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

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

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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.

Keywords: Cellulose; acid hydrolysis; alkali dissolution.

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-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 adsorbent cotton by sulfuric acid (H$_2$SO$_4$) hydrolysis with an emphasis on the reduction of free H$_2$SO$_4$ and salts. A modified version of the protocol was used for the preparation of CNCs [23,26].

Two glass beakers were labeled as CNC$_{30}$ and CNC$_{60}$. A 40 ml volume of 60% wt. H$_2$SO$_4$ 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. CNC$_{30}$ represents hydrolysis done for 30 min while CNC$_{60}$ 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.
2.5. Characterization of precursors, CNFs and CNCs

2.5.1. Scanning electron microscope (SEM) analysis

The surface morphological patterns of all the synthesized cellulose products and the precursors were examined using Zeiss sigma HDVP (Carl Zeiss GmbH, Oberkochen Germany) Scanning electron microscope (SEM) at different voltages (2-6 kV). The cellulose sample was initially gold-sputtered using Agar auto gold sputter.

2.5.2. Fourier transform infrared spectroscopy (FTIR)

Functional groups, present on the cellulose surface, were analyzed using Fourier transform infrared spectroscopy (FTIR) with Thermo Nicolet Nexus 8700 model (Thermo electron, Madison USA). The spectra were recorded in the range of 400 – 4000 cm\(^{-1}\) at 64 scans.

2.5.3. Brunauer–Emmett–Teller (BET) analysis

The surface area, pore diameter and pore volume of all samples were analyzed using BET analyser Tristar® II Plus (Micrometics, GA USA). The degassing temperature and time were 30 °C and 15 h, respectively.

2.5.4. X-ray Diffraction (XRD)

The XRD and the crystallite sizes of the samples were determined using PANalytical x-ray diffractometer, (PANalytical B.V., The Netherlands). Peak area and height from the measurements were used to determine the crystallite sizes based on full width at half maximum (FWHM) determinations using Sherrer’s equation:

\[
D = \frac{K\lambda}{B\cos\theta} \quad (1)
\]

where, D = crystalline size

- K = constant (0.89)
- \(\lambda\) = wavelength (Cuk\(\alpha\) = 0.154 nm)
- B = (FWHM) in (rad.)
- \(\cos\theta\) = 2 \(\theta\) peak
2.5.5. Zeta potential

The zeta potential measurements of the samples were conducted using Malvern Nano Zetasizer (Malvern instruments, Worcestershire UK) to measure the magnitude of the electrostatic or charge repulsion/attraction between particles of the fibers. The pH range for the measurements was chosen from 2 to 12.

2.6. Adsorption studies

Lead (Pb) adsorption experiments were conducted with CNFs at ca. 25 °C. The CNF was chosen for the adsorption studies based on its negative surface charge and the potential of various functional groups, present on the CNFs. The initial lead stock solution was prepared by dissolving the required amount of lead (II) nitrate (Pb(NO$_3$)$_2$) in deionized water. Dilution was used to prepare 50 mgL$^{-1}$ from the stock solution. A known amount of CNFs was added into a 15 ml tube containing 10 ml of 50 mgL$^{-1}$ lead solution. The mixture was agitated on a shaker at 80 rpm for 120 min. (equilibration time).

After the equilibrium time, the mixture was filtered and the residual lead concentration was analyzed using Atomic Absorption Spectroscopy (AAS). The percentage lead removal was determined using Eq. (2).

$$R\% = \frac{C_o - C_e}{C_o} \times 100$$  \hspace{1cm} (2)

where $R\%$ = percentage removal

$C_o = $ initial lead concentration (mgL$^{-1}$)

$C_e = $ final concentration of lead at equilibration time (mgL$^{-1}$)

3. Results and discussion

3.1. Fourier transform infrared (FTIR) spectroscopy

To analyze the functional groups on the parent material (medical absorbent cotton) and on CNFs and CNCs, FTIR analysis was performed. The nature of FTIR spectra presented in Fig. 1 and 2, are indicative of cellulose [27,28]. All synthesized materials showed peaks within two distinct regions. For the CNCs, significant peaks were observed within 3400-2700 cm$^{-1}$ and 1700-500 cm$^{-1}$. The peaks
recorded for the synthesized CNFs were also found between 3470-3070 cm\(^{-1}\) and 2250-540 cm\(^{-1}\). However, significant peaks recorded from the parent cotton were spread over most of the region. The O=C=O, present in the non-treated and bleached cotton, but absent in the dewaxed cotton, is assigned due to the presence of CO\(_2\) (Fig. 1). The partitioning of the significant peaks of synthesized cellulosics into two regions could only be attributed to the response in the change of frequency vibration from the original bonds of non-modified cellulose to newly formed bonds. This is in agreement with the fact that infrared spectrum of a molecule is formed from the absorption of electromagnetic radiation at frequencies that correlate to the vibration of the chemical bonds present in them [29]. Peaks between 1710 cm\(^{-1}\) and 1750 cm\(^{-1}\) were not found in any of the synthesized cellulosics in this study. This band is assigned as consequence of depolymerization [30,31]. Thus, the pretreatment and the subsequent extraction methods employed in this work ensured the structural integrity of all the forms of cellulose. The sharp peak at 1050 cm\(^{-1}\) present in all the parent materials (pretreated and non-treated cotton) is indicative of glucopyranose typical of cellulose and also showed that the pretreatment did not have any adverse effect on the parent material. A similar finding was also reported in another study [32]. The absorption band between 3500–3100 cm\(^{-1}\), which is the characteristic of stretching of –OH group of cellulose was present in all the analyzed samples [28,29,33,34]. However, the broadened nature of the peaks in that region (which was found with CNF D and CNF W samples) was vibrating with aliphatic amines (N-H) stretch due to the frequency vibrations of urea while the vibrations in the region of 1420–1370 cm\(^{-1}\) could be attributed to organic sulfates present in the thiourea [29,35].

Thioethers stretch C–S–C from the organosulfur group present in the CNFs vibrated within the region 660–630 cm\(^{-1}\). The glucopyranose reacted with NaOH (alkali) to cause “peeling” a conversion reaction of glucopyranoses by alkali [36] to shift the vibration from 1050 cm\(^{-1}\) to other forms, hence 1050 cm\(^{-1}\) peak was absent from synthesized CNFs. The presence of COO- stretch (860 cm\(^{-1}\)) on CNF D (Fig. 2. a) is stronger than CNF W (Fig. 2. b). There was no vibration at 1641 cm\(^{-1}\) on the parent
material (absorbent cotton; Fig. 1. a, b, and c) but it was observed in all synthesized cellulose samples, though the peak was significantly reduced in the CNC D1 sample. This is the frequency for absorbed water [26,37]. The methoxy stretch (CH$_3$-O-) at 2897 cm$^{-1}$ was present in all the synthesized CNCs (Fig. 3. a, b, c, and d). Although the presence of this functional group (CH$_3$-O-) is generally weak [29] amongst the CNCs, CNC D1 sample showed the weakest presence of this group (Fig. 3 c) compared to the other synthesized CNCs, which was probably as a result of prolonged interaction with H$_2$SO$_4$ and heat treatment during the hydrolysis process. From the sulfuric acid hydrolysis to obtain CNC, the peak from 1420-1300 cm$^{-1}$ is indicative of carboxylic acid [29]. This is a result of a typical deprotonation of the carboxyl group to form a carboxylate anion. The impregnation of CNCs by deprotonated carboxyl group might occur as a result of the termination of the hydrolysis with 1% NaOH.

The peak at 1205 cm$^{-1}$ is attributed to S=O linkage of inorganic sulfate peak of all the CNCs due to the esterification reaction [37], and the sharpness of the peak is an indication of the level of vibration of the band.

3.2. Scanning electron microscope (SEM) analysis

To better understand the effect of the various pretreatments, scanning electron microscopy (SEM) analysis was conducted with all cellulose samples. The SEM image of the fibers of the pretreated parent material (dewaxed and bleached absorbent cotton) shows a smooth and compacted surface with fewer signs of external fibrillation or fiber exfoliation, an evidence of the maintenance of the structural integrity of the parent material after pretreatment (Fig. 4 a and b). It was observed that the fiber structure varied in diameter (3.44-12.34 µm) after drying due to the contortion of the fibers. However, these diameters were smaller compared to the reported ones [11].

It is seen from Fig. 4 c and d that the fibers completely disappeared upon dissolution with alkali-urea-thiourea-water solution. These images showed a region of dried crystals of residual dissolution agents. The residuals are most likely due to the lack of co-precipitation reactions or the idling of the excess
dissolution agents which could not interact with the cellulose H-bonds. The particle size of the synthesized CNFs ranged between 20.72-29.30 nm (Smartiff image estimator). The CNF W sample showed similar structure as the CNF D, but could be differentiated from the CNF D by the presence of pronounce ridge-like protrusions. The SEM images of the CNFs in this study are consistent with freeze dried CNF [38], however the differences between CNF W and CNF D could be due to the influence of the nature of the crystals of the dissolution agent upon drying.

The flaky nature of all synthesized CNCs as seen in the SEM images (Fig. 4. e, f, g, and h) is typical characteristics of CNCs [20]. The width of the CNCs ranged between 12-70 nm and was consistent with other reports [39]. The broad surface or flat plate-like sheet as shown in (Fig. 4. f, g, and h) might be due to the lateral agglomeration of the nanofibers [20,40]. The stages of the fiber agglomeration processes during drying of synthesized celluloses are shown in Fig. 5 which was previously been described by [20]. It involves a series of steps which starts with the separation of free water from the cellulose fiber strand (I). The separated free water sublimes (as it has already turned into ice) to create spaces between the fibers (II). The aggregation process is initiated at stage (III) as a result of the existing H-bond between the fibers causing them to be drawn inward.

Significantly, the width of the pretreated CNC D1 was in the nanometer size, however, a previous study [20] recorded the width of CNC with freeze drying in the (µm) range. Comparatively, CNC B1 showed broader surface (Fig. 4 f). The CNC B30 sample showed rough surfaces (Fig. 4 e).

3.3. X-ray diffraction (XRD) analysis

To determine the extent of crystallinity of the synthesized cellulose samples, x-ray diffractograms were used. The patterns of different samples of cellulose, synthesized in this study, are presented in the Figs. 6 and 7. The patterns of CNC B1, CNC B30, CNC D1 and CNC D30 (Fig. 6) represent a typical semi-crystalline cellulose (I) pattern which is a proof that the optimized acid hydrolysis treatment maintained the structural integrity of the precursor. Four peaks were identified in line with ICDD database for semi-crystalline cellulose. A well-defined peak at $2\theta = 26.4^0$, a stretch of two
weak peaks between $2\theta = 16^0$ and $40^0$ ($17^0$ and $19.4^0$) and the last peak at $2\theta = 39.8^0$ with same acid hydrolysis of microcrystalline cellulose. Other workers [22], and [26] found similar patterns as found in this work but the peak at $2\theta = 39.8^0$ was absent. To better understand the nature of the first two peaks, it is worthy of noting that cellulose crystals are imperfect as a result of default amorphous sections in the structure [41].
The XRD patterns of the CNFs revealed both crystalline and amorphous nature of the fibers and a significant influence of the dissolution agents (alkali, urea, thiourea and water) was noticed. The presence of crystalline regions in a previously amorphous fiber is in line with [42], who found an increase in crystallinity of cellulose, treated with up to 8% NaOH. Various sharp peaks in the CNFs structure (Fig. 7) could likely be as a result of the influence of NaOH.

The crystalline sizes were determined using Sherrer’s approximation equation (as a result of not using all peaks in the diffractions and emphasizing on only one crystal lattice). The largest crystalline size of 33.3 nm was found with the untreated cellulose nanofibers (CNF W) and the smallest (23.29 nm) was for the bleached cellulose nanocrystals (CNC B1). The contribution of dried crystals from the dissolution agents cannot be ruled out. The approximated crystalline sizes for the cellulose samples are presented in Table 1.

3.4. Brunauer–Emmett–Teller (BET) analysis

The nitrogen adsorption-desorption isotherms and Barrett-Joyner-Halenda (BJH) adsorption-desorption isotherms from BET analyses were used to analyze the surface area, pore size distribution and pore volume of the CNCs and CNFs. The patterns of nitrogen adsorption-desorption and BET isotherms of different cellulose samples are presented in Fig. 8 and Fig. 9. The cellulose samples showed two distinct hysteresis loops. The CNCs was of type H1 hysteresis while the CNFs showed of type IV hysteresis 3 which is usual for raw cellulose and involves mesoporous adsorbents [43,44]. The hysteresis loop of the CNFs of this work was consistent with another study [45]. The BET surface area for CNC B1 was found to be 8 m²/g and an average surface area of 7 m²/g was recorded for CNC B30 and CNC D30 which indicates that fiber agglomeration was slightly higher with the bleached cotton. The least BET surface area among the CNCs was recorded for CNC D1 (0.54 m²/g) (Table 2). However, these surface areas, found in this study, were larger than CNCs prepared by acid hydrolysis reported elsewhere [46]. The BJH pore size distribution of the CNCs from adsorption isotherms was very sharp (Figs 8 b, d and h).
A higher pore volume was recorded for the CNCs compared to the CNFs (Table 2) which is consistent with another study [37]. This was however, expected since CNFs have a rigid and almost intact H-bond which can have an effect on the pore size. The H-bond of CNCs on the other hand, become flexible after hydrolysis which is seen in the pore size of this study. The surface area analyses of CNCs and CNFs show that CNCs have large surface area than CNFs (Table 2). This difference in surface area is to be expected since during synthesis, CNCs tend to aggregate fibers more than CNFs. The results also showed that the treated sample (CNF D) had a higher surface area, pore volume and pore diameter compared to the untreated one (CNF W). This indicates that the dewaxing pretreatment resulted in a greater swelling of the CNF D fibers compared to the non-treated (CNF W). This finding is consistent with a reported study [47]. Surface area and pore sizes determination is a complex venture since theoretical values vary from parent material to the next parent material [22]. The BET analysis results of cellulose samples are summarized in Table 2.

3.5. Zeta Potential

The zeta potential of all the cellulose samples was measured as a function of pH, and the results of different cellulose samples are presented in Fig. 10. Isoelectric points (IEP) were not observed for all the synthesized cellulose samples. This indicates that there is a greater effect of negatively charged surfaces and absence of the effect of protonation of treatment agents. The degree of negativity varied as a function of pH and increased with increasing pH except for CNC D30 (Fig. 10f) where there was a decrease in negativity at the highest pH of 12. Stronger negative charges were recorded with the CNCs where the average zeta potential was over -30 mV (at pH 12) except CNC B30 (Fig. 10 d) compared to the CNFs where an average of -20 mV (at pH 12). This is to be expected since hydrolysis with H₂SO₄ is known to impart sulfate groups on its surface and this results in a stronger negativity compared with HCl and other mineral acids [39]. In principle, decreasing pH invariably produces hydrogen ions (H⁺) to cause IEP in the presence of equalizing negative charges [48]. Since there was no IEP recorded in all the synthesized cellulose samples even at low pH, the strength of the negative
charges could also be attributed to the structural orientation of the cellulose. High face-edge oriented materials have been reported to cause greater negative charges [48,49].

The behavior and hence the default orientation of celluloses has been elusive [50], however edges of CNCs have been established to play a significant role in their interparticles interaction [50]. For the CNFs, thiocyanates from the dissolution agent, which was significantly present as well as COO- groups may be a probable cause of the negative surface charge. In the case of CNF D, the influence of alkoxide (CH₃CH₂OH → Na CH₃CH₂ONa + H₂) as a result of the ethanol washing during the pretreatment stage of the CNF D was not covered in this study however, it probably contributed to the higher surface negativity compared to the CNF W. The dried dissolution agent could also have contributed to their orientations which lead to the strong negative surface. The zeta potential results from this study were consistent with another study [46] who recorded no IEP of synthesized cellulose, though.

3.6. Adsorption study of CNFs

The adsorption efficiency of synthesized CNFs for lead (Pb(II)) removal from water was studied and results are presented in Fig. 11. It was found that CNF D sample showed the highest percentage of lead removal reaching an average of up to 91.49%. Furthermore, adsorption equilibrium was achieved in less than 20 min (Fig. 11a). The CNF W was able to remove ca. 66.48% Pb(II) after 130 min. (Fig. 11b). The efficiency of CNF D towards lead adsorption is most likely due to the electrostatic interaction between negatively charged CNFs surface and positively charged lead ions.

4. Conclusions

This work provides insights into aspects of CNFs obtained by dissolution of treated and untreated absorbent cotton in alkali-urea-thiourea solution as well as features of CNCs obtained by acid hydrolysis of treated absorbent cotton for different hydrolysis durations. Surface charges of the celluloses were highly negative and the CNCs had higher negativity averaging over -30 mV (at pH 12) compared to the CNFs of -20 mV (at pH 12). Furthermore, the BET surface area, pore volume
and pore diameter of the CNCs were found to be higher compared to the CNFs. The SEM images showed the porous nature of the CNFs and the flaky nature of the CNCs. The pretreatment options maintained the structure of the celluloses as none of the celluloses exhibited fiber degradation. The synthesized CNF D showed a better potential as an adsorbent with high lead removal efficiency (91.49%) and also had a slightly higher BET surface area (0.47 m²/g) and bigger pore diameter (59.87 Å) compared to waxed cellulose nanofibers (CNF W) (0.38 m²/g and 44.89 Å). The characterization results suggested that the materials can be used in different applications including nanocomposite synthesis and water treatability studies.

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References


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**Figure Caption**

**Table 1.** Crystalline sizes of all synthesized cellulose samples.

<table>
<thead>
<tr>
<th>Cellulose</th>
<th>Crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNC-B1</td>
<td>23.29</td>
</tr>
<tr>
<td>CNC-B30</td>
<td>24.90</td>
</tr>
<tr>
<td></td>
<td>CNC-B1</td>
</tr>
<tr>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>Surface area</td>
<td>8.00 m²/g</td>
</tr>
<tr>
<td>Pore volume (desorption)</td>
<td>0.02 cm³/g</td>
</tr>
<tr>
<td>Pore diameter (desorption)</td>
<td>113.39 (Å)</td>
</tr>
</tbody>
</table>

**Table 2.** Surface area, pore volume and pore diameter analyses of cellulose samples.
Fig. 1. FTIR spectra of non-treated medical absorbent cotton (a), bleached medical absorbent cotton (b) and dewaxed medical absorbent cotton (c).

Fig. 2. FTIR spectra of CNF D (a), non-treated cellulose nanofibers CNF W (b).
Fig. 3. FTIR spectra of CNC B1 (a) CNC B30 (b), CNC D1 (c) and CNC D30 (d).

Fig. 4. Scanning electron microscope (SEM) images of bleached cotton fibers (a), dewaxed cotton fibers (b), CNF D (c), CNF W (d), CNC B30 (e), CNC B1 (f), CNC D30 (g) and CNC D1 (h).
**Fig. 5.** Schematic representation of lateral agglomeration during the freeze drying of CNCs suspension. Source [20].

**Fig. 6.** XRD spectra of synthesized cellulose samples (CNC B1, CNC B30, and CNC D1) showing peak indices.

**Fig. 7.** XRD spectra of synthesized cellulose samples (CNF D and CNF W) showing peak indices.
Fig. 8. Nitrogen adsorption-desorption BET isotherms of CNC B1 (a), CNC B30 (c), CNC D1 (e), and CNC D 30 (g) and Barrett-Joyn-Halenda (BJH) pore size distribution plots (b, d, f and h).
**Fig. 9.** Nitrogen adsorption-desorption BET isotherms of CNF D (a) and CNF W (c) and Barrett-Joyner-Halenda (BJH) pore size distribution plots (b and d).
Fig. 10. Zeta potential as a function of pH of CNF D (a), CNF W (b), CNC B1 (c), CNC B30 (d), CNC D1 (e), and CNC D30 (f).
Fig. 11. Percentage removal of lead (Pb) by the synthesized CNF D (a) and CNF W (b) from aqueous solution as a function of time.