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Complete List of Authors:	Rai , Smriti ; The University of Georgia, Nanostructured Materials Lab Saremi, Raha; University of Georgia, Textiles, Merchandising & Interiors Sharma, Suraj; University of Georgia, Department of Chemistry Minko, Sergiy; The University of Georgia, Nanostructured Materials Lab

Environment-friendly nanocellulose-indigo dyeing of textiles

Smriti Rai,[a,b,c] **Raha Saremi,** [a,b,c] **Suraj Sharma,** [a,b*] **Sergiy Minko** [a,c,d *]

[1]Department of Textile, Merchandising, and Interiors, University of Georgia, Athens, Georgia, USA
[2]Innovative Materials Research Team, University of Georgia, Athens, Georgia, USA
[3]Nanostructured Materials Lab, University of Georgia, Athens, Georgia, USA
[4]Department of Chemistry, University of Georgia, Athens, Georgia, USA

* Corresponding e-mail: ssharma@uga.edu; sminko@uga.edu

Abstract

Dyeing of one pair of denim blue jeans consumes about 50-100 liters of water loaded with toxic reducing agents and alkali that remain effluent in wastewater. Here we introduce environmentally sound indigo-dyeing technology utilizing a high surface to volume ratio of nanocellulosic materials, which reduces water consumption up to a factor of 25 and eliminates the use of any reducing agent and alkali. This technology secures over 90% dye fixation compared to 70-80% of conventional dyeing. Lighter or darker shades are approached in a one-step process compared to the traditional vat dyeing with multiple (up to 8) dips in a reduced vat followed by oxidation. The dyeing process is as simple as the deposition of nanocellulose hydrogel loaded with natural indigo fine particles and chitosan over the cotton denim fabric or yarn. The generated nanofibrillated cellulose mesh-like conformal coating encloses indigo particles, whereas chitosan improves fixation and adhesion of the coating to fabrics via physical cross-linking.

Introduction

Textiles remain among major consumer products and one of the most elaborated human made materials with a history that spans over many centuries. The dark spot of this history is that the textile industry is one of the most significant pollutant sources since the Industrial Revolution in the late eighteenth century. In the twentieth century, the Earth population increased four-fold while the use of textile fibers increased 20-fold. The use of fibers continues to increase by about 3% a year, approaching the annual use in the U.S. of about 45 kg per person.[1] Denim fabric is not an exception, with an annual growth rate of more than 4%. The overall denim market was valued at over 90 billion dollars in 2017[2]. By 2018, more than 4.5 billion pairs of jeans were sold annually[2]. Cotton fiber denim products are biodegradable; however, their manufacturing remains less eco-friendly. The major environmental concerns related to the expansion of the use of denim cotton products is not limited to the consumption of energy and the use of fertilizers and chemicals at the agricultural stage of cotton fiber manufacturing. The process of dyeing of denim yarn is laborious, time-consuming, uses energy, toxic auxiliaries, and a substantial amount of water, 10-75 L per 1 kg of denim yarn for only the dyeing stage, depending on the target shade and structure of the yarn[3, 4].

Indigo, evidently, is the major pigment utilized for blue denim textiles. Indigo, although being considered a low-quality vat dye, is widely used in the denim industry because of its distressed look[5]. During the dyeing process, indigo is reduced into leuco indigo (see **Electronic Supplementary Information, ESI, Supporting Note, SN 1**) to make it soluble in water by adding a reducing agent (redox potential < −700 mV) in alkaline condition (pH 10-12). The most cost-efficient reducing agent is sodium hydrosulfite. However, it is readily oxidized in atmospheric oxygen, flammable during storage, and corrosive to wastewater pipe lines[6, 7]. During the wastewater treatment process, sodium hydrosulfite affects the aerobic processes and can form toxic hydrogen sulfide anaerobically from the sulfate present in the wastewater[7]. An alkali agent, caustic soda, is preferred for a combination with sodium hydrosulfite[8], but it is also known to be toxic to the environment, corrosive to the concrete waste line, and contribute to wastewater load[8]. A typical denim mill generates more than 400,000 tons of wastewater in a year in the dyeing process[9], which contains high amounts of salt effluents, indigo dye (20-30% of the initial load), and other metal traces[10-14]. The denim dyeing wastewater is not suitable for reuse or disposal because of a high chemical oxygen demand COD =520-3250 mg/L and a high pH level, among other parameters[9]. Due to the lack of expensive water treatment facilities in developing countries, untreated wastewater is usually discharged into nearby water streams. According to Greenpeace and other surveys, the water streams near the localities of denim dyeing mills are turning blue (**ESI**, **Figure S1**) and contain a high level of industrial pollution, causing skin diseases[15-18].

Using pre-reduced indigo (**PRI**) (catalytically hydrogenated indigo solution) could save up to 70% of the reducing agent and alkali[19], but it is too expensive and poses numerous challenges in shipping to prevent oxidation[19]. Newer technologies such as spray dyeing and foam dyeing can reduce significant amounts of water consumption[7, 19-23]. None of these novel techniques are widely adopted, especially in developing countries where most mills are situated because they require significant investments and maintenance[24].

An interesting approach was recently proposed by Dueber et al.[25] A resistant to oxidation indigo precursor indicant is obtained via microbial synthesis and deposited on the textile surface using a spray method. Then, the fabric is treated with β-glucosidase enzyme to hydrolyze indican into indoxyl. Indoxyl then is spontaneously oxidized to form indigo pigment. The methods are based on microbial synthesis and biocatalysis with no use of reducing chemicals. Further studies will provide quantitative information about dye fixation, color strength, and colorfastness of the colored fabrics.

For all the industrial technologies, the dyeing performance (dye fixation and colorfastness) remains at the same level as for the vat dyeing but, these techniques are based on the reduced indigo and hence make a similar negative environmental impact due to the use of toxic reducing agents. For higher shades, these methods use multiple deposition-oxidation steps with increased water consumption.

Synthetic indigo is produced from petroleum-based, highly toxic aniline, and other harmful intermediate chemicals[7]. The denim industry uses about 45500 tons of synthetic indigo, 84500 tons of sodium hydrosulfite, and 53500 tons of caustic soda each year[26, 27]. Cultivating and using natural indigo pigments (Indian or Japanese/Sukomo method) is a growing trend since recently. Combination of natural indigo with natural reducing agents (fructose, ferrous sulfate, henna, osage, and madder) and alkali from natural sources (wood ash, limestone, and wheat germ) are less environmentally harmful technologies[28]. However, the current technology to produce organic jeans is too expensive yet for mass production[28, 29].

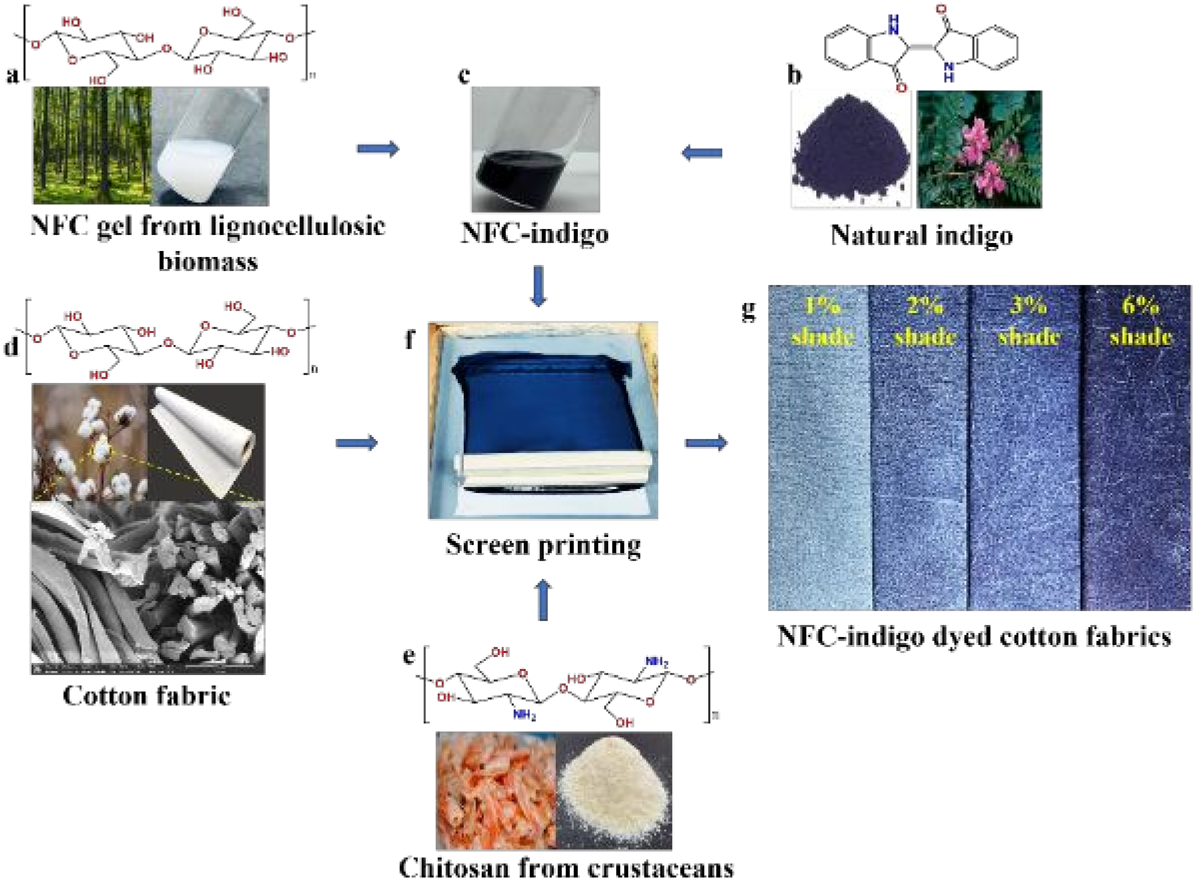

Figure 1. Schematic of NFC-indigo dyeing: (a) NFC gel prepared from wood pulp; (b) natural indigo powder, a product of plant *Indigofera Tinctorium*; (c) NFC-indigo; (d) cotton fabric, a product of natural cotton fibers; (e) chitosan, a product of deacetylation of chitin (food waste); (f) screen printing/ coating on the cotton fabric with NFC-indigo ; (g) Cotton fabric dyed with NFC-indigo and post-treated with chitosan The percentage shade is the amount of the indigo pigment expressed as a percentage of the weight of the undyed cotton textile.

Here, we demonstrate a cost-efficient indigo dyeing of cotton textiles, which is based only on biobased materials, including natural indigo (**ESI SN 1**), nanofibrillated cellulose (NFC) (**ESI SN 2**), and chitosan **(ESI SN 3)**) with no use of reduced indigo. The NFC-indigo dyeing technology eliminates the use of highly toxic auxiliaries (sodium hydrosulfite and caustic soda), consumes a reduced amount of indigo, and significantly reduces water usage. The developed method takes advantage of conformal web-like microscopic coatings formed by nanofibrillated cellulose around cotton fibers by entrapping indigo particles. The NFC-indigo dyeing formula consisting of nanofibrillated cellulose hydrogel (1 w% of cellulose content, ESI), natural indigo-particles, and a small fraction of a dispersing agent is coated over cotton textiles (**Figure 1**). The coated textiles are then post-treated with a chitosan aqueous solution for improved adhesion and stability of the coating (**Figure 1**).

Results and Discussion

The NFC-indigo dyeing of fabrics or yarns is conducted just in one step for any shade compared to conventional vat dyeing with multiple steps (up to 8 for dark-blue shades) by immersion in the oxygen-free dye bath with a leuco indigo solution followed by oxidation via exposure to the air. In the NFC-indigo dyeing method, a mixture of natural indigo particles and 1% NFC hydrogel is deposited once on the surface of the cotton fabric or yarn using a screen-printing technique or continuous flow padding process, respectively (**ESI Video 1** and **ESI Video 2**). This method requires no multiple reduction-oxidation steps.

Behind the simplicity of NFC-indigo dyeing technology, several mechanisms are responsible for securing the performance of the dyed fabric. NFC is a random material composed of cellulosic fibers typically 10-50 nm in diameter and several micrometers long with a broad size distribution. This results in an about 1:50 average aspect ratio of the microfibrils. The hydrogel contains 0.25% of carboxymethylcellulose (CMC). CMC is added as a pulp pre-treatment additive[30] for the efficient fabrication of NFC. NFC-hydrogel forms conformal flxible coatings upon deposition and evaporation of water. In the coating, NFC forms an entangled network with a random distribution of mesh sizes scalable with the fibril diameter. A very thin NFC coating on the surface of cotton fibers can be recognized by comparing the SEM images of the neat cotton fibers and coated ones in **Figure 2a** and **Figure 2b**, respectively. A reference sample of the NFC film on the glass slide reveals the mesh-like structure of the coating (**Figure 2c**). The experimentally measured cut-off diameter of particles that passed (>50%) through the NFC coating is 150 nm (**Figure 2j**).

Natural indigo particles are dispersed in an aqueous solution of a dispersing agent with an average diameter of 83±14 nm, as estimated with dynamic light scattering (DLS). However, they form aggregates on the surface of cotton fibers upon drying due to intermolecular hydrogen bonds[31, 32] with a 330 nm average size of the aggregates as measured by DLS for the particles extracted from the traditionally dyed cotton fabric (**Figure 2**). The aggregate size can also be estimated using SEM images (**Figure 2e-f**). These aggregates are caged in the fibrillar mesh form by NFC, as explained with pictorial sketches in **Figure 2i-j.** This engulfing of pigment aggregates with NFC is observed in SEM images of the reference NFC-indigo film on the glass slide (**Figure 2d,e**) and on the surface of cotton fibers (**Figure 2g-h**). More than 50% and 70% aggregated indigo particles with a diameter of 150 nm and 350 nm, respectively, retain in the coating as caged in the network.

In **Figure 2k-l,** at two different magnifications, we demonstrate for comparison the structure of the indigo-dyed cotton prepared by the traditional exhaustion method via dyeing of fabric or yarn in reduced leuco indigo. The indigo-particles are deposited in an aggregated form on the surface of cotton fibers. The difference in the structure of traditionally indigo dyed and NFC-indigo dyed becomes apparent from comparing the images **Figure 2g-h** with **Figure 2k-l**. In the traditional method, the reduced indigo particle aggregates are deposited on the surface of cotton fibers, while in the NFC-indigo dyeing method, the aggregates of indigo particles are engulfed by NFC fibrils.

Several bonding mechanisms contribute to the mechanical properties of the NFC network: hydrogen bonds, mechanical interlocking, electrostatic interactions, interdiffusion of cellulose molecules, and van der Waals forces[33]. In the latter work, it was found that the mechanical interlocking boosts the bond energy by a factor of 2. This contribution depends on the concentration of the entanglements and hydrogen bonds between cellulose molecules in the area of contacts of the fibrils when the concentration of entanglements depends on the aspect ratio of the fibrils. NFC coating swells in water (e.g., while washing of garments)[34, 35]. The mesh size could increase because of swelling and loss of some inter-fibril contacts when some fraction of small particles could be lost during washing. This loss of the particles is minimized by strengthening the entangled network with chitosan linear polysaccharide chains that secure additional hydrogen bonding and physical cross-linking via glucosamine units[36].

The same mechanism of fibrils entanglement and hydrogen bond formations improves adhesion between NFC coating and cellulose molecules of cotton fabrics, yarns, and fibers. Typical cotton fibers are 10-20 μm in diameter and 20-35 mm long. The cotton yarn is made of many twisted single staple (short) cotton fibers and hence has a hairy structure when fiber ends protrude from at the yarn surface. These fiber segments entangle with the NFC coating and provide an additional contribution to NFC adhesion to the cotton fabrics due to the increased contact area and mechanical interlocking. This effect is clearly visualized for NFC-indigo dyed yarn (**Figure 3**). The visual appearance of the NFC-indigo colored cotton yarns with different shades is demonstrated in a panel of **Figure 3a**. NFC fibrils entangle with the cotton fibers in the yarn and form a conformal shell and patches on the surface of the yarn (**Figure 3b-c**), while NFC reaches no interior part of the yarn (**Figure 3d**). This kind of pigment deposition over the cotton yarn is termed a ring effect, which is well known also for conventional indigo dyeing of cotton yarn shown here for reference (**Figure 3f**). This structure is visualized with an optical image showing a bundle of yarns (**Figure 3e** and **ESI Note 1**). We recently demonstrated that a combination of inter-entanglement and hydrogen bonds secured adhesion and stability of NFC coatings on textiles[37]. Such coatings were stable to multiple washing cycles for colored textiles with NFC-reactive dyes[38, 39].

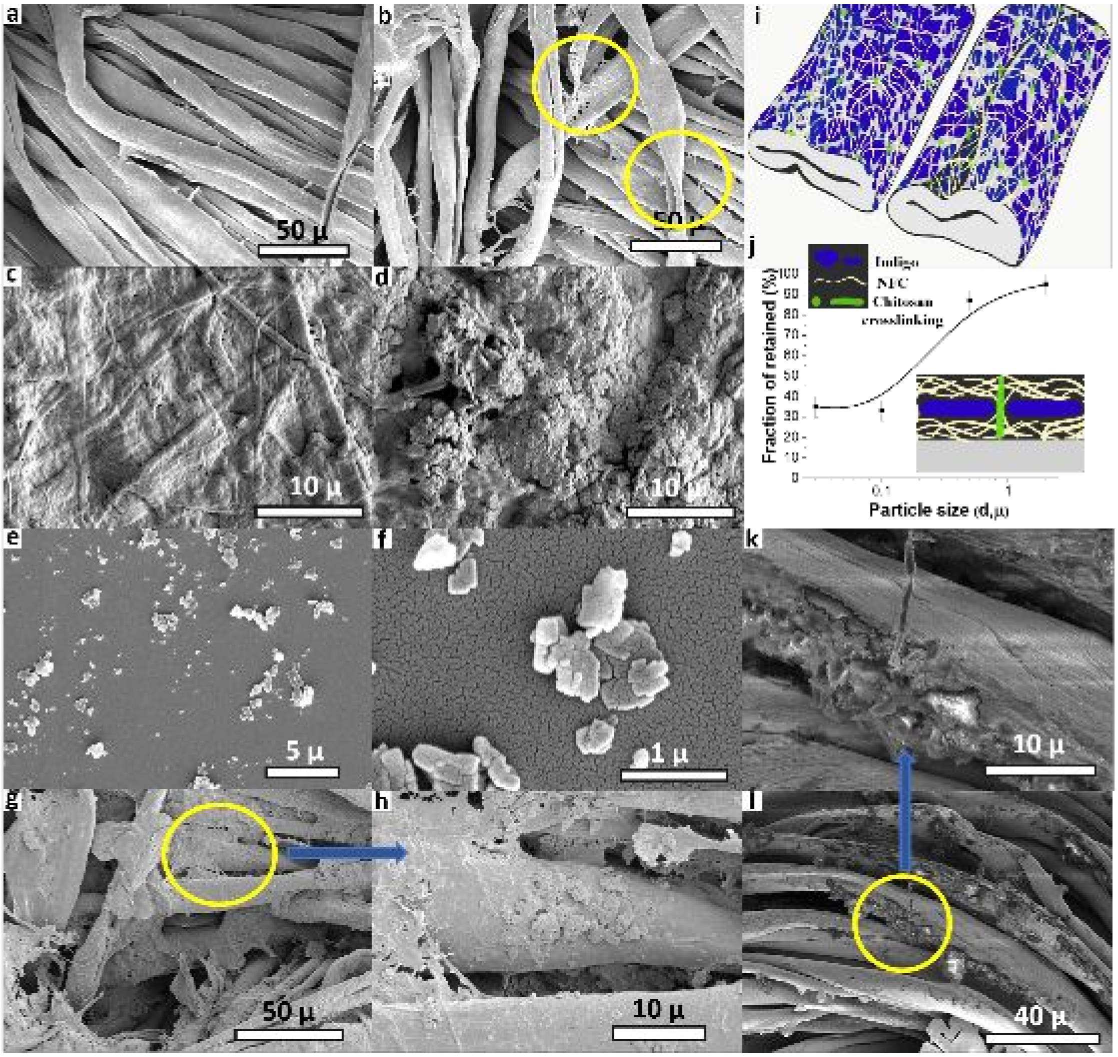

Figure 2: SEM images: (a) neat cotton fabric; (b) cotton fabric coated with NFC; (c) reference - 1% NFC gel (dried film) on the glass slide; (d) reference 1% NFC mixed with indigo, 6% (dried film); (e) and (f) indigo pigment particles on the glass slide; (i and j insets) pictorial representation of cotton fibers dyed with NFC-indigo (i) with an NFC mesh-like shell cross-linked with chitosan around cotton fibers with caged pigment particle in the NFC mesh, (j)

fraction of particles retained in the NFC mesh; the dotted line shows the cut-off size of 150 nm; insets show a schematic of the coating cross-section with retained indigo particles; (k) and (l) cotton fabric dyed with indigo by the traditional exhaustion method (dyeing of fabric in reduced leuco indigo). The circles point out well contrasted spots of interest for readers' convenience.

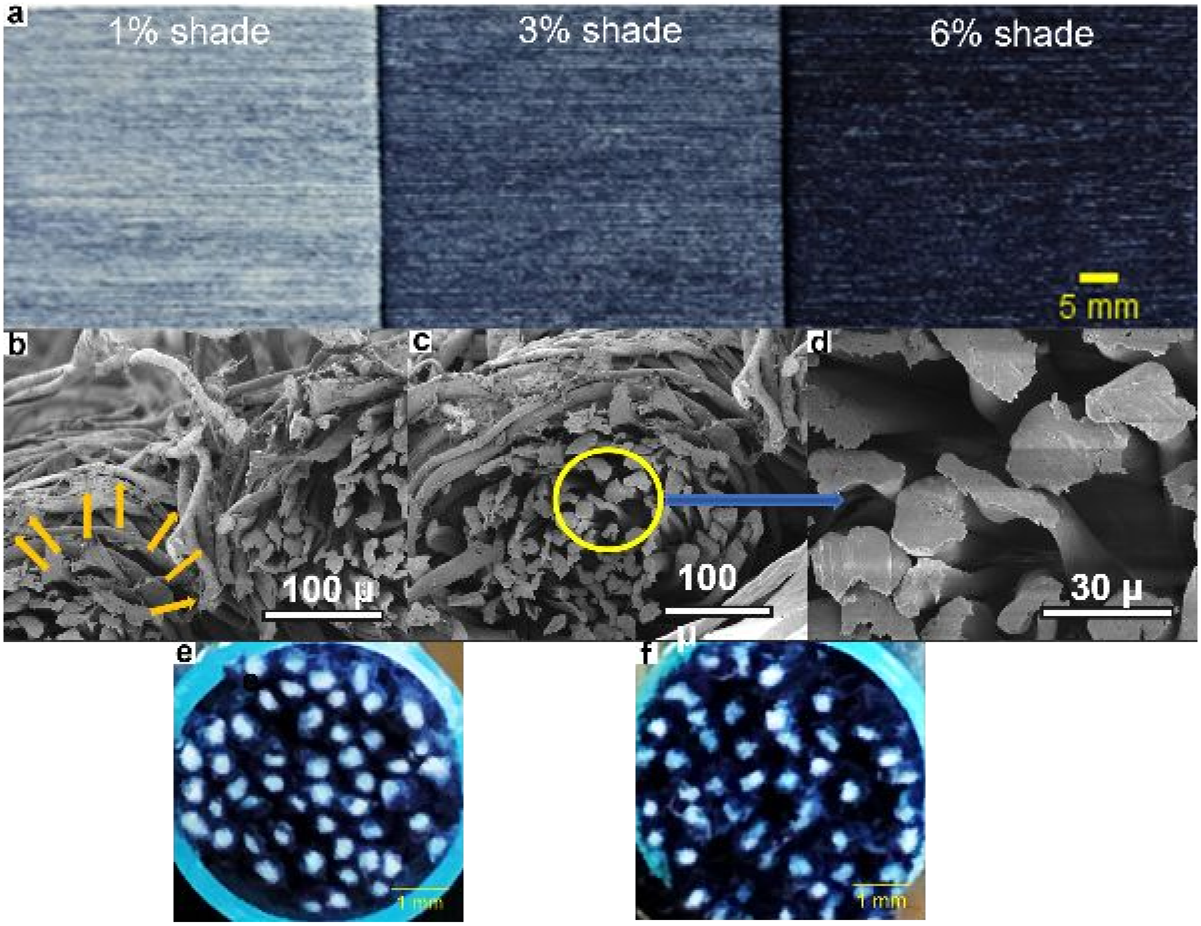

Figure 3. NFC-indigo dyed cotton yarn: (a) arrays of yarns colored with different shades; (b-d) cross-sectional SEM images of the dyed yarn; arrows point onto NFC fibrils entangled with single fibers located at the exterior part of the yarn; the circle shows the interior of the yarn and the magnification with no NFC fibers inside of the yarn; (e) and (f) optical images of the bundles of the indigo-dyed yarns using (e) NFC-indigo dyeing method and (f) conventional exhaustion method dyed yarn at 11.5 pH that show in both cases ring effect of dyeing the exterior part of the yarns.

Color performance for the NFC-dyed fabrics was estimated using commonly used metrics: color strength (K/S), dye fixation percentage (% F), and colorfastness. Color strength is defined as a ratio of absorbed (K) and scattered (S) light by the colored material[8]. Fixation is calculated by comparing the K/S ratio before and after washing using a standard protocol[8]. Colorfastness is the resistance of color fading, bleeding, or staining when actions such as laundering (washfastness) or rubbing (dry and wet crockfastness) are performed on dyed or printed textiles[8]. To elucidate the importance of the treatment with chitosan, we compared the results for chitosan treated materials with non-treated references for different shades (**Figure 4**). For example, before wash, K/S values for 6% shade samples were similar, 5.36±0.76 for reference, and 5.6±0.46 for chitosan treated samples. However, after wash, the K/S were 1.96±0.3 and 5.24±0.37, giving the fixation of 36±4.31% and 93±7.33% for reference and chitosan treated samples, respectively. Optical and SEM images of the NFC-indigo dyed reference and chitosan treated samples, both before and after washing, are shown in **Figure 4c**. The amount of the coating materials, as appears in SEM images, remains unchanged for chitosan treated samples after washing in contrast to the reference sample.

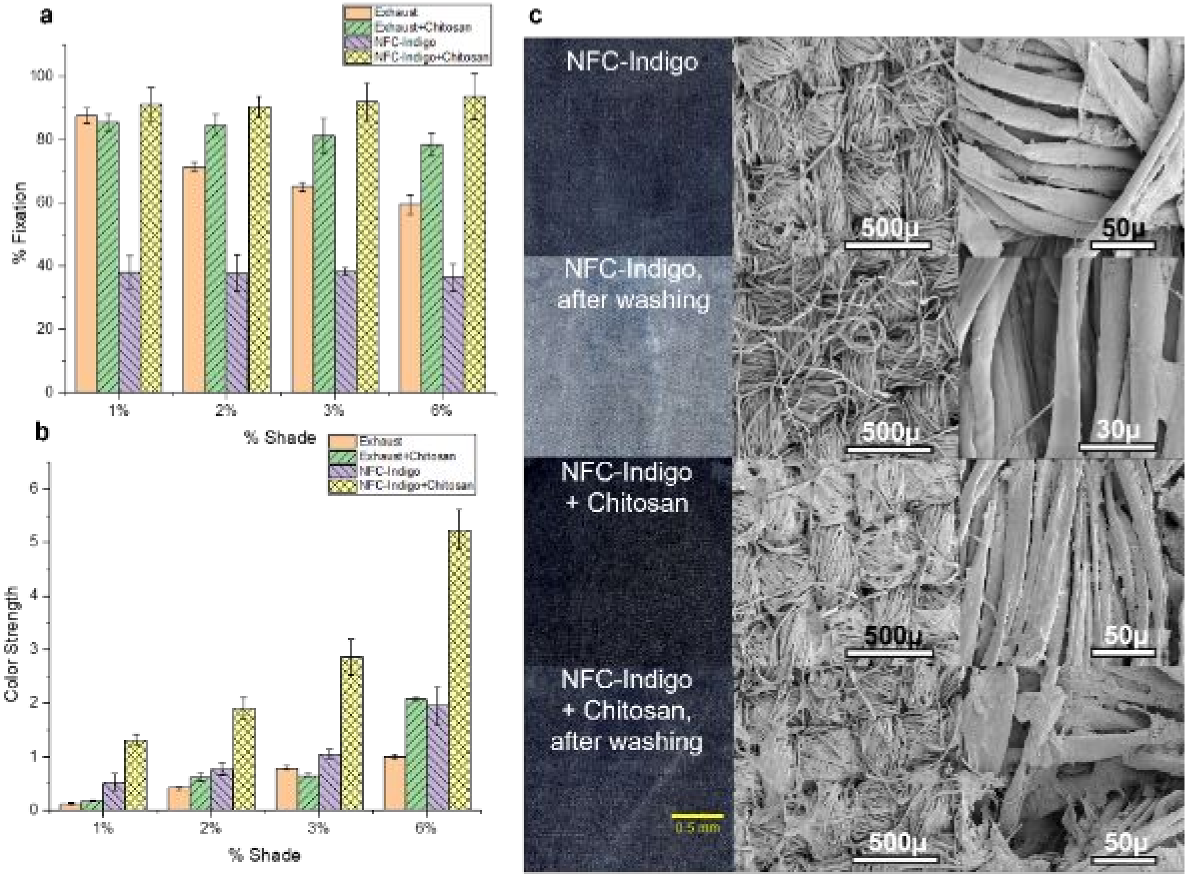

Figure 4. (a) Dye fixation (%F) and (b) color strength of NFC-indigo dyed denim for different % shade for samples post-treated with chitosan and non-treated reference sample (5 samples of 5 x 15 cm) compared with the traditional (Exhaust) and the traditional but modified with chitosan

(Exhaust + Chitosan) methods. (c) SEM and optical images of the 6% shade reference samples and samples post-treated with chitosan.

The dye fixation shows a minimal variation in the range of 90 to 93% when the fabric is post-treated with chitosan **(Figure 4a)**. The color strength increases with the percentage of indigo (**Figure 4b)**; hence any desired shade can be obtained by varying the indigo content in the NFC gel in one deposition step, unlike the conventional dyeing with indigo when multiple dipping is required to gain darker shades.

The developed NFC indigo-dyeing method was compared with the traditional exhaust method and the traditional method modified by the chitosan treatment (Figure 4a) for one step of the indigo-dye deposition. In terms of color strength, the NFC-dyeing method outperforms the traditional method with a factor of 5-10, depending on the shade level. The low level of indigo dye fixation is well known, and it is a reason for multistep deposition technology. In terms of dye fixation, the comparison is misleading since no one of the traditionally colored samples approached the color strength level of the NFC-indigo-chitosan method (Figure S4). Dye fixation for the traditional method is a decreasing function of shade, but for the NFC-indigo-chitosan method, it is independent of shade in the studied range (Figure 4a). The application of chitosan improves the dye performance in the traditional method, but indeed the levels of color strength and dye fixation remain well below the NFC-indigo-chitosan method. The effect of chitosan on the dye fixation for the NFC-indigo-chitosan method is in striking contrast with the traditional method. The latter indicates the differences in the dye fixation mechanisms.

If in the chitosan-modified traditional method, chitosan improves the adhesion of indigo particles and their aggregates to the surface of cotton fibers, in the NFC-indigo-chitosan method, chitosan strengthens the NFC network that cages indigo particles. In the latter case, the effect of hydrogen bonds is multiplied via the chitosan molecular associates bridging NFC fibrils of the NFC coatings. If the energy of a -OH…HO- hydrogen bond is about 5 Kcal/mol, but the energy of a -N-Ac ...H_2N- hydrogen bond in chitosan is 6.1 Kcal/mol.[40] These strong intermolecular hydrogen bonds make chitosan associates more hydrophobic and insoluble in DI water. This chitosan structure masks NFC network from molecules of water and lowers the swelling of the coating.

It is important to mention the role of the CMC additive. After deposition of the NFC coating, most CMC which is not strongly adsorbed on NFC and on cotton fibers, is washed out in washing cycles.

However, a strongly adsorbed CMC could facilitate swelling of the NFC coating in water.[30] At the same time, the strongly adsorbed negatively charged CMC forms a polyelectrolyte complex with chitosan, hence acting to reinforce the coating and its interaction with the cotton fabric.

The washfastness, wet, and dry crock fastness for most samples exceeded or met the standard requirements for indigo-dyed denim with grades 2, 1.5, and 3, respectively[41] (**Table S1**). Samples with a very dark shade demonstrated dry crock fastness with lower grades compared to lighter shades, likely because of a larger concentration of small indigo-pigment particles in the coating. This could be addressed by the optimization of indigo particles' aggregate size. These characteristics for the NFC-indigo-chitosan method are compared with the traditional exhaust method; note that these characteristics depend on K/S. For example, for the experimental data in Table S1, the samples prepared with 1% shade by the NFC-indigo-chitosan method (K/S=1.31) could be compared only with the sample prepared with 6% shade for the traditional method (K/S= 1.0). For all other samples, K/S values for the samples by the traditional method is substantially lower than those for the NFC-indigo-chitosan method.

We also compared the NFC-indigo-chitosan method with the exhaust method with no harsh chemical use (no alkali and reducing agent). In the latter case, the dye performance is much poorer than in the traditional method (Table S1).

It is noteworthy that comfort properties for the NFC indigo-dyed denim are not changed after NFC-indigo dyeing. The fabric samples were tested for a range of properties related to comfort: weight gain, thickness of the coating, bending length, and air permeability (**Table S2**). The weight gain was estimated as a very small count in a range from 1 to 3%, while the NFC coating thickness was in a range from 3 to 8 μm for color strength from 1 to 6, respectively. Bending stiffness is a quantitative measurement of the fabric hand. The bending length is the length of the rectangular strip of the material, which bends under its weight to a specified angle[42]. The longer the bending length, the stiffer the fabric. The increase in bending length was very low (approx. 8%) for samples post-treated with chitosan. The air permeability is estimated as the rate of airflow passing across the unit area of the fabric under a standard air pressure drop[42]. Our tests demonstrated no changes in air permeability in NFC coated fabrics. SEM images of the colored textiles (**Figure 2g**, **Figure 3b-c**, and **Figure 4c**) reveal that the NFC coating is deposited as a ring around the yarn with no deep intercalation into the interior yarn structure; consequently, the coating envelopes individual yarns with no blocking of the interstices (space between two yarns) and thus has no effect on the air permeability.

The results of the tests demonstrate that the NFC-indigo dyed denim fabric meets all major requirements while the colored fabric is fabricated by using much more efficient and environmentally sound technology compared to the traditional method. A typical traditional indigo dyeing range consists of pretreating vats, four to eight reduced indigo vats (dyebaths of 2000 liters each), and successive airing to produce a darker color of indigo blue, followed by multiple vats for washing to remove unfixed dye[43, 44]. The water usage in the dyeing process increases with the desired percentage shade, where approximately 10 to 75 liters of water per kg of yarn are used[3, 4]. The wastewater produced during this process contains high amounts of effluents and requires expensive water treatment facilities[9]. The ultrafiltration process can recover about 0.1g/liter of indigo; however, it is usually not pursued due to its cost compared to the cost of indigo[45].

Table 1. Comparison of materials consumption for NFC-indigo dyeing and traditional exhaust dyeing

Dyeing method	**Reducing agent (sodium hydrosulfite), g/kg of product**	**Alkali (27 % sodium hydroxide), ml/kg of product**	**Water, l/kg of product**
Conventional dyeing with pure indigo powder[3, 4]	44-262	110-656	10-75
Conventional dyeing with pre-reduced indigo[4, 19, 46]	13-79	33-197	3-5
NFC-indigo dyeing	None	None	2

Consumption of sodium hydrosulfite, caustic soda, and water to dye one kilogram of cotton with conventional and NFC-indigo dyeing is compared in **Table 1**. The estimation of water consumption includes only the dyeing stage. Any possible aqueous solution pre- and post-treatment and washing are excluded from the estimate. The treatment with chitosan (about 1 w% of the fabric) can add about 0.1 to 1 l/kg of water depending on the deposition method. No additional water consumption is associated with NFC production because it is made in an aqueous dispersion by the mechanical method in one step with no wastewater release. The NFC aqueous dispersion is directly used for the dyeing process (no drying).

The advantage of NFC-indigo dyeing technology is in the complete elimination of reducing agents, alkali, and also in a reduction in water usage up to a factor of above 25 when compared to conventional exhaust dyeing and by the factor of 2 when compared to dyeing with PRI. With over 90% dye fixation, an improvement of 10-20 percent point over the conventional method results in lesser indigo used to gain comparable color performance[13, 14, 47]. Additionally, the NFC-indigo dyeing method saves on energy and time-consuming parameters involved in the conventional indigo dyeing range, such as dipping time, oxidation time, and the number of dips to get the desired shade and effect. Moreover, washing with steel balls and rubbing during the crockfastness test exhibited the desired wash-off look due to deposition is very similar to the ring effect. It indicates that cotton dyed using the NFC-indigo method is also easy to work with various finishing methods such as stone washing, sanding to provide a personalized look to the final products.

Conclusions

The NFC–natural indigo dyeing technology is an eco-friendly and sustainable method of denim fabric dyeing. Post-treatment of chitosan significantly improved the dyeing performance of NFC-indigo dyed samples with better color strength and over 90% fixation in every percentage shade. There was no change in the comfort properties in terms of weight gain, bending stiffness, and air permeability. The surface morphology of coated and post-treated fabric offered a clear picture of the dyeing mechanism. The desired shade was obtained by adding the required amount of indigo as per the weight of the material to gain lighter or darker shade in a single coating. The method saves on chemical, energy, and water consumption by not using any harmful chemicals (reducing agents and alkali), eliminating the need for extensive multiple dipping, and saving water usage up to a factor of 25. This technology can be easily adapted and scaled as it requires a standard coating and printing technology with a one-step process to dye cotton textiles with indigo.

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Author contributions

S.M., S.S. conceptualization, methodology, review, and editing; S.R. methodology, NFC-indigo dyeing experiments, characterization, and writing. R.S. characterization methodology, experiments with the conventional dyeing, editing.

Conflict of interests

The authors declare no conflict of interest.

Keywords: nanocellulose; indigo; chitosan; cotton; textile

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