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Preparation of Cationic Cellulose as a Natural Flocculant/Sorbent and Its Application in Three Water Treatment Scenarios

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Abstract: In this study, cationic cellulose (CC) was prepared by etherifying commercial cellulose with (3-chloro-2 hydroxypropyl) trimethylammonium chloride (CHPTAC) in an alkaline medium. The prepared CC was characterized using Fourier transform infrared spectrometry (FTIR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and nuclear magnetic resonance (NMR). The characterization results affirmed the successful cationization of cellulose. Upon optimization of reaction conditions, a CC sample with a degree of substitution (DS) of 0.857 was achieved. The CC sample was then tested as a flocculant or sorbent in three environmental applications: algal harvesting, solid removal from dairy wastewater, and capture of methyl orange (MO) in dye wastewater. The effects of dose level and pH on flocculation/sorption performance were studied. Under the optimal dose level and pH conditions, up to 90.4% of dry algal biomass and 53.3% of suspended solids in the dairy wastewater were removed, as measured by standard jar testing. Around 64.2% of MO in the synthetic wastewater was sorbed on the prepared CC and removed, as determined by absorbance at 463 nm. The new CC preparation method exempts the pre-dissolution of cellulose in a solvent and is expected to promote the application of CC in water treatment and the alike scenarios.

Keywords: cationic cellulose; flocculant; wastewater; methyl orange; removal efficiency

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1. Introduction

Cellulose, the most abundant renewable biopolymer, has long been investigated as a green material to replace non-renewable materials and chemicals; however, its high crystallinity and highly ordered hydrogen bond network reduce the reactivity and solubility of cellulose, hindering its practical applications [1,2]. To overcome the constraints, various modification methods (including chemical and physical ones) have been reported. The most prevalent, conventional method is chemical surface treatment through reactions such as carboxylation, esterification, and nitration [3]. Chemical reagents such as alkalis and enzymes have been used to hydrolyze the crystalline and amorphous region of cellulose, causing a change in its structure and properties [4]. Efforts have been made to dissolve cellulose in organic solvents [5], alkali salts with urea and thiourea [6], deep eutectic

solvents [7], ionic liquids, and ionic liquids with co-solvents such as DMSO and DMAc [8]. Then, other reagents are added to react with the dissolved cellulose to produce the desired modified cellulose products, e.g., cationic cellulose and nanocellulose membranes [9].

However, the existing procedure has several limitations. The most renowned one is the non-biodegradability, volatility, toxicity, and high costs of the reagents/solvents required. Other limitations have also been identified. For example, in NaOH/urea aqueous solutions, the solubility of cellulose is contingent upon the temperature of the solvent (−10 to −12 °C), and spinning the solutions containing high concentrations of cellulose is unstable, which poses a challenge for industrial applications [10]. Various cationic groups have been successfully added to cellulose backbones. However, no successful use of N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) to substitute the hydroxyl groups of cellulose has been reported without first dissolving cellulose in a homogeneous or heterogeneous solvent system. In this study, we developed a new preparation method capable of producing cationic cellulose (CC), with a high degree of substitution (DS) (Figure 1). We further demonstrated the CC's three environmental applications: algal harvesting, the flocculation removal of solids from dairy wastewater, and the removal of methyl orange (MO) from synthetic textile wastewater. CC is a highly efficient flocculant that can function effectively across a broad pH range. Furthermore, it is non-toxic and has the added benefit of being readily biodegradable [11]. It has been used for pollutant removal from various types of wastewater [12–14]. This study further compared its flocculation characteristics in different application scenarios.

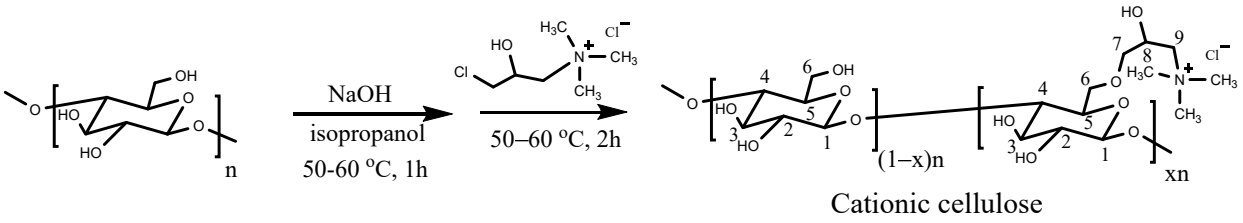


Figure 1. Preparation of cationic cellulose. In the first step, any of the OH groups may be deprotonated by NaOH. In the structure of the product, the ammonium unit may be attached to the oxygen on C_2, C_3, or C_6.

The dairy industry continues to grow in the Upper Midwestern U.S., raising a substantial challenge to manure management [15]. Dairy wastewater is characterized by high concentrations of total suspended solids (TSS), organic matter, nutrients, and potentially pathogenic microorganisms [16]. Effective solid–liquid separation capable of removing a substantial amount of organic solids from liquid or slurry manure can offer multiple benefits. These include the production of nutrient-rich organic solids, odor reduction in subsequent manure storage or treatment units, and improved economics of subsequent treatment processes due to reduced organic loading rates [17]. Excess nutrients are associated with the eutrophication of water bodies, causing hazardous algal blooms in aquatic ecosystems. Nutrient recovery through solid–liquid separation, especially with the aid of natural flocculants, can not only avoid the depletion of natural resources (e.g., phosphate ores) and water pollution but also promote a circular bioeconomy for agricultural production [18]. To our best knowledge, CC has not been tested for solid–liquid separation from dairy wastewater.

Microalgae have demonstrated great potential in nutrient removal and wastewater treatment [19]. They can be used as animal feed additives, biofuel production feedstock, and dietary or nutraceutical components in human nutrition [20,21]. A challenge to the microalgal bioeconomy is the lack of cost-efficient harvesting methods. Harvesting was estimated to account for 20–30% of the total algal biomass production cost. Technologies including flotation, sedimentation, filtration, flocculation, and centrifugation have been attempted [22–24]. Despite its great performance, the application of flocculation is impeded by difficulty in separating flocculants from harvested microalgal biomass. Specifically,

common flocculants such as aluminum sulfate, ferric sulfate, and polyacrylamide (PAM) are hard to remove from the settled flocs, and the presence of these flocculants poses a challenge to the downstream processing or utilization of algal biomass. Natural or bio-flocculants are therefore being actively pursued as substitute reagents [25].

The wastewater from the textile manufacturing industry can contain high concentrations of unused dyes, as well as surfactants and other organic compounds [26]. Various treatment methods, such as coagulation/flocculation, photocatalytic, advanced oxidation, and biological wastewater treatment (including both aerobic and anaerobic) have been attempted for dye removal [27,28]. Among them, coagulation/flocculation is considered one of the most practical methods [29]. To eliminate secondary pollution induced by chemical flocculants, CC as a natural flocculant was used to remove MO, a prevalent synthetic dye, from wastewater through its complexation with MO's sulfonate group—a process labeled as flocculation or sorption in the literature [30]. Only one study reported MO removal with modified CC, but the maximum sorption capacity was only 16.94 mg/g [30].

2. Materials and Methods

2.1. Materials

Microcrystalline cellulose (d = 1.5 g/cm^3) was purchased from MarkNature (Fullerton, CA, USA). Sigma-Aldrich (St. Louis, MI, USA) supplied the cationization reagent, CHPTAC (60 weight percent (wt%) in water, with d = 1.154 g/mL, molecular weight (MW) = 188.10 g/mol), isopropanol (91%), ethanol (99.5%), and deuterium oxide (D_2O). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Fisher Scientific (Hampton, NH, USA). All the reagents except for the cellulose were of analytical grade and were used as received without further purification.

2.2. Preparation of Cationic Cellulose

Five grams of commercial cellulose were placed into a 400 mL beaker and mixed with 200 mL of isopropanol. The mixture was stirred at 300 rpm for 30 min at room temperature. After that, 5.0 mL of a 1–4 M NaOH solution was added dropwise into the reaction mixture at 50–60 °C. The mixture was then stirred for another hour at the same temperature in the alkaline medium. For etherification, 3–10 mL (0.053–0.18 M; depending on the experimental setting) of CHPTAC (60 wt%) was added to the alkalized cellulose at 60 °C under vigorous stirring and the heat stirring continued for two more hours. After the mixture solution cooled down to room temperature, isopropanol was evaporated. The remaining part (cellulose plus water) was then stirred and filtered using a glass fiber membrane filter paper (pore size = 1.6 µm). The solid collected was rinsed and washed several times using ethanol (99.9%) to remove unreacted reagents and byproducts. The final product was air-dried overnight at 40 °C in a lab oven.

2.3. Characterization of Cationic Cellulose

For scanning electron microscopy (SEM) analysis, a thin coating of gold was applied onto a double-sided adhesive carbon tape containing a sample weighing approximately 1.0 mg. The tape was then examined with a Hitachi S-3400N SEM (Hitachi, Ltd., Tokyo, Japan) under an accelerating voltage of 10.0 kV, and images were captured at different levels of magnification to investigate the size and shape of cellulose granules. Fourier transform infrared spectroscopy (FTIR) analysis was performed using a PerkinElmer 100 FTIR spectrometer (Perkin Elmer Inc., Waltham, USA). CC powder and KBr were combined at a 2:98 (*w*/*w*) ratio, pressed into a transparent disk, and scanned 28 times at a resolution of 4 cm^{-1} to obtain a transmittance spectrum. The primary objective of this analysis was to identify the functional groups indicating the successful modification of cellulose [31].

Differential scanning calorimetry (DSC) analysis was conducted with a PerkinElmer 6000 DSC analyzer (Perkin Elmer Inc., Waltham, MA, USA). Approximately 10 mg of the CC sample was loaded into an aluminum sample pan, purged with N_2 at a flow rate of 20 mL/min, and subjected to heating from 20 to 450 °C at a ramp rate of 10 °C/min.

An empty pan used as a reference allowed for signal subtraction. The analysis aimed to compare the original cellulose with CC in terms of their glass transition temperature (T_g) and decomposition temperature. Any shift in these temperatures would indicate a successful modification. Nuclear magnetic resonance (NMR), specifically proton NMR (^{1}H NMR), was used to identify functional groups indicative of successful cationization. The analysis was conducted using a Bruker Avance 300 MHz NMR spectrometer. CC samples were dissolved in D_2O, and herein, D_2O also served as an internal standard. Chemical shifts in parts per million (ppm) were obtained using MestReC software. These analytical techniques were employed to characterize the morphology, functional groups, thermal properties, and chemical structure of the cationic cellulose samples, providing insights into the success of the modification process.

2.4. Degree of Substitution (DS)

DS is defined as the average number of hydroxyl groups substituted by quaternary ammonium groups at C-2, 3, and 6 in the backbone of cellulose. The nitrogen content of the cationically modified cellulose was determined using a TNT plus 826 test kit (Hach Company, Loveland, CO, USA) [32]. DS was calculated from the nitrogen content in cationically modified cellulose with Equation (1).

$$DS = \frac{162 \times N}{1400 - CR \times N} \quad (1)$$

where 162 = molecular weight of anhydrous glucose unit (AGU), N = percentage of nitrogen as determined by the nitrogen analysis, and CR = molecular weight of the cationic reagent.

2.5. Harvesting of Microalgae by Flocculation

Scenedesmus dimorphus UTEX 1237 was cultivated in the Bold's Basal Medium (BBM), as described by Ref. [19]. Dry algal biomass (DAB) concentration (mg/L) was determined gravimetrically by vacuum filtering 5 mL of microalgal suspensions through a 90 mm glass fiber filter, drying the microalgae-laden filter at 105 °C for one hour, weighing the filter on a microbalance, and subtracting the reading from the weight of the empty filter [33,34]. The initial DAB concentration was 1950 mg/L before the flocculation experiment. The flocculation experiment was conducted on a six-paddle jar tester (Phipps & Bird Model 7790-901B; Fisher Scientific Inc., Richmond, VA, USA) following a standard protocol described by Ref. [35]. First, 1.0 g of CC was mixed with 100 mL of deionized water and stirred for 30–40 min. The resulting flocculant solution was then added to 0.5 L of prescreened algae culture broth to achieve the desired dose levels (80, 125, 150, 200, and 250 mg/L). The flocculation experiment was replicated three times for each dose level using a jar tester. Before adding the flocculants, the pH of the microalgal culture broth in each jar testing beaker was 6.5. Coagulation was stimulated by intense stirring at 300 rpm for one minute, followed by gentle stirring at 20 rpm for 20 min to promote floc formation. The mixtures were given a 24 h settling period to allow the sedimentation of the flocs. Subsequently, liquid samples of approximately 5 mL were extracted from each beaker, with the sampling point approximately 2 cm below the surface. The DAB concentrations in the samples were determined gravimetrically as previously described.

2.6. Flocculation Removal of TSS from Dairy Wastewater

The flocculation experiment was conducted on a six-paddle jar tester following the procedure discussed in Section 2.5. Samples of dairy wastewater were collected from a free-stall dairy near Lake Benton, Minnesota, with around 2000 lactating cows. Sand lanes were used at the facility to separate sand bedding from manure wastewater. The samples were taken after the separation process. It is noteworthy that one of our previous studies [36] collected wastewater samples from the same facility but a year before the current study. Wastewater quality parameters including TSS were therefore slightly different.

2.7. Complexation Removal of Methyl Orange (MO)

One gram of MO was dissolved in 1 L deionized water and was further diluted to 100 ppm (1 ppm = 1 mg/L). To build a calibration curve, serial dilution to 2, 4, 6, and 8 ppm was performed. A 50 ppm MO solution was prepared from the 100 ppm stock solution to assess the complexation removal of MO by CC. Several factors were investigated, including the dose level of CC (50, 100, 150, 200, 250, and 300 ppm), pH (4–10), reaction temperature (20–60 °C), and reaction time (1–3 h). The solution was constantly stirred during the test. The pH of the solution was adjusted with 0.5 M NaOH and HCl and was recorded using a pH meter. Upon the completion of the reaction, the solution was centrifuged at 6000 RPM for 10 min. The supernatant was diluted by deionized water at a dilution ratio of 10 and measured for MO concentrations based on its absorbance at 463 nm using a visible light spectrophotometer (Spectrophotometer 721; Huanghua Faithful Instrument Co., Ltd., Changzhou, China) at 463 nm. MO removal efficiency (%) was calculated with Equation (2).

$$\text{MO reduction } (\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where C_0 and C_t are the initial and final MO concentrations, respectively. Dye sorption capacity (q_e) was calculated as:

$$q_e = \frac{(C_0 - C_t) \times V}{m_{cc}} \quad (3)$$

where V is the volume of the MO solution, and m_{cc} is the weight of CC added to the solution.

3. Results

3.1. Structural Analysis

A total of thirteen CC samples were prepared with different DS values. They were acquired by adjusting the preparation conditions such as NaOH concentration, CHPTAC concentrations, and reaction time. The concentration of NaOH was observed to be the most significant factor. DS reached its maximum value (0.857; determined by Equation (1) unless otherwise stated) as the NaOH concentration was increased to 3.0 M (with 0.124 M CHPTAC). Further increasing the NaOH concentration led to a slight decrease in DS values. The nucleophilicity of the hydroxyl groups in the cellulose backbone increases during the etherification of cellulose using cationic reagents and a strong base such as NaOH. The extra hydroxyl ions that NaOH releases may push the reaction equilibrium toward the product side. However, high NaOH concentrations may cause side reactions between the cationic reagent and sodium hydroxide, which can slow down the cationization processes. For simplicity, only two samples (DS = 0.540 and DS = 0.857) were submitted for structural analysis to verify the successful cationization of cellulose.

3.1.1. FTIR Spectrum

The incorporation of the quaternary ammonium group into the cellulose backbone was confirmed by FTIR (Figure 2). In both the modified and unmodified cellulose samples, several characteristic peaks were detected. These included a prominent peak at 3457 cm^{-1} representing the stretching vibration of the hydroxyl (-OH) [37]; a peak at 2901 cm^{-1} associated with the symmetrical vibration of the C-H bond [38]; and a peak at 1645 cm^{-1} primarily attributed to moisture absorbed by the cellulose samples [31]. Different from the unmodified sample, the modified samples showed a peak at 1484 cm^{-1}. The vibration of the C-N bond in the quaternary ammonium groups can be attributed to this, indicating the successful integration of trimethyl ammonium groups [36]. Furthermore, the absorption peak observed at 839 cm^{-1} was attributed to the deformation of the C-H bond within the glycosidic bond that connects the glucose units [12,39].

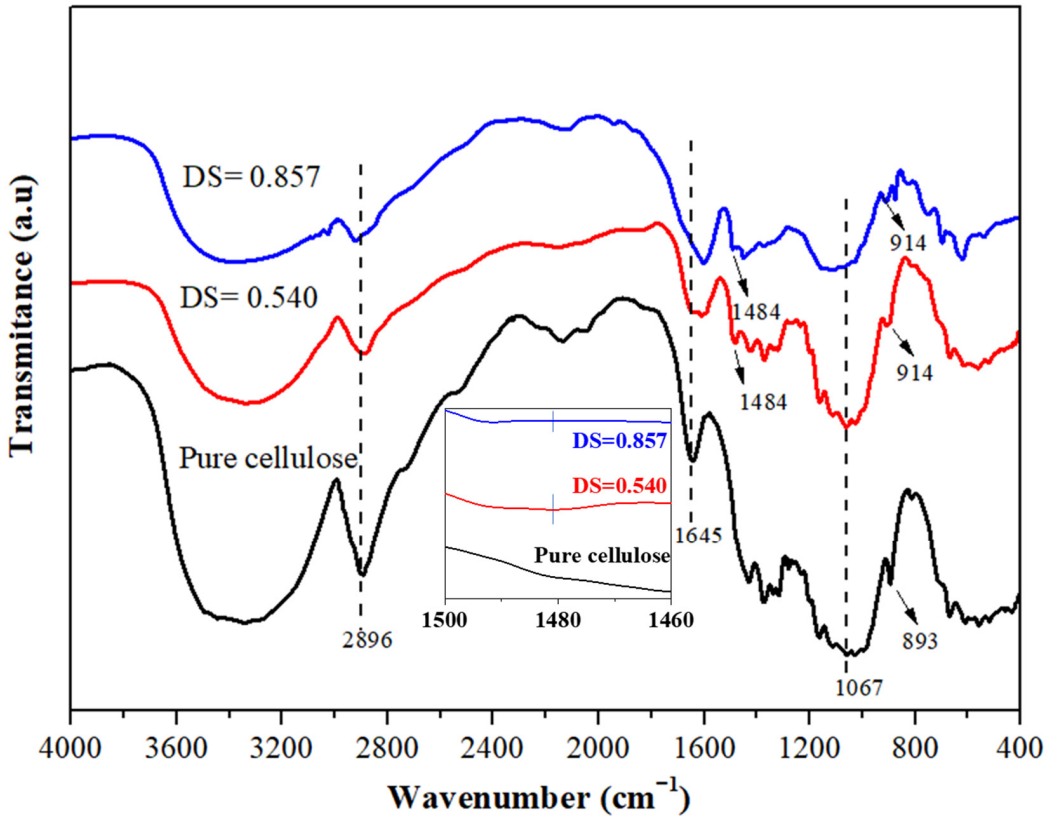


Figure 2. FTIR spectra of pure cellulose and cationic cellulose samples. Note: The relatively weak 1484 cm^{-1} peak of the DS = 0.857 sample was due to the deamination of CC after long-term storage.

3.1.2. DSC Thermogram

DSC analysis results supported the incorporation of cationic groups into the backbone of the cellulose (Figure 3). The endothermic and exothermic peaks were ascribed to the evaporation of levoglucosan formed from cellulose depolymerization, while the exothermic peaks were attributed to char formation [40]. The glass transition (T_g) temperatures of the DS = 0.540 sample (78.2 °C) and the DS = 0.857 sample (81.0 °C) were both slightly lower than that of unmodified cellulose (84.6 °C). DS exhibited a large influence on the thermal stability of the prepared CC samples. The DS = 0.857 sample decomposed at a slightly lower temperature (210–248 °C) than the DS = 0.540 sample (231–252 °C). Comparatively, the decomposition temperature of unmodified cellulose was 351 °C, indicating degraded thermostability after the cationic alteration of cellulose. The changes in DSC peaks after modification might also have resulted from changes in cellulose morphology and crystallinity levels before and after cationization reactions. Similar findings were reported in the literature [41–43].

3.1.3. NMR Spectrum

Certain challenges were encountered during NMR sample preparation. The samples were prepared by stir-mixing 0.2 g CC with 20 mL of deionized water. However, it resulted in a stable colloidal solution, and no solid settling was seen even after two days. To address the issue, the colloidal solution was further filtered with a 0.2 µm (in pore size) filter to a pre-weighed NMR tube. However, the filtrate remained cloudy. The water in the NMR tube was removed via vacuum drying (20 mbar and ~60 °C) until the mass of the solid residue became constant. D_2O was then added to the NMR tube and the tube was heated to ~90 °C for 30 s. Both H NMR and C NMR analyses were performed, but no signal was obtained during the C NMR analysis. The ^{1}H NMR spectra of the D_2O soluble portion of the two CC samples are shown in Figure 4. The hydrogen deuterium oxide (HDO) signal

at 4.80 ppm was used as the reference for chemical shifts, while the H_2O peak occurred at 4.81 ppm. The peak of the three methyl groups of the ammonium appeared at 3.27 ppm, and the integration of the peak was set to be 9H. The signals between 3.31 and 4.71 ppm were attributed to the Hs on the carbons of cellulose and carbon linkages between the ammonium group and the cellulose backbone. The integration of this shift range was 18.32H. The signal around 6.5 ppm and between 1.6 and 2.3 ppm (not shown) became stronger with an increase in DS.

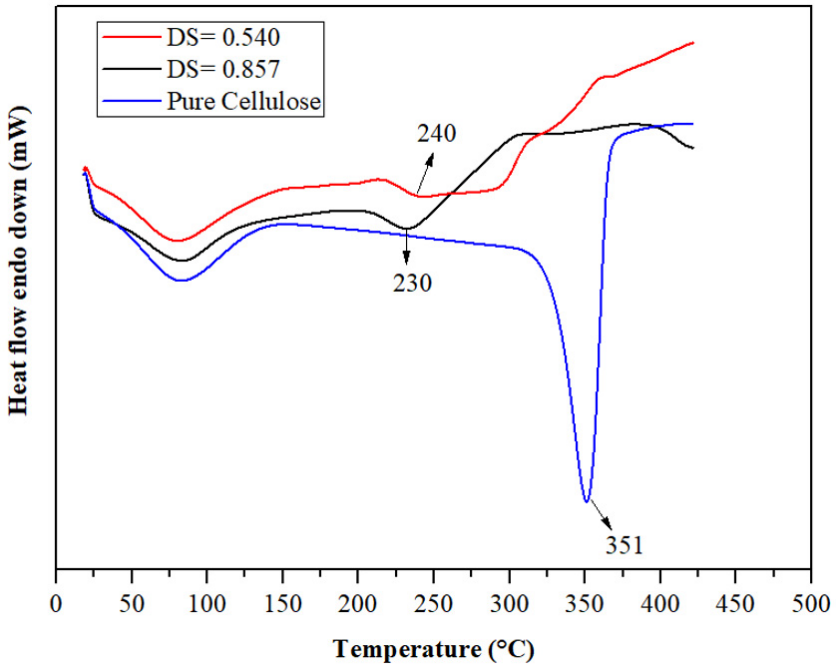


Figure 3. DSC thermograms of pure cellulose and cationic cellulose samples.

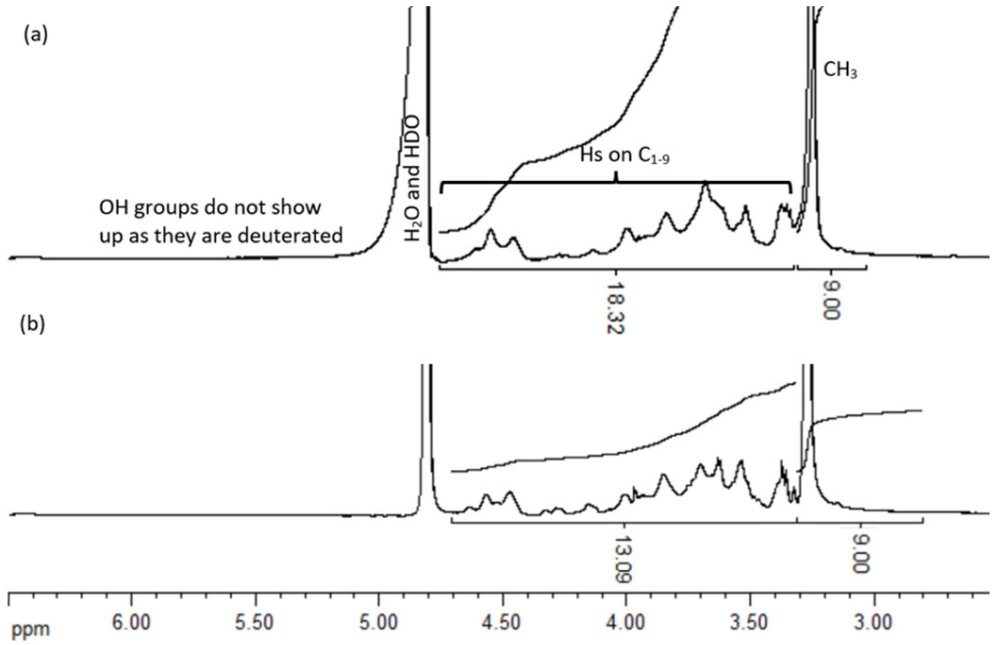


Figure 4. ^{1}H NMR spectra of two cationic cellulose samples: (**a**) DS = 0.540 and (**b**) DS = 0.857. Note that the water peak in (**a**) is much stronger, which reflects the lower solubility of the DS = 0.540 sample in D_2O as a result of the lower DS. Integration curves in (**a**) were truncated.

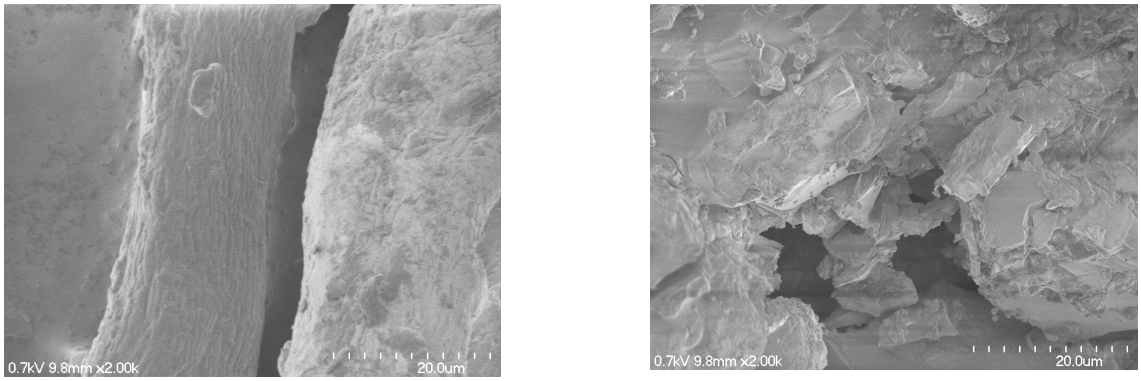
A stronger reaction condition or a longer reaction time would lead to more deamination-producing methyl ketone moieties. The moieties would further react among themselves to produce groups such as C=C-CH_3 and CH_3-CHR-OH that were seen in the regions mentioned above. The reactions could occur among modified cellulose polymers, leading to the formation of submicron cross-linked particles. These submicron colloidal particles did not aggregate due to the presence of positive ammonium groups on their surface. This explains the cloudiness of the acquired CC solutions and their persistency—the cloudiness did not disappear upon dilution or heating. The DS of the prepared CC sample was also calculated from the NMR results using Equation (4):

$$\mathrm{DS} = \frac{9/9}{(I_{H\ on\ C1-9} - 5)/7} \quad (4)$$

where the first 9 is the integration set for the methyl peak, the second 9 is the number of hydrogen atoms in one ammonium unit, $I_{H\ on\ C1-9}$ is the integration of signals of H atoms on carbons 1–9, 5 is the number of H on C (7–9), and 7 is the number of H on C (1–6) of an AGU. In this calculation, OH signals were not considered because they do not show up in the spectra due to deuteration by D_2O. The calculated DS values are 0.525 and 0.865, respectively. The values are close to those (0.540 and 0.857, respectively) derived from the nitrogen analysis (Equation (1)).

3.1.4. Scanning Electron Microscopy

The unmodified cellulose showed a regular cellulose structure (Figure 5), with individual fibers with smooth surfaces depicting less accessibility to the cationic reagent. After cationization, the morphology of the CC sample changed drastically, featuring a loose and porous structure. This is ascribed to the incorporation of quaternary ammonium groups (Figure 5b), suggesting that the surface area of cellulose significantly increased. Materials with loose and porous structures are preferred for adsorbing and flocculating contaminants from water [41,44,45]. Thus, it is anticipated that the prepared CC samples could deliver superior flocculation/sorption efficiency.



(**a**) (**b**)

Figure 5. SEM images of (**a**) pure cellulose fibers and (**b**) cationic cellulose with DS = 0.857.

3.2. Flocculation Experiments

3.2.1. Algal Harvesting

For algal harvesting, several CC samples differing in DS values were tested, but only the results of using the DS = 0.857 CC sample are presented here due to its better performance. The initial concentration of DAB was 1950 mg/L, while the pH of the algal culture was measured at 6.40. When the CC was added to the beakers containing the algal culture broth, there was a noticeable separation of solid particles settling at the bottom. However, in the control samples where no CC was added, there was no

stratification observed. This demonstrates that CC can be a highly effective flocculant for algal harvesting.

To further optimize the flocculation process, several CC dose levels were tested. DAB removal efficiency increased with the tested dose levels but started to taper off when the dose level exceeded 200 mg/L (Table 1). High flocculation efficiency at relatively low dose levels (several hundred mg/L) is characteristic of polyelectrolyte flocculants such as PAM and polystyrene sulfonic acid [46,47]. This study showed that CC behaves similarly to other polyelectrolyte flocculants. The best flocculant dose level depends on the properties of the microalgal suspension as well as flocculation mechanisms [48]. Influential factors may include the pH and chemical composition of the algal culture broth, the size and concentration of microalgae, the charge density on the microalgal cell surface, and the charge density of the flocculant [49].

Table 1. Flocculation of *Scenedesmus dimorphus* with prepared cationic cellulose at different dose levels.

CC Dose Level (mg/L)	Initial Algal Biomass (mg/L)	Final Algal Biomass (mg/L)	Removal of Dry Algal Biomass (%)
80	1950 ± 550	1016 ± 103	47.9
125	1950 ± 550	766 ± 103	60.7
160	1950 ± 550	450 ± 141	76.9
200	1950 ± 550	267 ± 24	86.3
250	1950 ± 550	183 ± 47	90.6
300	1950 ± 550	133 ± 24	93.0

For CC, the associated flocculation mechanisms include interparticle bridging and charge-patch. During interparticle bridging, fragments of dissolved cellulose polymer chains adhere to the surface of microalgal cells, while the rest of the chain extends into the surrounding solution, forming tails or loops. These loops and tails can then bind to other cells [50]. Mixing promotes collision and accordingly floc formation. In charge-patch, electrostatic interactions drive the positively charged CC polymers to the negatively charged microalgal cell surface. This creates a localized zone of charge inversion that subsequently attracts nearby algal cells with opposite charges [47]. Since pH affects both the surface charge of microalgal cells and the charge of CC polymers, a significant effect of pH was observed (Table 2). The finding is consistent with an earlier report [51].

Table 2. Effects of pH on removal efficiency (RE).

pH	Microalgae		Dairy Wastewater		Methyl Orange	
	Final DAB (mg/L)	RE (%)	Final TSS (mg/L)	RE (%)	Final MO (mg/L)	RE (%)
4	495 ± 212	74.6 ± 5.3	24,303 ± 100	53.4 ± 1.9	27.7 ± 1.8	44.5 ± 2.1
5	313 ±110	84.0 ± 5.3	23,216 ±126	54.8 ± 1.4	20.7 ± 4.1	58.7 ± 5.0
6	250 ± 126	87.2 ± 7.2	23,516 ± 122	54.3 ± 1.2	17.3 ± 0.5	65.3 ± 0.7
7	181 ± 174	90.5 ± 1.2	23,545 ± 358	54.2 ± 2.1	17.9 ± 1.3	64.3 ± 1.6
8	178 ± 420	90.9 ± 1.2	24,860± 178	51.8 ± 0.3	24.7 ± 2.2	50.7 ± 2.6
9	228 ± 112	86.3 ± 2.4	29,100 ± 187	43.5 ± 0.6	28.0 ± 2.7	44.0 ± 1.7
10	816 ± 532	58.2 ± 1.2	32,850 ± 161	36.2 ± 0.8	42.0 ± 4.1	16.0 ± 3.0

3.2.2. Solid–Liquid Separation of Dairy Wastewater

Flocculation experiments were conducted with prescreened (using a 35-mesh sieve) dairy wastewater with a TSS concentration of 51,466 mg/L and a pH value of 6.6. Only the results of the DS = 0.857 sample are presented here (Tables 2 and 3). The TSS reduction efficiency for dairy wastewater (47–53%) was lower than the DAB reduction efficiency for algal culture (47–90%). A difference in their solid compositions may account for this variation. The optimal dose level within the studied concentration range was 160 mg/L. Both under and overdosing could result in poor solid–liquid separation [52].

Table 3. Removal of TSS from dairy wastewater with prepared cationic cellulose at different dose levels.

CC Dose Level (mg/L)	Initial TSS (mg/L)	Final TSS (mg/L)	TSS Removal (%)
80	51,466 ± 675	26,685 ± 900	47.1
125	51,466 ± 675	25,735 ± 369	49.9
160	51,466 ± 675	25,350 ± 444	50.5
200	51,466 ± 675	24,270 ± 101	53.3
250	51,466 ± 675	24,700 ± 180	52.3

A natural flocculant that outperformed the CC was a commercial chitosan product with a 73% TSS reduction [53]. However, these two flocculants are not directly comparable. While for CC the positive charge is attributed to quaternary ammonium groups, for commercial chitosan flocculants such as chitosan acetate, it is caused by the protonation of amino groups [54]. Chitosan is extracted from crustacean shells as a fishery and aquaculture byproduct, and it has been extensively studied. However, due to logistic constraints, its application for livestock wastewater treatment in the U.S. Midwest appears to be less promising than CC and alike made from locally available agricultural byproducts.

The process of coagulation/flocculation is intricate, involving various mechanisms such as charge neutralization, sweep coagulation, inter-particulate bridging, and patch flocculation [55]. For CC, the ideal dose level for flocculation is related to charge density to destabilize the particles and the molecular weight of CC polymers to promote sweep coagulation and inter-particulate bridging. Excess CC could lead to net positive charges on the solid particle surface, causing electrostatic repulsion and thereby restabilizing the suspended solids [36]. The effect of pH was also substantial (Table 2). The greatest TSS reduction occurred at the pH range of 5–6. The molecular structure of cellulose could be damaged in a highly acidic environment, which may explain the decreased TSS removal below pH = 5 [56]. On the other hand, exposure to a high pH environment for an extended time may result in the alkaline hydrolysis of cellulose. The pH of raw dairy water is 8.0. Changes in pH may also alter the constituents of dairy wastewater, thereby affecting the flocculation efficiency. A similar observation was reported by Muniz et al. [57].

3.2.3. Methyl Orange

Effective removal of MO from the synthetic wastewater was achieved with the prepared CC (DS = 0.857) (Table 4). The dose level showed a large influence on MO removal. Raising the CC concentration from 50 to 200 mg/L resulted in an increase in MO removal efficiency from 24.3 to 51.8%. It could be ascribed to an increased number of sorption sites at elevated CC concentrations. However, a slight decrease in MO removal efficiency was observed when the dose level was over 150 mg/L, possibly due to the aggregation of CC decreasing the number of effective sorption sites.

Table 4. Methyl orange removal from synthetic wastewater with prepared cationic cellulose at different dose levels.

CC Dose Level (mg/L)	Initial MO (mg/L)	Final MO (mg/L)	MO Removal (%)	q_e (mg/g)
50	50	35.7 ± 2.2	24.3	243
100	50	31.0 ± 5.0	27.9	140
150	50	22.8 ± 0.7	53.0	177
200	50	22.5 ± 1.6	51.8	130
250	50	22.6 ± 2.6	49.4	99

The impact of pH on the removal of MO was further studied by fixing the dose level at 50 mg/L (Table 2). The greatest MO removal occurred at pH = 6. Upon dissolving in water, MO dissociates into Na^+ and MO ions. The sulfonate group ($R\text{-}SO_3^-$) is the only part of the MO ion structure that is hydrophilic, the rest is hydrophobic. MO and CC interact

primarily through the complexation of -SO_3^- in MO with the quaternary ammonium group in CC [58]. Hydrogen bonding between -OH in CC and tertiary amine in MO is another contributor to the interaction. A decrease in pH from neutral (pH = 7) would result in the increased availability of R-SO_3^- groups. However, MO becomes less soluble at pH < 3.5. As a result, the MO removal efficiency decreased when the pH dropped below 4 [59]. The MO-CC complexation weakens in an alkaline environment (pH > 7) because MO would primarily exist in the non-protonated form. It still offers weak electrostatic attractions to CC but no more strong hydrogen bonding remains. Furthermore, with an increased pH, OH^- starts to compete against MO for positively charged active sites in CC, which also causes a decline in MO removal [60].

4. Conclusions

CC was prepared from commercial cellulose via homogeneous etherification of cellulose with CHPTAC in an alkaline medium. CC samples with different DS values were obtained by adjusting reaction parameters. The optimal reaction conditions (for a maximized DS) were: a 4 h reaction time (alkalization and etherification), 0.124 M of CHPTAC, 3 M of NaOH, and a 60 °C reaction temperature. Structural characterizations (FTIR, DSC, SEM, and NMR) evidenced the successful introduction of a quaternary ammonium group to the cellulose backbone. A prepared CC sample with DS = 0.857 was tested as a flocculant/sorbent in three application scenarios. It delivered decent efficiency in capturing/removing algal biomass (up to 93.0%), TSS (up to 53.3%), and MO (up to 53.0%) from microalgal cultural broth, dairy wastewater, and synthetic dye wastewater, respectively. The efficiency can be further improved by altering the pH and the CC dose level. This study demonstrated the great potential of CC in wastewater treatment applications and is anticipated to promote further exploration of natural flocculants.

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