Cellulose nanocrystals derived from hemp agrowaste: A value-added biomass product for sustainable hemp farms

Abhishek Bhattacharjee[1], Ketul C. Popat[1,2,3], Yan Vivian Li[1,2,4]

[1]School of Advanced Materials Discovery, Colorado State University, Fort Collins

[2]School of Biomedical Engineering, Colorado State University, Fort Collins

[3]Department of Mechanical Engineering, Colorado State University, Fort Collins

[4]Department of Design and Merchandising, Colorado State University, Fort Collins

Keywords: Cellulose nanocrystal, hemp, agricultural waste, sustainability

Introduction: The Agriculture Improvement Act of 2018 legalized hemp cultivation in the USA. Since then, the production of hemp has been rapidly increasing. With an increase in the hemp production comes an increase in agricultural waste (agrowaste). The hemp agrowaste is rich in cellulose but is discarded as landfill. A sustainable reuse of this waste is necessary to reduce the amount of landfill from the increased hemp cultivation around the USA. Recently, nanocellulose such as cellulose nanocrystals (CNC) are gaining popularity as a reinforcing material because of its superior strength, sustainable source, and biocompatibility. Because hemp agrowaste is rich in cellulose, CNC can be sustainably produced from the discarded hemp agrowaste, which adds economical value to the waste products from the hemp farms. A popular method of producing CNC from a cellulosic source is hydrolysis method where hemicellulose and lignin are dissolved by a strong acid and pure cellulosic crystals are collected. However, before the acid hydrolysis, the cellulosic source needs to be pretreated. Generally, sodium hydroxide (NaOH) is used along with a bleaching agent for the pretreatment purpose. But these methods use a lot of toxic chemicals, water, and energy. To make the CNC preparation process more sustainable, recently enzymatic pretreatment was introduced which uses pectinase enzyme instead of NaOH and bleaching agent (Luzi et al., 2014). Also, a one-step CNC preparation method was recently developed where a strong oxidative agent (ammonium persulfate, APS) is used to hydrolyze lignin and hemicellulose from cellulosic source (Leung et al., 2010). In this work, CNCs were prepared from hemp agrowaste using three different synthesis methods: (1) alkaline pretreatment and acid hydrolysis, (2) enzymatic pretreatment and acid hydrolysis, and (3) one-step oxidation method using APS. The resulting products were characterized to study morphological and chemical properties of the CNCs. Future work includes applications of the resulting CNCs in nanofiber-based biosensors, antibacterial agents, and reinforcing materials.

Materials and methods: Hemp agrowaste were collected and grinded by using a commercial blender to make hemp powders. The hemp powder was used for subsequent processing to prepare CNC. For (1) alkaline pretreatment and acid hydrolysis method, the procedure described by de Rodriguez et al. (2006) and Henrique et al. (2013) was followed and CNC-alk was prepared. For (2) enzymatic pretreatment the work from Luzi et al. (2014) was adapted, however the acid hydrolysis procedure was same as the process (1). The CNC prepared from enzymatic pretreatment and acid hydrolysis was named as CNC-enz. The one-step oxidation technique (3) described by Leung et al. (2010) was followed to prepare CNC-APS. To characterize the chemical properties of CNCs, Attenuated Total Reflectance- Fourier Transform Infrared (ATR-FTIR) spectroscopy was used to collect spectra for raw hemp and prepared CNCs. For morphological analysis, optical microscope (OM) and scanning electron microscope (SEM) were used.

Results and Discussion: From the FTIR spectra analysis, it was found that the enzymatic pretreatment was inferior in removing pectin, wax, and other impurities from the hemp agrowaste compared to the alkaline pretreatment. The peaks at 1730 cm^{-1} and 1232 cm^{-1} wavenumbers are missing in the alkaline pretreated hemp waste, which indicates strong pretreatment reaction. However, these peaks were still present in the enzymatically pretreated hemp waste. There was no significant difference in the FTIR spectra between raw hemp waste and enzymatically pretreated hemp waste, indicating weak pretreatment reaction by pectinase enzyme. After acid hydrolysis treatment on both alkaline and enzyme pretreated hemp agrowaste, the cellulose content was improved which is indicated by increased intensity of peaks at wavenumbers 3328, 3331, 2897, 2894, 1031 and 1029 cm^{-1}. The most improved CNC content was found after the one-step oxidation method which produced CNC-APS. Intense peaks at wavenumbers 3328 and 1029 cm^{-1} indicates high cellulose content. Moreover, the peaks of pectin and lignin at 1730 and 1232 cm^{-1} was not observed for CNC-APS, which indicated successful removal of the impurities from hemp agrowaste. Figure 1 also showed the morphological analysis of the CNC-alk particles. OM image indicated several rod-shaped particles which is indicative of CNCs described in the literature. SEM images showed a network of rod-shaped particles (Figure 1).

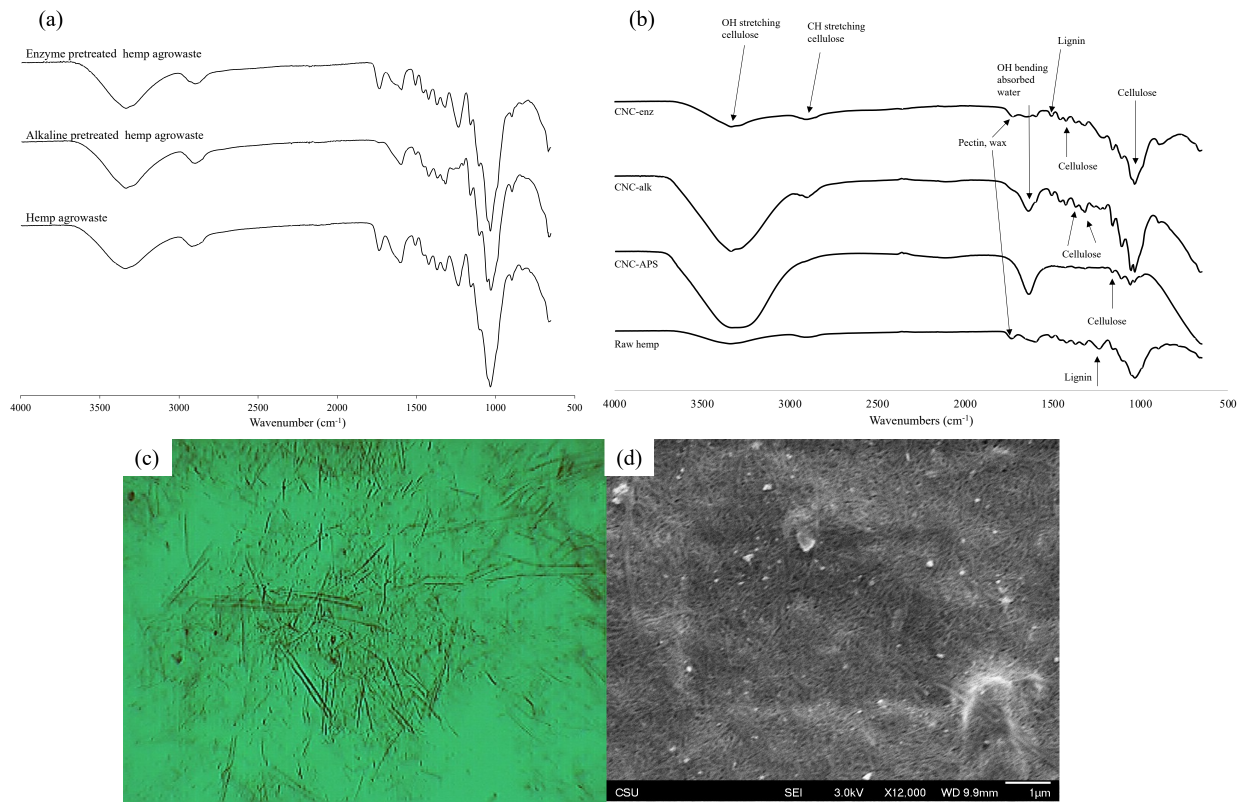

Figure 1. (a) ATR-FTIR spectra of alkaline and enzyme pretreated hemp agrowaste, (b) ATR-FTIR spectra of prepared CNCs, (c) OM and (d) SEM images of CNC-alk

Conclusion: Cellulose nanocrystals (CNC) are gaining popularity among material science communities due to its abundant source from plants and excellent mechanical properties. Moreover, CNCs derived from hemp are reported to be antimicrobial which offers potentials in biomedical applications. With an abundance in hemp cultivation around the USA, the agrowaste produced by hemp farms can be used for preparing CNCs via the methods described in this work. In future, the morphological, crystalline, and thermal properties of the CNCs will be evaluated. Additionally, the CNCs will be incorporated into materials such as electrospun nanofibers to improve the mechanical and antibacterial properties of the nanofibers.

References:

de Rodriguez, N. L. G., Thielemans, W., & Dufresne, A. (2006). Sisal cellulose whiskers reinforced polyvinyl acetate nanocomposites. *Cellulose*, *13*, 261-270. DOI: 10.1007/s10570-005-9039-7.

Henrique, M. A., Silvério, H. A., Neto, W. P. F., & Pasquini, D. (2013). Valorization of an agro-industrial waste, mango seed, by the extraction and characterization of its cellulose nanocrystals. Journal of Environmental Management, *121*, 202-209. DOI: 10.1016/j.jenvman.2013.02.054.

Leung, A. C. W., Hrapovic, S., Lam, E., Liu, Y., Male, K. B., Mahmoud, K. A., Luong, J. H. T. (2010). Characteristics and properties of carboxylated cellulose nanocrystals prepared from a novel one-step procedure. *Small*, *7*(3), 302-305. DOI: 10.1002/smll.201001715.

Luzi, F., Fortunati, E., Puglia, D., Lavorgna, M., Santulli, C., Kenny, J. M., & Torre, L. (2014). Optimized extraction of cellulose nanocrystals from pristine and carded hemp fibres. Industrial Crops and Products, *56*, 175-186. DOI: 10.1016/j.indcrop.2014.03.006.