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

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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

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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 μs/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

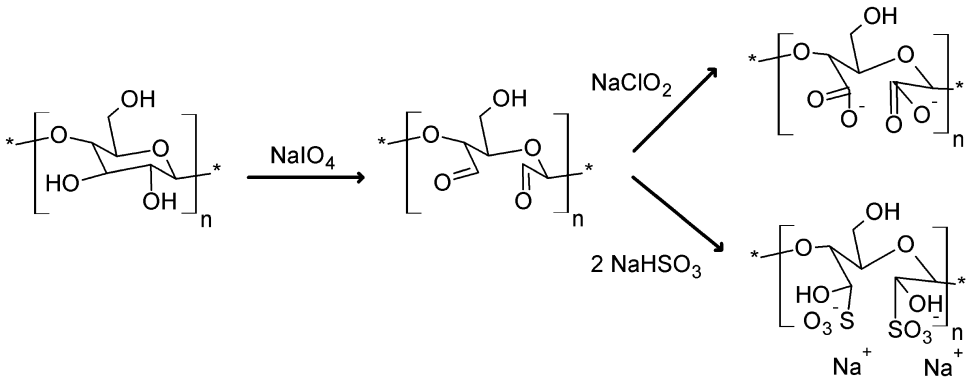

Fig. 1. Periodate oxidation of cellulose followed chlorite oxidation or bisulfite sulfonation reactions.

Finnish activated sludge wastewater treatment plant after the solids screen phase. Samples from 4 days were obtained. The characteristics of the wastewaters are shown in Table 1.

Synthesis of the anionic nanofibrillar cellulose flocculants

Anionic cellulose derivatives were synthesized with periodate oxidation following sodium chlorite oxidation (DCC) or sulfonation with sodium metabisulfite (ADAC). The DCCs and ADACs were synthesized as reported previously by Liimatainen et al. [25,37]. Briefly, aldehyde groups were produced on the cellulose pulp by oxidizing the vicinal hydroxyl groups of cellulose at positions 2 and 3 using sodium metaperiodate. The aldehyde groups of the dialdehyde celluloses (DAC) that formed were oxidized to carboxyls using sodium chlorite to form dicarboxylic acid cellulose (DCC) [37] or sulfonated by using sodium metabisulfite to form ADAC [25] (Fig. 1).

The charge density of the samples after they had been chemically treated was analyzed with conductometric titration using a procedure described by Katz et al. and Rattaz et al. [38,39]. The mass yields of the reactions were measured by weighing the products on an analytical balance. Treated celluloses were suspended in deionized water at a consistency of 0.5%. The anionic cellulose fibers were converted to nanofibrils by using a two-chamber high-pressure homogenizer (Invensys APV-2000, Denmark) with a pressure of 250–950 bar. The synthesis route and details of the reaction conditions are presented in Liimatainen et al. [25,37].

Characterization of the nanofibrillar anionic cellulose flocculants

Size of 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. Nanocelluloses were washed in a long plastic tube (diameter 4 mm) with 1000 ml of deionized water for 108 s with a flow rate of 7.5 ml/s. The particles flow in this tube at different average velocities according to their size such that the largest particles tend to stay in the middle of the tube longer at faster flow. Thus, these particles emerge first at the end of the long tube [40]. In a washer, a 5 ml of sample at the consistency of 0.1% was injected in a constant water flow, and four size categories were obtained by taking the samples after 60, 77, 86 and 95 s. The largest particles in the washed particle–water suspension were visualized with a charge-coupled camera (CCD) (resolution 1.6 μm) in a small cuvette, and the amount of material in the different categories was measured by filtration on a membrane (retention 0.2 μm) followed by weighing. Fractions were also collected for further analysis in field emission scanning electron microscopy (FESEM).

Imaging with FESEM

FESEM (Zeiss Ultra Plus) was used to study the morphology and size of chromatography washed nanofibrils in different fractions. As a pretreatment, samples were filtered to a polycarbonate membrane with 0.2 μm pores followed by rapid freezing with liquid nitrogen and freeze-drying in vacuum overnight. The dried samples were sputter-coated with platinum. A voltage of 10 kV and a working distance of 5 mm were used when the samples were sampled.

Coagulation–flocculation experiments

The flocculation performance of the anionic nanocelluloses was evaluated by measuring the residual turbidity and COD of the settled wastewater after the coagulation–flocculation treatment using a similar procedure as in standard jar testing. The wastewater (100 ml) was treated using only ferric coagulant or ferric coagulant and anionic nanocellulose. The experiments were conducted by adding a constant dosage of ferric coagulant (25 mg/dm^3 after the dosage was optimized) to a beaker containing the wastewater and stirring the suspension with a magnetic stirring bar at 200 rpm for 3 min. at room temperature. After the coagulation treatment, the nanocellulose solution (2.5–50 mg/dm^3) was added to the wastewater, and the suspension was stirred at 40 rpm for 15 min. Finally, the suspension was allowed to settle for 30 min. at room temperature. The turbidity of the supernatant was measured with a Hach Ratio XR turbidimeter (model 43900), and the COD of the supernatant was measured from the standardized test tubes (Hach) with a Hach Lange DR 2800 spectrophotometer.

Morphology and strength of flocs

A constant dosage of ferric coagulant (25 mg/dm^3) was added to a beaker containing 1000 ml wastewater, and the suspension was stirred with a magnetic stirring bar at 200 rpm for 3 min. at room temperature. After the coagulation treatment, the nanocellulose solution (5 or 10 mg/dm^3) was added to the wastewater, and the suspension was stirred at 40 rpm for 15 min.

The morphology and strength of the flocs that formed were determined with a custom-built MOFI (floc measurement environment) analyzer that includes tube flow imaging of the sample with a CCD camera (Fig. 2). Two hundred milliliters of flocculated wastewater were diluted to 1800 ml with deionized water in the mixing unit (Fig. 2). After dilution, the sample was pumped through a 5 mm cuvette, where the flocs were visualized with a CCD camera (resolution 3.6 μm). The sample was recirculated back to the mixing unit using a centrifugal pump. The rotation speed of the pump was 1400 rpm during the experiments, and the experiments were continued for 90 s. In this method, the flocs break due to the pumping and hydrodynamics forces of recirculation. Approximately 800–1000 images from every sample were taken; each image contained approximately 80 flocs. Thus, on average, more than 72,000 individual flocs were analyzed from every sample; therefore, the results are statistically reliable.

The morphology of the flocs was analyzed from the images of the CCD camera with the automated image analysis program presented by Koivuranta et al. [34]. The image analysis program calculates specific particle features in each image, for example, the total particle area, the number of particles and different shape factors such as form factor and roundness. Shape factors are calculated only for particles that are more than 100 μm^2 because the boundaries of small particles are usually difficult to define at the limits of resolution. The form factor (FF) is affected by the irregularity or roughness of the object's boundary. The FF is 1.0 for a perfect circle and below 1.0 for any other shape. Objects with irregular boundaries have a longer perimeter per surface area and therefore have smaller form factors. The form factor is calculated

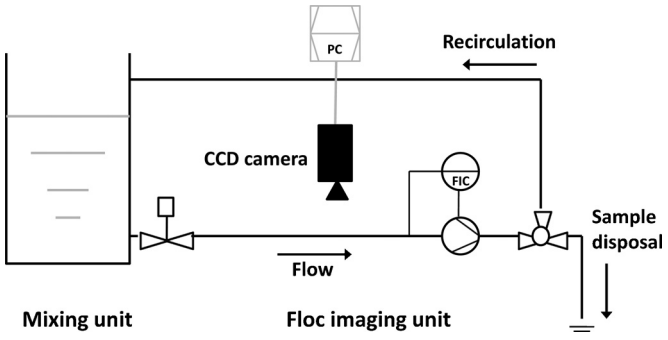

Fig. 2. Schematic illustration of floc measurement environment (MOFI).

Table 2
Charge of cellulose after synthesis, the yield after synthesis and number of passes through homogenizer.

Sample	Charge density (mmol/g)	Yield after synthesis (%)	Passes through homogenizer
ADAC I	0.357	90.5	5
ADAC II	0.507	88.3	3
ADAC III	0.507	88.3	5
DCC I	0.384	100	4
DCC II	1.750	66	1

from Eq. (1) as [34,41,42]:

$$FF = \frac{4\pi \times \text{area}}{\text{perimetre}^2} \quad (1)$$

Roundness (RO) (Eq. (2)) is defined as the ratio between the area of an object and the area of a circle with a diameter equal to the object's length [34,41,42]:

$$RO = \frac{4 \times \text{area}}{\pi \times \text{length}^2} \quad (2)$$

Roundness (RO) is 1.0 for a perfect circle.

Results and discussion

Characteristics of ADAC nanofibrillar flocculants

Number of anionic groups and size of nanofibrils

The FTIR spectrum of sulfonated cellulose is shown in our previous publication [26]. The sulfonation of cellulose was confirmed by the FTIR analysis, in which bands at 1131, 617 and 520 cm^{-1} associated with SO_2 vibrations at sulfonic acid groups, indicating the formation bisulfite containing compounds. Table 2 shows the anionic charge density of the cellulose and the mass yield of the samples after the chemical treatments. The anionic charge density of the DCC flocculants was higher than that of the ADACs. High charge also affected the viscosity of the samples, and the DCCs formed clear viscose gels with fewer passes through the homogenizer than the ADACs. The mass yield of the DCC samples after chlorite oxidation was from 100% to 66% and for the ADACs after sulfonation, from 90.5% to 88.3%. The dissolution losses during the oxidation pretreatments are strongly associated with the carboxyl content of the cellulose [37]. Thus, the yield would improve by using cellulose pulp with lower hemicellulose content.

Fig. 3 shows the mass proportions of different fractions from the chromatographic washer for the ADAC and DCC samples and the typical particles present in different fractions. Fraction 1 (FR 1) contains the largest particles, thus mainly non-fibrillated material and particle flocs. The second fraction (FR 2) contains fibrillated material, yet bunches of fibrils remain. According to the FESEM images, the measured widths of the particles in FR 2 ranged from approximately 60 to 20 nm while the length was assumed to be tens of micrometers. FR 3 contains highly fibrillated material that are approximately 10–4 nm wide and several micrometers long. FR 4 contains the finest material and rounder particles with a lower aspect ratio than the FR 2 or 3. The ADAC flocculants contained more fibrillated material in FR 2 and 3 and less non-fibrillated

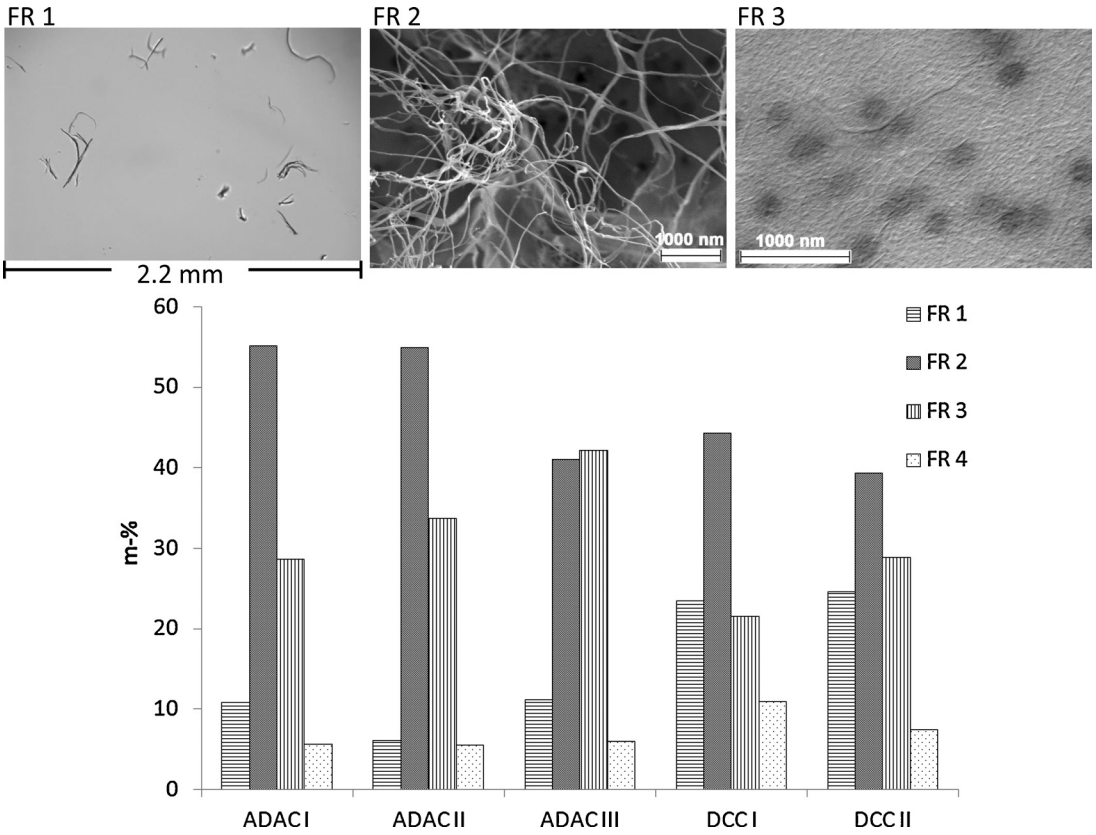

Fig. 3. Mass proportions of different fractions (FR 1–4) in the ADAC and DCC samples from the chromatographic washer and images illustrating the particles of different fractions.

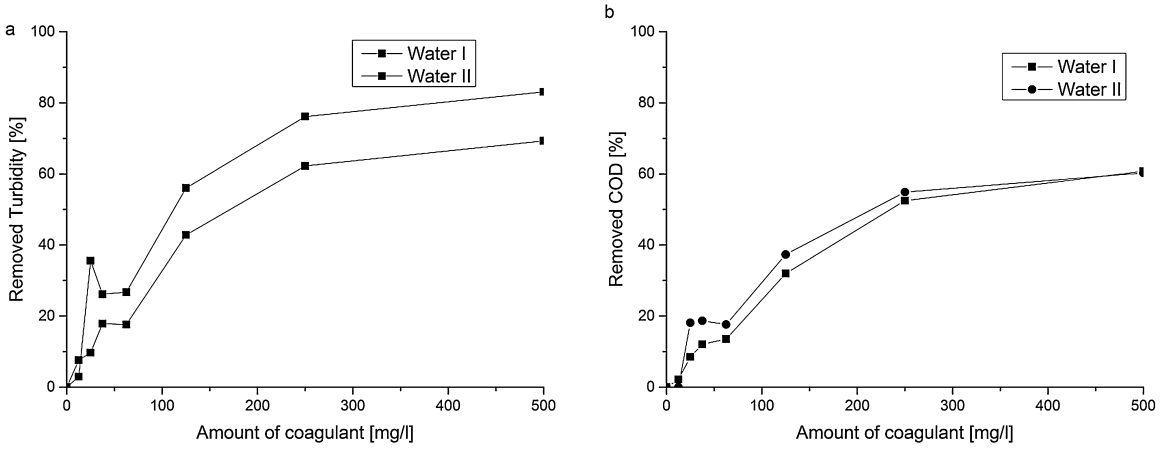

Fig. 4. Turbidity reduction and COD removal in wastewater samples I and II after coagulation treatment as a function of the coagulant dose. The settling time was 30 min.

material in FR 1 than the DCC flocculants, due to the higher number of passes through the homogenizer.

Coagulation–flocculation treatment

Optimization of coagulant dosage

The coagulation performance of ferric sulfate in terms of the turbidity and COD decrease in wastewater samples I and II (Fig. 4b) as a function of coagulant dosage are shown in Fig. 4. The decrease in turbidity increased up to a dosage of 250 mg/dm^3, after which the turbidity remained constant. Water II was more diluted than water I, which is also seen in the turbidity removal results (Fig. 4a). Thus, lower dry matter content did not have as high differences in the results of the COD removal (Fig. 4b). The same trend with the dosage of the ferric coagulant is seen in the COD removal, although the process is not as efficient as in the turbidity reduction.

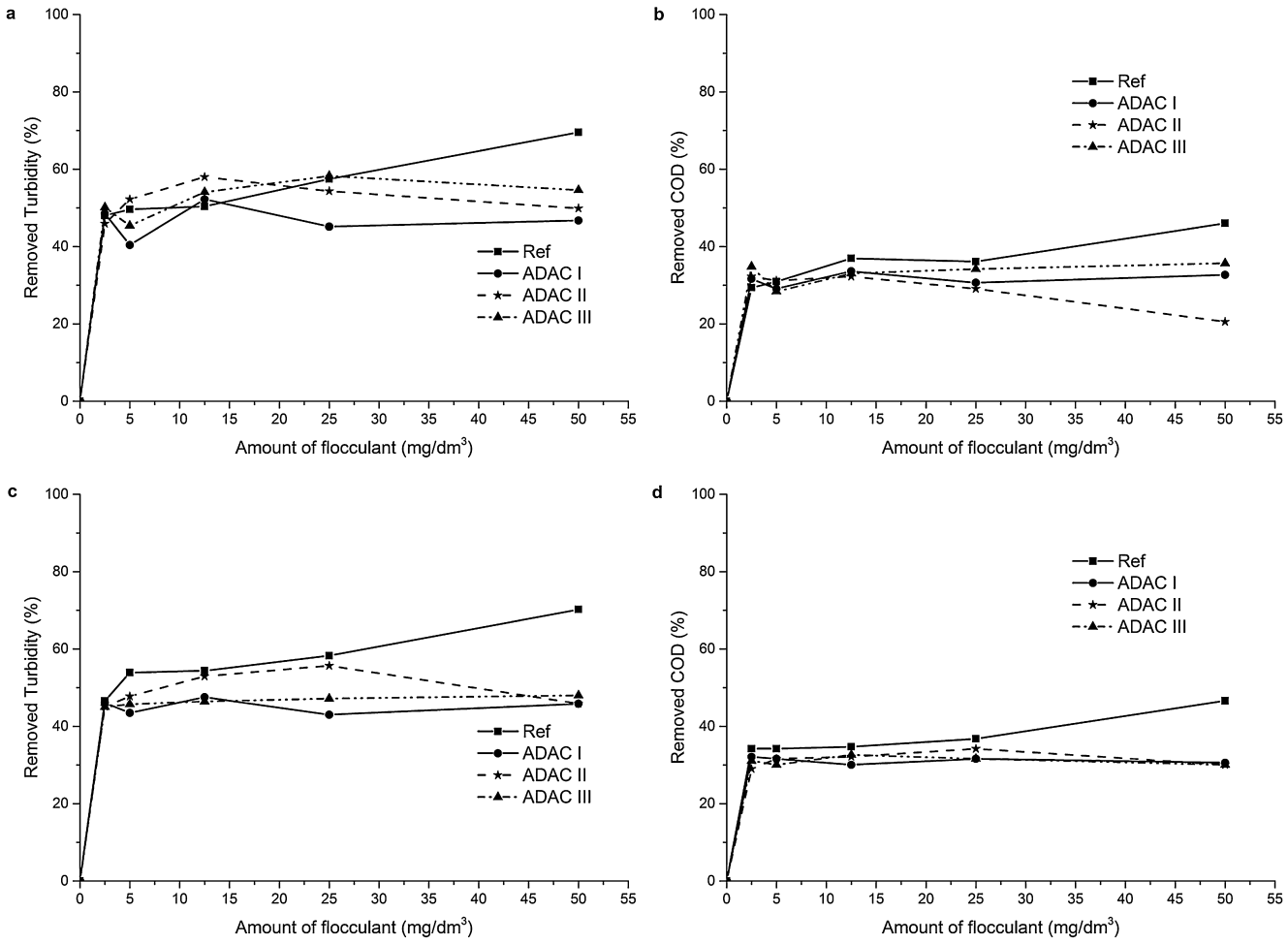

Fig. 5. Turbidity and COD removal of wastewaters (water I (a and b) and II (c and d)) after coagulation–flocculation treatment as a function of the dosage of ADAC nanofibril flocculants. The coagulant (ferric sulfate) dosage was 25 mg/dm^3, and the settling time was 30 min.

Influence of dosage of ADAC and DCC nanofibril flocculant on coagulation–flocculation treatment

Coagulation–flocculation treatments were performed by adding a constant dosage of ferric sulfate (25 mg/dm^3) to stirred wastewater after which the nanofibrillar cellulose flocculant was added to the coagulated wastewater. Fig. 5 shows the flocculation performance of the ADAC flocculants in terms of removed turbidity and removed COD as a function of flocculent dosage. In a previous article [28], the flocculation results for the DCCs showed good performance in the coagulation–flocculation treatment of municipal wastewater with small dosages. The results in Fig. 5 show that ADACs are even more effective in removing turbidity (Fig. 5a and c) and COD (Fig. 5b and d) with small dosages (2.5 mg/dm^3) compared to the performance of reference flocculant, and their performance is comparable to the commercial reference polymer. The flocculation results also show that the higher anionic charge of the ADACs provides a better result in removing turbidity, while the effect of the size of the flocculant was not as clear.

The flocculation results also show that the same decrease in turbidity and COD was reached with the ADAC dosage of 25 mg/dm^3 while dosage from 200 to 250 mg/dm^3 with coagulant alone was needed. Thus, the decrease in the chemical load was remarkable. Previously several different polysaccharides have proved to be efficient flocculants in wastewater treatments. However, their disadvantages have been rapid biological decomposition in aqueous solutions and required of high dosages [43,44]. Nanocellulose flocculants have in turn shown to possess high stability in aqueous suspensions over a long period of time [28] and good performance with low doses. The efficiency of coagulation–flocculation may still be improved by optimization of mixing speed and time and the pH [43].

Mechanism of flocculation with ADACs

We have previously shown that zeta potential of the waste water suspensions remained on a negative side during the whole coagulation–flocculation treatment in a pH range from 2 to 10 [28]. Consequently, it likely that cationic coagulant adsorbs on oppositely charged particle surfaces to give a non-uniform distribution of the surface charges [3,30] i.e., it forms cationic patches into anionic dirt particle surfaces. Anionic nanocelluloses create in turn bridges between dirt particles via these cationic patches. Sulfonic groups in ADAC have probably higher affinity towards iron patches of coagulant than the carboxyl acid groups, which may explain the better flocculation performance of ADACs compared to DCCs. Moreover, sulfonic group has likely larger degree of ionization than other functional groups in cellulose (e.g., hydroxyl or carboxyl groups), so the electrostatic affinity of sulfonic group towards metals may be stronger [45].

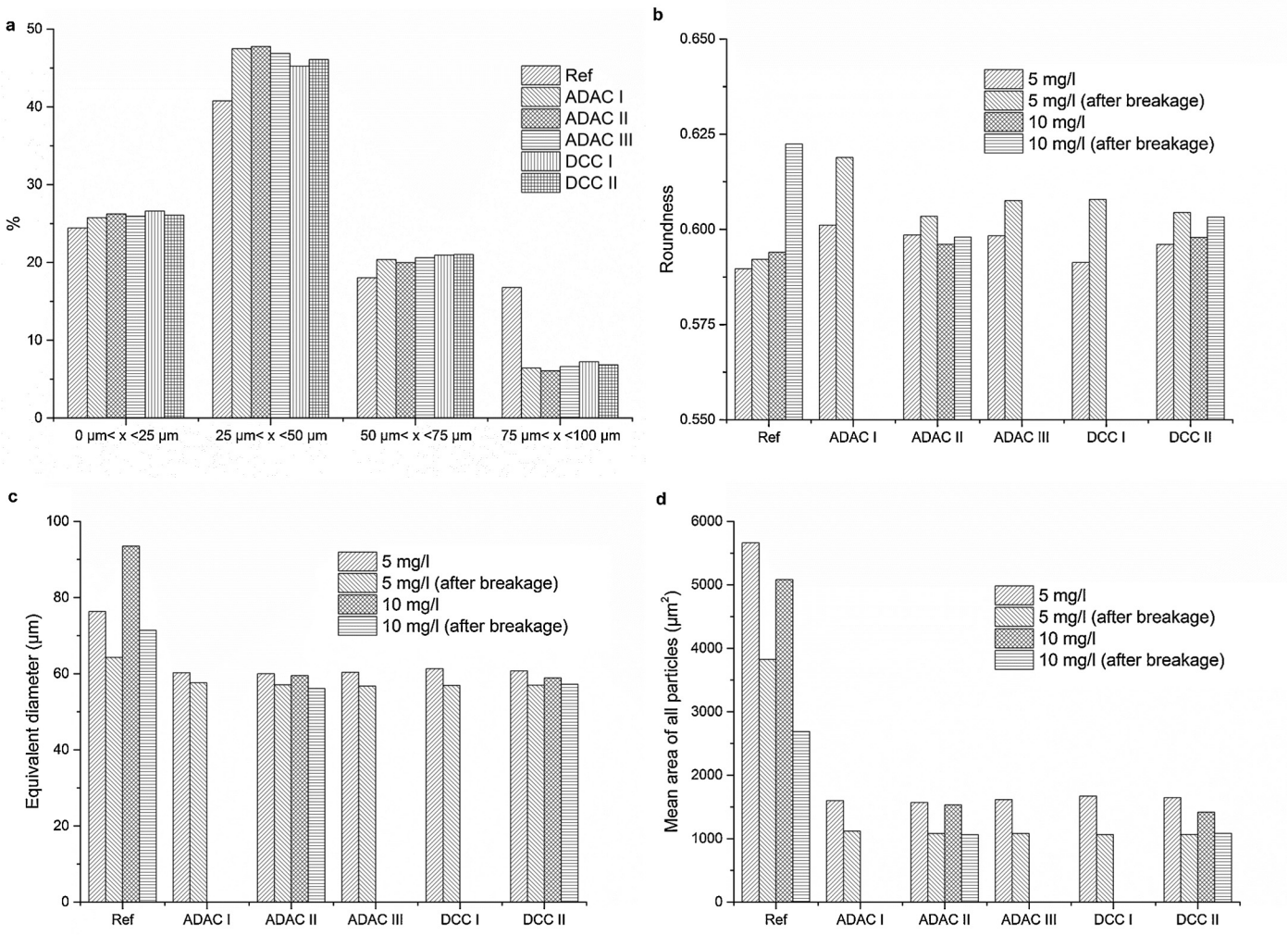

Fig. 6. Size distribution of the flocs formed with different polymers (a), roundness of the formed flocs (b), the equivalent diameter (flocs over 100 µm^2) (c) and the mean area of all particles (d) with different polymers before and after the flocks broke (dosage of flocculants: 5 or 10 mg/dm^3).

Morphology and strength of flocs

The morphology and strength of the flocs were followed by the MOFI analyzer. The particle size distribution, shown in Fig. 6a, shows that all flocculants had the same amount of smallest flocs (<25 μm), which is the size of the particles that do not settle down easily. The biggest flocs are clearly formed with a reference polymer, but the shapes of the flocs are not as round as with the nanocellulose flocculants (Fig. 6b). Fig. 6c shows the equivalent diameter for particles that have an area over 100 μm^2, while in Fig. 6d all the particles are included in calculating the mean area of all particles. Thus, in the mean area results the effect of a few really large flocs of the reference polymer dominated. The roundness and the density of the flocs have previously been observed promoting the efficiency of the water treatment [46,47]. Of the nanocellulose flocculants, ADACs formed the roundest flocs while the reference polymer had the
most irregular flocs, which broke easily into smaller round flocs (Fig. 6b–d). After the flocs broke, the reference polymer flocs had similar size than the nanocellulose flocs (Fig. 6c). Li et al. [29] showed that floc rupture is caused by surface erosion and large-scale fragmentation of flocs. The reference sample showed the largest differences during breaking in roundness, equivalent diameter and surface area values, which suggested that surface erosion and fragmentation affected floc breakage. Only minor changes in floc morphology were observed with nanocellulose flocculants, which indicates that more surface erosion than fragmentation existed. Natural polymers are also shear stable [48,49], which was also seen with the nanocellulose flocculants during pumping (Fig. 6). Also TEMPO-oxidized nanocelluloses in a flocculation of kaolin clay in combined treatment with CPAM were found to produce stronger flocs than CPAM alone [50]. Floc breakage depends on floc strength in tension, compression and shear, which are present in the wastewater treatment plants in turbulent flows and pumping [31]. In MOFI, flocculated wastewater is pumped through the imaging unit and circulated back in the mixing unit; thus, this floc measurement environment provides a realistic view of floc breakage.

In addition, the higher dosage of the polymers produced larger and weaker flocs with the reference polymer. However, the higher dosage with DCCs produced even smaller flocs, and with ADACs, the higher dosages seemed to have no effect; thus, the roundness (Fig. 6b) was slightly lower.

Conclusions

The ADAC bioflocculants possessed efficient flocculation performance in the coagulation–flocculation treatment of municipal wastewater. The performance was better than that reported earlier for DCCs. The turbidity reduction efficiency as well as the COD removal performance of the ADAC nanocelluloses were similar to those of the commercial reference polymer in low dosages, and the chemical consumption was significantly decreased compared to the consumption of ferric sulfite alone. The wastewater flocs produced with the nanocellulose flocculants were smaller and rounder than the flocs produced with the commercial reference polymer. Thus, the flocs produced with anionic nanocelluloses were more stable under shear than the flocs produced with the reference polymer.

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