Nanoj **Journal of Nanotechnology**
Vol. 5, N° 1, 2021

A publication of
CINCADER
Centre of Research and Training for Regional Development
Online at www.journals.cincader.org

ISSN 2522-6908
DOI: https://doi.org/10.32829/nanoj.v5i1.141

Improving Dyeing Properties of Cotton Fabrics to Natural Dyes with Cellulose Nanocrystals (CNCs)

[Mejora de las propiedades de teñido de telas de algodón a tintes naturales con nanocristales de celulosa (CNC)]

K.G.Rumesh Samarawickrama[a,*], U.G.S. Wijayapala[b], N.D. Wanasekara[c], C.A.N. Fernando[d]

[a,b,c] Department of Textile & Apparel Engineering, Faculty of Engineering, University of Moratuwa, Sri Lanka
[d] Department of Nano Science Technology, Faculty of Technology, Wayamba University of Sri Lanka Kuliyapitiy, Sri Lanka

* rumeshsnt@gmail.com

Received: 27 September 2021; Accepted: 16 October 2021; Published: 19 October 2021

Resumen

Los tintes naturales pueden generar menos problemas ambientales asociados con los agentes colorantes fabricados y el teñido de textiles. Pero, en el proceso de fijación de tintes naturales se utilizaron productos químicos llamados mordiente. La mayoría de las veces se utilizaron mordientes con sales metálicas y las sales metálicas no eran amigables con el medio ambiente. Por lo tanto, elimine la desventaja asociada con los colorantes naturales y el uso de nanopartículas. En esta investigación, se trató tejido de algodón con la nanopartícula de nanocristales de celulosa (CNC) como mordiente. El proceso de extracción de nanocristales de celulosa se realizó utilizando papel de filtro Whatman. Los nanocristales de celulosa obtenidos se analizarán y caracterizarán mediante el uso de herramientas seleccionadas como el análisis del tamaño de partículas y la espectroscopia de infrarrojos por transformada de Fourier (FTIR). Los procesos de mordiente de las telas de algodón se realizaron mediante dos tipos de métodos de pre-mordido y post-mordido. Los tres ingredientes naturales de las hojas de Mangifera indica (mango), hojas de Tectona grandis (teca) y hojas de Lannea coromandelica (fresno indio) se utilizaron para extraer los tintes naturales mediante el método de extracción acuosa. Los extractos de los procesos de tintura se realizaron antes y después de los procesos de mordiente. La muestra teñida desde la solidez del color hasta la luz, el lavado y el crocante se evaluaron de acuerdo con métodos estándar. Los nanocristales de celulosa dieron muy buena solidez del color a la luz, al lavado y al frotamiento cuando se tiñeron con las tres extracciones de tinte. En el presente estudio, se ha demostrado que el mordiente innovador de nanocristales de celulosa y el teñido natural con tres extracciones de tinte natural dan buenos resultados de teñido con tejido de algodón.

Palabras clave: Mordiente, nanocristales de celulosa, nanopartículas, algodón, extracción acuosa, solidez del color.

Please cite this article as: Samarawickrama K.G., Wijayapala U.G., Wanasekara N.D., Fernando C.A., Improving Dyeing Properties of Cotton Fabrics to Natural Dyes with Cellulose Nanocrystals (CNCs), Journal of Nanotechnology, vol. 5, no 1, 2021, pp. 1-8. https://doi.org/10.32829/nanoj.v5i1.141

Nanoj **Journal of Nanotechnology**
Vol. 5, N° 1, 2021

A publication of
CINCADER
Centre of Research and Training for Regional Development
Online at www.journals.cincader.org

ISSN 2522-6908
DOI: https://doi.org/10.32829/nanoj.v5i1.141

Abstract

Natural dyes can make less environmental problems associated with manufactured colouring agents and textile dyeing. But, the natural dyes fixing process was used chemicals called mordant. The most of times mordants were used metallic salts and metal salts mordants were not environmentally friendly. Therefore, remove the disadvantage associated with natural colorants and the use of nanoparticles. In this research, cotton fabric was treated with the nanoparticle of cellulose nanocrystals (CNCs) as mordant. The cellulose nanocrystals extraction process was done by using Whatman filter paper. The cellulose nanocrystals obtained will be further analyzed and characterized by using selected tools such as Particle size analysis and Fourier-transform infrared (FTIR) spectroscopy. The cotton fabrics mordanting processes were done by two types of pre-mordanting and post-mordanting methods. The three natural ingredients of Mangifera indica (Mango) leaves, Tectona grandis (Teak) leaves and Lannea coromandelica (Indian ash tree) leaves were used to extract the natural dyes using with aqueous extraction method. The extracts from dyeing processes were carried out after and before mordanting processes. The dyed sample from colour fastness to light, washing and crocking were assessed according to standard methods. The cellulose nanocrystals gave very good colour fastness to light, wash, and rubbing when dyed with all three dye extractions. In the present study, innovative mordant of cellulose nanocrystals and natural dyeing with three natural dye extractions have been shown to give good dyeing results with cotton fabric.

Keywords: Mordant, cellulose nanocrystals, nanoparticle, cotton, aqueous extraction, colour fastness

1. Introduction

Textile materials dyeing have been one of the oldest techniques practiced by ancient human civilization. The ancient time, textile materials have been dyed with natural dyes provided from animal and herbal sources (Cristea & Vilarem, 2006). But the introduction of synthetic dyes led to an almost complete replacement of natural dyes. However, synthetic dyes are synthesized from petrochemical sources (Erkurt et al., 2007). Therefore, synthetic dyes are gradually decreasing due to their toxicity, non-biodegradability, and associated serious health hazards like allergic and carcinogenicity, and increased environmental awareness (Republic, 2010). Natural dyes can be obtained from various parts of plants including roots, bark, leaves, flowers, and fruit, and other organic sources such as fungi and lichens (Frose et al., 2019).

Therefore, natural dyes have increased considerably high compatibility with the environment, non-toxicity, non-allergic effects and also become economically advantageous over synthetic dyes. Natural dyes can be applied to all types of natural fibers (Mehrabian et al., 2000). But, the problems associated with dying with natural dyes are low exhaustion colours and the poor fastness properties of dyed cotton fabrics (Siva, 2007). The problem can be overcome by using chemicals called mordants. Mordants are metal salts and commonly used alum, ferrous sulfate, copper sulfate, chrome, and stannous chloride (Satyanarayana & Chandra, 2013; Hwang et al., 1998). However, the metallic mordants were categorized by heavy metals category and the use of these chemicals during natural dyeing often puts question marks on the eco-friendliness and effect for human skin of natural dyes (Radhakrishnan, 2014).

Therefore, remove the disadvantages associated with natural colorants and the use of nanoparticles. The nanoparticles can provide high dye uptake for cotton fabrics. Because nanoparticles have a large surface area-to-volume ratio and high surface energy, thus presenting better natural dye affinity for cotton fabrics and leading to an increased colourfastness property of the dyed fabric (Wong et al., 2006). The nanoparticles can be synthesized in different methods and several nanoparticles can be used to improve the dye affinity with cotton fabrics (Hubbe et al., 2008; Beck-Candanedo et al., 2005). The research for we hope to use eco-friendly and

Nanoj Journal of Nanotechnology
Vol. 5, N° 1, 2021

ISSN 2522-6908
DOI: https://doi.org/10.32829/nanoj.v5i1.141
A publication of CINCADER
Centre of Research and Training for Regional Development
Online at www.journals.cincader.org

nontoxic type nanoparticle. Hence, this research selected cellulose-based nanoparticle of cellulose nanocrystals (CNCs). The cellulose nanocrystals are reported to be excellent materials because cellulose possesses fascinating characteristics such as sustainability, biocompatibility, biodegradability, nontoxicity and have the potential to be processed in industrial-scale quantities at low costs (Tang, 2016; Habibi et al., 2010). The cellulose nanocrystals have high surface area with a high amount of hydroxyl groups that give CNCs some extra natural properties. These hydroxyl groups on CNCs surfaces can be readily modified to achieve different surface properties and successfully bonding with natural polymers with dye molecules (Hubbe et al., 2018; Siqueira et al., 2010).

The present study has been selected cotton fabric treated with cellulose nanocrystals (CNCs) as mordant. The treatment process was done by two types of pre-treatment (pre-mordant) and post-treatment (post-mordant) methods. The cellulose nanocrystals extraction process was done by using Whatman filter paper. The cellulose nanocrystals obtained will be further analyzed and characterized by using selected tools such as Particle size analysis and Fourier-transform infrared (FTIR) spectroscopy. The three natural ingredients of Mangifera indica (Mango) leaves, Tectona grandis (Teak) leaves, Lannea coromandel (Indian ash tree) leaves were used to extract the natural dyes using with aqueous extraction method. The dyeing process was done by all parameters were optimized to obtain the maximum possible dye bath exhaustion and good colourfastness properties. All dyed fabric samples from analyzed by colourfastness properties (light, wash, and rubbing).

2. Materials and Methods

2.1. Fabric selection

A plain woven bleached cotton fabric was used for dyeing studies. Its characteristics were: mass per unit area of 132 g/m^2 and ends per inch (EPI) and picks per inch (PPI) of 60 and 48. The fabric was purchased by the local market of Colombo in Sri Lanka.

2.2 Leaves gathering and processing

The extraction of the dyes was carried out in three natural plant materials of *Mangifera indica* (Mango) leaves, *Tectona grandis* (Teak) leaves and *Lannea coromandelica* (Indian ash tree) leaves. These natural plant materials were collected from Sri Lankan villages. The collected fresh leaves were washed thoroughly with water to remove any impurities. The clean fresh leaves were dried in an oven at 40 °C until constant mass. The dry leaves were chopped into pieces and pulverized in the grinder. After the grinding process, grinded materials were stored in closed plastic containers.

2.3. Aqueous extraction process of natural dyes

The grinded dry leaves were immersed in distilled water for 24 h (weight ratio of 1:20) in a 1L flat-bottomed flask. The extractions were carried out on a hot plate, with the flask connected to a reflux condenser. The extraction was carried out at a boiling temperature of the water for 2 h. The extracted mixtures were filtered and separated from dye liquors.

2.4. Synthesize process of Cellulose Nanocrystals (CNCs)

The CNCs were isolated from No. 1 Whatman filter paper following a procedure that has been described previously. The filter paper 5.2 g of filter paper was blended with 250 mL of deionized water to form a pulp. The 98% Sulphuric acid (140 mL) was slowly added to this pulp under vigorous mechanical stirring (250 mL, 20 °C in the ice bath). The resulting suspension was held at 50 °C and magnetically stirred for 3.5 h to allow hydrolysis to take place and cooled to room temperature before centrifuging. Then, the mixture was cooled at room temperature and washed via centrifugation at 3400 rpm for 15 min and get supernatant solution from centrifuge canister.

Nanoj **Journal of Nanotechnology**
Vol. 5, N° 1, 2021

ISSN 2522-6908
DOI: https://doi.org/10.32829/nanoj.v5i1.141
A publication of
CINCADER
Centre of Research and Training for Regional Development
Online at www.journals.cincader.org

After, the process was repeated until the solution had a pH of 3–4. The solution was then dialyzed against distilled water until a pH value of 7 was obtained using the dialysis membrane.

2.5. Characterization of the cellulose nanocrystals (CNCs)
2.5.1. Particle size analysis
The particle size of the obtained CNCs was measured by a Zetasizer Nano ZS particle analyzer (Malvern Instrument, UK). The CNCs suspensions were diluted to a concentration of 0.01 % (w/v) with distilled water and sonicated for 5 min before the test. The measurements were performed in triplicate and the average data was reported.
2.5.2. Fourier transforms infrared spectroscopy (FTIR)
Fourier Transform Infrared (FTIR) Spectroscopy (Thermo Scientific Nicolet IS5-ATR) was used to obtain the spectrum of functional groups of the CNCs sample. The spectra were recorded in absorbance mode over the spectral range of 600-4000 cm^{-1}, with 32 scans for each spectrum and scanning resolution of 4 cm^{-1}.

2.6. Mordanting and Dyeing Conditions
2.6.1 Pre-treatment process (Pre-mordanting)
The pre-treatment process was carried out before the dyeing process and also called the Pre-mordanting process. In this process, bleached cotton fabrics were treated with cellulose nanocrystals as a mordant. The cotton fabrics were mordanted using 6g per liter of cellulose nanocrystals at 70 °C for 2 hours with MLR of 1:20.
2.6.2 Post-treatment process (Post-mordanting)
The post-treatment process was carried out after the dyeing process and also called the Post-mordanting process. In this process, dyed cotton fabrics were treated with cellulose nanocrystals as a mordant. The dyed cotton fabrics were mordanted using 6g per liter of cellulose nanocrystals at 70 °C for 2 hours with MLR of 1:20.
2.6.3. Dyeing Process
The dyeing processes were carried out at 65-70 °C for 2 hours with the dye extracts keeping MLR at 1:20. After the duration, the dyed fabric samples were rinsed thoroughly in cold water and allowed to dry at room temperature for overnight.

2.7. Colourfastness properties of dyed samples
The dyed samples were tested according to ISO testing standards. The colourfastness to light, washing, and rubbing were determined from standard test methods ISO 105- B02, 2013, ISO 105-C06 A1S:2010, ISO 105-X12:2016.

3. Results and discussions

Results of the analysis of the water samples before and after applying the treatment with titanium dioxide nanoparticles

3.1. Characteristics of cellulose nanocrystals (CNCs)

3.1.1. Evaluation of particle size analysis
The particle size and particle size distribution depending on the structure of the source sample, acid concentration, temperature, time, the procedure of hydrolysis, and the mechanical treatment. Figure 1 showed the particle size analysis of the cellulose nanocrystals sample. Although the size distribution of each sample varied from 4 – 8 nm and the distribution pattern was different.

Nanoj Journal of Nanotechnology
Vol. 5, N° 1, 2021

ISSN 2522-6908
DOI: https://doi.org/10.32829/nanoj.v5i1.141

A publication of
CINCADER
Centre of Research and Training for Regional Development
Online at www.journals.cincader.org

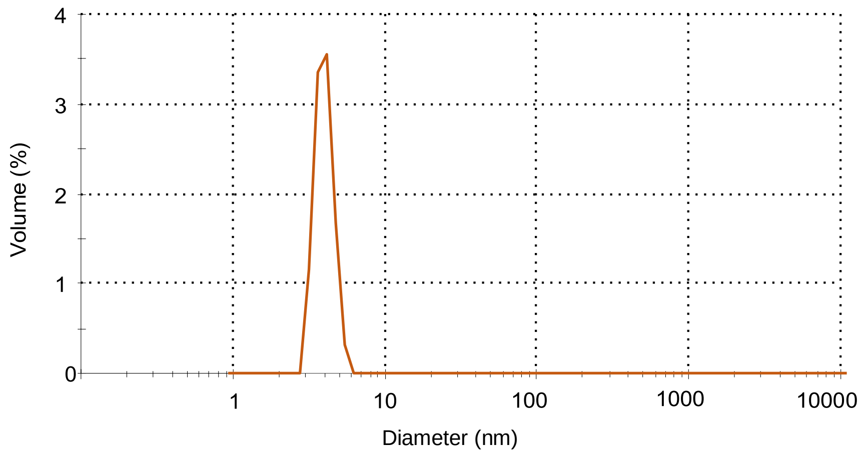

Figure 1 – Particle size analysis of cellulose nanocrystals sample

3.1.2. Evaluation of Fourier transforms infrared spectroscopy (FTIR)

Figure 2 shows an FTIR spectrum of cellulose nanocrystals sample in the wavelength range of 600-4000 cm^{-1}. The vibrations located at 3292 cm^{-1} and 3335 cm^{-1} are assigned to the inter-and intermolecular O-H group (Abidi et al., 2010; Pan et al., 2020). The peaks in the wavenumber range of 2750 – 2950 cm^{-1} are ascribed to C–H stretching vibration modes of –CH, $–CH_2$, and $–CH_3$ groups (Marchessault et al., 1960). The band at 1630 –1650 cm^{-1} is attributed to the CH_2–O–H bending or H–O–H bending vibration of absorbed water. The sharp absorbance band at 1429 cm^{-1} corresponds to asymmetric $–CH_2$ wagging indicates the crystallinity of the cellulose material (Lu & Hsieh, 2010). The bands located at 1315 cm^{-1} and 1334 $cm^{-}1$ are assigned to $–CH_2$ wagging and C–OH in-plane bending vibrations. The strongest bands at 1060 cm^{-1}, 1035 cm^{-1}, and 998 cm^{-1} are the vibrations of C–C, C–OH, and C–H ring and side group stretching vibrations (Rahimi Kord Sofla et al., 2016).

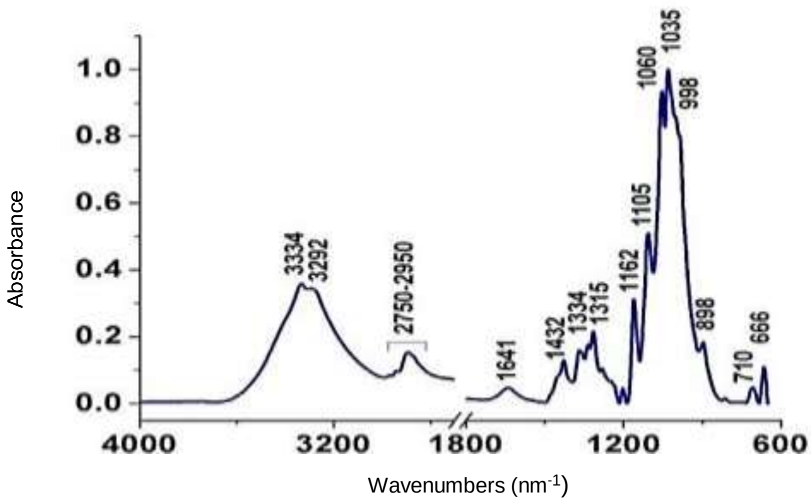

Figure 2 – FTIR spectrum of cellulose nanocrystals sample

Nanoj **Journal of Nanotechnology**
Vol. 5, N° 1, 2021

ISSN 2522-6908
DOI: https://doi.org/10.32829/nanoj.v5i1.141

A publication of
CINCADER
Centre of Research and Training for Regional Development
Online at www.journals.cincader.org

3.2. Colourfastness properties of dyed samples

Table 1 indicates the good colour fastness properties in all fastness tests carried out and which indicates that the ability of substantively of the dye molecules and fibers can be improvised by adding cellulose nanocrystals as a mordant. The colour fastness properties of all three dyes used are enhanced as a result of the addition of pre-mordanting and post-mordanting conditions with cellulose nanocrystals (CNCs). This shows that the cellulose nanocrystal is the mordant which helps to bind the dye molecules with cotton fibers resulting in stronger bonds. The cellulose nanocrystals gave very good colour fastness to light, wash, and rubbing when dyed with all three dye extractions.

Table 1 – Colourfastness results of dyed samples

Dye Type / CF	*Mangifera indica*				*Tectona grandis*				*Lannea coromandelica*			
LF	P_1M		P_2M		P_1M		P_2M		P_1M		P_2M	
	4		4		4		4		4		3-4	
WF	P_1M		P_2M		P_1M		P_2M		P_1M		P_2M	
	4		4		4-5		4		4-5		4	
RF	Dry		Wet		Dry		Wet		Dry		Wet	
	P_1M	P_2M	P_1M	P_2M	P_1M	P_2M	P_1M	P_2M	P_1M	P_2M	P_1M	P_2M
	4	4	4	3-4	4-5	4	4-5	4	4	4	4	4

(LF = light fastness, WF = wash fastness, RF = Rubbing fastness, P_1M = Pre-mordanting, P_2M = Post-mordanting)

4. Conclusions

The results of this research showed that the preparation of cellulose nanocrystals and its applying cotton fabrics with three natural dyes to represent an eco-friendly approach to the sustainable textile dyeing process. The three natural ingredients of Mangifera indica (Mango) leaves, Tectona grandis (Teak) leaves and Lannea coromandelica (Indian ash tree) leaves were used to extract the natural dyes using with aqueous extraction method. The cellulose nanocrystals were extracted using the sulfuric acid hydrolysis method with Whatman filter papers. The particle size diameters obtained were in the range of 4-8 nm for extracted cellulose nanocrystals and successfully investigated FTIR spectrum provide IR peak assignments for extracted cellulose nanocrystals. The cellulose nanocrystals were applied on bleached cotton fabrics samples using two mordanting methods of pre-mordanting and post-mordanting. The three natural dye extracts with dyeing processes were carried out at 65-70 °C for 2 hours with the dye extracts keeping MLR at 1:20. After the dying process, the dyed samples were analyzed by colourfastness properties (light, wash, and rubbing) using the standard ISO test method. The fastness test results indicate the good colour fastness properties in all fastness tests carried out and which indicates that the ability of substantively of the dye molecules and cotton fiber can be improvised by adding cellulose nanocrystals as a mordant. These test results revealed that it can be used in small-scale industries as well as large-scale industries.

ISSN 2522-6908
DOI: https://doi.org/10.32829/nanoj.v5i1.141

5. Acknowledgments
The author wishes to acknowledge the University of Moratuwa in Sri Lanka for the Support for testing and financial assistance through the SRC grant.

References

Abidi, N., Cabrales, L., & Hequet, E. (2010). Fourier transforms infrared spectroscopic approach to the study of the secondary cell wall development in cotton fiber. Cellulose, 17(2), 309–320. https://doi.org/10.1007/s10570-009-9366-1.

Beck-Candanedo, S., Roman, M., & Gray, D. G. (2005). Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspensions. Biomacromolecules, 6(2), 1048–1054. https://doi.org/10.1021/bm049300p.

Cristea, D., Vilarem, G., Improving light fastness of natural dyes on cotton yarn, Dyes and Pigments 70,238-245, (2006).

Erkurt, E. A., Ünyayar, A., & Kumbur, H. (2007). Decolorization of synthetic dyes by white-rot fungi, involving laccase enzyme in the process. Process Biochemistry, 42(10), 1429–1435.

Frose, A., Schmidtke, K., Sukmann, T., Juhász Junger, I., & Ehrmann, A. (2019). Application of natural dyes on diverse textile materials. Optik, 181(September), 215–219.

Habibi, Y., Lucia, L. A., & Rojas, O. J. (2010). CNC - Johnsy - habibi2010 [2].pdf. Chemical Reviews, 110, 3479–3500.

Hubbe, M. A., Rojas, O. J., Lucia, L. A., & Sain, M. (2018). Cellulosic nanocomposites: A review. International Journal of Interactive Mobile Technologies, 12(3), 929–980. https://doi.org/10.15376/biores.3.3.929-980.

Hwang, E.K., Kim, M.S., Lee, D.S. and Kim, K.B., Color development of natural dyes with some mordants. J. Korean Fiber Soc. 35: 490-497 (1998).

Lu, P., & Hsieh, Y. Lo. (2010). Preparation and properties of cellulose nanocrystals: Rods, spheres, and network. Carbohydrate Polymers, 82(2), 329–336. https://doi.org/10.1016/j.carbpol.2010.04.073.

Marchessault, R. H., Pearson, F. G., & Liang, C. Y. (1960). Infrared spectra of crystalline polysaccharides. Biochimica et Biophysica Acta, 45, 499–507. https://doi.org/10.1016/0006-3002(60)91486-4.

Mehrabian, S., Majd, A. and Majd, I., Antimicrobial effects of three plants (Rubia tinctorum, Carthamus tinctorius and Juglans regia) on some airborne microorganisms. Aerobiologia. 16 (3): 455-458 (2000).

Pan, L., Li, P., & Tao, Y. (2020). Preparation and properties of microcrystalline cellulose/fish gelatine composite film. Materials, 13(19), 1–15. https://doi.org/10.3390/ma13194370.

Radhakrishnan, S. (2014). Roadmap to Sustainable Textiles and Clothing. https://doi.org/10.1007/978-981-287-065-0.

Rahimi Kord Sofla, M., Brown, R. J., Tsuzuki, T., & Rainey, T. J. (2016). A comparison of cellulose nanocrystals and cellulose nanofibres extracted from bagasse using acid and ball milling methods. Advances in Natural Sciences: Nanoscience and Nanotechnology, 7(3). https://doi.org/10.1088/2043-6262/7/3/035004.

Republic, C. (2010). Dyeing and Fastness Properties of Natural Dyes Extracted from Eucalyptus Leaves Using Padding Techniques. 11(3), 346–350.

Satyanarayana, D. N. V, & Chandra, K. R. (2013). Dyeing Of Cotton Cloth with Natural Dye Extracted From Pomegranate Peel and its Fastness. International Journal of Engineering Sciences & Research Technology, 2(10), 1–6.

Siqueira, G., Bras, J., & Dufresne, A. (2010). Cellulosic bionanocomposites: A review of preparation, properties, and applications. Polymers, 2(4), 728–765. https://doi.org/10.3390/polym2040728.

Nanoj Journal of Nanotechnology
Vol. 5, N° 1, 2021
A publication of
CINCADER
Centre of Research and Training for Regional Development
Online at www.journals.cincader.org

ISSN 2522-6908
DOI: https://doi.org/10.32829/nanoj.v5i1.141

Siva, R. (2007). Status of natural dyes and dye-yielding plants in India. Current Science, 92(7), 916–925.

Tang, J. (2016). Functionalized Cellulose Nanocrystals (CNC) for Advanced Applications. Thesis, 8–69. http://hdl.handle.net/10012/10624.

Wong YWT, Yuen CWM, Leung MYS, Ku SKA, Lam HLI, (2006) Selected Applications on Nanotechnology in Textiles. AUTEX Resea.