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Flocculation of municipal wastewaters with anionic nanocelluloses: Influence of nanocellulose characteristics on floc morphology and strength

Terhi Suopajärvi *, Elisa Koivuranta, Henrikki Liimatainen, Jouko Niinimäki

[a] Fiber and Particle Engineering Laboratory, University of Oulu, P.O. Box 4300, FI-90014, Finland

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ABSTRACT

A wide variety of biopolymeric materials have been studied as flocculants in wastewater treatment to replace oil-based synthetic polymers. However, derivatives of cellulose, the most abundant biopolymer on earth, are still rarely used to treat wastewater. In this work, we first tested the flocculation performance of three anionic sulfonated (ADAC) nanocellulose flocculants, with variable charge densities in combined coagulation–flocculation treatment of municipal wastewater and compared the results with the performance of a commercial coagulant and a synthetic polymeric flocculant. Second, using an optical monitoring device (MOFI), we followed the morphology and strength of the formed flocs with three ADAC and two previously studied dicarboxyl acid nanocellulose (DCC) flocculants and a synthetic polymer. The decrease in turbidity and the COD removal performance of the ADAC nanocelluloses were similar to those of a commercial reference polymer in low dosages, with considerably decreased chemical consumption relative to coagulation with ferric sulfite alone. The wastewater flocs produced with the nanocellulose flocculants were smaller and rounder than those produced with the commercial reference polymer, but the flocs produced with the anionic nanocelluloses were more stable under shear than the flocs produced with the reference polymer.

Introduction

Colloidal solids from municipal or industrial wastewaters are purified conventionally by combining small impurity particles into larger aggregates or flocs, which can be easily removed by settling or flotation [1]. Aggregates are produced using coagulants, which are usually aluminum- or iron-based metal salts or synthetic short-chain polymers. Alternatively, aggregates can be produced with flocculants that are high-molecular-weight polymers or by using a combination of coagulants and flocculants. Effective performance of the metal salts typically requires high dosages causing high volumes of wastewater sludge [2] and harmful residual ionic load (especially aluminum) in the purified water [3]. To reduce the coagulant dosages and to save overall cost, synthetic polymers have been used in the combined coagulation–flocculation process for decades [3]. However, the current oil-based synthetic flocculants are neither readily biodegradable nor renewable, and consequently, natural polymers are gaining value in water treatment [4,5]. This is supported by the general global trend of replacing a large proportion of fossil resources with renewable materials in fabricating chemicals and materials [6].

Previously, biopolymeric materials, such as starch, guar gum [7], chitin [8], pectin [1] and algin [9] have been studied as flocculants in wastewater treatment. However, cellulose, the most abundant biopolymer on Earth, is still rarely used in wastewater treatment. Cellulose is cheap, biodegradable, biocompatible and renewable raw material [10,11], but has limited performance in its' native form. Introduction of new functional groups on the surface of cellulose results in increase of surface polarity and hydrophilicity, which enhance the interaction of cellulose with various compounds [12]. Moreover, nano-sized celluloses (nanocelluloses) have acquired extra advantage over conventional cellulose fibers due to very high surface area, aspect ratio and Young's modulus [10,13]. However, reports of using nanocelluloses as water chemicals are still rare, and they have mainly focused in adsorption of metals from diluted aqueous solutions [11,14–17].

One potential green method for producing cellulose flocculants is to introduce reactive aldehyde functionalities into cellulose with aqueous periodate oxidation, as reported earlier [18,19]. Lately Liimatainen et al. [20] showed that the expensive and harmful

* Corresponding author. Tel.: +358 294482415; fax: +358 8553 2405.
E-mail addresses: Terhi.Suopajarvi@oulu.fi (T. Suopajärvi), Elisa.Koivuranta@oulu.fi (E. Koivuranta), Henrikki.Liimatainen@oulu.fi (H. Liimatainen), Jouko.Niinimaki@oulu.fi (J. Niinimäki).

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Table 1
The characteristics of the wastewaters from the municipal wastewater treatment plant.

Wastewater	TSS[a] (mg/l)	TS[b] (mg/l)	pH	Conductivity ($\mu s\,cm^{-1}$)	COD[c] (mg/l)	Turbidity (NTU)
Water I	692	1134	7.29	909	749	156
Water II	294	801	7.38	909	452	198.5
Water III	649	1272	7.14	1070	879	215
Water IV	485	983	7.19	986	848	189

[a] Total suspended solids (SFS-EN 872).
[b] Total solids (SFS 3008:1990).
[c] Chemical oxygen demand (ISO 15705:2002).

periodate can be regenerated back to the reaction by using hypochlorite, which makes the reaction step more sustainable. The aldehyde groups of 2,3-dialdehyde cellulose (DAC) can easily and selectively be converted further into various functional groups such as carboxylic acids [21], sulfonates [22,23] or imines [24]. These cellulose derivatives which have disintegrated into nanocellulosics have shown good flocculation performance in model kaolin suspensions [25–27] as well as in municipal wastewaters [28].

The performance of flocculants in wastewater purification is determined by the morphology and strength of the flocs formed. The flocs should be strong enough to resist the shear stresses of the separation processes in wastewater treatment. Floc strength depends upon the inter-particle bonds between the dirt particles of the aggregate [29]. Densely packed aggregates have a high fractal dimension, while a lower fractal dimension results from large, highly branched and loosely bound structures [29]. In addition, the size and shape of the constituent particles of the flocs affect floc strength and the efficiency of the separation [29,30]. Flocs have two main breaking mechanisms: fragmentation, in which the floc is broken into two or more smaller flocs, and surface erosion, where single primary particles or small aggregates are eroded off the floc [29,31]. Breaking the flocs releases organics and increases the number of fine particles, as well as the distribution variability of broken particles that deteriorate not only dewatering of the sludge that forms but also the quality of the treated wastewater [32]. However, the development of a satisfactory technique for quantifying floc strength has proven to be difficult [33].

Our recent studies with anionic nanocelluloses in combined coagulation–flocculation treatment of municipal wastewater show that chemically modified anionic dicarboxyl acid (DCC) nanocelluloses are effective green alternatives for synthetic flocculants [28]. In this study, anionic sulfonated (ADAC) nanocellulose was first tested in combined coagulation–flocculation treatment of municipal wastewater. The effects of ADAC dosage on flocculation were studied by measuring the residual turbidity and the chemical oxygen demand (COD) of the settled suspension, and the results were compared with the performance of a commercial coagulant (PIX 105 A) and the combination of a coagulant and a synthetic polymeric flocculant (Fennopol K. 1396). Second, the morphology and strength of flocs formed with three ADAC and two DCC nanocelluloses and a synthetic polymer were optically monitored, as presented in [34].

Materials and methods

Raw materials and chemicals

Bleached birch (*Betula verrucosa* and *pendula*) chemical wood pulp obtained in dry sheets was used as the cellulose raw material to synthesize anionic cellulose derivatives after they had been disintegrated in deionized water. The polysaccharide content in the pulp was determined by using high-performance anion exchange chromatography (HPAEC-PAD) [35], the lignin content by using TAPPI-T 222 om-02 and the extractive content by using SCAN-CM 49:03. The cellulose content of the pulp was 74.8%, and the content of the hemicelluloses (xylan and glucomannan) was 24.7%. The amount of lignin was 0.4% and acetone soluble extractives 0.08%. The average (length-weighted) length and width of the pulp fibers, as determined with a Metso FiberLab image analyzer, were 0.90 mm and 19.0 μm, respectively. The fiber fines content, provided by the L&W STFI Fibermaster analyzer, was 3.4%. The pulp was washed and converted to sodium form [36], and the ζ-potential in the deionized water (conductivity $<5\,\mu s/cm$) was measured at 125 mV with a Mütek SZP-06 device. The degree of polymerization (DP) was 3817, as determined with a similar procedure described by Liimatainen et al. [27].

All chemicals used in the DCC and ADAC synthesis and characterization were obtained as p.a. grade from Sigma–Aldrich and were used without further purification. Deionized water (Millipore) was used throughout the work.

Ferric sulfate ($Fe_2(SO_4)_3$, PIX-105) and cationic polyacrylamide (Fennopol K1369) were obtained from Kemira, Finland, and were used as the inorganic coagulant agent and the reference flocculant in the experiments. These chemicals are commonly used in coagulation–flocculation treatment in wastewater treatment plants. Municipal wastewater samples were obtained from a

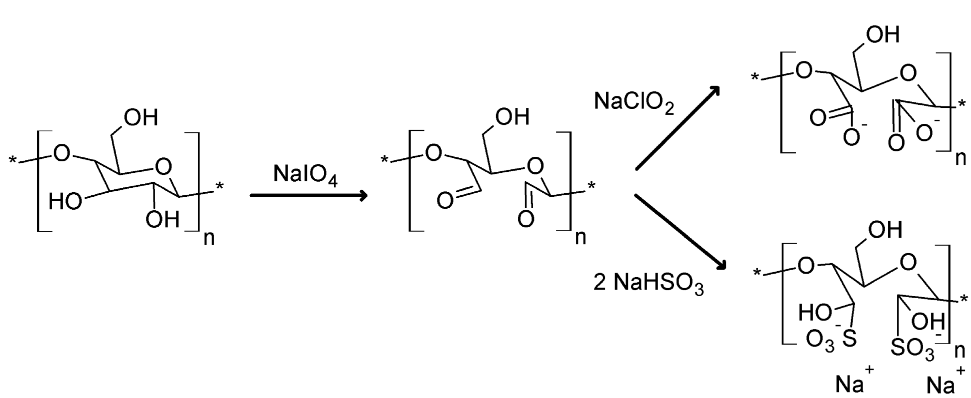

Fig. 1. Periodate oxidation of cellulose followed chlorite oxidation or bisulfite sulfonation reactions.