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Amine-Modified Chitosan Flocculant Synthesized via Single-Mode Microwave Method for Laundry Wastewater Treatment

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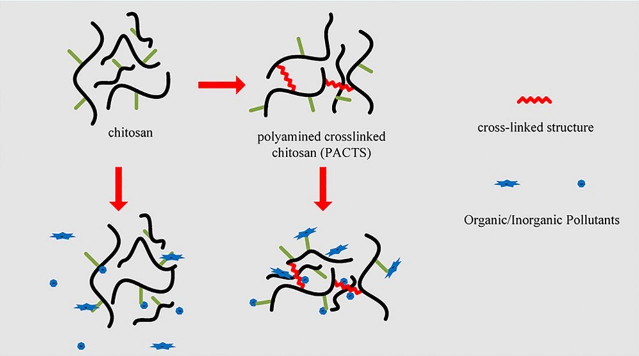

ABSTRACT: In this study, an effective and environmentally friendly polyaminated cross-linked chitosan (M-PACTS) flocculant was successfully synthesized via circular focus single-mode microwave synthesizer irradiation. Epichlorohydrin and tetraethylenepentamine were used as the cross-linking agent and active cationic reagent, respectively. The same formation was used to prepare cationic lightly cross-linked chitosan (C-PACTS) via the conventional heating method. The flocculant was characterized using Fourier transform infrared spectroscopy, X-ray diffraction analysis, and scanning electron microscopy. The flocculation capability of C-PACTS and M-PACTS was compared using laundry wastewater as a model pollutant. The pH, PACTS dosage, temperature, stirring rate, stirring time, and setting time were systematically investigated. The experimental results showed that circular focus single-mode microwave synthesizer irradiation was a more efficient method to modify chitosan. M-PACTS exhibited a higher capacity for turbidity and chemical oxygen demand (COD_{Cr}) removal. Under optimal conditions, the removal rate values of M-PACTS were up to 96% (turbidity) and 78% (COD_{Cr}). The proposed PACTS is suitable for treatment of polluted wastewater in an eco-friendly manner without causing secondary pollution.

1. INTRODUCTION

Wastewater treatment is important to human and environmental health.[1] As an important component of domestic sewage, laundry wastewater is discharged mainly from schools, hospitals, hotels, restaurants, residential areas, etc. This type of wastewater has high turbidity, micropollutants, and eutrophication materials; can affect the growth and reproduction of aquatic animals and plants; and has the potential for severe degradation of aquatic ecosystems.[2,3]

Typically, laundry wastewater predominantly contains surfactants, carboxymethyl cellulose, sodium tripolyphosphate, oils, dust particles, and a variety of microorganisms. Prolonged exposure to laundry wastewater can lead to skin keratosis, and the hazardous substances therein have toxic effects on the kidneys, gallbladder, and pancreas if they enter the bloodstream. Enzyme-containing detergents are used to hydrolyze the proteins on clothing to remove protein fouling. However, these alkaline proteases can also break down proteins on the surface of the skin and cause atopic dermatitis, eczema, etc. At low concentrations, all organic substances are present in the form of molecules and ions present in the water, forming a homogeneous system. At high concentrations, in the presence of suspended particulates, fine dispersed pollutants, and oil products, they may form colloid structures and act as stabilizers of emulsions and suspensions.[4]

The pollution in laundry wastewater results in high turbidity and chemical oxygen demand (COD), which are typical indicators for measuring sewage quality. Flocculation is typically used as a fast and efficient method for wastewater treatment. Through adsorption, bridging, and enmeshment effects, flocculants can dispose of suspended particles, colloids, and dissolved organic matter, and promote agglomeration by making "bridges" between these flocculants, causing them to agglomerate and precipitate out of solution.[5] Currently, inorganic polymers (metals salts) are the most commonly used flocculants for wastewater treatment. Specifically, polymeric ferric sulfate and polyaluminum chloride are the most extensively studied and applied reagents among them. Sometimes, to convert the smaller flocculants into larger particles, certain synthetic flocculant aids such as polyacrylamide (PAM) are added to the wastewater after the coagulation process. However, despite the high efficiency of inorganic

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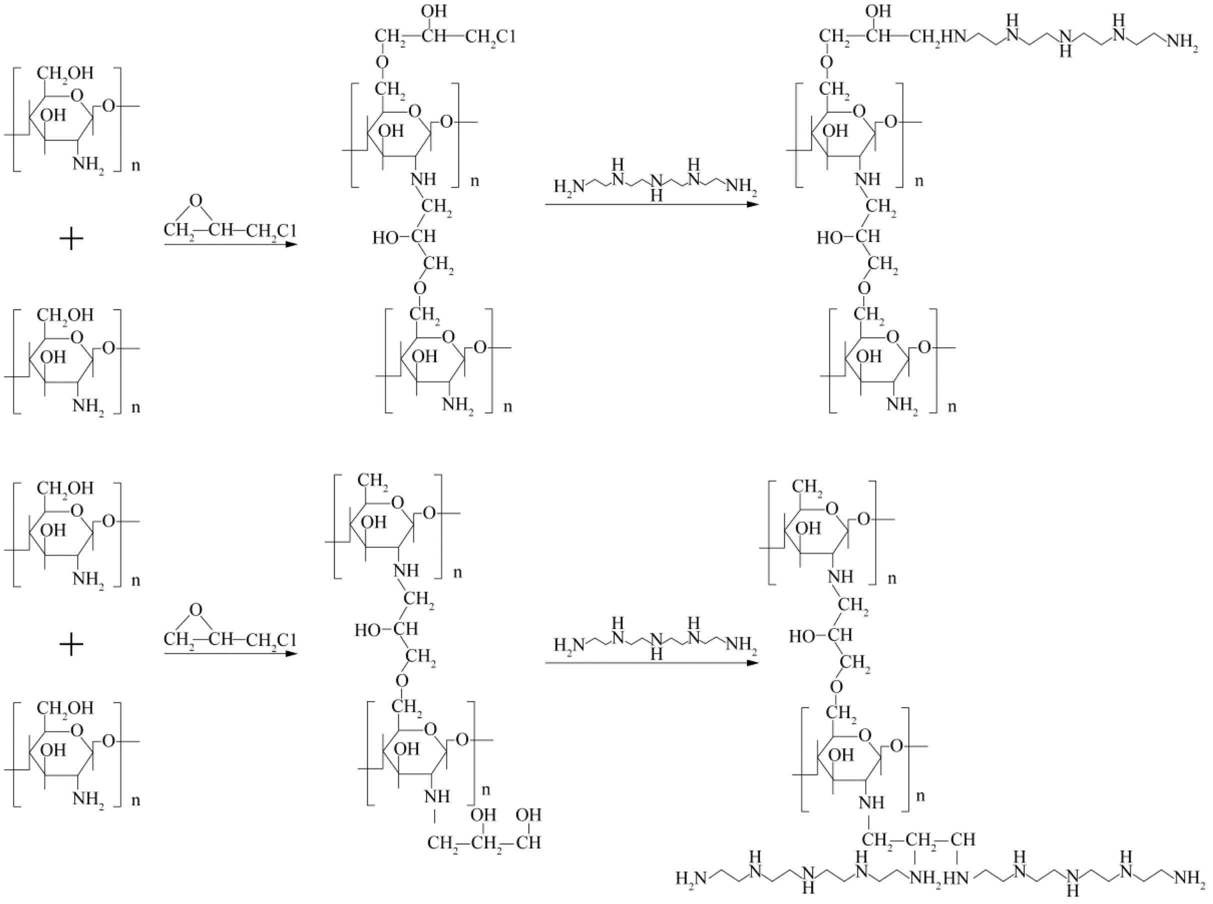

Figure 1. Equation for the preparation of the cationic lightly cross-linked chitosan (C-PACTS) flocculant.

flocculants, they can cause secondary pollution. For example, excessive flocculants can leave behind metallic elements, especially aluminum, which can accumulate within the brain neurons through drinking water and may impact memory and even lead to Alzheimer's disease.[6] Moreover, residues of coagulant aids such as PAM ultimately find their way into surface water and groundwater. These residues not only change the physical and chemical properties of water but also contribute to the pollution. For example, PAM degradation products (acrylamide) can damage the nervous systems of humans and animals.[7]

Synthetic organic polymeric flocculants and inorganic flocculants have been gradually replaced by a variety of environmentally friendly natural polymer flocculants such as starch[8] and cellulose[9] to cope with these problems. These natural polymers have abundant raw material availability and are nontoxic, readily biodegradable, and easy to modify.[10] Consequently, modified natural polymers have increasingly attracted the interest of researchers and have become a viable alternative choice in wastewater treatment.[11] Among the numerous natural biopolymers, chitosan (CTS) is the only one with amine groups, is widely found in many arthropods (such as insects and crustaceans) and fungi, and is the second most abundant biological polymer in nature after cellulose.[12] These two properties make the large-scale production and application of CTS possible. When amino groups are in an acidic environment, H^+ renders the whole molecule electropositive and promotes antimicrobial properties. Because most pollutants in water are electronegative, CTS has application prospects as a broad flocculant and heavy metal ion adsorbent.[13,14] Picos-Corrales et al. used CTS as a bioflocctulant to treat wastewaters from Sinaloa (Mexico). Jar test results showed that CTS exhibited high effectiveness in pollutant removal from different sampling zones (agricultural wastewater and river water) and led to 40% Mn removal from highly contaminated river water samples.[15]

Chemical modification could improve the performance of CTS. Although the conventional heating method has been used to modify CTS, it is a time-consuming and energy-intensive process. Single-mode microwave irradiation provides accurate and controllable synthesis energy for the reaction between chemical bonds.[16] Zhan et al. prepared a terpolymer (CDL) by microwave-assisted copolymerization.[17] Their results showed excellent flocculation efficiencies for acid black 172 and reactive orange C-3R simulated wastewater (100 mg/L) with removal ratios of 99.8% and 97.7% at a CDL concentration of 250 mg/L, respectively. In this study, a single-mode microwave irradiation synthesizer was adopted for the synthesis of polyaminated cross-linked CTS (M-PACTS) as a flocculant and compared with that synthesized by the conventional heating method. Two main water treatment evaluation indices, turbidity and COD_{Cr}, were tested under various parameters (dosage, pH, temperature, stirring rate, time, and setting time) to compare the flocculation performance of the products synthesized by the different methods. Here, we show that single-mode microwave irradiation could be an efficient tool to modify CTS.

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2. METHODS

Preparation of PACTS. All chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., and along with the water were of analytical grade.

Preparation of M-PACTS. CTS powder (0.5 g) was dissolved in 20 mL of 1% acetic acid solution. Subsequently, 3 mL of epichlorohydrin, 5 mL of ultrapure water, and 0.05 g of *p*-toluenesulfonic acid catalyzer were added to a long-neck flask. The mixture was heated to 80 °C to promote the ring-opening reaction of epichlorohydrin. Then, CTS and epichlorohydrin solutions were mixed and the pH of the mixed solution was adjusted to 7.0 by adding 0.1 mol L^{-1} NaOH. The prepared mixture was placed in a single-mode microwave synthesizer (Discover, CEM, USA) at 40 W and 80 °C until gel-like cross-linked CTS (CL-CTS) was obtained. The gel was smashed with a 200 mesh sieve and washed several times with ultrapure water to eliminate excess acetic acid.

The product obtained in the previous step was dispersed in 30 mL of ultrapure water. When the gel swelled in water to form a transparent and homogeneous colloidal solution, 10 mL tetraethylenepentamine was added to the solution and stirred for 2 h. Subsequently, this mixture was transferred into single-mode microwave reactor at 30 W, 70 °C. After the final purification step, the M-PACTS was preserved in a sealed environment.

Preparation of C-PACTS. The cationic lightly cross-linked CTS (C-PACTS) flocculant was synthesized by conventional heating according to the method described by Huang et al., and the equation is shown in Figure 1.[18]

The properties of the laundry wastewater (obtained from a student dormitory of Liaoning Shihua University) are listed in Table 1.

Table 1. Physicochemical Properties of Laundry Wastewater Used in the Study

parameter	value
appearance	purple-gray and turbid
T (°C)	20 °C
pH	6.2
turbidity (NTU)	62.1
COD_{Cr} (mg L^{-1})	1453.7
BOD (mg L^{-1})	382.5
TDS (mg L^{-1})	1213
conductivity (μS/cm)	457.6

Flocculation Experiments. All experiments were carried out using jar test equipment (Apex Instruments, Fuquay-Varina, NC, USA) with 500 mL of wastewater and a certain amount of PACTS under different parameters. Wastewater was sealed and stored in a dark environment at 4 °C before the experiments. The main steps of the experiments consisted of four consecutive stages: (1) adjusting the wastewater pH using dilute sulfuric acid (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}) within a range of 2−7; (2) adding PACTS to the pH-adjusted wastewater and stirring intensely under different rates and time values at a certain temperature to ensure even dispersion of PACTS; (3) after the fast stirring, performing slow stirring under different rates and time values at a certain temperature to investigate whether the stirring conditions could influence the process of adsorption and flocculation; (4) Adjusting the solution pH to 7 to reunite the smaller flocculants and then slowing it to settle for 40 min. Subsequently, the PACTS-pollutant flocculants were removed by filtering, and the clear liquid obtained was used to test the turbidity and COD_{Cr}.

The turbidity and COD_{Cr} values were measured using a turbidimeter and COD_{Cr} rapid detector, respectively. All experiments (except for the one on the temperature effect) were carried out at room temperature (20 ± 2 °C).

Analytical Methods. Fourier transform infrared (FT-IR) spectra of CTS, CL-CTS, and PACTS at wavenumbers between 400−4000 cm^{-1} were measured using WQF-520 FT-IR spectrometer (Beijing Beifen-ruili Analytical Instrument (Group) Co., Ltd., China). Scanning electron microscopy (SEM) of CTS and PACTS was performed using TSM-7900F (JEOL Ltd., Japan). X-ray diffraction (XRD) analysis was performed using D/max-RB X-ray diffractometer (Rigaku, Japan) operating at a voltage of 40 kV and current of 100 mA using Co Kα radiation. The pH was measured using PHS-25 acidimeter (Shanghai Lei-ci Instrument, China). The chemical oxygen demand (COD_{Cr}) was measured using a COD rapid detector (DR1010 rapid detector and DRB200 digestive machine, Hach, USA). Turbidity was determined using a turbidimeter (2100Q Turbidimeter, Hach, USA). The conductivity was measured at pre- and post-treatment stages using a conductivity detector (Sension7, Hach, USA).

3. RESULTS AND DISCUSSION

FT-IR Analysis. The spectrum of CTS, CL-CTS, and PACTS are shown in Figure 2. The main characteristic peaks of observed CTS were as follows: 3368 cm^{-1} (a broadening multiple peak generated by the overlapping of O−H stretch, N−H stretch, and interhydrogen bond), 2920 and 2871 cm^{-1} (methyl and methylene C−H stretch, respectively), 2360 and 2343 cm^{-1} (CO_2 asymmetric stretch), 1653 cm^{-1} (amide I band, C═O stretch), 1599 cm^{-1} (amide II band, N−H bending), 1423 cm^{-1} (C−N bending and C−H bending), 1381 cm^{-1} (amide III band, C−N stretch), 1325 cm^{-1} (C−H bending), 1261 cm^{-1} (C−N stretch), 1157 cm^{-1} (C−O−C stretch), and 1084 cm^{-1} (C−O stretch).[19]

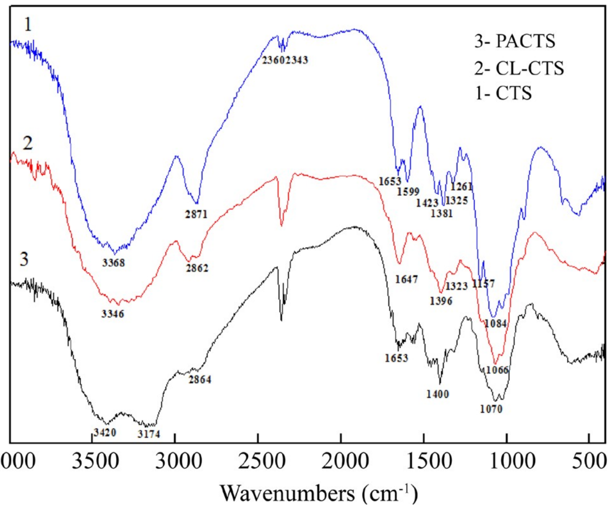

Figure 2. FT-IR spectra of chitosan (CTS), cross-linked chitosan (CL-CTS), and polyaminated cross-linked chitosan (PACTS).

Compared to CTS powder, the CL-CTS retained more characteristics than CTS. However, the 1599 cm^{-1} N−H bending and 1423 cm^{-1} C−N bending disappeared because of the cross-linking action between $-NH_2$ and −OH.

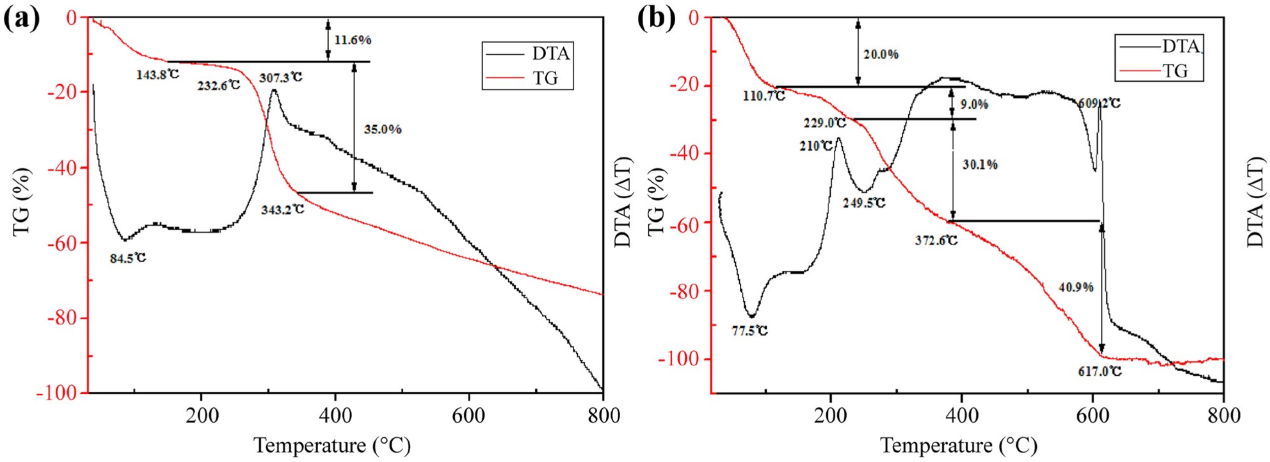

Figure 3. Thermogravimetry/differential thermal analysis of (a) CTS and (b) PACTS.

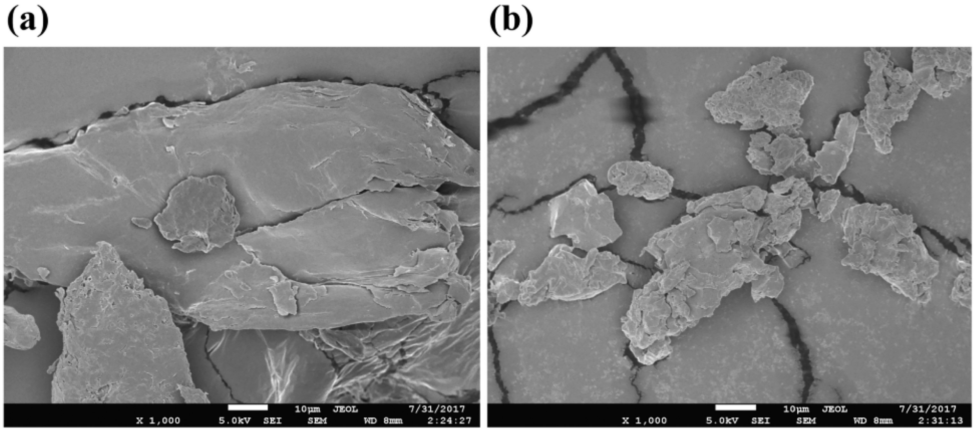

Figure 4. SEM images of (a) CTS and (b) PACTS.

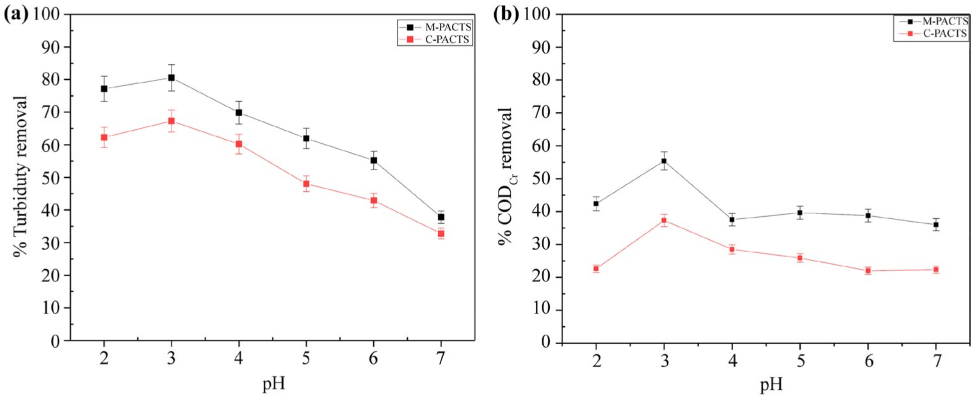

Figure 5. Influence of wastewater initial pH value on (a) turbidity and (b) chemical oxygen demand removal rates of M-PACTS and C-PACTS.

After the addition of tetraethylenepentamine, obvious changes to PACTS were observed at 3420 and 3174 cm^{-1} (N−H stretch). This indicates that abundant amino groups were introduced and the hydrogen bond effect caused the overlapping peaks (−OH and $-NH_2$) to shift to lower wavenumbers. Around 1650−1550 cm^{-1}, the deformation vibration of N−H reappeared in the plane and was reinforced. Moreover, 1472 cm^{-1} (asymmetric deformation of CH_2) and 1322 cm^{-1} (symmetric deformation of CH_2) became stronger, indicating that $-CH_2-$ was introduced by tetraethylenepentamine. However, a large number of amino groups can also increase the number of inter- or extra-molecular hydrogen bonds, causing the absorption peaks to shift to lower wavenumbers. All the above changes indicate that the target products were quickly and successfully synthesized via single-mode microwave irradiation.[18]

Thermogravimetry/Differential Thermal Analysis. Thermogravimetry/differential thermal analysis (TG-DTA) of CTS and PACTS is shown in Figure 3. The CTS DTA curve shows three stages of weight loss. In the first stage, the TG results showed approximately 11.6% weight loss due to the physically absorbed water escaping from the molecular

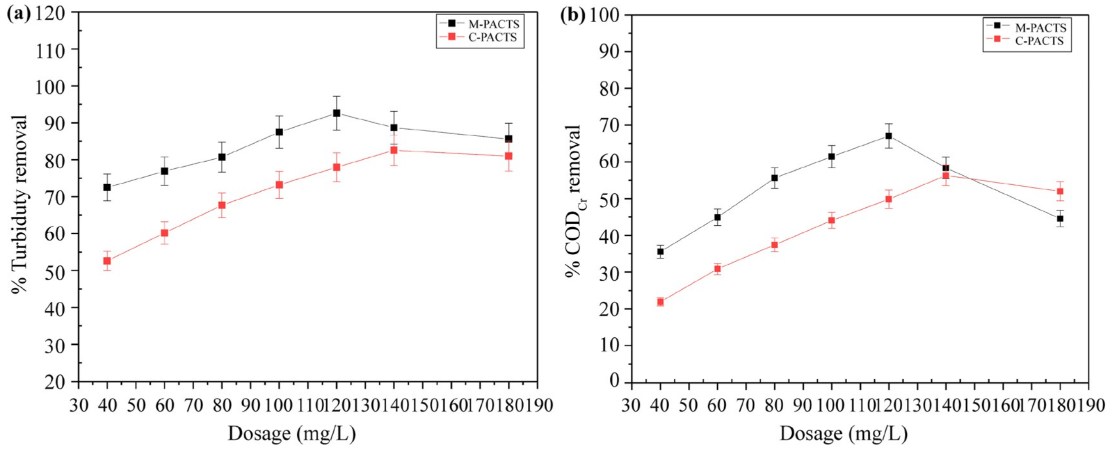

Figure 6. Influence of dosage on (a) turbidity and (b) COD removal rates for M-PACTS and C-PACTS.

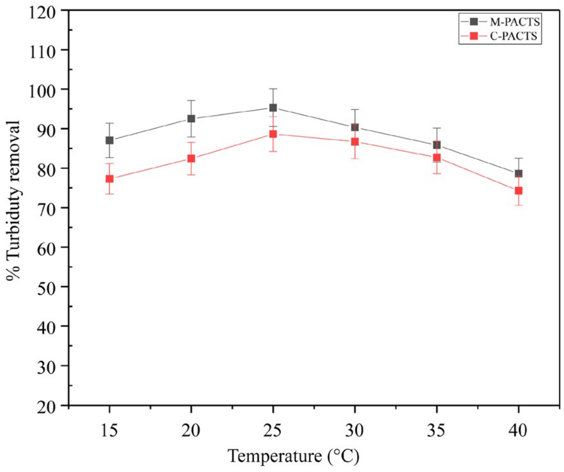

Figure 7. Influence of temperature on turbidity and COD$_{Cr}$ removal rates for M-PACTS and conventional C-PACTS.

structure and being fixed by hydrogen bonding, as demonstrated by the DTA endothermic peak at 84.5 °C. The second stage indicates that approximately 35.0% CTS powder was lost in the temperature range of 232.6 to 342.2 °C (with the maximum loss at 307.3 °C). This exothermic peak (307.3 °C) was mainly caused by strong decomposition that included the dehydration of CTS, breakage of glycosidic bonds, and partial decomposition of the acetylated and deacetylated units of the polymer (CTS rings were not completely decomposed). In the third stage, when the temperature rose to 800 °C, the mass of CTS dropped gradually because of the further fractionation of the CTS ring and the carbonization of organic matter. After chemical modification, the changes in the structure and the interactions between the different groups had a strong influence on the thermal stability of CTS.

PACTS also showed three stages of weight loss, but there were apparent differences compared to those of CTS. In the first stage, the temperature at which water loss occurred for PACTS was evidently lower than that for CTS, whereas the weight loss was higher than that of CTS. This was mainly caused by the cross-linking reaction and the introduction of amine groups. CTS cross-linked with epichlorohydrin to form a new space network structure. However, this reaction occurred on C2 $-NH_2$, and C6 $-OH$, which decreased the capacity to form H−O−H hydrogen bonds with water, making it easier for water to evaporate. This could also be confirmed from the TG curve, which indicated that the decomposition temperature of PACTS was much lower than that of CTS because the chemical modification destroyed its original crystalline structure. Beyond that, there was a final weight loss stage over 229.0−372.6 °C, which may be related to the degradation of the side amine chain and the fragmentation of cross-linking between CTS molecules.

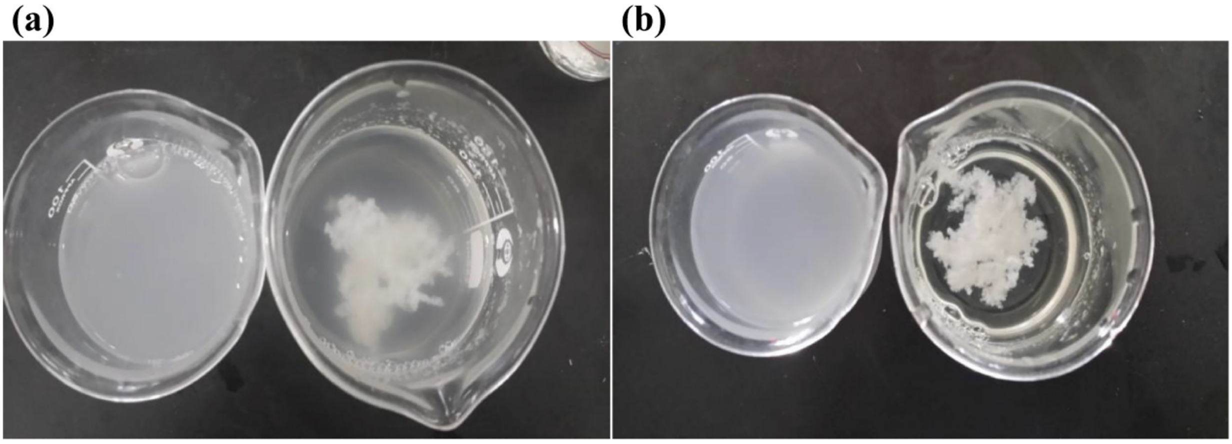

Figure 8. Comparison of laundry wastewater treatment with (a) C-PACTS and (b) M-PACTS in the laboratory environment.

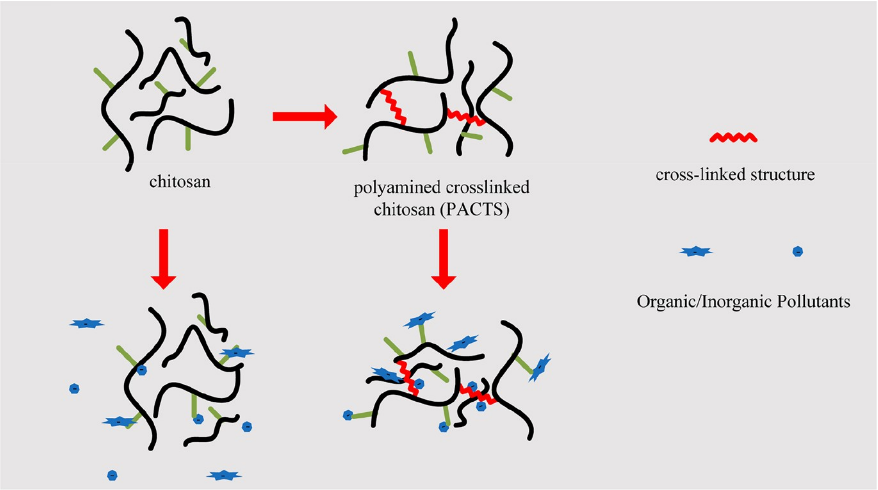

Figure 9. Flocculation mechanism diagram.

Table 2. Analysis of Effective Stirring Speed and Time at Two Flocculation Stages for M-PACTS

no.	A R_1 (rpm)	B T_1 (min)	C R_2 (rpm)	D T_2 (min)	turbidity removal (%)	COD_{Cr} removal (%)
1	1 (150)	1 (2.0)	1 (30)	1 (10)	93.3	68.8
2	1	2 (2.5)	2 (40)	2 (15)	93.9	70.2
3	1	3 (3.0)	3 (50)	3 (20)	94.8	75.9
4	1	4 (3.5)	4 (60)	4 (25)	95.2	75.5
5	2 (200)	1	2	3	94.2	75.3
6	2	2	1	4	95.7	76.2
7	2	3	4	1	94.1	66.2
8	2	4	3	2	96.2	73.7
9	3 (250)	1	3	4	95.9	78.2
10	3	2	4	3	94.8	75.1
11	3	3	1	2	97.0	72.6
12	3	4	2	1	94.3	70.8
13	4 (300)	1	4	2	96.3	75.5
14	4	2	3	1	94.5	71.3
15	4	3	2	4	95.2	75.7
16	4	4	1	3	93.5	68.2

	index of turbidity removal rate (%)					index of COD_{Cr} removal (%)			
	R_1	T_1	R_2	T_2		R_1	T_1	R_2	T_2
K_1	377.4	380.7	378.6	370.2	K_1	290.4	297.8	284.0	276.3
K_2	380.2	378.0	377.6	383.4	K_2	291.4	292.9	292.0	292.0
K_3	383.0	381.1	381.5	377.3	K_3	196.7	290.4	299.1	296.6
K_4	379.5	379.2	380.4	382.0	K_4	289.7	287.2	287.4	306.3
k_1	94.35	95.18	94.65	92.55	k_1	72.60	74.45	71.00	68.40
k_2	95.05	94.50	94.40	95.85	k_2	72.85	73.23	73.00	73.00
k_3	95.75	95.28	95.38	94.33	k_3	74.18	72.60	74.78	74.15
k_4	94.88	94.80	95.10	95.50	k_4	72.43	71.80	71.85	76.58
range	1.22	0.78	0.98	3.30	range	1.75	2.65	3.78	8.18
optimization	A_3	B_3	C_3	D_2	optimization	A_3	B_1	C_3	D_4

SEM Analysis. The SEM images are shown in Figure 4. After cross-linking and chemical modification, CTS lost its smooth laminar structure and formed a new irregular structure with side chains. This type of structure has a smaller size and higher surface area, which can be more favorable for capturing fine particles and colloids. Subsequently, the flocculants coagulated to form larger particles and precipitate.

Flocculation Effect of Laundry Wastewater and Removal of Turbidity and COD_{Cr}. To compare the water treatment efficiency of the different synthesis methods, we used PACTS produced via conventional heating (C-PACTS) and that produced via microwave irradiation (M-PACTS) as flocculants for the treatment of laundry wastewater. In the preparation of C-PACTS, the same dosage of reagents and materials was used as for M-PACTS, and a conventional hot plate stirrer with round-bottom flasks was used as an energy source.[18] Finally, several natural-polymer flocculants and inorganic flocculants were used for comparison.

pH Effect. For natural-polymer flocculants, especially CTS and its derivatives, pH is the most important factor influencing coagulation.[20] An acidic medium was used to provide H^+ for the amine group to enhance the electropositivity. After protonation, the acidic medium transforms the free $-NH_2$ into $-NH_3^+$. In the experiment, 500 mL wastewater was spiked with 40 mg of M-PACTS and C-PACTS (dry weight) at 20 °C, then stirred at 150 rpm for 3 min, followed by stirring at 50 rpm for 10 min. Finally, the pH of the wastewater was adjusted to 6. The influence of the initial pH of the wastewater on the turbidity and COD_{Cr} removal rate is shown in Figure 5. At the initial wastewater pH of 3, both C-PACTS and M-PACTS had the highest turbidity and COD removal rate, which is consistent with the results of Lu et al.[21] It is thus proven that the strongly cationic CTS derivative has the best performance at a lower pH. The highest water treatment capability at pH 3 can be explained by the enhanced electrostatic attraction and the reduction in hydrogen bonds. At a lower pH, more H^+ is provided to the amino groups, and the protonated amino groups enhance the electrostatic attraction between negatively charged colloids and positively charged adsorption sites. This enforces charge neutralization and adsorption bridging processes. However, at higher pH values between 4 and 7, more OH^- is available to compete with the anionic colloids and suspended particles of wastewater for the adsorption sites of PACTS. This decreases the number of adsorption sites and, consequently, the coagulation ability. From another aspect, the mass of amino groups in a neutral environment has a strong hydrogen bond effect, which causes high viscosity and low dispersibility of PACTS in wastewater. In an acidic solution, the protonated amino groups hinder the formation of hydrogen bonds, which also improves coagulation efficiency. However, when the pH is lower than 3, the fraction of PACTS may degrade under strongly acidic conditions, and a mass of H^+ leads to charge reversal on the colloid surface.

Dosage Effect. At an initial wastewater pH of 3, with other conditions remaining the same, the effect of the flocculant dosage on the turbidity and the COD removal rate is shown in Figure 6. We observed that with an increase in the flocculation dosage, both M-PACTS and C-PACTS showed increased turbidity and COD removal rates. The highest turbidity and COD removal rates were achieved at dosages of 120 and 140 mg/L for M-PACTS and C-PACTS, respectively. However, despite the higher dosage, the optimal turbidity and COD removal rates of C-PACTS were 82.3 and 56.1%, respectively, which are lower than those of M-PACTS (10.2 and 10.7%, respectively). Moreover, M-PACTS had a higher water content than C-PACTS because M-PACTS had a lower degree of cross-linking. This also indicates that there are more active sites ($-OH$, $-NH_2$) after grafting with tetraethylenepentamine. Furthermore, the high cross-linking degree results in an excessively compact interior structure, which probably hinders adsorption within PACTS. Through microwave irradiation, the cross-linking degree can be controlled more easily by regulating radiation power, temperature, and time in a shorter period (approximately 1/8 of the conventional heating method), and the grafting of tetraethylenepentamine is more efficient. Once the optimal dosage is exceeded, the excessive flocculants are adsorbed on the surface of the flocculants and then restabilize in the water, causing a reduction in flocculation performance. In addition, the excessive flocculants result in more residual soluble CTS derivatives. Finally, these organics dissolved in the water contribute to COD. This phenomenon can also be proven by the performance of C-PACTS. The higher degree of cross-linking and the lower viscosity contributed to the minimal soluble CTS derivatives in the flocculants. Therefore, the decrease in turbidity and COD removal rates was not evident with an increase in redundant flocculants.

Temperature Effect. At an initial wastewater pH of 3, the flocculant dosages were 120 and 140 mg/L for M-PACTS and C-PACTS, respectively, with other conditions similar as to what has been previously described. The results for the optimal wastewater temperature are shown in Figure 7. When the temperature was lower than 25 °C, the removal rates of turbidity and COD increased as the temperature increased. Nevertheless, when the temperature exceeded 25 °C, the flocculation efficiency decreased with the increase in temperature. This phenomenon can be explained as follows. First, the increasing temperature induced flocculants, suspended particles, and colloids to a faster diffusion rate. In addition, the higher temperature decreased the viscosity of the mixing water solution, which accelerated the flocculation reaction and promoted the setting and coagulation of the flocculants. Second, when the temperature exceeded a certain range, the movement of particles in the water system was too fast, leading to the formation of smaller flocculants with an unstable structure. These factors inhibited flocculation. Third, a higher temperature facilitated the dissolution of the soluble fraction in PACTS in acidic environments; therefore, the turbidity and COD increased again. Owing to the high cross-linking degree and less soluble structure, the flocculation performance of C-PACTS at high water temperatures may have been better than M-PACTS (>40 °C). However, based on practical situations and the principle of optimality, M-PACTS was still the most efficient for flocculation. At an optimal temperature (25 °C), M-PACTS exhibited a better performance with turbidity and COD removal rates reaching 95.1 and 70.1%, respectively. The comparison of wastewater treatment between C-PACTS and M-PACTS and the flocculation mechanism of the PACTS are shown in Figures 8 and 9.

Stirring Rate and Mixing Time Effect. When comparing the flocculation performance between M-PACTS and C-PACTS, the results clearly show that M-PACTS had a better water treatment ability. Thus, the study focused on M-PACTS in subsequent experiments. The stirring process was divided into fast and slow stirring. Previous studies have shown that fast stirring favors the dispersion of M-PACTS and particle collisions, but excessive stirring speed and time results in smaller and unstable flocculants. In contrast, slow stirring increases the size of the destabilization particles and enhances adsorption. Therefore, the effect of different combinations of stirring rate and stirring time on the removal rates of turbidity and COD was analyzed via four-factor and four-level orthogonal experiments. As shown in Table 2, for turbidity removal, the best combination was fast stirring for 3 min at 250 rpm, followed by slow stirring for 15 min at 50 rpm, and the sequence of influence level was D > A > C > B. The best COD removal was achieved when fast stirring for 2 min at 250 rpm, followed by slow stirring for 25 min at 40 rpm. The sequence of the influence levels was D > C > B > A.

The results show that the optimal removal rates of turbidity and COD could not be achieved under the same hydraulic conditions. Compared with the turbidity removal rates, the COD removal rates change significantly with stirring rates. This phenomenon indicates that PACTS has a higher stability and capacity to resist disturbance for stirring in turbidity removal, and a longer slow stirring time facilitates the adsorption of COD and other particles. Considering various factors, combination 9 can be considered as the best hydraulic condition (Table 2).

■ CONCLUSIONS

In this study, a single-mode microwave irradiation synthesizer was adopted for the synthesis of a PACTS flocculant. The proposed flocculant is environment-friendly, can be sustainably sourced, and creates no secondary pollution. To improve the efficiency and stability, we used epichlorohydrin and tetraethylenepentamine as the cross-linking and cationic reagents. The single-mode microwave irradiation significantly improved the synthesis and flocculation ability. The effects of pH, dosage, temperature, stirring conditions, and setting time was investigated to obtain the optimal flocculation conditions, which were found to be as follows: M-PACTS dosage of 120 mg/L, initial wastewater pH of 3, water temperature of 25 °C, stirring with a combination of fast stirring at 250 rpm (2 min) and slow stirring at 50 rpm (25 min), and setting time of 40 min. Under these conditions, the turbidity and COD removal rates were as much as 96 and 78%, respectively. Moreover, the experimental results also demonstrated that, in contrast to conventional heating method, single-mode microwave irradiation could indeed improve the reaction and flocculation efficiency. Because of the introduction of abundant amino groups, electrostatic adsorption between PACTS and particles plays a major role in wastewater treatment. In addition, charge neutralization and sweeping coagulation also contributed to the flocculation process. This study determined that the single-mode microwave irradiation method could efficiently and quickly synthesize cationic CTS flocculant. This method should be scaled up for industrial production, as it has significant potential to make a contribution to the development and application of bioflocculants.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. X.Z. drafted the main part of the paper and was responsible for the planning, implementation, and modification of the entire experiment. Z.T. participated in the experiment and analyzed the experimental results. C.M., L.L., and J.Y. coordinated the study and reviewed the manuscript. J.Y. provided financial help.

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■ ABBREVIATIONS

COD, chemical oxygen demand; EfOM, effluent organic matter; FT-IR, Fourier transform infrared spectroscopy; PACTS, polyaminated cross-linked chitosan; PAM, polyacrylamide; SEM, scanning electron microscopy; XRD, X-ray diffraction

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