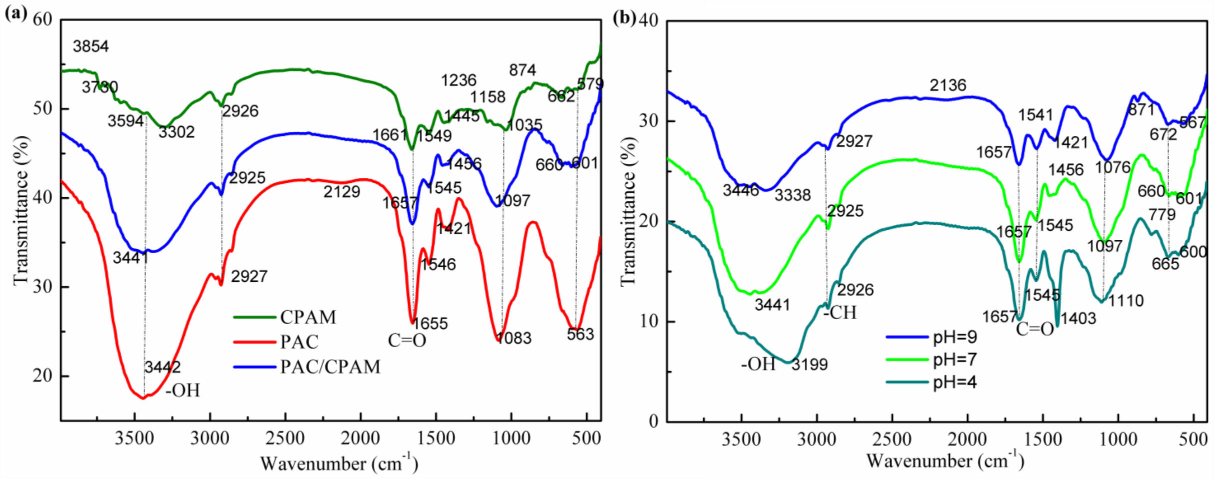

Fig. 6. The effect of (a) flocculants and (b) pH on FTIR spectra of flocs.

molecular weight. To investigate the changes of DOM, Figs. 7 and 8 primarily examine the three-dimensional fluorescence spectra under different pHs and different PAC dosages. As shown in Fig. 7, the raw water contains DOM of humus and protein, and the intensity of the fluorescence peak after removal had shown a tendency to decrease. The intensity of the fluorescence peak was faded at the pH values of 4 and 5, demonstrating that the flocculation treatment had excellent efficiency in removal of humus and protein.

As demonstrated in Fig. 8, the removal efficiency of DOM was investigated under different PAC dosages. The intensity of the central fluorescence peak representing the humus organic matter decreased progressively with the increase of PAC dosage. Meanwhile, the area of the fluorescence peak domain representing the humus was nearly constant with increasing PAC dosage. Thus, to find the peak value to compare the variation tendency of the humus content was necessary. Referring to Table S1, the maximum peak value appeared in the raw water of Fig. 8(a) and the PAC dosage in Fig. 8(b) were the minimum. The peak value of the fluorescence region of humus declined with the augmentation of PAC dosage, indicating that the removal efficiency of humic organic pollutants was ameliorated with the increase of PAC dosage.

3.2.3. Zeta potential analysis

Zeta potential is an interfacial parameter related to the low solubility condition of dissolved metals as the isoelectric points are reached [40]. The pH value of raw water was

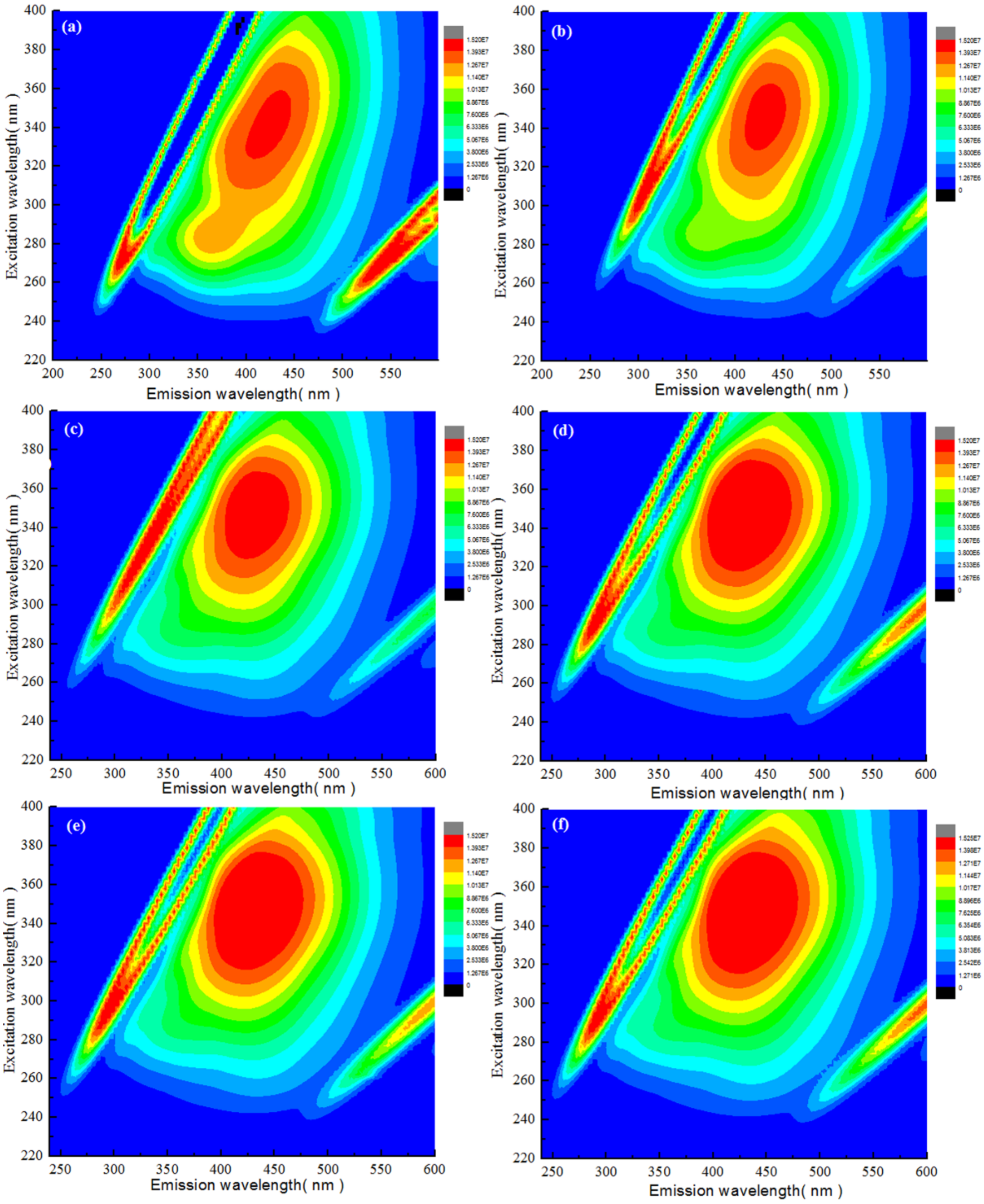

Fig. 7. The effect of pH on fluorescence spectra of supernatant after flocculation: (a) raw water, (b) pH = 4, (c) pH = 5, (d) pH = 6, (e) pH = 7, and (f) pH = 8.

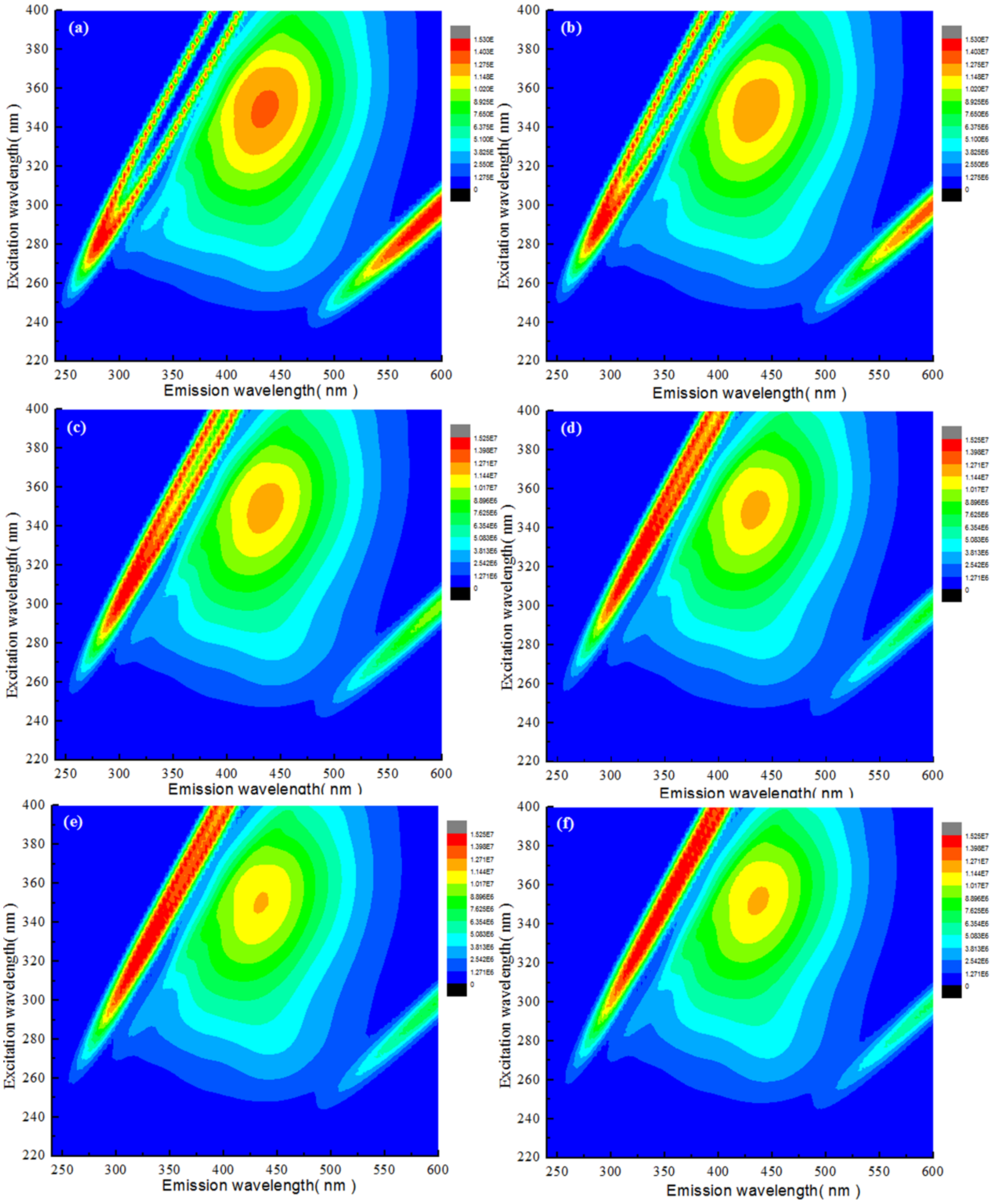

Fig. 8. The effect of PAC dosage on fluorescence spectra of supernatant after flocculation: (a) raw water, (b) 40 mg/L, (c) 60 mg/L, (d) 80 mg/L, (e) 100 mg/L, and (f) 120 mg/L.

adjusted by using dilute HCl and NaOH. The photograph of water samples before and after flocculation is shown in Fig. 9(a), and the zeta potential tested results are shown in Fig. 9(b).

As supernatant at high zeta potentials, the particles had major repulsive force and were hardly to be destabilized and agglomerated. The stability of colloid particles can be reduced with the decrease of zeta potential because of the decrease of repulsive force between the particles. As illustrated in Fig. 9(b), the zeta potential of supernatant was –24.7 to 1.9 mV at pH within 2–13. The results suggested that the dispersed pollutant particles are mostly negatively charged and remained stable because of repulsive force with each other. However, PAC is positively charged at acid and neutral pH, and CPAM is a cationic polymer, causing the increase in zeta potential [41]. Fig. 9(a) shows that at the pH value of 6–8, the colloidal impurities in water were most probable to be removed due to the neutralization of the flocculants.

3.2.4. Microscope image analysis

To compare the flocculation mechanism of different flocculants, observing the floc morphology is particularly

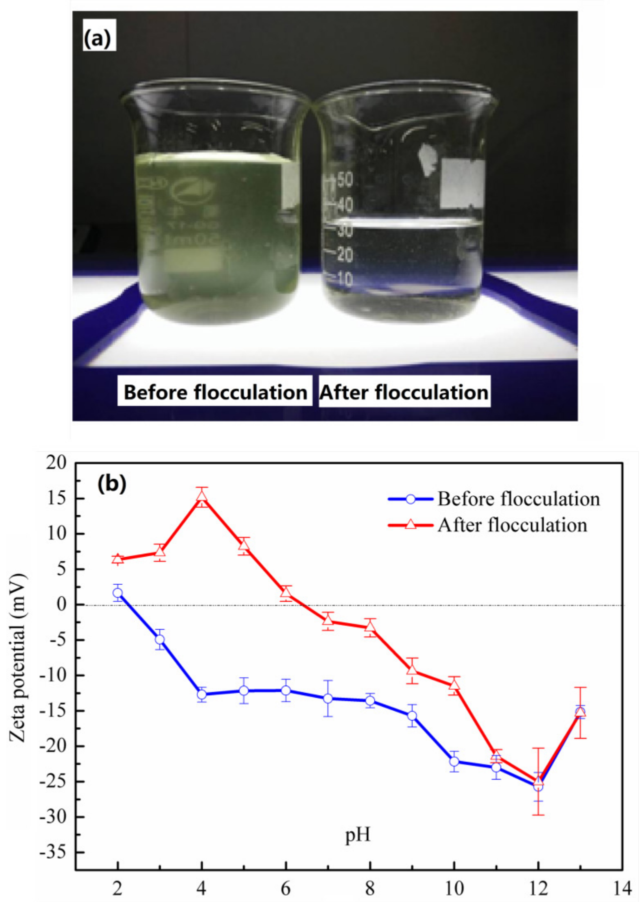

Fig. 9. comparison of (a) photograph and (b) zeta potential before and after flocculation.

necessary. The photograph of raw water at a magnification of ×100 before flocculation is presented in Fig. S3, and the photos before and after flocculation are illustrated in Fig. S4. In this experiment, the flocs by using PAC, CPAM, and PAC/CPAM were obtained for morphology analysis, and the results are exhibited in Fig. 10.

As presented in Fig. 10(a), the flocs gathered with a majority of algae and impurities by using PAC because of charge neutralization. The flocs remained relatively slack and loose ascribing to the less adsorption bridge effect. As shown in Fig. 10(b), the flocs aggregated intensively by using CPAM, attributed to adsorption and bridge effect of the organic polymer functioned [42]. The expansion of the polymer long chain was ascribed to the intense effect of adsorption bridging. However, owing to the lack of intensive electrical neutral effect, the supernatant was still dispersed by using CPAM alone. As displayed in Fig. 10(c), the flocs by using PAC/CPAM combined flocculant gathered a large majority of particles, and there was mucus-like transparent material, which was the polymer long chain of CPAM, was observed outside the granular pellet. In this circumstance, the generated flocs were compacted and stabilized. Accordingly, as illustrated in Fig. 11, the combined PAC/CPAM presented excellent flocculation property, completely exerting the electrical neutralization of PAC and the adsorption bridging of CPAM.

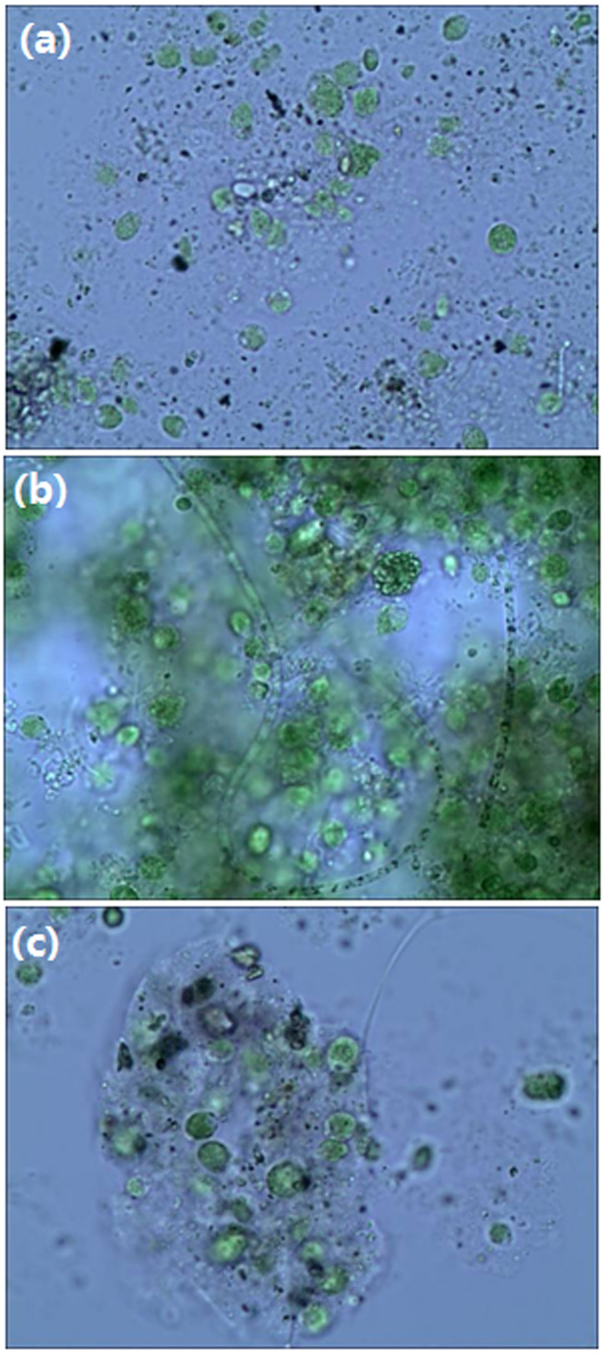

Fig. 10. The photograph of flocs at a magnification of ×100 by using flocculants of (a) PAC, (b) CPAM, and (c) PAC/CPAM.

4. Conclusion

In this research, the combined coagulant/flocculant PAC/CPAM chosen through comparison was used in flocculation of contaminated landscape water, and the possible flocculation mechanism was analyzed. The experimental results show that the removal efficiency in contaminated landscape water treatment was obtained at the following optimal conditions: PAC dosage of 120 mg/L, CPAM dosage of 0.4 mg/L, initial pH of 5–7, rapid stirring speed of 300 rpm, and settling time of 30 min. Furthermore, addition mode was investigated

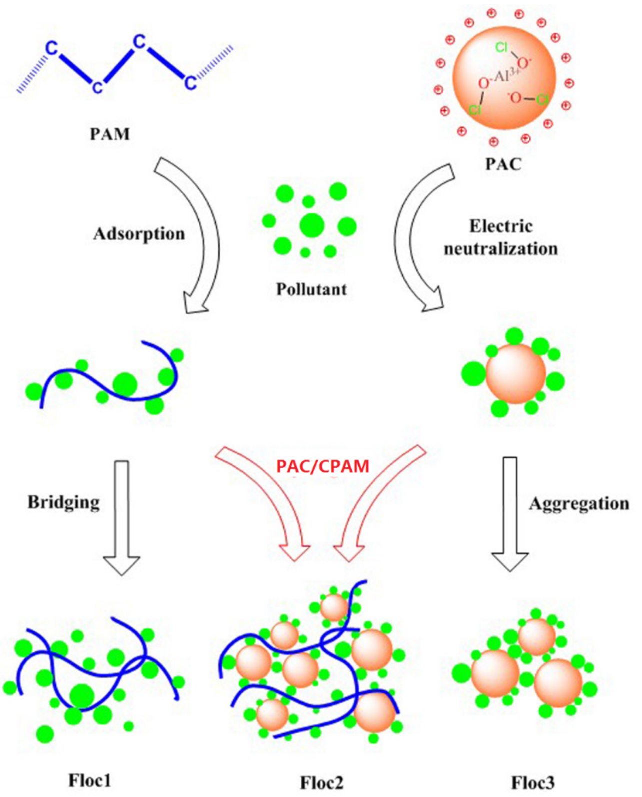

Fig. 11. Flocculation mechanism of CPAM, PAC, and PAC/CPAM.

to optimize the removal efficiency. The turbidity and UV_{254} removal efficiency could be enhanced under divided addition of PAC as CPAM used as coagulant aids. This condition enables thorough function of neutralization and adsorption bridging. The flocculation mechanism of the combined flocculant was further analyzed by microscopic observation, zeta-potential, FTIR, and EEM. The results show that the coagulant/flocculant could adequately exert the electrical neutralization of PAC and the adsorption bridging of CPAM. The flocculation experiments primarily removed the protein and humus-soluble organic matter from the contaminated landscape water. In addition, the PAC/CPAM not only can remove turbidity and UV_{254} splendidly but also has excellent removal efficiency on the TP and algae.

Acknowledgments

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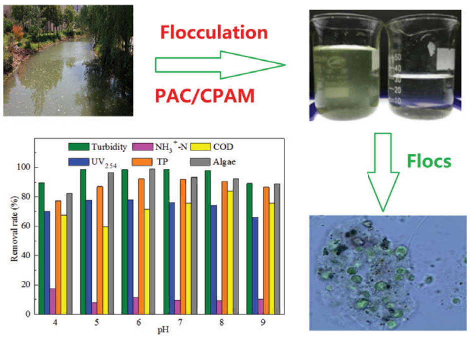
Supplymentary material



Graphical abstract

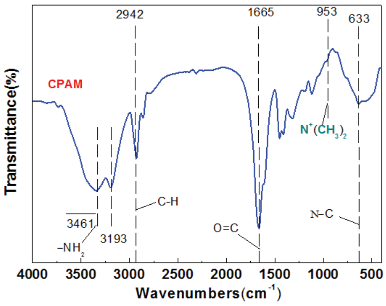


Fig. S1. FTIR spectrum of CPAM used in this study.

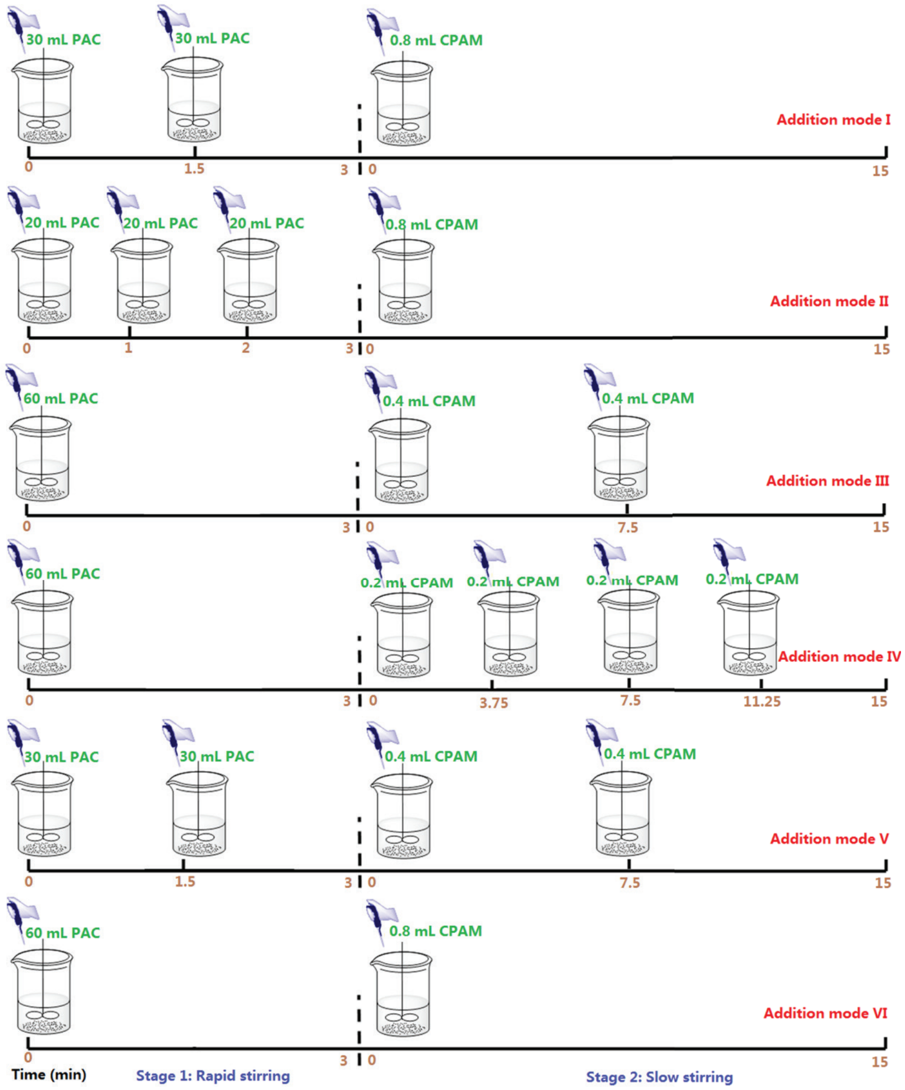


Fig. S2. Six different addition modes toward PAC/CPAM dosage and stirring time.

Table S1
Corresponds to the highest peak in Fig. 8

Number	(a)	(b)	(c)	(d)	(e)	(f)
Crest value	15,264,000	15,257,400	15,242,000	15,223,400	15,224,300	15,217,100

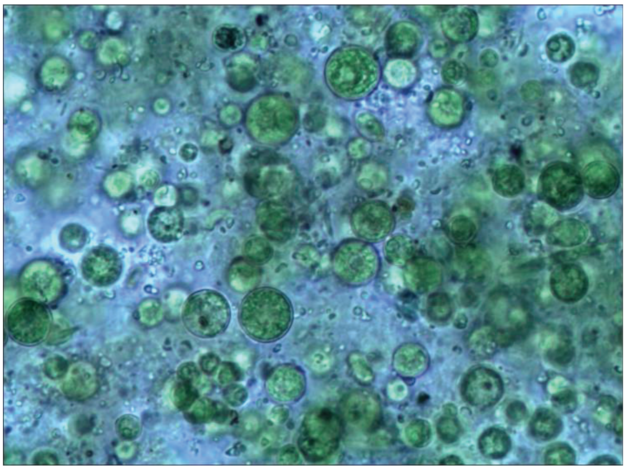


Fig. S3. The photograph of raw water at a magnification of ×100 before flocculation.

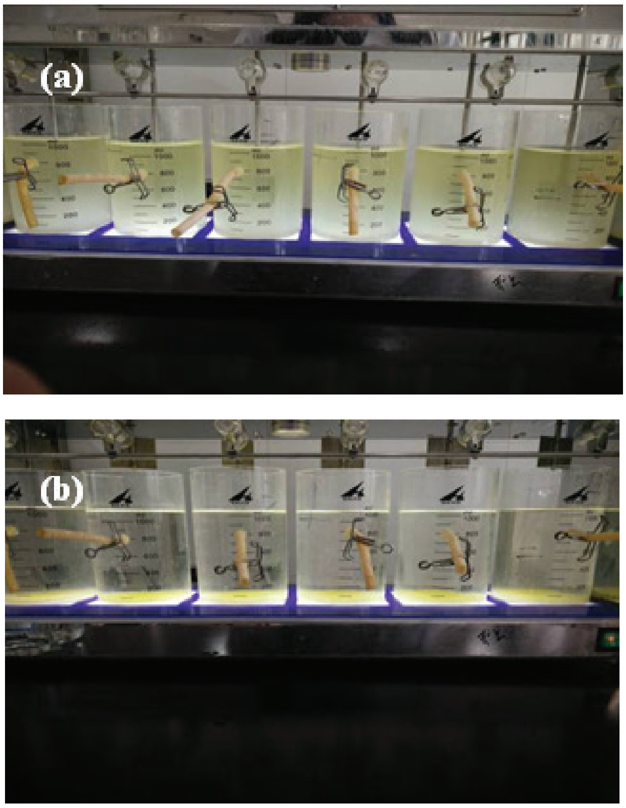


Fig. S4. Photos of (a) before flocculation and (b) after flocculation.