

Comparison of water adsorption properties of cellulose and cellulose nanocrystals studied by near-infrared spectroscopy and gravimetry

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Abstract. The adsorption properties of water molecules on cellulose and cellulose nanocrystals (CNCs), isolated from defatted rice bran (DRB) by 55% sulfuric acid hydrolysis under sonication were investigated. The powdered samples of cellulose and CNCs were analysed by using near infrared spectroscopy (NIR) and gravimetry at 38% and 55% humidities. Small amounts of samples were dried under vacuum at 120°C and the NIR spectra of the dry samples and their spectra during the adsorption water molecules were measured by using an NIR spectrometer equipped with a transmittance accessory and a DTGS detector. The quantitative adsorption of water molecules by the samples was determined by gravimetry. Second and fourth derivative profiles of the NIR spectra were used in understanding the chemistry of adsorption of water molecules and the adsorption processes by the samples.

The results show that the adsorption of water molecules by the cellulose samples gives rise to three prominent peaks that can be related to the water molecules engaged in hydrogen bonding with C2, C3 and C6-OH groups on the glucose units of the cellulose polymers. Furthermore, the cellulose nanocrystals adsorb twice as much of water as the cellulose polymer. It is also clear from the results that C2 and C3-OH groups in the glucose units adsorb water molecules at a faster rate than the C6-OH group and responsible for nearly 50% of the water adsorption.

Introduction

Cellulose is the most abundant natural polymer on the earth and also present in a wide variety of living species, such as plant, algae, fungi and bacteria. It is a polysaccharide with the common formula $(C_6H_{10}O_5)_n$ and consists of several linear chain of β -1,4-linked glucopyranose units that form a high-molecular-weight linear homopolymer. The repeating unit of this natural polymer is a dimer of glucose, known as cellobiose [1]. The inter-chain hydrogen bonding of cellulose is contributed by the presence of three hydroxyl (OH) groups. The strong hydrogen bonds between the -OH groups of cellulose molecules can stabilize the cellulose chain into a highly ordered structure through crystalline packing, giving the good strength and insolubility in most solvent. Some part of cellulose chains without -OH groups could not be stabilized laterally through hydrogen bonding, resulting in the formation of disordered amorphous regions which have lower density than crystalline regions and more available for hydrogen bonding with other molecules such as water [2]. Cellulose has received much attention for many applications in recent years, especially nanoscale cellulose materials. CNCs is a suitable nanomaterial for a wide range of applications such as synthesis of antimicrobial and medical materials, biosensing and stabilizing agent [3]. Several processes were used for CNC preparation, but the popular method is the hydrolysis using concentrated sulfuric acid, which gives nanocrystals with anionic sulfate half-ester groups on their surface through the esterification of hydroxyl groups. The strong acids can easily penetrate into amorphous parts, lead to remove the disordered amorphous fractions and leaves the highly crystalline parts, which exhibits a rod or needle-like structure [2]. Therefore, compared to original cellulose, which consisted of large amount of

amorphous region, CNCs present higher specific strength, modulus, surface area, and unique liquid crystalline properties. The morphology and properties of CNCs depend on the original cellulose. There are many natural raw material sources from agro-waste that have been used as a raw material for the production of CNCs. Recently, defatted rice bran (DRB) was used as a cellulosic source for the production of CNCs. Rice bran is a by-product of rice-milling and also the source of rice bran oil extraction, which leaves DRB as an agricultural waste [4]. Compared to cellulose, CNCs have the same chemical structure, but contain less amorphous part, less degree of polymerization and smaller particle size. The nanosized cellulose has a high surface area that probably attached by the other molecules such as water. The aim of this paper is to study and compare the water adsorption properties of CNCs compared to microcrystalline cellulose to show where and how water molecules are adsorbed. Near infrared spectroscopy was chosen as the preferred analytical technique. Christy [5-7] has used near infrared spectroscopy in combination with second and fourth-derivative techniques and gravimetry to show the water adsorption properties of silicagel and silicagel related materials [5-7]. A similar approach was used in following the adsorption behavior of water on cellulose and CNCs surface.

Experimental

Materials and preparation of the samples. Microcrystalline cellulose was purchased from Sigma-Aldrich. Cellulose nanocrystal (CNCs) was isolated from defatted rice bran (DRB) by 55% sulfuric acid hydrolysis under sonication. The size and zeta potential of CNCs were determined by nanoseries model S4700 (Malvern Instrument) and SZ-100 nanopartica series zetasizer (Horiba). Before measuring, all samples were dried at 120°C using a ceramic heater (BA Electric Bunsen from Electro thermal, Staffordshire, U.K.). A powerful vacuum pump (Edwards, West Sussex, U.K.) was used to evacuate the water adsorbed on sample and connected with K-type thermocouple to measure the temperature during heating. The NIR spectra measured and gravimetry of water adsorption of both cellulose and CNCs were investigated depend on the relative humidity (RH) of the surrounding. The humidity of the room during the measurements was 38%. Humidity of 55% was achieved by a glycerol/water system [8].

Near infrared (NIR) measurements. The NIR measurements were made using a Perkin-Elmer Spectrum One NTS FT-NIR spectrometer (Perkin-Elmer Ltd., Cambridge, U.K.) equipped with a transmittance accessory and deuterated triglycine sulfate (DTGS) detector. The dried sample was measured in close system first to avoid water adsorption, then exposed to air in the room. The increase in adsorption of water was followed by collecting NIR spectra every 5 min in the range of 10000-4000 cm^{-1} for 2-3 hours. All NIR spectra were transformed to log (1/R) format. The second and fourth derivative profiles of the spectra were calculated by an algorithm developed by Savitzky and Golay with a 19-point derivative width.

Gravimetric measurements. The gravimetric analysis of water adsorption was carried out by placing the dried sample on a Mettler electronic balance connected to a computer through an RS-232 port for data collection. The increasing of mass of sample was recorded twice every second using locally made software.

Results and discussion

The dynamic light scattering measurement presented the mean diameter of CNCs of 126.2 nm and zeta potential of -48.4 mV. Producing CNCs through sulfuric acid hydrolysis generated a negative charge on their surface which prevented the aggregation of CNCs [2]. The cellulose that used in this study was microcrystalline cellulose, which has a particle size of 51 μm . Water molecules are found to be adsorbed on both of cellulose and CNCs surface. In the literature, water adsorption of the other carbohydrate polymers such as amylose, amylopectin and acyclic oligosaccharides of α -glucose were investigated using NIR spectroscopy and gravimetry [8, 9]. The analysis revealed that the

carbohydrate skeleton and OH groups did not adsorb in the range of 5300-5000 cm^{-1} . The only adsorption in this range came from the combination frequencies of the OH stretching and bending vibration frequencies of the water molecule. The water molecular adsorption on glucose units of cellulose or CNCs by hydrogen bonding is shown in Fig. 1. Each OH group of a glucose unit can form hydrogen bond with one water molecule. According to NIR spectrum displayed only one OH combination bands for each OH group of glucose which belong to the symmetric OH stretching vibrations of water molecules [10].

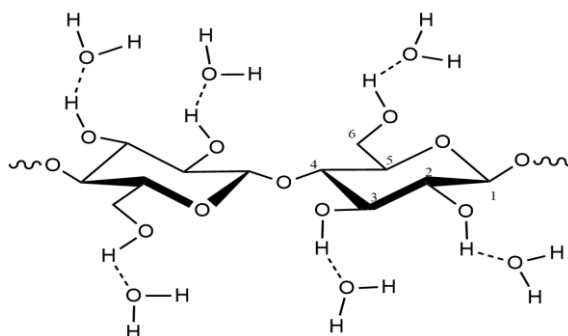


Fig. 1. Model for adsorption of water molecule on cellulose and CNCs.

The near infrared spectra of the each dry sample was measured first. Then the sample was exposed to surrounding air and their adsorption evolution was followed in regular time intervals (Fig. 2). The NIR spectrum exhibited a unique peak in the range of 5300-5000 cm^{-1} because of the combination frequency of water molecular OH stretching and bending vibrations. All spectra revealed increase in intensity of the peak representing the OH combination frequencies. The results revealed that at a relative humidity of 38% CNCs could adsorb water molecule for 155 min until it became saturated. This adsorption was at a rate faster than cellulose. However, the OH combination peak appears as a single peak. The second-derivative profiles as shown in Fig. 3 revealed more structure lying under the peak. Moreover, it is obviously seen that there are three prominent bands for cellulose and two prominent bands for CNCs in fourth-derivative profiles of the NIR spectra in the range of 5300-5100 cm^{-1} .

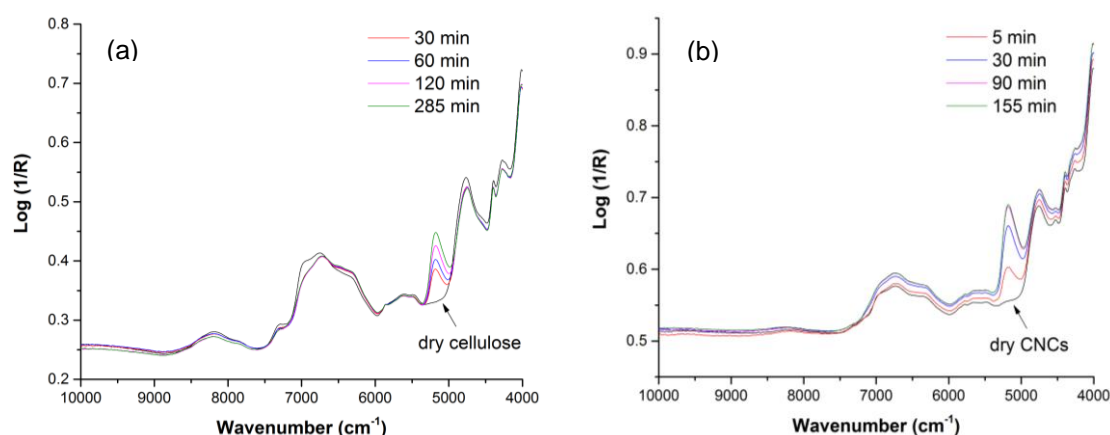


Fig. 2. NIR spectrum of (a) cellulose (b) CNCs before and after adsorption of water

Several other carbohydrate polymers and their derivatives exhibited similar spectral structure in the NIR range of 5300-5100 cm^{-1} and presented the assigning of these bands to water molecules bound to specific OH groups in glucose units [8, 9]. The water molecules adsorbed on to the C2-OH and C3-OH groups give rise to an adsorption band at 5240 cm^{-1} for cellulose and 5250 cm^{-1} for CNCs. The band at 5212 cm^{-1} from cellulose spectra comes from the water molecules adsorbed on C6-OH groups, whereas the CNCs spectra exhibited the peak at 5216 cm^{-1} . The adsorption of water molecules on C1-OH position present only in cellulose spectra at 5168 cm^{-1} . This suggests that CNCs have

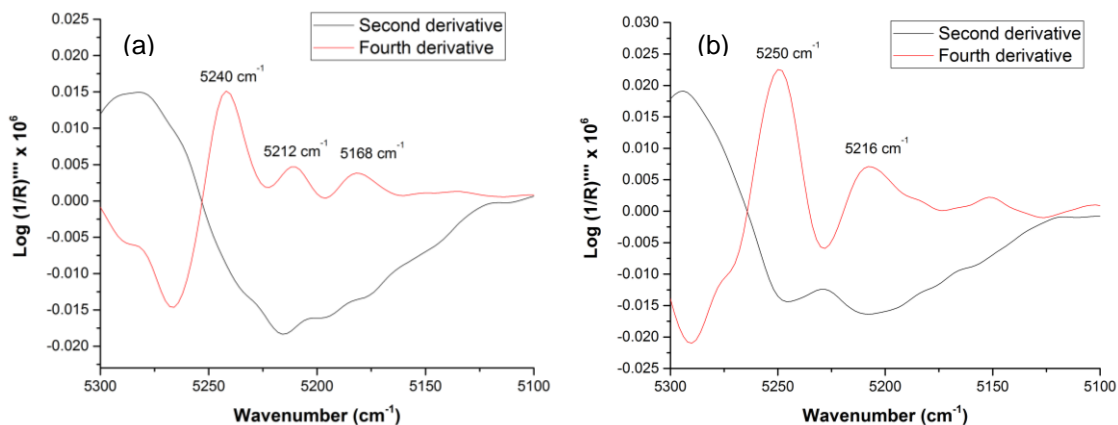


Fig. 3. Second and fourth-derivative profiles of NIR spectra of (a) cellulose and (b) CNCs with adsorbed water molecules in range of 5300-5100 cm^{-1} .

stronger inter-molecular hydrogen bonding through C1 and C4-OH than cellulose. This results in low availability of the C1 and C4-OH groups on glucose units of CNCs for forming hydrogen bond with water molecules. All of these bands of CNCs exhibited slight gradual red shift compared to the relative bands of cellulose. The associated red shift occurs because the water molecules form weaker hydrogen bonding with CNCs than cellulose [11], implying that the inter-molecular hydrogen bonding of CNCs molecules are stronger.

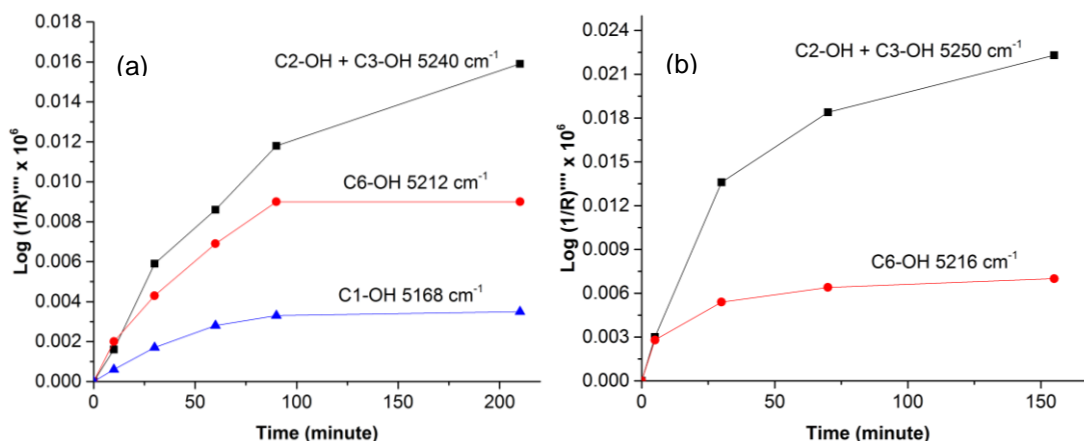


Fig. 4. Time correlations of the intensities of the fourth-derivative bands, which related to the rate of water adsorption of (a) cellulose and (b) CNCs.

The rates of increase in the intensities, which related to the adsorption of water molecules onto C1-OH, C2-OH, C3-OH and C6-OH positions of cellulose and CNCs are shown in Fig. 4. The results indicated that combination bands of C2-OH and C3-OH groups have the highest adsorption rate for both of cellulose and CNCs. Moreover, CNCs had the highest adsorption rates of these bands compared to cellulose. The unfavorable energetic position of C6-OH groups in glucose units led to a low rate of water adsorption in both of cellulose and CNCs [12]. The hydroxyl groups at the C6 position were found to be favorably engaged in an inter-molecular hydrogen bonding that lead to the formation of a crystalline part of cellulose and CNCs [13]. Thus, C6-OH groups are less available hydrogen bonding with water molecules than C2 and C3-OH groups. Furthermore, previous work revealed that C2 and C3-OH groups is a better hydrogen bond donor [14], resulting more capability to form hydrogen bonding with water molecule.

The gravimetric analysis was used to measure the amounts of water adsorbed by dried samples at different humidities (Fig. 5). Both cellulose and CNCs can adsorb more water at the higher humidity. In addition, the results demonstrated that CNCs have relatively higher adsorption and adsorb twice as much of water molecules as the cellulose polymer. The mass of water adsorbed by CNCs had much higher rates of adsorption of water molecules compared to cellulose during the first

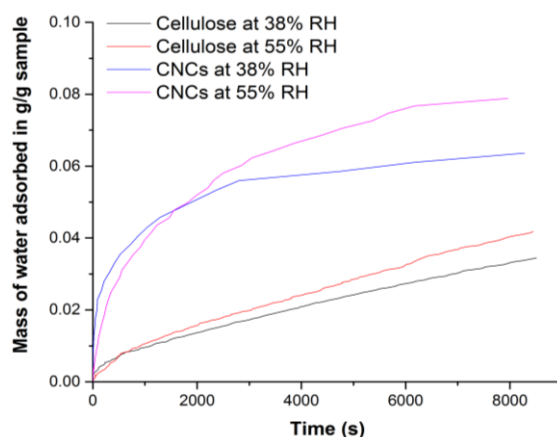


Fig. 5. The mass of water adsorbed by cellulose and CNCs as a functions of time at 38% and 55% relative humidity.

30 minutes then reached equilibrium at 50 and 100 minute for 38% and 55% relative humidities respectively. The mass of water adsorbed by cellulose increased gradually. CNCs have the smaller particle size than cellulose, thus it has more surface area that can form a large number of hydrogen bonding with water molecules.

Conclusions

The second and fourth-derivative profiles of NIR spectra were used to study the adsorption of water molecules on cellulose and CNCs. The results showed that the water molecules were preferentially attached on C2-OH and C3-OH groups by these two polymers. However, CNCs have high rate of adsorption of water molecules compared to cellulose. This is in agreement with gravimetric measurement, which used to investigate the quantitative adsorption of water molecules by the dried samples. As can be seen from the results, cellulose adsorbs lower amounts of water molecules at the same humidities compared to CNCs. The results also reveal that the combination of near infrared spectroscopy and derivative techniques can provide valuable information about water molecular adsorption onto solid surfaces containing polar groups.

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