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Coagulation–flocculation treatment of municipal wastewater based on anionized nanocelluloses

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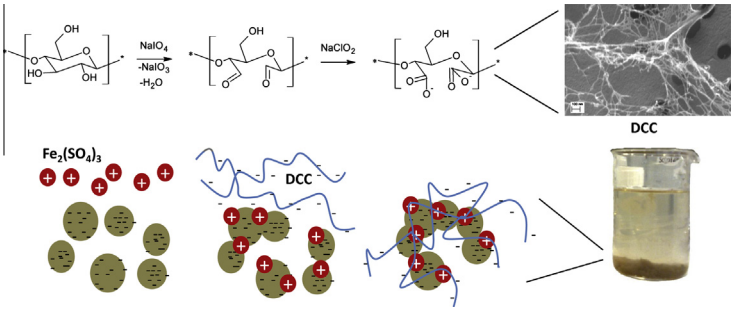
HIGHLIGHTS

- We produced nanofibrillar dicarboxylic acid cellulose samples with variable charge.
- Anionic nanofibrils were tested in the flocculation of municipal wastewater.
- Combined coagulation–flocculation treatment resulted good performance.
- Results with anionic nanofibrils were comparable with commercial reference polymer.
- High charge and nanofibril content gave the best flocculation performance.

GRAPHICAL ABSTRACT



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ABSTRACT

The synthetic polymers normally used in the coagulation–flocculation treatment of waste water are in most cases derived from oil-based, non-renewable raw materials. Consequently, there has been a growing interest in replacing them with more sustainable natural bio-based alternatives. However, derivatives of cellulose, which is the most abundant biopolymer on earth, are still scarce. In this work dicarboxylic acid nanocellulose (DCC) flocculants were produced by nanofibrillation of periodate and chlorite-oxidized celluloses with a homogenizer. The flocculation performance levels of five such anionic nanocelluloses with variable charge densities were examined in the coagulation–flocculation treatment of municipal waste water and the results compared with the performance of a commercial coagulant and a synthetic polymeric flocculant. In addition, the aldehyde and carboxyl content, charge density (CD), size and stability of each DCC were determined in an aqueous solution. The results showed that all the DCCs synthesized were able to flocculate waste water very efficiently, and the dosages required were similar to that of the commercial reference flocculant. The combined coagulation–flocculation treatment of municipal wastewater resulted in a lower residual turbidity and COD in a settled suspension, with considerably reduced total chemical consumption relative to coagulation with ferric sulphite alone. A high charge density and high nanofibril content of the DCC flocculant gave the best flocculation performance. The DCCs showed high stability in aqueous suspensions over a long period of time and good performance within the chosen pH range.

1. Introduction

Coagulation–flocculation treatment is commonly used to reduce the turbidity of municipal and industrial waste water, the coagulants in question typically being divalent or trivalent metallic

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salts or polymers that have low solubility in the pH range used [1]. Metal salts hydrolyze rapidly in waste water to form cationic species, which are adsorbed by negatively charged dirt particles, resulting in simultaneous surface charge reduction [2]. Polymers have been used in the coagulation–flocculation process for decades to reduce coagulant dosages, the volume of sludge and the ionic load of the waste water (especially the level of aluminium), and to save overall costs [3].

The polymers used in coagulation–flocculation treatment are commonly synthetic poly-acrylamides, poly-acrylic acids and poly-styrene sulphonic acids and their derivatives, which are not readily biodegradable [4,5]. Moreover, they may also contain unpolymerized monomers and additives that are neurotoxic and carcinogenic [6,7]. Also, synthetic polymers are produced from oil-based raw materials, which make them non-renewable chemicals. Consequently, there has been a growing interest in replacing oil-based flocculants with more sustainable natural bio-based alternatives.

Many natural-based flocculants are environmentally friendly and biodegradable, with good flocculating ability [8,9]. These include biopolymeric materials such as starch, guar gum, chitin, pectin and algin [4], and some derivatives of natural carbohydrates such as dextran [10] and pullulan [11] have also been investigated for these properties. Derivatives of cellulose, which is the most abundant biopolymer on earth, are nevertheless still scarce. One potential and environmentally sustainable method of producing cellulose flocculants is to introduce reactive aldehyde functionalities into cellulose by aqueous periodate oxidation, as has been reported earlier [12,13]. The aldehyde groups of 2,3-dialdehyde cellulose (DAC) can easily be converted further and in a selective manner to various functional groups such as carboxylic acids [14], sulphonates [15,16] or imines [17]. Recently Liimatainen et al. [18] have investigated the use of anionic (ADAC) and cationic cellulose (CDAC) derivatives [19] in the flocculation of kaolin suspensions, with promising results, showing that anionic cellulose nanoparticles resulted in better flocculation performance than the corresponding fully water-soluble derivatives [18]. Also Hokkanen et al. [20] used modified nanofibrillated celluloses to remove heavy metals from aqueous solutions with promising results.

In the present research aldehyde groups of DAC pulp fibres were converted to carboxylic acids and these anionic cellulose derivatives (DCC) were nanofibrillated with a homogenizer. The flocculation performance of five anionic dicarboxylic acid (DCC) nanocelluloses produced in this way with variable charge densities was examined in the context of the coagulation–flocculation treatment of municipal waste water. The effects of DCC dosage and pH on flocculation were studied by measuring residual turbidity and COD of the settled suspension and compared the results with the performance of a commercial coagulant (PIX 105 A) and a commercial combination of a coagulant and a synthetic polymeric flocculant (Fennopol K 1396). In addition, the aldehyde and carboxyl content, charge density (CD), size and stability of each DCC were determined in an aqueous solution.

2. Materials and methods

2.1. Raw material and chemicals

Bleached birch (*Betula verrucosa* and *B. pendula*) chemical wood pulp obtained in dry sheets was used as a cellulose raw material for the synthesis of anionic cellulose derivatives after disintegration in deionized water. The polysaccharide content of the wood pulp was determined using high performance anion exchange chromatography (HPAEC-PAD) [21], the lignin content by the TAPPI-T 222 om-02 procedure and the extractive content by the SCAN-CM 49:03 method. The chemical composition of the cellulose material is shown in Table 1.

The average (length–weighted) length and width of the pulp fibres, as determined with a Metso FiberLab image analyzer, were 0.90 mm and 19.0 μm, respectively. The fines content, as indicated by an L&W STFI Fibermaster analyzer, was 3.4%. The pulp was washed and converted in sodium form, as Liimatainen et al. [22] previously reported, and the ζ-potential measured in deionized water (conductivity <5 μS/cm) with a Mütek SZP-06 device was −125 mV. The degree of polymerization (DP) was 3817, as determined by a similar procedure to that Liimatainen et al. [19] previously described.

All of the chemicals used in the synthesis and characterization of DCC were of p.a. grade as obtained from Sigma–Aldrich and were used without further purification. NaH_2PO_4 (Sigma), NaCl (Merck), CH_3COOH (Merck), $NaCH_3COO$ (Oy FF Chemicals), Na_2HPO_4 (Fluka), $NaHCO_3$ (Merck) and Na_2CO_3 (J.T. Baker), all of which were of p.a. grade, were used as received to prepare the buffers. Deionized water (Millipore) was used throughout the work.

PIX-105 A ferric sulphate ($Fe_2(SO_4)_3$) and Fennopol K1369 (cationic polyacrylamide) were obtained from Kemira, Finland, and were used in the experiments as an inorganic coagulant agent and a reference flocculant. These chemicals are commonly used in coagulation–flocculation wastewater treatment plants. The municipal wastewater samples were obtained on three separate days from a Finnish activated sludge plant after the screen phase. The characteristics of wastewater samples are shown in Table 2.

2.2. Synthesis of the nanofibrillar dicarboxyl acid cellulose (DCC) flocculant

Anionic dicarboxyl acid cellulose (DCC) derivatives with variable charge densities (DCC *I–V*) were synthesized by the periodate and chlorite oxidation of cellulose in the manner Liimatainen et al. [23] reported previously. In brief, dicarboxyl groups were introduced into the cellulose pulp by first oxidizing the vicinal hydroxyl groups at positions 2 and 3 in the cellulose using sodium metaperiodate to produce aldehyde groups and subsequently oxidizing the aldehyde groups to carboxyls using sodium chlorite (Fig. 1). FTIR spectra of the cellulose samples treated with periodate and chlorite were recorded using a Bruker FT-IR spectrometer (USA). The samples were prepared by pressing 2 mg of dry sample into a pellet with 200 mg of KBr.

The aldehyde content of the periodate oxidized cellulose was determined using an oxime reaction, as Sirviö et al. [13] previously reported, while the carboxyl content after the chlorite oxidation was analyzed by conductometric titration using a procedure described by Rattaz et al. [24] and Katz et al. [25]. The mass yields of the reactions were measured by weighing the products on an analytical balance. The periodate and chlorite-oxidized celluloses were suspended in deionized water at a consistency of 0.5%, and the pH of the suspensions was adjusted to ~7.5 using NaOH. The anionic cellulose fibres were converted to nanofibrils using a two-chamber high-pressure homogenizer (Invensys APV-2000, Denmark) with a pressure of 250–950 bar. The suspensions were passed through the homogenizer one (DCC V), three (DCC II-IV), or four times (DCC I) until clear, gel-like samples were obtained. The synthesis route and details of the reaction conditions are presented in Liimatainen et al. [23].

2.3. Characterization of the nanofibrillar anionic cellulosic flocculants

2.3.1. Size of the flocculants

A fractional size analysis of the nanocellulose flocculants was conducted with a chromatographic washer based on the continuous water flow within a long tube. The nanocelluloses were