NANOCELLULOSE-BASED DYEING OF COTTON-RICH TEXTILES: A SUSTAINABLE SOLUTION FOR THE TEXTILE INDUSTRY

by

SMRITI RAI

(Under the Direction of Suraj Sharma and Sergiy Minko)

ABSTRACT

This research introduces an environmentally sound indigo-dyeing and cotton/polyester dyeing technology utilizing a high surface-to-volume ratio of nano cellulosic materials. Nanofibrilliated cellulose (NFC) is an engineered material composed of cellulosic fibers typically 10-50 nm in diameter and several micrometers long with a broad size distribution, resulting in about 1:50 average aspect ratio of the microfibrils. This dyeing technology involves coating cotton fibers with NFC loaded with dye molecules or particles, where NFC forms an entangled network of nanocellulose fibrils. This research study is divided into two parts.

In the first study on natural indigo-based nanocellulose gel (NFC-NI) dyeing, cotton samples are coated with nanocellulose hydrogel (mixed with natural indigo particles) and post-treated with chitosan. Nanocellulose gel acts as a carrier for indigo particles, whereas chitosan is a physical crosslinking agent, improving the fixation and adhesion of nanocellulose gel with indigo particles. This method provides lighter or darker shades in a one-step process as opposed to the traditional method, where several dips are required in a reduced vat followed by oxidation to develop darker shades. This one-step technology secures over 90% dye fixation compared to 70-80% of conventional dyeing, comparable colorfastness properties, eliminates the use of reducing agents or alkali, and saves water up to a factor of 25. Moreover, the NFC-NI dyed fabric has antimicrobial properties which are safe for apparel and medical textiles without compromising comfort properties.

In the second study, nanocellulose gel-based dyeing of cotton/polyester blend fabric provides one-step uniform coloration via the deposition of the colored (reactive dyes) nanocellulose fibrils on cotton fibers and sublimation of disperse dye into polyester fibers, followed by post-treatment with chitosan. Nanocellulose gel acts as an anti-migrating agent for disperse dye during sublimation in polyester fibers. In contrast, the reactive dyed nanocellulose is physically linked with the cotton fibers, coloring the whole fabric in a one-step process. Chitosan post-treatment improves color strength, fixation, and adhesion of dyed nanocellulose gel. NFC-based dyed cotton/polyester fabric achieved similar color performance, fastness properties, enhanced anti-wrinkle properties compared to the conventional dyeing method, and reduced water and auxiliaries usage up to factors of 18 and 20, respectively.

INDEX WORDS: Nanocellulose, Nanotechnology, Textile Dyeing, Eco-friendly, Sustainable, Indigo, Chitosan, Cotton, Cotton/Polyester Blend, Antimicrobial, Antiwrinkle.

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DEDICATION

I would like to dedicate this dissertation to my parents, husband, sister, brother-in-law, son, niece, and other family members. Thank you all for giving me the strength to follow my dream.

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INTRODUCTION AND LITERATURE REVIEW

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 has been one of the most significant pollutant sources since the Industrial Revolution. In the 20th century, while the world population increased 4-fold, a 20-fold increase in the use of textile fibers has worsened the situation. 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] Textile dyeing and treatment is responsible for 20 percent of industrial water pollution (4% is not treatable), and about 5 trillion liters of water is used in textile dyeing yearly.[2-4] Removal of dyes from the effluent is an expensive process. 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 have changed it's color (Figure 1.5) and contain a high level of industrial pollution, causing skin diseases.[5-9]

Nanocellulose nanotechnology is an emerging area of research and one that holds great promise for sustainable textile functional coatings for dyeing and coloration. Nanocellulose is engineered from cellulose, a renewable and biodegradable polymer abundant in nature. Conventional dyeing technologies are water and energy-intensive, loaded with harmful chemicals.[10] This approach offers great potential to develop environmentally friendly and sustainable textile dyeing technology.

This research introduces environmentally friendly and sustainable indigo dyeing and cotton/polyester dyeing technology utilizing a high surface-to-volume ratio of nano cellulosic materials. This nanocellulose nanotechnology involves coating cotton and cotton/polyester fibers with nanofibrilliated cellulose loaded with dye molecules or particles, followed by chitosan posttreatment, which improves the fixation and adhesion of the coating to fabrics via physical cross-linking. For indigo dyeing of cotton fabric, this one-step technology secures over 90% dye fixation compared to 70-80% of conventional dyeing, comparable colorfastness properties, eliminates the use of reducing agents or alkali, and saves water up to a factor of 25. For cotton/polyester blend fabric, this technology provides similar color performance, fastness properties, enhanced anti-wrinkle properties compared to the conventional dyeing method, and reduced water and auxiliaries usage up to factors of 18 and 20, respectively.

The remainder of this chapter consists of a literature review on nanocellulose nanotechnology, synthetic and natural dyes, chitosan, indigo and indigo dyeing, and dyeing of cotton/polyester blends.

1.1 Nanotechnology

Nanotechnology is the application of engineered materials and structures at the atomic and molecular levels (1-100 nanometers in dimension).[11] Nanomaterials are engineered materials with one or more dimensions in the nanometer range, which come from the sources of inorganic and organic materials (metal, metal oxides, carbon (fullerenes)).[12, 13]

Nanotechnology has diverse applications across various fields, including but not limited to electronics and computing, medicine and healthcare, energy, food and agriculture, water filtration, consumer products, and the environment, among others.[11, 14] Some notable benefits could be drug delivery systems, diagnostics and medical technology, nanoimaging instruments (STM, AFM etc.), food packaging, nanoelectronics, fuel cells, thin films for solar cells and other applications, and functional coating to name a few.[11, 14, 15]

Nanotechnology has been used in textiles for the last two decades to impart or enhance mechanical, physical, and chemical properties.[12, 13] The coating with nanoparticles is the most common method used in nanotechnology for surface modification.[16] Nanofiber and nanoparticle doped nanocomposite and nanorods are other forms of nanomaterials used in medical textiles and filtration textiles.[17, 18] The advantage of using nanomaterials in textiles is to improve textile performance and serviceability without compromising the inherent comfort and aesthetic. Nanomaterials are known for their larger surface area, which enhances the intrinsic properties of the material in comparison to its bulk counterpart, as a significant portion of the atoms are located on the surface.[12, 19] It also provides the opportunity for lower loading.[12] For example, TiO_2 nanoparticle is a well-known photocatalyst for generating hydrogen. It has a larger surface area per unit mass and volume than the bulk material size, leading to an increase in the effectiveness of absorbing and scattering UV radiation, and thus can be applied to textiles for UV blocking, antistatic, wrinkle resistance, and antibacterial properties.[20, 21] Other application of nanotechnology in textiles involves optical displays, sensors, piezoelectric, strength enhancement and coloration.[21, 22]

While nanotechnology has many advantages for the textile industry, the release of nanomaterials from textile products could pose some serious environmental and health concerns through wastewater, landfill, recycling, or skin contact.[17] The surface area and the surface chemistry of nanomaterials, product life cycle, and product design, as well as the composition of washing liquid and washing procedure, determine the extent of these risks.[12, 17, 21] For example, nano-silver and nano-titanium oxide containing textiles (socks, blankets, shirts, pants) release Ag and TiO_2 into sweat and washing liquid which are toxic to aquatic animals and may affect bacteria in sewage treatment plants.[21] Earthworms could consume nanomaterials that could travel through the food chain and ultimately affect humans.[23]

1.2 Nanocellulose

Nanocellulose (NC), on the other hand, has great potential for a wide range of applications in textiles because of its sustainability, biodegradability, biocompatibility, high surface area, and specific strength.[24, 25] Nanocellulose nanotechnology holds great promise for sustainable applications including functional coatings. Nanocellulose nanotechnology offers possibilities such as improved durability, self-cleaning, and water- or dirt-repellent features that hold great promise for sustainable applications.[16] Nanocellulose is engineered material from cellulose (Figure 1.1), which is an abundant biopolymer found in wood, plant fibers, marine animals, algae, fungi, and bacteria.[26, 27] Cellulose does not occur in nature as a single polymer chain but instead forms a bundle of approximately 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.[26, 28]

Nanocellulose has a large surface area (~10^3 m^2/g) and facile reactivity arising from abundant surface hydroxyls [29, 30]. There are three types of nanocellulose: nanocrystalline cellulose (NCC), nanofibrillated cellulose (NFC), and bacterial nanocellulose (BNC). BNC is secreted extracellularly by bacteria called *Gluconacetobacter*. Cellulose nanocrystals are single crystals formed under acid hydrolysis.[26] NFC is manufactured from many different sources, including wood pulp, bleached kraft pulp, and bleached sulfite pulp using a homogenizer or microfluidizer.[26] It has both amorphous and crystalline regions and tends to form a web-like network.[31, 32]

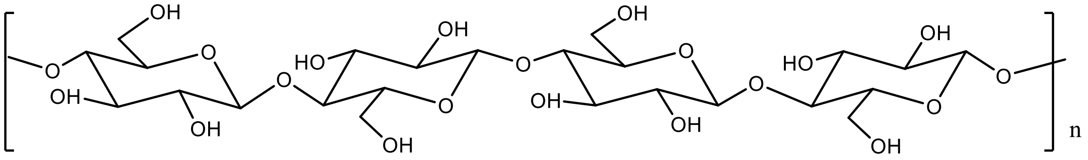


Figure 1.1: Chemical structure of cellulose with reactive OH groups.[27]

The hydrogen bond between the abundant hydroxyl groups due to the high aspect ratio of the cellulose polymers in nanocellulose gel gives rise to the highly ordered conformation of the nanocellulose fibril network, forming a matrix that can hold nanoparticles and act as carriers during application over textiles.[33] For example, when combined with NFC gel, the TiO2 nanoparticles are immobilized and prevented from agglomerating. The NFC gel also acts as a dispersing agent for loading TiO_2, which enhances photocatalytic activity.[33]

Using nanocellulose nanotechnology in textile dyeing significantly reduces the amount of toxic chemicals and water, which are otherwise released in our natural streams polluting water, soil, and human health.[30] Researchers showed that a combination of inter-entanglement and hydrogen bonds secured the adhesion and stability of NFC coatings on textiles.[34] Such coatings are stable to multiple washing cycles for colored textiles with NFC-reactive dyes.[30, 35]

1.3 Synthetic and Natural dyes

There is a growing concern for toxicity and environmental hazards posed by synthetic dyes and auxiliaries used in the textile industry. Synthetic dyes are predominantly used in the textile dyeing industry due to their high performance and availability. Though these dyes are high-performing, they require a lot of water, energy, and chemicals that can harm health and the environment.[10] An average-sized textile mill consumes 1.6 million liters of water to process approximately 8000 kg of fabric.[4] Approximately 40 percent of water used in textile dyeing and finishing contains about 8000 chemicals released without any treatment.[4, 36] Natural dyes, on the other hand, are eco-friendly and sustainable but usually lack the high performance of their synthetic counterparts. The need for green and sustainable technology revitalized interest in the utilization of natural dyes over the past last few decades. This has stimulated the cultivation of natural dye plants such as madder and indigo.[37-39] Natural dyes extracted from these renewable resources are environmentally friendly. No harmful chemical is used during the extraction process, and the waste produced is compostable.[37, 38, 40] The final product is commercially available in powder form in the commercial market. Apart from being environmentally friendly, many natural dyes have functional properties such as antibacterial, anti-fungal, UV protection, insect repellent, and flame retardancy.[41-48] But, most natural dyes do not have an affinity towards cellulosic substrates such as cotton and require pre-treatment with heavy metal mordants, and multiple dyebath for deeper shade, posing environmental threats similar to synthetic dyes.[49] The biggest drawbacks of natural dyes are reproducibility and lower colorfastness properties in comparison to synthetic dyes.[49] For all-natural dyes to be green and used commercially; we need appropriate and standardized dyeing techniques without sacrificing the quality of dyed textiles materials. To overcome the above-mentioned issues, recently, researchers have started exploring the use of nanotechnology in dyeing with natural dyes. Fabric dyed and printed with natural dye nanoparticles showed better color performance and fastness properties.[50-52] Dyeing with encapsulated dye particles in nanometric silica through the sol-gel process showed better color absorption and colorfastness properties without using any mordants.[53]

1.4 Chitosan

Chitosan is a polysaccharide (Figure 1.2) having more than 5000 glucosamine units, obtained from deacetylation of chitin, poly-(1,4)-2-acetamido-2-deoxy-β-D-glucose.[54, 55] Chitin is the second most abundant natural polymer found in the shells of a crustacean, such as a crab, shrimp, crayfish, and cell wall of some fungi (Basidiomycetes, Ascomycetes, Zygomycetes, and Deuteromycetes).[56] [55, 57] Properties such as antibacterial, antitumor, and low immunogenicity of chitosan have drawn the attention of researchers in textile, polymer, biomedical field.[57, 58] Although the exact mechanism of antimicrobial activity of chitosan is unknown, researchers have proposed that there is an interaction between positively charged chitosan molecules and negatively charged microbial cell membranes that leads to the leakage of proteinaceous and other intracellular constituents[59]. Chitosan also acts as a chelating agent and binds with metal traces, inhibiting the production of toxins and microbial growth.[59] chitosan forms Schiff base (C=N double bond) between the aldehydic carbonyl group of cotton and an amino group of chitosan, contributing to antimicrobial activity (bacterial reduction up to 96-100% and inhibition zone 1.3-1.5 cm) and introduce the cationic site in cotton polymer by free $–NH_2$ group.[60] [61] S. Islam et al. studied that polyester fabrics treated with chitosan also showed a bacterial reduction of about 99% and anti-odor properties.[62]

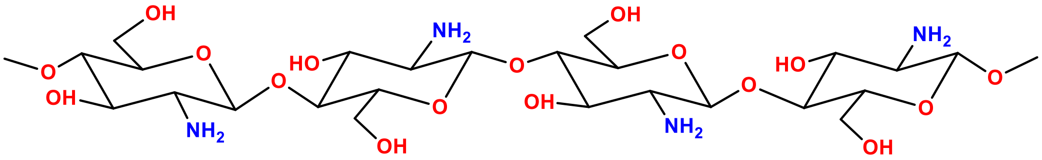


Figure 1.2: Chemical structure of chitosan.

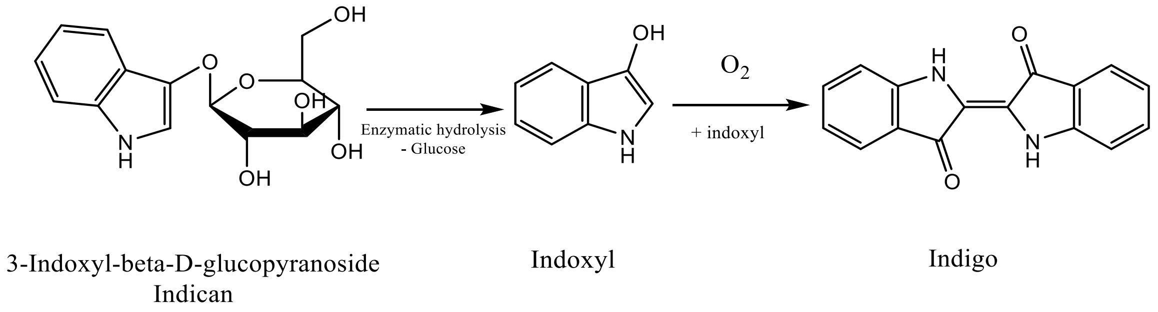
FTIR spectroscopic analysis also shows that chitosan can form a hydrogen bond as a crosslinking agent between the $-NH_2$ group of chitosan and the -OH group of cellulose. [63, 64] The amine group, $–NH_2$, which gets protonated cationic form ($–NH_3+$) in an acidic solution, forms a crosslink in contact with cotton by hydrogen bonding and maybe by ion-dipole interactions. [63, 64] The research also showed that the treatment contributed to increased abrasion resistance, stiffness, crease recovery properties, and antimicrobial activity.[64] Oktem et al. mention that the treatment with chitosan does not show durability to repeated washing; therefore, researchers use polycarboxylic acids such as 1,2,3,4-Butanetetracarboxylic acid (BTCA) and citric acid with chitosan.[61] The treatment of cotton with the mixture of polycarboxylic acid and chitosan contributes to the esterification reaction between polycarboxylic acid and hydroxy groups of chitosan as well as with cellulose; also, the free carboxylate groups can react with the amino groups of chitosan resulting in a salt linkage contributing to antimicrobial activity. [61] In another study, chitosan used in combination with citric acid as a crosslinking agent in the presence of sodium hypophosphite imparted antimicrobial properties to cellulosic fibers using UV- irradiation.[65]

In other studies, pre-treatment of cotton with chitosan is carried out to impart cationic sites in the fiber before dyeing with reactive dye and acid dyes for improved dye absorption.[63, 66] A hundred percent fixation is exhibited by cotton fabrics, which are ink-jet-printed with pigment-based inks and post-treated with 1% chitosan due to the strong film-forming property of chitosan due to intramolecular and intermolecular hydrogen bonding.[67]

1.5 Indigo and Indigo Dyeing

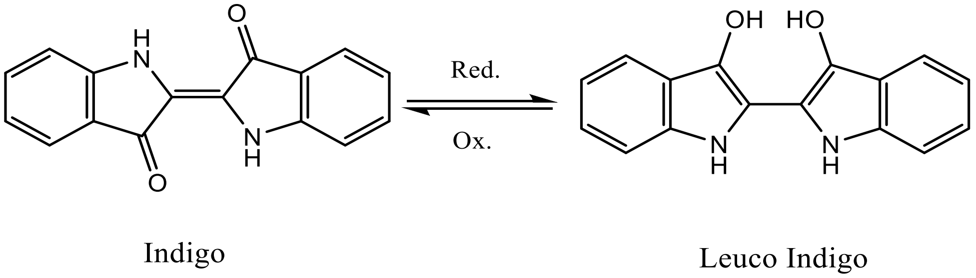
The usage of Natural indigo (NI) dates back as far as 7000 BC.[68] Recently, there has been a growing awareness and concern regarding pollution control, with an increasing consciousness of pollution control leading to a resurgence in the use of natural dyes such as natural indigo.[69] Natural indigo (2,2'- Bis (2,3-dihydro-3- oxoindolyliden) (I) is a vat dye that is manufactured by biosynthesis of leaves and stems of indigo plants containing indican in *Indigofera. tinctorium* and *P. tinctorium*; isatan B and indican in *Is. tinctoria* to yield indoxyl, which transforms rapidly into indigo by oxidation.[69, 70]

Due to the high demand for indigo, in 1865, the German chemist Adolf von Baeyer began synthesizing synthetic indigo. Still, it was not until 1897 that BASF successfully launched its synthetic "Indigo Pure BASF."[70] For commercial production of synthetic indigo, crude oil (petroleum) is chemically transformed into benzene, which, in turn, is converted into aniline in the presence of nitric acid, sulfuric acid, metal catalysts, and heat. Aniline is converted into *n*-phenyglycinein by the *N*-methylation process in the presence of formaldehyde, hydrogen cyanide, and sodium hydroxide and converted into indoxyl in the presence of potassium hydroxide, sodium hydroxide, and sodium amide, which is oxidized to get indigo.[70]



(I)

Figure 1.3: Biosynthesis of Natural Indigo.



(II)

Figure 1.4: Reduction of Indigo into leuco indigo and vice versa.

Dyeing with indigo is a complex process and requires careful consideration of several parameters. Indigo is a nonionic vat dye, an insoluble pigment comprising the carbonyl group (C=O) as chromophore and alkylamino group (-NHR) as auxochrome.[71] During dyeing, the aggregates of indigo are converted into a soluble leuco indigo (II) anionic form of ion size 1.3 nm in the presence of a reducing agent under the alkaline condition and develop substantivity towards cellulosic fibers.[71, 72] After diffusion, the dye molecules are adsorbed on the cellulose via hydrogen bonds and oxidized to form submicron to micron size pigment particles in the presence of oxygen.[71, 73] Indigo is deposited over the surface of the cotton fibers with the exhaustion of only 10-20 % as compared to other vat dyes with the exhaustion of 70-95%, showing lower colorfastness properties and thus called a poor vat dye.[74, 75] To have better exhaustion and color performance, the multiple immersion and oxidation for a shorter period of 10-15 sec and 120 sec, respectively, for approximately 2% dye uptake each dip, are employed.[76] Continuous dosing of indigo and chemicals is performed to avoid shade variations. Well-monitored steps lead to 70 to 80% fixation of indigo after washing.[77-79] Commercially, indigo dyeing for denim is a continuous process involves pretreating (scouring, mercerization), bottoming (sulfur dyes), dyeing, topping (sulfur, reactive, vat dyes), post-treating (washing), and drying. During dyeing, the wetted cotton yarns go through multiple dips and nips in leuco indigo vats (1-5 g/L) and oxidation by air to gain the desired percentage shade, and after dyeing, the yarns are sized before weaving[80, 81]. Bottoming or topping is a dyeing of yarns with black (or other) sulfur dyes before or after, respectively, is required to produce darker/deeper blue shade or different dyeing performance[80]. Indigo dyeing for denim is unique as it does not require uniform dyeing across the cross-section of yarns. Instead, indigo particles aggregate layer by layer on the surface of yarn after each dipping without penetrating the yarn.[76] This phenomenon is called the ring dyeing effect, which gives the denim a distressed look (wash down effect).[79] The size of the ring effect can be increased by decreasing the pH from 13 to 11 in the same alkalinity.[79] The color yield of indigo on denim yarn is the highest in the mono-ionic form (HO-indigo-O^-) of reduced indigo within the range of 10.8 to 11.2 pH.[79] Also, enough ionization of cotton fiber (cellulose-O^-) happens at pH 11 of dyebath, favoring ring effect due to higher affinity, higher strike rate (rate of exhaustion), and lower penetration of the dye.[79]

Typically, a mixture is prepared by manually combining 34% of indigo pigment powder in an open-air environment. The mixture also includes a 3% complexing agent, 31% sodium hydrosulfite, 29% sodium hydroxide, and a 1% stabilizing agent. The resulting mixture is allowed to react for 2 hours.[72, 82] In very few mills, this unhealthy dusty operation has been replaced by pre-dispersed pigment or pre-dissolved reduced indigo solution.[72] To maintain the required redox potential of over -700mV, alkaline condition of pH 10-12, and dyeing quality, the extra amount of indigo, reducing agent, and alkali are added simultaneously as the air gets introduced while dyeing in open condition.[72] The most cost-efficient reducing agent is sodium hydrosulfite. However, it is susceptible to oxidation in the presence of oxygen. It is also flammable and should be handled with caution. Additionally, it can be corrosive to wastewater pipelines.[70, 83] Sodium hydrosulfite affects the aerobic processes during the wastewater treatment process.[70] It can also form toxic hydrogen sulfide anaerobically from the sulfate present in the wastewater.[70] An alkali agent, caustic soda, is preferred with sodium hydrosulfite. Still, it is also known to be toxic to the environment, corrosive to the concrete waste line, and contributes to wastewater load.[71] Most of the indigo dyeing mills are in developing countries. Xintang (China) is known as the denim capital of the world, where, with the spread of indigo mills, the east river has turned blue with a chemical odor unsuitable for drinking and other human consumption (Figure 1.5). Xinzhou village was once fertile and well-known for fishing but is no longer suitable for farming and fishing. Bangladesh is the second leading clothing exporter in the world after China, where a lack of environmental regulations and enforcement has turned their water bodies very toxic and harmful to flora and fauna. Unregulated management of these mills exerts negative impacts on the local and global environment.[8]

The denim market represents approx. 5% of the total apparel market and has been experiencing continuous growth.[84] The overall denim market was valued at over 90 billion dollars in 2017.[85]. By 2018, more than 4.5 billion pairs of jeans were sold annually.[85] The denim industry uses about 45,500 tons of synthetic indigo, 84,500 tons of sodium hydrosulfite, and 53,500 tons of caustic soda each year.[86, 87] Of the total wet processing of denim, the dyeing process consumes about 42% of water (10–75 L per kg of denim yarn for the dyeing stage and approx. 150 L/kg in total, including washing), which is more than 400,000 tons of water in a year in one mill [88]. The wastewater produced during this process contains high amounts of effluents such as salts (sulfites and sulfates), indigo dye (20-30%), and other metal traces.[77, 78, 82, 89, 90] The denim dyeing wastewater is not suitable for reuse or disposal. It requires expensive water treatment facilities because it has a pH of 8.9-12.7, COD (mg/l) of 520-3250, and color (Pt-Co) of 650-10,1000, among other parameters.[88]

Figure 1.5: A Greenpeace campaigner takes a water sample from a polluted river near Dadun Village, Xintang, Zengcheng (2010). Credit: © Lu Guang / Greenpeace.

Researchers have proposed alternatives to reduce water and chemical effluents, such as using dyes with the highest possible fixation, biodegradable dyes and auxiliaries, minimizing wash-off, or recycling.[91] As an alternative to hydrosulfite, many ecofriendly reducing agents have been studied, such as bacterial reduction, Alpha-hydroxy ketones, glucose, thiourea dioxide, iron(ii)salts, sodium borohydride, and electrochemical reduction.[70, 83, 92-98] The electrochemical reduction method minimizes chemical use and controls redox potential. The indirect electrochemical using mediator, direct electrochemical with the radical process, graphite electrodes, and electrocatalytic hydrogenation are examples of electrochemical reduction methods.

However, the main disadvantage is that electrochemical reduction requires high surface area electrodes and energy consumption. Alpha-hydroxy ketones are a biodegradable reducing agent that has the capacity of -810mV redox potential (such as hydroxy acetones, acetoin, glutaroin, adipoin, α-hydroxycarbonyls) to reduce indigo. However, the hydroxy acetones do not perform well at 11.5 – 12 pH and produce a very foul smell. Glucose is another eco-friendly reducing agent which is used to reduce sulfur dyes. However, it requires boiling temperature and more oxidation time to perform efficiently. Thiourea dioxide, used by some dyeing mills, has a stronger reduction capability than sodium hydrosulfite, but it requires 100°C and is not economically viable. Sodium borohydride can be used as a reducing agent, but the slow reaction in vat dyeing is the limitation. A two-component system, ferrous hydroxide complexed with gluconic acid, citric acid, tartaric acid, or triethanolamine in the presence of sodium hydroxide, is a good reducing agent proposed by many researchers. A promising approach is bacterial reduction, where bacteria such as Clostridium isatidis, Amphibacillus and Oceanobacillus have successfully been used to reduce indigo. Nevertheless, bacterial reduction requires further study to reach consistency in results. Studies have used natural reducing agents such as date palm, apple, banana, and its peal, bokbunja (*Rubus coreanus Miq.*) sludge. The advantage of using natural materials is that they are eco-friendly and biodegradable; however, they pose the problem of irreproducibility and inefficiency due to the inconsistency of natural composition. An interesting approach recently proposed by Dueber et al.[99] involves obtaining oxidation resistant indigo precursor indican via microbial synthesis and depositing it onto the textile surface using a spray method. Subsequently, the fabric is treated with a β-glucosidase enzyme to hydrolyze indican into indoxyl.[99] Indoxyl then undergoes spontaneous oxidation to form indigo pigment.[99] The methods are based on microbial synthesis and biocatalysis without reducing agents.[99] Further studies will provide quantitative insights into dye fixation, color strength, and colorfastness of the colored fabrics

Many denim dyeing mills use 40% pre-reduced indigo or PRI (e.g., Dystar indigo by Dystar, Denisol indigo by Archroma), which contains significantly less amount of aniline (less than 1% of dye), up to 70% less reducing agent and alkali and up to 15% less indigo dye [100]. PRI is an indigo solution that is reduced in an oxygen-free environment by the catalytic (Raney nickel) hydrogenation process [70, 72, 101]. The disadvantage related to PRI is that it requires 20-ton tanks under some nitrogen pressure, and these tanks need to be shipped back to the indigo supplier[72]. In addition, the use of PRI requires dyebath injection equipment, which is an added cost to a denim manufacturer and, ultimately, to consumers [72]. The recently developed foam indigo dyeing technology for denim yarns utilizes pre-reduced indigo and inert gas to produce foam during the dyeing process. In this method, dyeing is performed in an enclosed system that saves water and energy, improves efficiency, reduces chemical footprints, and gives a better color performance compared to conventional dyeing methods [72, 102, 103]. However, none of these techniques are widely adopted in developing countries, mostly because they require costly investments in these technologies, and the additional costs may not be passed on to the consumers. [104]

Cultivating and using natural indigo pigments (Indian or Japanese/Sukomo method) has recently become a growing trend. The 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.[38] Researchers studied that fabrics dyed with natural indigo also have functional properties such as anti-odor, UV resistance, and antibacterial properties with an inhibition zone of 3.7-3.5 cm.[105] However, the current technology for producing organic jeans is too expensive for mass production.[38, 106]

1.6 Dyeing of Cotton/Polyester blends

Cotton/polyester blended fabrics, one of the most widely used blended fabrics, hold over 7 billion market value (2016).[107] When cotton is blended with polyester, fabric exhibits better durability and dimensional stability, is crease-resistant and easy to care and has moderate moisture absorption due to polyester fiber, antistatic, and less pilling due to cotton fiber.[10, 108] Cotton and polyester dyeing and finishing mills consume 70 to 250 liters of water for one kilogram of textiles[109]. During the preparation, dyeing, and finishing, the cotton consumes 0.5-397 grams/kg, and polyester consumes 3-1776 grams/kg of chemicals.[109] More than 50% of the chemicals end up as affluent in the waste water with high levels of pollutants such as COD- 118-1387 mg/l, pH 8.2-8.9, color-374-1496 Pt-Co.[109] Conventionally, the cotton/polyester blended fabric is dyed using two dyes: reactive, vat, direct, sulfur, or azoic, to dye cotton and disperse dye for polyester fibers[10, 71, 75, 108, 110]. Due to its bright shades with excellent fastness properties, reactive dyes are preferred for coloring cotton in cotton/polyester blended fabrics.[75] Traditionally, cotton/polyester are dyed in two-bath systems (batch methods), where each fiber is dyed in a separate bath. In the most conservative two-bath method, where polyester fibers are dyed, first, using disperse dyes at 130°C, then the reduction clearing is performed to remove the superficial color using strong reducing agents ($Na_2S_2O_4$ and NaOH at 70°C) and dispersing agents.[75, 108, 110] Then the cotton fiber is dyed using reactive dye, and finally, the fabric is rinsed and scoured to remove any hydrolyzed dye. A total of nine cycles of washing is required, which consumes approx. 64-100 liters of water and an enormous amount of chemicals.[111, 112] The conservative two-bath method takes approx. 10-12 hours, but provides excellent colorfastness properties due to the intermediate washing process.[71, 75, 110] Sometimes, as required, the blended fabrics are dyed with only one class of dyes to produce reserve shade.[10, 71] Reserve shade is attained when the blended fabric is dyed either with disperse dye or reactive to dye either polyester fabric or cotton fiber; for example, if the fabric is dyed with reactive dye, the cotton fibers are dyed, and the polyester fibers remain undyed showing white dots all over the fabric. However, when the blends are dyed with both classes of dyes, the union (solid), cross, or shadow shade is achieved.[10, 71, 110] A union shade is achieved when both fibers in the blends are dyed with same hue, depth and tone to develop a solid shade[10, 71, 110]. A cross shade is obtained when the two fibers are dyed with different hues such as orange- black with the same or different shades (percentage).[10, 71, 110] A shadow shade is obtained when the blend is dyed at different percentage shades (for example, 1% reactive dye and 3% disperse dye).[10, 71, 110] In the less conservative, reverse two-bath method, the cotton fibers are first dyed with reactive dye, then polyester fibers are dyed with disperse dyes.[75, 108, 110] After the reactive dyeing, the fabrics are rinsed several times to remove salt, alkali, and hydrolyzed reactive dyes.[75, 108, 110] The reduction clearing is avoided after disperse dyeing to avoid damage of reactive dye; instead, alkaline scouring is performed, reducing the total time to approx. 7-8 hours.[75, 108, 110] A rapid one-bath dyeing can also be performed where reactive dyes are combined with disperse dye in one bath. There are many processes (cold bath to hot bath) used in the industry for one-bath dyeing using a careful selection (to avoid interactions) of types of reactive dyes and disperse dyes and the sequence in which the salt, alkali and other auxiliaries are added for exhaustion and diffusion of dyes either at two stages or at one stage.[10, 75, 108, 110, 113] For example, the dye bath is prepared by adding reactive (highly exhaustive (HE-Brand)) and disperse dyes at the pH of 5-6 with a dispersing agent and an anti-reducing agent for reactive dyes. The temperature is raised rapidly to 95°C and then gradually to 130°C for 30-40 minutes for adsorption and diffusion of disperse dyes. The temperature is then reduced to 80°C, and salt is added. After 15-20 minutes, the alkali is added, and then dyeing is continued for 40-60 minutes for the fixation of reactive dyes.[10] In one bath dyeing, the total time is reduced to 4-5 hours and water consumption to approx. 48 liters per kilogram of fabric but the colorfastness properties are compromised due to the absence of intermediate washing.[10, 111] Continuous dyeing methods are used to dye longer continuous yards (approx. 11000 yards) of fabric.[10, 75] In the continuous range the disperse dye is padded first, thermofixed and then reactive dye is padded, steamed, or vice versa, or both the dyes are padded together. For one bath dying, both dyes are padded in presence of alkali, salt, urea and an anti-migration agent (sodium alginate or CMC).[10] During thermofixing method, transfer of disperse dyes to polyester fiber occurs though vapor phase at 200-220°C from cellulose fiber.[10] In a semi-continuous method the combination of pad and batch methods are used as per the requirement of color, color performance and overall cost.[10]

Researchers have been developing efficient dyeing methods to reduce the water, chemicals, and energy conservation to dye cotton/polyester blended textiles. Ahmed et al. combined the scouring and bleaching process for cotton fiber in the blend during reduction clearing after the polyester was dyed with disperse dye using NaOH and H_2O_2 and saved water by 26% and time by

15%.[114] In another study, researchers explored that increasing the temperature of trichloroacetic acid (TCAA) as a medium of dyeing can change from acidic to basic for subsequent dyeing with disperse dye and later with reactive dye in one bath pad dry fixation method.[115] Deo et al. reduced the pollution load of Biochemical Oxygen Demand (BOD) by 10.47% and Chemical Oxygen Demand (COD) by 14.38% in one bath dyeing using formic acid instead of acetic acid in dyeing the polyester part of the cotton/polyester blended fabric.[116] In the second part of this study, researchers reused water used in conventional two-bath dyeing, reduction clearing, and washing, and overall saved water by 85.04%[116]. They achieved comparable dyeing performance in both cases compared to the conventional two-bath dyeing.[116] Lee et al. achieved good dyeing properties with reactive-disperse dye based on 1-substituted derivatives of hydroxyparid-6-one to dye cotton/polyester fabric in one bath dyeing at pH5 compared to two bath dyeing using two different dyes.[117] Maeda et al. and Zhou et al. used supercritical carbon dioxide as a solvent instead of water in one bath dye method and used monofluorotriazine and s-triazine reactive group of reactive-disperse dye respectively, to dye cotton/polyester blended fabric[112, 118]. They found a better dyeing performance than the thermofixing method when the dyeing is performed at 393 K and 20 Mpa.[118] However, reactive-disperse dyes (union dyes) are limited because they offer solid shades on specific blend ratios of blended textiles.[10] Monochlorotriazine and pyrimidinyl reactive dyes in combination with several alkali stable disperse dyes are found most suitable for one-step dyeing at alkaline 9-9.5 to neutral pH conditions at 125°C for 45 minutes.[119, 120] In another study, the cotton/polyester blended fabric is pretreated with an azeotropic solvent mixture (Acetone, Ethyl alcohol, Chloroform; and Acetone, Methyl acetate, N-Hexane) to improve the dye uptake of reactive and disperse dye in one bath dyeing.[121] Imran et al. used Blue FFG pigment (α type) to color the cotton/polyester blended fabric by a one-step pad-dry-cure method.[122] In many studies, surface modification of blended textiles has been studied to have one bath dyeing of cotton polyester fabrics.[123-125] In a study, the cotton/polyester blended fabric is treated with sodium 2-(2,3-dibromopropionylamino)-5-(4,6-dichloro-1,3,5-triazinylamino)-benzenesulfonate (DBDCBS) either before or during dyeing with only disperse dye in one bath dyeing.[123] DBDCBS reacts with cotton and creates affinity towards the -OH and -NH2 group of disperse dyes.[123] Ristic et al. and Hilal et al. studied the effects of the treatment of polyester with NaOH, chitosan, and a combination of both in one bath dye with only reactive dyes.[124, 126] NaOH carries out alkaline hydrolysis of polyester, terminating the -CO group and leaving the -OH group creating a site for the reactive dye to react, and the deposition of chitosan imparts -OH group and $-NH_2$ group on polyester as well as cotton to attract reactive dyes in the blended fabric.[124, 126] In a similar study, the cotton/polyester fabric is pre-treated with chitosan to dye with direct dyes in one bath dyeing.[125] In another study, researchers studied the dyeability of cotton/polyester blended with direct/reactive dyes after the treatment with both corona discharge and chitosan[127]. The corona discharge enhances the hydrophilicity of both the fibers by forming -CO, -C=O and -COOH groups and improves the dyeability.[127] Zhang et al. used cationic dyes to dye cotton/polyester fabrics in one bath dyeing at low temperature after the treatment with β-cyclodextrin modification with crosslinking agents (BTCA, citric acid, acetic acid and adipic acid).[128] They found that β-cyclodextrin modification with citric acid improve the hydrophilicity of polyester and thus the dyeability at 70°C.[128]

This study uses Reactive Red 120 (Figure 1.6) to dye the cotton fibers of 50-50 cotton/polyester blended fabric. Reactive dyes are anionic dyes that form a covalent bond with cellulosic fiber.[10, 71] In general, all reactive dyes have three parts, reactive site (A), chromogen with water solubilizing group (C), and bridge between reactive site and chromophore (B).[10, 71] Reactive red 120 is categorized as highly exhaustive (H-E) dye suitable for exhaust dyeing of cellulosic fibers with higher fixation at 85°C with a lesser amount of salt and alkali.[10, 71] H-E dyes have two chromogens and two monochloro-s-triazine reactive groups, which provide more affinity towards the fiber, impair hydrolysis, and impart stability towards higher temperatures during dyeing.[10, 71, 129] For this reason, H-E dyes are also suitable to be used in one-bath dyeing of cellulosic/polyester blends due to their stability at high temperature (130°C) for high pressure (HTHP) dyeing or pad-dry-cure methods.[10, 71, 129] The suggested hydrolysis mechanism in the alkaline condition, in the given time, the bis(monochloro-s-triazine) reactive dye is hydrolyzed to monochloromonohydroxybis-s-triazine dye.[130] Eventually, monochloromonohydroxybis-s-triazine is hydrolyzed to bis(monohydroxy-s-triazine) dye. The same hydrolysis mechanism occurs in the presence of cellulose-OH of cotton fiber.[130]

The other dye used in this study is Disperse Red 1 (Figure 1.7). Disperse dyes are water-insoluble nonionic dyes and are used to dye hydrophobic fibers like polyester, nylon, and cellulose acetate.[10, 71] Disperse dyes are retained in the fibers by hydrogen bonds and van der Waals forces.[10, 71] Disperse Red 1 is an aminoazobenzene disperse dye and is used in polyester and cotton-polyester blended dyeing at high temperatures with moderate to excellent fastness properties.[10, 131, 132] Disperse dyes are milled with dispersing agent to have even dispersion in the bath.[10]

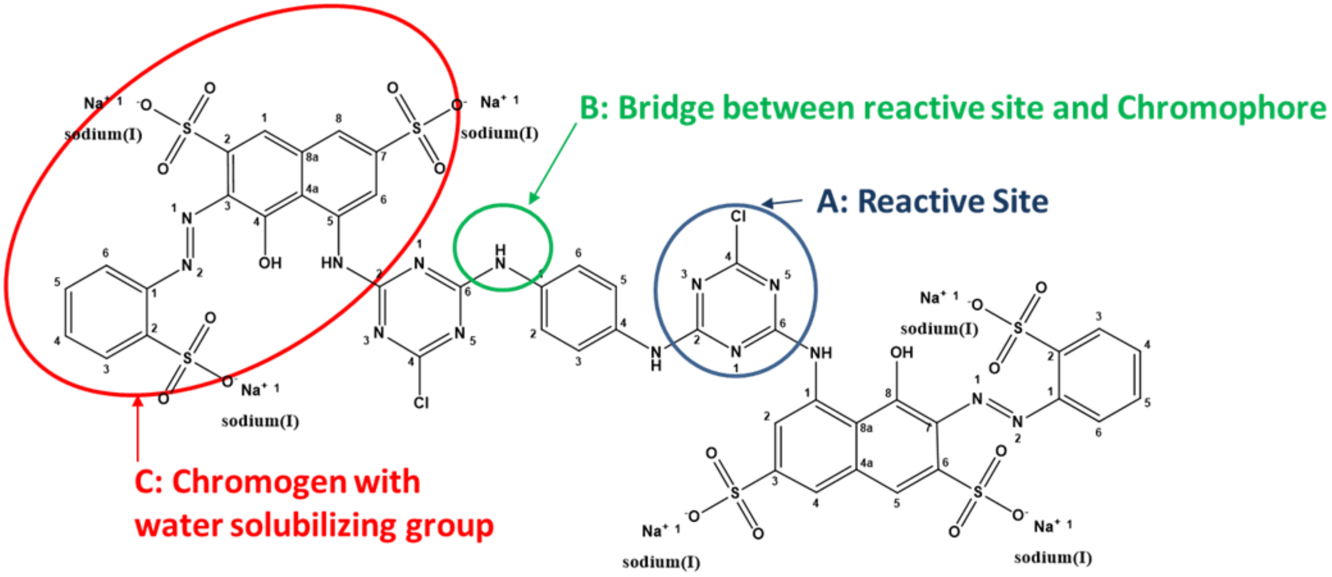


Figure 1.6: : Structure of various parts of C.I. Reactive Red 120.

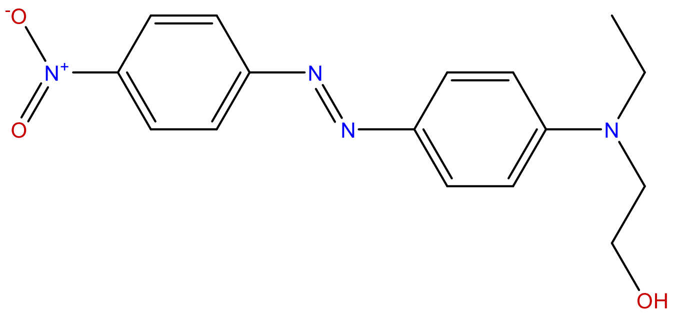


Figure 1.7: Structure of C.I. Disperse Red 1.

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As mentioned in sections 1.5 and 1.6 on indigo dyeing and dyeing of cotton/polyester fabric, the current industrial dyeing technology is one of the most significant pollutant sources in the world. For indigo dyeing, using pre-reduced indigo (PRI) (catalytically hydrogenated indigo solution) could save up to 70% of the reducing agent and alkali[133], but it is too expensive and poses numerous challenges in shipping to prevent oxidation.[133] Newer technologies, such as spray dyeing and foam dyeing, can reduce significant amounts of water consumption. [91, 100, 133-136] None of these novel techniques are widely adopted, especially in developing countries where most mills are situated, because they require significant investments and maintenance.[137]

Researchers have also been developing efficient dyeing methods to reduce water and chemicals and conserve energy to dye cotton/polyester blended textiles, which includes combining treatment process[114], using alternative dyeing mediums, conditions, dyes,[112, 115-118] and chemicals, surface modifications (chemical or physical).[30, 124-128] Despite technological advances, textile dyeing and finishing industries produce significant water and air pollutants - most of them are untreatable and pose health and environmental hazards.[138]

Recently, the dyeing of cotton fabric using reactive dyes was developed using nanocellulose nanotechnology, and the effect of various polycarboxylic acids was analyzed. [30, 35] This technology offers great promise for an environmentally friendly and sustainable dyeing method. This study brings nanocellulose nanotechnology to denim and cotton/polyester blended fabric, analyzes the antimicrobial activity of chitosan post-treatment, compares the effects of other cross-linking agents, the impact of particle size on fixation and color performance, and studies rheological properties. The next section discusses specific research objectives undertaken in this dissertation.

1.7 Research Objectives

1.7.1 Study 1: Eco-friendly Nanocellulose based Natural Indigo Dyeing of Cotton (Chapters 2-4)

The objectives of this study are:

- To develop a dyeing technique using NFC gel with natural indigo dye particles that yield good color performance and colorfastness to samples dyed with conventional indigo cotton dyeing.
- To study the effects of chitosan as a cross-linking agent on NFC– indigo dyed fabric
- To compare the chitosan with other crosslinking agents such as itaconic acid and a combination of itaconic acid with chitosan.
- To determine the optimum indigo particle size via ball milling for NFC-NI formulation for
- To determine the antimicrobial activity on cotton fibers coated with NFC-NI and post-treated with chitosan.

1.7.2 Study 2: Sustainable Nanocellulose based Dyeing of Cotton/Polyester Blended Textiles (Chapter 5)

The objectives of this study are:

- To develop a dyeing technique using NFC gel with a reactive dye for reserve shade that yields good color performance and colorfastness to samples dyed with conventional cotton/polyester blend dyeing.

- To develop a dyeing technique using NFC gel with disperse dye for reserve shade that yields good color performance and colorfastness to samples dyed with conventional cotton/polyester blend dyeing.
- To develop a dyeing technique using NFC gel with reactive and disperse dye for cross/ shadow shade that yields good color performance and colorfastness to samples dyed with conventional cotton/polyester blend dyeing.
- To study the effects of chitosan as a cross-linking agent on NFC – reactive dye/disperse (or combination) dyed cotton/polyester blend fabric.

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CHAPTER 2

ENVIRONMENT-FRIENDLY NANOCELLULOSE-INDIGO DYEING OF TEXTILES[1]

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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 the fixation and adhesion of the coating to fabrics via physical cross-linking.

2.1 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's 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 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 to make it soluble in water by adding a reducing agent (redox potential < -700 mV) in alkaline conditions (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 (Figure 2.5) 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.

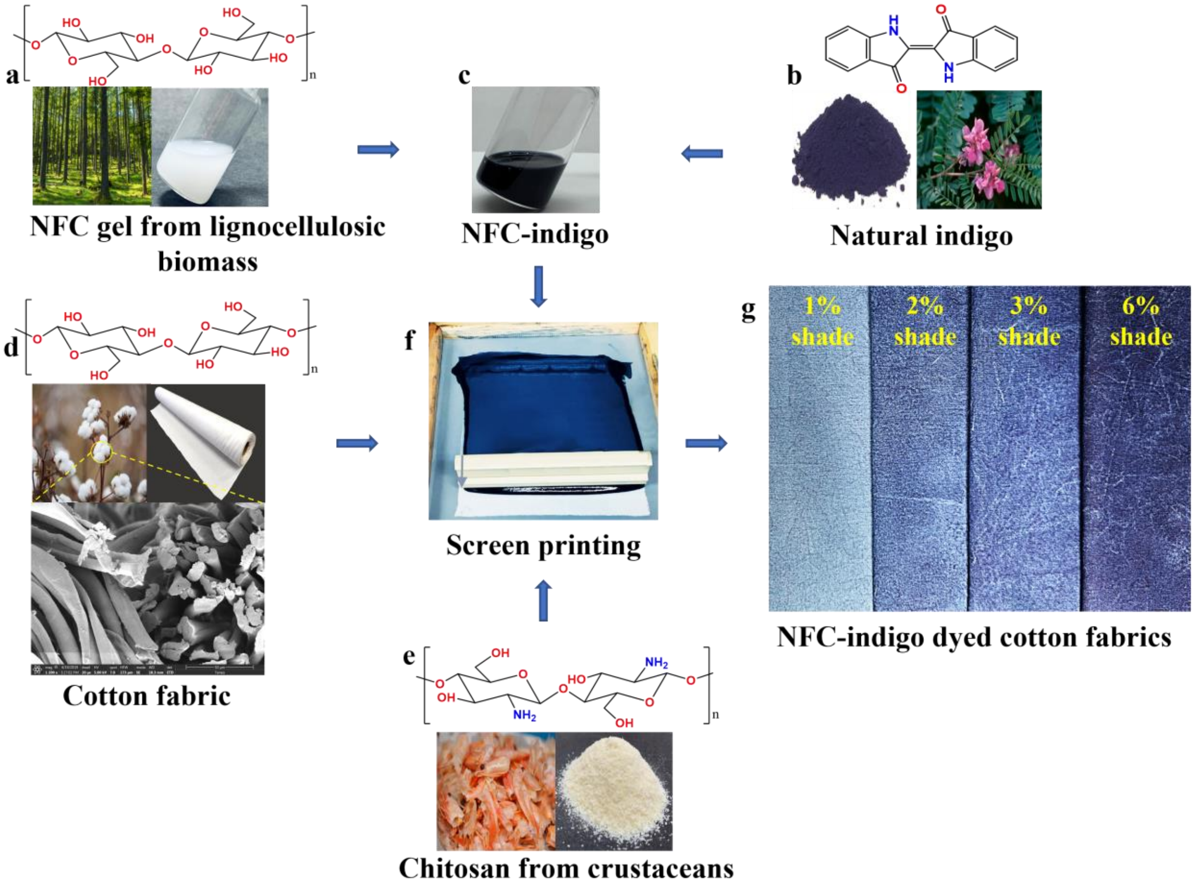

Figure 2.1: Schematic of NFC-indigo dyeing: (a) NFC gel prepared from wood pulp; (b) natural indigo powder, a product of plant Indigofera Tinctorium; (c) NFC-indigo; (d) cotton fabric, a product of natural cotton fibers; (e) chitosan, a product of deacetylation oof chitin (food waste); (f) screen printing/ 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.

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].

Here, we demonstrate a cost-efficient indigo dyeing of cotton textiles, which is based only on biobased materials, including natural indigo, nanofibrillated cellulose (NFC), and chitosan 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), natural indigo-particles, and a small fraction of a dispersing agent is coated over cotton textiles (Figure 2.1). The coated textiles are then post-treated with a chitosan aqueous solution for improved adhesion and stability of the coating (Figure 2.1).

2.2 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. 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 plasticizer and a co-gelation additive for the fabrication of NFC. NFC-hydrogel forms conformal flexible coatings upon deposition and evaporation of water. CMC is a water-soluble polymer, but upon drying of the NFC coating, NFC is adsorbed on the surface of the fabric. However, CMC is dissolved and removed in the washing cycles. 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 2.2a and Figure 2.2b, respectively. A reference sample of the NFC film on the glass slide reveals the mesh-like structure of the coating (Figure 2.2c). The experimentally measured cut-off diameter of particles that passed (>50%) through the NFC coating is 150 nm (Figure 2.2j).

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[30, 31] with a 330 nm average size of the aggregates as measured by DLS for the particles extracted from the traditionally dyed cotton fabric (Figure 2.2). The aggregate size can also be estimated using SEM images (Figure 2.2e-f). These aggregates are caged in the fibrillar mesh form by NFC, as explained with pictorial sketches in Figure 2.2i-j. This engulfing of pigment aggregates with NFC is observed in SEM images of the reference NFC-indigo film on the glass slide (Figure 2.2d,e) and on the surface of cotton fibers (Figure 2.2g-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 2.2k-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 2.2g-h with Figure 2.2k-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[32]. 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)[33, 34]. 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[35].

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 2.3). The visual appearance of the NFC-indigo colored cotton yarns with different shades is demonstrated in a panel of Figure 2.3a. NFC fibrils entangle with the cotton fibers in the yarn and form a conformal shell and patches on the surface of the yarn (Figure 2.3b-c), while NFC reaches no interior part of the yarn (Figure 2.3d). 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 2.3f). This structure is visualized with an optical image showing a bundle of yarns (Figure 2.3e). We recently demonstrated that a combination of inter-entanglement and hydrogen bonds secured adhesion and stability of NFC coatings on textiles[36]. Such coatings were stable to multiple washing cycles for colored textiles with NFC-reactive dyes[37, 38].

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 2.4). 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 2.4c. 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.

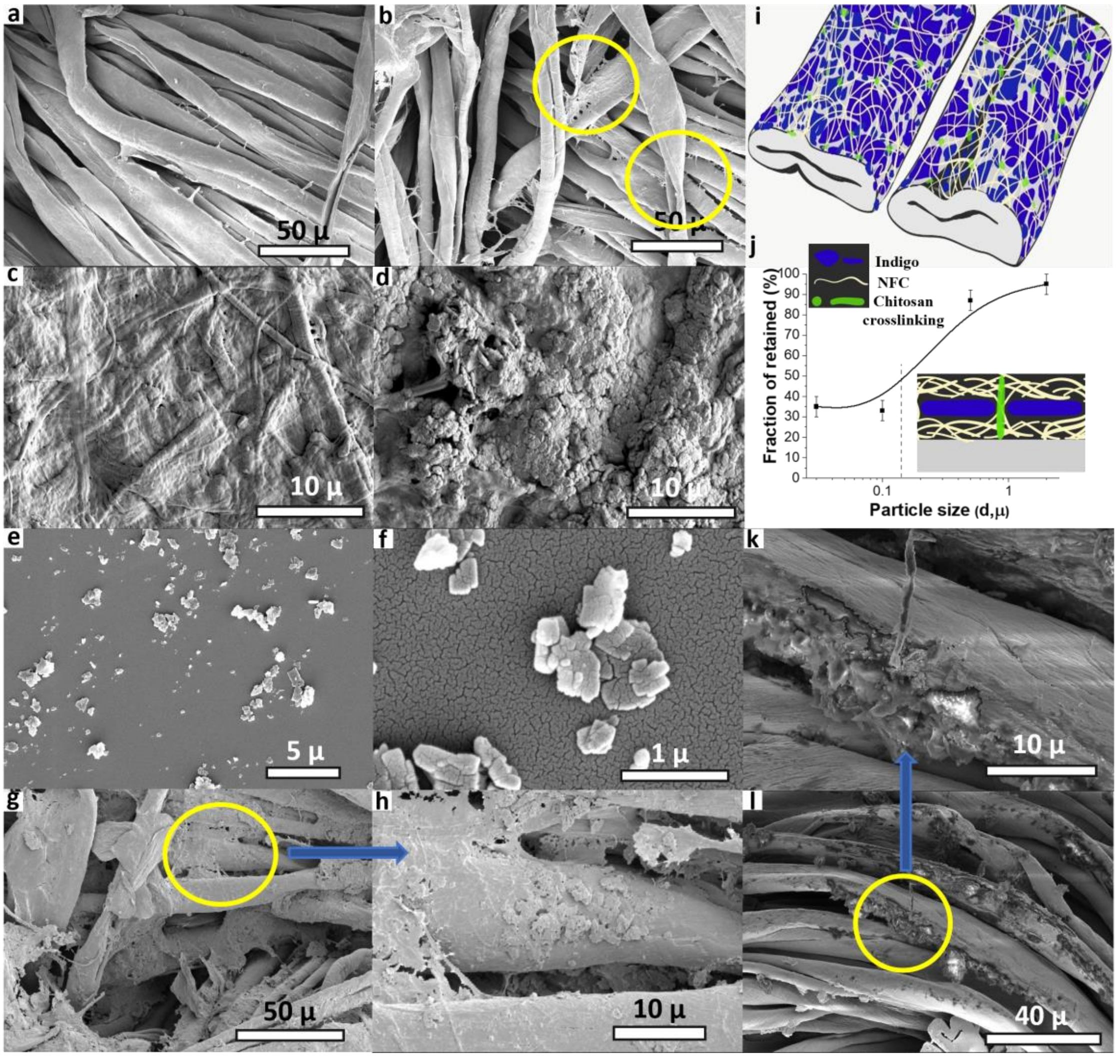

Figure 2.2: SEM images: (a) neat cotton fabric; (b) cotton fabric coated with NFC; (c) reference - 1% NFC gel (dried film) on the glass slide; (d) reference 1% NFC mixed with indigo, 6% (dried film); (e) and (f) indigo pigment particles on the glass slide; (i and j insets) pictorial representation of 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

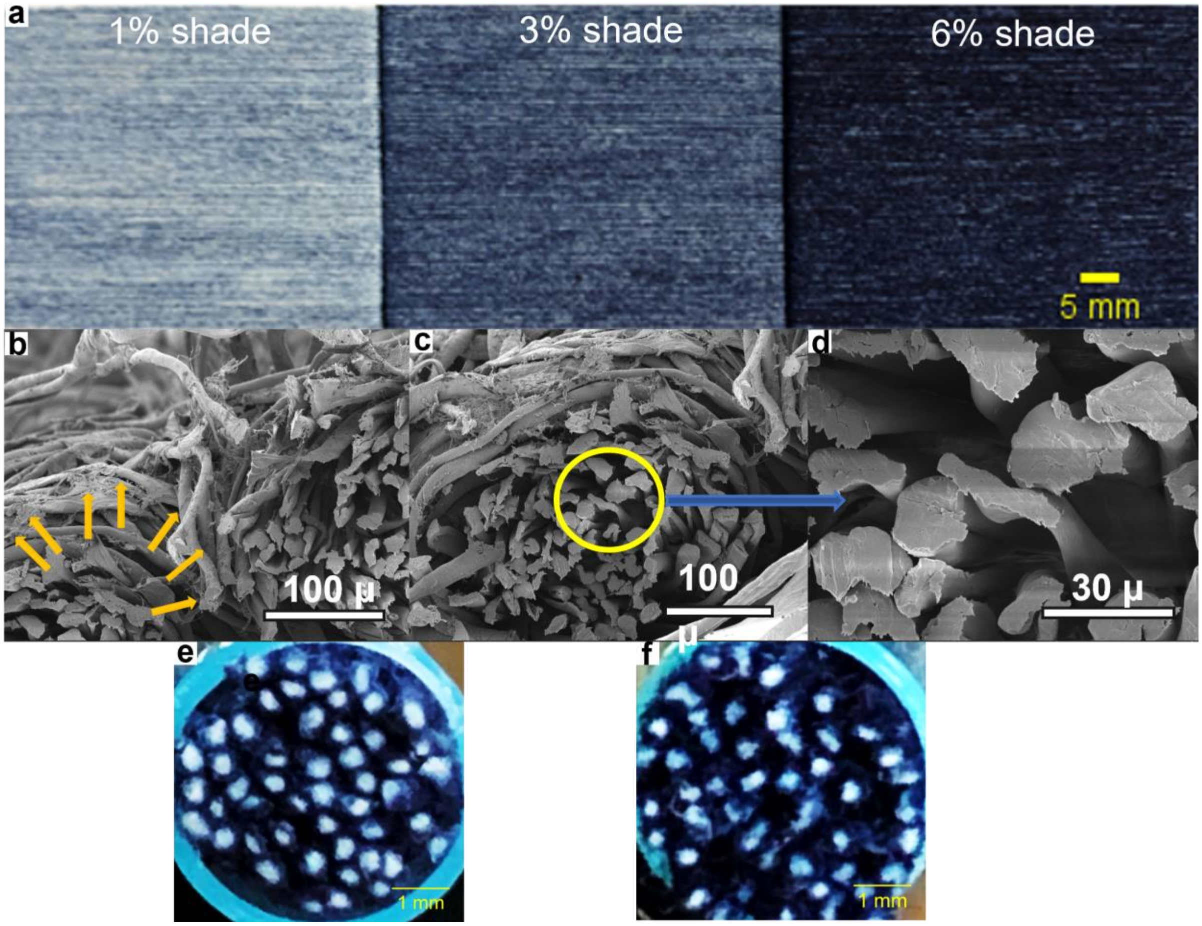

Figure 2.3: NFC-indigo dyed cotton yarn: (a) arrays of yarns colored with different shades; (b-d) cross-sectional SEM images of the dyed yarn; arrows point onto NFC fibrils entangled with single fibers located at the exterior part of the yarn; the circle shows the interior of the yarn and the magnification 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.

The dye fixation shows a minimal variation in the range of 90 to 93% when the fabric is post-treated with chitosan (Figure 2.4a). The color strength increases with the percentage of indigo (Figure 2.4b); 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.

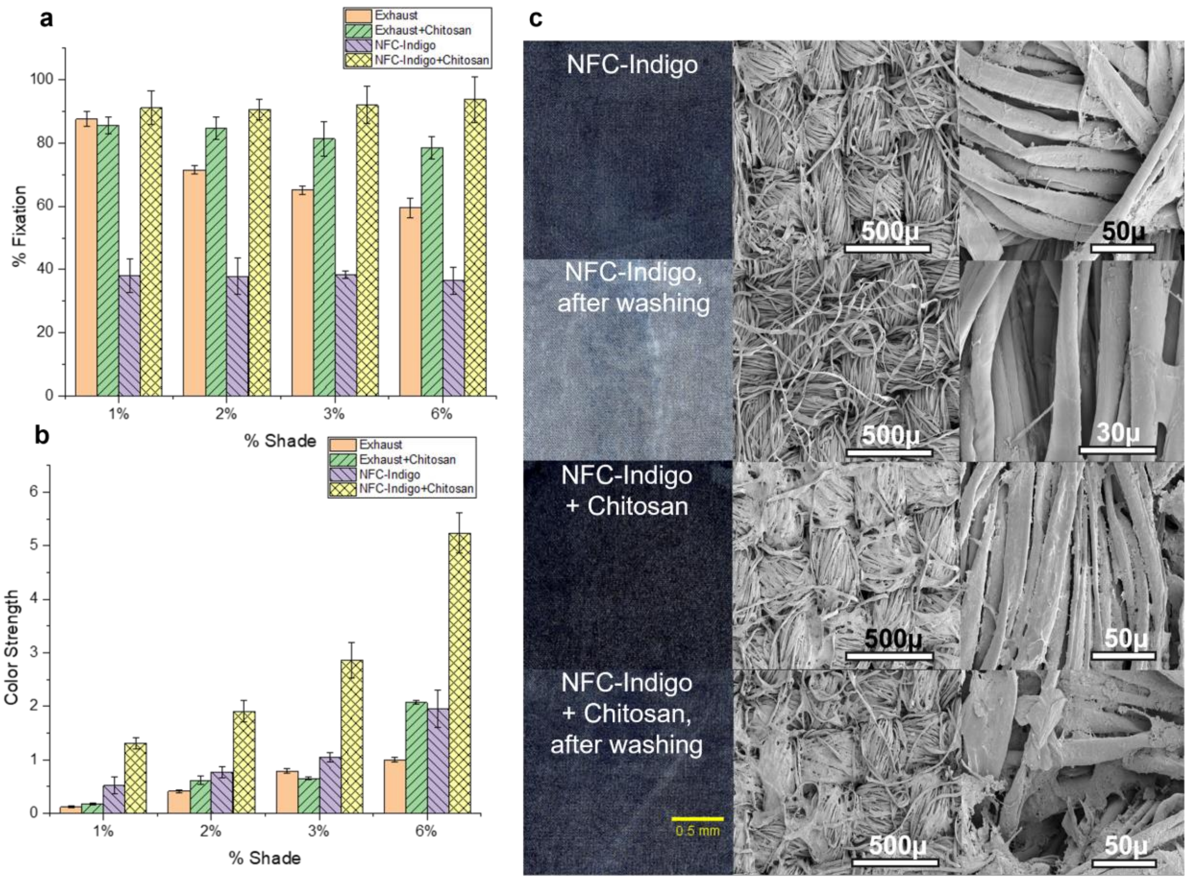

Figure 2.4: (a) Dye fixation (%F) and (b) color strength of NFC-indigo dyed denim for different % shade for samples post-treated with chitosan and non-treated reference sample (5 samples of 5 x 15 cm) compared with the traditional (Exhaust) and the traditional but modified with chitosan (Exhaust + Chitosan) methods. (c) SEM and optical images of the 6% shade reference samples and samples post-treated with chitosan.

The developed NFC indigo-dyeing method was compared with the traditional exhaust method and the traditional method modified by the chitosan treatment (Figure 2.4a) 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 2.8). 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 2.4a). 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.[39] 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.

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[40] (Table 2.2: Colorfastness ratings of NFC-indigo dyed fabrics.Table 2.2). 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 2.2, 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 2.2).

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 2.3). 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[41]. 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[41]. Our tests demonstrated no changes in air permeability in NFC coated fabrics. SEM images of the colored textiles (Figure 2.2g, Figure 2.3b-c, and Figure 2.4c) 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.

Table 2.1: 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, 45]	13-79	33-197	3-5
NFC-indigo dyeing	None	None	2

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[42, 43]. 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[44]. Consumption of sodium hydrosulfite, caustic soda, and water to dye one kilogram of cotton with conventional and NFC-indigo dyeing is compared in Table 2.1. 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, 46]. 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.

2.3 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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2.5 Supplementary Information

2.5.1 Materials and Methods

Materials and Reagents

Bleached, desized, un-mercerized 100% cotton print fabric (99.7 g/m^2) was purchased from Testfabrics, Inc, PA USA. The 100% cotton rotor spun yarn (unscoured, un-mercerized, and 6cc) was provided by Mount Vernon Mills, Trion, Georgia. Natural indigo (*Indigofera tinctoria*) was obtained from Dharma Trading Company, CA, USA. Carboxymethylcellulose sodium salt with a molecular mass of 90 kg/mol, chitosan with a molecular mass range of 19-375 kg/mol, and acetic acid were purchased from Sigma-Aldrich and used as received. Anhydrous sodium carbonate and triton X-100 (nonionic dispersing agent) were purchased from J.T. Baker and used as received. AATCC 1993 standard detergent WOB was received from AATCC. Formamidinesulfinic acid (thiourea dioxide) was purchased from Acros. Polystyrene latex beads suspension 2.5% in the water of a size 30 nm (L5155), 100 nm (L9902), 500 nm (L1403), and 2 μm (L4530) were purchased from Sigma-Aldrich.

Fabrication of Nanocellulose

As per a published protocol[1], kraft pulp sheets were knife-milled three times using a mesh sieve (pore size 500 μm). Cellulose powder was mixed with hot water (1-5% cellulos powder in water) and carboxymethylcellulose sodium salt (CMC, 0.25% in water). CMC was used as a plasticizer to accelerate the halogenation process (Rebinder effect[2]). The mixture was then delaminated into nanosized fibrils during 4-5 passes in a high-pressure homogenizer (APV 1000) to produce 1-5% nanofibrillated cellulose (NFC) hydrogel[1]. The cellulose concentration was adjusted to 1% in the hydrogel by dilution with water. The presence of CMC contributes to the gel formation. The nano-size cellulose fibers are 10 to 50 nm in diameter and up to several micrometers in length with an average aspect ratio of 1:50.[3]

Scouring of Cotton Fabric

The fabric was subjected to water at 60°C with AATCC standard reference detergent in 1:20 material liquor ratio. After 10 min, the sodium carbonate was added, and then the temperature was elevated to 80°C and maintained for another 35 minutes. After that, the samples were thoroughly rinsed in a similar amount of water twice and were dried at room temperature.

Coating of Cotton Textiles with NFC-indigo Formula

Agglomerated natural indigo of the average size of approximately 259 µm was ground using mortar and pestle to make it in powder form. The NFC-indigo formula was prepared by mixing the natural indigo powder with NFC hydrogel in amounts calculated in units of shade (pigment weight in % of the weight of the fabric for coloration). In the experiments, 1, 2, 3, and 6% shade was mixed with 1% NFC gel and 0.01% nonionic dispersing agent (Triton X-100). The mixture was stirred using a magnetic stirrer and then coated over damp, pre-scoured cotton fabric samples using a screen printer for even and thin coating. Coated samples were dried in the oven at 120°C for 60 minutes. Samples of cotton yarn were coated at the continuous passage of the yarn through the NFC-indigo formulation and dried in a tube furnace.

Post-Treatment of Coated Textiles

A chitosan solution was prepared by dissolving 1% chitosan in the water of 1:10 material to liquor ratio in the presence of 2% acetic acid (as per the volume of water) using a magnetic stirrer [4]. Each percentage shade of the sample was divided into two groups. One group was post-treated with the chitosan solution and the other group was not treated. For the post-treatment, the fabrics were dipped in chitosan solution for 15 minutes and then nipped using a manual rubber roller. The post-treated samples were dried at 150°C for 15 min. Likewise, samples of yarn were also treated in a chitosan aqueous solution and then cured.

Washing of samples

Each sample of size 5 cm x 15 cm was subjected to the colorfastness to laundering, home & commercial: accelerated, AATCC test method 61-2013-2A to perform the washing process with 25 steel balls) with Atlas Launder-Ometer (AATCC standard instrument), which is equivalent to 5 laundry cycles. For bending length and air permeability, the five home-laundering (washing/drying) procedure was performed on samples of sizes 2.5 cm x 20 cm and 20 cm x 20 cm according to AATCC Standard Method 124 using a standard reference detergent. Soluble in water CMC is rinsed out in the washing step.

Control samples

Four sets of exhaust dyed control samples were produced. The first sets of samples were dyed with indigo (1, 2, 3, and 6% shade) in the presence of thiourea dioxide (twice the amount of indigo) and 4g/l of sodium hydroxide in a material liquor ratio of 1:200. The powdered indigo and sodium hydroxide were mixed in water and heated to 50°C, thiourea dioxide was added and allowed to reduce the indigo. Then presoaked samples were dyed by dipping it for 1 minute and after taking it out, excess liquor was squeezed out. The fabric was then hanged to oxidize for 2 minutes. The second set was produced by post-treating dyed samples with chitosan, similar to

NFC-indigo dyed fabrics. The third set of samples were dyed with indigo (1, 2, 3, and 6% shade) without the presence of thiourea dioxide and sodium hydroxide. Lastly, the fourth set of samples were produced by post-treatment of samples dyed with indigo (1, 2, 3, and 6% shade) without the presence of thiourea dioxide and sodium hydroxide. All samples were dried at 100°C for 20 minutes and subjected for washing as mentioned above.

Characterization

The fabric samples were conditioned overnight at 65±2% relative humidity and 20±1°C temperature for testing and characterization of color performance and comfort properties.

Dyeing performance of colored fabrics:

Dye fixation (%F) is given by

$$\%F = \frac{K/S \text{ after Wash}}{K/S \text{ before Wash}} \times 100$$

The color strength (K/S) of the coated samples was measured at all wavelengths (400 to 700 nm at 10 nm interval) using a Macbeth Color Eye 7000A Spectrophotometer. It was calculated using the built-in software of color matching using the Kubelka–Munk equation given by:

$$K/S = \frac{(1\text{-}R)^2}{2R}$$

where K is the absorption, S is the scattering, and R is the reflectance. The K/S value of coated samples at the maximum wavelength of absorbency (λ_{max} 630-650 nm) was reported.

The washfastness of the samples was evaluated using Colorfastness to laundering, home & commercial: accelerated, AATCC test method 61-2013-2A to perform the washing process with 25 steel balls) with Atlas Launder-Ometer (AATCC standard instrument). Colorfastness to crocking (dry and wet) was evaluated using Colorfastness to crocking crockmeter AATCC test method 8-2016 by using SDL atlas, M238BB Electronic Crockmeter. The color change for washfastness and color staining for crock fastness ratings were obtained using Macbeth Color Eye 7000A spectrometer. To evaluvate the colorfastness properties of the NFC-indigo dyed fabric, the standard minimum colorfastness requirement for denim fabrics was referred to Standard Specification for 100% cotton denim fabrics (ASTM D6554/D65554M-14)[5].

Comfort properties of colored fabrics

The samples of original and coated fabrics were initially incubated in an oven at 100°C for 20 min, and then in a desiccator for 20 min. The dry weight of coated and non-coated samples was measured to calculate the percentage weight gain:

$$\%\ \text{Weight Gain}=\frac{\text{Weight after wash-Weight before coating}}{\text{weight before coating}}\times 100$$

The thickness of NFC coatings was calculated based on weight gain as

$$\text{Thickness of coating}=\text{Initial thickness of cotton fabic}\times\%\ \text{Weight gain}$$

The stiffness test on the warp side of the samples (ASTM D1388—18 Standard Test Method for Stiffness of Fabrics) was carried out using the cantilever test with IDM Stiffness Cloth Tester S0013. Air permeability test was performed (ASTM D737—18 Standard Test Method for Air Permeability of Textile Fabrics) using Textester FX 3300 Air permeability tester.

Dynamic light scattering (DLS) measurements

Indigo particle size was measured using the DLS Malvern Zetasizer Nano-ZS instrument. The size of ground indigo particles was estimated in a particle dispersion of 0.01% Triton X-100 aqueous solution. Samples of indigo particles extracted from the fabric, dyed by exhaustion method, were prepared by extracting the particles at 60°C at the agitation of the fabric sample in 0.01% Triton X-100 aqueous solution.

Particle retention test with NFC-based filters

A 5 µL sample of a 2.5% polystyrene latex fluorescent-labeled beads suspension of each bead size was diluted in 20 mL of deionized water. Each diluted suspension was filtered through an NFC-coated fabric in a Büchner funnel and vacuum suction. The filtrate solution was collected, and its fluorescence intensity was measured using a spectrofluorometer (Fluorolog-3, HORIBA Scientific, USA) at the specific excitation and emission wavelengths of fluorescent particles. The calibration plot was used to estimate the fraction of the particles retained on the filter.

2.5.2 Supporting Figures

Figure 2.5: A Greenpeace campaigner takes a water sample from a polluted river near Dadun Village, Xintang, Zengcheng (2010). Credit: © Lu Guang / Greenpeace

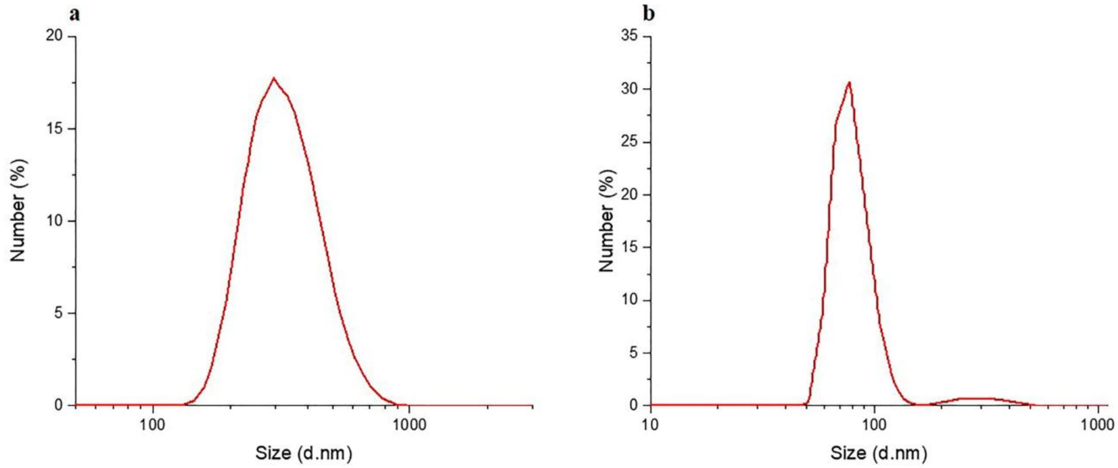


Figure 2.6: Indigo particles size distribution by dynamic light scattering: (a) natural indigo particle dispersed in the aqueous solution of dispersing agent, an average diameter is 83 ± 14 nm; (b) reference experiment: indigo particles extracted from the denim f fabric colored using traditional dyeing method by reduction of leuco-indigo; an average diameter is 331 ± 44 nm.

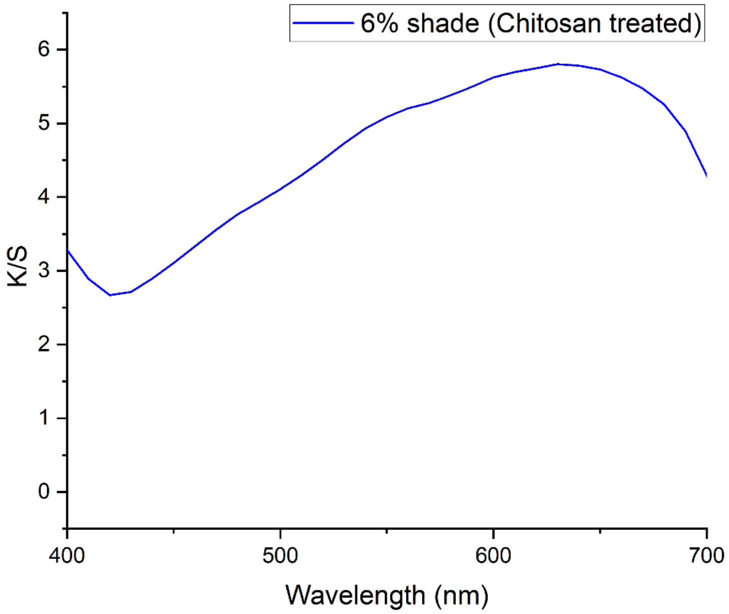


Figure 2.7: Color strength wavelength function of the chitosan post-treated 6% shade NFC-indigo dyed sample.

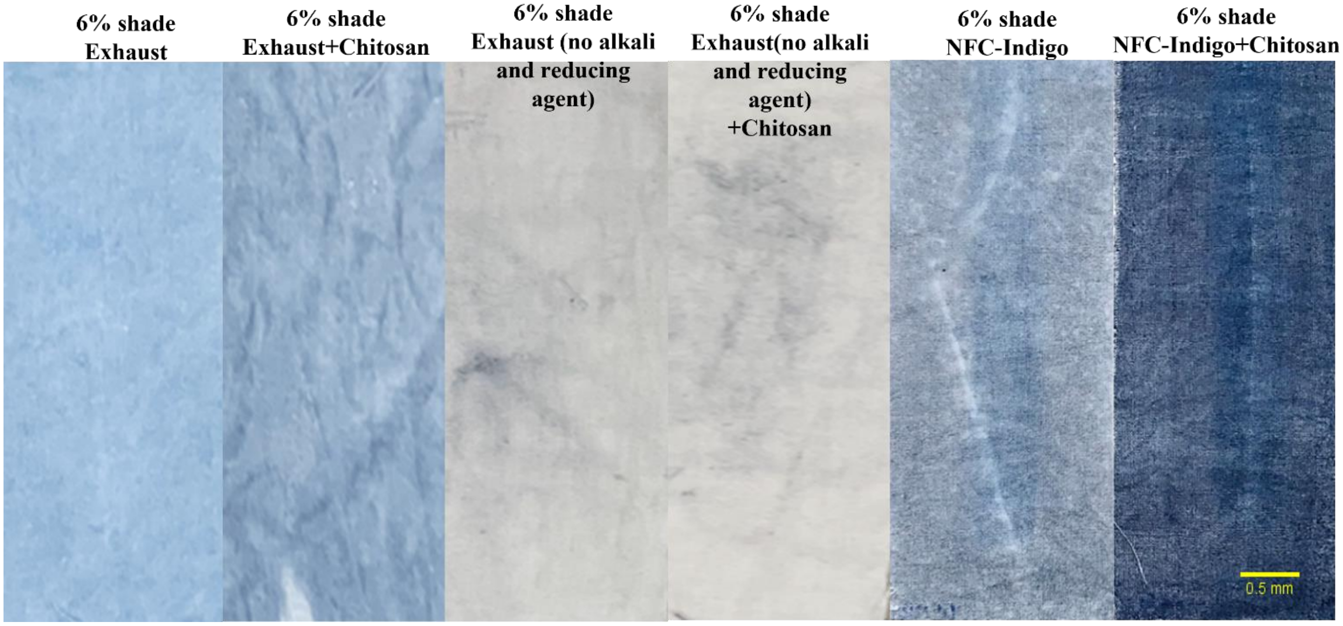


Figure 2.8: Optical images of 6% shade samples of exhaust dyed and NFC dyed samples with or without postreatment with chitosan (washed).

2.5.3 Supporting Tables

Table 2.2: Colorfastness ratings of NFC-indigo dyed fabrics.

% shade of NI (wof)	**Exhaust**	**Exhaust + Chitosan**	**Exhaust (no alkali and reducing agent)**	**Exhaust (no alkali and reducing agent) +Chitosan**	**NFC-Indigo**	**NFC-Indigo +Chitosan**
1% Shade						
K/S	0.12 ± 0.02	0.18 ± 0.01	0.06 ± 0.03	0.08 ± 0.01	0.52 ± 0.16	1.31 ± 0.1
% Fixation	87.54 ± 2.33	85.54 ± 2.69			38.11 ± 5.39	91.14 ± 5.35
Washfastness	4.17 ± 0.29	4.33 ± 0.29			3.17 ± 0.5	2.78 ± 0.25
Dry Crockfastness	4.17 ± 0.29	4.17 ± 0.29			4.17 ± 0.29	3.17 ± 0.29
Wet Crockfastness	4.17 ± 0.29	4 ± 0			3.83 ± 0.29	2.83 ± 0.29
2% Shade						
K/S	0.41 ± 0.03	0.62 ± 0.08	0.04 ± 0	0.14 ± 0.05	0.77 ± 0.11	1.91 ± 0.2
% Fixation	71.52 ± 1.24	84.69 ± 3.59			37.94 ± 5.76	90.6 ± 3.29
Washfastness	4.33 ± 0.29	4.17 ± 0.29			3.33 ± 0.6	2.94 ± 0.35
Dry Crockfastness	3.5 ± 0	3.33 ± 0.58			4.17 ± 0.29	2.83 ± 0.29
Wet Crockfastness	3.5 ± 0	3.33 ± 0.58			3.5 ± 0	2.67 ± 0.29
3% Shade						
K/S	0.79 ± 0.05	0.65 ± 0.02	0.04 ± 0.01	0.09 ± 0.01	1.05 ± 0.08	2.86 ± 0.34
% Fixation	65.18 ± 1.29	81.33 ± 5.56			38.35 ± 1.23	91.97 ± 5.92
Washfastness	4.17 ± 0.29	4.5 ± 0			3.17 ± 0.33	2.5 ± 0.33
Dry Crockfastness	2.5 ± 0	3.33 ± 0.29			3.83 ± 0.29	2.33 ± 0.29
Wet Crockfastness	2.83 ± 0.29	3.33 ± 0.29			3.17 ± 0.29	2.33 ± 0.29
6% Shade						
K/S	1.00 ± 0.05	2.07 ± 0.04	0.10 ± 0.03	0.12 ± 0.05	1.96 ± 0.35	5.24 ± 0.37
% Fixation	59.5 ± 3.01	78.59 ± 3.58			36.56 ± 4.32	93.73 ± 7.33
Washfastness	4.17 ± 0.29	4.33 ± 0.29			3.28 ± 0.42	2.61 ± 0.19
Dry Crockfastness	2.67 ± 0.29	2.83 ± 0.29			3 ± 0	1.5 ± 0
Wet Crockfastness	3.17 ± 0.29	3.33 ± 0.29			2.17 ± 0.29	1.5 ± 0

Table 2.3: Comfort properties of NFC-dyed fabrics.

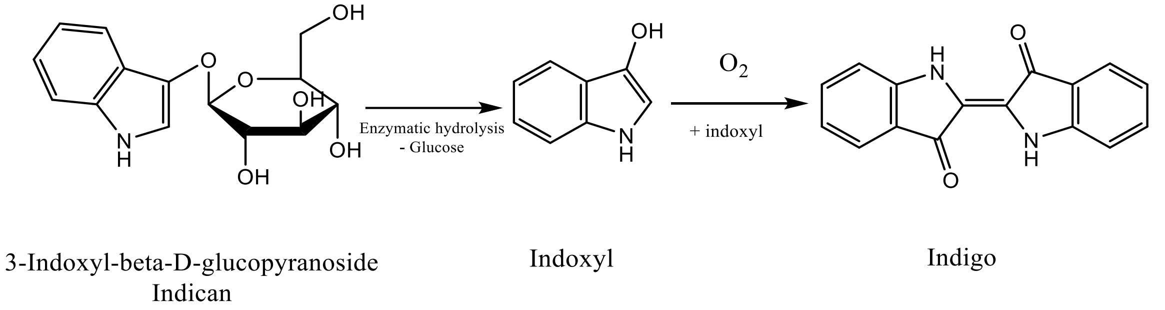
% Shade of NI (wof)	**NFC-Indigo**	**NFC-Indigo +Chitosan**
Initial measurements, Thickness of fabric 296.25 ± 3.98 µm, Bending length: 1.99 ± 0.13 cm, Air permeability: 56.32 ± 2.71 cfm		
1% Shade		
K/S	0.52 ± 0.16	1.31 ± 0.1
% Fixation	38.11 ± 5.39	91.14 ± 5.35
Weight gain* %	-0.78 ± 0.09	1.11 ± 0.39
Thickness of coating (µm)	-	3.28 ± 1.15
Bending length (cm)	2.04 ± 0.14	2.16 ± 0.03
Air permeability (cfm)	51.9 ± 1.15	48.57 ± 0.55
2% Shade		
K/S	0.77 ± 0.11	1.91 ± 0.2
% Fixation	37.94 ± 5.76	90.6 ± 3.29
Weight gain* %	-0.31 ± 0.21	1.39 ± 0.04
Thickness of coating (µm)	-	4.11 ± 0.11
Bending length (cm)	2.08 ± 0.09	2.16 ± 0.16
Air permeability (cfm)	50.33 ± 2.15	48.5 ± 0.61
3% Shade		
K/S	1.05 ± 0.08	2.86 ± 0.34
% Fixation	38.35 ± 1.23	91.97 ± 5.92
Weight gain* %	-0.60 ± 0.24	1.28 ± 0.22
Thickness of coating (µm)	-	3.79 ± 0.65
Bending length (cm)	2.08 ± 0.08	2.16 ± 0.11
Air permeability (cfm)	50.8 ± 0.70	47.3 ± 0.98
6% Shade		
K/S	1.96 ± 0.35	5.24 ± 0.37
% Fixation	36.56 ± 4.32	93.73 ± 7.33
Weight gain* %	-1.33 ± 0.20	2.65 ± 0.27
Thickness of coating (µm)	-	7.85 ± 0.79
Bending length (cm)	2.11 ± 0.16	2.17 ± 0.17
Air permeability (cfm)	50.57± 1.27	47.5 ± 0.85

* negative weight is due to the loss of some fibers to rinsing solutions

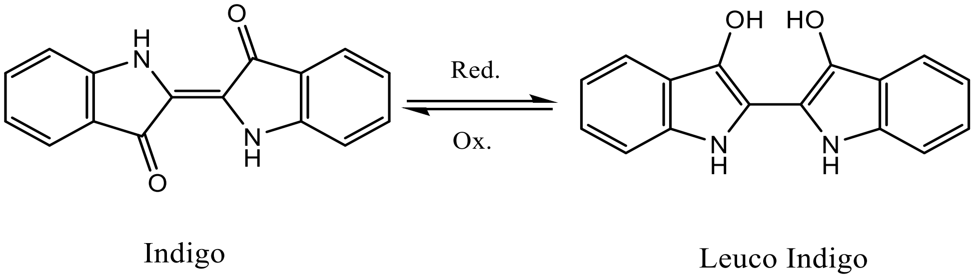
2.5.4 Supporting Notes

Supporting Note 1. Indigo

The uses of natural indigo go as far back as 7000 BC[6]. Recently, with an increasing consciousness of pollution control, the revival of natural dyes, including natural indigo, has occurred[7]. Natural indigo (2,2'- Bis (2,3-dihydro-3- oxoindolyliden) (I) a vat dye which is manufactured by biosynthesis of leaves and stem of indigo plants containing indican in *Indigofera. tinctorium* and *P. tinctorium*; isatan B and indican in *Is. tinctoria* to yield indoxyl, which transforms rapidly into indigo by oxidation[7, 8].



(I)



(II)

Due to the high demand for indigo, in 1925, BASF synthesized the commercially viable indigo[8]. For commercial production of synthetic indigo, crude oil (petroleum) is, first, chemically transformed in benzene, which, in turn, is converted into aniline in the presence of nitric acid, sulfuric acid, metal catalysts, and heat. Aniline is converted into the *n*-phenyglycinein by the *N*-methylation process in the presence of formaldehyde, hydrogen cyanide, and sodium hydroxide and converted into indoxyl in the presence of potassium hydroxide, sodium hydroxide, and sodium amide, which is oxidized to get indigo[8].

Dyeing with indigo is a complicated process and requires a series of parameters to be looked after. Indigo is a nonionic vat dye, which are insoluble pigments comprising of the carbonyl group(C=O) as chromophore and alkylamino group (-NHR) as auxochrome[9]. During dyeing, the aggregates of vat dyes are converted into a soluble Leuco indigo (II) anionic form of ion size 1.3 nm in the presence of reducing agent under the alkaline condition and develop substantivity towards cellulosic fibers[9, 10]. After diffusion, the dye molecules adsorbed on the cellulose via hydrogen bonds and oxidized to form submicron to micron size pigment particles in the presence of oxygen[9, 11]. Indigo is deposited over the surface of the cotton fibers with the exhaustion of only 10-20 % as compared to other vat dyes with the exhaustion of 70-95%, showing lower colorfastness properties and thus called a poor vat dye[12, 13]. To have better exhaustion and color performance, the multiple immersion and oxidation for a shorter period of 10-15 sec and 120 sec, respectively, for approximately 2% dye uptake each dip, are employed[14]. Continuous dosing of indigo and chemicals is performed to avoid shade variation. Well monitored steps lead to 70 to 80% fixation of indigo after washing[15-17]. Commercially, indigo dyeing for denim is a continuous process involves pretreating (scouring, mercerization), bottoming (sulfur dyes), dyeing, topping (sulfur, reactive, vat dyes), post-treating (washing), and drying. During dyeing, the wetted cotton yarns go through multiple dips and nips in leuco indigo vats (1-5 g/L) and oxidation by air to gain the desired percentage shade, and after dyeing, the yarns are sized before weaving[18, 19]. Bottoming or topping is a dyeing of yarns with black (or other) sulfur dyes before or after, respectively, is required to produce darker/deeper blue shade or different dyeing performance[18]. Indigo dyeing for denim is unique as it does not demand uniform dyeing through the cross-section of yarns, instead of the indigo particle aggregates over the surface of the yarns layer by layer after each dipping and does not penetrate inside[14]. This phenomenon is called the ring dyeing effect, which is desired to develop a trendy distressed look (wash down effect) in denim easily[17]. The size of the ring effect can be increased by decreasing the pH from 13 to 11 in the same alkalinity. [17] The color yield of indigo on denim yarn is highest in the mono ionic form (HO-indigo-O^-) of reduced indigo within the range of 10.8 to 11.2 pH.[17] Also, enough ionization of cotton fiber (cellulose-O^-) happens at pH 11 of dyebath favoring ring effect due to higher affinity, higher strike rate and lower penetration of the dye.[17]

Supporting Note 2. Nanocellulose

Cellulose is an abundant biopolymer found in woods, plant fibers, marine animals, algae, fungi, and bacteria comprised of glucose monomeric units covalently bonded by β 1-4 glucosidic bond. The degree of polymerization depends on the source of cellulose (from 10 000 to 15000)[20, 21]. Cellulose in plant walls occurs in the form of elementary fibrils composed of cellulose chains. Aggregation between cellulose chains and microfibrils occurs due to van der Waals forces and hydrogen bonding[20, 22]. There are three types of nanocellulose (engineered, nano-structured cellulose[23]): nanocrystalline cellulose (NCC), nanofibrillated cellulose (NFC), and bacterial nanocellulose (BNC). BNC is secreted extracellularly by bacteria called *Gluconacetobacter*. NFC comes from many different sources, including wood pulp, bleached kraft pulp, and bleached sulfite pulp via mechanical processing, using a homogenizer or microfluidizer. NFC has both amorphous and crystalline regions and tends to form hydrogels due to the entanglement of high aspect ratio NFC fibers[21, 24, 25]. NCC is fabricated by chemical treatment of biomass with mineral acids or oxidizing agents[20]. NCC particles have a lower aspect ratio as compared to NFC and higher crystallinity. All types of nanocelluloses have a very high surface area with the surface decorated by OH functional groups[23]. In this work, we selected NFC due to the high aspect ratio of fibrils capable of generating an entangled network that cage pigment particles.

Supporting Note 3. Chitosan

Chitosan is a polysaccharide with more than 5000 glucosamine units, obtained from the deacetylation of chitin, poly-(1,4)-2-acetamido-2-deoxy-β-D-glucose[26, 27]. Chitin is the second most abundant natural polymer found in the shells of crustaceans such as crab, shrimp, and crayfish [27]. Properties such as antibacterial, antitumor, and low immunogenicity of chitosan have drawn the attention of researchers in textile, polymer, and biomedical fields[28]. FTIR spectroscopic analysis shows that chitosan is capable of forming a hydrogen bond between -NH_2 group of chitosan and -OH group of cellulose acting as a cross-linking agent[29, 30]. Chitosan introduces cationic sites on the cotton surface owing to –NH_2 functional groups in glucosamine units. Treatment of textiles with chitosan contributed to an increase in abrasion resistance, stiffness, and crease recovery properties along with antimicrobial activity[30].

Supporting Note 4. Cost-factor

We focused only on the stage of indigo-dyeing of cotton fabrics with the major goal to reduce the use of harsh chemicals. We can make only a very rough estimation of the cost factor. The combination of indigo+NFC+chitosan makes only 1-2 w% of the colored fabric. Current prices of NFC < $50/kg, chitosan about $5/kg. Adding these components to the fabric will add about $0.5/kg fabric, but we should subtract the costs of water and chemicals that are avoided by NFC dyeing technology. A typical price of indigo-colored cotton fabric is $3/kg. It is apparent that the proposed technology will have a minimal impact on the price but it provides substantial improvements of the environmental impact.

2.5.5 Supporting References

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CHAPTER 3

THE ADVANCEMENT OF SUSTAINABLE AND ECO-FRIENDLY WITH NANOCELLULOSE-INDIGO GEL DYEING OF COTTON[2]

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[2] Rai, S., S. Sharma, and S. Minko. To be submitted to Dyes and Pigments.

ABSTRACT

Dyeing with indigo is a water, chemical, and energy-intensive process. Our previous study introduced a novel one-step nanocellulose-based natural indigo (NFC-NI) dyeing of cotton post-treated with chitosan.[1] This technology eliminated the use of chemicals and auxiliaries and reduced water usage up to a factor of 25. This research is the progression of NFC-NI dyeing technology as a "green" alternative to the conventional indigo dyeing process. Here, alternative cross-linking agents, chitosan, itaconic acid, and a mixture of chitosan and itaconic acid were considered, and their dyeing and comfort properties were examined and compared with the conventional dyeing technology. Post-treatment with chitosan and the combination of chitosan and itaconic acid outperformed the other alternatives and were comparable to each other. Additionally, the rheological properties and optimum indigo particle sizes were also evaluated. No significant change was observed in the rheological properties of nanofibrillated cellulose by adding indigo. The particle size in the 240-300 nm range provided the best results in terms of fixation and color strength.

3.1 Introduction

Among all blue dyes, indigo is the most popular blue dye used in the textile industry. The uses of natural indigo (from species *Indigofera tinctoria*) go as far back as 7000 BC.[2] Due to the high demand for indigo, in 1865, the German chemist Adolf von Baeyer began synthesizing synthetic indigo. Still, it was not until 1897 that BASF successfully launched its synthetic "Indigo Pure BASF." Although considered a low-quality vat dye, indigo is widely used in the denim industry because of its distressed look due to its poor colorfastness properties.[3] The denim industry uses approximately 95% of 50,000 tons (or more) of synthetic indigo produced yearly.[4] The indigo dyeing process involves pretreating (scouring), bottoming (sulfur dyes), dyeing (multiple dip) followed by airing for oxidation, topping, post-treating (washing), and drying, all carried out as a continuous process. Various parameters are involved in the effective dyeing with indigo, such as the amount of indigo, alkali concentration to maintain pH, reducing agents to maintain solubility, dipping and oxidation time, and the number of dips to get desired shade and effect.[5, 6]

Sodium hydrosulfite and sodium hydroxide are the most commonly used reducing agent (the redox potential of over -700mV) and alkali (pH 10-12), respectively, to make indigo soluble in water.[7, 8] They are economical and produce the best results among other reducing agents and alkali. But they are toxic, corrosive to equipment, drainage, and treatment facilities and are detrimental to the environment.[9, 10]

Researchers have proposed alternatives to reduce water and chemical effluents, such as using biodegradable dyes, and auxiliaries, minimizing wash-off, or recycling dyeing baths.[11] Alternative eco-friendly reducing agents such as bacterial reduction, alpha-hydroxy ketones, glucose, thiourea dioxide, iron(ii)salts, sodium borohydride, electrochemical reduction, β-glucosidase enzyme to hydrolyze indican into indoxyl have been studied.[9, 10, 12-19]. Most denim dyeing mills now use 40% Pre-reducing indigo (PRI) (e.g., Dystar indigo by Dystar, Denisol indigo by Archroma) produced by the catalytic hydrogenation process. PRI involves reducing indigo paste using a Raney nickel catalyst at a hydrogen pressure in alkaline conditions, which contains significantly less aniline (less than 1% of dye), up to 70% less reducing agent and alkali, and up to 15% less indigo dye.[20] [21] Although, PRI is much more expensive than indigo powder, it still requires the use of sodium hydrosulfite and caustic soda during dyeing.

Our previous study introduced an alternative indigo dyeing technology, which provides a one-step process to dye cotton fabric.[1] In this method, nanofibrillated cellulose gel mixed with indigo particles (NFC-NI) was coated over the cotton fabric and then post-treated with chitosan.[1] Traditionally, dyeing with indigo requires several dips in reduced vat followed by oxidation to develop darker shades. With this technology, to get the desired percentage shade, indigo particles (natural or synthetic) are added to the nanocellulose gel based on the weight of the fabric, allowing it a one-step process.[1]This unique method reduces the time- and energy-consuming steps involved with traditional indigo dyeing and provides an environmentally friendly dyeing process by not using any reducing agent or alkali and saving water up to a factor of 25.[1] This technology provides better fixation (over 90%) with comparable washfastness and rub fastness without altering comfort properties. This paper discusses advancements in NFC-NI dyeing technology. The study investigate the impact of using alternative cross-linking agents, namely chitosan (C), itaconic acid (IA), and a combination of chitosan and itaconic acid (IA+C) on the dyeing performance. Subsequently, the effect of in situ method of mixing NFC and indigo were examined. Additionally, the rheology of different NFC-NI formulations were studied. Finally, the role of particle size of indigo were investigated in fixation and color strength.

3.2 Materials and methods

3.2.1 Materials and Reagents

Bleached, desized, un-mercerized 100% cotton print fabric (2.94 ounces/yard^2) was purchased from Testfabrics, Inc, PA, USA. Natural indigo (*Indigofera tinctoria*) was obtained from Dharma Trading Company, CA, USA. Other chemicals used in the study were carboxymethylcellulose sodium 90 kD (Sigma- Aldrich), AATCC 1993 standard detergent WOB, sodium carbonate, anhydrous (J. T. Baker), itaconic acid, 99+% (Aldrich), chitosan, practical grade-mol wt 190000-375000 Da (Aldrich), sodium hypophosphite hydrate, hygroscopic (Aldrich), formamidinesulfinic acid (thiourea dioxide), 99% (Acros) and triton X- 100 (nonionic dispersing agent) (J. T. Baker). The conventionally dyed fabric was obtained from Mount Vernon Mills, Trion, Georgia.

3.2.2 Production of Nanocellulose[22]

Kraft pulp sheets were knife-milled three times using a mesh sieve (pore size 500 μm). 1% Cellulose powder and carboxymethylated cellulose (plasticizer, 0.25% in water) were mixed with hot water. The mixture was then delaminated into nanosized fibrils during 4-5 passes in a high-pressure homogenizer to produce 1% nanocellulose (NFC) hydrogel. The resulting NFC exhibits nanofibrils with a diameter of 10-50 nm and a length of several micrometers, and a surface area of 430 m^2/g.[22]

3.2.3 Scouring of cotton fabric[1]

The fabric was subjected to water at 60°C with AATCC standard reference detergent (WOB) in 1:20 M:L. After 10 minutes, the sodium carbonate was added, and then the temperature was brought to 70 to 80°C and maintained for another 35 minutes. After that, the samples were thoroughly rinsed twice in a similar amount of water and dried at room temperature.

3.2.4 Coating of cotton fabric with NFC-NI Formulation gel

The coating was performed using the procedure mentioned in chapter 2.[1] Tiny, agglomerated beads of natural indigo of the average size of approximately 259 µm were ground using mortar and pestle to make it in powder form. Approx. 95% of the obtained powder had an average diameter of 83±14 nm, while the remaining 5% fell within the range of 200-500 nms.[1] In experiments 1, 2, 3, and 6% natural indigo powder (% shade) on the weight of the fabric (wof) was mixed with 1% nanocellulose gel in the presence of 1% dispersing agent (on the weight of NFC gel). The mixture was stirred using a magnetic stirrer and then coated over damp, pre-scoured cotton fabric samples using a screen printer for even and thin coating (Figure 3.1). Coated samples were dried in the oven at 120°C for 60 minutes.[1] To prepare the in situ NFC-NI, the required indigo amount was added to the homogenizer to produce 1% nanocellulose gel.

3.2.5 Post-treatment of coated fabric[1]

Three different post-treatment solutions were prepared. For the first solution (IA), 8% itaconic acid (wof) was dissolved in the water (1:10 M:L) by using a magnetic stirrer, and then 4% sodium hypophosphite (wof) was mixed in the solution.[23] The second solution (IA+C) was prepared by dissolving 1% chitosan (wof) in the water in the presence of 2% acetic acid (as per the volume of water) using a magnetic stirrer, and then 8% itaconic acid (wof) with 4% sodium hypophosphite (wof) was added in the solution. Finally, the third solution (C) was prepared by dissolving 1% chitosan (wof) in water in the presence of 2% acetic acid (as per the volume of water) using a magnetic stirrer.[24]

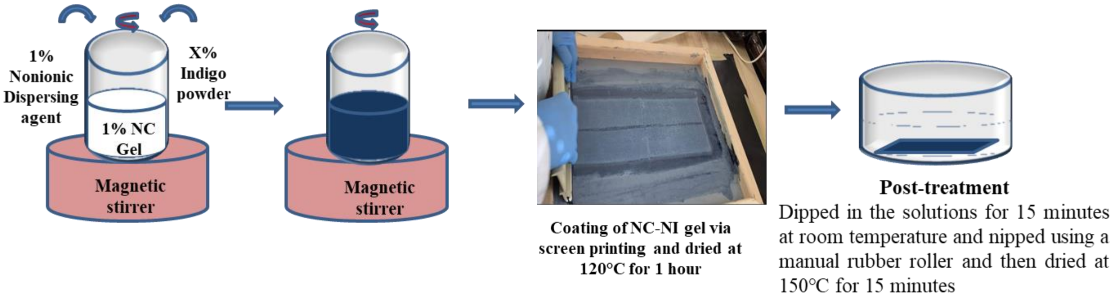

Figure 3.1: Preparation of NFC-NI gel, screen printing, and post-treatment of cotton samples.

Each % shade of the sample was divided into three groups, so one group was post-treated with one post-treatment solution. For post-treatment, the fabrics were dipped in these solutions for 15 minutes and then nipped using a manual rubber roller. The post-treated samples were dried at 150°C for 15 minutes. The reference samples (R) were prepared without subjecting them to any post-treatment.

3.2.6 Coating cotton fabric with indigo particles mixed in chitosan solution

As mentioned in section 3.2.5, the chitosan solution was prepared by dissolving 1% chitosan (wof) in water in the presence of 2% acetic acid (as per the volume of water) using a magnetic stirrer. 6% indigo particle (wof) (denoted as 1% chitosan (wof) +6% NI) was dispersed in the solution in the presence of 1% dispersing agent (as per the volume of water). For comparison, another solution was prepared by dissolving 1% chitosan (as per the volume of water) in the presence of 2% acetic acid (as per the volume of water) using a magnetic stirrer. Then, 6% indigo particles (wof) were dispersed in the presence of 1% dispersing agent (as per the volume of water) (denoted as 1% chitosan (vow) +6% NI). These two dispersions were coated over the fabric via screen printing, dried at 150°C for 15 minutes, and subjected to testing as other samples.

3.2.7 Washing of samples[1]

Each sample of size 2"×6" was subjected to 'colorfastness to laundering, home & commercial: accelerated, AATCC test method 61-2013-2A' to perform the first washing process (with 25 steel balls) to determine fixation and color strength using atlas Launder-Ometer (AATCC standard Instrument) which is equivalent to 5 laundry cycles. The five home-laundering (washing/drying) procedure was performed according to AATCC Standard Method 124 using a standard reference detergent ("AATCC Detergent 1993") to the samples for testing bending length (1"×8") and air permeability (8"×8").

3.3 Characterization

The fabric samples were conditioned overnight at 65±2% relative humidity and 20±1°C temperature to test and characterize color performance and comfort properties.[1]

3.3.1 Dyeing performance of colored fabrics[1]

Dye fixation (%F) is given by:

$$\%F=\frac{\text{K/S after Wash}}{\text{K/S before Wash}} \times 100$$

The color strength (K/S) was measured at all wavelengths (400 nm to 700 nm at 10 nm intervals) using a Macbeth Color Eye 7000A Spectrophotometer. It was calculated using the built-in software of color matching using the Kubelka–Munk equation given by:

$$K/S=\frac{(1\text{-}R)^2}{2R}$$

where K is the absorption coefficient, S is the scattering coefficient, and R is the sample's reflectance. The K/S value of coated samples at the maximum wavelength of absorbency (λ_{max} 630-650 nm) was reported.

The washfastness of the samples was evaluated using 'colorfastness to laundering, home & commercial: accelerated, AATCC test method 61-2013-2A' to perform the washing process with 25 steel balls with Atlas Launder-Ometer (AATCC standard instrument). Colorfastness to crocking (dry and wet) was evaluated using 'colorfastness to crocking: Crockmeter method, AATCC test method 8-2016' by using SDL atlas, M238BB Electronic Crockmeter. The color change for washfastness and color staining for crock fastness ratings were obtained using Macbeth Color Eye 7000A spectrometer. To evaluate the colorfastness properties of the NFC-NI dyed fabric, the standard minimum colorfastness requirement for denim fabrics was referred from 'Standard Specification for 100% cotton denim fabrics' (ASTM D6554/D65554M-14)".[25]

3.3.2 Comfort properties of colored fabrics[1]

The original and coated fabrics samples were initially incubated in an oven at 100°C for 20 min, and then in a desiccator for 20 min. The dry weight of coated and non-coated samples was measured to calculate the percentage weight gain:

$$\%\ \text{Weight Gain}=\frac{\text{Weight after wash-Weight before coating}}{\text{weight before coating}}\times 100$$

The thickness of the coating was calculated based on weight gain as

$$\text{Thickness of coating} = \text{Initial thickness of cotton fabric} \times \%\ \text{Weight Gain}$$

The stiffness test on the warp side of the samples (ASTM D1388—18 Standard Test Method for Stiffness of Fabrics) was carried out using the cantilever test with IDM Instrument Stiffness Cloth Tester – S0013. An air permeability test was performed (ASTM D737—18 Standard Test Method for Air Permeability of Textile Fabrics) using Textester FX 3300 Air permeability tester.

3.3.3 Rheology

The rheological properties were evaluated using Modular Compact Rheometer (MCR) 302 (Anton Paar) with Rheoplus software. The parallel plate with a gap of 0.5mm (PP20/MRD/TI-SN32701) was used for measurement with the normal force of 1.03N at the temperature of 23°C. The shear rate sweep ranged from 0.01 to 100 per second.

3.3.4 Dynamic light scattering (DLS) measurements[1]

The indigo powder was mixed with water in the presence of the nonionic dispersing agent at room temperature. The solution was diluted, and the particle sizes were measured by a dynamic light scattering method using Malvern Zetasizer Nano-ZS with a disposable micro cuvette.

3.3.5 Statistical analysis

A simple linear regression analysis was performed to test the significance of particle size on fixation. Also, ANOVA test was performed to test the whether K/S values of synthetic dyes are significantly higher than that of natural dyes.

3.4 Results and Discussion

3.4.1 Color performance of NC-NI coated fabrics

Figure 3.2 and Figure 3.3 compare the dye fixation percentage (%F) and color strength (K/S) of NFC-NI and NFC-NI in situ coated fabrics with different post-treatments. The dye fixation and the color strength in NFC-NI dyeing depend on the adhesion of nanocellulose loaded with indigo particles to the fabric.[1] The post-treated fabric showed significantly better dye fixation than the reference samples. As mentioned in the previous study, the reference samples and chitosan showed fixation of 36-38% and 90-93%, respectively.[1] The fixation percentage of IA post-treated samples was 50-60%, which can be explained by the esterification of cotton and cellulose by itaconic acid in the presence of sodium hypophosphite.[23] The samples post-treated with IA+C showed fixation in the 82-92% range. This improved fixation can be explained by the adhesion of NFC by cross-linking (esterification of cellulose and chitosan) in the presence of catalyst sodium hypophosphite.[26] The post-treatment of cotton fabric with chitosan (C) and chitosan combined with itaconic acid (IA+C) displayed better fixation than the post-treatment with only itaconic acid (IA) in every percentage shade. Notably, the fixation percentage is generally higher (90-93%) with minimal variation across different shades when the fabric is post-treated with chitosan only. The difference between the post-treatment with (C and IA+C) and without chitosan (IA only) suggests that chitosan plays a significant role as a cross-linking agent and in the fixation of the indigo particles. It is also important to mention that a fractional escape of indigo particles (blue) was observed in the solution when the samples were post-treated with IA or IA+C. However, no noticeable leakage was observed when post-treated with chitosan. To elucidate the difference between the various post-treatment is shown in Figure 3.4 which shows the comparable optical pictures of NFC-NI coated samples of 6% shade, post-treatments with IA, IA+C and C, and reference samples.

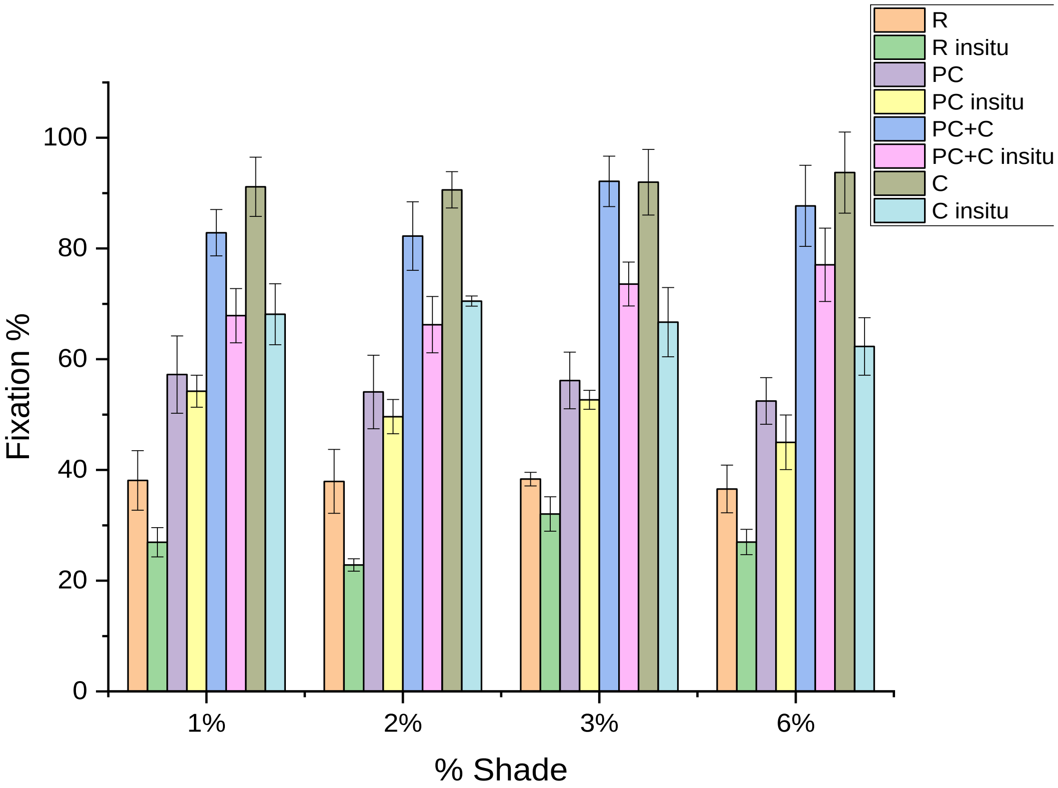

Figure 3.2: Dye Fixation percentage (%F) of coated samples for different % shade of NI, posttreatments, and reference sample (5 samples of 2’’x 6"). (R: Reference, IA: Itaconic Acid, IA+C: Itaconic Acid w/ Chitosan, C: Chitosan).

The color strength (K/S) increases with the increase in the amount of indigo particles in the nanocellulose gel. The results of the color strength correlate with the results of the dye fixation. Since the K/S increases with percentage shade, any desired shade can be obtained by varying the percentage shade of indigo particles in nanocellulose gel, unlike the conventional dyeing with indigo where multiple dipping is required to gain darker shade.

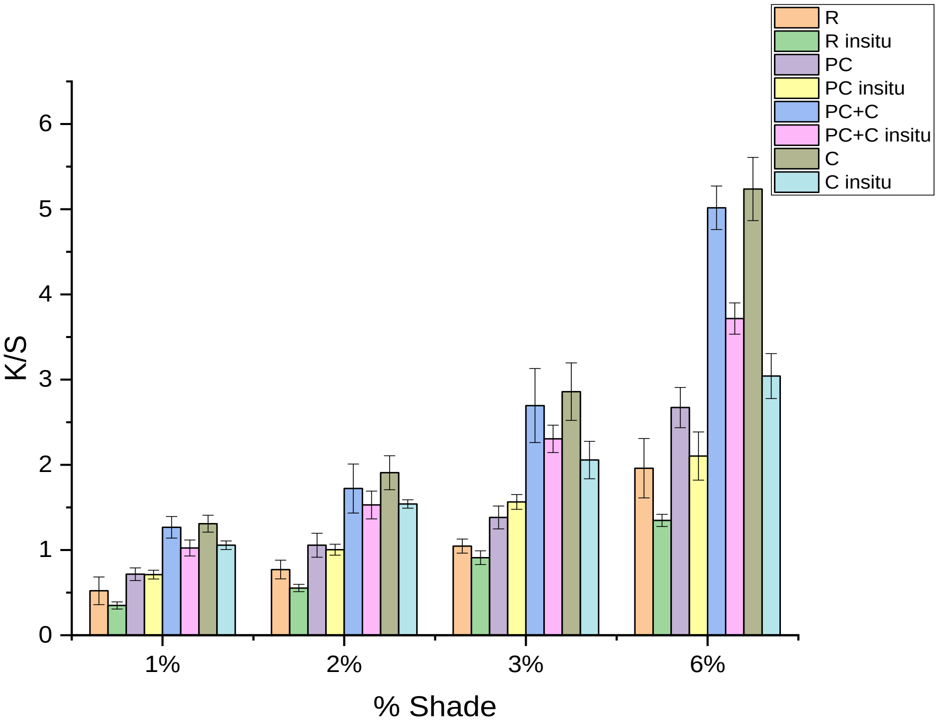

Figure 3.3: Color Strength of coated samples for different % shade of NI, posttreatments, and reference samples (5 samples of 2’’x 6"). (R: Reference, IA: Itaconic Acid, IA+C: Itaconic Acid w/ Chitosan, C: Chitosan).

However, the samples coated with in situ NFC-NI overall showed lower fixation and lower K/S in the reference and all post-treatments. Hence, mixing indigo with NFC in in situ was not the appropriate method and was not considered for further characterization.

The samples coated with 1% chitosan (wof) + 6% NI performed poorly, having only 1.84±0.26 K/S value and only 56% fixation, as shown in Table 3.5. Whereas 1% chitosan (vow) + 6% NI dispersion was not uniform. Indigo particles aggregated as soon as they were added to the chitosan solution (Figure 3.7.) These aggregates were very large to pass through the screen during coating and did not color the fabric.[27] Compared to NFC gel, chitosan could not encage or hold the particles, resulting in poor color strength and fixation (Figure 3.8, Table 3.5).

Table 3.1 summarizes the colorfastness properties of the reference and the post-treated samples. The samples' washfastness exceeded the standard requirement (grade 2). The samples post-treated with itaconic acid (IA) generally showed good dry and wet crockfastness, while the fixation was in the range of only 50 to 60% (Figure 3.2). Wet crockfastness ratings also meet the standard specification's minimum requirement (grade 1.5). However, dry crockfastness ratings do not meet the minimum requirement (grade 3) when coated with 3% and 6% NFC-NI gel and post-treated with chitosan (C) or chitosan and itaconic acid (IA+C). The high surface area of the NFC exposes the loaded indigo particles that come off in rubbing in wet conditions.[22] Optical images of the coated samples are shown in Figure 3.4. The approaches to improve colorfastness performance by NFC-NI-based dyeing are ongoing.

Further, wash fastness to 50 laundry washes were performed for 6% shade samples post-treated with C and IA+C and compared with 6% shade dyed fabric with the traditional method (three dips and oxidation) and a commercial denim twill weave fabric (with warp yarn dyed with synthetic indigo and weft undyed). The performance of NFC-NI coated samples was comparable to the conventionally indigo-dyed fabric for each laundry cycle, as shown in Table 3.2.

Table 3.1: Colorfastness ratings of NFC-NI coated samples for different % shade of NI, posttreatments, and reference samples (3 samples of 2" x 6"). (Grading is according to AATCC grey/ stain scale of 1–5, where 1 is very poor, and 5 is excellent.[25])

% Shade of NI (wof)	**Reference with no post-treatment (R)**	**Post-treatment with polycarboxylic**	**Post-treatment with polycarboxylic**	**Post-treatment with chitosan (C)**
Washfastness				
1%	3.17 ± 0.5	2.78 ± 0.25	3.06 ± 0.77	2.78 ± 0.25
2%	3.33 ± 0.6	2.56 ± 0.42	3.44 ± 0.92	2.94 ± 0.35
3%	3.17 ± 0.33	2.44 ± 0.92	2.78 ± 0.54	2.5 ± 0.33
6%	3.28 ± 0.42	2.28 ± 0.79	3.06 ± 0.69	2.61 ± 0.19
Dry Crockfastness				
1%	4.17 ± 0.29	4.17 ± 0.29	3.33 ± 0.58	3.17 ± 0.29
2%	4.17 ± 0.29	3.83 ± 0.29	3 ± 0	2.83 ± 0.29
3%	3.83 ± 0.29	3.5 ± 0.5	2.33 ± 0.29	2.33 ± 0.29
6%	3 ± 0	3 ± 0.5	1.67 ± 0.29	1.5 ± 0
Wet Crockfastness				
1%	3.83 ± 0.29	3.83 ± 0.29	2.5 ± 0	2.83 ± 0.29
2%	3.5 ± 0	3.5 ± 0	2.17 ± 0.29	2.67 ± 0.29
3%	3.17 ± 0.29	2.67 ± 0.29	2.17 ± 0.29	2.33 ± 0.29
6%	2.17 ± 0.29	2.33 ± 0.29	1.5 ± 0	1.5 ± 0

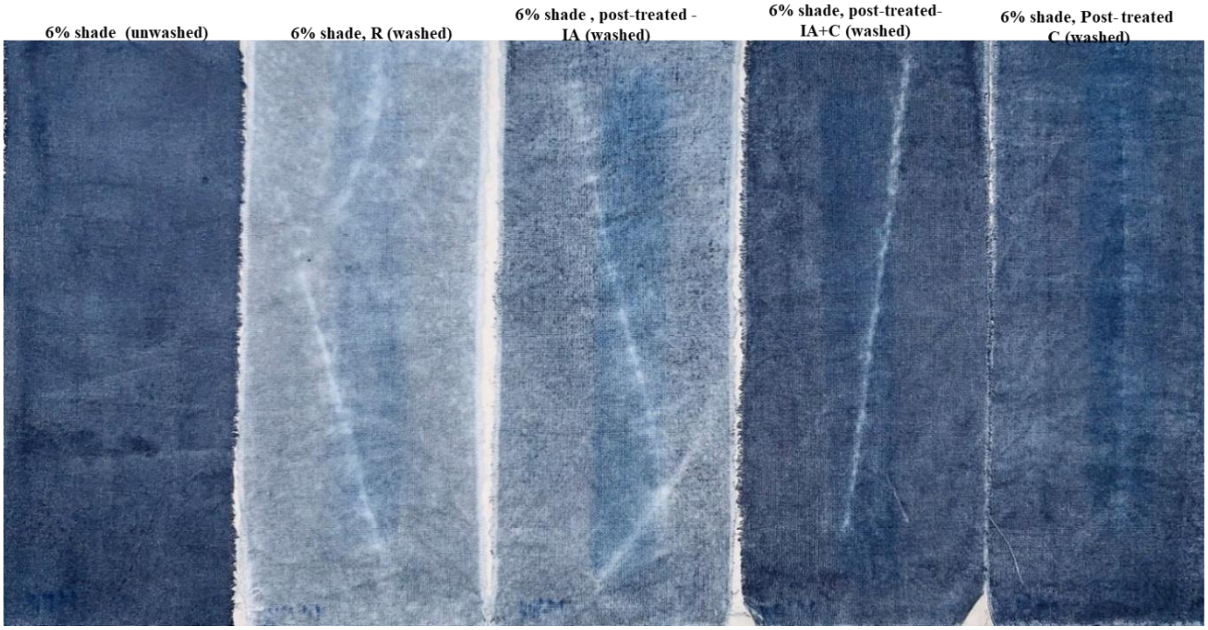

Figure 3.4: Optical pictures of coated samples of 6% shade of NI, posttreatments, and reference samples (5 samples of 2’’x 6"). (R: Reference, IA: Itaconic Acid, IA+C: Itaconic Acid w/ Chitosan, C: Chitosan).

3.4.2 Comfort properties of colored fabrics

Table 3.3 reports the comfort properties of NFC-NI dyed fabrics in terms of weight gain, the thickness of the coating, bending length, and air permeability. Overall no significant change in the comfort properties of the fabric was observed after NFC-NI dyeing. The results indicate a direct relationship between the adhesion of nanocellulose and the fixation of the indigo particles.[1] Generally, the maximum weight was observed in the 6% shade for each treatment, indicating that weight increases with the increase in indigo particles. Among them, the most weight gain occurred when the coated samples were post-treated with IA+C, followed by post-treated with C in all percentage shades. A higher weight gain in IA+C samples indicates the formation of an ester bond with nanocellulose and chitosan in the presence of sodium hypophosphite. [26] The thickness of the coating ranges from 2 to 11µm, and the maximum thickness occurred for samples post-treated with IA+C followed by the samples post-treated with C in every percentage shade. Bending stiffness is a quantitative measurement of the fabric hand.

Table 3.2: Colorfastness ratings of NFC-NI coated samples for 6 % shade of NI, with C and IA post-treatment (3 samples of 2" x 6"). (Grading is according to AATCC grey/ stain scale of 1–5, where 1 is very poor, and 5 is excellent.[25]).

Number of laundry washes	NFC-NI+C	NFC-NI+IA+C	Traditional method	Commercial denim fabric
5	3.22 ± 0.42	3.11 ± 0.35	2.56 ± 0.19	2.78 ± 0.19
10	3.44 ± 0.25	3.22 ± 0.75	3.89 ± 0.1	4.28 ± 0.25
15	3.61 ± 0.25	3.56 ± 0.82	4.11 ± 0.25	4.22 ± 0.1
20	3.67 ± 0.73	2.89 ± 0.51	3.72 ± 0.38	4.17 ± 0.17
25	3.78 ± 0.84	3.50 ± 0.60	4.28 ± 0.19	4.00 ± 0.29
30	3.94 ± 0.42	4.22 ± 0.25	4 ± 0.33	4.44 ± 0.1
35	4.06 ± 0.25	4.00 ± 0.44	2.78 ± 0.79	4.28 ± 0.25
40	4.06 ± 0.25	4.44 ± 0.25	3.83 ± 0.44	4.00 ± 0.29
45	4.22 ± 0.19	4.33 ± 0	4.61 ± 0.19	4.44 ± 0.1
50	4.22 ± 0.10	4.39 ± 0.19	4.44 ± 0.25	4.44 ± 0.25

The bending length is the length of the rectangular strip of material that bends under its own weight to a specified angle.[28] The longer the bending length, the stiffer the fabric. In every category, the increase in bending length was very low, with the highest being approx. 8% for samples treated with IA+C and C. The maximum increase, approx. 8% in the bending length was for the samples coated with IA+C and C. Air permeability is the rate of airflow passing perpendicularly through a known area under a standard air pressure differential between the two surfaces of a textile material.[28] The coating affects air permeability by causing a change in the length of the airflow path through a fabric. The maximum but insignificant loss in air permeability was observed after the IA+C and C post-treatments than in IA.

3.4.3 Rheological properties of NFC-NI

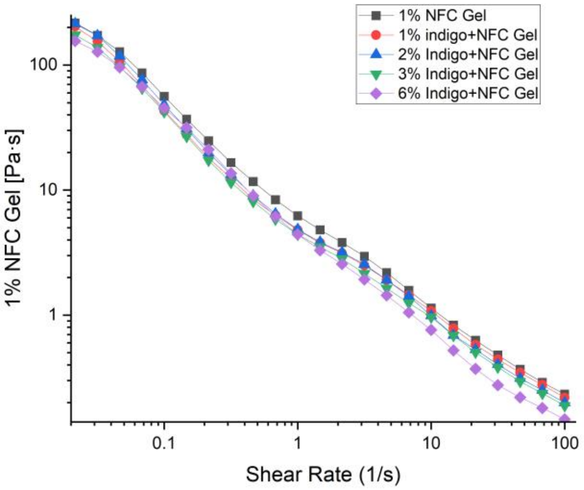

Figure 3.5: Viscosity of 1% NFC and 1,2,3,6% NFC-NI gels.

The rheological properties of 1% NFC and 1, 2, 3 and 6% NFC-NI are shown in Figure 3.5. Notably, no significant change occurred in the rheological properties of NFC by adding indigo. The zero shear viscosity was found as 185, 172, 159, 135, and 117 Pa.s for 1% NFC and 1,2,3 and 6% NFC- NI, respectively, and the viscosity at the shear rate 100 per second was observed at 0.234, 0.219,.0.200, 0.189, and 0.147 Pa.s, respectively. NFC-NI exhibited shear-thinning properties similar to 1% NFC. It was observed that increasing the amount of indigo added to NFC decreased the viscosity. Adding particles results in the disruption of hydrogen bonds between the nanofibrils of cellulose, leading to a decrease in entanglement and subsequently reducing the viscosity of the NFC.[29]

Table 3.3: Comfort properties of coated samples for different % shade of NI, post-treatments, and reference samples (weight gain -5 samples of 2" x 6"; bending length- 3 samples of 1" x 8"; and air permeability – 3 samples of 8" x 8").* negative weight gain and change in thickness due to the loss of fiber to rinsing solutions.

% Shade of NI (wof)	**Reference with no post-treatment (R)**	**Post-treatment with polycarboxylic acid (IA)**	**Post-treatment with polycarboxylic acid & chitosan (IA+C)**	**Post-treatment with chitosan (C)**
Weight gain* %				
1%	-0.78 ± 0.09	1.36 ± 0.34	2.3 ± 0.23	1.11 ± 0.39
2%	-0.31 ± 0.21	0.62 ± 0.3	1.87 ± 0.73	1.39 ± 0.04
3%	-0.60 ± 0.24	1.01 ± 0.29	2.21 ± 0.4	1.28 ± 0.22
6%	-1.33 ± 0.20	1.27 ± 0.45	3.74 ± 0.6	2.65 ± 0.27
Thickness of coating (µm), Initial thickness of fabric 296.25 ± 3.98 µm				
1%	-2.31 ± 0.26	4.02 ± 1.00	6.81 ± 0.68	3.28 ± 1.15
2%	-0.91 ± 0.62	1.83 ± 0.88	5.53 ± 2.16	4.11 ± 0.11
3%	-1.77 ± 0.71	2.99 ± 0.85	6.54 ± 1.18	3.79 ± 0.65
6%	-3.94 ± 0.59	3.76 ± 1.33	11.0 ± 1.77	7.85 ± 0.79
Bending length* (cm), Initial bending length- 1.99 ± 0.13 cm				
1%	2.04± 0.14	2.09 ± 0.02	2.10 ± 0.14	2.16 ± 0.03
2%	2.08 ± 0.09	2.09 ± 0.02	2.10 ± 0.04	2.16 ± 0.16
3%	2.08 ± 0.08	2.09 ± 0.09	2.18 ± 0.06	2.16 ± 0.11
6%	2.11 ± 0.16	2.11 ± 0.05	2.14 ± 0.13	2.17 ± 0.17
Air permeability (cfm), Initial air permeability - 56.32 ± 2.71 cfm				
1%	51.9 ± 1.15	51.33 ± 1.16	48.9 ± 2.19	48.57 ± 0.55
2%	50.33 ± 2.15	50.2 ± 1.55	48.83 ± 0.59	48.5 ± 0.61
3%	50.8 ± 0.70	49.9 ± 1.91	47.23 ± 0.38	47.3 ± 0.98
6%	50.57± 1.27	49.6± 1.71	48.07 ± 1.99	47.5 ± 0.85

3.4.4 Particle Size Analysis

In NFC-NI dyeing, the particle size of indigo plays an important role. In our previous study, the particle size of indigo during mixing to NFC was 83±14 nm.[1] However, the caged aggregate size of indigo in the coating over fabric was 150-350 nm resulting in more than 90% fixation with chitosan post-treatment.[1] Hence, fixation and color strength analysis were performed by various particle sizes of indigo aggregates. Different particle sizes were obtained by ball milling the indigo particles at various time duration (1min, 3min, 5min, 7 min, and 10 min) with 7 steel balls. These indigo particles were mixed with 1% NFC to prepare 6% NFC-NI formula as mentioned in section 2.4. The results are summarized in Table 3.4. The highest fixation and K/S were observed for particle size 244-290 nm when natural indigo was ball milled for 5-7 min. This range is the optimum range of indigo particle size for the NFC fibrils to encase the particles to have a fixation of around 95%. The increase or decrease in the particle size beyond this range decreased the fixation rate. Based on this result, synthetic indigo (with an average aggregate size of about 170 um) was ball milled for 5 minutes giving a particle size of 305±37.48 nm. The resulting K/S and fixation were 7.92±0.79 and 94.38±3.76, respectively. It is important to note that synthetic indigo results in better K/S than natural indigo with the same % shade due to its manufactured purity. The ANOVA test also showed that the K/S of synthetic indigo is significantly higher (at 5% level of significance) than that of natural indigo (Table 3.6). Natural indigo contains red or other color pigments because of its natural raw material.[30] This analysis proves that particle size is vital in NFC-NI dyeing fixation. Table 3.7 shows the regression analysis of the impact of particle size on the fixation of NFC-NI dyeing. The independent variables are the particle size of the indigo after milling for different minutes, and the coefficients are the estimated effect of each variable on the fixation. The standard error is a measure of the uncertainty of the coefficient estimate, and the t-statistic is a ratio of the coefficient to the standard error. A higher t-statistic and the corresponding low p-value (p-value < 0.001) means that the coefficients are statistically significant, that is, the particle size significantly affects the fixation. A high R-square (R^2=0.99) implies a good fit for the regression model.

Table 3.4: Color Strength, Dye Fixation percentage (%F), of 6% NFC-NI dyed samples prepared using various particle sizes obtained by ball milling at various time duration.

Ball milled indigo	**1 min**	**3 min**	**5 min**	**7 min**	**10 min**
Particle size (nm)	484.3±89.19	369.5±27.85	290.0±29.69	244.8±12.27	226.0±2.09
K/S	5.15±0.06	5.27±0.42	5.77±0.33	5.34±0.2	5.63±0.34
%F	86.48±1.17	87.00±6.45	95.85±5.37	97.31±1.78	89.84±4.07

The above-prepared NFC-NI with various indigo particle sizes were coated in cellulose film (model to mimic cotton fabric with smooth surface) to study and estimate the particles' dispersion and the coating's thickness under the SEM. There was no visible difference in the dispersion of the particles and thickness of the coating between any of the NFC-NI gels prepared with various particle sizes. The thickness of the coating measured from the SEM pictures was 1.44±0.08um. Figure 3.6(a) and (b) show examples of SEM pictures for the top and cross-sectional view of the coated film, respectively.

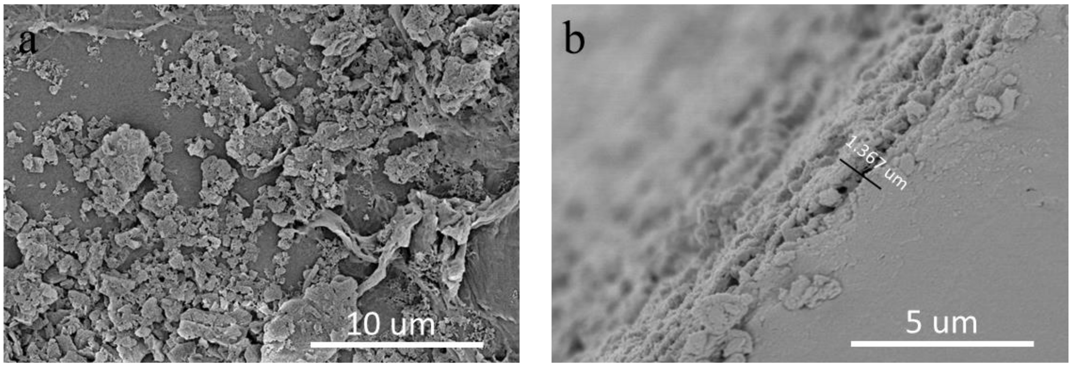

Figure 3.6: SEM pictures for the top (a) and cross-sectional (b) view of the coated cellulose films.

3.5 Conclusions

In this study, the cotton fabric was coated with 1,2,3 and 6% shade of nanofibrillated cellulose-natural indigo gel and post-treated with chitosan, polycarboxylic acid (itaconic acid), and a combination of polycarboxylic acid and chitosan. Overall, the chitosan-treated NFC-NI coated samples exhibited the best dyeing performance with the highest K/S values and over 90% fixation in every percentage shade. Chitosan act as cross-linking agent due to its intramolecular and intermolecular hydrogen bonding with nanocellulose and cotton fabric. Also, there was no significant change in the comfort properties in terms of weight gain, bending stiffness, and air permeability. There was also no significant change in the rheological properties of nanocellulose gel with the addition of indigo particles. Finally, the particle size of 240-300 of indigo particles performed the best for better fixation and color strength.

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3.7 Supplementary Information

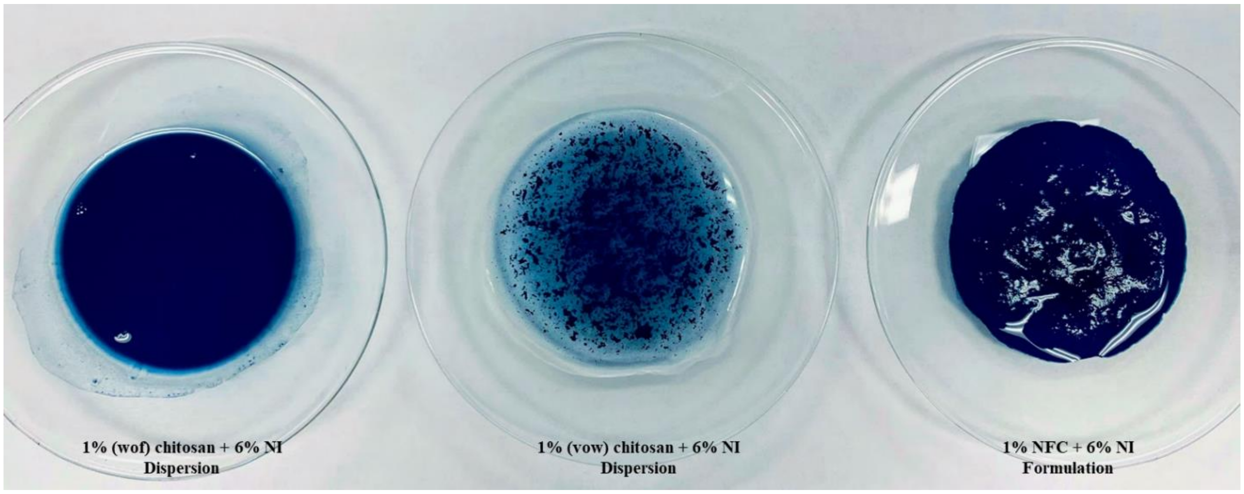


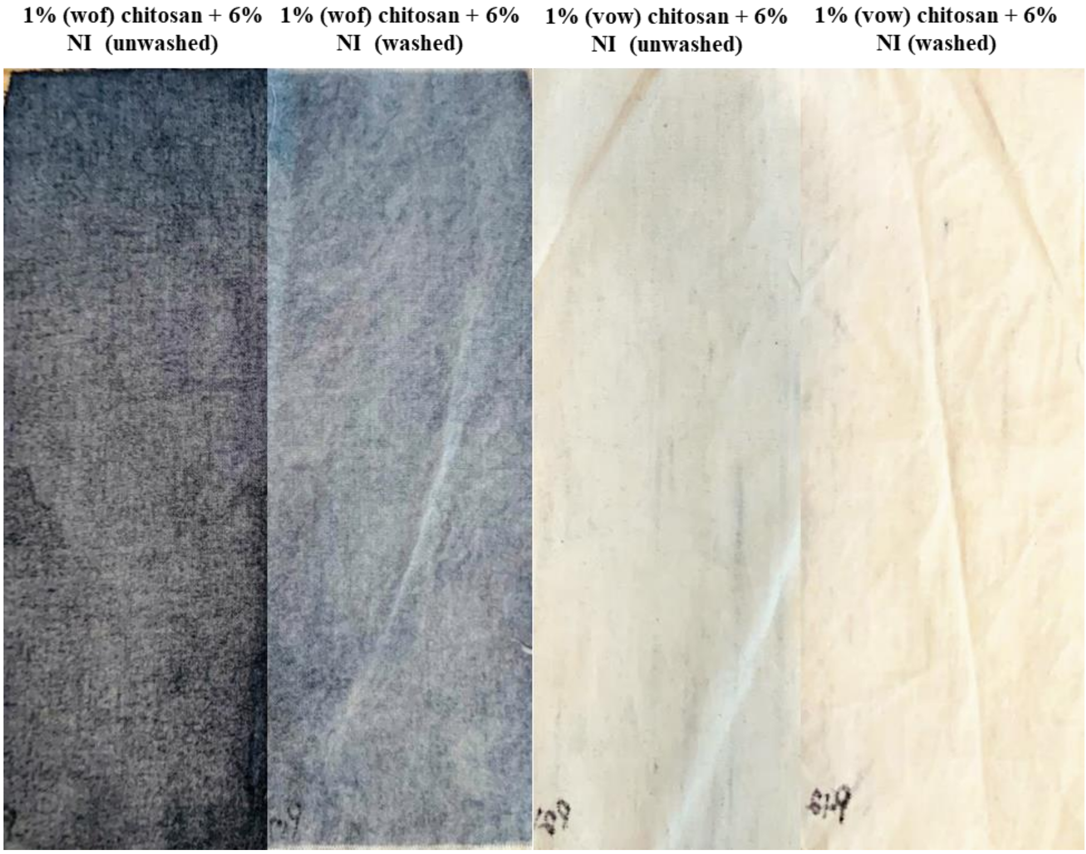
Figure 3.7: Optical images showing difference in dispersion of NI particles in 1% chitosan solution (wof), 1% (vow) chitosan solution and 1% NFC gel.(wof= as per the weight of fabric, vow = as per volume of water.)

Table 3.5: Color strength (K/S), Fixation (%) and Colorfastness ratings of coated samples 1% chitosan (wof)+6% NI dispersion and 1% (vow) chitosan+ 6% NI dispersion. (Samples size of 2" x 6"). (Grading is according to AATCC grey/stain scale of 1–5, where 1 is very poor, and 5 is excellent.) [25]

Samples	**K/S**	**Fixation (%)**	**Washfastness**	**Dry Crockfastness**	**Wet Crockfastness**
1% (wof) Chitosan + 6%NI	1.84±0.26	56.46±4.05	2.08±0.11	2.75±0.35	2.00±0.00
1% (vow) Chitosan + 6%NI	0.12±0.02	n/a	n/a	n/a	n/a

Table 3.6: Test of difference in K/S value of natural and synthetic dyes.

	Natural Indigo	Synthetic Indigo
Mean (K/S)	5.77	7.92
Variance	0.11	0.63
t Stat	-4.47	
P(T<=t) one-tail	0.02	



1% (wof) chitosan + 6% NI (unwashed) | 1% (wof) chitosan + 6% NI (washed) | 1% (vow) chitosan + 6% NI (unwashed) | 1% (vow) chitosan + 6% NI (washed)

Figure 3.8: Optical images of coated samples 1% chitosan (wof)+6% NI dispersion (washed and unwashed), 1% (vow) chitosan+ 6% NI dispersion (washed and unwashed)

Table 3.7: Regression analysis to test the impact of particle size on fixation. *

R Square = 0.99 Observation = 25			
Independent variables	Co-efficient	Standard error	t-statistic
X_1	0.18	0.004	45.21
X_3	0.24	0.005	45.48
X_5	0.33	0.006	50.11
X_7	0.39	0.008	50.87
X_{10}	0.39	0.009	46.96

*The dependent variable is fixation of NFC-NI dyeing. X_i is the particle size when indigo particles are milled for i minutes. See Table 3.4 for corresponding numbers.

CHAPTER 4

ANTIBACTERIAL ACTIVITY OF SUSTAINABLE NATURAL INDIGO DYED COTTON TEXTILE[3]

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[3] [3] Rai, S., V. Mohakar, V. Reukov, S. Sharma, and S. Minko. To be submitted to ACS Applied Polymer Materials.

ABSTRACT

This paper examines the antibacterial property of NFC-NI dyed cotton fabric using qualitative (AATCC TM 147) and quantitative (AATCC TM1 100) methods against gram-positive (*S. aureus*) and gram-negative (*E. coli*) bacteria. The NFC-NI dyed cotton fabric post-treated with chitosan showed a 99% reduction in bactericidal activity. This efficacy remained after 30 laundry washes. The antibacterial activity results were supported by FTIR analysis of dyed samples. The results were compared with conventionally dyed cotton fabric.

4.1 Introduction

The demand for antimicrobial textiles has increased, especially in the post-COVID era.[1] The market for antimicrobial textiles was valued at \$11.79 billion in 2023 and is estimated to grow to \$16.33 billion by 2027.[1] Antimicrobial textiles can inhibit or kill harmful microbes (bacteria, viruses, and fungi), preventing Healthcare-Acquired Infections (HAI) and odor.[2] They are used in medical apparel, footwear, sportswear, furnishings, and industrial textiles.[2] These textiles (natural or synthetic) are treated with active antimicrobial agents such as synthetic organic compounds such as triclosan, metals and metallic salts (ex. Ag+ Cu+), quaternary ammonium compounds, and biobased agents.[2-4] Although synthetic and metal ions are well known for their antimicrobial activity and durability, they are hazardous to health and the environment.[3, 4] Alternative biobased antimicrobial agents are gaining popularity due to their eco-friendliness and biodegradability while providing equally durable antimicrobial activity.[3-5]

Chitosan is a well-studied and documented biobased antimicrobial agent with antibacterial, anti-fungal, anti-viral, antitumor, anti-odor, and low immunogenicity properties.[6-8] It is widely used in many applications such as pharmacology, wastewater treatment, pesticide formulation, biomedical accessories, textile auxiliary, and finishing agents.[6-11] Chitosan is a polysaccharide having more than 5000 glucosamine units obtained from deacetylation of chitin, poly-(1,4)-2-acetamido-2-deoxy-β-D-glucose.[12, 13] Chitin is the second most abundant natural polymer found in the shells of a crustacean, such as a crab, shrimp, crayfish, and cell wall of some fungi (Basidiomycetes, Ascomycetes, Zygomycetes, and Deuteromycetes).[6, 13, 14] Although the exact mechanism of the antimicrobial activity of chitosan is unknown, researchers have proposed that there is an interaction between positively charged chitosan molecules and negatively charged microbial cell membranes that leads to the leakage of proteinaceous and other intracellular constituents.[12] Chitosan acts as a chelating agent and binds with metal traces, inhibiting the production of toxins and microbial growth.[12] Chitosan also forms Schiff base (C=N double bond) between the aldehydic carbonyl group of cotton and the amino group of chitosan, contributing to antimicrobial activity and introducing the cationic site in cotton polymer by free $–NH_2$ group.[13, 15] The $-NH_2$ group in an acidic solution gets protonated cationic form ($–NH_3+$) and crosslinks with the -OH group of cotton by forming hydrogen bonds and ion-dipole interactions.[15, 16] The formation of hydrogen bonds makes chitosan a non-leaching antibacterial agent with no adverse impact on human skin.[3]

In our previous study, we introduced a sustainable nanocellulose-based indigo dyeing (NFC- NI) technology[17], saving water up to a factor of 25 and eliminating toxic chemicals (salt and alkali) compared to conventional dyeing. The dyeing process involves coating with nanocellulose loaded with the required amount of natural indigo particles over the cotton fabric and then post-treatment with 1% chitosan (as per the weight of the fabric). The nanocellulose mesh-like coating entraps the indigo particles, and chitosan improves the fixation and adhesion of the drying. This technology offers over 90% fixation and comparable color fastness properties without compromising the comfort properties such as hand (bending length), air permeability, and weight gain. This paper examines the antimicrobial activity of chitosan in nanocellulose-based indigo dyed samples.

4.2 Materials and Methods

4.2.1 Materials

Bleached, mercerized 100% cotton twill fabric (186 g/m^2) was purchased from Testfabrics, Inc, PA, USA. Natural indigo (Indigofera tinctoria) was purchased from Dharma Trading Company, CA, USA. Carboxymethylcellulose sodium salt with a molecular mass of 90 kg/mol, chitosan with a molecular mass of 190000-375000 Da, and acetic acid were purchased from Sigma-Aldrich and used as received. Anhydrous sodium carbonate and triton X-100 (nonionic dispersing agent) were purchased from J. T. Baker and used as received. AATCC 1993 standard detergent WOB was received from AATCC. Formamidinesulfinic acid (thiourea dioxide) was purchased from Acros.

4.2.2 Methods

Samples produced to study and compare the antimicrobial activities are mentioned in Table 4.1.

Table 4.1: Fabric samples to compare antimicrobial activities.

Samples	AATCC 147	AATCC 100
Cotton fabric (untreated)	x	
Chitosan treated cotton fabric	x	
Conventionally dyed (6% shade) cotton fabric with indigo	x	
Conventionally dyed (6% shade) cotton fabric with Indigo and post-treated with chitosan	x	x
Conventionally dyed (6% shade) cotton fabric with Indigo and post-treated with chitosan after 30 laundry washes	x	x
NFC- NI coated (6% shade) cotton fabric post-treated with chitosan	x	x
NFC- NI coated (6% shade) cotton fabric post-treated with chitosan after 30 laundry washes	x	x

4.2.3 Conventional dyeing of cotton fabric with indigo

Samples were dyed with indigo (6% shade) in the presence of thiourea dioxide (twice the amount of indigo) and 4g/l of sodium hydroxide in a material liquor ratio of 1:50.[18] The powdered indigo and sodium hydroxide were mixed in water and heated to 50°C; thiourea dioxide was added and allowed to reduce the indigo. Then presoaked samples were dyed by dipping them for 1 minute, and excess liquor was squeezed out after taking it out. The fabric was then left to hang and undergo oxidation for 2 minutes. This process of dipping and oxidation is repeated two more times to acquire 6% shade.

4.2.4 NFC-NI based dyeing of cotton fabric

The production of nanocellulose protocol is described elsewhere.[17, 19] To describe it briefly, Kraft pulp sheets were knife-milled three times using a mesh sieve (pore size 500 µm). Cellulose powder was mixed with hot water and carboxymethylcellulose sodium salt (0.25% in water). The mixture was then delaminated into nanosized fibrils during 4-5 passes in a high-pressure homogenizer to produce 1% nanofibrillated cellulose (NFC) hydrogel.

The scouring of fabric was performed to remove any sizing and other impurities. The fabric was subjected to water at 60°C with AATCC standard reference detergent in a 1:20 material liquor ratio. After 10 min, the sodium carbonate was added, and then the temperature was elevated to 80°C and maintained for another 35 minutes. After that, the samples were thoroughly rinsed twice in a similar amount of water and dried at room temperature.[17]

The indigo was mixed with NFC gel, as explained in our previous study.[17] The NFC-indigo formula was prepared by mixing the natural indigo powder with NFC hydrogel in amounts calculated in units of shade (pigment weight in % of the weight of the fabric for coloration). In the experiments, 6% shade was mixed with 1% NFC gel and 0.01% nonionic dispersing agent (Triton X-100). The mixture was stirred using a magnetic stirrer and then coated over damp, pre-scoured cotton fabric samples using a screen printer for even and thin coating. Coated samples were dried in the oven at 120°C for 60 minutes.

4.2.5 Post-treatment of dyed and undyed cotton with chitosan

A chitosan solution was prepared by dissolving 1% chitosan (as per the weight of the fabric) in the water at a 1:10 material liquor ratio in the presence of 2% acetic acid (as per the volume of water) using a magnetic stirrer.[20] The fabric samples were dipped in chitosan solution for 15 minutes and nipped using a manual rubber roller. The post-treated samples were dried at 150°C for 15 min. After treatment, the samples were hand washed with cold water with some AATCC detergent and rinsed thoroughly. After washing, the samples were dried at room temperature.

4.2.6 Laundering procedure

To determine the antibacterial activity of the samples after 30 laundry washes, the samples were subjected to 6 cycles of colorfastness to laundering, home & commercial: accelerated, AATCC test method 61-2013-2A to perform the washing process (with 25 steel balls) with Atlas Launder-Ometer (AATCC standard instrument), which is equivalent to 5 laundry cycles.

4.2.7 Antibacterial activity analysis

The qualitative (AATCC Test Method 147-2016) and quantitative methods (AATCC Test Method 100-2012) are performed on each sample to determine the antimicrobial activity. AATCC-147 was performed to detect the bacteriostatic activity (interferes with the multiplication, growth, or activity of bacteria) of textile materials by assessing the diminishing amount of growth across a streak of *S. aureus* 6538 and *E. coli* 10536. Prior to initiating the test, 15 mL (± 2 mL) of sterilized molten agar (Tryptic Soy Agar) was poured into a standard (15 x 100 mm) flat-bottom Petri dish. The agar was then allowed to cool and form a firm gel before inoculation. *S. aureus* 6538 and *E. coli* 10536 were prepared separately in liquid culture mediums (Tryptic Soy broth - TSB) and standardized by dilution (Serial Dilution) in sterile distilled water. The bacterial inoculum was prepared from a 24h broth culture. Five streaks (approx. 60 mm long and 10 mm apart) were made with a sterile cotton swab without disrupting the surface of the agar plate. The sample fabrics were cut into rectangles measuring 2 x 5 cm, placed transversely across the inoculum streaks, and incubated for 24 hours at 37°C to ensure the bacteria's optimal growth. Finally, zones of inhibition and bacterial growth under the samples were observed.

AATCC-100 test was performed to detect the bactericidal activity against *S. aureus* (gram positive) and *E. coli* (gram negative). Each culture was suspended in a small amount of tryptic soy broth, spread on the tryptic soy agar plate, and incubated at 37°C for 24h. Two single colonies were picked up with an inoculating loop from the agar plate, suspended in a 10 mL nutrient broth, and incubated for 18h at 37°C. A final concentration of 10-50 x 10^6 colony-forming units per milliliter (CFU/mL) was prepared by diluting each culture with a sterile tryptic soy broth. These diluted culture solutions were used for the antimicrobial test. Fabric samples were cut into pieces of 4.8 cm diameter. A 100 mL flask was prepared to contain 1 mL of the bacterial dilution (10 – 50 x 10^6 CFU/mL), and samples were placed in them. All flasks were loosely capped and placed on an incubator at 37°C for 24 hrs. Then, the fabric was neutralized with 100ml of DI water. A series of dilutions were prepared using the buffer solution, and 0.1 mL of the dilution was placed in a tryptic soy agar plate. The inoculated plates were incubated at 37°C for 18–24 hrs. Cells were counted using the Viable plate count method. The percentage reduction (*R*) of bacteria was calculated by using:

$$R=\left(\frac{B-A}{B}\right)\times 100$$

where A and B are the surviving cells (CFU/mL) from the test samples in the flasks incubated over a 24 h contact period and the control (untreated cotton) after 0 h contact time, respectively.

4.2.8 Tensile Strength

The tensile strength of dyed fabrics was also analyzed to understand the effects of NFC and chitosan present in the NFC-NI dyeing. The tensile strength was performed according to the ASTM D5035-11(2019): Standard Test Method for Breaking Force and Elongation of Textile Fabrics (Strip Method).

4.2.9 FTIR Analysis

The Fourier transform infrared spectroscopy was performed using The PerkinElmer Spectrum™ 3 to identify chemical and functional groups in the wavenumber 4000-800 cm^{-1}. The analysis was done using Spectragryph.

4.3 Results and Discussion

The results of AATCC test method 147 to detect the bacteriostatic activity (interferes with the multiplication, growth, or activity of bacteria) of the samples against gram-positive (*S. aureus*) and gram-negative (*E. coli*) bacteria are shown in Figure 4.1-Figure 4.7. No growth of bacteria was observed on the samples (underneath the samples) treated with chitosan after 24 hours of incubation (Figure 4.2, Figure 4.4-Figure 4.7). In contrast, the samples without chitosan treatment showed bacterial growth (Figure 4.1, Figure 4.3). Notably, the samples after 30 washes also exhibit similar antimicrobial activity as samples with no laundry washes. The absence of an inhibition zone demonstrates that chitosan is a non-diffusible (non-leaching) antibacterial agent.

(a) ***S. aureus*** **(b)** ***E. Coli***

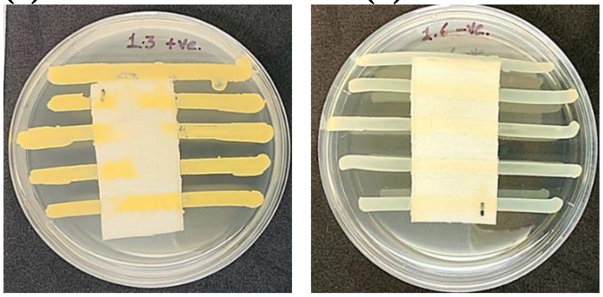

Figure 4.1: Cotton fabric (untreated).

(a) ***S. aureus*** **(b)** ***E. Coli***

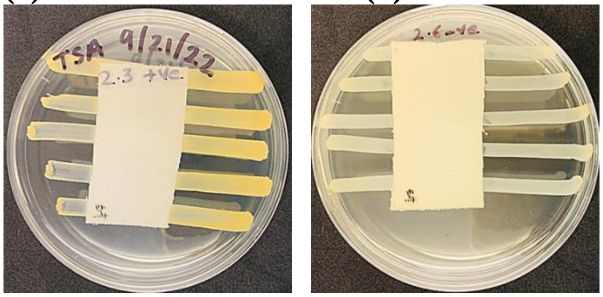

Figure 4.2: Chitosan treated cotton fabric.

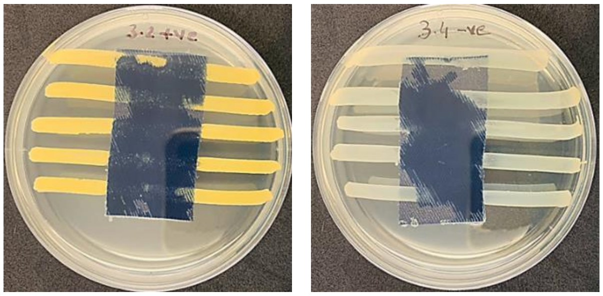

Figure 4.3: Conventionally dyed (6% shade) cotton fabric with indigo.

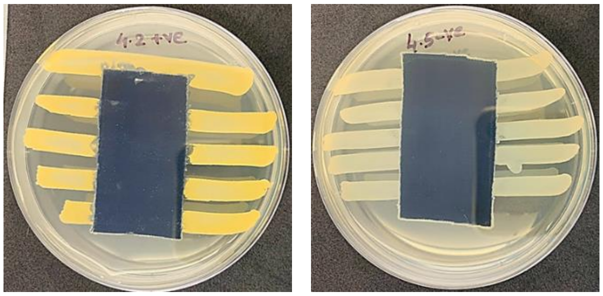

Figure 4.4: Conventionally dyed (6% shade) cotton fabric with indigo and post-treated with chitosan.

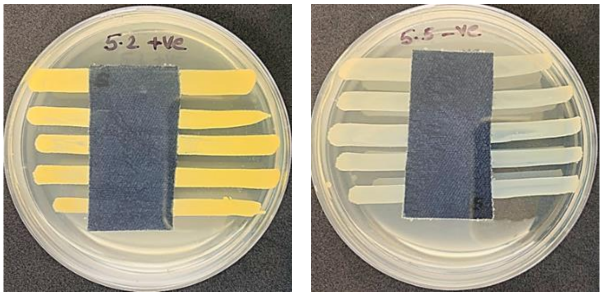

Figure 4.5: Conventionally dyed (6% shade) cotton fabric with indigo and post-treated with chitosan after 30 laundry washes.

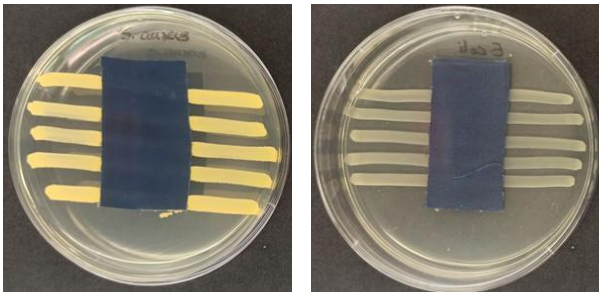

Figure 4.6: NFC- NI coated (6% shade) cotton fabric post-treated with chitosan.

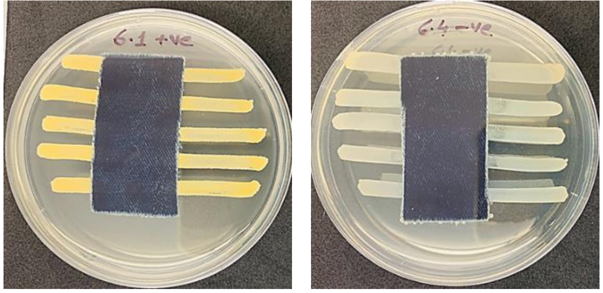

Figure 4.7: NFC- NI coated (6% shade) cotton fabric post-treated with chitosan after 30 laundry washes.

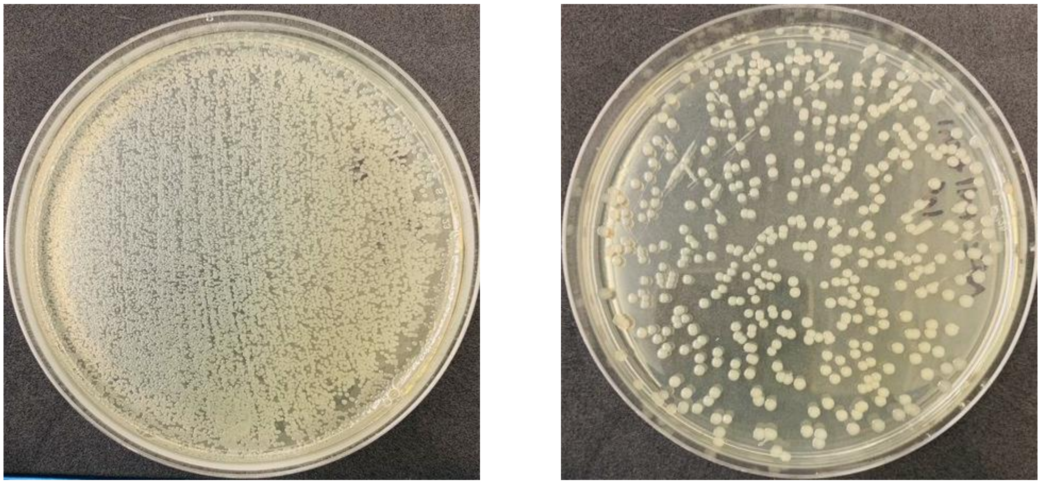

Figure 4.8: AATCC 100: Example of plates showing growth of gram-negative (E. coli) bacteria (a) untreated cotton and (b) NFC- Indigo Dyed cotton fabric after 24 hours.

Table 4.2: Percentage reduction in bacteria against *S. aureus* and *E.Coli* in conventionally and NFC-NI dyed cotton fabric.

Types of Bacteria	**Cotton + Indigo + Chitosan**	**Cotton + Indigo + Chitosan (30 washes)**	**Cotton + NFC+ Indigo + chitosan**	**Cotton + NFC+ Indigo + Chitosan (30 washes)**
S. aureus (Gram +ve)	99.30±0.71	95.96±0.42	99.20±0.00	98.75±0.07
E. coli (Gram -ve)	98.75±0.07	96.45±1.71	98.75±0.07	98.65±0.07

AATCC test method 100, quantitative method was performed to determine the bactericidal (kills bacteria) activity of the NFC indigo dyed samples compared to conventional dyed fabric with indigo and post-treated with chitosan after 24 hours of exposure to the gram-positive (*S. aureus*) and gram-negative (*E. coli*) bacteria. Table 4.2 reports the percentage reductions of bacteria against untreated cotton fabric at zero hours. Chitosan was extremely effective against both types of bacteria, with approximately 99% reduction for both conventionally dyed and NFC-

NI dyed fabric. The efficacy remained high after 30 laundry washes and decreased marginally to 98% and 96% for NFC-NI and conventional dyed fabrics, respectively. Chitosan is a durable, bactericidal antibacterial agent, and its antimicrobial activity was enhanced in the presence of NFC (Figure 4.8). NFC coating can increase the surface area of the coated cotton due to its high aspect ratio nanofibrils and thus increase the sites for hydrogen bonds for chitosan, ultimately increasing the durability of the chitosan as an antibacterial agent.[17, 21] The NFC-NI-dyed fabric has inherent antibacterial properties, which can be safely used for apparel and biomedical purposes. The SEM pictures of conventionally (a) and NFC-NI dyed (b) cotton fiber with indigo is shown in Figure 4.9 for reference.

Figure 4.10 shows the tensile strength of various samples. The tensile strength of cotton fiber decreased when the fabric was dyed with indigo using the conventional exhaust method. The loss in tensile strength could be due to the reduction and oxidation of indigo during the dyeing process.[22] The chitosan post-treatment does not appear to make any difference for neat cotton fiber or when it is dyed with the conventional method. However, when the fabric is dyed using the NFC-NI method and post-treated with chitosan, the tensile strength increases by approximately 16% compared to neat cotton fabric and by approximately 35% compared to the conventionally dyed fabric, which indicates that the combination of NFC and chitosan synergically increase the tensile strength.[21] The increase in tensile strength is contributed due to the increase in hydrogen bonds formed between the cotton fibers NFC and chitosan cross linking.[17, 21]

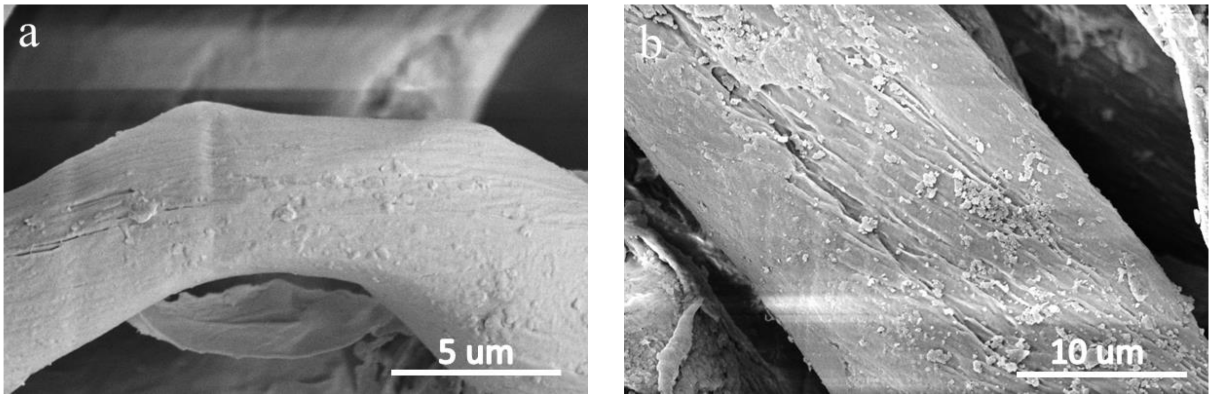

Figure 4.9: SEM pictures of (a) conventionally indigo-dyed cotton fiber and (b) NFC-NI dyed cotton fiber.

FTIR spectroscopy was performed to identify the organic materials, chemical bonds, and molecular structure present in the sample. A peak at a specific wavelength indicates an explicit chemical bond after scanning the sample in the infrared light source. The FTIR spectra of NFC-NI dyed samples compared with conventional dyed and post-treated with chitosan are presented in Figure 4.11. The chemical interaction of cotton dyed with indigo and post-treated with chitosan is determined by the change of the peak and intensity of the peak of the characteristic spectra. The characteristic absorption of cotton dyed with indigo appears at 1600-1650 cm^{-1} for C=C stretching and the peak at 1633 cm^{-1} for the ketone group (C=O) of indigo dye, respectively.[23] The characteristics spectra of cotton and cotton with chitosan are visible in the 3600 to 2800 cm-1 range, representing hydrogen bonds (-O-H and -N-H). Other peaks that characterize cotton or cellulose are around 2893, 1462, and 1023 cm^{-1}, attributed to C–H stretching, CH_2 asymmetric bending, and C–O stretching vibrations, respectively.[24] The characteristic absorption in 1600 to 1370 cm^{-1} corresponds to the free $–NH_2$ group, representing the introduction of the cationic site by chitosan in the cotton polymer.[15] Notably, all peaks intensified in the presence of NFC, which indicates that the bonds are either more in number or stronger, resulting in better antibacterial activity after 30 laundry washes.[25] The sharp peak at 1629 cm-1 and 1633 cm-1 (overlapped with C=O of indigo) exhibits the formation of C=N, Schiff base by the interaction of the aldehydic carbonyl group of cellulose and the amino group of chitosan, responsible for antibacterial activity, prominently visible at NFC-NI dyed cotton and conventionally indigo cotton and post-treated with chitosan, respectively[15, 24].

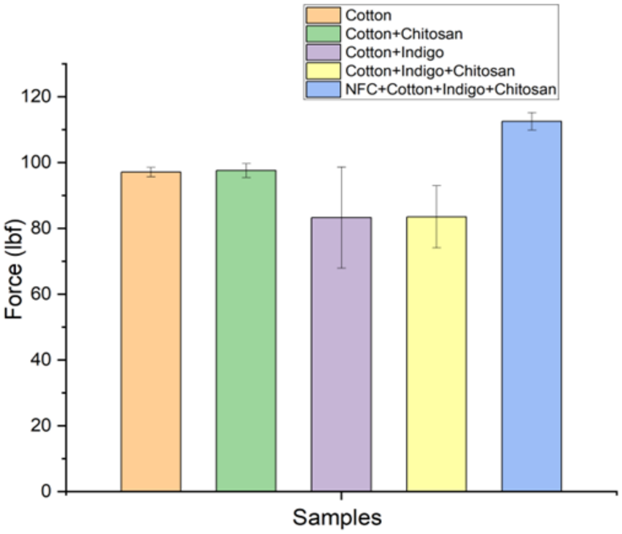

Figure 4.10: Tensile strength of samples

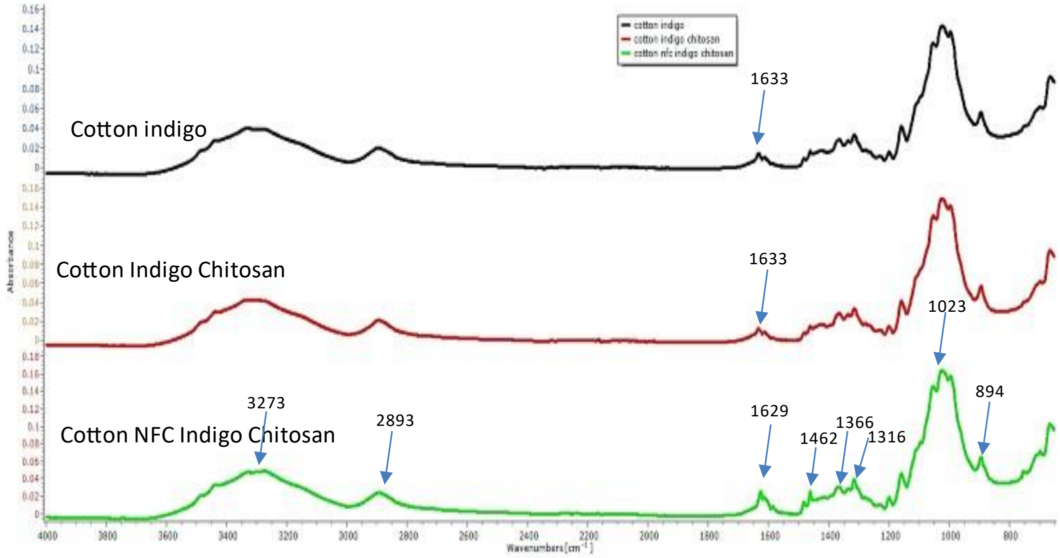

Figure 4.11: FTIR spectra of NFC-NI dyed samples, conventionally indigo dyed samples, and chitosan post-treated samples.

4.4 Conclusions

The novel NFC-indigo-dyed fabric is eco-friendly and sustainable and possesses antibacterial properties. The dyeing process involves coating fabric with indigo-loaded NFC and post-treatment with chitosan as a crosslinking agent. Chitosan also acted as an antibacterial agent, which performed with a reduction of 99% against gram-positive (*S. aureus*) and gram-negative (*E. coli*) bacteria. The dyed fabric is durable, exhibiting about 98% bacterial reduction after 30 laundry washes, and performed better than conventionally indigo dyed and post-treated with chitosan.

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CHAPTER 5

SUSTAINABLE, NANOFIBRILLATED CELLULOSE-BASED TEXTILE DYEING TECHNOLOGY FOR COTTON/POLYESTER BLENDS[4]

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[4] [4] [4] Rai, S., S. Sharma, and S. Minko. To be submitted to Green Chemistry.

ABSTRACT

Nanofibrillated cellulose (NFC) gel-based dyeing of cotton/polyester blend fabric provides one-step uniform coloration via the deposition of the colored (reactive dyes) nanocellulose fibrils on cotton fibers and sublimation of dispersed dye into polyester fibers, followed by post-treatment with chitosan. NFC gel acts as dispersing and anti-migrating agent to disperse dye during sublimation on polyester fibers. At the same time, the reactive dyed nanocellulose is physically linked with the cotton fibers, thereby coloring the whole fabric in one step process. Chitosan, a physical cross-linking agent for cotton/polyester fabric, improves the adhesion of dyed nanocellulose gel and, consequently, fixation (over 80%) and colorfastness properties. NFC-based dyeing reduces water and auxiliaries usage by a factor of 18 and 20, respectively.

5.1 Introduction

Cotton/polyester blended fabrics, one of the most widely used blended fabrics, hold over \$7 billion in market value (2016).[1] When cotton is blended with polyester, fabric exhibits better durability and dimensional stability, crease-resistance, and easy care due to polyester fiber, while moderate moisture absorption, antistatic, and less pilling due to cotton fiber.[2, 3] With the increasing demand for multifunctional and easy care textiles, the need for cotton/polyester blended textiles is also growing.[1] However, dyeing both fibers in a blend with good color performance brings challenges. Conventional cotton-polyester blend dyeing uses significant water and chemicals during preparation, dyeing, and finishing.[4] Over 50% of the chemicals are discharged as effluent into the wastewater, which contains high levels of pollutants, including COD (118-1387 mg/l), pH (8.2-8.9), and color (374-1496 Pt-Co).[4]

Conventionally, the cotton-polyester blended fabric is dyed using two types of dyes: anionic dyes (reactive, vat, direct, sulfur, or azoic) to dye cotton and nonionic or disperse dye for polyester fibers.[2, 3, 5-7] Reactive dyes are preferred for coloring cotton in cotton/polyester blended fabrics due to their ability to produce bright shades with excellent fastness properties.[6] The fabric can be dyed by using either reactive, disperse or both dyes to obtain different shades.[2, 5, 7] A reserve shade (Figure 5.15a-b) is attained when only one component of the blended fabric is dyed while the other remains undyed, showing white dots all over the fabric. When the blends are dyed with both classes of dyes, a union (solid), cross, or shadow shade is achieved. A union shade is achieved when both fibers in the blends are dyed with the same hue, depth, and tone to develop a solid shade. A cross shade (Figure 5.15c-d) is obtained when the two fibers are dyed with different hues, such as orange-black, with the same or different shades (percentage). A shadow shade is obtained when the blend is dyed at different percentage shades (for example, 1% reactive dye and 3% disperse dye).

The following four types of processes are used to dye cotton/polyester blended fabric using either batch-wise, continuous, or semi-continuous methods: a conservative two-bath, a less conservative reverse two-bath, a rapid one-bath, and a rapid reverse one-bath system.[2, 3, 5-9]

In a conservative two-bath system (batch method), where each fiber is dyed in two separate baths, the polyester fibers are dyed first, and then a reduction clearing is performed to remove the superficial color using reducing ($Na_2S_2O_4$ and NaOH) and dispersing agents. The cotton fiber is dyed in the second bath using a reactive dye. Finally, the fabric is rinsed and scoured to remove any hydrolyzed dye. This process requires nine cycles of washing and takes approx. 10-12 hours, but it provides excellent colorfastness properties due to the dye fixation and removal of unbound dyes in the intermediate washing process. In a less conservative, reverse two-bath method, cotton fibers are first dyed with reactive dye, then polyester fibers are dyed with disperse dyes, taking 7-8 hours. In rapid one-bath dyeing, the total time is reduced to 4-5 hours, but the colorfastness properties are compromised due to the absence of intermediate washing.

In a continuous range, the disperse dye is padded, thermofixed, and then reactive dye is padded, steamed, or vice versa. In one bath of continuous dyeing, both the dyes are padded together along with an enormous amount of alkali, salt, urea, anti-migration agent, and other auxillaries. In a semi-continuous method, the combination of pad and batch methods is used as per the shade, color performance, and overall cost.

Researchers have been developing efficient dyeing methods to reduce water and chemicals and conserve energy to dye cotton/polyester blended textiles, which includes combining treatment process[9], using alternative dyeing mediums, conditions, dyes,[10-14] and chemicals, and surface modifications (chemical or physical).[15-20] Despite technological advances, textile dyeing and finishing industries produce significant water and air pollutants - most of them are untreatable and pose health and environmental hazards.[21]

Here, we demonstrate sustainable one-step cotton/polyester blended fabric dyeing using biodegradable nanofibrilliated cellulose (NFC). NFC is an engineered hydrogel made of highly entangled cellulose nanofibers obtained by the defibrillation process of cellulosic biomass using a mechanical process. When deposited on the surface of fabrics, NFC fibers form a mesh-like film (Figure 5.2a) owing to the interfiber entanglements and interfiber interactions via hydrogen bonds, Van der Waals forces, electrostatic interactions, and mechanical interlocking.[22] NFC has a high surface area, resulting in a high load of dye molecules and pigments.[15, 23] It has a strong affinity toward cellulosic substrates like cotton due to hydrogen bonding from abundant surface hydroxyls after drying.[15] Utilizing these properties of NFC, we developed the one bath coloration method for cotton/polyester blended fabrics when the NFC mesh-like coating plays a double role; namely, it binds and holds the reactive dye (Reactive) on the surface of cotton fibers and facilitates the coloration of polyester fibers with the disperse dye (Disperse).

5.2 Results and Discussion

A series of dyeing formulations were prepared by blending the NFC hydrogel with reactive, disperse, and their combinations The NFC-Reactive formulation (Figure 5.1f) is used to produce reserve shade with reactive (Figure 5.1g), NFC-Disperse (Figure 5.1h) to produce reserve shade with disperse (Figure 5.1i), and NFC-Reactive+Disperse (Figure 5.1d) to produce cross shade with both reactive and disperse dyes (Figure 5.1e).

The formulations were deposited on the surface of the cotton/polyester blended fabrics using the screen printing technique for uniform and thin coating. The corresponding NFC coating on the bladed fabrics was examined using scanning electron microscopy (SEM) (Figure 5.2f-h and j-l). The neat cotton/polyester is shown for reference in (Figure 5.2e, i). The NFC with added reactive, disperse and their mixtures were coated on a glass substrate, dried, and imaged as well for reference (Figure 5.2b-d).

As was previously reported[23], the post-treatment of NFC textile coatings with a bio-based cross-linking agent, chitosan, can substantially improve the resistance of the coating to machine-washing. The effect of post-treatment with chitosan on the color performance of the blended fabric was studied at annealing temperatures (60°C, 130°C, 150°C, and 170°C). Various post-treatment techniques with chitosan were also studied at an annealing temperature of 170°C. The detailed procedure is described in the supplementary notes. We evaluated the color performance of the dyed sample with and without (reference) post-treatment and compared the results with the conventional exhaust dyeing methods (control) using the dye fixation (% F), color strength (*K/S*), and standard test methods of color fastness (wash and crocking). The conventional exhaust dyeing was performed with a 1:50 liquor ratio to achieve the color strength closer to the NFC-based dyed samples.

Table 5.1 summarizes the dyeing performance of the dyed fabrics. The reserve shade with reactive dye (Figure 5.1g, Figure 5.16b) was obtained by coating the fabric with NFC gel loaded with reactive dyes, which gets anchored over the cotton fibers leaving the polyester fibers uncoated and uncolored. The fixation of the reactive dyes on the coated fabrics depends on the adhesion of the dyed nanocellulose fibrils to the fabric. The alkalinity of the gels aids in the adhesion of fibrils to the cotton.[24] NFC-Reactive (reference) yields higher K/S and provides comparable fixation to the conventional method (control). The chitosan post-treatment improves fixation significantly but slightly lowers K/S due to dye bleeding in the chitosan post-treatment solution, which can be prevented using the spray post-treatment method (Table 5.3). The chitosan post-treatment also improves color fastness properties, and the results are similar to the conventionally dyed fabric. A slightly lower wet and dry crockfastness compared to the control samples can be attributed to material transfer due to the larger surface area of nanocellulose.

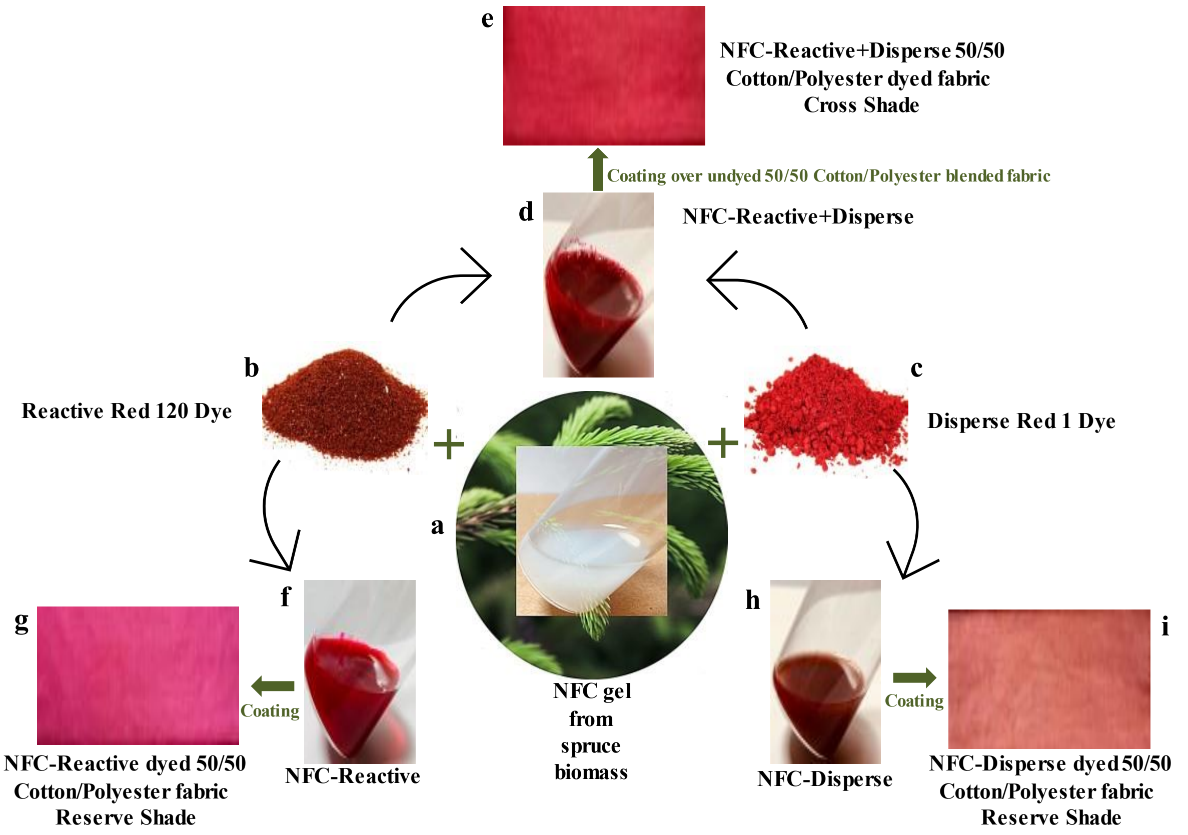

Figure 5.1: Schematic of NFC-based dyeing: (a) 0.5% NFC gel prepared from wood (Exilva F 01-V); (b) reactive red 120 dye c) disperse red 1 dye; (d) NFC-Reactive formulation (1 % shade); (e) NFC-Disperse formulation (1 % shade) (f) NFC-Reactive+Disperse formulation (1 % shade each); (g) 50/50 cotton/polyester blend fabric ; (h) screenprinting/coating on the fabric with NFC-Dye; (i) fabric dyed with NFC-Reactive (1 % shade) ; (j) fabric dyed with NFC-Disperse (1 % shade) ; (k) fabric dyed with NFC-Reactive+Disperse (1 % shade each) . The percentage shade (% shade) is the amount of dye powder expressed as a percentage of the weight of the undyed Cotton/ polyester blend fabric.

In the case of NFC-Reactive+Disperse based dyeing, the reactive dyes are absorbed by the nanofibrils, and the disperse dyes are entrapped in the NFC entanglement. After coating, the nanofibrils cover the surface of the cotton fibers, and upon drying, the nanofibrils get attached to the cotton fiber and entrapped disperse particles diffuse locally and uniformly into the polyester fibers and thus producing a cross shade (Figure 5.1e, Figure 5.16d). This process also reduces the chances of interaction between reactive and disperse dyes, limiting cross-staining episodes. Overall, both reference and post-treated show significant improvement in K/S and fixation with comparable colorfastness properties compared to the control sample.

Table 5.1: Dyeing Performance of NFC-Reactive (reserve shade), NFC-Reactive+Disperse (cross shade) and NFC-Disperse (reserve shade) dyed fabric. *Exhaust dye at 1:50 liquor ratio. [1]NFC-Reactive dyeing with no post-treatment. [2] NFC-Reactive+Disperse dyeing with no post-treatment. [31]NFC-Disperse dyeing with no post-treatment. †Post-treatment at 170°C with 15 min dipping time.

	Reactive Red 120 (Reserve Shade)			**Reactive Red 120+Disperse Red 1 (Cross Shade)**			**Disperse Red 1 (Reserve Shade)**	
	Control* (one-bath)	**Reference[1]**	**Post-treatment†**	**Control* (two-bath)**	**Reference[2]**	**Post-treatment†**	**Control* (one-bath)**	**Reference[3]**
K/S	2.22±0.04	3.12±0.13	3.06±0.13	3.84±0.06	6.91±0.29	6.73±0.63	2.58±0.09	2.18±0.15
Fixation (%F)	75.03±2.02	73.32±4.82	84.42±3.14	70.95±5.35	81.40±2.05	80.47±3.01	48.06±1.76	86.42±3.92
Washfastness	4.39±0.19	3.56±0.42	4.56±0.10	3.94±0.10	3.50±0.24	4.56±0.10	3.83±0.17	5.00±0.00
Dry Crockfastness	4.83±0.29	4.00±1.06	4.67±0.29	4.67±0.29	4.50±0.00	4.50±0.00	4.50±0.00	3.83±0.29
Wet Crockfastness	4.00±0.00	2.83±0.35	3.17±0.29	3.50±0.00	2.50±0.00	2.17±0.29	3.33±0.58	2.89±0.38

When the fabric is coated with NFC-Disperse, the disperse dye is diffused inside the polyester fiber, and the NFC coating (no color/white) covers the cotton fiber, producing a reserve shade (Figure 5.1i, Figure 5.16c). As the lingering nanocellulose is washed away during the washing process, leaving the polyester with a uniformly diffused color, the fixation is greatly improved to more than 85% compared to the control sample, which is less than 50%. Due to chitosan post-treatment (Table 5.5), NFC coating (no color/white) stays on the fabric resulting in a significantly lower fixation (less than 40%). Since NFC effectively disperses the dispersed dye particles and acts as an antimigration agent or migration inhibitor, a leveling agent lowers fixation as it acts as a retarder for dye diffusion (Table 5.5).[7]

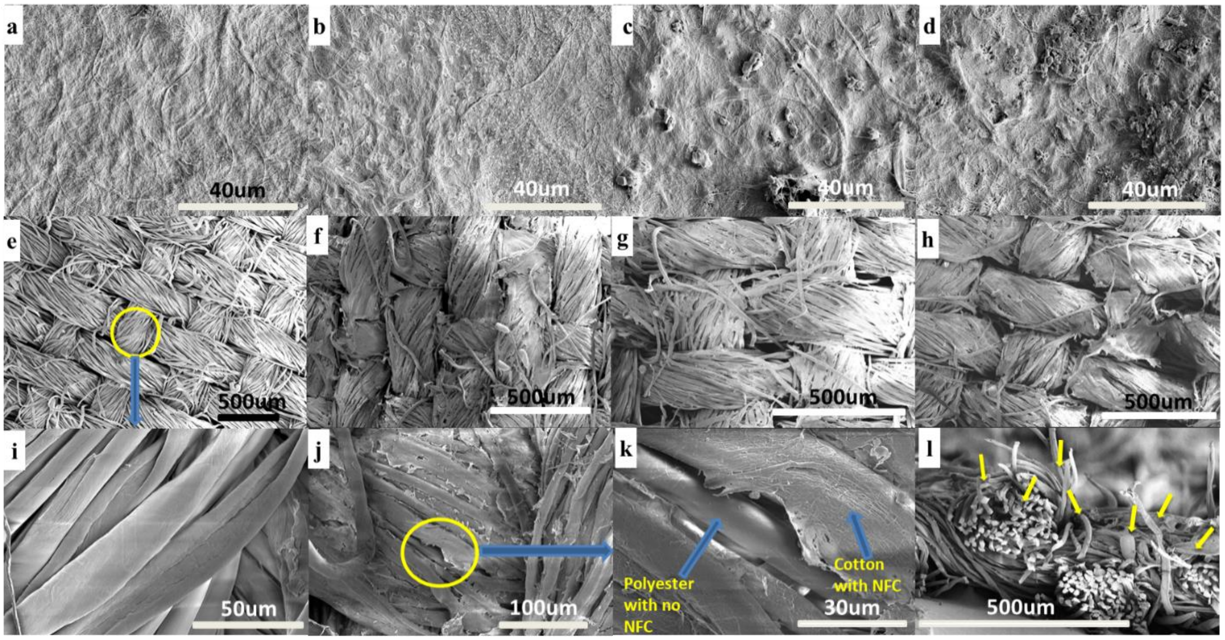

Figure 5.2: SEM Images: (a) Reference 0.5% NFC gel (dried film) ; (b) NFC-Reactive (dried film); (c) NFC-Disperse (dried film); (d) NFC-Ractive+Disperse (dried film); (e) neat 50/50 cotton /polyester blend fabric (f) NFC-Reactive dyed cotton/polyester blend fabric; (g) NFC-Disperse dyed cotton/polyester blend fabric; (h) NFC-Reactive+Disperse dyed cotton/polyester blend fabric; (i) larger magnification of cotton/polyester blend; (j and k) larger magnification of NFC- Reactive+Disperse dyed fabric with cotton fibers covered with reactive dyed NFC and polyester dyed with disperse dye; (l) cross section of NFC-Reactive+Disperse dyed fabric. The circles point out well-contrasted spots of interest for readers' convenience.

The NFC-Dye (reactive, disperse or both) dyed fabrics were also evaluated for comfort related properties and compared with undyed fabric in terms of weight gain, the thickness of the coating, bending length, air permeability, and wrinkle recovery (Table 5.3-Table 5.6). A detailed description of all characterization protocols is mentioned in the supplementary information. Overall, no substantial change was noticed in the comfort related properties due to coating. The weight gain and thickness of the coating of NFC-dyed fabrics were analyzed to estimate the amount of the deposited NFC. The weight gain and NFC coating thickness were observed to be less than 2% and 5µm, respectively, indicating that a coating method similar to screen printing is applicable for NFC-based dyeing. Bending stiffness measures fabric hand. The stiffness of the fabric increases with bending length, which is the standard length and width of the fabric that bends under its own weight to a specific angle.[25] The initial measurement of the bending length was 1.31±0.07, which increased from 1.60±0.03 to 1.85±0.09 for NFC-based dyed fabrics. The air permeability test provides the airflow rate passing through a unit area of fabric under a standard pressure drop. The coating is visible on the individual cotton fibers in the SEM image of the fabric cross-section (Figure 5.21), which does not bridge the interstices between the yarns and thus does not affect the air permeability. One of the characteristics of cotton/polyester blend fabric is superior anti-wrinkle properties to cotton fabrics due to the presence of resilient polyester fiber. Wrinkle recovery measures how fabrics recover from folding deformation in the dry state.[25] A higher recovery angle implies a better anti-wrinkle property. NFC-based dyeing increases the anti-wrinkle recovery angle for every shade. Tensile strength measures the force necessary to break a fiber given by maximum load.[26] The chitosan post-treatment generally improves the tensile strength of the fabric, and the results are comparable to the conventionally dyed control sample.

Table 5.2: Comparison of consumption of water and auxiliaries of NFC-based dyeing with exhaust dyeing. *M:L ratio is 1:30.

1% shade wof	**Exhaust Dyeing***		**NFC-based Dyeing**
Reactive Dyeing (Reserve Shade)			
Salt (gm/kg)	900		96
Alkali (gm/kg)	450		48
Other Auxiliaries (gm/kg)	NA		0
Water (l)	28.65		3.18
Disperse Dyeing (Reserve Shade)			
Auxiliaries (gm/kg)	120		0
Water (l)	29.88		3.18
Reactive + Disperse Dyeing (Union/Cross/Shadow Shade)			
	2-bath	**1-bath**	
Salt (gm/kg)	900	2100	96
Alkali (gm/kg)	450	600	48
Other Auxiliaries (gm/kg)	120	225	5
Water (l)	58.53	27.075	3.18
Washing (water (l))	48	40	20
Post-treatment			
chitosan (gm/kg)			1
acetic acid (ml)			20
Water (l)			1

The significant advantage of NFC-based dyeing is that the whole process is eco-friendly and sustainable. Moreover, the use of salt and alkali is reduced, and other auxiliaries like urea, acid, pH sliding agents, and other chemicals are also eliminated. Table 5.2 summarizes the materials used to dye 1 kg of fabric by NFC-based dyeing and the exhaust dyeing for a 30:1 liquor ratio. For exhaust dyeing, the liquor ratio ranges from 5:1 to 30:1 depending on the type of equipment used (for example, 5-10:1 for jet, 10-20:1 for jigger, and 20-30:1 for winch), and from 0.6:1 to 2:1 for continuous dyeing.[2, 7] A detailed comparison is provided in Table 5.7. For reserve shade with reactive dye, NFC-based dyeing uses approximately 1/10th of salt and alkali and does not use any other chemicals and auxiliaries, while for cross-shade, the NFC-based dying saves more than 1/20th and 1/10th of salt and alkali. A continuous process with a 2:1 liquor ratio uses 400 grams and 100 grams of urea for reserve shade with reactive dye and for cross shade, respectively, whereas none is used in NFC-based dyeing (Table 5.7). In the case of reserve shade with disperse dye, NFC-based dyeing does not use any chemicals and auxiliaries.

The exhaust dyeing process uses 29 to 59 liters of water per kg of fabric, and the resulting wastewater contains a high amount of effluents. The NFC-based dyeing reduces water usage up to a factor of 9 for reserve shade and 18 for cross shade, respectively. Water consumption during chitosan post-treatment is approximately 1 liter per kg of the fabric. It is worth mentioning that, intuitively, there will be minimal washing and rinsing in NFC-based dyeing as very little to no chemicals are used, reducing the water effluent and the water treatment cost.

The common issues of conventional dyeing, such as tailing, ending, listing, random staining, dark spots, and chemical pad bleeding, can be avoided with NFC-based dyeing. The NFC-Reactive+Disperse formulation can be applied using techniques similar to printing for thin, uniform coating in one step, followed by thermofixing, post-treatment using the spray, drying, and washing.

5.3 Conclusion

In conclusion, NFC-based dyeing proves to be a sustainable and efficient method for dyeing cotton/polyester blend fabric, allowing for the production of reserve, union/cross shades. This technology minimizes the usage of salt, alkali, and other auxiliaries, making it an environmentally friendly option. With over 80% fixation and comparable colorfastness properties, NFC-based dyeing ensures excellent results while maintaining the fabric's comfort properties such as weight gain, bending length, and air permeability. Moreover, it enhances anti-wrinkle properties, adding value to the fabric. Notably, NFC-based dyeing achieves significant water savings, up to 18 times less water consumption, and reduces auxiliary consumption by a factor of 20 compared to conventional exhaust dyeing methods. Overall, NFC-based dyeing offers a promising alternative that combines sustainability, efficiency, and improved performance in the textile dyeing process.

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5.5 Supplementary Information

5.5.1 Supporting Notes

Nanocellulose

Nanocellulose is engineered material from cellulose (Figure 5.3), which is an abundant biopolymer found in wood, plant fibers, marine animals, algae, fungi, and bacteria.[1, 2] Cellulose does not occur in nature as a single polymer chain; instead, it forms a bundle of approximately 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.[3, 4] Nanocellulose has a large surface area ($\sim 10^3$ m^2/g) and facile reactivity arising from abundant surface hydroxyls.[5, 6] There are three types of nanocellulose: nanocrystalline cellulose (NCC), nanofibrillated cellulose (NFC), and bacterial nanocellulose (BNC). BNC is secreted extracellularly by bacteria called *Gluconacetobacter*. Cellulose nanocrystals are single crystals formed under acid hydrolysis.[4] NFC is produced utilizing many different bio sources, including wood pulp, bleached kraft pulp, and bleached sulfite pulp, using a homogenizer or microfluidizer.[4] It has both amorphous and crystalline regions and tends to form a web-like network.[7, 8]

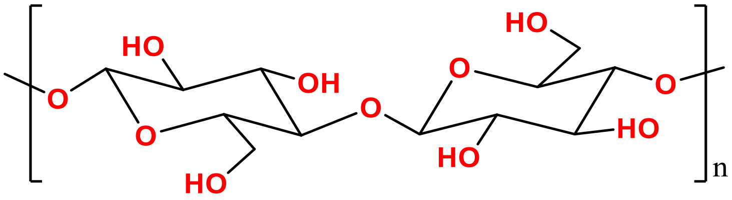

Figure 5.3: Chemical structure of cellulose with reactive OH groups.

The hydrogen bond between the abundant hydroxyl groups, facilitated by the high aspect ratio of the cellulose polymers in nanocellulose gel, leads to the formation of a highly ordered conformation in the nanocellulose fibril network. This network acts as a matrix capable of accommodating nanoparticles and serving as carriers during their application onto textiles.[9]

Chitosan

Chitosan is a polysaccharide (Figure 5.4) having more than 5000 glucosamine units, obtained from deacetylation of chitin, poly-(1,4)-2-acetamido-2-deoxy-β-D-glucose.[10, 11] Chitin is the second most abundant natural polymer found in the shells of a crustacean, such as a crab, shrimp, crayfish, and cell walls of some fungi (Basidiomycetes, Ascomycetes, Zygomycetes, and Deuteromycetes). [11-13] The antibacterial, antitumor, and low immunogenicity properties of chitosan have garnered significant attention from researchers in the textile, polymer, and biomedical fields.[12, 14]

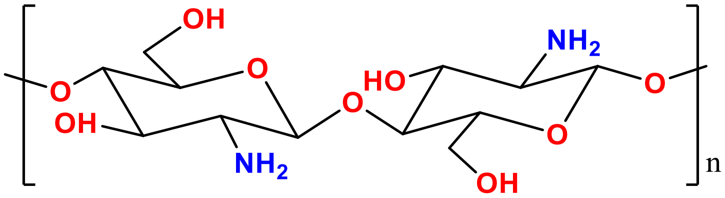

Figure 5.4: Chemical structure of chitosan.

FTIR spectroscopic analysis reveals that chitosan can act as a cross-linking agent, forming hydrogen bonds between the -NH2 group of chitosan and the -OH group of cellulose.[15, 16] In an acidic solution, the amine groups (-NH2) of chitosan become protonated, resulting in the formation of a cationic form (-NH3+). These protonated amine groups can form cross-links with cotton through hydrogen bonding and potentially through ion-dipole interactions.[15, 16] The research also showed that the treatment also contributed to an increase in abrasion resistance, stiffness, and crease recovery properties along with antimicrobial activity.[16]

Dyeing of Cotton/Polyester blends

Conventionally, the cotton-polyester blended fabric is dyed using two types of dyes: anionic dyes (reactive, vat, direct, sulfur, or azoic) to dye cotton and nonionic or disperse dye for polyester fibers.[17-21] Reactive dyes are preferred for coloring cotton in cotton/polyester blended fabrics due to their ability to produce bright shades with excellent fastness properties.[19] Traditionally, cotton/polyester are dyed in two-bath systems (batch methods), where each fiber is dyed in a separate bath. In the most conservative two-bath method, polyester fibers are dyed, first, using disperse dyes at 130°C (under mild acidic condition), then the reduction clearing is performed to remove the superficial color using strong reducing agents ($Na_2S_2O_4$ and NaOH at

70°C) and dispersing agents.[19-21] Then the cotton fiber is dyed using reactive dye, and finally, the fabric is rinsed and scoured to remove any hydrolyzed dye. A total of nine cycles of washing is required, which consumes approx. 64-100 liters of water and an enormous amount of chemicals.[22, 23] The conservative two-bath method takes approx. 10-12 hours, but provides excellent colorfastness properties due to the intermediate washing process.[18-20] In the less conservative, reverse two-bath method, the cotton fibers are first dyed with reactive dye, and then polyester fibers are dyed with disperse dyes.[19-21] After the reactive dyeing, the fabrics are rinsed a couple of times to remove salt, alkali, and hydrolyzed reactive dyes.[19-21] The reduction clearing is avoided after disperse dyeing to avoid damage of reactive dye; instead, alkaline scouring is performed, reducing the total time to approx. 7-8 hours.[19-21] Rapid one-bath dyeing can also be performed where reactive dyes are used in combination with disperse dye in one bath. There are many processes (cold bath to hot bath) used in the industry for one bath dyeing using a careful selection (to avoid interactions) of types of reactive dyes and disperse dyes and the sequence in which the salt, alkali and other auxiliaries are added for exhaustion and diffusion of dyes either at two stages or at one stage.[17, 19-21, 24] For example, the dye bath is prepared by adding reactive (highly exhaustive (HE-Brand)) and disperse dyes at the pH of 5-6 with a dispersing agent and an anti-reducing agent for reactive dyes. The temperature is raised rapidly to 95°C and then gradually to 130°C for 30-40 minutes for adsorption and diffusion of disperse dyes. The temperature is then reduced to 80°C, and salt is added. After 15-20 minutes, the alkali is added, and then dyeing is continued for 40-60 minutes to fix reactive dyes.[17] In one bath dyeing, the total time is reduced to 4-5 hours and water consumption to approx. 48 liters per kilogram of fabric, but the colorfastness properties are compromised due to the absence of intermediate washing.[17, 22] Continuous dyeing methods are used to dye longer continuous yards (approx. 11000 yards) of fabric.[17, 19] In the continuous range, the disperse dye is padded first, thermofixed and then reactive dye is padded, steamed, or vice versa, or both the dyes are padded together. For one bath dying, both dyes are padded in presence of alkali, salt, urea and an anti-migration agent (sodium alginate or CMC).[17] During thermofixing method, transfer of disperse dyes, from cellulose fiber deposited during padding, to polyester fiber occurs through vapor phase at 200-220°C.[17] In a semi-continuous method the combination of pad and batch methods are used as per the requirement of color, color performance and overall cost.[17]

Sometimes, as per the requirement, the blended fabrics are dyed with only one class of dyes to produce reserve shade.[17, 18] Reserve shade is attained when the blended fabric is dyed either with disperse dye or reactive to dye either polyester fabric or cotton fiber; for example, if the fabric is dyed with reactive dye, the cotton fibers are dyed, and the polyester fibers remain undyed showing white dots all over the fabric. However, when the blends are dyed with both classes of dyes, the union (solid), cross, or shadow shade is achieved.[17, 18, 20] A union shade is achieved when both fibers in the blends are dyed with the same hue, depth, and tone to develop a solid shade.[17, 18, 20] A cross shade is obtained when the two fibers are dyed with different hues such as orange-black with the same or different shades (percentage).[17, 18, 20] A shadow shade is obtained when the blend is dyed at different percentage shades (for example, 1% reactive dye and 3% disperse dye).[17, 18, 20]

Reactive Red 120

In this study, Reactive Red 120 (Figure 5.5) is used to dye the cotton fibers of 50-50 cotton/polyester blended fabric. Reactive dyes are anionic dyes that form a covalent bond with cellulosic fiber.[17, 18] In general, all reactive dyes have three parts (Figure 5.5), reactive site (A), chromogen with water solubilizing group (C), and bridge between reactive site and chromophore (B).[17, 18] Reactive red 120 is categorized as a highly exhaustive (H-E) dye suitable for exhaust dyeing of cellulosic fibers with higher fixation at 85°C with a lesser amount of salt and alkali.[17, 18] H-E dyes have two chromogens and two monochloro-s-triazine reactive groups, which provide more affinity towards the fiber, impair hydrolysis and impart stability towards higher temperature during dyeing.[17, 18, 25] For this reason, H-E dyes are also suitable to be used in one-bath dyeing of cellulosic/polyester blends due to their stability at high temperature (130°C) for high pressure (HTHP) dyeing or pad-dry-cure methods.[17, 18, 25] The suggested hydrolysis mechanism under alkaline conditions indicates that, within a given time frame, the bis(monochloro-s-triazine) reactive dye undergoes hydrolysis to form the monochloromonohydroxybis-s-triazine dye.[26] Eventually, monochloromonohydroxybis-s-triazine is hydrolyzed to bis(monohydroxy-s-triazine) dye. The same hydrolysis mechanism occurs in the presence of cellulose-OH of cotton fiber.[26]

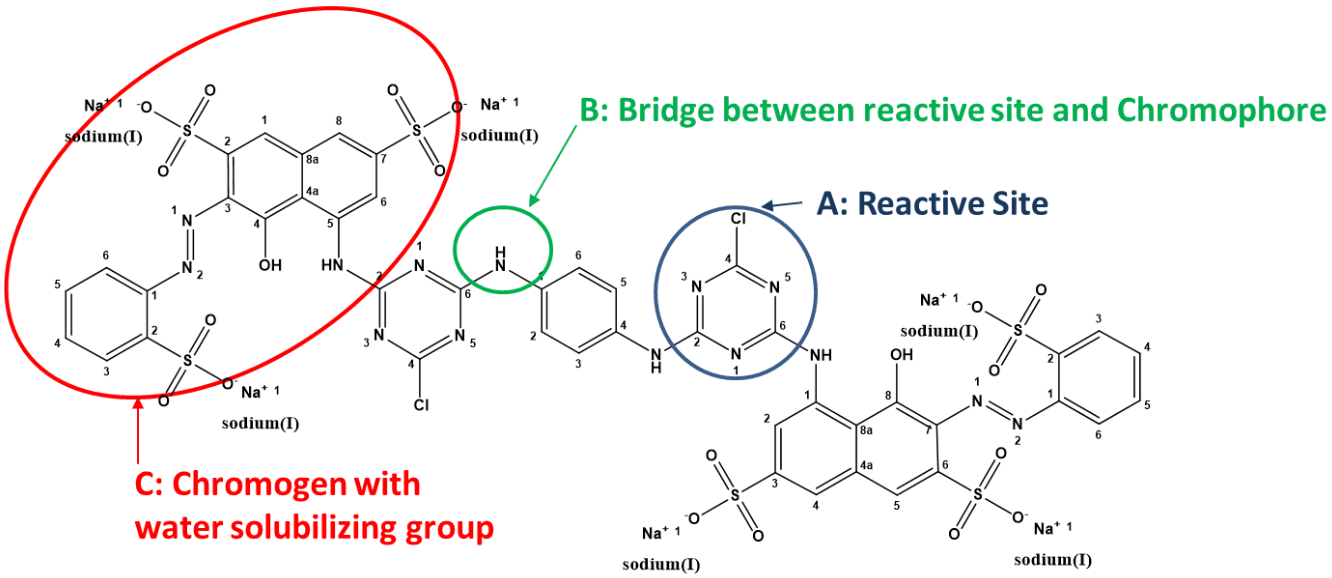

Figure 5.5: Structure of various parts of C.I. Reactive Red 120.

Disperse Red 1

The other dye used in this study is Disperse Red 1 (Figure 5.6). Disperse dyes are water-insoluble nonionic dyes and are used to dye hydrophobic fibers like polyester, nylon, and cellulose acetate.[17, 18] Disperse dyes are retained in the fibers by hydrogen bonds and van der Waals forces.[17, 18] Disperse Red 1 is an aminoazobenzene disperse dye used in polyester and cotton-polyester blended dyeing at high temperature (130°C) with moderate to excellent fastness properties.[17, 27, 28] Disperse dyes are milled with dispersing agent to have even dispersion in the bath.[17]

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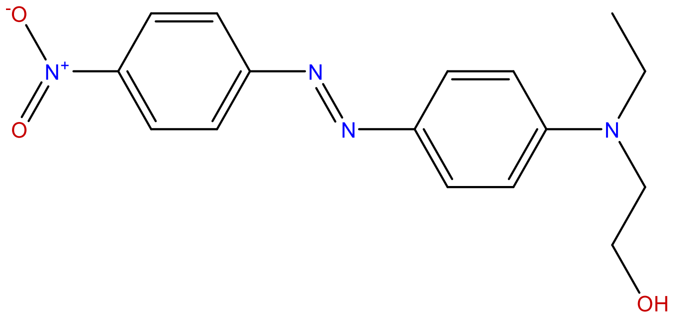

Figure 5.6: Structure of C.I. Disperse Red 1

5.5.2 Materials and Reagents

50/50 cotton/polyester fabric (104 g/m^2) was purchased from Testfabrics, Inc, PA USA. The 9% Nanocellulose gel (Exilva F 01-V) was generously donated by Borregaard AS. The Reactive Red 20, Disperse Red1, Chitosan with a molecular mass range of 19-375 kg/mol, acetic acid, were purchased from Sigma-Aldrich. Anhydrous sodium carbonate and triton X-100 (nonionic dispersing agent) were purchased from J.T. Baker. AATCC 1993 standard detergent WOB was received from AATCC. Formamidinesulfinic acid (thiourea dioxide) was purchased from Acros.

5.5.3 Scouring of Cotton/Polyester blend Fabric

The fabric was subjected to water at 60°C with AATCC standard reference detergent in a 1:20 material liquor ratio. After 10 min, the sodium carbonate was added, and then the temperature was elevated to 80°C and maintained for another 35 minutes. After that, the samples were thoroughly rinsed in a similar amount of water twice and dried at room temperature.

5.5.4 Coating of Cotton Textiles with NFC-Dye Formula

In this study, we used NFC provided by Borrregard AS, named **Exilva®**. Exilva® is sourced from Norway Spruce in Scandinavian forests with a typical diameter of 10-100 nm, length of 200-300um, and surface area of 200 m^2/gram.[29, 30] 0.5% of Exilva NFC's demonstrate sheer thinning properties as shown in Figure 5.7.[31, 32]

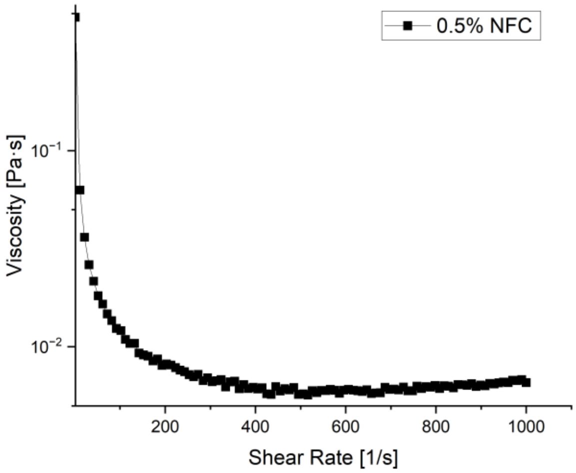

Figure 5.7: Viscosity of 0.5% NFC

The 9% NFC was diluted to 0.5% NFC by adding water with the help of a high-speed stirrer. To prepare NFC-Reactive formulation[6] (Figure 5.1f, Figure 5.8), 1% reactive dye on the weight of fabric (wof) was mixed with 0.5% NC gel and stirred using a magnetic stirrer for 15 minutes at 60°C. Then, Glauber's salt (30 g/L) was added, and the temperature was raised to 80-85°C. After 30 minutes, the temperature was reduced to 60°C, and alkali (sodium carbonate) (15 g/L) is added and stirred for 15 minutes. This formulation is only used for reserve shade with reactive dye. The reference SEM (Figure 5.2b) reveals the NFC-Reactive formulation dry film where the salt crystal can be seen in the mesh. The formulation was then coated over the fabrics at room temperature (Figure 5.1g). The fabrics were then dried at 130°C for 1 hour. Upon drying, the colored nanocellulose fibrils form a web-like coating mainly over the cotton fibers of the blend fabric, leaving polyester fibers uncolored (Figure 5.1g, Figure 5.2f, Figure 5.2j, Figure 5.16b). The alkali swells the cotton fibers, creating spaces for nanofibrils that get deposited in those spaces and trapped there upon drying. Swelling of cotton and nanocellulose also occurs during the washing process, which is minimized with post-treatment of the chitosan. The exact mechanism of swelling also takes place during dyeing with reactive dyes of cotton or cellulose in the presence of alkali (pH11).[18]

NFC-Reactive+Disperse formulation is prepared, first, by dyeing the NFC nanofibrils with reactive dye using the same procedure as earlier. Then 1% disperse dye and 0.48% (wof) dispersing agent are added at room temperature, and the mixture is stirred again for 15 minutes. This formulation is used for producing cross-shade only (Figure 5.1d, Figure 5.9). NFC-reactive+disperse dyeing takes advantage of aminoazobenzene disperse dye's sublimation property and increased affinity towards the polyester in the alkaline condition of the NFC-Reactive+Disperse formulation (pH11).[33] In the alkaline condition, the solubility of aminoazobenzene disperse particles is also minimal.[33] Disperse dye particles get suspended/trapped in the nanofibrils network, sublime during drying, and diffuse in the polyester fiber. The aminoazobenzene disperse dye take-up increases with the increase of pH due to the basicity of the amino groups.[33] However, the increased affinity created the problem of patchy or unlevelled dyeing. Adding some (0.15% as per the volume of water used in the nanocellulose gel or 0.48% wof) non-ionic dispersing agent as a leveling agent, however, improved the uniformity of the colored fabric. Non-ionic dispersing agents act as a retarder by forming surfactant micelles, which attract the dye particles, slow the diffusion rate, and produce level dyeing.[20]

The NFC-Disperse formulation (Figure 5.1h, Figure 5.10) was prepared by adding 1% disperse dye (wof) with or without 0.15% nonionic dispersing agent. This formulation is used for reserve shade with disperse dye. This formulation is used for reserve shade with disperse dye. The NFC gel acts as an anti-migrating and dispersing agent, ensuring uniform distribution of the disperse dye particles, which leads to their diffusion in the polyester fibers uniformly over the fiber surface. We found that the leveling agent significantly lowers the fixation of disperse dye because it also acts as a retarder for dye diffusion.[20] Thus, it indicates that NFC itself is enough to effectively disperse the disperse dye particles and act as an antimigration agent or migration inhibitor for uniform diffusion.

The prepared formulation is applied to the samples using the screen-printing technique at room temperature, followed by drying the fabric at 130℃ for 1 hour to promote adhesion of the dyed NFC gel and facilitate the sublimation process of the disperse dye (Figure 5.11).

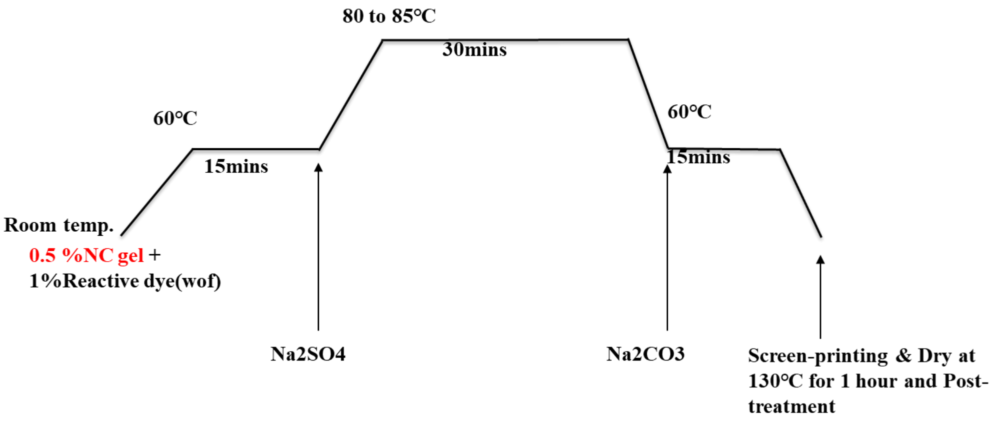

Figure 5.8: Preparation profile of NFC-Reactive for reserve shade

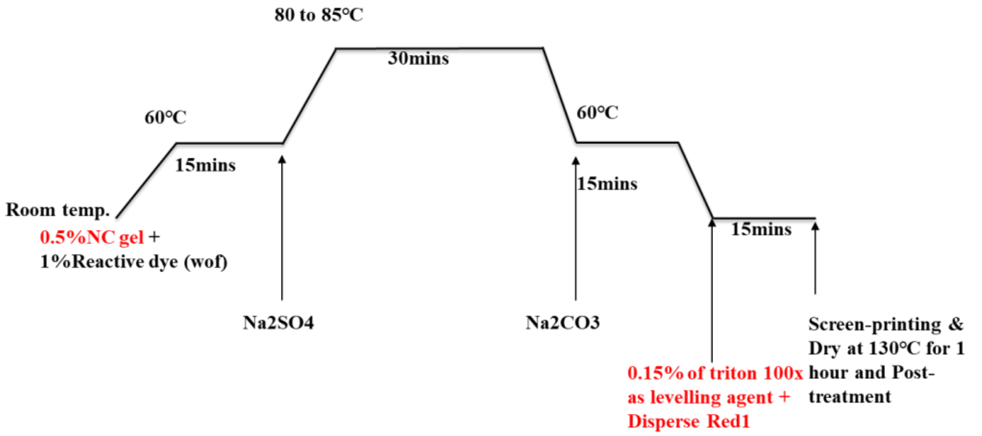

Figure 5.9: Preparation profile of NFC-Reactive+Disperse for cross shade

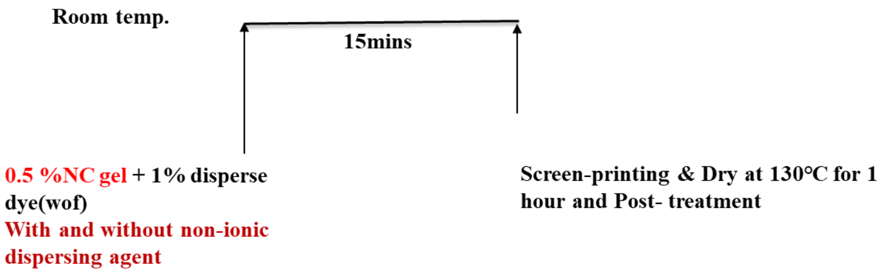

Figure 5.10: Preparation profile of NFC-Disperse for reserve shade.

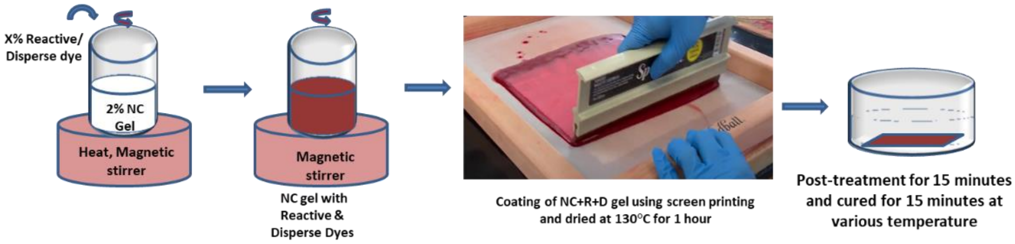

Figure 5.11: Schematics of NFC-Dye dyeing of cotton/polyester blend.

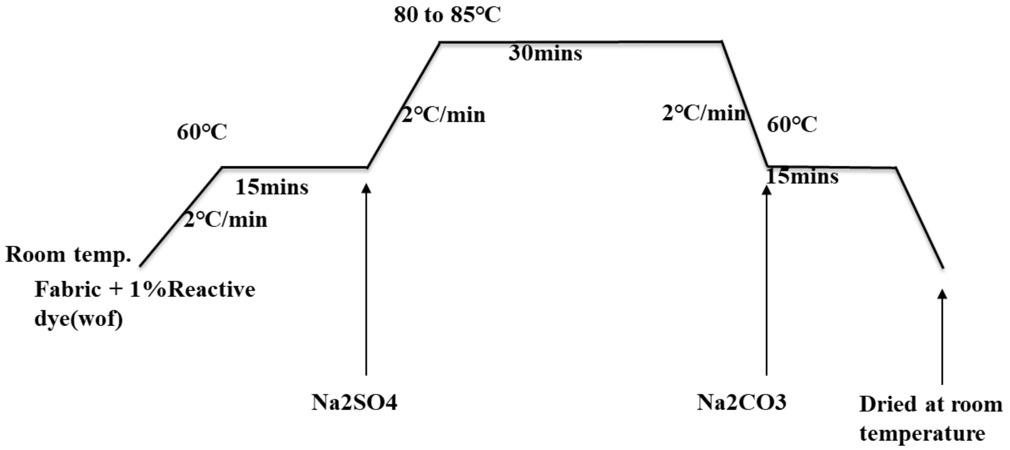

Figure 5.12: Dyeing profile of cotton/polyester blend with Reactive Red 120 (control- reserve shade).

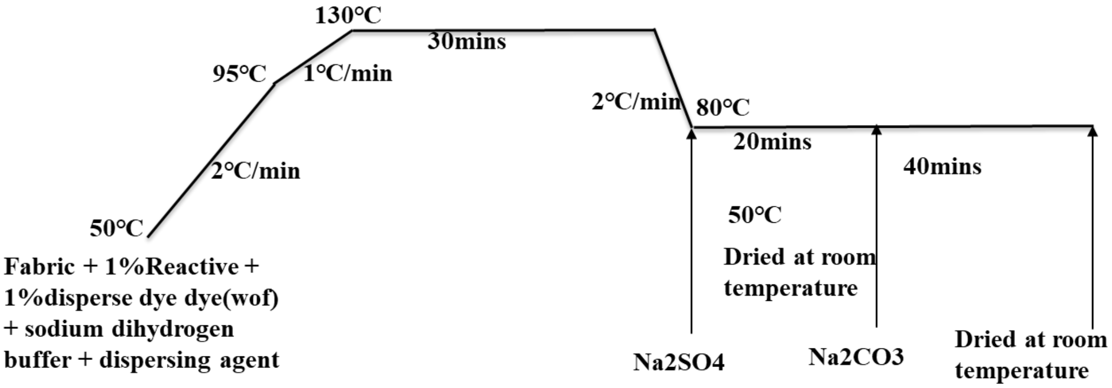

Figure 5.13: Dyeing profile of cotton/polyester blend with Reactive Red 120 + Disperse Red 1 (control- cross shade).

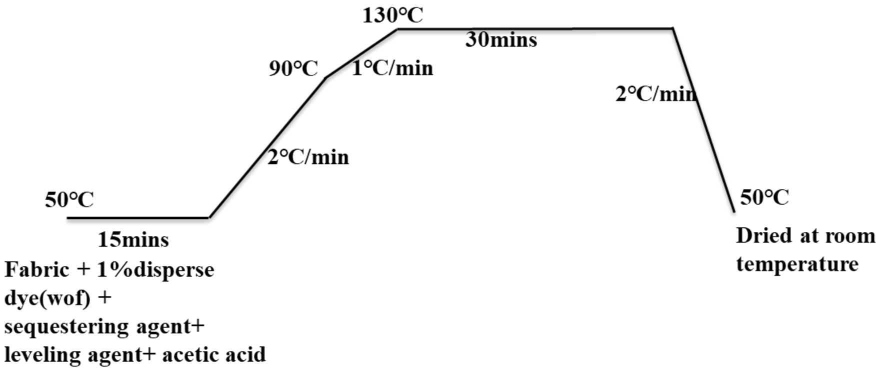

Figure 5.14: Dyeing profile of cotton/polyester blend with Disperse Red 1 (control- reserve shade)

5.5.5 Post-Treatment of Coated Textiles

A chitosan solution was prepared by dissolving 1% chitosan (wof) in the water of 1:10 material to liquor ratio in the presence of 2% acetic acid (as per the volume of water) using a magnetic stirrer[34]. The coated fabric was dipped in the solution for 15 minutes and cured at 60, 130,150, and 170°C temperatures. For comparison, the two other post-treatment methods were performed and cured at 170°C. In the first method, the dipping time was changed to enough time at which the sample soaks the solution, which was 10 seconds, and then cured at 170°C. In the second method, the chitosan solution was sprayed uniformly on the sample and allowed to stand for 15 minutes before curing. Chitosan post-treatment strengthens the entangled network of nanocellulose and cotton with additional hydrogen bonds and cross-linking through glucosamine units.[35]

5.5.6 Washing of samples

Each sample of size 5 cm x 15 cm was subjected to 'The Colorfastness to Laundering, Home & Commercial: accelerated, AATCC test method 61-2013-2A' to perform the washing process without steel balls) with Atlas Launder-Ometer (AATCC standard instrument). For bending length, air permeability, and anti-wrinkle, the washing procedure was performed with a similar material liquor ratio as per AATCC test method 61-2013-2A.

5.5.7 Control samples

The control samples were dyed using two baths and one bath method to produce cross shade. For the two-bath method, the samples are first dyed with reactive dye, washed, and then dyed with disperse dye. To produce reserve shade, the samples were dyed either with reactive dyes or disperse dyes for comparison. The dyeing of the control sample is done using the Ahiba IR pro dying machine with a 1:50 M:L ratio. The dyeing procedures are as follows.

Reactive dyeing: 1% reactive red 120 dye (wof) was dissolved in water (room temperature). The presoaked samples were fed into a dyeing machine with the solution. The temperature was raised to 60°C at 2°C /min. 30 gms/liter of Glauber's salt was added after 15 minutes, and the temperature was raised to 85°C and maintained for 30 mins. The temperature was then reduced to 60°C, and 15 gms/liter of sodium carbonate was added. The dyeing was continued for another 15 mins, and finally, the samples were dried at room temperature and subjected to testing (Figure 5.12).[17]

Disperse dyeing: 1% disperse red 1 dye (wof) was dispersed in water with 1.2 g/liter of non-ionic dispersing agent/leveling agent in the presence of 2% of acetic acid (of the total volume of water) and 1.2 grams /liter sequestering agent (EDTA) at 50°C. Presoaked samples were inserted into the dispersion and fed into the dyeing machine. Then the temperature was raised to 90°C and 130°C rapidly. After 30 mins, the temperature is lowered to 50°C. The samples were dried at room temperature and subjected to testing (Figure 5.13).[24]

Reactive + Disperse dyeing (1 bath): 1% reactive red 120 dye (wof) and disperse red 1 (wof) was dissolved in water at 60°C in the presence of 0.5 g/liter sodium dihydrogen phosphate and 1g/liter of a dispersing agent. Presoaked samples were fed into the dyeing machine. Then the temperature was raised initially to 90°C and then to 130°C rapidly. After 30 minutes of dyeing, the temperature was lowered to 80°C, and 70g/liter of Glabaur's salt was added. The dyeing continued for 15 mins, and then 20g/liter of sodium carbonate was added. After 40 minutes, the samples were dried at room temperature and subjected to testing (Figure 5.14).[17]

5.5.8 Characterization

The fabric samples were conditioned overnight at 65±2% relative humidity and 20±1°C temperature for testing and characterization of color performance and comfort properties.

Dyeing performance of colored fabrics:

Dye fixation (%F) is given by

$$\%F=\frac{K/S\ \text{after Wash}}{K/S\ \text{before Wash}}\times 100$$

The color strength (K/S) of the coated samples were measured at all wavelengths (400 to 700 nm at 10 nm interval) using a Macbeth Color Eye 7000A Spectrophotometer. It is calculated using the built-in software of color matching using the Kubelka–Munk equation given by:

$$K/S=\frac{(1\text{-}R)^2}{2R}$$

where K is the absorption, S is the scattering, and R is the reflectance. The K/S value of coated samples at the maximum wavelength of absorbency is reported.

The washfastness of the samples was evaluated using 'The Colorfastness to Laundering, Home & Commercial: accelerated, AATCC test method 61-2013-2A' (with 25 steel balls) with Atlas Launder-Ometer (AATCC standard instrument). Colorfastness to crocking (dry and wet) was evaluated using 'The Colorfastness to Crocking Crockmeter AATCC Test Method 8-2016' by using SDL atlas, M238BB Electronic Crockmeter. The color change for washfastness and color staining for crock fastness ratings were obtained using the Macbeth Color Eye 7000A spectrometer.

Comfort properties of colored fabrics

The original and coated samples were incubated in an oven at 100°C for 20 minutes and then in a desiccator for 20 minutes. The dry weight of coated and non-coated samples was measured to calculate the percentage weight gain:

$$\%\ \text{Weight Gain}=\frac{\text{Weight after wash-Weight before coating}}{\text{weight before coating}}\times 100$$

The thickness of the coating was calculated using.

Thickness of coating=initial thickness of cotton fabric×% Weight Gain

The stiffness test on the warp side of the samples (ASTM D1388—18 Standard Test Method for Stiffness of Fabrics) was carried out using the cantilever test with IDM Stiffness Cloth Tester S0013. Air permeability test was performed (ASTM D737—18 Standard Test Method for Air Permeability of Textile Fabrics) using Textester FX 3300 Air permeability tester.

SEM analysis

SEM analyses were performed for NFC dyed fabric, NFC films, NFC-Dye films

Tensile Strength

The tensile strength of dyed fabrics was also analyzed to understand the effects of alkali (pH11) present in the formulation in the polyester fiber during dyeing and the presence of acid during post-treatment on cotton. The tensile strength was performed according to the ASTM D5035-11(2019): Standard Test Method for Breaking Force and Elongation of Textile Fabrics (Strip Method).

Wrinkle recovery

The wrinkle recovery was performed using AATCC Test Method 66-(2017): Wrinkle Recovery of Woven Fabrics: Recovery Angle Method.

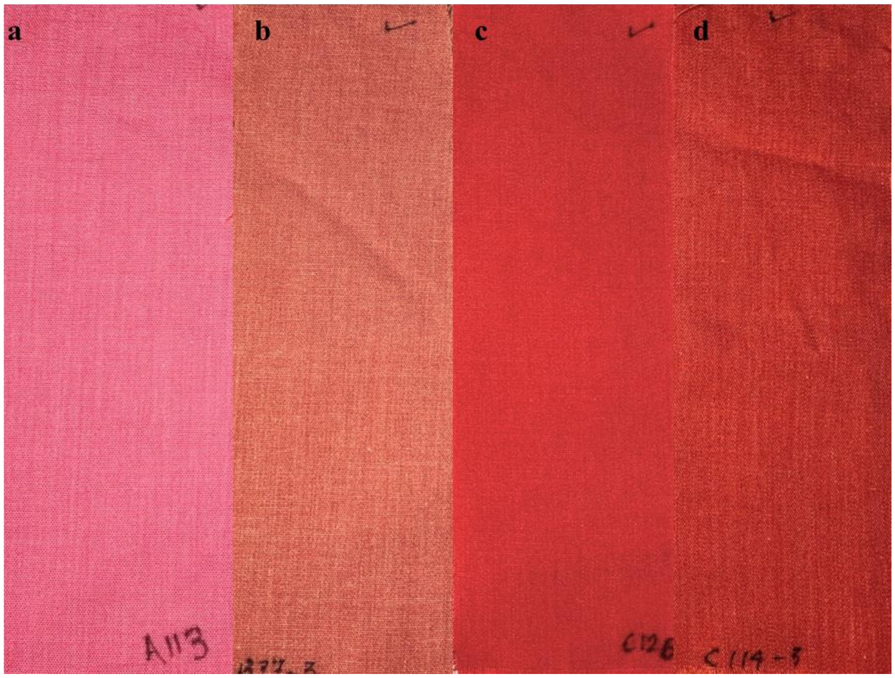

Figure 5.15: Exhaust Dyed Fabrics (controls): a: Reactive dyed fabric with undyed white polyester (reserve shade). b: Disperse dyed fabric with undyed white Cotton (reserve shade), c & d: Reactive+Disperse dyed fabric with both fibers dyed (cross shade) with 1 bath and 2 baths, respectively.

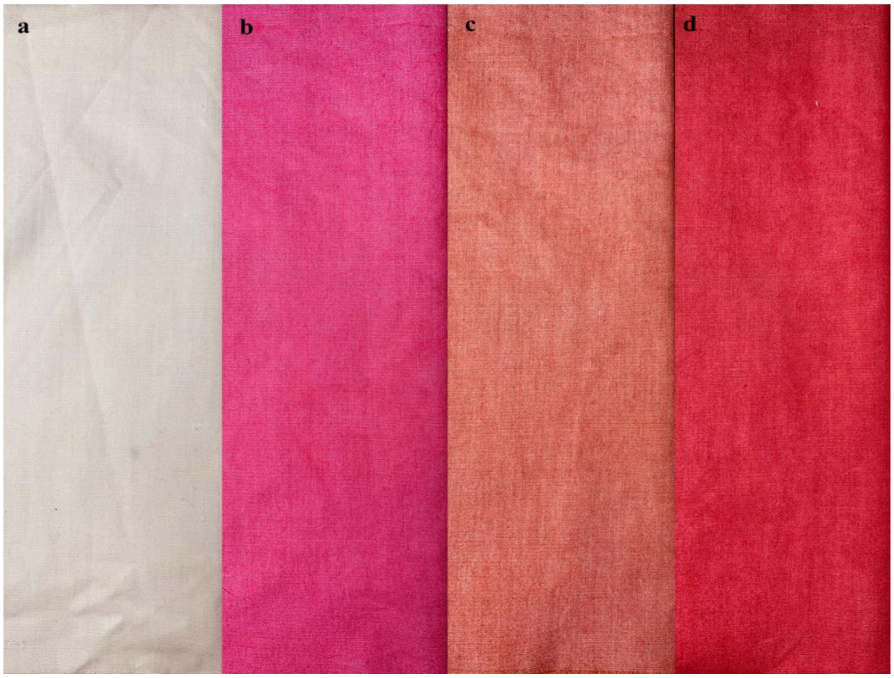

Figure 5.16 NFC-Dye Dyed Fabrics: a: undyed cotton/polyester fabric, b: NFC-Reactive dyed fabric with undyed white polyester (reserve shade). c: NFC-Disperse dyed fabric with undyed white Cotton (reserve shade), d: NFC-Reactive+Disperse dyed fabric with both fibers dyed (cross shade).

Table 5.3: Dyeing Performance of NFC+Reactive dyed fabric (reserve shade). * One bath exhaust dye at 1:50 liquor ratio. † NFC+Reactive dyeing with no leveling agent and no post-treatment.

1% shade of Dye (wof) **Reactive Red 120 (Reserve Shade)**	**Control***	**Reference†**	**Post-treatment with chitosan**					
			60°C	**130°C**	**150°C**	**170°C**		
			(Dipping time: 15 min)	(Dipping time: 15 min)	(Dipping time: 15 min)	(Dipping time: 15 min)	(Dipping time: 10 sec)	Sprayed. Standing time: 15 min
K/S	2.22±0.04	3.12±0.13	3.01±0.09	2.64±0.16	2.50±0.08	3.06±0.13	2.88±0.15	3.51±0.11
Fixation (%F)	75.03±2.02	73.32±4.82	82.67±2.12	75.27±2.94	77.78±2.68	84.42±3.14	78.50±1.45	81.50±1.03
Washfastness	4.39±0.19	3.56±0.42	4.50±0.00	4.39±0.19	4.22±0.25	4.56±0.10	4.44±0.10	4.56±0.10
Dry Crockfastness	4.83±0.29	4.00±1.06	5.00±0.00	5.00±0.00	5.00±0.00	4.67±0.29	5.00±0.00	4.33± 0.58
Wet Crockfastness	4.00±0.00	2.83±0.35	2.83±0.29	3.17±0.29	3.50±0.29	3.17±0.29	2.83±0.29	2.67±0.29
Weight gain %		0.50±0.43	0.45±0.41	1.43±0.42	1.11±0.47	0.66±0.91	0.78±0.54	1.02±1.81
Thickness of coating (μm) **Fabric: 245.45 ± 3.31**		1.24±1.05	1.10±1.01	3.52±1.03	2.73±1.16	1.62±2.23	1.91±1.33	2.15±2.91
Tensile Strength (lbf) **Fabric: 69.01±4.73**	62.71±1.85	56.39±1.11	70.34±1.00	64.82±2.42	68.99±3.05	65.11±0.43	63.59±6.41	62.86±0.17

Table 5.4: Dyeing Performance of NFC+Reactive+Disperse dyed fabric (reserve shade). * Exhaust dye at 1:50 liquor ratio. † NFC-Reactive+Disperse dyeing with no post-treatment

1% shade of Dye (wof) **Reactive Red 120 (Reserve Shade)**	**Control* (One-bath)**	**Control* (Two-bath)**	**Reference †**	**Post-treatment with chitosan**					
				60˚C	**130˚C**	**150˚C**	**170˚C**		
				(Dipping time: 15 min)	(Dipping time: 15 min)	(Dipping time: 15 min)	(Dipping time: 15 min)	(Dipping time: 10 sec)	Sprayed. Standing time: 15 min
K/S	9.43±0.15	3.84±0.06	6.91±0.29	6.53±0.45	4.87±0.60	5.93±0.69	6.73±0.63	7.10±0.37	7.71±0.06
Fixation (%F)	62.86±2.79	70.95±5.35	81.40±2.05	86.82±1.90	78.46±4.66	83.03±3.30	80.47±3.01	78.13±2.98	83.01±0.66
Washfastness	4.22±0.19	3.94±0.10	3.50±0.24	3.50±0.00	3.61±0.35	3.89±0.10	4.56±0.10	4.61±0.42	4.56±0.10
Dry Crockfastness	4.50±0.00	4.67±0.29	4.50±0.00	3.33±0.29	3.83±0.29	4.17±0.29	4.50±0.00	4.83±0.29	4.33±0.29
Wet Crockfastness	2.67±0.29	3.50±0.00	2.50±0.00	1.50±0.00	1.50±0.00	1.83±0.29	2.17±0.29	2.33±0.29	2.33±0.29
Weight gain %			0.70±0.30	0.53±0.35	1.13±0.73	1.01±0.49	0.52±0.83	0.61±0.77	1.99±1.28
Thickness of coating (µm) **Fabric: 245.45 ± 3.31**			1.72±0.74	1.30±0.86	2.77±1.08	2.47±1.20	1.28±0.27	1.50±1.89	4.88±3.14
Tensile Strength (lbf) **Fabric: 69.01±4.73**	65.62±0.26	58.82±7.02	54.15±6.11	65.03±0.62	66.66±0.86	62.31±2.62	65.88±2.32	65.73±0.29	61.21±3.89

Table 5.5: Dyeing Performance of NFC-Disperse dyed fabric (reserve shade). * One bath exhaust dye at 1:50 liquor ratio. † NFC-Disperse dyeing with no post-treatment. † NFC-Disperse dyeing with leveling agent and no post-treatment. ††Post-treatment at 170°C.

1% shade of Dye (wof) **Disperse Red 1 (Reserve Shade)**	**Control***	**Reference† (no leveling agent)**	**Reference† (with leveling agent)**	**Post-treatment††**
K/S	2.58±0.09	2.18±0.15	2.43±0.10	2.33±0.13
Fixation (%F)	48.06±1.76	86.42±3.92	53.34±1.69	38.97±1.81
Washfastness	3.83±0.17	5.00±0.00	3.39±0.35	4.50±0.29
Dry Crockfastness	4.50±0.00	3.83±0.29	4.50±0.00	5.00±0.00
Wet Crockfastness	3.33±0.58	2.89±0.38	3.33±0.29	4.00±0.50
Weight gain %		0.18±0.00	0.00±0.00	1.21±0.29
Thickness of coating (µm) **Fabric: 245.45 ± 3.31**		0.00±0.00	0.00±0.00	2.98±0.72
Tensile Strength (lbf) **Fabric: 69.01±4.73**	60.47±0.50	68.20±2.11	64.26±10.79	60.77±1.76

Table 5.6: Comfort properties. *Post-treatment at 150°C. †No Post-treatment.

Comfort Properties of post-treated samples*				
	Initial Measurements	**Reactive Red 120 (Reserve Shade)**	**Reactive Red 120+Disperse Red 1 (Cross Shade)**	**Disperse Red 1† (Reserve Shade)**
Bending length (cm)	1.31 ± 0.07	1.85±0.09	1.60±0.03	1.82±0.03
Air permeability (cfm)	105.67 ± 5.58	88.17±2.27	96.37±6.77	87.77±9.72
Wrinkle recovery (degrees)	262.60˚ ± 16.99	280.67±12.70	282.00±12.10	269.33±12.90

Table 5.7: Comparison of consumption of water and auxillaries of NFC-based dyeing with various M:L ratios of exhaust dyeing and continuous dyeing.M:L ratio: 5-10:1 for jet, 10-20:1 for jigger, and 20-30 for winch, and 0.6-2:1 for continuous dyeing.

1% shade wof	**Exhaust Dyeing**				**Continuous Dyeing**		**NFC-based Dyeing**
M:L	**1:5**	**1:10**	**1:20**	**1:30**	**1:0.6**	**1:2**	
Reactive dyeing (Reserve shade)							
Salt (gm/kg)	150	300	600	900			96
Alkali (gm/kg)	75	150	300	450	12	40	48
Urea (gm/kg)	na	na	na	na	120	400	none
Anionic surfactant (gm/kg)	na	na	na	na	na	na	none
Nonionic surfactant (gm/kg)	na	na	na	na	na	na	none
Swelling agent (gm/kg)	na	na	na	na	na	na	none
Migration inhibitor (gm/kg)					0.6	2	
Water (l)	4.775	9.55	19.1	28.65	0.4674	1.558	3.18
Disperse dyeing (Reserve shade)							
Urea (gm/kg)	0	0	0	0	na	na	none
Dispersing agent (gm/kg)	5	10	20	30	0.6	2	none
Sequestering Agent (gm/kg)	5	10	20	30	0.6	2	none
Acetic acid (ph-5)	5	10	20	30	3	10	none
Levelling agent (gm/kg)	5	10	20	30	7.2	24	none
Migration inhibitor (gm/kg)	na	na	na	na	12	40	none
Water (l)	4.98	9.96	19.92	29.88	0.5886	1.962	3.18
Reactive + Disperse Dyeing (Union/Cross/Shadow Shade): 1-bath							
Salt (gm/kg)	350	700	1400	2100	0	0	96
Alkali (gm/kg)	100	200	400	600	6	20	48
Urea (gm/kg)	0	0	0	0	30	100	none
Buffer ph5-6	2.5	5	10	15			none
Dispersing agent (gm/kg)	5	10	20	30	0.6	2	none
Levelling agent (gm/kg)	5	10	20	30	0.6	2	5
Anti-reducing agent (gm/kg)	25	50	100	150	na	na	none
Migration inhibitor (gm/kg)	na	na	na	na	12	40	
Reduction inhibitor (gm/kg)	na	na	na	na	3	10	
Water (l)	4.5125	9.025	18.05	27.075	0.5478	1.826	3.18
Washing (water (l))	48 (2-bath), 40 (1-bath)				na		20
Post-treatment							
chitosan (gm/kg)							1
acetic acid (ml)							20
Water (l)							1

5.5.9 Supporting References

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CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

This research presents the development of NFC-based dyeing technology for denim and cotton/polyester blended fabrics. The NFC–NI dyeing technology offers an eco-friendly and sustainable approach to dyeing denim fabric. Post-treatment of chitosan significantly improves the dyeing performance of NFC-indigo dyed samples, resulting in improved color strength and over 90% fixation across all percentage shades. The desired shade is achieved by adding the required amount of indigo relative to the weight of the material, allowing for a lighter or darker shade in a single coating. The method saves on chemical, energy, and water consumption by eliminating the use of any harmful chemicals such as reducing agents and alkalis, eliminating the need for extensive multiple dipping, and reducing water usage by a factor of up to 25.

Comparison with different cross-linking agents (chitosan, polycarboxylic acid (itaconic acid), and a combination of polycarboxylic acid and chitosan) demonstrated that chitosan-treated NFC-NI dyed samples exhibit superior dyeing performance with the highest color strength and fixation. Chitosan acts as a cross-linking agent through its intramolecular and intermolecular hydrogen bonding with nanocellulose and cotton fabric. Furthermore, no significant change was observed in the comfort properties, including weight gain, bending stiffness, and air permeability. Further studies showed no significant change in the rheological properties of nanofibrillated cellulose by adding indigo. The particle size in the range of 240-300 nm provided the best results in terms of fixation and color strength.

Moreover, NFC-NI-dyed fabric possesses inherent antibacterial properties appropriate for apparel and medical textiles. Chitosan acts as a non-leaching antibacterial agent, demonstrating a

99% reduction against gram-positive (*S. aureus*) and gram-negative (*E. coli*) bacteria. The dyed fabric exhibits durability with approx. 98% bacterial reduction even after 30 laundry washes outperforming conventionally indigo-dyed fabric post-treated with chitosan. The FTIR analysis confirms the presence of the characteristic and intense peak of Schiff base (known for antibacterial activity) in samples with NFC.

NFC-based dyeing for cotton/polyester blend fabric produced reserve, union/cross shades while using the bare minimum amount of salt and alkali and eliminating the need of other auxiliaries. This method achieves over 80% fixation with comparable colorfastness properties and no significant change in comfort properties while also enhancing antiwrinkle properties. Additionally, NFC-based dyeing saves water by a factor of up to 18 and reduces auxiliaries consumption by a factor of up to 20 compared to conventional exhaust dyeing methods.

6.2 Future Work

In this study, only 1% chitosan (wof) was used as a crosslinking agent to have better fixation and K/S values of the NFC based dyed cotton or cotton/polyester blended textile. Further studies with various concentrations of chitosan should be studied to achieve improvement in colorfastness properties.

Also, screen printing was used for uniform dispersion and thin coating. Other techniques, such as roller printing, knife coating, and padding, should be explored, which could be particularly useful for scaling up this technology for commercial production.

Although this study compared the water and chemical usage of NFC based dyeing with conventional dyeing methods, gate-to-gate life cycle impact assessment should also be performed for both indigo dyeing and cotton/polyester dyeing to understand the eutrophication potential, carbon footprint and sustainability of the NFC based dyeing.

In addition to indigo, reactive and disperse dyes to dye cotton and cotton/polyester blend fabric, other vat dyes, sulphur dyes, direct dyes and natural dyes of various hues should also be explored.

Finally, NFC based dyeing should be applied to other fiber contents textiles and their various blends (also yarns) such as polyamides (nylon, silk, wool), regenerated cellulose (rayon and acetates).