



# Cationic nanocelluloses in dewatering of municipal activated sludge



Terhi Suopajarvi\*, Juho Antti Sirviö, Henrikki Liimatainen

Fiber and Particle Engineering Unit, P.O. Box 4300, FI-90014 University of Oulu, Finland

## ARTICLE INFO

### Article history:

Received 18 August 2016

Received in revised form 18 November 2016

Accepted 19 November 2016

Available online 21 November 2016

### Keywords:

Activated sludge  
Cationic nanocellulose  
Cellulose nanofibril  
Centrifugal analysis  
Flocculation

## ABSTRACT

This study used cationic nanocelluloses (CNFC I and II) produced by nanofibrillizing periodate oxidized and aminoguanidine hydrochloride reacted wood cellulose as flocculation agents for municipal activated sludge. For both CNFC I and II, the diameters ranged from about 2–8 nm. Lengths ranged from hundreds of nanometers for CNFC I and about 50–100 nm for CNFC II. The charge densities for CNFC I and II were 1.07 and 1.70 meq g<sup>-1</sup>, respectively. The study examined the flocculation performance of the two CNFCs in the conditioning treatment of municipal activated sludge and compared the results with the performance of both a commercial coagulant and polyelectrolyte (polyacrylamide). Results showed that both CNFC I and II were able to flocculate activated sludge efficiently at effective doses similar to those of the commercial cationic polymer and at doses lower than the reference coagulant. Their efficiency in reducing turbidity was nearly as good as that of the synthetic reference polymer, and their COD was even better than that of the synthetic reference polymer. The performance of CNFC II was slightly better than that of CNFC I. In centrifugation analyses, the use of both CNFCs resulted in dense sludge cakes with moderate swelling and good colloidal-removal efficiency.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

The activated-sludge process is highly efficient for removing organic loads from wastewater and is the most widely used biological treatment in wastewater purification. About 71,000 municipal wastewater treatment plants (WWTPs) operating in the area of the EU, which includes Iceland, Norway, and Switzerland [1], produced approximately 10 million tons (dry matter) of sewage sludge annually from 2003 to 2006, and that amount has been increasing continually [2,3]. This activated sludge commonly contains more than 90% water and exhibits poor dewaterability that is related to the presence of extracellular polymeric substances (EPS), which possess negative surface charges and hydrophilic structures [4,5]. Often, sludge dewatering must be enhanced by chemical conditioning before mechanical water removal. Conditioning increases particle sizes by combining small, colloidal particles into larger, cohesive aggregates. This chemical conditioning is done using inorganic, multivalent cationic coagulants such as aluminum (Al) or iron (Fe) salts or with synthetic polyelectrolytes such as synthetic polyacrylamides (PAM) [6–11]. However, PAM and its derivatives pose a number of environmental problems, as the intermediate products of their degradation are

hazardous and their monomers are highly toxic. In addition, these polymers are derived from oil-based, non-renewable raw materials [12,13]. Furthermore, the use of inorganic salts increases both sludge volume and the ionic load of the sludge and the treated water [14]. Consequently, there is a need for sustainable, natural, bio-based alternatives for conditioning wastewater sludge.

Biodegradability is one of the most important environmental aspects of water chemicals, as it determines their long-term ecological effects [15]. In view of the increased demand for sustainable water-treatment technologies, natural polymers have been widely investigated as a means of replacing synthetic and inorganic water chemicals [16]. Natural polymers consist mainly of polysaccharides and their derivatives, and they have been studied widely in various water-chemical applications [17]. Of all the natural polysaccharides, cellulose is the most abundant, and it could be a primary chemical resource in the future [16,18]. Therefore, the modification and use of cellulose as a water chemical in wastewater treatments are attractive. Previously, we studied various functionalized nanocelluloses as water chemicals in flocculation of model kaolin waters [19–22], real wastewaters [19,23–25], and in metal adsorption [23,26,27]. The results have been promising and indicate that functionalized nanocelluloses are potential future water chemicals and may also be used to condition wastewater sludge. In particular, cationic nanocelluloses could have potential for this purpose, since sludge consists mainly of anionic solids.

\* Corresponding author.

E-mail address: [terhi.suopajarvi@oulu.fi](mailto:terhi.suopajarvi@oulu.fi) (T. Suopajarvi).

The present study aimed to produce cationic cellulose nanofibrils and measure their performance in conditioning municipal activated sludge. Two cationic nanocellulose flocculants (CNFC I and II) were produced by nanofibrillizing periodate oxidized and aminoguanidine-reacted wood celluloses using a microfluidizer. The conditioning performance of both CNFCs was examined by flocculating municipal activated sludge. The results were compared with the performance of a commercial coagulant and a synthetic PAM flocculant.

## 2. Materials and methods

### 2.1. Raw materials and chemicals

Dry sheets of bleached birch (*Betula pendula*) chemical kraft pulp was used as the cellulose raw material. Pulp was disintegrated in deionized water before the syntheses of CNFCs. The characteristics of the pulp were as presented elsewhere [24].

All chemicals used in the synthesis and characterization of the nanocellulose materials were p.a. grade and were obtained from Sigma-Aldrich (Germany). They were used without any further purification. The chemicals used to prepare the buffers for charge-density measurement by polyelectrolyte titration were 0.1/1 M NaOH and HCl (Merck, Germany),  $\text{NaH}_2\text{PO}_4$  (Sigma-Aldrich, Germany), NaCl and  $\text{CH}_3\text{COOH}$  (Merck, Germany),  $\text{NaCH}_3\text{COO}$  (Oy FF Chemicals, Finland),  $\text{NaH}_2\text{PO}_4$  (Fluka, Germany),  $\text{NaHCO}_3$  (Merck, USA),  $\text{Na}_2\text{CO}_3$  (J.T. Baker, USA), and  $\text{NaNO}_2$  (Sigma-Aldrich, Germany). All were p.a. grade, and all were used as received. Deionized water was used throughout the work.

PIX-105 (ferric sulphate,  $\text{Fe}_2(\text{SO}_4)_3$ ) and Fennopol K5060 (cationic polyacrylamide) were obtained from Kemira (Finland), and were used as an inorganic coagulant agent and a reference polyelectrolyte, respectively.

Samples of municipal activated sludge were collected from the aeration tank of a local municipal WWTP from Oulu, Finland. Table 1 shows the main characteristics of the samples.

### 2.2. Fabrication of CNFC flocculants

Fig. 1 shows the functionalization of the cellulose using two-step reaction paths based on regioselective oxidation [28]. In the first reaction step, the vicinal hydroxyl groups at positions 2 and 3 in the cellulose were oxidized to aldehyde groups using sodium metaperiodate to produce dialdehyde cellulose (DAC). Two separate DAC samples were prepared with differing aldehyde contents: DAC I had an aldehyde content of  $1.68 \text{ mmol g}^{-1}$ , and DAC II had an aldehyde content of  $2.84 \text{ mmol g}^{-1}$  [28]. To synthesize DAC I, 6 g of cellulose pulp was mixed with 4.92 g of sodium metaperiodate in aqueous solution for 3 h at  $55^\circ\text{C}$ . DAC II was produced in the same way as DAC I, except the reaction temperature was set at  $75^\circ\text{C}$ . Then, cationic celluloses (CDAC I and II) were synthesized from the DAC samples using aminoguanidine hydrochloride, as described previously by Sirviö [29]. To synthesize CDAC I, 7.44 g of aminoguanidine hydrochloride was diluted in 200 ml of deionized water, pH was adjusted to 4.5 with 0.1 M of HCl solution, 4 g of DAC I was added, and the solution was mixed at room temperature for 72 h. CDAC II was synthesized the

same way except the amount of aminoguanidine hydrochloride used was 12.56 g. Both products were purified by filtration and washing with deionized water. The cationized celluloses were Nanofibrillated into cationic nanocelluloses, CNFC I and CNFC II, using the microfluidizer M-110EH-30 (Microfluidics, USA). The CDAC I sample at the consistency of 1% was passed once through 200- $\mu\text{m}$  and 100- $\mu\text{m}$  chambers and then once 200- $\mu\text{m}$  and 87- $\mu\text{m}$  chambers. The CDAC II sample at the consistency of 0.5% was passed once through 200- $\mu\text{m}$  and 87- $\mu\text{m}$  chambers using 2000 bar pressure.

### 2.3. Characterization of CNFCs

#### 2.3.1. Optical transmittance

Transmittance of the prepared CNFC suspensions was measured with a Hach Lange DR 2800 spectrophotometer (USA) at a wavelength range of from 340 to 800 nm at a consistency of 0.1%.

#### 2.3.2. Charge density

The polyelectrolyte titrations were performed at a solids content of 0.1% mixed with the appropriate buffer using a Mutek PCD 03 particle-charge detector (USA). The CNFCs were titrated with  $1 \text{ meq dm}^{-3}$  of anionic PES-Na (sodium polyethenesulphonate) while the sign of the sample charge was monitored.

#### 2.3.3. Transmission electron microscopy

The visualization of CNFCs was performed with a Tecnai G2 Spirit transmission electron microscope (TEM) (FEI Europe; Eindhoven, The Netherlands). A droplet of the dilute sample was dosed on top of a carbon-coated copper grid treated with polylysine, and the excess amount of the sample was removed from the grid by touching the droplet with a corner of a filter paper. Negative staining of the samples was performed by placing a droplet of uranyl acetate (2%w/v) on top of each specimen. The excess amount of the uranyl acetate was removed with filter paper as described above. Grids were dried at room temperature and analyzed at 100 kV under standard conditions.

#### 2.3.4. Dewatering experiments

Next, 1000 ml samples of activated sludge were treated with CNFC, ferric coagulant, or cationic flocculants. To keep the content of solids constant, the proper amount of water was added to the sludge samples with low doses of flocculation aid. After the flocculation aid was added, the sludge samples were stirred with a magnetic stirring bar at 200 rpm for 2 min at room temperature. Then, 1000 ml of flocculated sample was placed in a measuring glass and allowed to settle for 30 min, after which the volume of the sludge was measured. The turbidity of the supernatant was measured with a Hach Ratio XR turbidimeter (model 43,900; USA) and its chemical oxygen demand (COD) was measured using standardized Hach test tubes and a Hach Lange DR 2800 spectrophotometer (USA).

#### 2.3.5. Sludge settling during centrifugation

During centrifugation, an analytical centrifuge (LUMifuge, L.U. M. GmbH; Germany) was used to evaluate the CNFCs' sludge dewatering and flocculating performance. The centrifuge consisted of a light source, a rotor above which the sample cells containing the suspension were horizontally positioned, and a Charge-Coupled Device (CCD) line sensor below the rotor. The centrifuge simultaneously measured light transmission at 800 nm over the plastic sample cells as a function of time and position, so local alterations in particle concentration and the position of the solid-liquid interface during separation could be detected by changes in light transmission [30]. Flocculation performance was determined from the height of the sludge cake formed, swelling of the cake and

**Table 1**  
Characteristics of the activated sludge samples from the municipal WWTP.

Sample	pH	Conductivity [ $\mu\text{S/cm}$ ]	TSS [g/L]	TS [g/L]
Activated sludge I	6.80	644	4.32	4.74
Activated sludge II	6.68	777	4.50	5.12

TTS = total suspended solids, TS = total solids.

Download English Version:

<https://daneshyari.com/en/article/6477270>

Download Persian Version:

<https://daneshyari.com/article/6477270>

[Daneshyari.com](https://daneshyari.com)