Application of coagulant obtained through charge reversal of sawdust-derived cellulose nanocrystals in the enhancement of water turbidity removal

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Keywords: sawdust, cellulose nanocrystals, charge-reversal, coagulation, turbidity

Abstract
Sawdust-derived cellulose nanocrystals (CNC) were functionalized using hexadecyltrimethylammonium bromide (HDTMA-Br) as a cationic surfactant to produce novel coagulant for application in reducing water turbidity. The modified CNC was characterized using Fourier transform infra-red spectroscopy, x-ray diffraction, scanning electron microscopy, transmission electron microscopy and zetametry. Upon functionalization, the surface charge was reversed from $-39 \text{ mV}$ to $+22 \text{ mV}$ by introducing amine group to the CNC matrix. The microscopic analyses revealed that CNC has a narrow particle size range and rod-like morphology. The XRD analysis showed increased peak intensity upon modification, indicating enhanced crystallinity of the CNC; and an additional peak around $30.1^\circ$ appeared, which was attributed to the presence of HDTMA on the surface of CNC. Turbidity tests was conducted using both simulated and environmental water samples, and the effects of CNC modification reaction time, solution pH, coagulant dosage and initial turbidity levels were evaluated. Results reveal that turbidity reduction increased with an increase in reaction time and coagulant dosage, and decreases in initial turbidity level and solution pH. The performance of the modified CNC coagulant in turbidity reduction complied with the South African national standard (SANS 241:2015) for drinking water quality.

1. Introduction

The increase in industrialization, urbanization and anthropogenic activities in recent times are responsible for the high level of suspended and colloidal particles found in water cycles, which commonly result in high turbidity of water [1]. Turbidity is an optical quality of water that gives the appearance of ‘cloudiness’; thus, masks the presence of bacteria, algae and parasites which are harmful to human. Moreover, according to the United States Environmental Protection Agency (EPA) suspended particles less than 10 $\mu\text{m}$ pose great health problems because they could penetrate deep into the lungs or bloodstream. As such, they are capable of causing premature death in people with heart or lung disease [2]. Therefore, the World Health Organization (WHO) recommends that turbidity should not exceed 1 Nephelometric Turbidity Unit (NTU) before chlorination [3]. Consequently, efficient reduction of turbidity up to and below the allowable limit is required before water can be certified fit for consumption.

Suspended solids in water can be removed by sedimentation and filtration; however, these techniques are inefficient [3, 4]. To improve the process so as to handle suspended solids in the size range 0.1–10 $\mu\text{m}$ more advanced water treatment technology [4]. Coagulation/flocculation (CF) process is a widely used water treatment technique and has been found to be the most efficient in the removal of suspended particles and colloids [5]. One of the distinct advantages of the CF process is its simplicity and ease of application as primary, secondary or tertiary treatment process [6–8]. The effectiveness of CF process has been ascribed to the type of
coagulant used. Therefore, highly efficient, cost-effective and eco-friendly coagulant is required in order to meet up the water quality regulatory standards.

Chemically synthesized coagulants commonly used in industries are highly efficient in turbidity reduction. However, they may also pose some problems to the treated water because hazardous chemicals from these coagulants may leach into the process water during the water treatment procedure, thereby introducing more pollutants into the system which requires further purification [9]. It is, therefore, necessary to explore coagulants involving non-toxic, biodegradable, eco-friendly, renewable, readily available and low-cost materials, which could serve as a substitute for the traditional inorganic salts and polymer materials. In this regard, the development of an efficient and eco-friendly coagulants which utilize nanocellulose extracted from wood as a base material have been reported [10–14]. However, due to the constant demand for wood as a result of its numerous primary industrial applications [15], an alternative source is required for sufficient cellulose extraction.

The forestry, timber, pulp and paper (FTPP) industries play important role in the economy of South Africa and contribute about 4% to the country’s manufacturing gross domestic product (GDP). Therefore, maximizing the capital effectiveness of FTPP operations is a focus area for the industry and government as a way of increasing revenues [16]. One promising approach to achieving this is by adapting the bio-refinery concept. Currently, the FTPP industry extracts about 47% value from trees and the rest of the material are lost as waste [16]. Hence, the extraction of cellulose nanocrystals (CNC) from waste sawdust instead of the wood itself would be a worthy venture. This innovation would also enhance the disposal of waste sawdust by-products in an economically and environmentally acceptable manner, which is another critical issue facing the FTPP sector [17, 18]. The problem is further compounded by impending government regulations which will limit or prohibit landfilling all together as a way of waste disposal. Therefore, the use of waste sawdust as a source of cellulose nanocrystals extraction is highly beneficial in all ramifications [19].

This work is part of a wider project on bio-refinery technologies which aims to develop various downstream processes for converting sawdust-derived CNC into high value chain products. The sawdust-derived CNC was charge-reversed and evaluated as coagulant for turbidity reduction. Jar test experiments were carried out using simulated water and environmental water sourced from the local water industry. Modification reaction time, coagulant dosage, solution pH and initial turbidity were varied to evaluate the coagulant performance in meeting the South African National Standards (SANS 241:2015) [20, 21]. The physicochemical properties such as functional groups, structures and surface charge were also investigated and where applicable the coagulant properties were related to the performance achieved during water treatment.

### 2. Material and methods

#### 2.1. Material

Cellulose nanocrystals (CNC) suspension was obtained from DST-CSIR Biorefinery, Durban (South Africa), where it was extracted and processed from sawdust. Hexadecytrimethylammoniumbromide (HDTMA-Br), sodium hydroxide and hydrochloric acid were obtained from Sigma-Aldrich, South Africa. Turbid water was simulated by mixing a known amount of kaolin with water. In addition turbid environmental water samples were obtained from three different sources in South Africa (Weltevrede water treatment works (WTW), Bronkhorstspruit WTW and TB hall dam). All chemicals used were of analytical grade.

#### 2.2. Methods

##### 2.2.1. Surface re-engineering of cellulose nanocrystals (CNC)

The details of CNC extraction from sawdust has been reported elsewhere [19]. The procedure involved a one pot synthesis route using deionized water and sulphuric acid, which were subsequently ultra-sonicated to afford cellulose nanocrystals suspension. Cellulose nanocrystals naturally have highly electronegative surface ions which are responsible for the stability of CNC in aqueous solutions. These electronegative ions are oxygen atoms whose anionic natures were enhanced by the presence of lone pairs of electron. These anionic groups are nucleophiles, which facilitate the coordination of the CNC with cations [22]. The suspended particles in water also possess negative charges on their surface; thus, repulsion occurs when CNC and suspended particles are in contact in water. Consequently, surface modification of CNC is required in order to induce positive charges on the surface for efficient coagulation of suspended solids. The structure of cellulose nanocrystals has abundant OH groups, which serve as sites for several reactions and allow for the modification of surface charge. Different cationic surfactant may be used as modifier to increase the performance of CNC. Hence, HDTMA-Br was used in this study. This was achieved by adding 1 g of HDTMA-Br to a reactor containing 10 g CNC in 40 ml deionized water and constant stirring was maintained to allow for homogenous mixture. The reaction time was...
varied from 30 min to 4 h and thereafter the resulting slurry was centrifuged and then rinsed several times to ensure complete removal of excess chemicals.

2.2.2. Characterization of synthesized cellulosic coagulants and flocs formed
Suitable analytical techniques were used to characterize the raw CNC, modified CNC and flocs formed after coagulation process. For charge density determination, zeta potential measurement was conducted using zetasizer nanoseries (Malvern instruments, UK). Evaluation of the crystallinity of CNC was conducted by x-ray diffraction analysis, using x-ray diffractometer (XRD) (PANalytical Empyrean) which utilises a monochromatic Cu Kα radiation (λ = 0.154 06 nm), and over a scan range of 5.0149°–89.9809°. High score plus program was used for the phase identification. The CNC samples used for XRD analysis were oven dried for 12 h at 50 °C prior to the analysis. Fourier transform infrared- attenuated total reflectance (FTIR-ATR) was used to explore the functional groups present in the material, using a Perkin Elmer Spectrum 100 spectrometer recorded in the 500–4000 cm\(^{-1}\) range and at a resolution of 4 cm\(^{-1}\). The samples used for FT-IR analysis were also oven dried for 12 h at 50 °C. The external morphologies were studied by SEM analysis using a JEOL JSM-7600F Field Emission Scanning Emission Microscope (FESEM), running at 2 kV accelerating voltage. The particle sizes were measured by transmission electron microscopy (TEM) analysis, using a JEM-2100F field emission electron microscope run at 200 kV and the particle size distribution analysis using image J software. CNC samples used for electron microscopic analyses were prepared by placing a drop of a diluted solution of the sample in ethanol on a carbon grid (400 mesh, agar). The excess solvent was whisked away with a paper tip and the sample was allowed to dry completely at room temperature.

2.2.3. Coagulation studies
Jar test experiments were conducted in 1 L beakers on each six gang stirrers. The tests were conducted using surface modified CNC coagulant under different conditions, while the volume of turbid water in each beaker was fixed at 500 ml for all the experiments. Rapid mixing of the solution was conducted for 2 min at 200 rpm, and then followed by slow mixing in order to allow floc formation for 15 min at 65 rpm. Finally, the water in the beakers was allowed to settle for 30 min. Samples were taken from 2.0 cm below the surface of the beakers for water analysis using turbidity meter. The coagulant performance was evaluated by varying modification reaction time, solution pH, coagulant dosage and initial turbidity level. In addition, the performance of modified CNC coagulant was also tested using environmental water samples obtained from three different sources.

3. Results and discussion

3.1. Characterization results

3.1.1. Fourier transform infra-red spectroscopy
The FTIR spectra of the unmodified CNC, modified CNC, HDTMA-Br and CNC flocs formed during coagulation are presented in figure 1. In the spectra, a band around 2920 cm\(^{-1}\) corresponds to the C–H vibration of SP\(^3\) hybridized carbon [23] which confirms the presence of saturated bond around the carbon atom. The broad band in the range 3286–3486 cm\(^{-1}\) is ascribed to the O–H stretching vibration of water molecules. This band becomes broader after coagulation, indicating an increase in hydrogen bonding [24]. The spectrum of the HDTMA-Br displays two peaks in the region 2851–2919 cm\(^{-1}\) which are assigned to the asymmetric and symmetric CH\(_2\) vibrations, and the peak at 3018 cm\(^{-1}\) is due to the symmetric CH\(_3\)–N vibration [25]. The peaks at 700, 2851 and 2919 cm\(^{-1}\) could be attributed to adsorbed HDTMA-Br found on the surface of the modified CNC, since these peaks were also observed in the FT-IR spectrum of HDTMA-Br. A band around 1000 cm\(^{-1}\) is the C–O stretching vibration, while the band at 1435 cm\(^{-1}\) is attributed to the CH\(_2\) vibration and has been regarded as the crystallinity band in any cellulosic material [26–28]. The intensity of this peak was slightly stronger in the modified CNC, suggesting an increase in crystallinity of this material after modification process. The weak band around 1765 cm\(^{-1}\) is due to the C=O stretching vibration [29] of hemicellulose carbonyl group.

3.1.2. Scanning/transmission electron microscopic analyses
The external morphologies obtained from SEM analyses are shown in figure 2(a) which presents the image of raw CNC (unmodified), (b) modified CNC, and (c) flocs after coagulation using modified CNC. The micrograph of pristine CNC (unmodified) shows a surface with granular particles and fibers with irregular shape. Upon modification there is an onset of regularity of CNC (see figure 2(b)). However, the laminar crystals observed on the surface of the unmodified CNC are not as clear as those in the modified and after-coagulation forms of CNC. This suggests that HDTMA-Br adsorbed on the external surface of the modified CNC forming an organic coating [30]. As such, the cationic HDTMA species bonded to the negatively charged CNC through cation exchange, and the hydrophobic interactions formed a stable organic rich coating on the external surfaces.
of the CNC. During coagulation, there was spherical shaped flocs formation across the surface of modified CNC (see inset figure 2(c)). Similar floccules formation is reported in the literature [31].

The internal morphology of the cellulose nanocrystals samples was analysed using transmission electron microscopy (TEM) and is presented in figure 3. The micrograph of pristine CNC displayed rod-like fibres with average particle size in the range 6 to 36 nm (figure 3(a)). This is also supported with corresponding particle size distribution histogram of the pristine CNC presented in figure 3(c). The nanofibers become more pronounced and intertwined on the surface upon modification (figure 3(b)), which is attributed to the effect of chemical interaction and continuous stirring [32]. Similar morphology has been reported for CNC in another study [33].
3.1.3. X-ray diffraction (XRD) analysis

The XRD analysis was performed in order to evaluate the crystalline structure of pristine CNC and also determine the impact of modification. The x-ray diffraction pattern of unmodified CNC presented in figure 4 shows a typical diffraction pattern of type I cellulose with diffraction peaks at 16.4° and 22.2° (C₆₀H₈₈O₈ and C₂H₁₉₂N₆₄O₁₆). Modification of CNC with HDTMA-Br did not considerably change the cellulose type. However, an additional crystalline peak around 30.1° appeared after modification which could be ascribed to the presence of HDTMA-Br on the surface [34]. It is observed that the modified CNC shows higher intensity than the unmodified CNC which is indicative of its higher crystallinity. Hence, the reaction of CNC with HDTMA-Br might be responsible for enhanced crystallinity on the surface of CNC. Similar observation was reported in the literature [35]. Coagulation of suspended solids resulted in changes in x-ray diffraction patterns. The appearance of other additional peaks around 60.1° and 75° (Al₁₂O₁₈N₁₆Si₄) could be ascribed to the interactions between modified CNC and suspended solids in kaolin simulated water. Overall, the phases identified on cellulose nanocrystal used in this study were similar to the reported characteristics of pure cellulose reported in other studies [34, 36].

3.1.4. Zeta potential studies of the coagulants

The electro kinetic potential of CNC in colloidal dispersions was determined by net charge analysis referred to as zeta potential. It reflects the effective charge on the particles and is, therefore, related to the electrostatic repulsion between similar charges. The zeta potential has proven to be very relevant to the control of colloidal stability and flocculation processes between the particles [37]. The apparent charge density at pH 7 for unmodified CNC was found to be −39 mV, indicating that the sawdust-derived CNC was negatively charged. Charge reversal of CNC from −39 mV to +22.0 mV was observed upon modification with cationic surfactant (HDTMA-Br). The resulting surface reengineered CNC was subsequently used for the coagulation of suspended solids in water.
3.2. Coagulation results

3.2.1. Effect of modification reaction time on turbidity reduction

Pristine CNC was reacted with HDTMA-Br for 1/2, 2 and 4 h in order to explore the effect of reaction time on coagulation performance. Figure 5 summarizes the jar test results obtained for two different initial turbidity levels. Different amounts of kaolin in water were used to simulate the two turbidity levels: 50 and 20 NTU. In figures 5(a) and (b), the turbidity of the filtered water was expressed as a function of coagulant dose for three different surface modification reactions time. Performance of a commercial coagulant R2T2 was also included for purposes of comparison only. It is generally observed that turbidity reduction increases with an increase in coagulant dose. This can be explained in terms of the electro kinetic properties of suspended solids in water and inherent charge on coagulant. Suspended solids are negatively charged and due to coulombic repulsive forces, are dispersed in water resulting in high turbidity. Upon the use of surface modified CNC coagulant, the suspended solids were destabilized; hence, van der Waals forces and surface adsorption became dominant [38, 39]. Consequently, the suspended particles flocc together, and settle (sedimentation). Any particles left in the water after sedimentation are easily removed by filtration leading to low water turbidity. Indeed, a target turbidity value <1 NTU (SANS 241:2015) [39] of filtered water was achieved, suggesting that modified CNC is a potential coagulant with application value. It must be noted though from the data presented in figure 5 that overdose of coagulant does not enhance turbidity reduction but by contrast results in increased turbidity as...
observed with R2T2. This is due to resuspension of particles at high coagulant dose because particles acquire positive charges and repel one another. When different modification regimes are compared, it is observed that when pristine CNC was reacted with HDTMA-Br for 4 h, the resulting coagulant exhibited the highest performance, although marginally, over most of the dosage levels (figures 5(a) and (b)). As a result, CNC obtained after 4 h of modification reaction time was used in the subsequent jar test experiments.

3.2.2. Effect of solution pH
The pH of drinking water varies from one source to another, but ideally should be between pH 6.5–8.5 [40]. In this work, we studied the performance of modified CNC at pH 6, 7 and 8 using initial turbidity level of 20 NTU. The results are presented in figure 6, in which the turbidity level of the filtered water is expressed as a function of coagulant dose for various pH values. It can be seen that it was possible to achieve the target turbidity value of <1 NTU. Another characteristic of the results depicted in figure 6 is that pH affects the performance of the modified CNC; turbidity reduction improves as pH reduces. This observation may be explained by considering two aspects. First, in acidic media the coagulant is more positively charged. This enhances coulombic attraction between the positively charged coagulant and the negatively charged particles in water. The second aspect relates to the reduction of the hydrogen bonding sites available in the coagulant leading to more effective formation of bridge bonds and neutralization of the charges [41, 42].

3.2.3. Effect of initial water turbidity
The performance of the surface modified CNC was further evaluated by varying the initial turbidity level of the water between 10 to 100 NTU, using coagulant dosage from 0 to 20 mg L⁻¹. Figure 7 presents the results obtained after the filtration process. It can be seen that performance is affected by initial turbidity level and coagulant dose. When the initial turbidity values are between 10 and 50 NTU, performance improves with an increase in coagulant dose and it is possible to achieve the filtered water turbidity target value of <1 NTU. For raw water of 100 NTU, it is observed that an increase coagulant dosage helps improve performance but it is not possible to achieve the filtered water turbidity target of <1 NTU within the limit of coagulant dose used. As already explained, formation of flocs may either occur through charge neutralization or bridging. When the raw water turbidity is very high, the coagulant loses its ability to effectively neutralize the inherent negative charges of particles in water. As a consequence, elevated levels of final water turbidity is observed.

3.2.4. The performance of modified CNC on reduction of turbidity of environmental water
The environmental water samples obtained from two drinking water treatment plants and a dam in South Africa were also tested to ascertain the performance of modified CNC. Coagulation/flocculation experiments were conducted under the same conditions of flash mixing, slow mixing and settling time. Initially, the three water samples sourced from TB Hall dam, Bronkhorstspruit WTW and Weltevreden WTW were analyzed and found to contain suspended solids with turbidity levels of 13.96, 13.99 and 34.5 NTU, respectively. The turbidity reduction efficiencies of modified CNC in these 3 different water matrices were evaluated and are presented in
Results indicate that it is possible to lower raw water turbidity to values < 1 NTU at coagulant dosages between 5 and 10 mg l\(^{-1}\). Such low coagulant dosages for environmental water suggest that modified CNC coagulant is not only highly efficient but also would render water treatment to be highly cost effective.

4. Conclusions

In this study, surface re-engineering of cellulose nanocrystals (CNC) derived from sawdust was carried out in order to develop a novel coagulant, which was characterized and evaluated for the reduction of turbidity in both simulated and real water samples. The surface functionalization was achieved using HDTMA-Br and the following features were discovered: the material was highly porous with narrow particle size range and rod-like morphology. Fourier transform infrared analysis revealed that the functional groups responsible for higher performance of modified CNC were carboxylic and alky chain. X-ray diffraction analysis of the particles revealed the presence of additional phases upon modification which were attributed to HDTMA-Br. In water turbidity reduction, modified CNC coagulant exhibited higher performance compared to R2T2, a commercial coagulant used as reference. The excellent performance was attributed to the CNC charge-reversal upon modification.
Charge neutralization and bridging mechanisms are thought to be responsible pathway for the coagulation of the particles from water samples. The performance of the coagulant was affected by solution pH, coagulant dose and initial turbidity level. It seems that modified CNC was more effective at lower turbidity levels. Overall, the modified CNC exhibited high performance, was able to reduce water turbidity to values < 1 NTU; the South African national standard (SANS 241:2015) maximum allowable value.

Acknowledgments

The authors wish to acknowledge the funding from the Department of Science and Technology-Republic of South Africa under ‘Biorefineries Consortium’, and our collaborator, Prof. Bruce Sithole (CSIR-DURBAN/UKZN, South Africa) for supplying cellulose nanocrystals material.

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