

# Sustainable Cationic Cellulose for Highly Efficient Flocculation of Suspended Particles

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## Research Article

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# Abstract

Sustainable, cationic cellulose bio-flocculants with various amino group contents were successfully prepared by a feasible chemical crosslinking with polyethyleneimine (PEI). The flocculation performances of diverse PEI-grafting cellulose (CE-PEI) were evaluated to purify sewage sludge treatment. Further, the preparation conditions and flocculation mechanism of CE-PEI were investigated. Benefiting from the high surface positive charges and the supramolecular structure of PEI, the results indicate that CE-PEI could remove the turbid Kaolin suspension effectively. The efficiency of CE-PEI for removing the turbid in Kaolin suspension is 98.2%. Flocculation kinetic results indicated that charge neutralization was the dominant mechanism for the flocculation process. And then, the small Kaolin particles agglomerate together to form large flocs by the function of adsorbing, gathering, and enwrapping. Thus, this work not only exploits a promising application of cellulose as a bio-flocculant but also provides a feasible approach to efficiently purify high turbidity wastewater.

## Introduction

With the accelerated development of industrialization and urbanization, an enormous quantity of high turbidity wastewater was produced by the paper-making, printing and dyeing, leather, livestock, agriculture, building industries, which aggravates the process of water purification. To address the problem and create a sustainable future, a variety of technologies, such as membrane filtration (Jamshidifard et al. 2019; Zhao et al. 2020; Gao et al. 2020), adsorption (Dong et al. 2016; Vakili et al. 2019; Liu et al. 2020), oxidation (Chen et al. 2020), coagulation/flocculation (Guo et al. 2018; Zhao et al. 2021) and micro-biological treatment (Wang et al. 2019) have been employed for water purification. Among them, flocculation is deemed to be the most favorable method for wastewater treatment because of its advantages of low cost, easy operation, and high efficiency for suspended colloid removal (Carvalho et al. 2018; Essandoh et al. 2019). However, severe problems of massive dosage, chemical sludge recycling, corrosively restrict the application of inorganic metal-based flocculants such as iron, aluminum, and titanium salts in turbid water purification (Zou et al. 2017; Wang et al. 2019). Whereas in fact, effective organic flocculants, for example, polyacrylamide (PAM) and its derivatives were exploited to reduce water turbidity (Chen et al. 2019; Chen et al. 2020). However, the high flocculation performance of PAM can be achieved by the addition of coagulant aids (e.g.  $\text{CaCl}_2$ ). Meanwhile, the coagulant aids resulting in a large number of loose-sludges. Moreover, organic PAM is synthesized from petrochemical resources, and cannot be biodegraded after environmental restoration, resulting in secondary pollution. Thus, the design and development of sustainable and degradable bio-flocculants with high flocculation performance is vital for wastewater purification.

Cellulose, as the most abundant natural bioresources, has great potential for the removal of various pollutants due to its marvelous properties of biodegradability, nontoxicity, cheap and widely available (Salehizadeh et al. 2018; Shak et al. 2018; Noor et al. 2020). It is well known that functional modification of cellulose can be easily obtained, due to its sufficient hydroxyl groups on the surface. Thereby, a series of anionic groups such as carboxyl groups, phosphate groups, and sulfo groups,

were introduced to improve the removal ability of cellulose for cationic dyes or heavy metal ions (Rodríguez et al. 2011; Fu et al. 2017; Wang et al. 2020). For example, Li et al. (Li et al. 2020) successfully prepared carboxylated cellulose filters by TEMPO-mediated oxidation and presented excellent adsorption capacity for cationic dyes and heavy metal ions. Ge et al. (Ge et al. 2016) and Zhang et al. (Zhang et al. 2016) prepared cationic cellulose fiber by introducing polyethyleneimine (PEI) for the removal of heavy metal ions. Besides, Dicarboxyl cellulose flocculant was manufactured by periodate oxidation for the removal of kaolin suspension assisted with  $\text{CaCl}_2$  as a coagulant (Zhu et al. 2015; Zhu et al. 2015). However, to the best of our knowledge, the employment of cationic cellulose as bio-flocculant for the direct removal of suspended particles from wastewater has been rarely reported.

Hence, this work is to exploit the potential of cellulose bio-flocculant for efficiently removing suspended particles and reducing the turbidity of water. On the basis of abundant surface hydroxyl groups of cellulose, amine-rich cellulose bio-flocculants have been fabricated by a feasible chemical crosslinking with branched polyethyleneimine (PEI). The obtained cellulose bio-flocculants have a supermolecular structure and large amounts of positively charged amine groups, exhibiting outstanding flocculation performance for suspended kaolin particles without any coagulant aid. Further, generated flocs, zeta potential, and flocculation kinetics were evaluated for understanding the flocculation mechanism.

## Materials And Methods

### *Materials.*

Cellulose ( $M_w = 20000$ ) and glutaraldehyde (25 wt%) were acquired from Macklin Biochemical Co., Ltd. (Shanghai, China). Kaolin and Polyethylenimine ( $M_w = 600$ ) was provided by Aladdin Chemical Reagent Co., Ltd. (Shanghai, China).

### *Fabrication of cellulose bio-flocculant.*

Amine-rich cellulose bio-flocculants were fabricated by chemical crosslinking with branched polyethyleneimine (PEI) in a heterogeneous system, according to our previous report (Chen et al. 2018). Briefly, Cellulose (1.0 g) was dispersed in distilled water (100 mL) to swell for 12 h. Desired amounts of PEI were doped into cellulose suspension under mechanical stirring. Crosslinking reaction was started by introducing glutaraldehyde as a cross-linking agent, under vigorous stirring at different temperatures for 3h. Finally, PEI-grafted cellulose (CE-PEI) was extracted by suction filtration and adequately washed. The surface charge density of CE-PEI was adjusted by varying the reaction conditions, correspondingly the products are denoted as CE-PEI 1, CE-PEI 2, CE-PEI3, and CE-PEI 4. The sample codes of the CE-PEI and relevant synthesis conditions were list in Table 1.

Table 1 The codes and synthesis conditions of CE-PEI and their amino contents and  $\zeta$ -potentials

Samples	CE-PEI [wt%]	Temperature (°C)	Glutaric dialdehyde (g)	Amino group contents (mmol/L)	$\zeta$ -potentials (mV)
CE-PEI 1	1:1	45	1.5	17.5	51.4
CE-PEI 2	1:1	55	1.5	12.5	50.3
CE-PEI 3	2:1	45	2	6.7	42.1
CE-PEI 4	1:2	55	2.5	1.625	39.7

### Characterization.

The surfacetopography of samples was investigated by using Field Emission Scanning Electron Microscopy (FESEM, vltra55, German). Chemical crosslinking reaction was demonstrated using Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 5700, Thermo, USA). Zeta potential of samples was measured using NanoSizer Nano-ZS90 (Malvern, UK). The contents of amino groups of samples were tested using titration method. CE-PEI (0.02 g) was added into 50 mL of HCl solution (0.1 M) with mildly stirring for 6 h. The consumption of HCl was checked by the titration of NaOH (0.1 M) with phenolphthalein as an indicator. The contents of amino groups were calculated using the following Eq. (1) (Donia et al. 2012; Sun et al. 2014).

$$\text{Amino group contents} \left( \frac{\text{mmol}}{\text{g}} \right) = \frac{(C_i - C_e) \times 50}{0.02} \quad (1)$$

where  $C_i$  and  $C_e$  are initial concentration and equilibrium concentration of HCl solution (mol/L), respectively.

### Flocculation performance for suspended particles

The flocculation performance of CE-PEI for suspended particles from wastewater was assessed, by using Kaolin standard suspension with 500 mg/L as a model. Briefly, CE-PEI was added into 40mL of Kaolin suspension and stirred at 200 rpm for 1 min. Finally, a slow stirring at 50 rpm for 5 min was used to floc aggregation. Subsequently, setting for sedimentation without stirring. After sedimentation, the change of turbidity and zeta potential of the system was tested using Turb 550 turbiditor and NanoSizer Nano-ZS90. The flocs size was determined using Mastersizer 2000 (Malvern). The setting height was measured by adding 100 mL Kaolin suspension into a beaker (1 L) cylinder with optimal dosage of cellulose bio-flocculants at 5 min intervals. The effects of CE-PEI dosages (0-10 mg), suspension pH values (3-11), and settling time (0-30 min) on flocculation behavior were investigated in detail. Each test was performed three times.

## Result And Discussion

### Characterization of cellulose bio-flocculant

On the basis of the abundant surface hydroxyl groups of cellulose, cellulose bio-flocculant can be easily fabricated by crosslinking reaction with PEI and glutaraldehyde (Scheme 1). The grafting reaction is verified by FTIR spectra in Fig 1a. After grafting, the characteristic peak of cellulose from  $3349 \text{ cm}^{-1}$  shifts to  $3417 \text{ cm}^{-1}$  in CE-PEI

associated with the overlapping of O-H and N-H stretching vibration (Cheng et al. 2014). Three new peaks at 1656, 1579 and 1430  $\text{cm}^{-1}$  appear, corresponding to bending vibration of N-H, stretching vibration of C=N and C-N, respectively (Park et al. 2014). This indicated the successful Schiff base reaction between aldehyde group (-COH) of glutaraldehyde and  $\text{-NH}_2$  of PEI. Moreover, the typical C-O-C stretching vibrations of cellulose polysaccharide at 1057-1160  $\text{cm}^{-1}$  shift to a larger wavenumber, indicating that the formation of new ether bond between glutaraldehyde and cellulose. In addition, the occurrence of  $\text{-CH}_2\text{-}$  stretching vibrations at 2923 and 2848  $\text{cm}^{-1}$  and C-H bending vibration at 771  $\text{cm}^{-1}$  also confirms the successful grafting of PEI. The content of amino groups and the surface zeta potential of CE-PEI can be controlled by adjusting the reaction conditions, including the ratio of cellulose and PEI, reaction temperature, and glutaraldehyde amount. Fig 1b and Table 1 show that the amino group content and the zeta potential of CE-PEI 1 presented the maximum value of 17.5 mmol/g and 51.4 mV, revealing a positively charged surface due to the existence of multiple amino groups. The morphology of cellulose and CE-PEI was observed using FESEM and displayed an irregular shape (Fig 1c and d). The surface of cellulose is smooth. After PEI modification, many micro-cracks were found along with the cellulose microfibers, which can facilitate the adsorption of pollutants.

#### *Flocculation performance of CE-PEI for Kaolin particles*

To understand the relationship of surface property-activity, four bio-flocculants with different amino group content and zeta potential were employed to assess the removal of Kaolin particles. Here, the effects of CE-PEI dosage, pH value, setting time on flocculation performances were investigated in detail. Variation in turbidity, zeta potential, floc size, interface height of system was determined.

#### *Effect of CE-PEI dosage*

The effect of CE-PEI dosage on the residual turbidity and average floc size of the Kaolin suspension was studied and shown in Fig 2. In Fig 2a, the turbidity of the suspension all declined sharply with the increase of CE-PEI dosages until minimum values at corresponding optimal dosage, subsequently a tiny increase. Compared with CE-PEI 4, the turbidity removal efficiencies of CE-PEI 1, CE-PEI 2, and CE-PEI 3 are higher because of active site increases with the amount of amino group. The turbidity of Kaolin suspension significantly reduced from initial to 480 NTU to 8.7 NTU for CE-PEI 1 with 6 mg. The removal efficiency approached a maximum value of 98.2% higher than that of CE-PEI 2 (95.7%) and CE-PEI 3 (97.1%). However, the turbidity tiny increased when the dosage was 10 mg, which revealed that charge neutralization is dominant during the flocculation process. Positively charged CE-PEI neutralizes the surface negative charge in Kaolin particles to generate insoluble floc. Whereafter flocs further aggregate, grow, and settle down, consequently resulting in turbidity reduction. Nonetheless excessive flocculants lead to the destabilization of flocs due to the electrostatic repulsion between the initial flocs, which is further demonstrated by the average floc size.

Fig 2b shows the change of the average floc size as the increase of CE-PEI dosages. Increasing CE-PEI dosages from 2 to 8 mg, the average floc size remarkably increased, subsequently decreased when the dosage

reaches 10 mg. Maximum floc sizes produced by CE-PEI 1, CE-PEI 2, CE-PEI 3, and CE-PEI 4 reached  $48.6 \pm 0.9$ ,  $45.0 \pm 1.4$ ,  $38.7 \pm 2.6$ , and  $36.4 \pm 1.9$   $\mu\text{m}$ , respectively, which gradually enlarged with the increase of amino group contents of four CE-PEI. Adding CE-PEI, positively charged flocculants have been transferred from the solution phase to the surface of Kaolin particles to generate insoluble flocculant-kaolin complexes through charge neutralization. The flocculant-kaolin complexes still have vacant active sites for absorbing other Kaolin particles which can produce bridging actions between Kaolin particles, consequently, forming larger flocs with a 3D network structure. Simultaneously, the flocs with a large size further capture small flocs and residual kaolin particles in the system via the capture effect and sweeping (Li et al. 2015). All these resulted in the optimal rate value for the precipitation of particles. Excessive flocculants might impart a positive electric charge to Kaolin particles to cause electrostatic repulsion. Additionally, at higher flocculants dosages could cover most of the available sites on the suspended particles, leading to ignorable bridging action. Thus, the floc size decreased.

#### *Effect of pH*

Fig 3 shows the variation in turbidity and zeta potential of the suspension as a function of pH values. Introducing CE-PEI into suspension, residual turbidity of the system was declined at pH 3-7 but increased when pH increased from 8 to 12 (Fig 3a). Moreover, CE-PEI 1 displayed the best Kaolin removal of CE-PEI can reach 94.9% at pH 7.0. Notably, Kaolin standard suspensions are negatively charged within the entire pH range (Hosseinpour et al 2020). The zeta potential of the system became increases and then decreases with increasing pH values (Fig 3b). Increased zeta potential could be because that the electronegative charges on the Kaolin particle surface were neutralized by the electropositive CE-PEI. The decrease might be due to the deprotonation of amino groups, where the negative surface charges on the CE-PEI increased at alkaline conditions. The maximum zeta potential of the system was found at pH 5.0. Moreover, it is clearly that the zeta potential of the system approached zero at pH 6.4-7.0 with different CE-PEI flocculants, revealing that the charge neutralization effect performed a dominant role in the flocculation process. By contrast, CE-PEI 4 showed higher turbidity reduction and zeta potential under an alkaline condition which revealed that contrasted with charge neutralization, bridging action and/or adsorption played a role in the flocculation process.

#### *Effect of settling time*

The time dependence of settling property was investigated turbidity and settling height of Kaolin suspension. As shown in Fig 4a, the turbidity of Kaolin suspension sharply decreased within the first 5 min, the reduction slightly fluctuated in the range of 78.3-85.0% corresponding to four CE-PEI flocculants with different surface properties. Fig 4b further displayed a rapid sedimentation process in view of the remarkable decline in interface height. Moreover, higher amino group content, faster settling velocity. These results showed that the sedimentation of most flocs was accomplished in a short time. With an increasing settling time from 5 to 30 min, remnant turbidity decreased slowly because the growth of small flocs is slowly adverse to settlement. The best removal efficiency of the Kaolin turbidity of CE-PEI reached 98.2% in 30 min.

*Flocculation kinetics and mechanism*

Table 2 The rate constants and correlation coefficients (R<sup>2</sup>) for flocculation of Kaolin by CE-PEI at different initial concentrations

Flocculant doses (ppm)	Kinetics of aggregation of particles		Frequency of collisions of particles	
	$k_1(\times 10^{-14} \text{ count}^{-1} \text{ s}^{-1})$	$k_2(\times 10^{-3} \text{ s}^{-1})$	$k(\times 10^{-14} \text{ s}^{-1})$	$R^2$
50	1.43	11.03	1.08	0.95602
100	2.02	24.91	1.44	0.96712
150	143.89	4.08	10.51	0.98228
200	192.37	79.78	8.96	0.9815
250	123.26	85.15	6.33	0.95766

To further explain the flocculation mechanism, flocculation kinetics of representative CE-PEI 1 was investigated through blending flocculants (2-10 mg) into 40 mL of Kaolin suspension with rapid stirring (200 rpm) and then settling for 30 min. The supernatant was collected for kinetic analysis. The flocculation process is a mainly bimolecular reaction, thereby, the aggregation and collision of particles were determined according to the flocculation kinetic models, expressed as Eq(2) and Eq(3), respectively.

$$\frac{d(N_t/N_0)}{dt} = -N_0 k_1 \left(\frac{N_t}{N_0}\right)^2 + k_2 \frac{N_t}{N_0} \quad (2)$$

$$\sqrt{\frac{N_0}{N_t}} = 1 + \frac{1}{2} k N_0 t \quad (3)$$

where  $N_t$  is the concentration of kaolin particles at  $t$  (s).  $N_0$  is the initial concentration of kaolin particles, which can be calculated by considering the particle diameter (1.2  $\mu\text{m}$ ) and density of kaolin (2.6  $\text{g cm}^{-3}$ ).  $k_1(\text{s}^{-1})$  and  $k_2(\text{s}^{-1})$  is the kinetic constant for the particle aggregation and aggregate breakage, respectively.  $k(\text{s}^{-1})$  is the rate constant for particle collisions.

The theoretically simulated curves were fitted and the results are shown in Fig 5 and Table 2. The concentration of Kaolin particles was shown a remarkable reduction at the initial 60 s when CE-PEI 1 was added to the system, then gradually declined or remained stable with increased flocculation time, which revealed that the excellent adsorption-flocculation-sedimentation of CE-PEI for Kaolin, as show in Fig 5a. The concentration of Kaolin particles at a lower dosage (50-100 mg/L) and a higher dosage (250 mg/L) were higher than those at the intermediate dosage (150-200 mg/L). It's due to the number of positive charges on CE-PEI 1 was not enough to completely neutralize the negative charges on the surface of Kaolin particles at the low dosage. An excessive

dosage led to electrostatic repulsion and cage effect caused by CE-PEI at higher dosages covering most of the available sites on each particle. Thus, the rate for aggregation of Kaolin particles decreased. As shown in Table 2, the rate constant  $k_1$  and  $k_2$  for particle aggregation and aggregate breakage increased with increasing flocculant dosages from 50 to 200 mg/L except for  $k_2$  at 150 mg/L.  $k_1$  and  $k_2$  obtained with 250 mg/L were  $123.26 \times 10^{-14} \text{ s}^{-1}$  and  $85.15 \times 10^{-3} \text{ s}^{-1}$ , respectively. This shows that the floc generated at high dosage was harder than floc formed at low dosage due to the steric and electrostatic repulsion forces among particles. Moreover, the minimum  $k_2$  of  $4.08 \times 10^{-3} \text{ s}^{-1}$  was found at the dosage of 150 mg/L, which indicated a moderate CE-PEI could improve the floc strength and stability. Further, the maximum  $k$  of  $10.51 \times 10^{-14} \text{ s}^{-1}$  was also found at 150 mg/L which indicated that collision between particles was effective at the optimal dosage, and increase or reduction dosages will cause the decrease in the value of  $k$  (Peng et al. 2010). At a low dosage, the interaction including charge neutralization and bridging action between CE-PEI and Kaolin particles was very weak, it's due to the low-density positive charge in the system, leading to lower  $k$ . There were significant positive correlations between the value of  $k$  and the dosage of CE-PEI resulting from more positive charges and adsorption sites on the flocculants, which is beneficial for accelerating the molecular collisions. However, an excess of CE-PEI caused steric and static repulsion and reduced the number of effective junction points causing decreased  $k$ .

Therefore, according to the analysis on the flocculation performances and flocculation kinetics, the assumed flocculation mechanism of CE-PEI for Kaolin particles was proposed and illustrated in Fig. 6. The stabilization of Kaolin suspension was destroyed by the addition of positively charged CE-PEI via charge neutralization, and numerous small aggregates generated. These aggregates collided and further agglomerated with regional electrostatic attraction and supramolecular structure of CE-PEI through bridging action. These larger netlike aggregates could further capture the suspended Kaolin particles by capture and sweeping effect, forming heavier and denser flocs, finally sedimentation.

## Conclusion

In this work, a series of sustainable cationic cellulose bio-flocculants with various amino group contents were successfully prepared by a feasible chemical crosslinking with PEI and glutaraldehyde. The flocculation performances of diverse CE-PEI bio-flocculants were evaluated to purify turbid Kaolin suspension. Further, the flocculation kinetics and flocculation mechanism were investigated. Benefiting from the high surface positive charges and supramolecular structure, CE-PEI bio-flocculants with amino group contents of 17.5 mmol/g displayed the best turbidity removal efficiency with the dosage of 0.15 mg/mL, sedimentation time of 30 min at pH 7.0. The residual turbidity of Kaolin suspension decreased from the initial 480 NTU to 8.6 NTU, a 98.2% reduction. Flocculation kinetic results illustrated that the interaction of aggregation and collision between CE-PEI bio-flocculants and Kaolin particles was sufficient for the flocculation process at the optimal CE-PEI dosage. Moreover, charge neutralization was the dominant mechanism for the flocculation of CE-PEI on Kaolin. Thus, this work not only exploits a

promising application of cellulose as a bio-flocculant but also provides a feasible approach to efficiently purify high turbidity wastewater.

## Declarations

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### *Conflicts of interest*

All authors declared no conflict of interest.

### *Availability of data and material*

The datasets used or analyzed during the current study are available from the first author on reasonable request.

### *Code availability*

Not applicable

### *Authors' contributions*

**Zhen Li:** Investigation, Data curation, Writing-original draft. **Wenli Gong:** Investigation, Data curation. **Xuan Chen:** Methodology. **Ranju Meng:** Format and layout. **Yanhong Ding:** Characterization. **Lin Liu:** Supervision, Review & editing, Funding acquisition. **Juming Yao:** Conceptualization, Writing-review & editing.

### *Ethics approval*

Not applicable

### *Consent to participate*

Not applicable

### *Consent for publication*

Not applicable

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## Figures

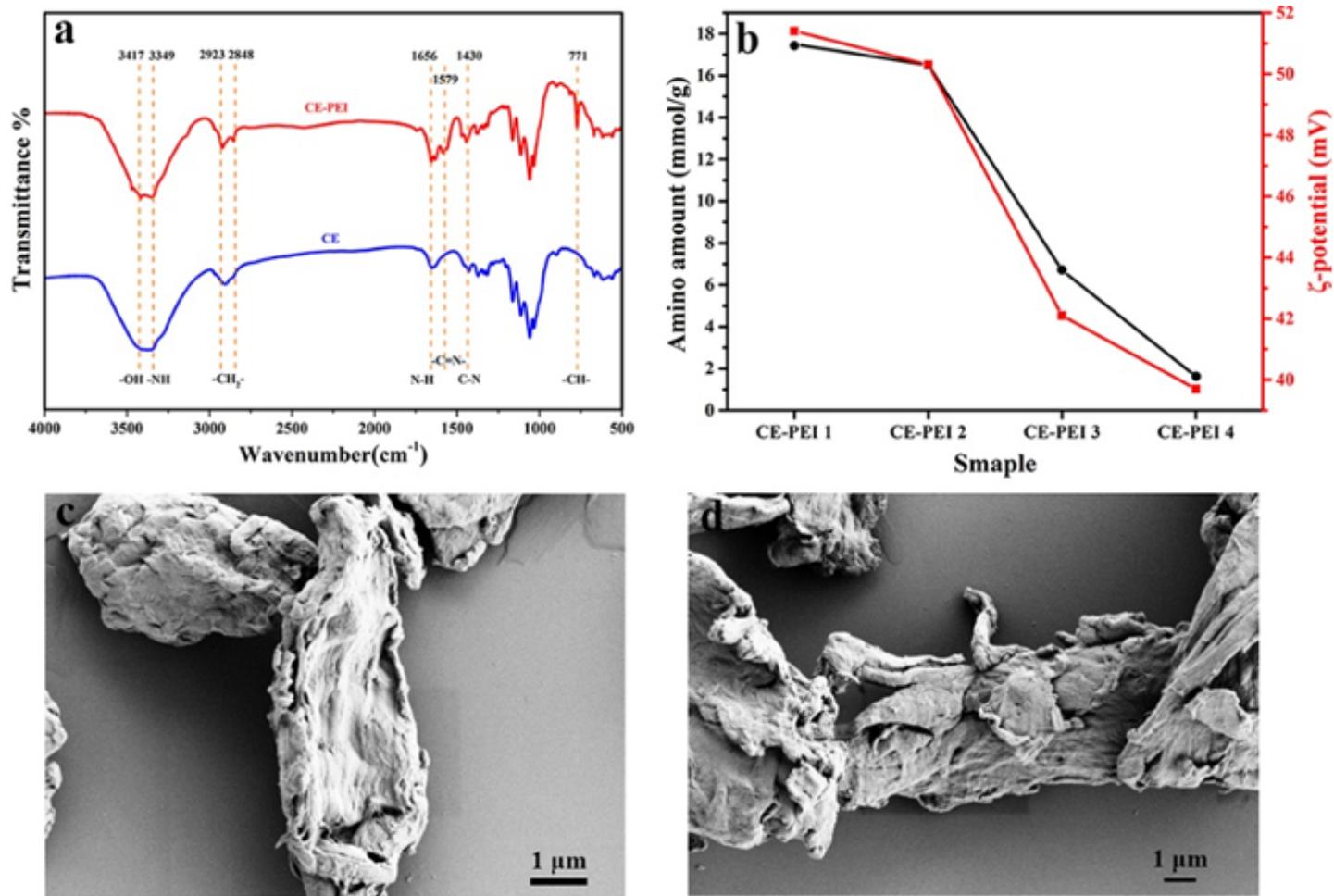


Figure 1

FT-IR spectra of the CE and CE-PEI (a). Amino group contents and zeta potentials of different CE-PEI (b). FESEM images of the original CE (c) and CE-PEI (d)

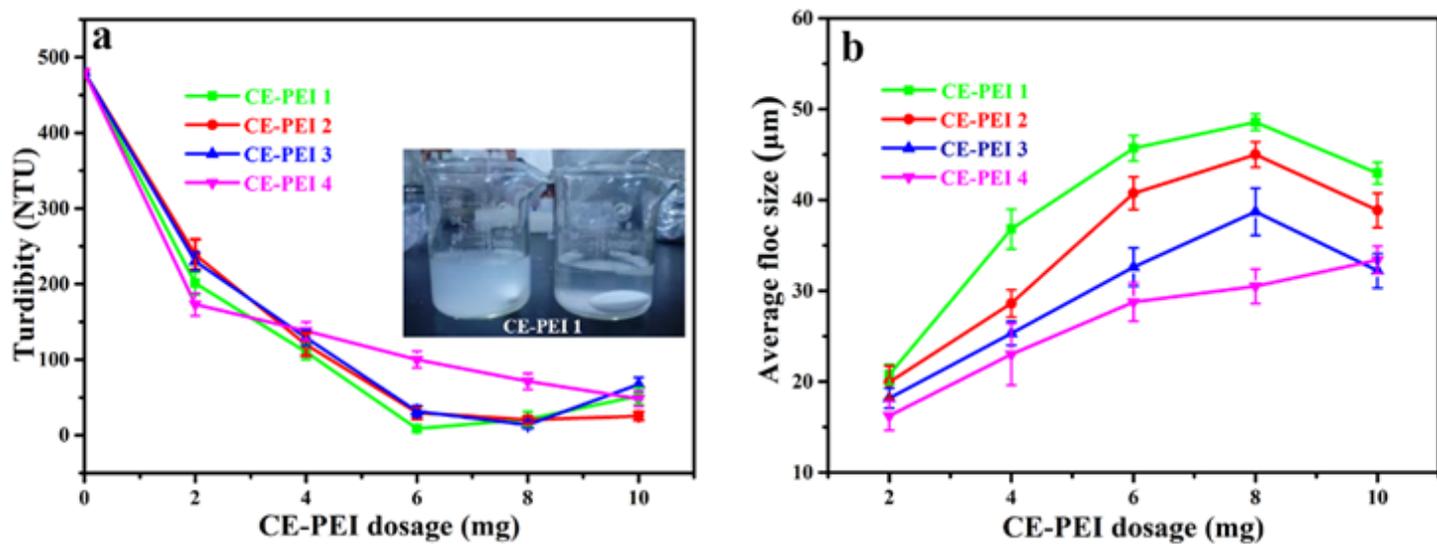


Figure 2

Effect of CE-PEI dosages on the turbidity (a) and floc size (b)

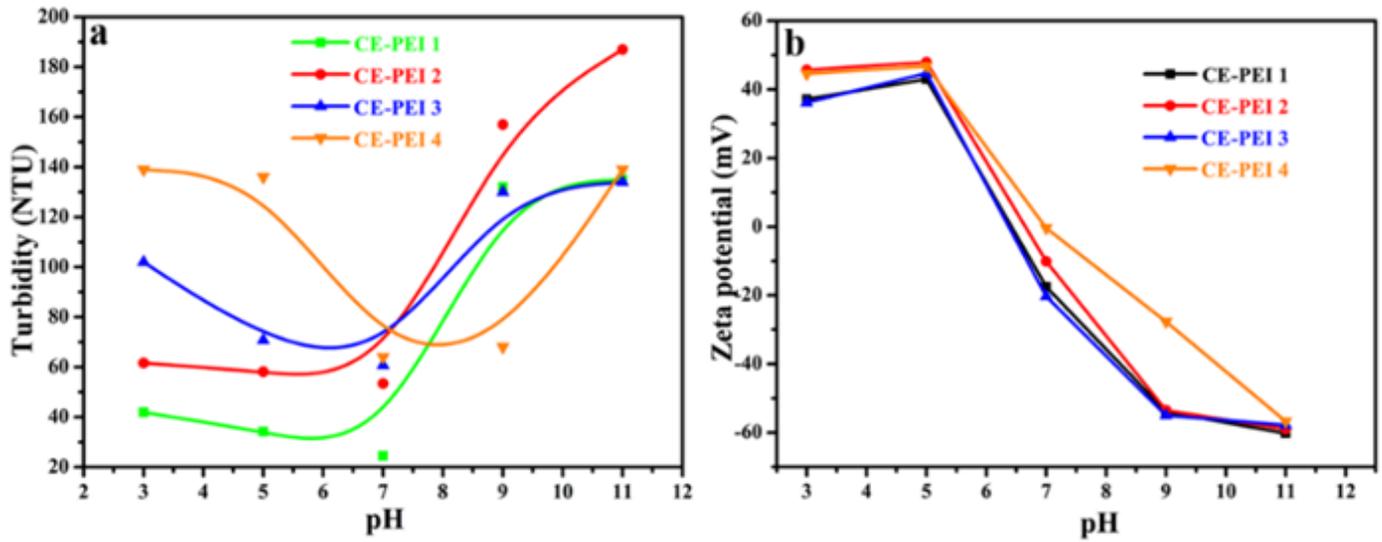


Figure 3

Effect of pH on the turbidity (a) and Zeta potential (b) of kaolin solution

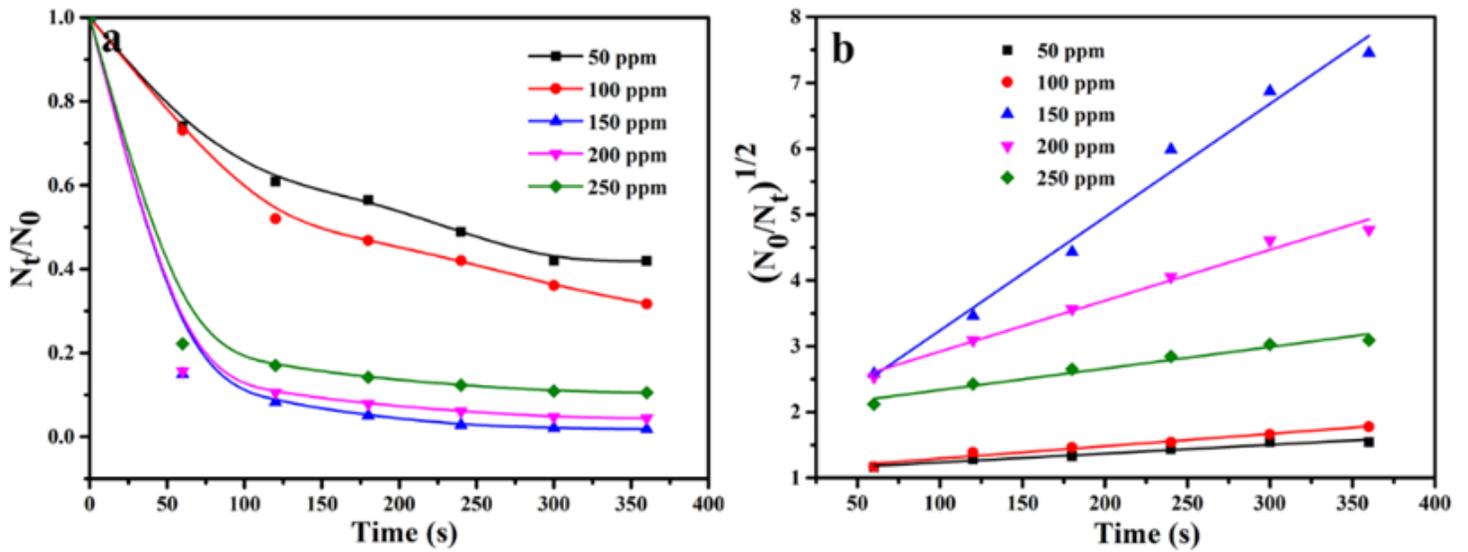


Figure 4

Effect of time on the turbidity (a) and of interface height (b) kaolin solution

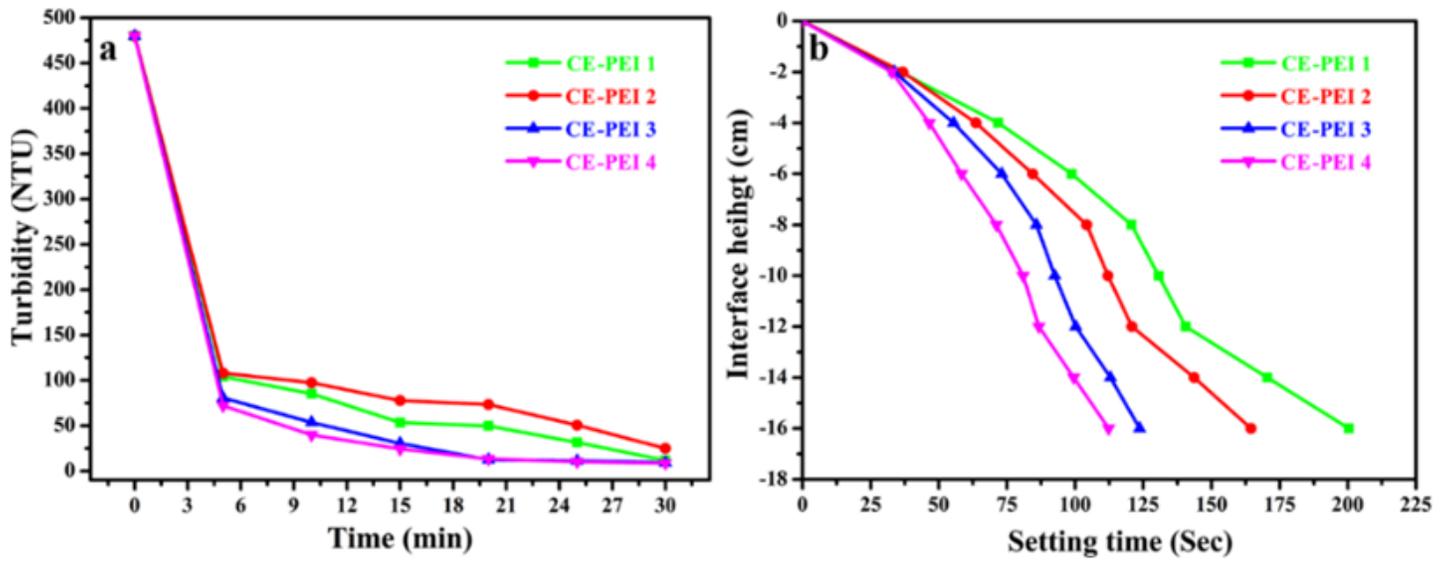


Figure 5

Kinetic curves of flocculation of Kaolin by CE-PEI at different initial concentrations

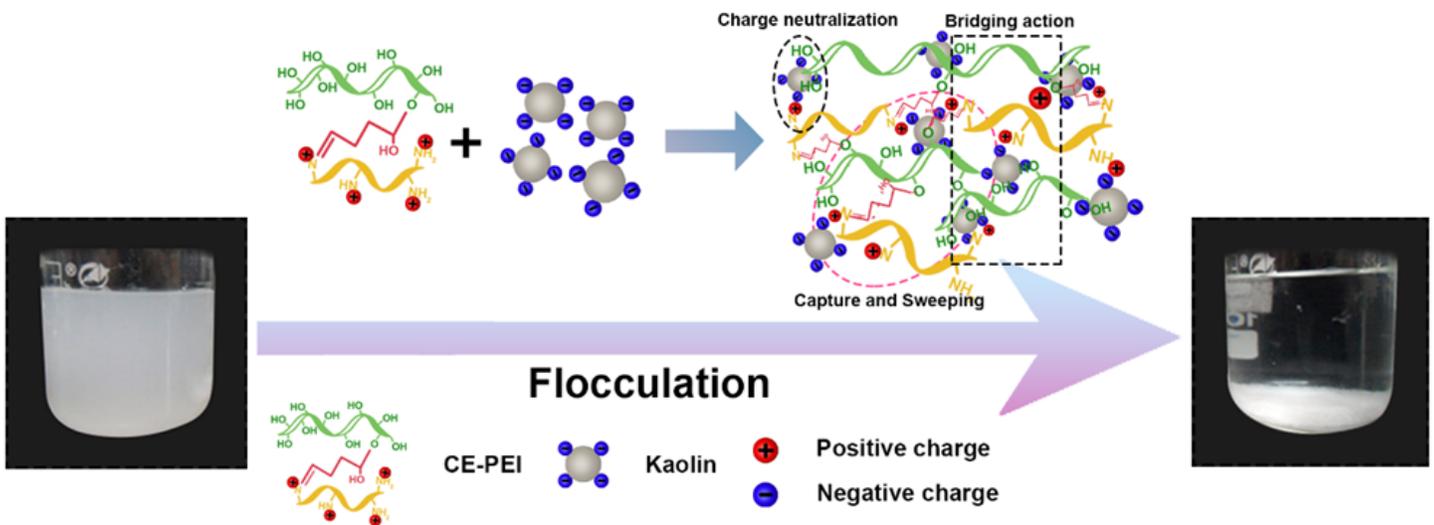


Figure 6

Proposed flocculation mechanism of CE-PEI for Kaolin particles