The optimization of novel nanocellulose gel-reactive dye coating for textile applications

Brian J. Lee[2], Sandy Daubenmire[1], Eliza Lee[1], Raha Saremi[1], Smriti Rai[1], Anuradhi Liyanapathiranage[1], T. N. Sriram[2], Abhyuday Mandal[2], and Suraj Sharma[1]*

Abstract

The conventional dyeing process which is practiced mostly in our textile industry to dye cotton has a high amount of water consumption and consequently releases a massive amount of wastewater which leads to economic cost, and environmental impact associated with the removal of reactive dye from the effluent. Nanocellulose gel, when combined with a reactive dye, can be applied as a coating to cotton fabric. This novel dyeing approach significantly reduces water usage, generation of wastewater, and treatment costs. The study suggests that the application of nanocellulose gel-dye coating to cotton fabrics improves the colorfastness of the fabrics. However, dye-nanocellulose gel coating also lightens the fabric color. Therefore, the gel to dye ratio, in grams/milliliter, must be retained roughly under 0.40 to yield the same color as fabric dyed directly without a nanocellulose coating.

Keywords: reactive dye, nanofibrillated cellulose (NFC), statistical analysis, dye coating, dyeing

Introduction

CELLULOSE is an abundant biopolymer found in wood, plant fibers, marine animals, algae, fungi, and bacteria.[1] Cellulose does not occur in nature as a single polymer chain, but instead forms a bundle of ~36 individual units called elementary fibrils. Elementary fibrils bundle together to form microfibrils. Microfibrils have a diameter between 20 to 50 nm. Aggregation between microfibrils tends to occur due to van der Waals forces and hydrogen bonding.[1-2] Each microfibril can be described as strings of cellulose crystals connected by amorphous regions along its length.[3] There are two types of nanocellulose, cellulose nanocrystals, and nanofibrillated cellulose (NFC). Cellulose nanocrystals are single crystals formed under acid hydrolysis whereas nanofibrillated cellulose has both amorphous and crystalline regions and tends to build a web-like network.[1]   NFC is the type of nanocellulose discussed in this article.

NFC is manufactured from many different sources including wood pulp, bleached kraft pulp, and bleached sulfite pulp. The pretreated pulp suspension is transformed into nanocellulose by subjecting it to high delamination forces through a homogenizer or microfluidizer.[1] Turbak et al. patented microfibrillated cellulose as a new kind of cellulose.[4] Wood pulp suspension was passed several times through a high-pressure Gaulin homogenizer with a narrow orifice. Homogenization defibrillated the wood pulp to obtain a viscous gel.[1, 4] The microfluidizer from Microfluidics Corporation is an alternative to the homogenizer. The wood suspension is pushed through the thin z-shaped chambers under pressures of 30,000 psi or below. Multiple passes are necessary to increase the degree of fibrillation.[5]

Pre-treatment of cellulose suspension has been studied to produce fibers that are less stiff and cohesive.[1] TEMPO-mediated oxidation pre-treatment is currently the most commonly used pre-treatment. Sodium hypochlorite is added to the cellulose suspension with the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and sodium bromide, pH setting of 10-11, and room temperature conditions. C6 primary hydroxyl groups are converted to carboxylate groups, resulting in separation between fibrils. Other pretreatment methods include enzyme treatment, carboxymethylation, and acetylation of cellulose suspension.[1]

NFC has many potential applications, such as films and paper coatings for food packaging. The food industry is interested in packaging that will reduce environmental contamination and increase shelf life. The barrier properties of food packaging influence shelf life and impede food degradation.[6] Aulin, Gallstedt, and Lindstrom reported that the carboxymethylated NFC films showed low oxygen permeability with no relative humidity. However, the oxygen transmission rate increases dramatically after 70% relative humidity.[7] A separate study by Syverud and Stenius revealed that non-treated NFC films also had very low air permeability with the oxygen transmission rates of 17.0 and 17.8 ml m^{-2} day^{-1}, which are within the range of the recommended oxygen transmission rate (10-20 ml m^{-2} day^{-1}).[8] Aulin, Gallstedt, and Lindstrom also produced carboxymethylated NFC coatings for unbleached kraft and greaseproof paper. The air permeability of the papers decreased from 69,000 and 660 nm/Pa s, respectively, to 4.8 and 0.2 nm/Pa s, respectively, with the addition of the NFC coating.[7] The low air permeability of NFC is thought to be influenced by NFC crystalline regions.[7-8] The more crystalline material is, the

[1] Department of Textiles, Merchandising, and Interiors, University of Georgia, Athens, GA, USA
[2] Department of Statistics, University of Georgia, Athens, GA, USA
*Corresponding author: Suraj Sharma, Ph.D.; Associate Professor, UGA

Queries and Responses: author.colourage@gmail.com

lower its air permeability tends to be.[6] NFC tends to show low air permeability in low relative humidity, but its tendency to absorb water could be problematic because the high relative humidity will increase its air permeability.[7-8]

NFC has also been considered for printing applications to improve the print quality of papers.[1] Taking a similar approach to paper printing, NFC, combined with a reactive dye, can be applied as a dye coating to cotton fabrics for a novel dyeing process. Reactive dyes are synthetic dyes that covalently bond to the hydroxyl groups in cellulose. Reactive dyes were first developed in 1956 by ICI. Since then reactive dyes have become popular because of their bright colors, the range of shades, and fastness properties. Reactive dyes tend to be water soluble, which lends to its ease of application.[9,10,11]. They typically consist of four chemical groups. The reactive group reacts with the cellulose. The water solubilizing group causes reactive dyes to be soluble in water. The chromophore group gives the dye its color. The bridging group connects the reactive group to the chromophore group. Under alkaline conditions, the hydroxyl groups in cellulose (Cell-OH) can become cellulosate anions (Cell-O-) (equation 1). The cellulosate anions react with the dye's reactive group (Dye-X) and form a covalent bond (Dye-O-Cell) (equation 2). However, cellulose competes with water for the formation of covalent bonds with the reactive dye. This competing hydrolysis reaction results in a portion of the reactive dye that is not bound or reacted with cellulose (Dye-OH) (equation 3).[4,12,13]

Cell-OH +OH- ↔ Cell-O- + H_2O [1]
Cell-O- + Dye-X → Dye-O-Cell + X- [2]
OH- + Dye-X → Dye-OH +X- [3]
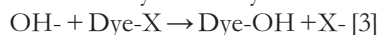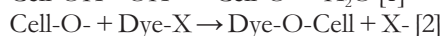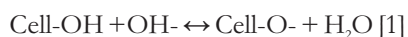
Conventionally, the dye is dissolved and circulated in the dyebath and through the material. The temperature is slowly raised from ambient to fixation temperature. Salt is added to the dye bath in portions. The dye is absorbed into the fabric fibers in the presence of the high electrolyte concentration. Next, alkali is added and circulated through the dyebath. Fixation of dye to the fabric takes place under the presence of the alkali. The dye reacts with material or the water in the bath. The dyeing of material is followed by a lengthy washing off period, which removes all hydrolyzed and unfixed dye from the material.[14,9]

Textile dyeing and washing off processes tend to be highly water intensive. Since typically 50-75% of reactive dye reacts with the fabric, the remaining 25-50% of the unreacted or hydrolyzed dye remains in the effluent.[9] Reactive dye in the effluent must be treated either on-site or at municipal sewage plants. Removal of reactive dye from the effluent is an expensive process. Continuous dyeing could lower the amount of reactive dye in the effluent and decrease the cost of water treatment. Some innovations include dyeing at lower liquor ratios and using pad-dry-pad-steam, cold pad-bath, pad-dry-thermofix, or pad-steam techniques.[9,15] Surface modifications using chemical and physical methods are the leading technologies for sustainable dyeing. Plasma treatment is an effective method in changing the morphology of the fibers and functional groups on the textile surface.[16]

In our previous study, (Kim et al.)[17], we developed an environmentally sound textile dyeing technology with nanofibrillated cellulose that can decrease the amount of salt, and alkali used in the dyeing of cotton by order of magnitude without any compromise on dyeing performance compared to the other commonly used methods (Table1).

NFC dyeing technique has many advantages over the other dyeing methods. It consumes ten times less water, dye and dye auxiliaries. It also minimizes water consumption and dye discharge during the textile washing process offering cost reduction benefits to the industry. It promises more than 80% dye fixation and excellent dye performance. NFC dyeing technology involves dyeing of nanocellulose first and then depositing NFC dye dispersion on the fabric surface. Hence, the dye fixed to nanocellulose is converted to a fibrous pigment (in the nano-scale). NFC ensures the permanent retention of dye molecules via a combination of strong hydrogen bonds and fibrous (entanglements) mechanism of adhesion. As a result, the NFC dyeing technique achieves good dye fixation and minimizes dye discharge during the washing process. NFC increases the versatility of dyeing fabrics and fabric blends of different textiles, such as cotton, nylon, polyester and blended fabrics. NFC dye dispersion can be optimized for batch or continuous dyeing process using different deposition methods such as knife-coating, spraying, and printing. NFC is compatible with different dyes such as reactive, indigo, sulfur and vat dyes. It makes consistent dye dispersions with different monochromatic reactive dye color systems (red, blue, black and yellow) and trichromatic color shades (e.g., brown shade). And it also has a lower carbon footprint compared to the conventional dyeing method.

We also performed a gate-to-gate life assessment which proves the reduction in eutrophication potential and wastewater effluent load which is a more eco-friendly process for textile dyeing.[17]

| Table 1 : The materials for dyeing 1 kg of cotton (1% dye on the weight of fabric (owf)[17]				
	Reactive Dye	Salt (Na_2SO_4)	Alkali (Na_2CO_3)	Water
Conventional dyeing	10 g	1200 g	76 g	19 L (up to 100L depending on the method of dyeing)
NC-based dyeing		120 g	7.6 g	1.9 L

The objective of the current study is to optimize the amount of nanocellulose gel to dye ratio that yields high colorfastness and comparable L*a*b* color values to the control (samples with dye solution but without nanocellulose gel).

Materials and Methods

Materials

Commercially available kraft pulp and carboxymethylcellulose sodium salt (Sigma Aldrich, St. Louis,

MO) were used to manufacture nanocellulose gel. Key ingredients of nanocellulose gel-dye coated cotton fabrics included reactive red 120 dye (*Figure 1*, Sigma Aldrich, St. Louis, MO), sodium carbonate (J. T. Baker, Center Valley, PA), sodium chloride (J. T. Baker, Center Valley, PA), bleached desized cotton print cloth (Testfabrics, West Pittston, PA), and standard powder detergent.

Fig. 1: Reactive Red 120
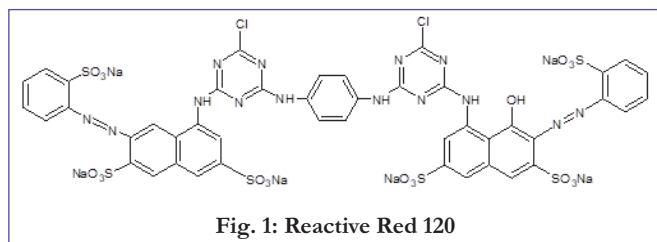
Methods

Nanocellulose gel production

Kraft pulp was processed through a hammer mill once and then through a knife mill three times to form a cellulose powder. 30 grams cellulose powder, 5 grams carboxymethylcellulose sodium salt, and 500 milliliters of deionized water were mixed in a beaker with stirring. The mixture was passed through an SPX APV 1000 homogenizer under 700 bar pressure for 20 minutes until a gel was formed.

Particle size distribution measurement

Water was added to knife milled cellulose for suspension and six percent nanocellulose gel for dilution. The samples were analyzed with a NICOMP particle sizing system using NICOMP distribution.

Imaging of nanocellulose gel and NanoFibrillated Cellulose (NFC)

In order to image the nanocellulose microfibrils, 6% nanocellulose gel was diluted to 2% and then filtered through a 12 ml syringe containing glass wool sandwiched between two layers of 2.5 μm filter paper. Transmission electron microscope grids were added to the nanocellulose and allowed to air dry for a few seconds. The nanocellulose fibrils were imaged using an FEI Tecnai20 Transmission electron microscope at 200 kV. One droplet of 2% NFC gel was diluted to 1 % on a microscope slide and allowed to dry into a thin film. The thin film was viewed with an Olympus optical microscope under 5x magnification.

Formation of nanocellulose gel dye paste and application to cotton fabric

Ten grams of deionized water, 0.1 grams reactive red 120 dye, 0.1 grams sodium carbonate, 0.4 grams sodium chloride, and 0.2 grams detergent, used as a wetting agent, were mixed to make the dye solution and stirred using an Innova 2000 shaker for 30 minutes at 100 rpm.

The dye solution and nanocellulose gel were mixed in a petri dish (*Figure 2*). The ratio of the weight of gel to the amount of dye solution was selected as follows: 5 g to 1 ml, 5 g to 2 ml, 5 g to 3 ml, 5 g to 4 ml, 5 g to 5 ml, 10 g to 1 ml, and 10 g to 2 ml. Nanocellulose gel-dye mixture was rolled with a laboratory dyeing roller over pre-wetted cotton fabric heated to 65°C. For control cotton samples, dye solution without nanocellulose gel was applied directly over the pre-wetted cotton fabric. Samples were dried at 120°C for 90 seconds by using a Mathis dryer. Fabric samples were then placed in the conditioning chamber. Wet and dry crocking was performed on treated fabrics with an SDL Atlas M238BB Electronic Crockmeter, and L*a*b* color measurements were taken with a Macbeth Color Eye 7000A.

Fig. 2: Dye and Nanocellulose Gel Paste

Statistical analysis

Separate statistical analyses were carried out for wet and dry crocking data as well as L*a*b* color space data. A linear regression model was fitted for the crocking data. For the L*a*b* color space data, two different statistical methods were employed to determine the gel to dye ratio for retaining the same color as the control. While the first method examines the three-color values L*, a* and b* separately; the second method evaluates them simultaneously by considering the color difference, ΔE(CMC). For the first method, three separate linear or quadratic regression models were fitted for the three-color values L*, a*, and b*, respectively, and in each case, the more parsimonious linear regression was chosen, if the quadratic term was not statistically significant. Using the fitted models, the acceptable ranges of gel to dye ratios were determined for each of the three color attributes. For the second method, the color difference ΔE(CMC) was calculated, for each sample, and fitted with a quadratic model to identify the gel to dye ratio for which ΔE(CMC) ≤ 1 indicates no color difference.

Results and Discussion

Nanocellulose gel characterization

The image from transmission electron microscopy (TEM, *Figure 3*) presents isolated nano-sized cellulose fibers with width and length range from 10 to 50 nm and up to several micrometers, respectively. NFC gel also exhibits a wide range of viscosity as a function of shear rate (*Figure 4*), which is an essential feature for printing/coating. Suspensions of NFC tend to have shear thinning properties, which may be caused by the packing aggregation of nanofibrillated cellulose fibrils.[1] The shear thinning property of gel allows for ease application of the nanocellulose gel coating.

The nanocellulose gel has specific properties that may influence its ability to make a good dye coating for textiles. For instance, NFC is known to contain a high amount of hydroxyl groups.[1] Due to its nano-dimension, the specific surface area of NFC fibers is expected to be substantially large. Its surface chemistry will determine the number of reactive sites available to react with the reactive dye. NFC also consists of crystalline and amorphous regions,[1] and its degree of crystallinity may impact the affinity of the dye for reaction with nanocellulose.
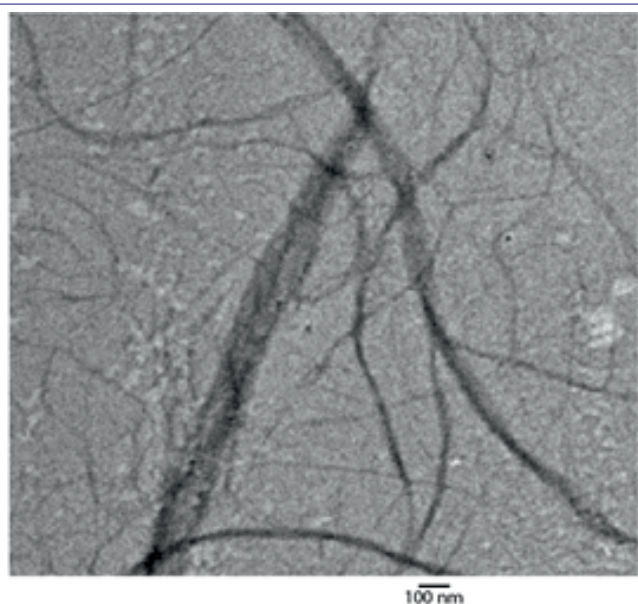

Fig. 3: Transmission Electron Microscopic Image of NFC

Colorfastness evaluation

As seen from *Figure 5*, for dry crocking, the colorfastness remained constant as the nanocellulose gel to dye ratio increases. Whereas, for wet crocking, the colorfastness level increases significantly as the nanocellulose gel to dye ratio increases. The linear regression model yields 83.8% and 3.27% values of multiple R^2 for wet and dry crocking, respectively. As expected, the regression coefficient for a gel to dye ratio was statistically significant for the wet crocking, but not for the dry crocking. The analysis of wet crocking data indicated that for each unit increase in the gel to dye ratio, the colorfastness level could be predicted to rise by 0.202 (Table
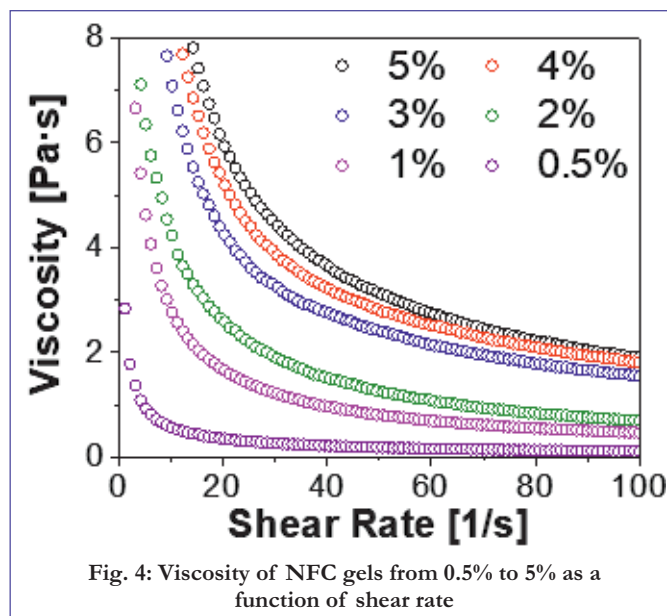

Fig. 4: Viscosity of NFC gels from 0.5% to 5% as a function of shear rate

2). In other words, these results suggest that a higher gel to dye ratio is desirable. Recommendations of the optimal gel to dye ratio will be made based on these results that are discussed further in this article.
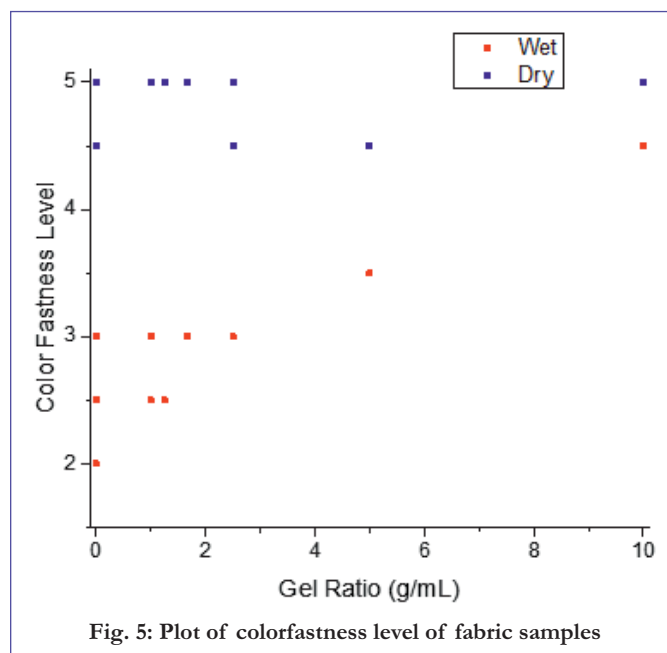

Fig. 5: Plot of colorfastness level of fabric samples

Table 2: Regression summary corresponding to colorfastness test				
	Estimate	**Std. Error**	**t Value**	**P value**
Intercept	2.491	0.0895	27.829	5.7E-13
Gel to Dye Ratio	0.202	0.246	8.201	1.7E-6

Gel to Dye ratio for retaining dye's color

Individually evaluating L*, a*, and b*

We determined, based on L*a*b* color space values through reflectance, the optimal gel to dye ratio that would yield a color

close to the color of the control. As the gel to dye ratio increased, an increasing trend was observed in L* and a decreasing trend in both a* and b* (*Figure 6*). The rising trend of L* suggests that the dye's color is getting lighter. Decreasing a* signifies a reduction in red and decreasing b* indicates an emerging presence of blue. The b* value close to 0 for the control confirms that the original dye incorporates a purely red color composition. The three trends combine to illustrate the increasing deviation from the dye's original color, with the gel to dye ratio increasing.
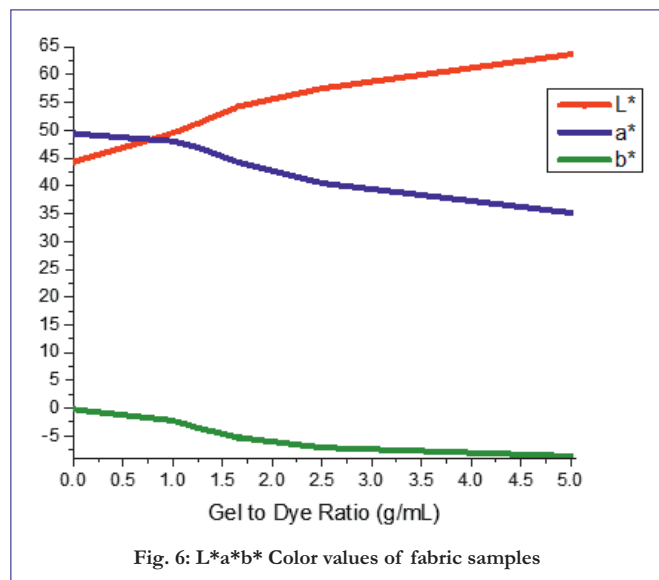

Fig. 6: L*a*b* Color values of fabric samples

For the analysis, we fitted a quadratic regression for L*, linear regression for a*, and a log transformation regression for b*. The one-way ANOVA test for L*, a*, and b* all indicated the significance of the gel to dye ratio in the resulting color of the fabric after the dyeing process (Tables 2-5). We used the coefficients from this analysis to determine the optimal gel to dye ratios significantly close to the L*a*b* color values of the control. If the difference between the sample's and the control's L*a*b* values were less than 2.20, 1.85, and 1.50, respectively, no color difference was reported.

Table 3: Regression summary corresponding to L*				
	Estimate	Std. Error	t Value	P value
Intercept	44.013	0.581	75.811	5.1E-6
Gel to Dye Ratio	6.756	0.578	11.698	0.001
(Gel to Dye Ratio)^2	-0.562	0.105	-5.367	0.013

Table 4: Regression summary corresponding to a*				
	Estimate	Std. Error	t Value	P value
Intercept	49.842	0.806	61.846	4.1E-7
Gel to Dye Ratio	-3.047	0.326	-9.338	7.3E-4

Table 5: Regression summary corresponding to b*				
	Estimate	Std. Error	t Value	P value
Intercept	2.311	0.0931	24.810	1.6E-5
Gel to Dye Ratio	-0.413	0.0377	-10.950	3.9E-4

In order to retain the original dye's L*a*b* values, the three models predict that the gel to dye ratio must be less than 0.39, 0.76, and 0.48, respectively. The lower end of all three intervals returned a negative number. Thus the ranges were cut off at the lower endpoint of zero. Therefore, if the gel to dye ratio is under 0.39, all three of L*, a*, and b* should pass the color comparison test against the control, which has no nanocellulose gel. With the gel to dye ratio of 0.39, our analysis predicts that the colorfastness level will increase by 0.079 when tested with wet crocking.

Evaluating ΔE(CMC)

Equation (4) calculated the total color difference, ΔE:

$$\Delta E\ (CMC) = \sqrt{\left(\frac{\Delta L^*}{lS_L}\right)^2} + \sqrt{\left(\frac{\Delta C^*}{cS_C}\right)^2} + \sqrt{\left(\frac{\Delta h^o}{S_h}\right)^2} \quad (4)$$

The symbols represent the following factors: ΔL = L* difference, ΔC = C* difference, Δh = h* difference, l = luminosity factor, c = chroma factor, S_L = compensation for lightness, S_c = compensation for chroma, SH = compensation for hue. We followed the precedent set by Khatri et al. and chose l:c ratio of 2:1. 18

Table 6: ΔE (CMC) values at different gel to dye ratios	
Gel to Dye Ratio	**ΔE(CMC)**
0	0
1.00	3.177
1.25	4.757
1.67	7.454
2.50	10.473
5.00	14.881

For this statistical analysis, the gel to dye ratio was the explanatory variable, and the ΔE(CMC) value was the response variable (Table 6). Because the dataset showed an exponential trend, a log transformation was applied and fitted with a quadratic regression (Table 7). We added to each ΔE(CMC) value to have only positive numbers for the response. The multiple R^2 for this model was 98.77%, with adjusted R^2 of 97.95%, which indicated a good and proper fit.

Table 7: Regression summary corresponding to log(ΔE(CMC)+1), with quadratic fit				
	Estimate	Std. Error	t Value	P value
Intercept	0.008	0.129	0.601	0.589
Gel to Dye Ratio	1.503	0.128	11.734	0.001
(Gel to Dye Ratio)2	-0.194	0.023	-8.362	0.004

In the fit, we looked for the gel to dye ratio that yielded log(2), which would correspond to ΔE (CMC) = 1 prior to the transformation. Using the coefficients derived from the analysis, the maximum gel to dye ratio to ensure ΔE (CMC) ≤ 1 was found to be 0.434. With this gel to dye ratio, the predicted
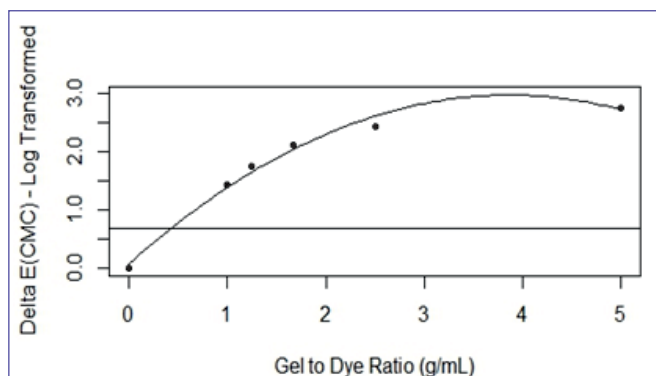
Fig. 7: Observed log(ΔE(CMC)+1) values and the fitted regression line. The horizontal line represents the maximum ΔE(CMC) value for no color difference

increase in the colorfastness for wet crocking was 0.088. *Figure 7* plots log(ΔE(CMC)+1) and its fitted regression line, with a horizontal line at the maximum value representing no color difference from the control. The plot reflects a concave positive relationship between color difference measure and gel to dye ratio. The graph provides the visual location of maximum gel to dye ratio denoting no color difference, as the intersection of the fitted line and the horizontal line.

Conclusions

NFC presented in this paper is a biodegradable material engineered into a nanocellulose hydrogel by a homogenization process. The cellulose is ground and homogenized into a gel - a suspension of nanometer size fibrils. Nanocellulose gel with its ease of application would make a good dye coating for the innovative textile application. Based on our previous research, this paper focuses on the optimization of the amount of nanocellulose gel to dye ratio for good color performance. Through the statistical analysis, we determined that the colorfastness level would increase with higher gel to dye ratio. Through a separate analysis for L*, a*, and b*, we recommend a gel to dye ratio less than 0.39 for a color comparison test. From the combined analysis of ΔE(CMC), a gel to dye ratio less than 0.43 is recommended. Combining all three results, we conclude that a gel to dye ratio of approximately 0.4 will yield optimal performance and an effect comparable to the control.

Acknowledgments

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