



Pretreatment assisted synthesis and characterization of cellulose nanocrystals and cellulose nanofibers from absorbent cotton



Emmanuel Abu-Danso^{a,*}, Varsha Srivastava^b, Mika Sillanpää^{b,c}, Amit Bhatnagar^a

^a Department of Environmental and Biological Sciences, University of Eastern Finland, FI-70211, Kuopio, Finland

^b Laboratory of Green Chemistry, Lappeenranta University of Technology, Sammonkatu 12, Mikkeli, 50130, Finland

^c Department of Civil and Environmental Engineering, Florida International University, Miami, FL, 33174, USA

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ABSTRACT

In this work, cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs) were synthesized from absorbent cotton. Two pretreatments viz. dewaxing and bleaching with mild alkali were applied to the precursor (cotton). Acid hydrolysis was conducted with H₂SO₄ and dissolution of cotton was achieved with a mixture of NaOH-thiourea-urea-H₂O at −3 °C. Synthesized cellulose samples were characterized using FTIR, XRD, SEM, BET, and zeta potential. It seems that synthesis conditions contributed to negative surface charge on cellulose samples and CNCs had the higher negative surface charge compared to CNFs. Furthermore, BET surface area, pore volume and pore diameter of CNCs were found to be higher as compared to CNFs. The dewaxed cellulose nanofibers (CNF D) had a slightly higher BET surface area (0.47 m²/g) and bigger pore diameter (59.87 Å) from attenuated contraction compared to waxed cellulose nanofibers (CNF W) (0.38 m²/g and 44.89 Å). The XRD of CNCs revealed a semi-crystalline structure and the dissolution agents influenced the crystallinity of CNFs. SEM images showed the porous nature of CNFs, the flaky nature and the nano-sized width of CNCs. Synthesized CNF D showed a better potential as an adsorbent with an average lead removal efficiency of 91.49% from aqueous solution.

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1. Introduction

The current shift towards the green economy in process industry has led to the preference for low-cost natural materials that are renewable, have no or minimum negative impact on the environment and are generally unique in physiochemical properties. One of such materials is cellulose [1] which is the most abundant polymer in nature. Cellulose is present in plants [2], bacteria and tunicates [3] as well as in some animals [4]. The chemical composition of cellulose reveals a linear homopolysaccharide chain of β-1,4-linked anhydro-D-glucose units which is hydrophobic, fibrous and physically tough but with different degrees of polymerization (DP) depending on the source [1,5]. Cellulose has been used in various applications such as in the food industry, material coating, flexible films, and in medical applications including tissue growth manipulation [6]. Cellulose-rich biomass waste from agriculture and forestry (such as plant residues, wood waste, peat, cattle manure and others) has been used as a feedstock for biochar production

[7,8]. In environmental protection, cellulose has been used for the removal of arsenic from soil [9,10] and from water [11,12]. Cellulose has also been used for the removal of various aquatic pollutants such as fluoride [11], Congo red dye [13]. Although cellulose has a fundamental structure, the chemical composition can be influenced by genotypic and environmental factors as found in cellulose from cotton [14]. Cotton is composed of ca. 85–90% of cellulose [15] and a traditional source of cellulose nanostructures [14]. Different cotton types including regular cotton and cotton linters may have modified structures [16,17] however, available literature on nano-size cellulose from cotton provide less information on factors that can influence the structure [18].

The current challenge is the synthesis of cellulose that will allow manipulation of the internal structures to conform to nanoscale and also enable the integration of different materials. One typical challenge is the prevention of negative effects of the H-bond in cellulose nanofiber (CNF) bundles after drying [19]. The difficulty is the disengagement of water molecules within the CNFs [20], although the distances among CNFs in a stable suspension are reasonably wide to prevent fibril clustering [21]. Improvement of synthesized cellulose fibrils is multifaceted because preparation processes will eventually determine the nature of the fibrils. The current focus therefore, is on the various pretreatment and post-

* Corresponding author.

E-mail addresses: emmanuel.abu-danso@uef.fi (E. Abu-Danso), amit.bhatnagar@uef.fi (A. Bhatnagar).

treatment methods that will result in improved cellulose structure, suitable for novel products as well as other applications. The caveat in choosing pretreatment agent is to study the effect closely since the composition can have a degrading effect on cellulose [21]. If a preparation process leads to avoidance of degradation as well as control the influence of the H-bond, this might be the preferred option. One option to obtain cellulose from cotton is a facile dissolution with alkali by using NaOH-thiourea-urea-H₂O solution as a cotton dissolution agent [11,21], however, this procedure is less reported. In contrast, acid hydrolysis of cellulose, to produce cellulose crystals, is a well-known process and has been reported widely [22,23]. Treatment of cellulose with sulfuric acid (H₂SO₄) produces cellulose crystal and negatively charged surface from the esterification of hydroxyl (OH) groups by sulfate ions from the H₂SO₄, to form a stable cellulose suspension [24,25].

This work focuses on the optimization of cellulose nanofibers (CNFs) and crystals (CNCs) from medical absorbent cotton by prior pretreatments viz. dewaxing (with toluene and ethanol 2:1 v/v) and bleaching with mild alkali (0.1% NaClO₂). The CNCs and CNFs were obtained by following the procedures as reported in the literature with some modifications. This procedure has been less reported with cotton. Moreover, the frail nature and the risk of fiber damage in the process makes it difficult to work with cotton.

The resulting products (CNCs and CNFs) were characterized by various spectroscopic techniques viz. Fourier transform infrared microscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) and zeta potential to get an insight on the physicochemical properties of synthesized materials. Finally, the potential of CNFs as an adsorbent for Pb(II) removal from water was studied.

2. Materials and methods

2.1. Chemicals

Medical absorbent cotton was procured from a local pharmacy shop in Kuopio, Finland. Dialysis sacks, sodium chlorite and toluene were purchased from Sigma-Aldrich (Germany). Ethanol was purchased from Altia Oyj, (Finland), while urea and thiourea were purchased from Merck-Schuchardt, (Germany). Sodium hydroxide and sulfuric acid were purchased from Fisher scientific (UK) and (VWR, Germany), respectively.

2.2. Pre-treatment of precursor

The precursor (medical absorbent cotton) was divided into two parts. One part was subjected to dewaxing and the other part was used for bleaching. Deionized water was used in all the experiments.

2.2.1. Dewaxing

To achieve expedited and unimpeded dissolution of the cotton fiber, dewaxing method was selected to better expose the fibers by removing residual wax. The medical absorbent cotton was dewaxed by following a modified version of the protocol used by other researchers [23,26]. Briefly, ca. 10 g of cotton was placed in a Soxhlet extraction apparatus attached to a round bottom flask containing toluene and ethanol (2:1 v/v). The cotton was boiled (90–100 °C) in the Soxhlet apparatus on a heater for 4 h. Further, the dewaxed cotton was then placed in a beaker containing 200 ml ethanol for 30 min, washed and filtered after 30 min. The dewaxed cotton was then placed in an oven (Memmert 100–800, Schwabach-Germany) and dried at 80 °C to constant weight, cut into smaller sizes and stored for the next procedure.

2.2.2. Bleaching

Bleaching as a fiber cleansing procedure is commonly performed using relatively unstable hydrogen peroxide (H₂O₂). To avoid reagent instability in the procedure, a mild alkali as the bleaching agent was used in this study. Medical absorbent cotton (ca. 10 g) was placed in a solution of 0.1% sodium chlorite (NaClO₂) in a beaker. The beaker containing the solution and the cotton was then placed in the oven at 80 °C for 4 h. The bleached cotton was washed with deionized water to remove the sodium chlorite and dried in the oven at 80 °C to constant weight.

2.3. Synthesis of cellulose nanofibers (CNFs)

Cellulose nanofibers (CNFs) were obtained based on a method reported elsewhere [11,21] with some modifications. A solution of 8% NaOH-6.5% thiourea-8% urea-77.5% deionized H₂O (by weight) was prepared in a beaker and kept in the freezer to cool to –3 °C. Approximately 3.3 g of the dewaxed medical absorbent cotton was immediately dispersed into the cooled solution and stirred vigorously for approximately 10 min to form a cellulose solution. The solution was transferred into a cooking blender (OBH Nordica) and further agitated to break up recalcitrant fibers. The solution was transferred into centrifuging tubes and centrifuged (Biofuge Stratos Heraeus instruments, Kendro Lab. Germany) at 7500 rpm for 10 min to separate the undissolved particles and bubbles from the solution. The solution was then placed in a refrigerator and frozen completely and subsequently placed in a freeze dryer (Christ alpha 1-2, Biotech, Germany) and dried for 96 h. The dried cellulose was then pulverized to powder with mortar and pestle and stored. The procedure was repeated with non-treated medical absorbent cotton and the CNFs obtained from the two syntheses were named as CNF D and CNF W. (D represents dewaxed sample and W represents sample with wax).

2.4. Synthesis of cellulose nanocrystals (CNCs)

Cellulose nanocrystals (CNCs) were obtained from medical absorbent cotton by sulfuric acid (H₂SO₄) hydrolysis with an emphasis on the reduction of free H₂SO₄ and salts. A modified version of the protocol was used for the preparation of CNCs [23,26].

Two glass beakers were labeled as CNC₃₀ and CNC₆₀. A 40 ml volume of 60% wt. H₂SO₄ was poured into each glass beaker and placed on a hot magnetic plate (Heidolph MR3001, Germany). The bleached cotton (ca. 4.0 g) was dispersed into each of the two beakers to start the hydrolysis for 30 min and 60 min respectively, at ca. 45 °C under continuous stirring. The hydrolysis was terminated after set times with deionized water and centrifuged at 7500 rpm for 10 min. The supernatant was discarded only if not turbid to avoid sample loss. Centrifuging was repeatedly done until the supernatant turned turbid. The obtained suspensions were neutralized with aliquots of 1% NaOH. The suspensions were then dialyzed in deionized water for ca. 4 days. The resultant cellulose suspension was ultrasonicated (UP400S Hielscher, Germany) at 1 cycle, 80 amplitude to break up recalcitrant fibers. The sample was then frozen completely and freeze dried for 96 h. CNC₃₀ represents hydrolysis done for 30 min while CNC₆₀ represents hydrolysis done for 60 min.

The procedure was repeated for dewaxed medical absorbent cotton and the CNCs so obtained from the syntheses were labeled (CNC B1, CNC B30, CNC D1 and CNC D30), where B1 and B30 represent bleached cotton acid hydrolyzed for 60 min and 30 min while D1 and D30 represent dewaxed cotton acid hydrolyzed for 60 min and 30 min respectively.

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