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Short communication

The reuse of wastepaper for the extraction of cellulose nanocrystals

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ABSTRACT

The study reports on the preparation of cellulose nanocrystals (CNCs) from wastepaper, as an environmental friendly approach of source material, which can be a high availability and low-cost precursor for cellulose nanomaterial processing. Alkali and bleaching treatments were employed for the extraction of cellulose particles followed by controlled-conditions of acid hydrolysis for the isolation of CNCs. Attenuated total reflectance Fourier Transform Infrared (ATR FTIR) spectroscopy was used to analyze the cellulose particles extracted while Transmission electron microscopy images confirmed the presence of CNCs. The diameters of CNCs are in the range of 3–10 nm with a length of 100–300 nm while a crystallinity index of 75.9% was determined from X-ray diffraction analysis. The synthesis of this high aspect ratio of CNCs paves the way toward alternative reuse of wastepaper in the production of CNCs.

1. Introduction

Cellulose, a type of polysaccharides, which is in abundant consists of both crystalline phase and amorphous region. The removal of the amorphous region by acid hydrolysis results in the formation of highly ordered (crystalline) structure, the cellulose nanocrystal (CNCs). Reviews in the field of cellulosic nanomaterial has been reported by Moon, Martini, Nairn, Simonsen, and Youngblood (2011), Lin, Huang, and Dufresne (2012), Klemm et al. (2011) and Azizi Samir, Alloin, and Dufresne (2005). The geometry and characteristic of CNCs made it an ideal material for various potential applications such as in biomedical (Wang & Roman, 2011), gel nanomaterial (Heath & Thielemans, 2010), polymer nanocomposite membrane (Paralikar, Simonsen, & Lombardi, 2008), and polymer electrolyte (Azizi Samir, Alloin, Gorecki, Sanchez, & Dufresne, 2004).

Preparation of CNCs can be achieved through isolation of cellulose particles from many sources such as tunicate (Anglès & Dufresne, 2000), bacteria (Roman & Winter, 2004), ramie (Peresin, Habibi, Zoppe, Pawlak, & Rojas, 2010), sisal (Garcia De Rodriguez, Thielemans, & Dufresne, 2006), cotton (Uddin, Araki, & Gotoh, 2011), *mengkuang* leaves (Sheltami, Abdullah, Ahmad, Dufresne, & Kargarzadeh, 2012) and wood pulps (Dong et al., 2012).

Wastepaper, being a cellulose biomass provides a potential source of raw material for the production of CNCs. Several million tons of paper which are produced and used globally undoubtedly gives rise to a tremendous amount of wastepaper. Despite recycling efforts, wastepaper continues to constitute considerably to the municipal and industrial waste. Recycling of wastepapers results in a lower grade paper due to shortening of the fiber length and the paper quality is far poorer than a paper made from virgin pulps. Since the maximum ratio of paper-to-paper recycling is reported to be 65% (Ikeda, Park, & Okuda, 2006), this results in the production of large quantities of by product which ultimately have to be disposed. With higher cost of producing paper from recycled paper, and disposal of waste fibers unfit for use, finding alternative ways to recycle wastepaper is a necessity. Due to its cellulosic content, wastepaper has the potential as a source material for the production of cellulose nanocrystals (CNCs). The production of CNCs from wastepaper would provide an alternative to paper recycling and possibly address the issue of byproducts arising from paper to paper recycling.

To the best of our knowledge, the use of wastepaper as the raw material for the extraction of CNCs has not been reported. In this work, the extraction of cellulose particles from wastepaper was carried out by subjecting wastepaper to alkali and bleaching treatments followed by controlled-condition of acid hydrolysis for the isolation of CNCs. The aim of the alkali treatments is to ensure

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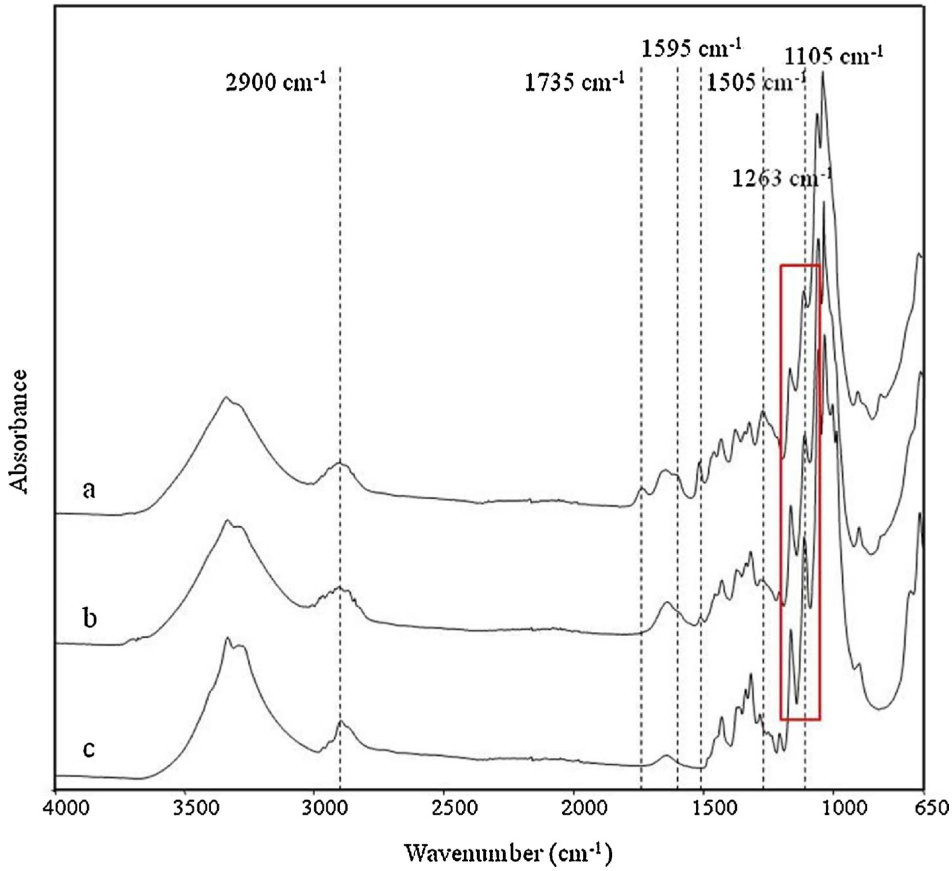

Fig. 1. FTIR spectra of (a) raw wastepaper, (b) treated wastepaper, and (c) pure cellulose.

the hydrolysis of hemicelluloses and removal of undesirable amorphous type polymer components, while the bleaching treatment is primarily aimed at removing lignin (Cherian et al., 2010; Li et al., 2009; Ndazi, Nyahumwa, & Tesha, 2007). Successful treatment will result in the extraction of semicrystalline cellulose particles.

Physical chemical characterizations were carried out by ATR FTIR spectroscopy, scanning electron microscopy (SEM), transmission electron microsopy (TEM), and X-ray diffraction (XRD).

2. Experimental

2.1. Extraction of cellulose particles

The wastepaper used in this work was sourced from old newspaper, cut into small pieces and boiled for more than 12 h, during which distilled water was added periodically. It was then ground to form a slurry, filtered and rinsed several times with distilled water. The slurry was re-boiled and treated with 5% (w/v) reagent grade sodium hydroxide, NaOH (Merck) followed with 2% (v/v) of reagent grade sodium hypochlorite, NaClO (Rinting Scientific). The slurry was then filtered and washed with distilled water until neutral pH was achieved. The resulting material was analyzed using ATR FTIR Spectroscopy to confirm the presence of cellulose particles from the source material. Cellulose powder was purchased from (Sigma-Aldrich) and was used as a reference material.

2.2. Preparation of cellulose nanocrystals

The procedure for the preparation of CNCs was adapted from Sheltami et al. (2012) whereby CNCs were obtained by acid hydrolysis of the pretreated source material using 60% (v/v) H_2SO_4 solution at 45 °C with constant stirring. The optimum reaction time was

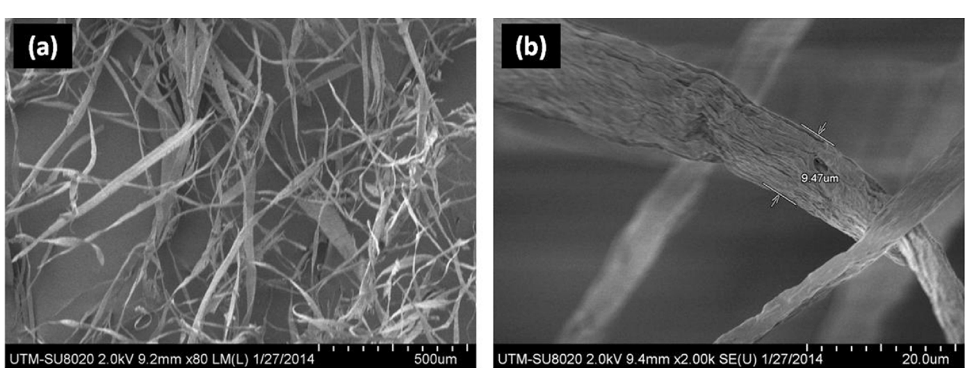

Fig. 2. FESEM images of cellulose particles extracted from wastepaper at (a) 80× magnification (b) close-up of the individual fiber at 2000× magnification.

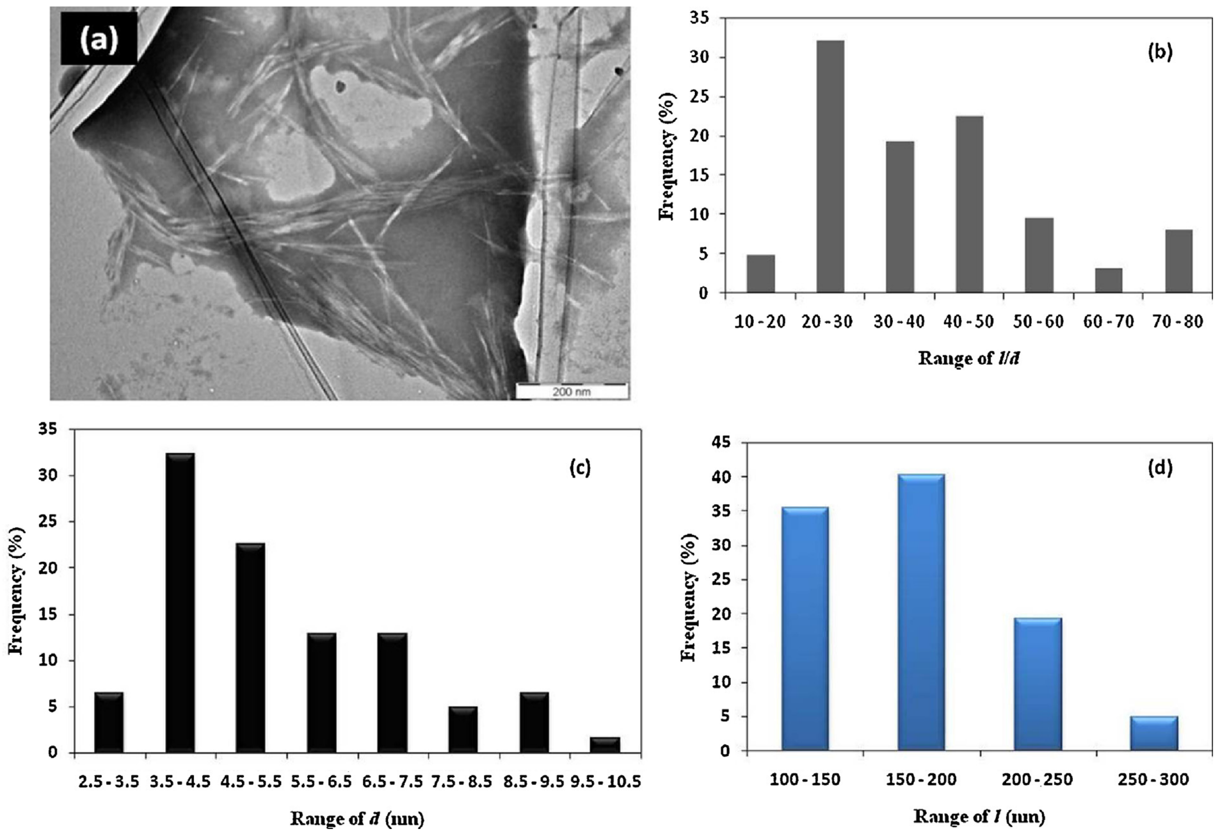

Fig. 3. (a) TEM image of CNCs, (b) distribution of aspect ratio, (c) diameter and (d) length of CNCs.

fixed at 1 h with pretreated solution to acid ratio of 1:2 (v/v). The mixture was diluted with distilled water followed by centrifugation to remove spent acid. The suspension was then subjected to dialysis against distilled water until a constant pH was obtained.

2.3. Imaging analysis

The morphology of the extracted cellulose particles were observed by Field emission scanning electron microscope (FESEM) (Hitachi SU8020) with an accelerating voltage of 2 kV and sample was gold coated to prevent charging. Transmission electron microscopy (TEM) images and dimensions of the cellulose nanocrystals were recorded on TEM Philips CM12 operating at 80 kV. The suspension of cellulose nanocrystals was deposited on the grid and left for 5 min. The grid was then stained using 2% phosphotungstic acid (PTA) for 5 min and dried before analysis.

2.4. X-ray diffraction (XRD)

The crystallinity of the wastepaper and CNCs in comparison with pure cellulose was studied using an X-ray diffractometer (D5000, Siemens) equipped with Cu*K*α radiation (λ = 0.1541 nm) in the 2θ range 5–70°. The operating voltage was 40 kV, and the current was 30 mA.

3. Results and discussion

3.1. Extraction of cellulose particles

The ATR FTIR spectra of raw wastepaper, treated wastepaper and pure cellulose are shown in Fig. 1. The C═O band observed at ~1735 cm^{-1} in raw wastepaper spectrum, assigned to the acetyl stretching from hemicelluloses (Alemdar & Sain, 2008), was no longer observed in the treated wastepaper spectrum, indicating that the alkali treatment has successfully removed hemicelluloses (Ndazi et al., 2007). The observed bands at ~1505 cm^{-1} and ~1595 cm^{-1} in the wastepaper spectrum, ascribed to C═C in-plane aromatic vibrations indicates the presence of lignin while the band located at 1263 cm^{-1} is attributed to C—O—C stretching from ether linkage of lignin. The absence of these bands in FTIR spectrum of the treated wastepaper (in similar comparison with pure cellulose spectrum) suggests the effectiveness of bleaching treatment in removing lignin (Cherian et al., 2010).

The C—C ring breathing band and C—O—C glycoside ether band at ~1155 cm^{-1} and ~1105 cm^{-1}, respectively, is attributed to the presence of cellulose in the wastepaper (Garside & Wyeth, 2003). The intensities of these bands, i.e. at ~1155 cm^{-1} and 1105 cm^{-1} increased after the treatment process with respect to the relative intensity of polysaccharide components. The band at 2900 cm^{-1}, observed in all samples corresponds to C—H stretching vibration reflecting the general organic content (Garside & Wyeth, 2003).

The FESEM micrographs (Fig. 2a) show the fibrous structure of the cellulose particles extracted from the wastepaper after both pretreatments process. The diameters ranged from 5–40 μm and a longitudinal examination of the cellulose is shown in Fig. 2b.

3.2. Isolation of cellulose nanocrystals

The extracted cellulose particles were used for the isolation of CNCs. Transmission electron microscopy image (Fig. 3a) indicates rod-like structures of CNCs with some of the individual CNCs arranged longitudinally due to hydrogen bonding (Heath & Thielemans, 2010). The distribution of their aspect ratio, diameters and length are shown in Fig. 3b, c and d, respectively. More than 70% of the CNCs has an aspect ratio in the range 20–50. The diameter of the CNCs ranged from 3 to 10 nm while the length ranged from 100

Table 1
Geometrical dimensions of CNCs prepared from various source material.

Source material	Length (nm)	Diameter (nm)	References
Wastepaper	100–300	3–10	This study
Cotton	100–150	10–15	Uddin et al. (2011)
Tunicate	500–1000	10	Anglès and Dufresne (2000)
Bacteria	100–1000	5–10	Roman and Winter (2004)
Ramie	100–250	3–10	Peresin et al. (2010)
Sisal	100–500	3–5	Garcia De Rodriguez et al., 2006
Mengkuang leaves	200 (average)	10–20	Sheltami et al. (2012)
Wood pulps	190–660	17 (average)	Dong et al. (2012)
	100–200	3–4	Araki, Wada, Kuga, and Okano (1998, 1999)
	100–150	4–5	Beck-Candanedo, Roman, and Gray (2005)
Avicel	90 ± 50	10 ± 4	Liu et al. (2011)

to 300 nm with an average value of ∼4 nm and ∼170 nm, respectively. This diameter is similar to the values reported for CNCs obtained from bacterial (Roman & Winter, 2004), ramie (Peresin et al., 2010) and sisal (Garcia De Rodriguez, Thielemans, & Dufresne, 2006). The average diameter and length of the CNCs are lower than the average value of 17 nm and 380 nm reported for CNCs extracted from wood pulps, respectively (Dong et al., 2012). The aspect ratio of the CNCs is higher when compared to the value of 10–15 for CNCs produced from Avicel (Liu, Chen, Yue, Chen, & Wu, 2011). The geometrical dimensions of CNCs prepared from various source materials are summarized in Table 1. The resultant CNCs suspension was approximately 0.04% (i.e. 0.44 mg/mL) by weight and the yield was ca. 19%. This yield is slightly lower compared to the value of 20% for CNCs extracted from microcrystalline cellulose by Valentini, Bon, Fortunati, and Kenny (2014). On the other hand, the percentage yield of CNCs obtained from wood pulps is higher (33–50%), as reported by Dong et al. (2012).

3.3. X-ray diffraction studies

X-ray diffraction analysis was conducted to probe the crystallinity of the cellulosic particles. The XRD patterns for the wastepaper, CNCs and pure cellulose are shown in Fig. 4a, b and c, respectively. The XRD spectra show the highest diffraction peak ca. $2\theta = 22.7^\circ$, which corresponds to the crystalline structure of cellulose I, whilst the low diffraction peak ca. $2\theta = 18^\circ$ represents the amorphous background (Sheltami et al., 2012). Based on the diffraction pattern, the crystallinity index (*CrI*) was calculated using Segal's method (Segal, Creely, Martin, & Conrad, 1959) from the following relation:

$$CrI = \left(\frac{I_{22.7} - I_{18}}{I_{22.7}}\right) \times 100\%$$

The *CrI* values listed in Table 2 indicates that the crystallinity index for the CNCs (75.9%) increased after chemical extraction of the wastepaper (65.8%). On the other hand, the *CrI* of pure cellulose is higher due to the higher proportion of cellulose I crystallites present. This observation is further corroborated by X-ray diffraction pattern of the samples as shown in Fig. 4. The *CrI* for the CNCs is higher than the value of CNCs extracted from pineapple leaf fibers (73.6%) by Cherian et al. (2010) and CNCs from *mengkuang* leaves (69.5%) reported by Sheltami et al. (2012). However, it is lower than CNCs from Avicel (81%) by Filson and Dawson-Andoh (2009).

Table 2
Crystallinity index of the wastepaper, CNCs and pure cellulose.

Samples	2θ (amorphous) (°)	2θ (crystalline) (°)	*CrI* (%)
Wastepaper	18.1	22.8	65.8
CNCs	18.1	22.6	75.9
Pure cellulose	18.0	22.7	91.0

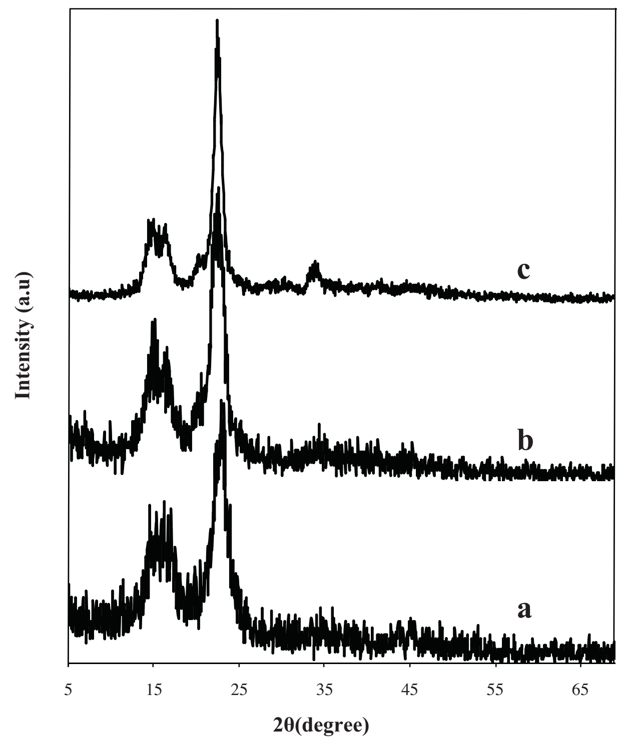

Fig. 4. X-ray diffraction patterns of (a) wastepaper, (b) CNCs and (c) pure cellulose.

4. Conclusion

The preparation of CNCs from wastepaper via simple pretreatment and hydrolysis process was discussed. FTIR analysis supports the effectiveness of the pretreatment while TEM observation indicates the nano-dimension of the CNCs with a length ranged in 100–300 nm. The crystallinity index of the extracted CNCs (75.9%) is comparable to other reported values. Given the abundance of wastepaper, and the need to reduce waste generated from paper to paper recycling, the study has demonstrated that wastepaper, specifically newspaper can serve as a precursor for the production of CNCs, while providing an alternative to paper recycling.

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