Environmentally Sound Textile Dyeing Technology with Nanofibrillated Cellulose

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Supplementary Information

Methods

Production of NFC hydrogel. Kraft pulp sheets (provided by Weyerhaeuser, Dacula, GA) were knife-milled three times using a mesh sieve with a pore size of 500 μm to the order of tens of micrometers in width and hundreds of micrometers in length. Milled cellulose powders were mixed with hot water and carboxymethyl cellulose (CMC) (0.25% in water, average molecular weight 250 kD, Sigma-Aldrich). The mixture was processed to nano-size fibers during 2-3 passes in a high-pressure homogenizer (APV-1000, SPX Flow Technology). The prepared NFC hydrogel (Figure S1) remained stable and showed no signs of phase separation or precipitation for many months (Zeta potential: -45±5 mV).



Figure S1. Homogenization process: (left to right) cellulose pulp sheet, knife mill, high-pressure homogenizer, and stable NFC hydrogel containing NFC fibers.



Figure S2. (a) TEM (scale bar 200 nm) and (b) AFM images of NC fibers (0.1 wt% in water); (c) Viscosity of the NFC gels from 0.5% to 5% as a function of shear rate.

Estimation of specific surface area by methylene blue method. Methylene blue (from Ward's Science) was dried at 110°C for several hours before use. A methylene blue solution was prepared with deionized water and its absorbance at 660 nm was analyzed by a UV-Vis spectrophotometer (Shimadzu 2401). This wavelength corresponds to the absorption peak of the molecule.¹ In a typical example, 0.36 g of cotton fibers or dry NFC fibers were immersed in 45 mL of various concentrations of methylene blue solutions (from 10 μ M to 25 mM) for one day, in which all surfaces in the cellulosic fibers were occupied by methylene blue molecules (see Figure S3a). The reduction in the adsorption intensity at 660 nm after one day of immersion corresponds to the amount of adsorbed methylene blue on the surfaces of cotton and NFC fibers. From the calibration curve of neat methylene blue solutions at various concentrations (Figure S3b), the methylene blue adsorption per gram of fiber (mg/g) was calculated and then converted to the specific surface area of cellulosic fibers, *S*_{cf}, by using the equation below,

$$S_{cf} = \frac{N_{MB} \times a_{MB} \times N_A}{M_{MB}}$$
(S1)

where N_{MB} equals to the molecular weight of methylene blue (M_{MB}) multiplied by the number of moles of methylene blue per gram of fiber needed to form a monolayer; a_{MB} is the molecular footprint of methylene blue (130 Å²)²; and N_A is Avogadro's number. N_{MB} was taken at the maximum of methylene blue adsorption in Figure 1d and 1e.



Figure S3. (a) The absorbance spectra of methylene blue solutions after the immersion of cotton fabric for 1 to 23 hours. The reduction of absorbance intensity stabilizes after 4 hours of immersion, indicating that all of the surfaces in cotton fibers are occupied by the absorption of methylene blue molecules. (b) The absorbance of methylene blue solution at 660 nm in various concentrations. Linear fit gives an R² value of 99%. (c-d) Adsorption of methylene blue on cotton and NFC fibers as a function of methylene blue concentration.

Fabrication of the NFC-dye and coloration of cotton fabrics. Reactive Red 120 dye molecules (Sigma Aldrich, chemical structure shown in Figure S4a) were incorporated into NFC hydrogels with Na_2SO_4 and Na_2CO_3 as a salt and alkali, respectively, by a simple mixing under ambient conditions to produce the NFC-dye mixture. The weight percent of the NFC gel determines the liquor ratio, which is the weight ratio of water to dry cellulose fibers. The NFC-dye was applied to both sides of the cotton fabric (bleached desized cotton, style #400, 102 g/m², purchased from

Testfabrics, Inc., USA) by manual squeegee printing. In a typical example, a 2" by 5.1" piece of cotton fabric whose mass was *c.a.* 0.7 g was coated by 1.4 g of the NFC-dye. The procedure shown in Figure S4b was used to produce a cotton reference by an exhaust dyeing method. Table S1 summarizes the amount of dye and dye auxiliaries used in the coloration of the cotton fabrics (four 2" by 5.1" swatches, total 2.8 g). After dyeing, the colored fabrics were dried at 120°C for one hour, followed by a wash-off in which the four colored swatches were boiled in 1 liter of deionized water for 30 minutes (liquor ratio 370:1) and subsequently dried under ambient conditions. The rinse water after wash-off was collected to determine the concentration of dye molecules in the effluent.



Figure S4. (a) Chemical structure of Reactive Red 120 used in this study and (b) the sequence of the exhaust dyeing method.



Figure S5. Process flow for conventional exhaust dyeing and NC-based dyeing.

Table S1. Quantitative comparison of dye and dye auxiliaries to produce four 2" by 5.1" cotton fabrics (one batch, total 2.8 g) by exhaust dyeing and NFC-based dyeing (based on 10%).

1% dye	Reactive	Water	Dye	Weight	Salt	Alkali
owf	Red 120		concentration	of dry	(Na ₂ SO ₄ , 64	(Na ₂ CO ₃ , 4
20:1 liquor	dye			NC	g/L)	g/L)
ratio						
Exhaust	28 mg	53 g	0.36 mM	N/A	3.4 g	0.21 g
dyeing						
NFC-based	28 mg	5.3 g	3.6 mM	280 mg	0.34 g	0.021 g
dyeing						

	L*	a*	b*
Exhaust dyeing	52.57 ± 0.63	55.38 ± 0.48	0.35 ± 0.38
Exhaust dyeing with a low conc. of dye auxiliaries	67.37 ± 0.09	38.97 ± 0.8	-4.92 ± 0.04
NFC-based dyeing	52.75 ± 0.70	58.31 ± 0.69	2.61 ± 1.01

 Table S2. Colorimetric values of dyed cotton swatches.

Dyeing performance of colored fabrics. After dyeing, reflectance spectra of fabric specimens were measured using a color spectrophotometer (Macbeth Color-Eye 7000A) equipped with Color I QC software from X-Rite. L*, a*, b*, and K/S values of the dyed samples were recorded with the following instrumental settings (illuminant D65, aperture size 75 mm², specular included). The dyeing performance of colored cotton fabrics was evaluated by dye exhaustion (*E*) and dye fixation (*F*). Dye exhaustion is a measure of how many dye molecules are consumed and absorbed on to textile fibers during a dyeing process, which is determined by the ratio between the absorbance of a dyeing solution associated with dye molecules employed before and after dyeing. To determine the dye exhaustion of the NFC-dye, a supernatant solution was collected by centrifugation at 13000 rpm for 30 minutes. The concentration of reactive dye in the supernatant and stock solution without NFC fibers was determined by the absorbance of solutions at 510 nm (corresponding wavelength for Reactive Red 120) using a UV-Vis spectrophotometer (UV-2401PC, Shimadzu). For a reference for the exhaust dyeing method, dyebath solutions before and after dyeing were sampled and compared.

$$E = \frac{A_o - A_d}{A_o} \tag{S2}$$

where E: dye exhaustion, A_o : initial absorbance, A_d : absorbance after dyeing.

Dye fixation is a measure of how many dye molecules are permanently fixed on fabric surfaces during dyeing, which is determined by the ratio between the color strength of colored fabrics associated with dye molecules employed before and after wash-off. After wash-off, the color strength was measured at 510 nm to determine dye fixation. Higher dye exhaustion and dye

fixation indicate more efficient and economical dyeing processes as well as producing less dye in the effluent from dyeing and wash-off.

$$F = \frac{C_s}{C_o}$$
(S3)

where F: dye fixation, C_o : initial color strength, C_s : color strength after wash-off.

Colorfastness and stiffness of colored fabrics. To determine colorfastness properties, crocking (dry and wet) and laundering tests were performed based on AATCC Test Method 8-2013 and 61-2013 2A,³ respectively. Stiffness of a colored fabric was evaluated by measuring the bending length of a fabric under its own mass by using the Cantilever Test, ASTM D1388.

Preparation of a fiber specimen for cross-sectional SEM. The polyethylene film method was used to prepare cross-sections of fabric specimens. Fibers/fabrics were placed in disposable polyethylene pipettes and the polyethylene/fiber sandwich was then placed between two glass microscope slides on a hot plate until the polyethylene melted. After cooling down, the polyethylene/fiber sandwich was cut in thin slices using a sharp razor blade. The thin slices were subsequently gold-coated by sputtering.

Cellulose model film. The cellulose model film was spun on a silicon wafer from a cellulose solution in LiCl / *N*,*N*-dimethylacetamide. The silicon wafer was freshly prepared by a base piranha treatment followed by dipping in a 1% polyethylenimine solution. The spin-cast cellulose film was rinsed with deionized water to remove the LiCl and dried under ambient conditions. The root-mean-square roughness of the cellulose films was 0.5 nm. NFC hydrogel (1%) was deposited on the cellulose model film by spin casting and baked at 120°C overnight. The thickness of the cellulose and NFC film was determined to be 85 nm and 25 nm respectively by ellipsometry. The bilayer film was subjected to washing by dipping in a detergent solution (0.3 g/L) at 50°C for an hour with magnetic stirring.

Figure S6. AFM images of (a) NC gels deposited on regenerated cellulose film and (b) the same film after washing, indicating good adhesion of nanocellulose fibrils on the cellulose model film.

Life cycle inventory analysis (LCIA). All input and output data used in this study were obtained from bench scale experimental data, literature sources and the LCI databases - GREET version 1.3.0, Ecoinvent v.2.2 and USLCI v.1.6.0. The collected data were then scaled up for producing 1 kg of dyed cotton fabric on dry basis. The U.S. LCI database was used to extract data for each of the chemicals and materials used in this study. For some chemicals, the European database was selected as similar technologies were used to manufacture the selected chemicals. Table S2 summarizes the inventory data for manufacturing 1 kg of dyed cotton fabric using two different dyeing methods. The experimental data obtained from NFC preparation including knife milling and homogenization, and the data for dyeing cotton fabrics with the reactive dye (Reactive red 120) and NFC-dye were used in this analysis. The data for wastewater treatment using granular activated carbon (GAC) were collected from the literature.^{4, 5}

Input (Unit)	Exhaust	NC-based	
	dyeing	dyeing	
Cotton fabric dyeing process			
Bleached Cotton fabric (kg)	1	1	
$Na_2SO_4(g)$	1216	121.6	
Na_2CO_3 (g)	76	7.6	
Reactive red 120 (g)	10	10	
Kraft bleached pulp (g)	-	116.64	
Carboxymethylcellulose (g)	-	0.48	
Total deionized (DI) water (L)	389	38.9	
DI water for nanocellulose preparation	$\lambda I/A$	1.0	
(L)	IN/A	1.9	
DI water for dyeing (L)	19	N/A	
DI water for rinsing (L)	370	37	
Total electricity (kwh)	36.76	5.85	
Electricity for nanocellulose	N/A	1 37	
preparation (kwh)		1.57	
Electricity for dyeing (kwh)	1.59	N/A	
Electricity for drying (kwh)	0.8	0.8	
Electricity for rinsing (kwh)	34.37	3.44	
Electricity for water recycle (kwh)	-	0.016	
Transport, truck, average fuel (tkm)	0.26	0.048	
Wastewater treatment			
Hard coal (kg)	0.017	0.0142	
Steam (kg)	0.10	0.085	
Deionized water (L)	0.20	0.17	
Heat, hard coal combustion (MJ)	1.52	1.30	
Heat, natural gas combustion (MJ)	1.96	1.68	
Electricity (kwh)	0.086	0.032	
Transport, truck, combination, average			
Fuel (tkm)	0.14	0.12	
Output (Unit)			

Table S3. Life cycle inventory data for one kg of cotton fabric using two dyeing methods.

Cotton fabric dyeing process						
Dyed cotton fabric (kg)	1	1				
Particulate >10um (g)	N/A	16.64				
Heat waste (MJ)	26.47	3.95				
Heat waste from nanocellulose	NT/ 4	0.00				
preparation (MJ)	IV/A	0.89				
Heat waste from dyeing (MJ)	26.47	3.06				
Water evaporated (kg)	0.7	1.67				
Wastewater treatment						
Treated effluent (L)	389.59	37.37				
Heat waste (MJ)	0.76	0.62				
Reactive Red 120 (mg)	241.28	213.01				
CO ₂ (g)	3.25	2.77				
$NO_{x}(g)$	1.08	0.92				

Figure S7. Flow diagram for wastewater treatment by GAC absorption.

Figure S8. Comparative life cycle assessment impacts of dyed cotton fabrics (1 kg) using exhaust and NC-based dyeing methods.

References

- C. Kaewprasit, E. Hequet, N. Abidi and J. P. Gourlot, *The Journal of Cotton Science*, 1998, 2, 164-173.
- 2. J. C. Santamarina, K. A. Klein, Y. H. Wang and E. Prencke, *Canadian Geotechnical Journal*, 2002, **39**, 233-241.
- 3. *AATCC Technical Manual*, American Association of Textiles Chemists & Colorists, 2015.
- 4. X. Gabarrell, M. Font, T. Vicent, G. Caminal, M. Sarrà and P. Blánquez, *The International Journal of Life Cycle Assessment*, 2012, **17**, 613-624.
- I. Muñoz, J. Peral, J. Antonio Ayllón, S. Malato, M. José Martin, J. Yves Perrot, M. Vincent and X. Domènech, *Environmental Engineering Science*, 2007, 24, 638-651.