TECHNICAL UNIVERSITY OF LIBEREC
Faculty of Textile Engineering

MULTIFUNCTIONAL COTTON FABRIC WITH NANO TIO_2 LOADED CELLULOSE

Bandu Madhukar Kale

SUMMARY OF THE THESIS

Title of the thesis:	Multifunctional Cotton Fabric with Nano TiO_2 Loaded Cellulose
Author:	Bandu Madhukar Kale
Field of study:	Textile Technics and Materials Engineering
Mode of study:	Full-time
Department:	Department of Material Engineering
Supervisor:	prof. Ing. Jiří Militký, CSc.

Committee for defense of the dissertation:

Chairman: doc. Ing. Vladimír Bajzík, Ph.D.	FT TUL, Department of Textile Evaluation
Vice-chairman: prof. Ing. Jakub Wiener, Ph.D.	FT TUL, Department of Material Engineering
Members of the committee: prof. Dr. Ing. Mir. Černík, CSc. (opponent)	The Institute for Nanomaterials, Advanced Technology and Innovation TUL
prof. Ing. Jaroslav Šesták, DrSc., Dr.h.c.	The Czech Academy of Sciences, Institute of Physics
doc. Ing. Ladislav Burgert, CSc.	Univerzita Pardubice, Fakulta chemicko-technologická
doc. Mgr. B. Lapčíková, Ph.D. (opponent)	Tomas Bata University in Zlín, Faculty of Technology
doc. Mgr. I. Lovětinská Šlamborová, Ph.D.	FP TUL, Department of Chemistry
Ing. Jan Marek, CSc.	INOTEX spol. s r.o., Dvůr Králové n. L.
Ing. Jana Šašková, Ph.D.	FT TUL, Department of Material Engineering

The dissertation is available at the Dean's Office FT TUL.

Liberec 2017

ABSTRACT

Cotton is a leading textile fibre due to its unique properties such as hydrophilicity, biodegradability, durability, good dyeability, and relatively low cost. However, now a day's people want cotton fabric to be smart, which can give comfort according to weather conditions. Self-cleaning, antibacterial, antifungal and permanently stiff textiles are becoming important due to market demand, and broad research is being done in this areas. Nanoparticles such as Titanium dioxide (TiO_2), Zinc oxide (ZnO), Copper oxide (CuO), Silver (Ag), Carbon nanotubes (Singlewalled carbon nanotubes (SWCNTs), Multiwalled carbon nanotubes (MWCNTs) show excellent functional activity towards light. Nano TiO_2 is the most environment-friendly and relatively cheap among all other nano particles. TiO_2 can be applied on different substrates such as activated carbon, stainless steel and glass. Researchers have coated TiO_2 on cotton fabric by various methods such as in-situ suspension polymerization with nano TiO_2-acrylatecopolymer and functionalizing cotton fabric with nano sized TiO_2. However, they do not claim that fabric is stable against washing.

In this thesis, a new route to make cotton fabric self-cleaning and permanently stiff by coating cellulose-TiO_2 on its surface is demonstrated. Cellulose solution was prepared by dissolving 10% cellulose in aqueous sulphuric acid (60%) or Sodium hydroxide-Urea-Thiourea solvent system. TiO_2 with different concentrations (1, 3, 5 and 10 % TiO_2 on the weight of cellulose) was dispersed in cellulose solution and coated on the surface of cotton fabric by padding machine. The surface morphologies of pure cotton fabric, cellulose and cellulose-TiO_2 coated cotton fabric were observed on scanning electron microscope (SEM). Simulation method was developed to quantify amount of cellulose II by using X-ray diffraction patterns on Mercury software. Effect of cellulose coating on dyeing was investigated with Reactive dyes.

Self-cleaning ability of cellulose-TiO_2 coated cotton fabric was investigated with Orange II dye and wine stain under UV light. Antibacterial and antifungal activity was studied according to international standards. Results revealed that samples coated with more than 3% TiO_2 showed strongest inhibition efficiency against Staphylococcus aureus (SA), Methicillin resistant Staphylococcus aureus (MRSA) bacteria's. Antifungal testing results showed that the photo-catalytic activity of titanium dioxide nanoparticles allows a disinfection of cotton fabric from fungal colonization. The amount of cellulose II in cotton fabric increased slightly after solvent treatment. However, breaking strength also increased by cellulose coating. Air and water vapor permeability were hardly affected. The stiffness of cellulose coated cotton fabric increased substantially. Degradation of orange II dye was increased with increasing TiO_2 concentration and irradiation time. The samples coated with 1, 3 and 5% TiO_2 were stable against washing up to 20 washing cycles for both self-cleaning and stiffness properties. However, 10% TiO_2 coated sample does not show similar stability against washing due to poor dispersion of TiO_2 in cellulose solution.

Keywords: Cotton fabric, cellulose, self-cleaning, stiffness, antibacterial, antifungal, Titanium dioxide.

ABSTRAKT

Bavlna je díky svým jedinečným vlastnostem jako je hydrofilita, biodegradabilita, trvanlivost, dobrá barvitelnost a relativně nízká cena významným textilním materiálem. Dnes však lidé očekávají od bavlněné tkaniny i další vlastnosti, díky nimž poskytuje bavlna komfort podle počasí. Vzhledem k požadavkům trhu roste význam samočisticích, antibakteriálních, antimykotických a nemačkavých textilií, které jsou předmětem rozsáhlého výzkumu. Nanočástice jako TiO_2, ZnO, oxid měďnatý, Ag nebo uhlíkové nanotrubice (SWCNTs nebo MWCNTs) vykazují vynikající funkcionalizační aktivitu na světle. Nanočástice oxidu titaničitého jsou nejšetrnější k životnímu prostředí a ve srovnání s ostatními nanočásticemi i relativně levné. TiO_2 lze aplikovat na různé substráty jako je aktivní uhlí, nerezová ocel nebo sklo. Výzkumníci aplikují TiO_2 na bavlněné tkaniny různými způsoby, jako je in situ suspenzní polymerace s nano TiO_2-akrylátovým kopolymerem a funkcionalizace bavlněné tkaniny nanočásticemi TiO_2. Nicméně tyto tkaniny nejsou odolné v praní.

Tato práce se zabývá přípravou samočisticí ztužené bavlněné tkaniny potažené celulózou a TiO_2. Celulózový roztok se připraví rozpuštěním 10% celulózy ve vodném roztoku 60% kyseliny sírové a nebo v rozpouštěcí směsi z hydroxidu sodného, močoviny a thiomočoviny. TiO_2 o různých koncentracích (1, 3, 5 a 10% TiO_2 z hmotnosti celulózy) se disperguje v roztoku celulózy a nanese na povrch bavlněných tkanin klocováním. Povrchová morfologie čisté bavlněné tkaniny a bavlněné tkaniny povrstvené celulózou a celulózou s TiO_2 byla pozorována rastrovacím elektronovým mikroskopem (SEM). Pro kvantifikaci celulózy II byla vyvinuta simulační metoda s použitím rentgenové difrakce na softwaru Mercury. Vliv celulózového povrstvení na barvitelnost byl zkoumán pomocí reaktivních barviv.

Samočisticí schopnost bavlněné tkaniny potažené celulózou a TiO_2 byla zkoumána pomocí barviva Orange II a skvrn od vína pod UV světlem. Antibakteriální a protiplísňový účinek byl testován podle mezinárodních norem. Výsledky ukázaly, že vzorky potažené více než 3% TiO_2 vykazovaly nejsilnější inhibiční účinek na bakterie Staphylococcus aureus (SA) a methicillinu rezistentní Staphylococcus aureus (MRSA). Protiplísňové testy ukázaly, že fotokatalytická aktivita nanočástic oxidu titaničitého umožňuje dezinfikovat bavlněnou tkaninu od kolonií plísní. Množství celulózy II v bavlněné tkanině se po ošetření rozpouštědlem mírně zvýšilo. Celulózový povlak také zvýšil pevnost do přetrhu bavlněné tkaniny. Prodyšnost a paropropustnost prakticky nebyly ovlivněny. Tuhost bavlněné tkaniny potažené celulózou se podstatně zvýšila. Degradace barviva Orange II se zvyšuje s rostoucí koncentrací TiO_2 a dobou ozařování. Pokud jde o tuhost i samočisticí vlastnosti, vzorky potažené 1, 3 a 5% TiO_2 byly odolné v praní do 20 pracích cyklů. Nicméně vzorek potažený 10% TiO2 nevykazoval podobnou stabilitu v praní v důsledku špatné dispergovatelnosti TiO_2 v roztoku celulózy.

Klíčová slova: bavlněná tkanina, celulóza, samočištění, tuhost, antibakteriální, protiplísňový, oxid titaničitý

Table of contents

1. Introduction

Cotton fibre is one of the most common natural and leading textile fibre due to its unique properties such as hydrophilicity, biodegradability, durability, good dyeability, and relatively low cost [1]. Despite the excellent properties of cotton fabrics, some characters like the inherently hydrophilic property, impotent antimicrobial activity, low strength and poor sensitivity to the UV light, confine their wide applications, especially in some high-end areas for medicine, personal healthcare, functional textile and self-cleaning [2-4]. Therefore, value addition to cotton by functionalization has generated considerable academic and industrial attention, not only due to their potential use in physical, thermal, biological and medical protection, but also to meet the constantly evolving demand from consumers for advanced materials. Self-cleaning fabric materials are a research area that has accumulated huge interest over the years. The original idea of self-cleaning textiles envisioned a scenario where tablecloths and men's suits shrug off coffee, tea, wine and other stains; or where large awnings, tents and other architectural structures stay spotlessly clean without requiring any washing or cleaning. Due to the remarkable developments made in this field during the last few decades, the concept of self-cleaning widened to include apparel that cleanses itself of body odour, curtains that rid themselves of tobacco odours to stay 'ever fresh', and hospital sheets that disinfect themselves to reduce the incidence of cross infections[5]. A strategy that is commonly adopted for the purpose of self-cleaning is to modify the textile surface with photocatalytic nanoparticles such as Titanium dioxide (TiO_2) and Zinc oxide (ZnO) [6, 7]. TiO_2 as a cheap, nontoxic, highly efficient, stable, and ecologically friendly photo catalyst, has been proved to be an excellent catalyst in the degradation of organic pollutants [8].

Cotton fabric is widely used in the apparel and household fields because of its good hygroscopicity, moisture regain and heat-resistant quality [9]. However, because of its poor stiffness and crease recovery, its application is restricted in some situations. As a differential fabric, stiff cotton fabric is important to many industries, such as applications to suit jackets, curtains and luggage. For comfort in hot environment people prefer to have some distance between skin and cloth and that why most of the Asian and African countries use stiff cotton fabric due to high temperature. Starch is mainly being used to make cotton fabric stiff. However, it does not give permanent effect. Cellulose is not soluble in water so it can replace starch if it is coated on the surface.Antibacterial activity is very interesting and demanding properties of cotton fabrics [10-13].

In recent years, the commercial market for antibacterial fibers has grown rapidly due to the increased need of consumers. Polymeric materials, such as cotton, wool and flax, provides an excellent substrate for bacteria growth because they are contaminated easily with microorganisms under the appropriate environmental conditions [14]. Microbial proliferation eventually causes damage to the fiber materials and induces human infections [15]. Nano particles like TiO_2, ZnO, CuO, Ag, carbon nanotubes etc. show excellent antibacterial activity. TiO_2 is most environment-friendly [16] among all other nano particles and shows multifunctional ability, that‘s why it was selected for coating with cellulose. There are several methods and techniques researchers have introduced to make cotton fabric functional by coating nanoparticles on the surface, in-situ polymerization, depositing nanoparticles on the surface etc. However, these methods lacking in durability. To overcome with this proplem, the new route has been introduced herein to make cotton fabric multifunctional by coating cellulose-TiO_2 nanoparticles on the surface of cotton fabric.

2. Purpose and the aim of the thesis

Overall aim of this study is to develop a cellulose-TiO_2 coated cotton fabric and its characterization for organic stain degradation, inhibition efficiency against bacteria's, disinfection of cotton fabric from fungal colonization, stiffness, mechanical properties, X-ray diffraction, durability of cellulose-TiO_2 against washing and comfort properties such as air and water vapor permeability for multifunctional applications. Orange II dye and wine have been selected for investigation of self-cleaning propeties and ImageJ software has been used to analyze stain degradation under UV light. The bacterias such as Escherichia coli (EC), Klebsiella pneumonia (KP), Staphylococcus aureus (SA), Methicillin resistant staphylococcus aureus (MRSA) have been used to study antibacterial activity of coated fabric. X-ray diffraction patterns based simulation model was used to understand the effect of solvent on the structure of cellulose.

The specific objectives are as follows,

a) investigation of morphology of cellulose-TiO_2 coated cotton fabric
b) investigation of photocatalytic self-cleaning ability by degradation of orange II dye and wine stain under UV light.
c) evaluation of antibacterial and antifungal properties of cellulose-TiO_2 coated cotton fabric
d) investigation of stiffness, mechanical and comfort properties of cellulose coated cotton fabric
e) effect of cellulose coating on dyeing, colour strength and related parameter with reactive dyes
f) durability of cellulose-TiO_2 coated cotton fabric against washing.
g) development of simulation method to quantify amount of cellulose I, II and amorphous content by X-ray diffraction.

3. Overview of the current state of the problem

Self-cleaning and permanently stiff textiles are becoming important due to market demand, and broad research is being done in this area [5, 17, 18]. TiO_2 can be applied on different substrates such as activated carbon, stainless steel and glass [19]. TiO_2 shows extraordinary photocatalytic activity since it has a high sensitivity to light [20]. Nano TiO_2 has the ability to decompose dye pollutant such as Acid Orange [21], Methylene Blue [22], C.I. Acid Blue-9 [23], Methyl Orange [24, 25], Ethyl violet dye [26], C.I. Reactive Red 2 [27] and photocatalytic decomposition of some air pollutants [28]. Recently some researches have coated TiO_2 on cotton fabric by in-situ suspension polymerization with nano TiO_2-acrylate copolymer [29] and functionalizing cotton fabric with nano sized TiO_2 [30]. However, durability is major concern with these methods. Starching is commonly used for increasing stiffness of cotton fabric by applying starch [31, 32] to them. Application of starch is widely used for increasing the bending rigidity of collars and sleeves of men's shirts and the ruffles of girl's petticoats. However, that notwithstanding, the stiffness arising from starching isn't permanent due to the fact that when the fabrics are washed, starch dissolves in water [33] therefore leading to loss of fabric stiffness, and hence a need to reapply starch after each washing cycle. Cellulose is insoluble in water, therefore coating fabrics with cellulose leads a lasting and permanent stiffness effect unlike starch which is soluble in water whose stiffness is temporary [34].

In recent years, researchers have been trying to make cotton fabric self-cleaning and antibacterial in different ways such as: antibacterial finishing of cotton by microencapsulation[12], by synthesizing Photo bactericidal porphyrin-cellulose nanocrystals [35], Treating cotton fabric by SBA-15-NH_2/polysiloxane hybrid containing tetracycline [36], plasma treatment and ZnO/Carboxymethyl chitosan composite finishing [37], self-cleaning by copper (II) porphyrin/ TiO_2 visible-light photocatalytic system [20], coating with nano TiO_2-acrylate copolymer [29], Nano TiO_2 coating after treatment of cotton fabric with carboxylic acids such as oxalic, succinic, and adipic acids [38], functionalizing cotton fabric with p-BiOI/ n-TiO_2 heterojunction [39], bleaching and cationized cotton using nanoTiO_2 [10]. However, these methods do not give durable ability to kill bacteria's. Research elsewhere has utilized various cellulose coated substrates for various applications such as high oxygen barrier and targeted release properties cellulose [34, 40], extension of the shelf life of rainbow trout fillets [41], bioactive composite coating [42], wood coatings [43] for active packaging [44] etc. Cellulose does not melt before decomposition and is insoluble in common organic solvents. Cellulose is a highly stable compound and its stability is primarily attributed to strong intra- and intermolecular hydrogen bonding leading to a remarkably stable fibrillar structure [45]. Solvents like 60% Sulfuric acid (H_2SO_4) [46], Ionic Liquid [47, 48], N-Methylmorpholine N-oxide (NMMO)[49], Sodium hydroxide-carbon disulfide (NaOH-CS_2) [50], Dimethyl acetate/ Lithium chloride (DMAc/ LiCl) [51] can readily dissolve cellulose. Thus, there is a scope for cellulose coating on cotton fabric after dissolution since both the molecules are same and there will be exchange of hydrogen bonding for permanent change. Due to interlinkage between coated celluose and cotton cellulose, coated cellulose will not be washed away unlike starch. Hypothesis is that cellulose can carry nanoparticles and hold for long duration after coating with help of hydrogen bonding between coated cellulose and cotton fabric cellulose.

Coating with cellulose-TiO_2 addresses four main uses: self-cleaning, antibacterial, antifungal and stiffness. For coating cellulose-TiO_2, Urea-Thiourea-NaOH solvent system and 60 % H_2SO_4 solution were selected for cellulose dissolution. Urea-Thiourea-NaOH solvent system dissolves cellulose directly at -12°C [52] and 60 % H_2SO_4 is powerful and has the ability to breakdown cellulose chains directly. The Degree of Polymerization of cellulose decreases after dissolution in 60% H_2SO_4 [46]. This report, therefore, presents the findings of the investigation of the microstructural, self-cleaning, antimicrobial, stiffness and comfort properties of cellulose-TiO_2 coated cotton fabric for possible applications.

4. Methods used, studied material

4.1 Materials

Cotton plain weave fabric with the 0.28 mm thickness, 125.2 g/cm2, 97.3% porosity, density of 30warps/cm and 25 weft/cm was obtained from Tepna Nachod, Czech Republic. TiO_2 nanoparticles (Degussa-P25) were purchased from Evonik industries with the average particle size of 50 nm. Vian Biocel V Mg-bisulfite softwood pulp was supplied by Lenzing Biocel Paskov A.S. Urea was purchased from Pentachem. Thiourea, sulfuric acid, and NaOH were purchased from Lachner, Czech Republic. Reactive Red 240, Blue 49, and Yellow 95 reactive dyes were purchased from Synthesia a.s. Sulfuric acid waspurchased from Lach-ner, Czech Republic. Sodium carbonate wasobtained from P-Lab a.s Czech Republic. The Orange II dye was usedas a stain and it was obtained from Sigma Aldrich.

4.2 Methods

4.2 Cellulose Coating

4.2.1 Cellulose dissolution

a) Dissolution in 60 % Sulphuric acid

Viscose fibers were used as a sourse of cellulose to prepare cellulose solution. 60 % of sulphuric acid soltion was prepared by dissolving 60 g of sulphuric acid in 40 g of water. Prepared solution allowed to cool down at room temprature (20-25° C). 10 g of viscose fibers were dissolved in 90 g of 60 % Sulphuric acid solution at room temperature under continuous stirring for 30 min.

b) Dissolution of cellulose in Urea-Thiourea-NaOH Solvent system

The solvent system was prepared by mixing 8g of Urea, 6.5 g of Thiourea and 8g of NaOH in 77.5g of water by stirring. Various concentrations of cellulose pulp (0, 1, 3, and 5 %) were dissolved in the urea–thiourea–NaOH–water solvent system at -12° C by mechanical stirring.

4.2.2 Dispersion of TiO_2 nanoparticles in cellulose solution

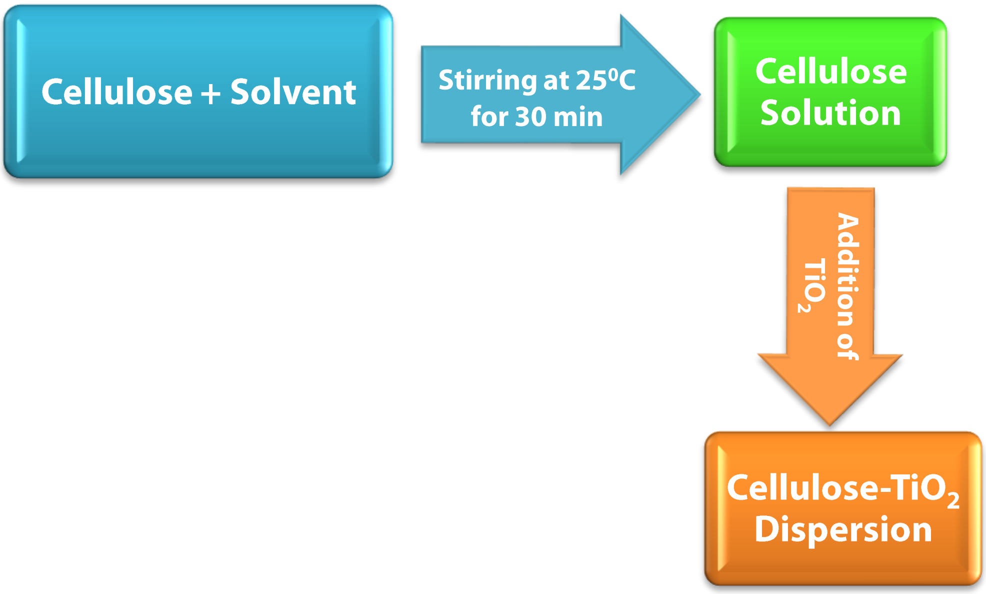


Figure 1. Dissolution and dispersion of TiO_2

Cellulose solution was prepared by dissolving cellulose in direct solvents such as 60% Sulfuric acid and NaOH-urea-thiourea. Figure 1 shows the schematic representation of dissolution and dispersion process. TiO_2 nanoparticles with diffrent concentration (1,3,5,and 10% on the weight of cellulose) were dispersed in cellulose solution. Mixture of Cellulose solution and TiO_2 nanoparticles were stirred at room temperature for 5 min. Prepared cellulose-TiO_2 soltion was used for coating.

4.2.3 Padding

The cellulose - TiO_2 solution was applied on the surface of cotton fabric (4g) by roller padding machine at room temperature (15-20 $^{\circ}$C). The time used for padding was 20 seconds and same time used to treat fabric with solvent (60 % H_2SO_4). Fabric was washed after padding by aqueous solution of 100 g/l Sodium carbonate, followed by water until neutralization. The coated fabrics were dried at 60 $^{\circ}$C for 30 min and pressed using an electric iron. The concentration of cellulose added is as shown in Table 1. Starching to cotton fabric was done according to procedure given in US patent no 2,693,042 [53] to compare stiffness property with cellulose coated cotton fabric.

Table 1. Amount of cellulose coating on 4 g of cotton fabric

Sample description	Weight of fabric after coating [g]	Added cellulose-TiO_2/ g of fabric
0 % (Without TiO_2)	4.2415	0.0603
1 % TiO_2	4.2355	0.0588
3 % TiO_2	4.2366	0.0591
5 % TiO_2	4.2383	0.0595
10 % TiO_2	4.2392	0.0598

4.3 Dyeing with reactive dyes

Dyeing bath was prepared by dissolving NaCl (50 g/l), Na_2CO_3 (20 g/l) and reactive dye in distilled water. The dyeing was done at 70 °C for 60 min with fabric-liquor ratio 1:50. The dyeing was carried out with 3 %, 9 % and 15 % of dye concentration (%w/w). Then dyed samples were washed with hot (80 °C) water and dried at 70 °C in hot air convection oven for 30 min.

4.3.1 Effect of cellulose coating on dyeing properties

Reflectance of the coated and uncoated fabric samples were measured on spectrophotometer (Datacolor 110TM Switzerland) at λmax and Kubalka–Munk equation was used to determine K/S value of the both fabrics:

$$\frac{\boldsymbol{K}}{\boldsymbol{S}}=\frac{(\mathbf{1}-\boldsymbol{R}_{\boldsymbol{\lambda max}})^{\mathbf{2}}}{\mathbf{2}\boldsymbol{R}_{\boldsymbol{\lambda max}}} \qquad (1)$$

where K is the coefficient of absorption; Rλ is the reflectance of the fabric at peak wavelength and S is the coefficient of scattering;

The relative color strength and color difference between cellulose coated dyed samples and uncoated dyed samples were calculated by using following formula:

$$\textbf{Relative color strength}\ (\%)=\frac{\textbf{K/S of coated sample}}{\textbf{K/S of uncoated sample}}\ \mathbf{100} \qquad (22)$$

$$\Delta\boldsymbol{E}=\sqrt{(\Delta\boldsymbol{L})^{\mathbf{2}}+(\Delta\boldsymbol{a})^{\mathbf{2}}+(\Delta\boldsymbol{b})^{\mathbf{2}}} \qquad (3)$$

Where $\Delta L = L_{Coated}$- $L_{unCoated}$; $\Delta a = a_{Coated}$- $a_{unCoated}$; $\Delta b = b_{Coated}$- $b_{unCoated}$; L is lightness, ‘a’ explain redness or greenness and ‘b’ indicate yellowness or blueness [56].

4.3.2 Fastness properties

The coated samples were washed according to the standard conditions given in the test method ISO 105-C06 [57] to assess staining of adjacent fabrics and change in the color after washing. Rubbing fastness of both coated and uncoated samples were evaluated according to the test method ISO 105-X12 [58]. The coated fabrics were evaluated for their perspiration fastness using the test method ISO 105-E04 [59].

4.4 Charactrization and measurements

4.4.1 Scanning Electron Microscopy (SEM)

The surface morphologies of the control, cellulose coated and cellulose-TiO_2 coated cotton fabric surfaces were investigated using a TS5130 Vega-Tescan Scanning Electron Microscope with accelerating voltage of 20kV. The samples were sputter coated with gold to increase the surface conductivity.

4.4.2 Simulation method to calculate amount of cellulose II by x-ray diffraction

PANalytical X'Pert³ X-ray powder diffractometer was used to analyze crystal structure of coated and control cotton fabric. The fabric samples were run at angle 8° to 70° in steps of 0.017. Cellulose II was estimated by following AD French's simulation method [50-52]. The published coordinates of the asymmetric units of cellulose Iβ and cellulose II containing crystallographic information file was downloaded from the supplementary material of the AD French paper [50-52]. The whole contents was copied into a note pad, and a = 7.784° A for Iβ unit cell was changed to 7.906°A for cotton fabric cellulose and saved in .cif file format. The Mercury 3.5.1 program [53] was used to simulate diffraction patterns. The Full Width Half Maximum (FWHM) was set at 1.5° 2θ and the CuKα wavelength was set at 1.54056°A. For the preferred orientation, a March–Dollasefactor of 2.0 [54] was applied to the (0 0 1) plane. The pattern of cellulose II at 9° FWHM [51] was used to incorporate amorphous fraction of cellulose.

4.4.3 Mechanical properties

In order to understand the effect of 60 % H_2SO_4 solvent on the mechanical properties of cotton fabric, samples with dimensions 15 X 5 cm were tested for the breaking strength, elongation and modulus of control and cellulose-TiO_2 coated fabrics were measured according to ISO 1924-2 [55] standard test method on Testometric M250-2.5 machine (UK). Five number of samples were tested and statistical treatment was done.

4.4.4 Photocatalytic properties

The Orange II dye and wine were used as a stain for the experiments. Stained samples were irradiated under UV light as a function of time to see the effect of TiO_2 on degradation of stain. Philips TL 6W/05 CE UV tubes (400-320 nm) were used for irradiation of stain. After irradiation, the fabric samples were scanned on the scanner at 300 dpi and the scanned images were analyzed by 'Image J' software [54, 55]. ImageJ is an open source Java image processing program inspired by NIH Image[55]. It runs on any computer with a Java 1.8 or later virtual machine. Downloadable distributions are available for Windows, Mac OS X and Linux. ImageJ has a strong, established user base, with thousands of plugins and macros for performing a wide variety of tasks. ImageJ can display, edit, analyze, process, save and print 8-bit, 16-bit and 32-bit images. It can read many image formats including TIFF, GIF, JPEG, BMP, DICOM, FITS and "raw". It supports "stacks", a series of images that share a single window. It is multithreaded, so time-consuming operations such as image file reading can be performed in parallel with other operations. It can calculate area and pixel value statistics of user-defined selections. It can measure distances and angles. It can create density histograms and line profile plots. It supports standard image processing functions such as contrast manipulation, sharpening, smoothing, edge detection and median filtering [56]. Ten number of samples were analysed for photocatalytic degradation. Blue colour intensity was taken into consideration since it was only changing. Figure 2 shows the process to analyze stain degradation by ImageJ.

Procedure of image analysis by ImageJ software

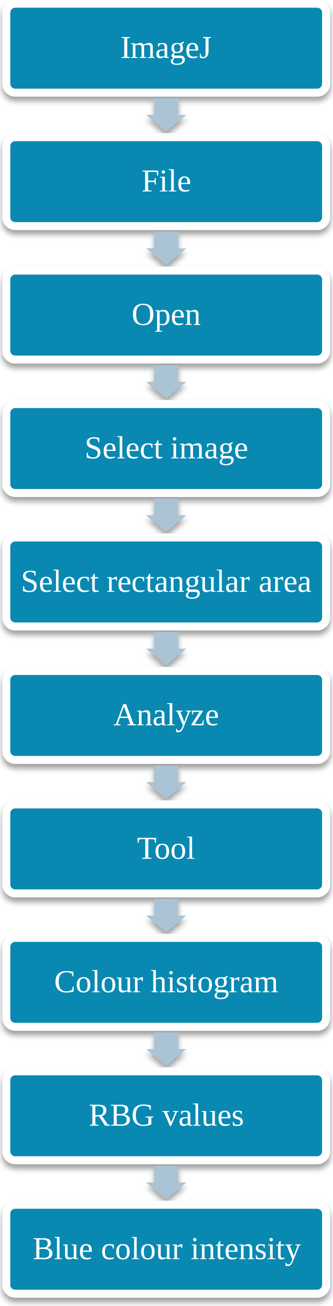


Figure 2. Method to analyze photocatalytic degradation of stain by ImageJ

4.4.5 Stiffness of treated fabric

The bending force of fabric was measured on TH-7 instrument [61]. The device TH-7 (figure 3) was developed in Department of Textile Evaluation at Technical University of Liberec by Dr. Ludmila Fridrichova. It was developed by means of innovation of device TH-5 on which only rectangle samples sized 2.5 cm 5 cm could be measured. The differences between model of device TH-5 and TH-7 and the essential innovations that were realized on the older device TH-5 is given below.

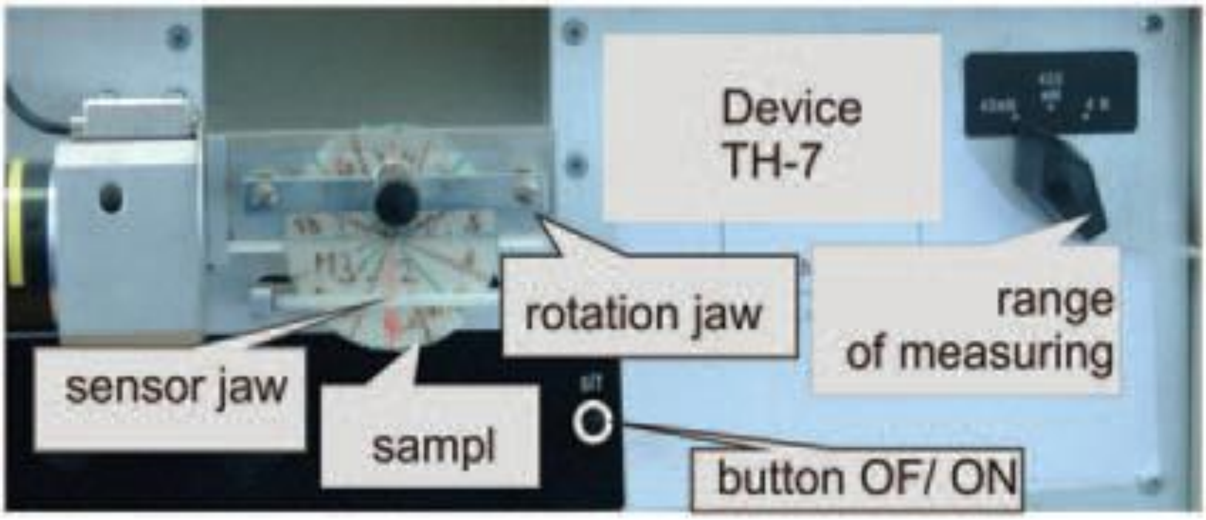


Figure 3. Device TH-7 [57].

1. The clamping and sensor jaw was extended so that the device could be used for measuring rectangular, square and circular samples.
2. The revolving clamping jaw was designed so that it could turn in both directions, which enabled one to draw the whole hysteresis loop of bending (figure 4).
3. The sensor jaw was adjusted so that the bending power could be scanned in both directions: face– face and back–back. The sensor jaw is U-shaped.
4. There are Teflon tubes on the sensor jaw that reduces the coefficient of friction between the tube and the bent fabric.
5. To control the device and store the measured data, new software was developed. The output of the measuring is a hysteresis loop (curve). The data are stored in a data file (csv) and at the same time in a graphic file (png), as shown in figure 4.
6. Device TH-7 also enables one to measure the cyclical strain of the sample. It is possible to set 10 cycles of automatic bending at maximum. The values of every cycle are recorded, as well as the final average value.

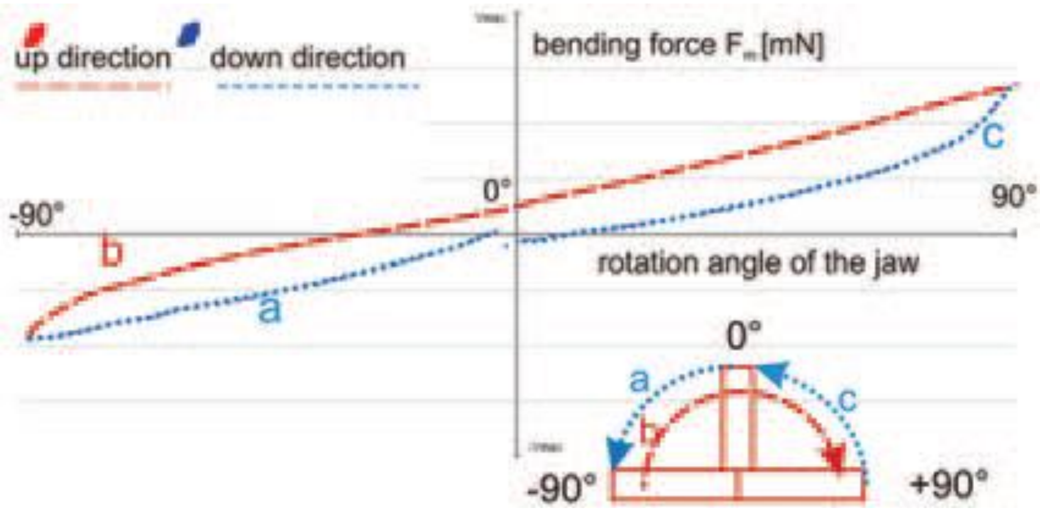


Figure 4. Hysteresis loop of bending from device TH-7 [57].

The device enables the measuring of non-textile materials, for example paper, foils and membranes; however, it was constructed mainly for measuring fabrics. It has three ranges of measured bending force. The range of measuring force of bending is from 40 to 4000 mN. The output from the device is the value of bending force Fm [mN]. This value can be measured for various sample widths, with 50 mm being the maximum and the minimum being unlimited.

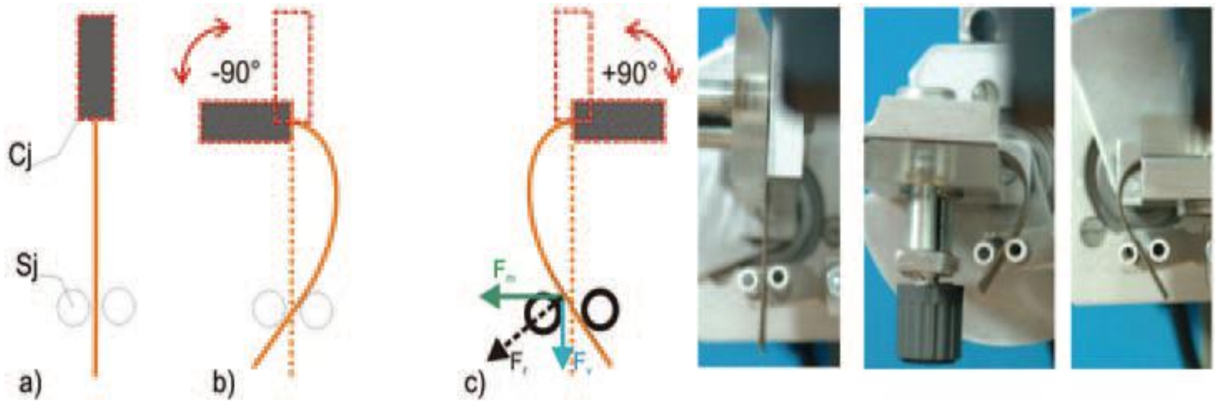


Figure 5. Scheme and photography of bending sample on device TH-7. [57].

The suggested length of the sample is 50 mm; however, textiles of 25 mm minimum length can be measured, too. Materials whose thickness does not exceed 1.5 mm can be bent. The distance between the clamping and the sensor jaws is 14 mm. The scheme and photography of bending the fabric on device TH-7 is given in figure 5 [Cj: clamping jaw; Sj : sensor jaw, it is scanning bending force (F_m= F_h horizontal force component); F_r: resultant force; F_v: vertical force. (a) Sample in zero position. (b) Sample turned to position +90 face–face. (c) Sample turned to position -90° back–back]. The output value from device TH-5 or TH-7 is bending force Fm. The calculation of bending moment Mo [Nm] is described for the older model, device TH-5, according to the standard CˇSN 80 0858, where Mo ¼ Fm k, k ¼ 0.604 for samples of 2.5 cm width. There is more information in the article by Naujokaityte et al- [58]. If we want to compare the mutual bending behavior of textiles that were measured only on device TH-7, it is possible to work only with the value of bending force Fm [Nm], so it is not necessary to convert Fm to the value of bending rigidity B [Nm2 /m], or to the bending moment M [Nm]. Stiffness was calculated by multiplying bending force to 0.008. Five number of samples were tested and standard deviation was calculated.

4.4.6 Quantitative evaluation of anti-bacterial activity (AATCC–100)

American Association of Textile Chemists and Colorists (AATCC) standard methods such as AATCC 147 and AATCC100 were used to investigate antibacterial activity of cellulose-TiO_2 coated cotton fabric. Four different bacterial strains, Escherichia coli (EC), Klebsiella pneumonia (KP), Staphylococcus aureus (SA), Methicillin resistant staphylococcus aureus (MRSA) respectively were used.

AATCC 147: The sample with dimensions 18x18 mm was wetted in distilled water and placed on moist filter paper (in distilled water). Both sample and filter paper were placed together in petri dish and then dish was closed. After 15 minutes of UV radiation exposure, the sample was placed on blood agar. The blood agar plates were individually inoculated with bacterial stains at a concentration of 10^5 CFU / ml. The samples were cultivated in incubator at 37 °C for 24 hours**.**

AATCC100: The sample wetted in distilled water with the dimension of 18x18 mm was placed on wet filter paper and then together placed in covered petri dish. The sample was placed into sterile container and exposed to UV radiations for 15 minutes. Thereafter 50µl of bacterial stain (inoculums) was applied on the sample and allowed to wick through the sample stack. The inoculated swatches incubated for 24 hours at 37^oC; thereafter a neutralizing broth composed of 50ml of saline was added and container was shaken so as to release the inoculums from the test swatches and into the neutralizing broth. The bacteria present in this liquid was obtained as the percentage reduction [59].
The percentage reduction of bacteria was calculated using the following formula:

$$(\boldsymbol{B}-\boldsymbol{A})\frac{\mathbf{100}}{\boldsymbol{B}}=\boldsymbol{R} \tag{4}$$

Where R is the percentage reduction; A and B are the number of bacteria recovered from the inoculated treated and untreated fabrics.

4.4.7 Evaluation of antifungal properties of coated fabric

The antifungal properties were measured using the following fungi mixture in aqueous suspension at a concentration of 10^6 CFU/ml: Penicillium digitatum (CCM F-382), Rhizopus stolonifer (CCM F-445), Cladosporium sphaerospermum (CCM F-351), Chaetomium globosum (CCM 8156). Three samples of cotton fabric coated with TiO_2, each with area of about 4 cm^2, with different concentrations of TiO_2 (0, 1, 3, 5 and 10%) were placed on agar medium [Malt agar, Cadersky-Envitek, Ltd, Brno, Czech Rep.] and inoculated with a suspension of testing moulds. Incubation of the tested sample was conducted for two weeks at a temperature of 22 ± 3 °C, at daylight (near a window). After the test, evaluation of antifungal properties was done on the basis of visual assessment according to the EN 14119, 2003 Standard [60] by determining degree of mould growth on the surface of fabric samples.

The rating system for mold growth was as follows:
0 – no visible growth evaluated microscopically,
1 – no visible growth evaluated with the naked eye but clearly visible microscopically,
1 – growth visible with naked eye, covering up to 25% of tested surface,

2 – growth visible with naked eye, covering up to 50% of tested surface,
3 – considerable growth, covering more than 50% of tested surface,
4 – Very intense growth, covering all tested surface.

4.4.8 Air and water vapor permeability

The air permeability of control and coated cotton fabrics was analyzed using a Textest FX instrument according to the ASTM D2986 standard test method. The air permeability was measured at pressure of 200 Pa and range of 3. The measuring principle depends on measurement of the air flow through the fabric under a certain pressure gradient Dp. The water vapor permeability was analyzed using a Permetest device (Sensora Instruments) with the fast skin model according to the ISO 11092 standard.

4.4.9 Durability of stiffness and photocatalytic properties

Durability of Cellulose-TiO_2 coated fabrics for stiffness and photocatalytic properties against repeated washing were evaluated by washing TiO_2-Cellulose coated cotton fabrics according to modified AATCC (American Association of Textiles Chemists & Colorists) test method 61 (2A)-1996 [66]. After washing, samples were analyzed for stiffness and photocatalytic properties. The fabric was washed with 4g per liter (g/l) detergent at 40 °C for 1hr. Washed fabrics were further evaluated for stiffness and stain degradation.

5 Summary of the results achieved

5.1 Morphology of cellulose and cellulose-TiO_2 coated cotton fabric

To investigate the change in the surface morphology of the coated cotton fabric, scanning electron microscopy was used to estimate the influence of the modification process on the fabric. These images (figure 6) are of cellulose coated cotton fabric in which coating was done with dissolved pulp in NaOH-urea-thiourea solvent system. Cross sectional and surface images of cellulose-coated and uncoated cotton fabrics are presented in figure 6. These micrographs reveal that the applied cellulose formed a film on the surface of the cotton fabric, covering the spaces between yarns. This formed film is attached to the surface of cotton fabric by intermolecular hydrogen bonding. The hydrogen bonds from between coated cellulose and cotton fabric cellulose because strong solvent NaOH-urea-thiourea or 60% H_2SO_4 has been used to dissolve cellulose for coating. Solvent molecules interact with cotton fabric cellulose and try to dissolve and bring both cellulosic phase together.

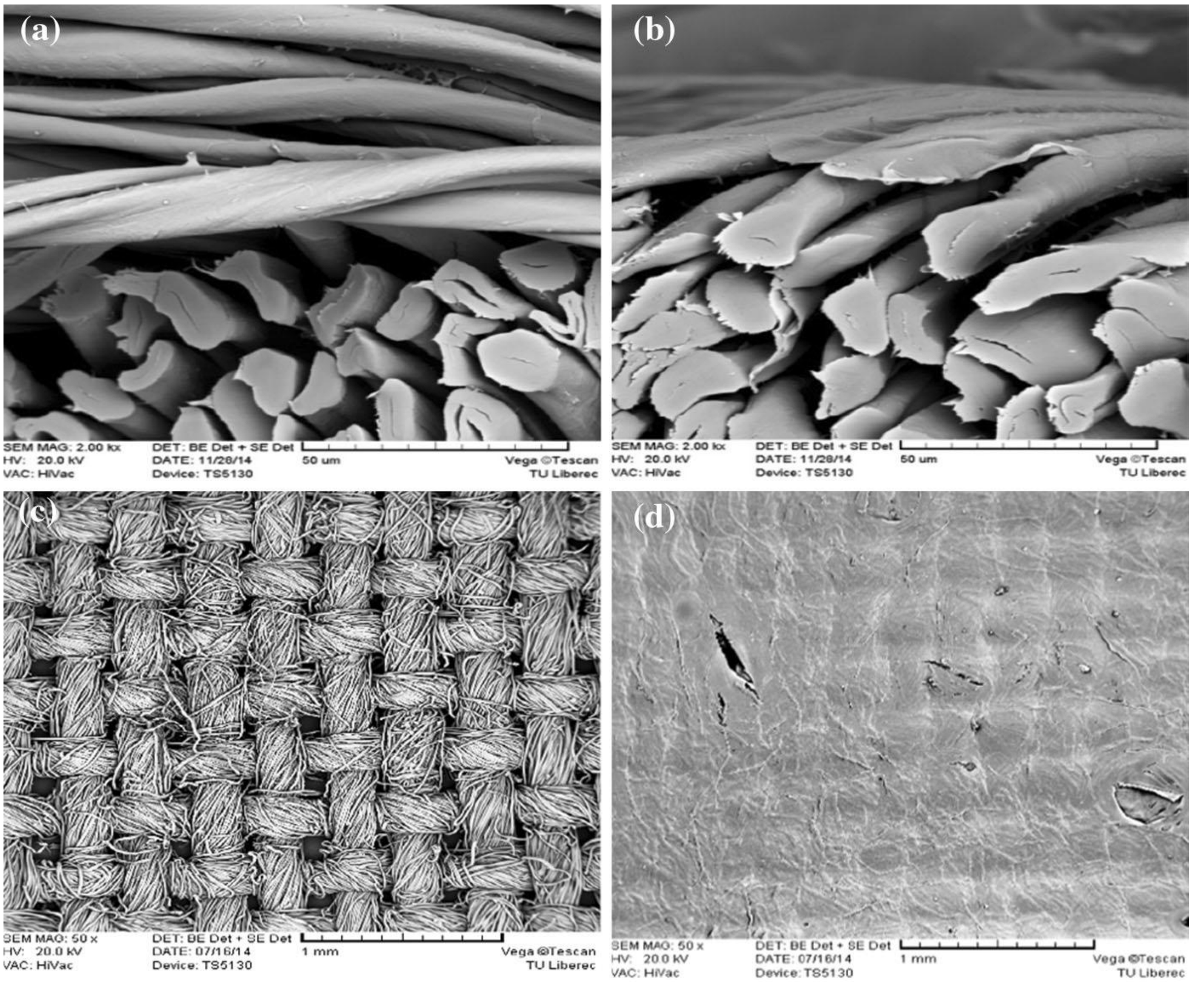


Figure 6. SEM images of (a, c) uncoated cotton fabric and (b, d) cellulose-coated cotton fabric

During this process coated cellulose and cotton fabric cellulose form intermolecular hydrogen bonding. This interchain linkage help coated cellulose to stay attached to fabric. Figure 7 (a–f) show the morphological changes inducted by the coating of cellulose-TiO_2 on the surface of the cotton fabric. It isapparent from the micrographs that coated cellulose forms a thinfilm on the fiber surface. Figure 7 (c–f) show the white particles on the surface and these white particles in the micrographs confirm that TiO_2 was successfully coated with the cellulose on the surface. Micro-graphs also reveal that coated cellulose holds the TiO_2 particles by forming the film on fabric surface. Solvent (60% H_2SO_4) molecules interact with cotton fabric cellulose therefore forming an interchain linkage between dissolved cellulose and coated cellulose as a result of this linkage, celluloseis not easily washed away by water. It is not possible to detect the interchain linkage by spectroscopic technique because both themolecules are same. X-ray diffraction pattern of solvent treated cotton fabric (figure 24) shows some changes in the structure of cellulose. Cellulose II content increases slightly and proves the interaction between solvent and cotton fabric during coating.

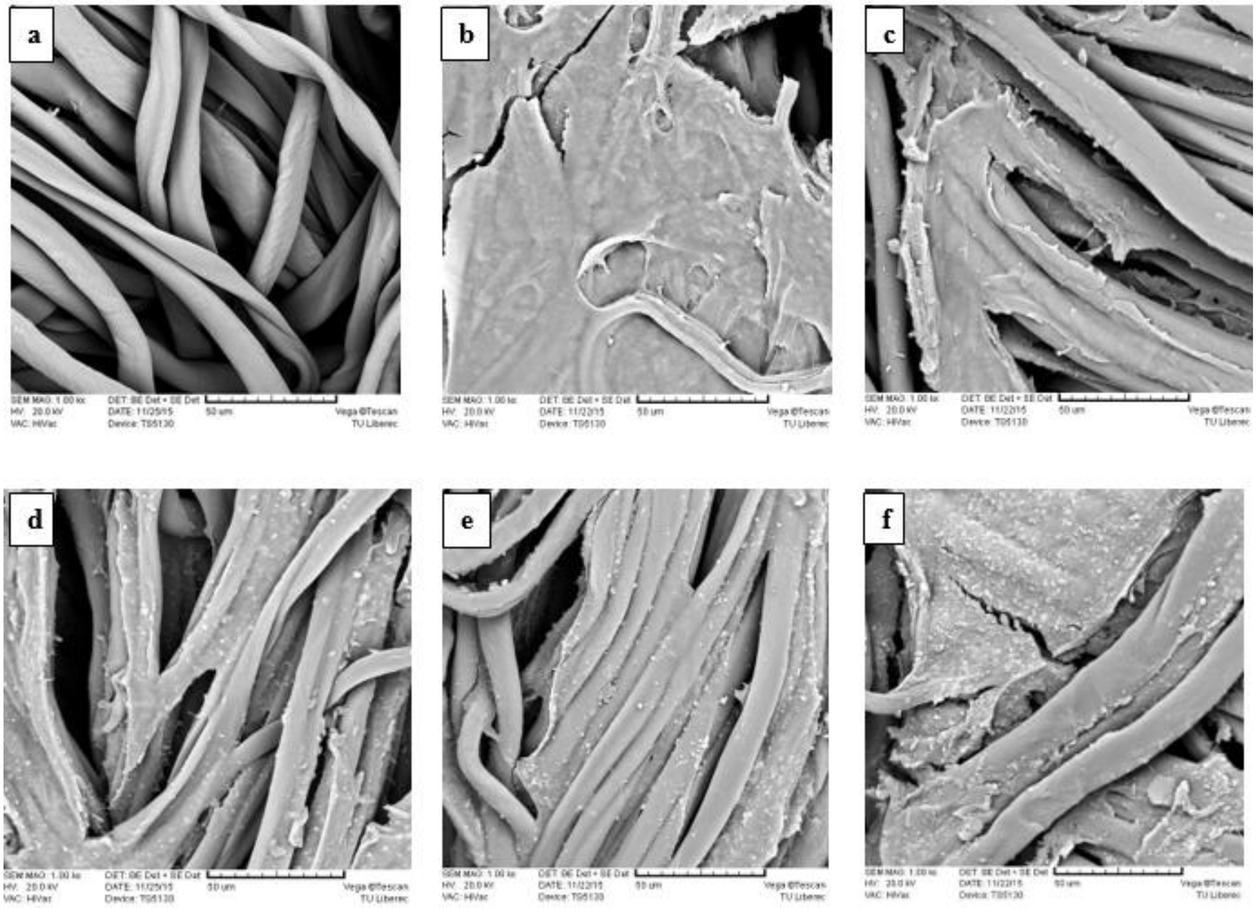


Figure 7. SEM photographs of TiO_2 - cellulose coated cotton fabric a) Control, b) 0% TiO_2, c) 1 % TiO_2, d) 3% TiO_2, e) 5 % TiO_2, f) 10% TiO_2.

5.2 Photocatalytic degradation of orange II under UV light

Cotton fabrics coated with cellulose-TiO_2 were analyzed for self-cleaning using photocatalytic degradation of orange II dye under UV light irradiation. Figure 8 shows scanned images of TiO_2 coated cotton fabric with various concentrations after irradiation under UV light at diffrent time of intervals. In figure 9, the exponential curves are form of the equation $B=B_0+(B_\infty-B_0)\ (1^{-e-kt})$. Here B is calculated intensity, B_0 is observed highest intensity, $B\infty$ is the intensity of pure cotton fabric without stain, k is constant and t is time. Significant discoloration of orange II dye was observed at 5 and 10 % TiO_2 coated samples. Evaluation of Orange II by ImageJ software is shown in figure 9. ImageJ software measures the intensity of color by using the color histogram tool. Here when sample becomes whiter, the value (counts) of color intensity increases that means it is measuring the whiteness of the sample. It is clear from figure 8 and 9 that degradation rate increases with increasing concentration of TiO_2 and time of irradiation. Coated samples with 1 and 3 % TiO_2 showed some degradation too but low as compared to 5 & 10 % due to low concentration. Figure 9 also shows that degradation of orange II increases with increasing irradiation time and TiO_2 concentration. Undyed control sample gave 249.7 counts whereas the dyed sample gave 186.6 counts and all the samples were compared in this range. All the TiO_2 coated samples show the photocatalytic properties and are therefore capable of stain degradation.

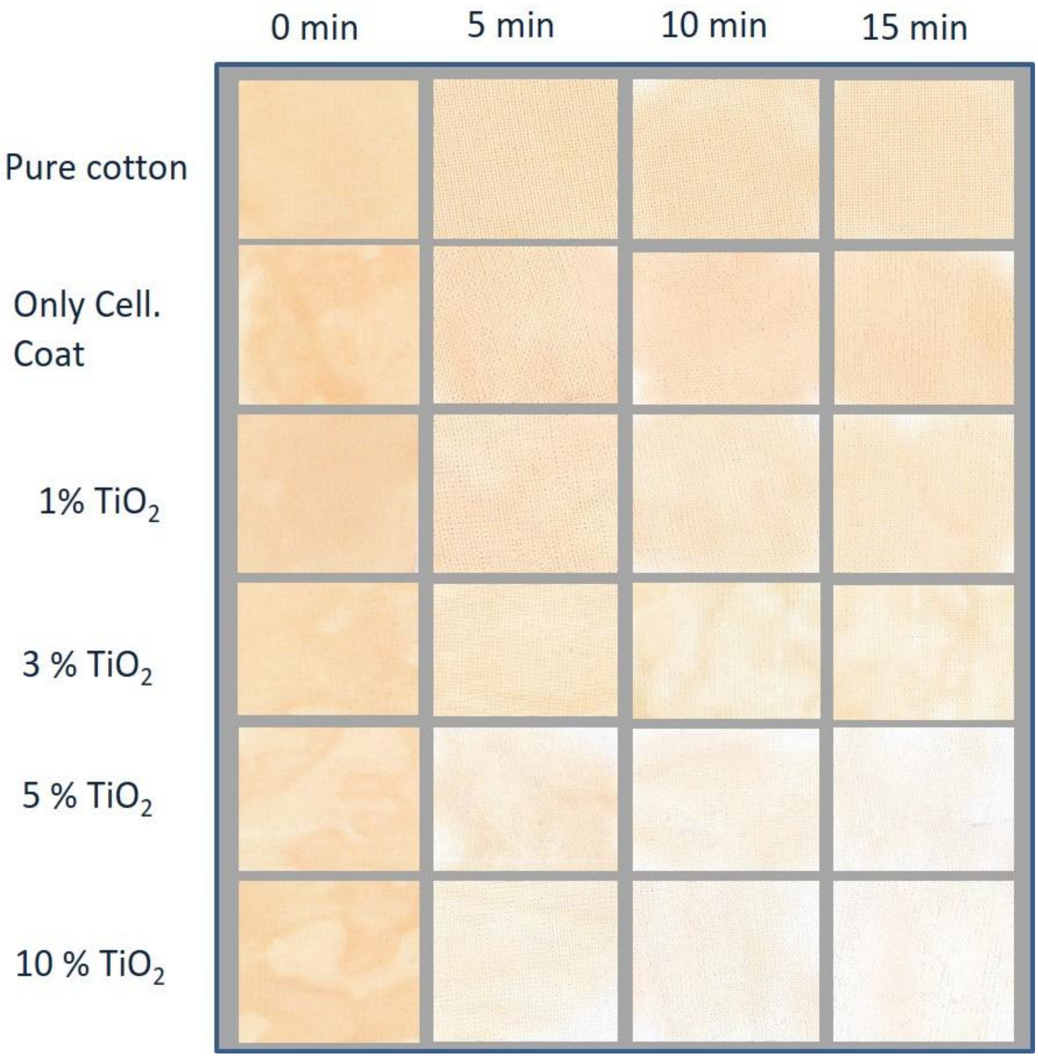


Figure 8. Degradation of Orange II under UV-visible light irradiation on cellulose-TiO_2 coated samples.

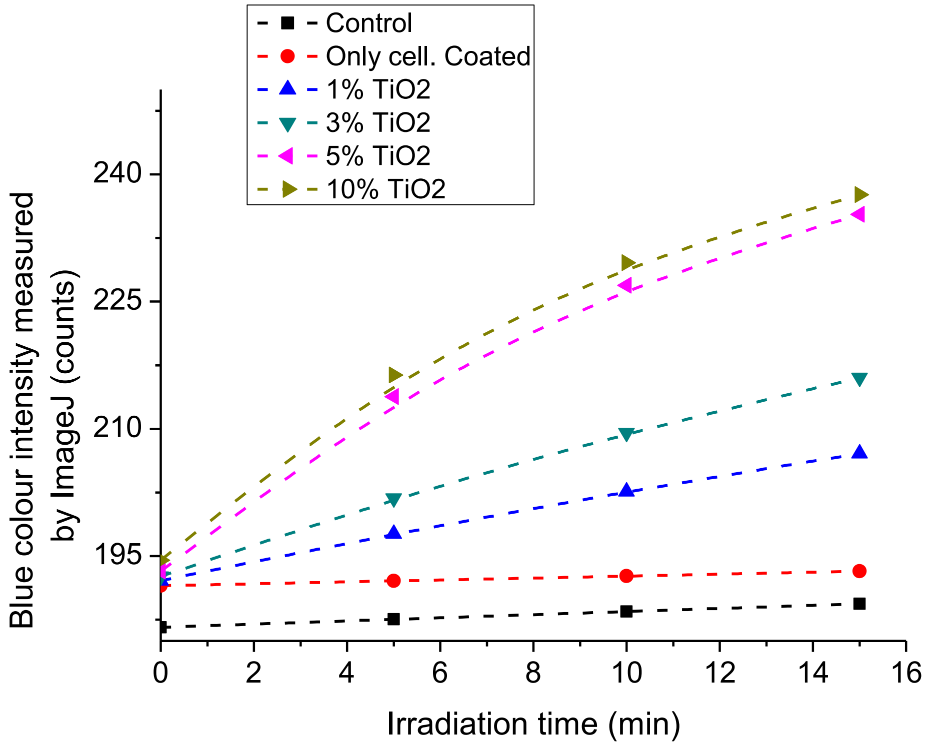


Figure 9. Evaluation of orange II degradation by ImageJ.

5.3 Wine stain degradation

The photocatalytic self-cleaning ability of TiO_2-cellulose coated cotton fabric with red wine stain was observed by irradiating samples under UV light. Irradiated coated cotton fabric samples were scanned on the scanner and then evaluated by using ImageJ software. Figure 10 shows the scanned images of control, only cellulose coated and 1, 3, 5 and 10% TiO_2-cellulose coated cotton fabric with red wine stain after 15 minutes of irradiation under UV light. It is clear from the figure 10 that red wine stain of 3, 5 and 10% TiO_2-cellulose coated samples was degraded whereas control, only cellulose coated samples remained unaffected. Due to low concentration of TiO_2 in 1% coating sample shows less degradation of wine stain.

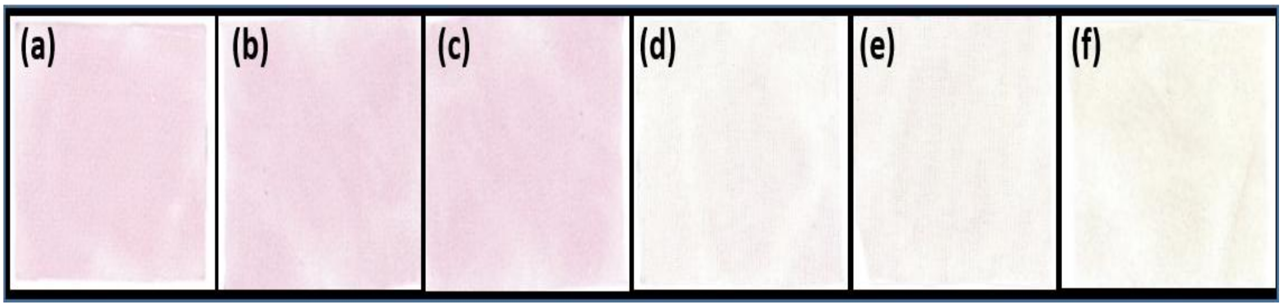


Figure 10. Scanned pictures of (a) Control (b) only cellulose coated and (c) TiO_2-cellulose coated cotton fabric after irradiation of red wine stain under UV light

Effect of TiO_2 concentration on wine stain degradation was evaluated by using ImageJ software. It is observed in figure 11 that degradation of stain increases with increasing irradiation time and concentration of TiO_2. Samples coated with 3, 5 and 10% TiO_2 shows significant discoloration of stain after irradiation under UV light for 15 minute. 1% TiO_2 coated cotton fabric shows least amount of degradation after UV light irradiation because of less concentration of TiO_2. Thus, from these results it is clear that degradation of stain depends on amount of TiO_2 in coating.

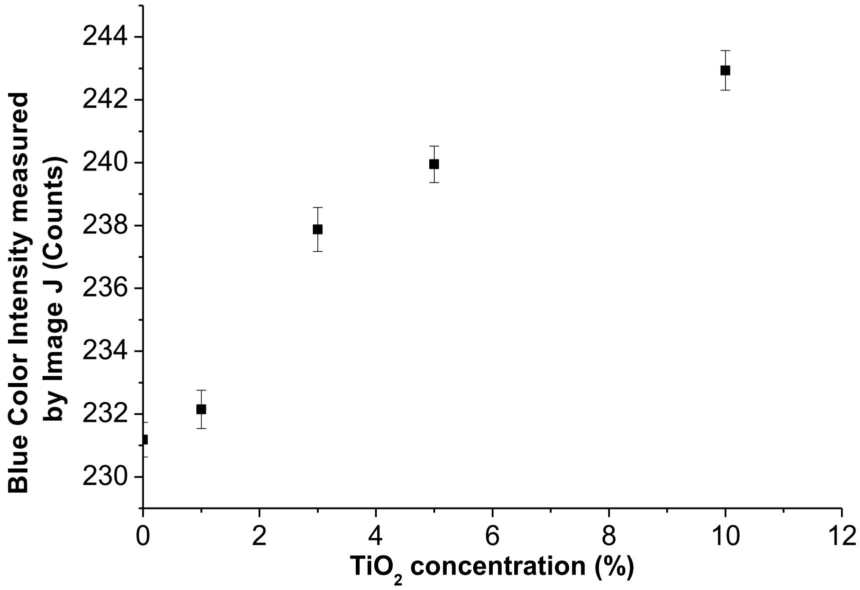


Figure 11. Effect of TiO_2 concentration on wine stain degradation

5.4 Durability of cellulose-TiO_2 coated cotton fabric for self-cleaning ability

To study the effect of washing on the self-cleaning ability of cellulose-TiO_2 coated cotton fabric, the fabric was washed with 4g per liter (g/l) detergent at 40 °C for 1hr. Figure 12 shows the effect of washing on self-cleaning ability of coated fabrics.

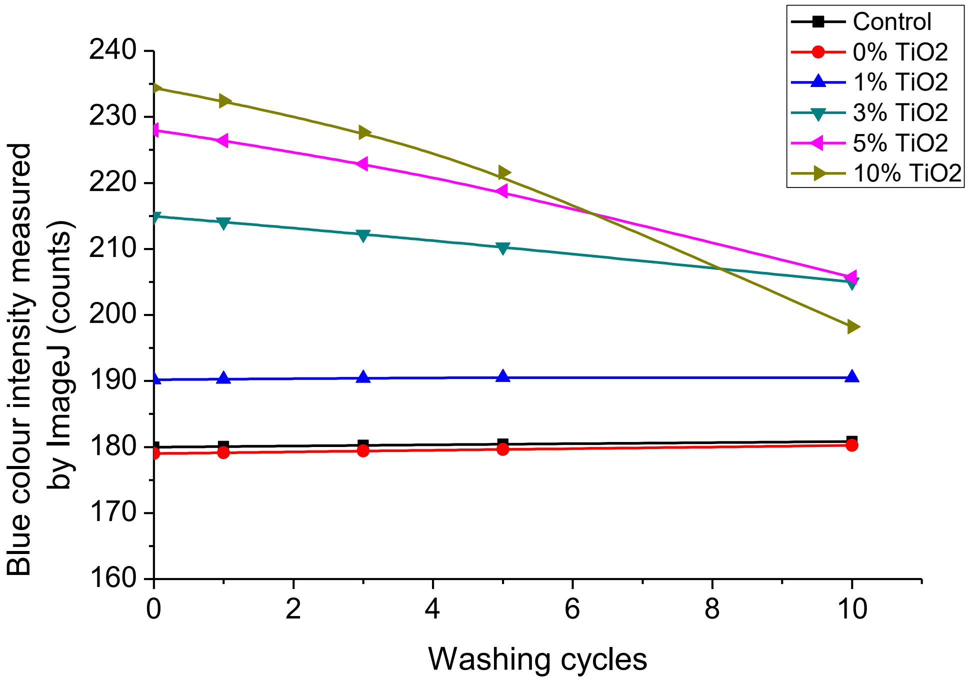


Figure 12. Effect of washing on stain degradation

In figure 12, the exponential curves are form of the equation $B=B_0+(B_\infty-B_0)\ (1^{-e-kw})$. Here B is calculated intensity, B_0 is observed highest intensity, $B\infty$ is the intensity of pure cotton fabric without stain, k is constant and w is washing cycle. Coated samples with 1, 3 and 5% TiO_2 show very good durability against washing up to 10 cycles. The sample coated with 10% TiO_2 showed poor durability because TiO_2 was not dispersed homogeneously in cellulose solution due to the higher concentration and is illustrated in the SEM images (figure 7 f). It is apparent from figure 12 that stain degradation starts decreasing after 1st washing for 3, 5, and 10 % TiO_2 coated cotton fabric, however, the ability to degrade the orange II dye stain still persists upto 10 washing cycles with all cellulose-TiO_2 coated samples. The fabric ability to degrade stain dropping after first cycle of washing because loosely attached cellulose was washed away with water. Therefore, this study confirms that significantly higher level of stain degradation is preserved as compared to uncoated fabric.

5.5 Rubbing effect on wine stain degradation

Textile materials frequently go through rubbing so it is neccesary to investigate its effect on self-cleaning ability of cellullose-TiO_2 coated cotton fabric. The cellulose-TiO_2 coated cotton fabric was tetsed against rubbing on abrasion and pilling tester for different cyles such as 0, 5, 10, 50, 100 cyles. Samples coated with 5 and 10% TiO_2 (on the weigth of cellulose) shows excellent results againt rubbing upto 100 cyles. 3% TiO_2 coated sample shows significant decrease in self-cleaning ability.

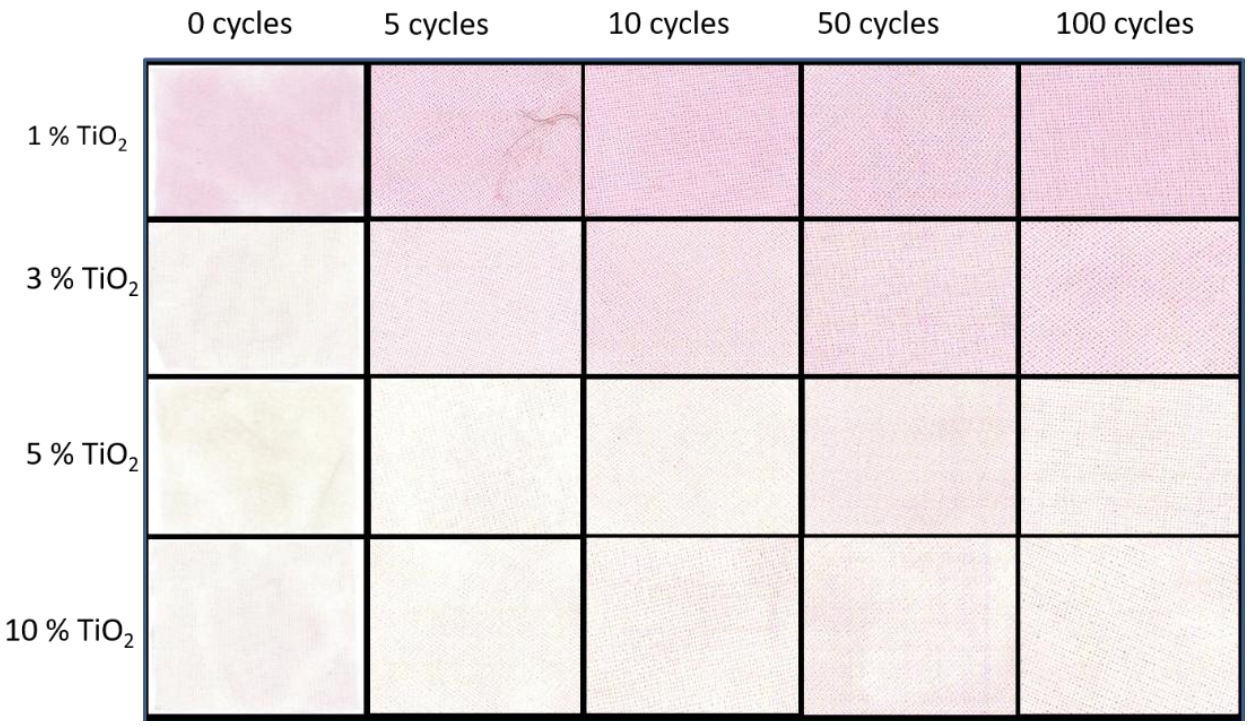


Figure 13. Scanned images of wine stain degradation of rubbed samples after 15 minuts of UV irradidition

The trend show that with increasing concentration of TiO_2 the stablity against increasing of coated samples. Figure 13 shows the pictorial images of wine stain degradation after 15 minutes of UV irradiation. Evaluation of waine stain degradation after rubbing 100 cycles by ImageJ is shown in figure 14. The origin lab software was used to plot this graph and B-spline function used to draw curve for smotthness. There is some amount of drop in stain degradation between 1-10 rubbing cycles in all samples but not very significant. This is happening because loosely attached cellulose-TiO_2 ging away at initial abrasion. After 10 cycles of rubbing there is no substantial change on wine stain degradation under UV irradiation for 15 min. Trend shows that stain degradation decreases with decreasing concentration of TiO_2 as rubbing cycles increases. Therefore, cellulose-TiO_2 coated cotton fabric is stable against rubbing.

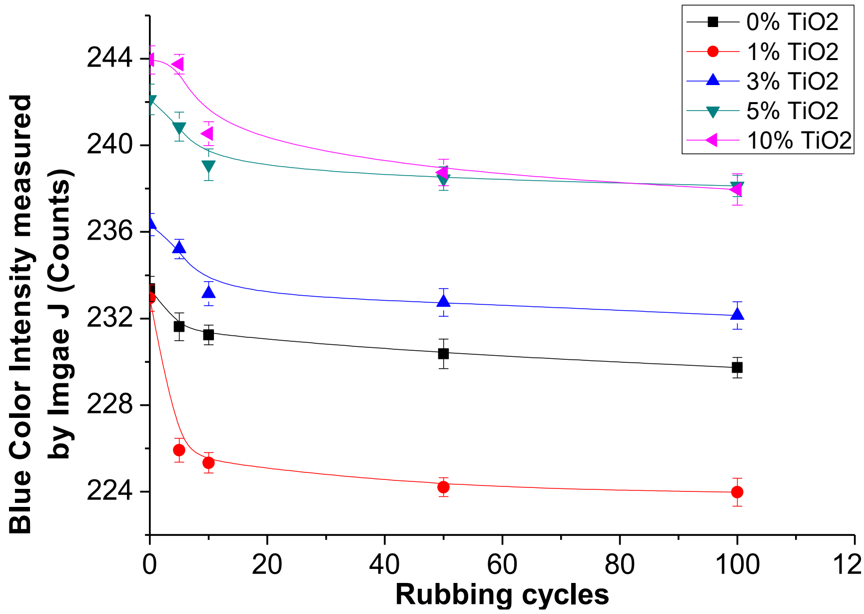


Figure 14. Evaluation of rubbing effect on wine stain degradation after 15 min of UV irradiation by ImageJ

5.6 Stiffness

5.6.1 Stiffness of cellulose coated cotton fabric in Urea–Thiourea–NaOH solvent system

Different concentrations of cellulose solution were prepared by dissolving cellulose in the Urea–Thiourea–NaOH–Water solvent system. The cellulose concentration was increased up to 5 % by decreasing the water concentration. This solvent can clearly dissolve a maximum of 6 % cellulose, but such 6 % solution has very high viscosity and is difficult to apply to fabric. The prepared cellulose solution was applied on cotton fabric by using roller padding to increase its stiffness permanently. The stiffness of the control as well as coated cotton fabrics was measured using a TH-7 instrument [57]. Figure 15 shows the effect of cellulose coating on the stiffness of the cotton fabric. The cotton fabric with 5 % cellulose coating showed very high stiffness compared with the other samples. From figure 16 it is also clear that the stiffness increased with increasing cellulose concentration. The SEM micrographs in figure 6 reveal that the coated cellulose was attached homogeneously to the fabric surface, which is why the stiffness was high and permanent. The coated cellulose was homogeneously distributed over the fabric surface because, during coating, the solvent molecules try to dissolve the fabric cellulose and link cellulose chains together. It is not easy to prove such linking by spectroscopic methods, because both molecules are the same. However, from the results of SEM imaging and the washing study, it is clear that there is a link between both kinds of cellulose chains, which is why the coated cellulose was not removed by the water during washing.

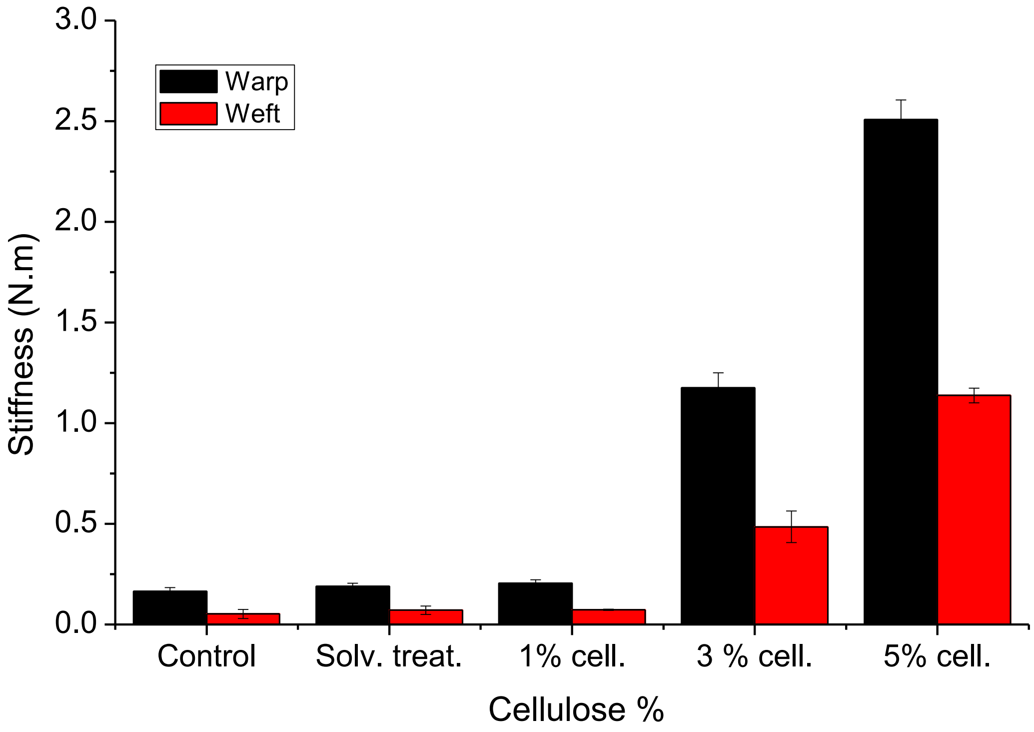


Figure 15. Stiffness of uncoated and coated samples.

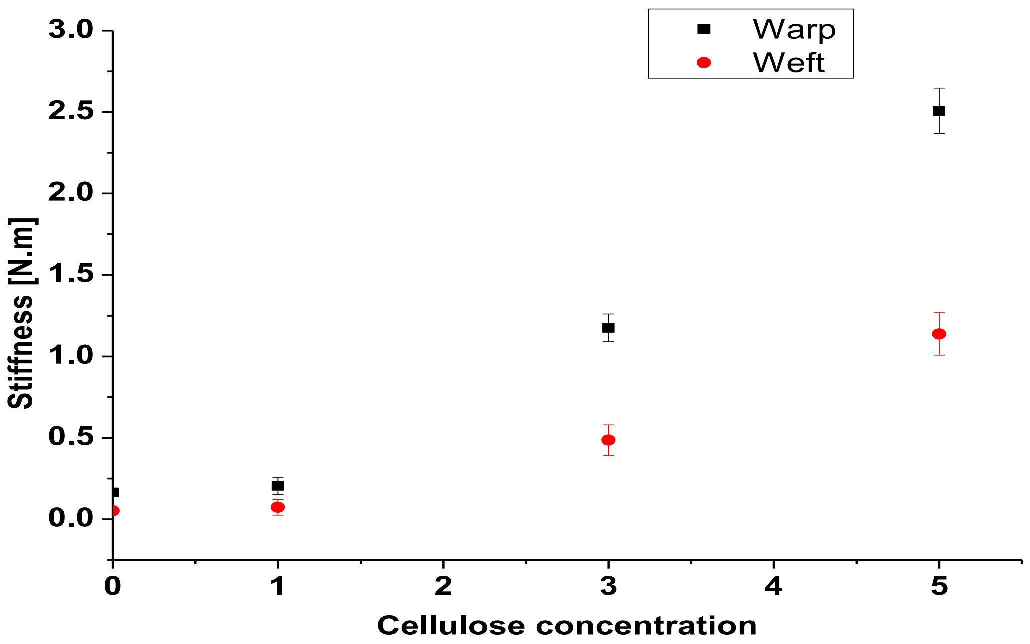


Figure 16. Effect of cellulose concentration on stiffness of cotton fabric

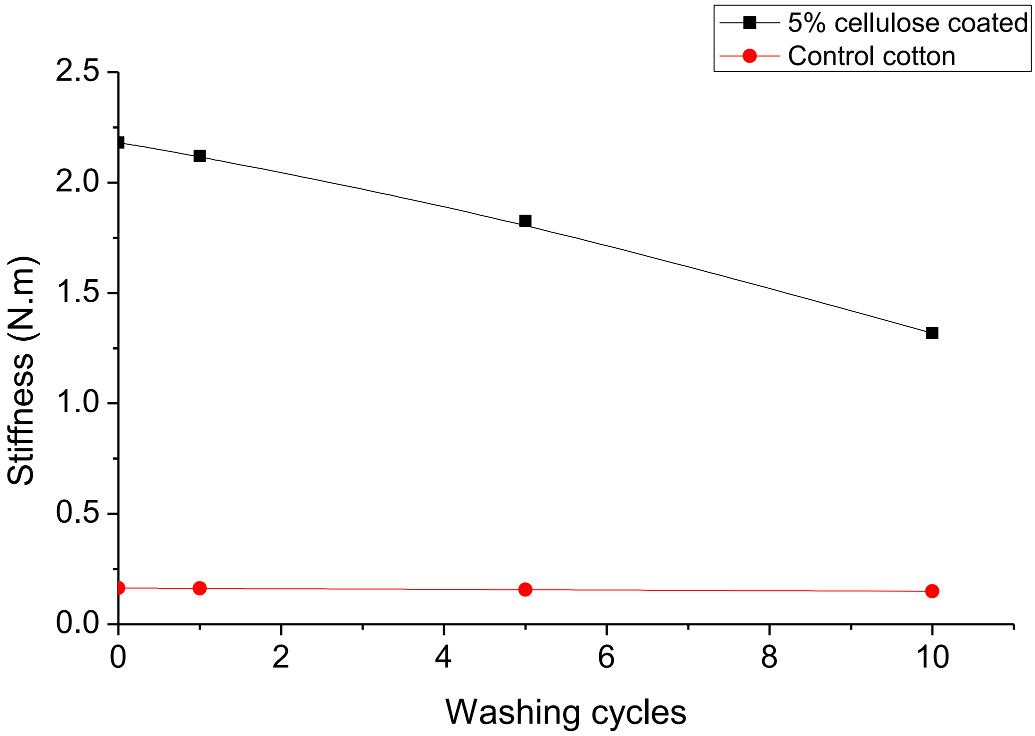


Figure 17. Durability of only cellulose coated cotton fabric against washing

Figure 17 shows the effect of washing on the stiffness of the cotton fabric. In figure 17, the exponential curves are form of the equation $B=B_0+(B_\infty-B_0)\ (1-e^{-kw})$. Here *B* is calculated stiffness, B_0 is observed highest stiffness in sample, $B\infty$ is maximum stiffness (3 N.m), *k* is constant and *w* is washing cycle. This study was carried out with the 5 % cellulose-coated sample. Samples were washed with 4-gpl soap detergent at 40 °C. Figure 17 shows that the stiffness decreased slightly after the first washing, but thereafter there was no drastic change, and the stiffness remained high even after 10 washing cycles. There was no significant drop in stiffness after 5 washing cycles, because the stiffness decreased by only 0.29 N m between 5 and 10 washing cycles. This indicates that there is no need to reapply cellulose solution like starch. This study confirms that the stiffness obtained after applying cellulose to the surface of cotton fabric is permanent.

5.6.2 Stiffness of cellulose-TiO_2 coated cotton fabric in 60% Sulfuric acid solution

Stiffness is a special property of the fabric. It is a tendency of the fabric to keep standing without support. The bending force was measured to calculate the stiffness of the fabric on TH-7 instrument. Figure 18 compares the stiffness of control fabric with cellulose-TiO_2 coated cotton fabric. It is clear from figure 18 that the stiffness increases significantly when the cotton fabric is coated with cellulose. The stiffness was slightly decreased when TiO_2 was added to the cellulose solution because viscosity of cellulose solution decreases after mixing TiO_2. Xu et al explain how viscosity decreases after adding small amount of nanoparticles in to solution [61]. Viscosity decreases after adding TiO_2 in cellulose solution because nanoparticles reduce the polymer chain entanglement. Stiffness of all coated samples was higher than the control cotton fabric sample and comparable to starched sample. Stiffness of coated samples is in the range of 1.07 - 1.22 Nm. Solvent treated cotton fabric shows similar stiffness to control cotton fabric that means there was no effect of solvent treatment on stiffness of cotton fabric. Hence, cellulose coating increases the stiffness of cotton fabric significantly.

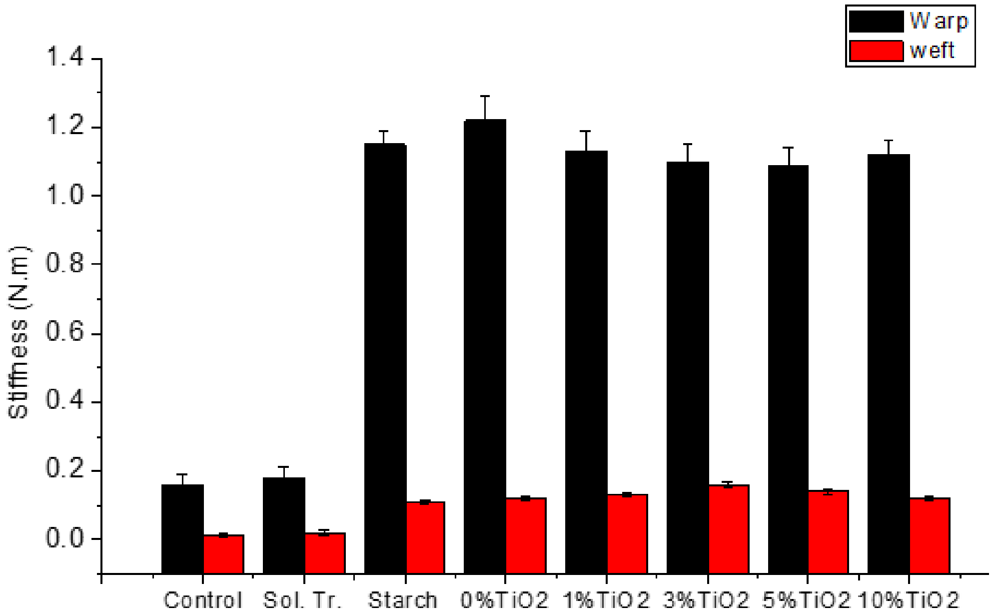


Figure 18. Stiffness of control, Solvent treated (Sol. Tr.), Starched, only cellulose (0% TiO_2) and cellulose-TiO_2 coated cotton fabric.

5.7 Durability stiffness against washing of cellulose-TiO_2 coated cotton fabric

To study the effect of washing on stiffness of cellulose-TiO_2 coated cotton fabric, the fabric was washed with 4 g/l detergent at 40^0C for 1 hr. Figure 19 shows the effect of washing on stiffness of coated fabrics. Coated samples with 1, 3 and 5 % TiO_2 show very good durability against washing up to 20 cycles.

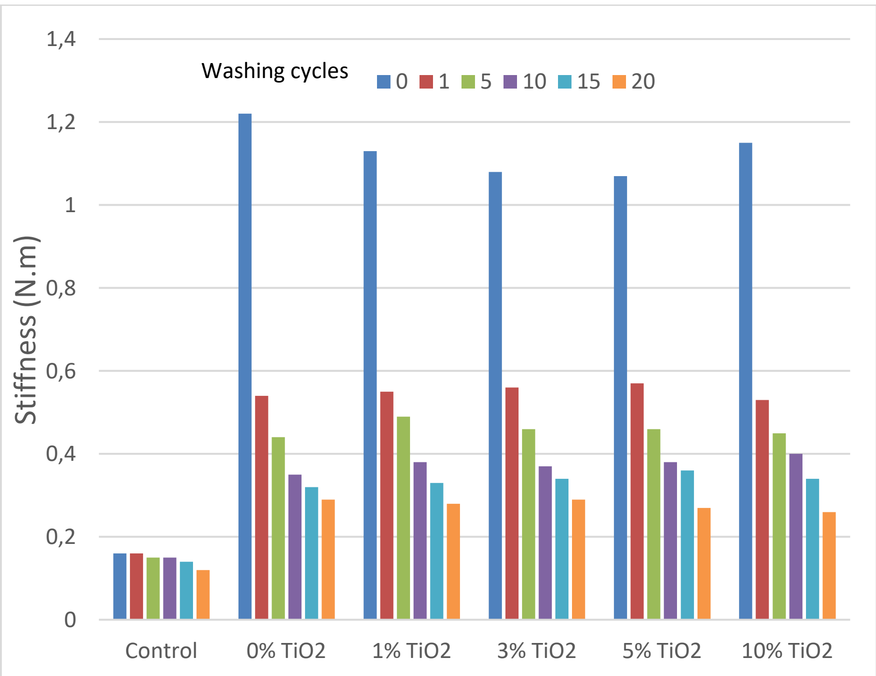


Figure 19. Durability of stiffness against washing

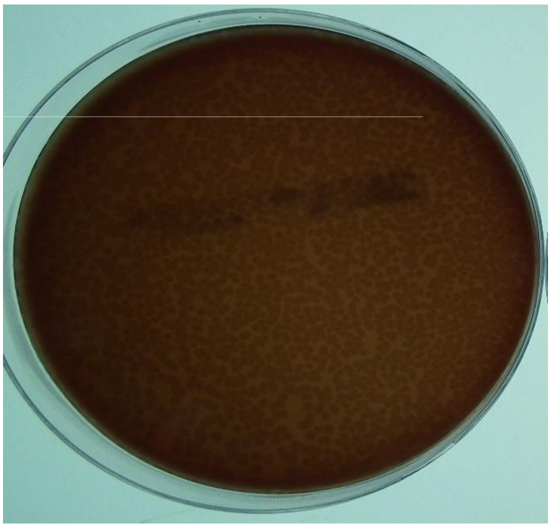
It is apparent from the figure 19 that stiffness decreased after 1st washing. However, the stiffness was stable after first washing with all cellulose-TiO_2 coated samples as compare to starched fabric. The fabric stiffness dropped after first cycle of washing by 0.68 Nm because loosely attached cellulose was washed away with water. There is no significant drop in stiffness after first washing because the stiffness was slightly decreased until after the 20th cycle of washing. Therefore, there is no need to reapply cellulose solution unlike starch. This study confirms that significantly higher level of stiffness is preserved as compared to starched fabric.

5.8 Antibacterial activity of cellulose-TiO_2 coated cotton fabric

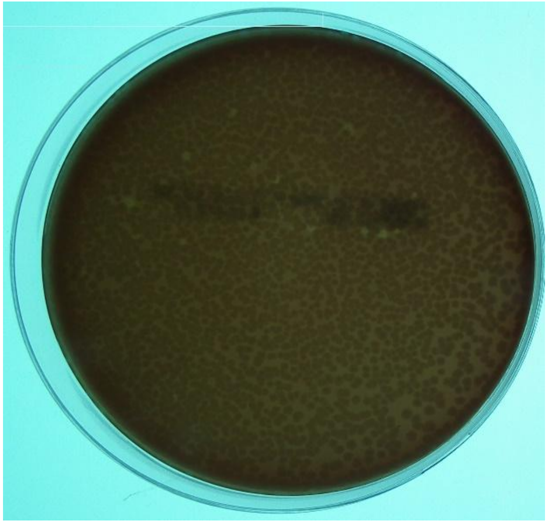
Effect of TiO_2 coating on the growth of bacterias such as Escherichia coli G- CCM 2024, Klebsiella pneumoniae G- CCM 2318, Stapgylococcus aureus G+ CCM 226 a MRSA (methicillin-resistant Staphylococcus aureus) G+ CCM 4223 were investigated. Figure 20 & 21 show the pictures of bacterial growth on coated and uncoated cotton fabric against S. aureus (figure 20) and MRSA (figure 21). Table 2 reflects the observation of bacterial reduction by AATCC 100. Table 2 shows that compact bacteria's were obtained in case of G-ve Escherichia coli (EC) and Klebsiella pneumonia (KP) bacterias. Table 3 gives the percentage reduction/multiplication of the test bacteria (G+ve S. aureus and MRSA) confirmed quantitatively utilizing the AATCC100 method. It is observed that the coating of fabrics with TiO_2-cellulose had a positive reduction of S. aureus bacteria and MRSA bacteria. The effectiveness of the anti-microbial activity increased with increase in the concentration of the TiO_2 coating.

Table 2. Observation of bacterial reduction by AATCC 100

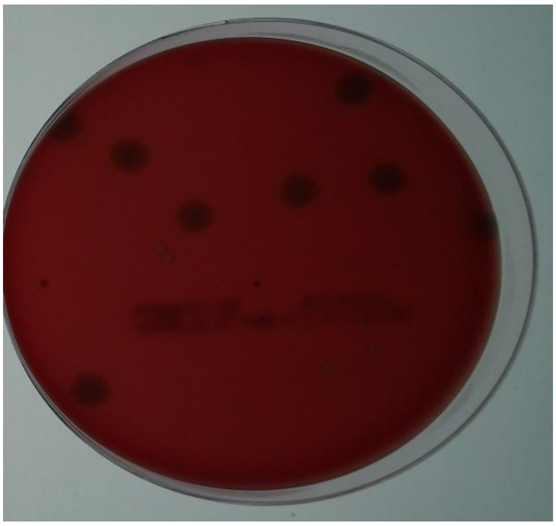
Method: AATCC100	Control	Cellulose coated	1% TiO_2	3% TiO_2	5% TiO_2	10% TiO_2
Escherichia coli 10^5 CFU/ml	Compact bacteria occurrence	Compact bacteria occurrence	Compact bacteria occurrence	Compact bacteria occurrence	Compact bacteria occurrence	Compact bacteria occurrence
Klebsiella pneumoniae 10^5 CFU/ml	Compact bacteria occurrence	Compact bacteria occurrence	Compact bacteria occurrence	Compact bacteria occurrence	Compact bacteria occurrence	Compact bacteria occurrence
Staphylococcus aureus 10^5 CFU/ml	960	900	68	32	22	17
MRSA 10^5 CFU/ml	104	120	98	42	34	22



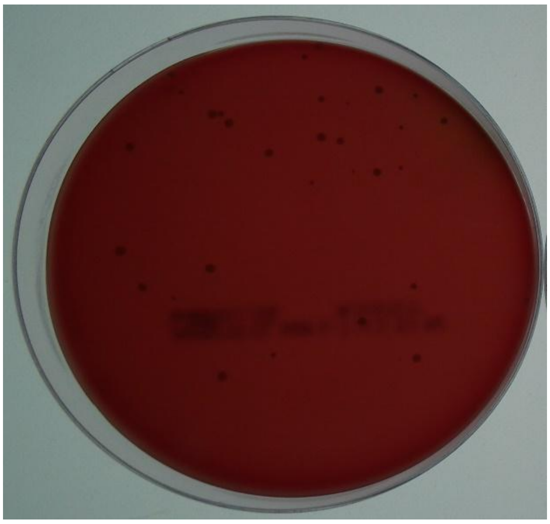
Control



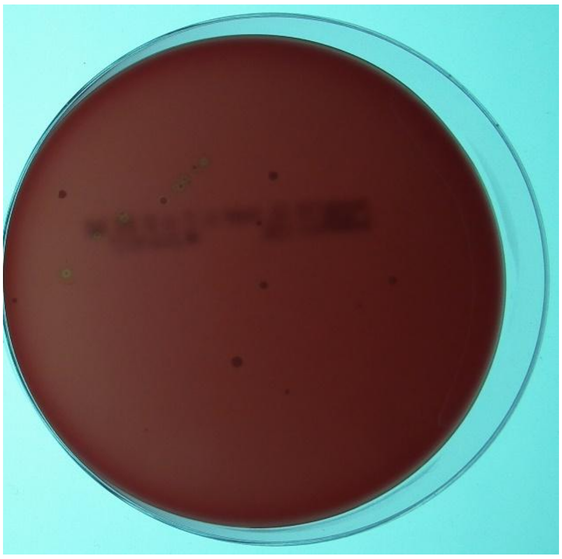
1% TiO_2



3% TiO_2

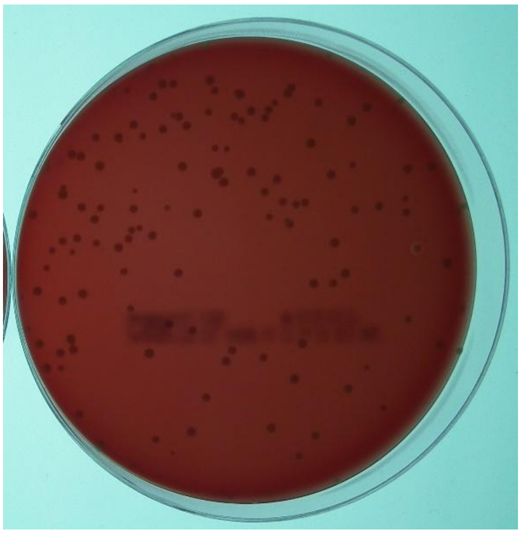


5% TiO_2

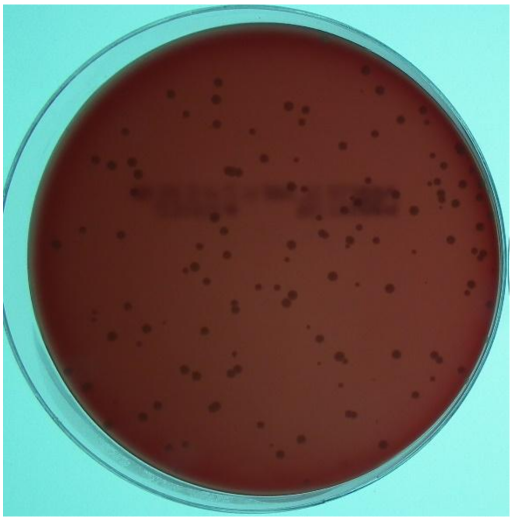


10% TiO_2

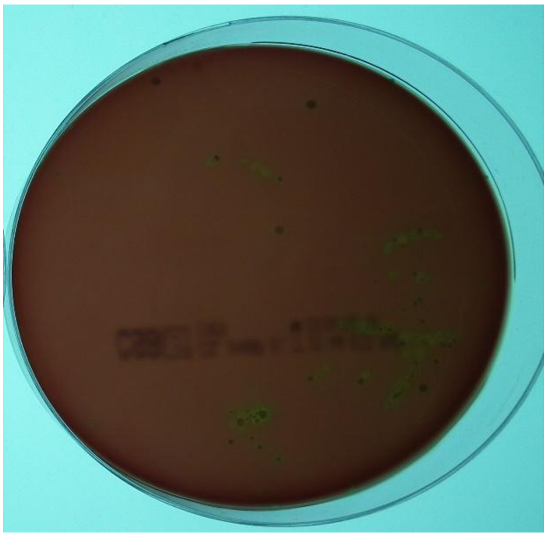
Figure 20. Antibacterial activity against Staphylococcus aureus bacteria



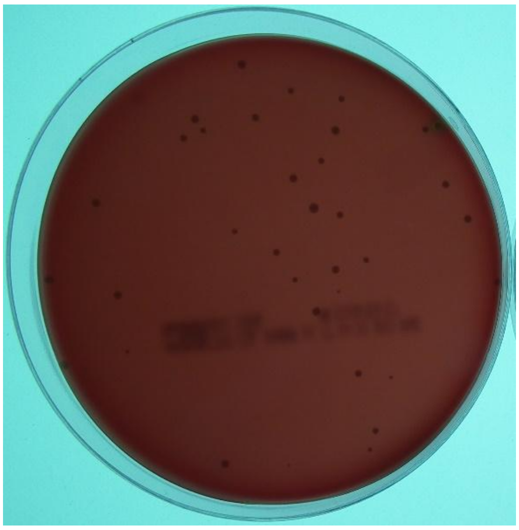
Control



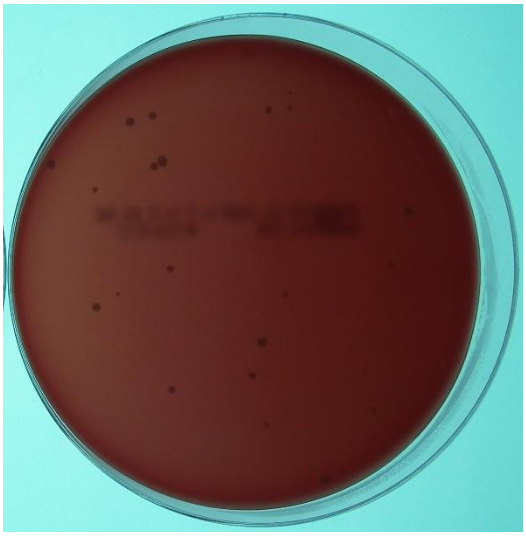
1% TiO_2



3% TiO_2



5% TiO_2



10% TiO_2

Figure 21. Antibacterial activity against Methicillin-resistant Staphylococcus aureus

Fabrics treated with 1% TiO_2 had the lowest S. aureus bacterial reduction. However, with an increase in the concentration of TiO_2, there was a high jump from 6.3% to 96.7% reduction of S. aureus bacteria on 3% TiO_2 treated fabrics. These results confirm that sample coated with 3, 5 and 10% TiO_2-cellulose show strongest inhibition efficiency against bacteria's. The effectiveness of the anti-microbial activity increased with increase in the concentration of the TiO_2 coating. Fabrics treated with 1% TiO_2 had the lowest S. aureus bacterial reduction, however with an increase in the concentration of TiO_2, there was a high jump from 6.3% to 96.7% reduction of S. aureus bacteria on 3% TiO_2 treated fabrics. Therefore, sample coated with 3, 5 and 10% TiO_2-cellulose show strongest inhibition efficiency against G+ bacteria's and compact bacterias occurred against G- bacterias. Same samples were analysed according to AATCC147 standatrd method to investigate antibacterial activity. Unlike AATCC100, the results from AATCC147 (Table 4) shows no effect of cellulose-TiO_2 coating on G-ve bacterias such as Escherichia coli (EC) and Klebsiella pneumonia (KP). Also there is no effect of coating on G+ve Staphylococcus aureus (SA) and Methicillin resistant staphylococcus aureus (MRSA).

Table 3. Quantitative evaluation of bacterial reduction

Test Sample	Bacterial Reduction/Multiplication	
	Staphylococcus aureus (SA)	Methicillin-resistant Staphylococcus aureus (MRSA)
Control	-	-
1% TiO_2	6.3	13.3
3% TiO_2	96.7	65.0
5% TiO_2	97.7	68.3
10% TiO_2	98.2	81.6

Table 4. Evaluation of antibacterial testing by AATCC 147

Method: AATCC147	Control Cotton fabric	Cellulose coated cotton fabric	1 % TiO_2	3 % TiO_2	5 % TiO_2	10 % TiO_2
Escherichia coli 10^5 CFU/ml	No effect	No effect	No effect	No effect	No effect	No effect
Klebsiella pneumoniae 10^5 CFU/ml	Halo zone not clear ∅ 1,74 mm	No effect	No effect	No effect	No effect	No effect
Staphylococcus aureus 10^5 CFU/ml	Halo zone not clear ∅ 4,93 mm	No effect	No effect	No effect	No effect	No effect
MRSA 10^5 CFU/ml	No effect	No effect	No effect	No effect	No effect	No effect

5.9 Evaluation of antifungal activity of cellulose-TiO_2 coated cotton fabric

Antifungal activity of TiO_2 coated cotton fabric was evaluated with mixture of Penicillium digitatum (CCM F-382), Rhizopus stolonifer (CCM F-445), Cladosporium sphaerospermum (CCM F-351), Chaetomium globosum (CCM 8156) fungi's in aqueous suspension at a concentration of 10^6 CFU/ml. Figure 22 (a, b, c, d and f) shows the results of antifungal test. The surface of agar in the Petri dishes was completely covered with fungi (filamentous hyphae forming the mycelium) in the first 4 days. However, the filamentous hyphae (mycelium) started to lose from the surface over the second week.

Figure 22. Antifungal activity of (a) Control (b) 1% TiO_2 (c) 3% TiO_2 (d) 5% TiO_2 and (e) 10 % TiO_2 coated cotton fabric

Finally, the samples containing the titanium dioxide of 5 and 10% were most cleared. The reason of this antibacterial activity is photocatalytic effect of TiO_2, but this effect occurred slowly and later (during the second week of cultivation). The amount of fungi decreased with increasing concentration of TiO_2 from the beginning. Thus, long-term antifungal effect was observed on samples of cotton fabrics coated with TiO_2 at concentration of 5% or higher and according to the EN 14119, 2003 Standard [60] the grow of fungi ranged between degree 2 (high concentration of TiO_2) and 4 (low concentration of TiO_2) on the samples.

5.10 Investigation the effect of cellulose-TiO_2 coating and strong solvent on cellulose structure by X-ray diffraction patterns

5.10.1 Effect of cellulose-TiO_2 coating and 60% Sulfuric acid on structure of cellulose

X-ray diffraction patterns were obtained to detect TiO_2 and to investigate the effect of 60 % H_2SO_4 solvent on cotton fabric. Figure 23 shows the X-ray diffraction patterns of the control and cellulose-TiO_2 coated cotton fabric. The characteristic peak at 2θ 25.4° shows the presence of TIO_2 in 3, 5 and 10 % TiO_2 coated cotton fabric. 1 % TiO_2 coated cotton fabric does not show this peak presumably due to the lower concentration of TiO_2. It can be seen from figure 23 that the peak height of TiO_2 at 25° increases with increasing concentration of TiO_2. X-ray diffraction spectra of the control and cellulose-TiO_2 coated cotton fabric exhibited main characteristic diffraction peaks at 14.7°, 16.3°, and 22.4° of cellulose I. The small peak at 12.3° and the bigger shoulder at 20° confirm the presence of cellulose II in both control and the solvent treated samples. The control cotton fabric (figure 24) shows the peak of Cellulose II because of the chemical treatments used during the fabric processing to improve the properties of cotton, such as dimensional stability, reactivity, luster etc. The amount of cellulose II was estimated by simulation method [62-64]. The 'a' value ($I\beta$ unit cell) was adjusted to 0.7906 nm from 0.7784 nm, because less perfectly ordered cotton cellulose.

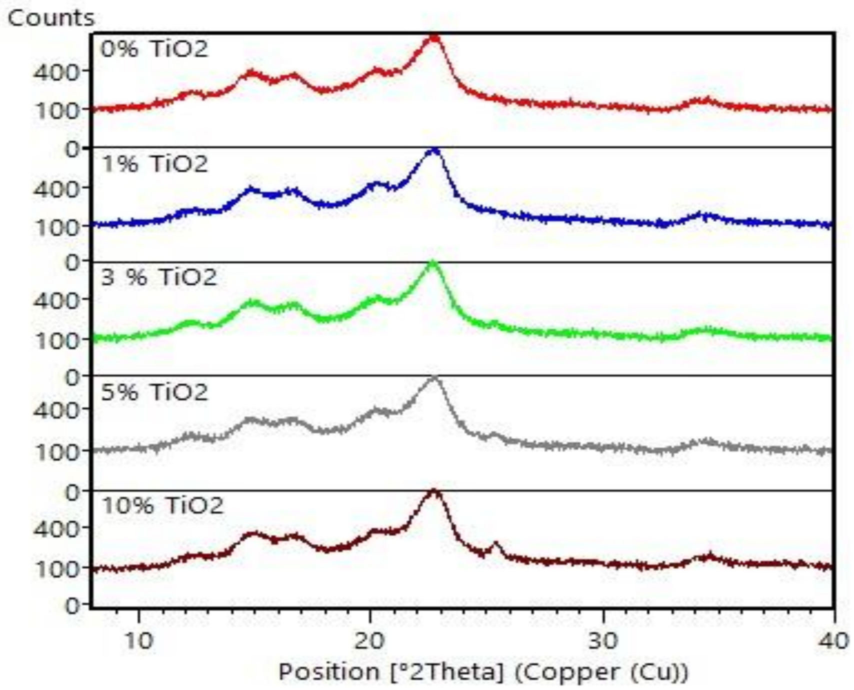


Figure 23. X-ray diffraction patterns of cellulose-TiO_2 coated cotton fabric

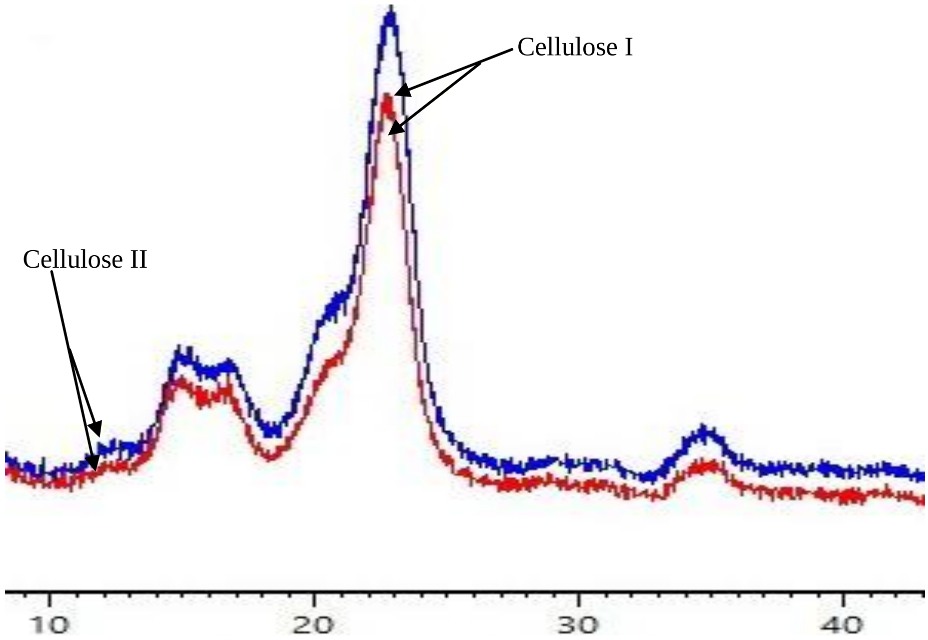


Figure 24. Diffraction pattern of Control (red curve) and solvent (without cellulose) treated (blue curve) cotton fabric

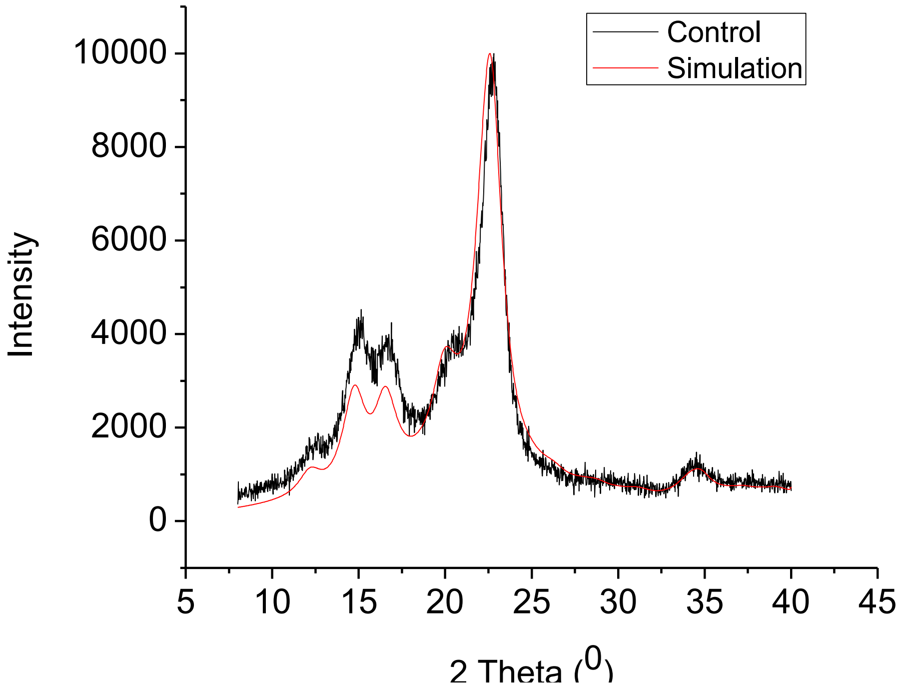


Figure 25. Diffraction pattern of control cotton fabric fitted with simulated pattern

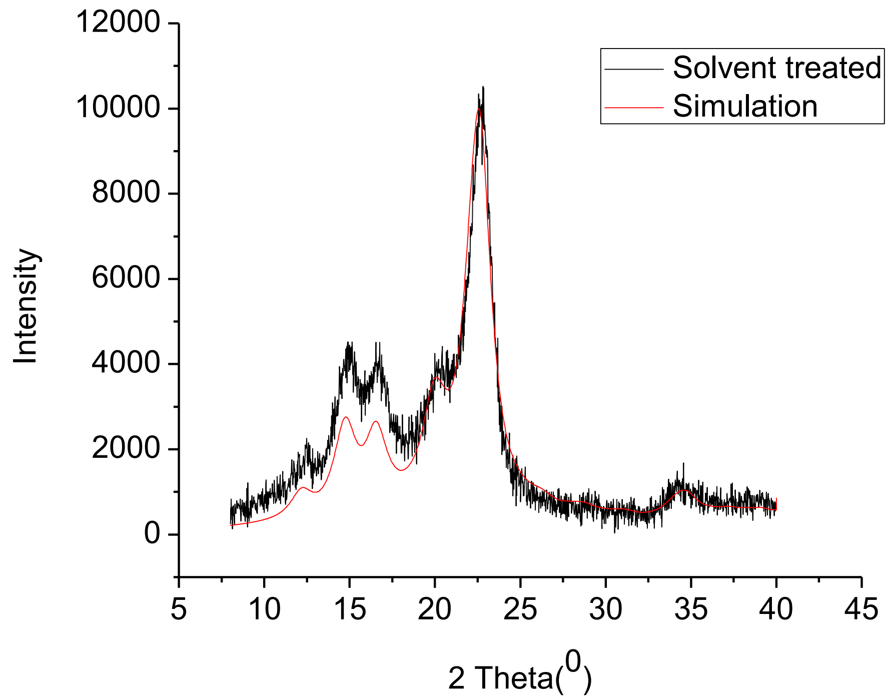


Figure 26. Diffraction pattern of 60 % H_2SO_4 treated cotton fabric fitted with simulated pattern.

The basic idea of this simulation is to fit combined x-ray diffraction patterns of cellulose I, II and amorphous fractions obtained from Mercury 3.0 program with diffraction pattern of treated sample to quantify cellulose fractions. Diffraction intensities, output by the Mercury program from the Cambridge Crystallographic Data Centre, have several uses including comparisons with experimental data. Calculated intensities from different polymorphs can be added in varying proportions using a spreadsheet program to simulate patterns such as those from partially mercerized cellulose or various composites.Amorphous cellulose significantly influences the diffraction pattern and that is why it was included in the simulation. To incorporate amorphous fraction into the simulation, the diffraction pattern of Cellulose II at 9 deg. FWHM was used [63]. Figure 25and 26 are the diffraction patterns of 60 % H_2SO_4 solvent treated and control cotton fabrics respectively fitted with corresponding simulated pattern. Table 5 shows the composition of cellulose in 60% H_2SO_4 solvent treated and control cotton fabric. Solvent (60 % H_2SO_4) treated cotton fabric shows 22.2 % cellulose II, which slightly higher than the control sample (16.9 %), that means there is an effect of the solvent on cotton fabric during coating. The effect of solvent on structure of cotton fabric was negligible because the treatment time was of 20 sec duration at room temperature which was the same conditions used for cellulose coating.

5.10.2 Effect of NaOH-Urea-Thiourea-Water solvent system on cellulose structure

The effect of the urea–thiourea–NaOH–water solvent system on the cotton fabric was analyzed using X-ray diffraction analysis. Figure 27 shows an overlay of the X-ray diffraction spectra of the original (black) and regenerated (red) cellulose pulp, while figure 28 shows an overlay of the X-ray diffraction spectra of control (black) and urea–thiourea–NaOH–water-treated (red) cotton fabric. In figure 27, the characteristic peak of cellulose I at 16.20° is missing for the regenerated pulp cellulose while the peaks at 12.3° and 21.20° show that the structure of the pulp cellulose has been converted from cellulose I to II. The X-ray diffraction spectra and overlapping peak resolution of the control and solvent-treated cotton fabric show main characteristic diffraction peaks at 14.7°, 16.3°, and 22.4° for cellulose I. The small peak at 12.3° and larger shoulder at 20° show the presence of cellulose II in both samples (figure 28) with slightly more in the solvent-treated (red curve) sample. The control cotton fabric showed peak of cellulose II because of the chemical treatments used during fabric processing to improve properties of cotton such as its dimensional stability, reactivity, luster, etc. [65]. The amount of cellulose II was estimated by the simulation method [62-64]. The *'a'* value was adjusted to 0.7906 nm because of the less perfectly ordered cotton cellulose. Amorphous cellulose significantly influenced the diffraction pattern and was therefore included in the simulation. The diffraction pattern of cellulose II with FWHM of 9° was used for amorphous cellulose[63] in the simulation. Figures 29 and 30 show the diffraction pattern of the control and solvent-treated cotton fabrics, respectively, fit with the corresponding simulated pattern.

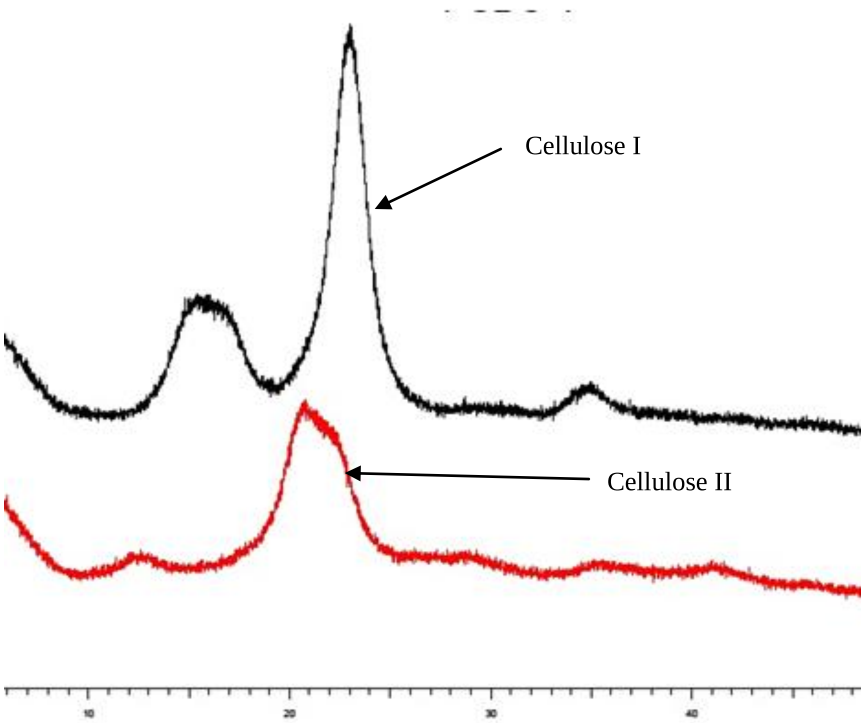


Figure 27. X-ray diffraction pattern and analysis of original (Black) and regenerated (Red) cellulose pulp.

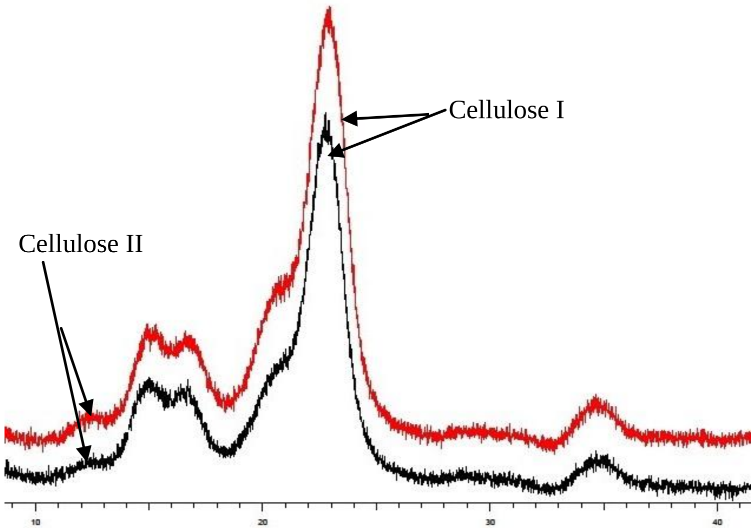


Figure 28. X-ray diffraction pattern and analysis of control (black) and solvent treated cotton fabric (Red).

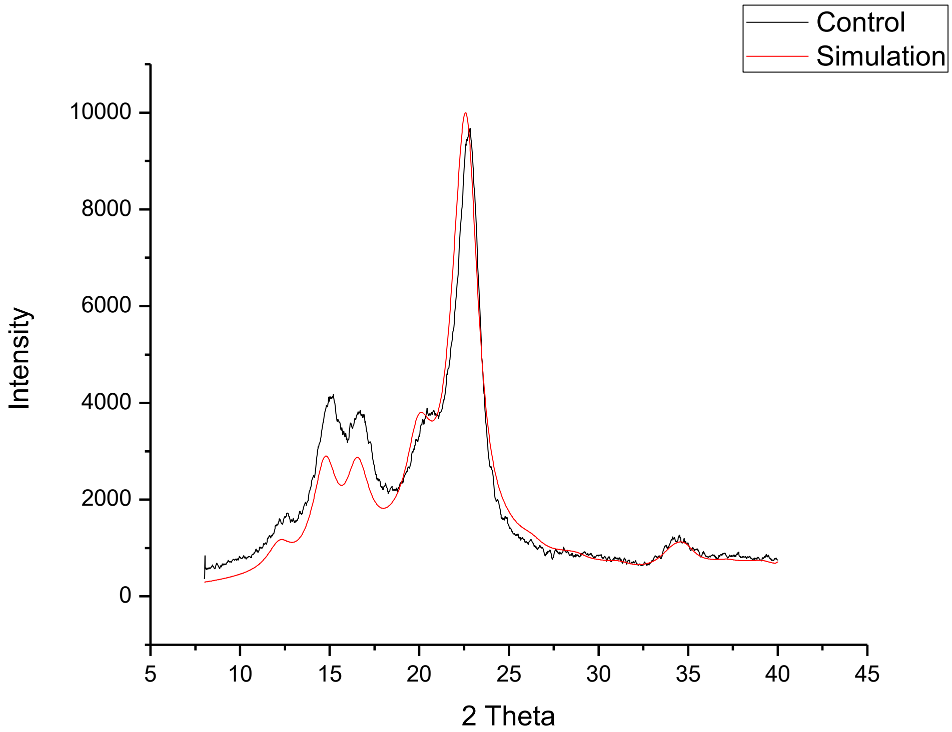


Figure 29. Diffraction pattern of control cotton fabric fitted with simulated pattern.

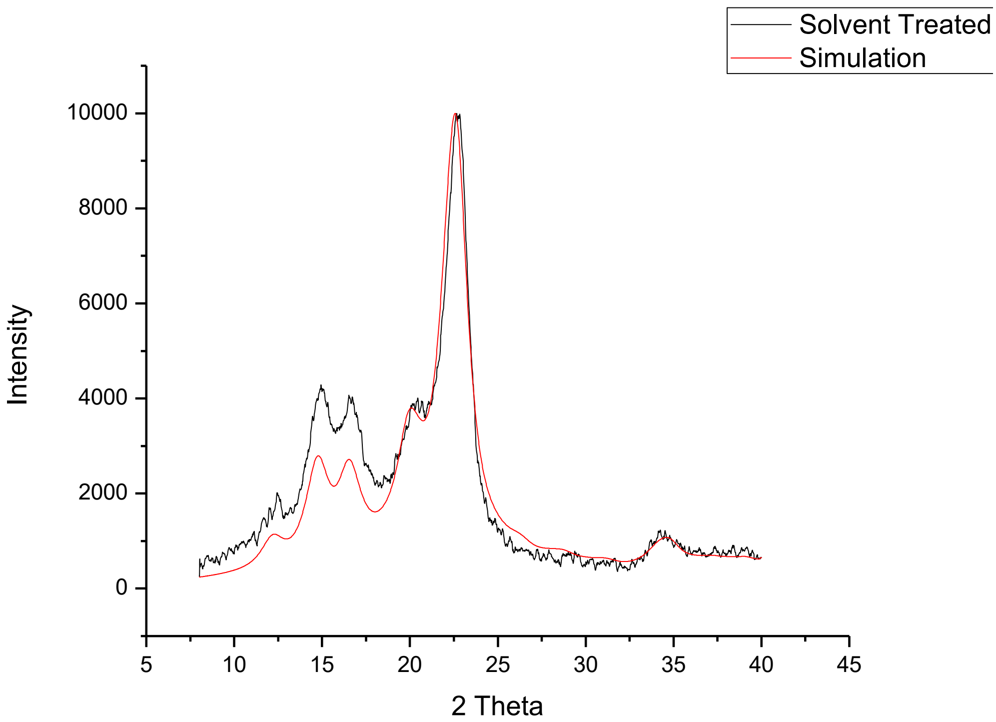


Figure 30. Diffraction pattern of solvent treated cotton fabric fitted with simulated pattern.

Table 5 presents the composition of cellulose in the control and solvent-treated cotton fabric. Solventtreated cotton fabric showed a slightly greater amount of cellulose II (21.5 %) compared with the control sample (16.9 %), indicating a solvent effect on the cotton fabric during coating. The effect of the urea–thiourea–NaOH–water solvent system on the structure of the cotton fabric was small because the treatment time was just 20 second at room temperature, with the same conditions used for cellulose coating.

Table 5. Estimation of cellulose fractions

Sample description	Cellulose I [%]	Cellulose II [%]	Amorphous cellulose [%]
Control cotton fabric	47.5	16.9	35.6
NaOH-Urea-Thiourea-Water	45.2	21.5	33.3
60 % H_2SO_4 treated cotton fabric	44.7	22.2	33.1

5.11 Colour strength and related parameter

The K/S value of the dyed fabric was directly proportional to the amount of dye present in the fabric. The relative color strength (%) and K/S values of the cellulose-coated dyed samples are presented in Table 6 from which it is clear that the K/S values of the cellulose-coated dyed fabrics were lower than for control dyed samples. Dye uptake decreased as the cellulose concentration was increased, as reflected in the observed values. Reactive Blue 49 dye showed better dyeability than Reactive Red 240 or Reactive Yellow 95. The lower K/S values for the cellulose-coated cotton fabrics are related to the applied cellulose.

Table 6. Spectrophotometric analysis of dyed sample

Dye Content [% owf]	Dye	Cellulose concentration [%]	L*	a*	b*	ΔE	K/S	Standard Deviation [σ] K/S	C.I. (Half size) K/S	Relative color strength [%]
3	Reactive Red 240	Control	53.22	61.15	2.25	0	7.29	0.65	0.81	100
		1	59.33	62.21	2.75	6.22	2.54	0.38	0.47	34.87
		3	61.34	62.98	3.23	8.38	2.36	0.25	0.31	32.45
		5	63.75	63.26	3.56	10.81	2.25	0.32	0.40	30.97
	Reactive Yellow 95	Control	81.51	16.63	66.91	0	8.15	0.45	0.56	100
		1	82.59	17.26	67.49	1.37	3.74	0.85	1.05	45.98
		3	82.87	15.14	61.93	5.37	3.07	0.63	0.78	37.72
		5	84.32	21.28	73.46	8.51	3.21	0.56	0.70	39.45
	Reactive Blue 49	Control	24.91	-3.89	-18.1	0	20.47	0.25	0.31	100
		1	25.12	-3.45	-17.18	1.04	13.72	1.32	1.64	67.03
		3	27.25	-2.77	-15.99	3.34	13.3	1.25	1.55	64.98
		5	28.32	-2.45	-15.58	4.47	12.49	1.71	2.12	61.04
9	Reactive	Control	42.17	59.55	13.72	0	20.75	0.61	0.76	100

	Red 240	1	47.26	61.1	5.66	9.65	12.14	1.98	2.46	58.51
		3	48.37	61.85	5.72	10.37	8.79	1.59	1.97	42.36
		5	49.98	62.12	5.85	11.38	7.7	1.92	2.38	37.15
	Reactive Yellow 95	Control	73.32	15.53	69.91	0	21.73	0.31	0.38	100
		1	75.59	16.26	67.49	3.39	13.67	0.92	1.14	62.92
		3	80.87	16.64	66.93	8.19	12.1	1.45	1.80	55.69
		5	82.32	17.12	62.46	11.79	8.71	2.1	2.61	40.09
	Reactive Blue 49	Control	16.11	-4.22	-15.1	0	26.63	1.21	1.50	100
		1	16.92	-3.35	-14.68	1.26	23.28	1.82	2.26	87.41
		3	17.25	-3.67	-14.09	1.61	22.59	1.61	2.00	84.83
		5	18.32	-3.75	-13.78	2.61	17.12	1.77	2.20	64.31
15	Reactive Red 240	Control	37.94	57.92	14.72	0	24.91	1.10	1.37	100
		1	46.1	58.1	5.56	12.26	13.46	1.55	1.92	54.05
		3	47.21	58.98	5.61	13.04	12.4	1.20	1.49	48.32
		5	47.42	59.23	5.67	13.17	9.14	1.65	2.05	36.7
	Reactive Yellow 95	Control	69.32	14.63	66.91	0	25.74	0.85	1.05	100
		1	72.52	17.26	59.49	8.49	16.13	1.62	2.01	62.67
		3	74.38	15.14	58.93	9.46	15.46	1.23	1.53	60.05
		5	75.13	21.28	59.46	11.55	11.71	1.10	1.37	45.48
	Reactive Blue 49	Control	12.11	-5.45	-13.01	0	29.68	0.52	0.65	100
		1	15.02	-4.55	-12.88	3.04	25.6	0.95	1.18	86.26
		3	15.95	-4.87	-12.19	3.96	24.78	1.09	1.35	83.49
		5	16.41	-3.95	-11.78	4.71	18.69	1.32	1.64	62.99

The possible cause of this decrease is that the coated pulp cellulose was mercerized after dissolution, reducing dye uptake by the fabric because it was on the surface. Table 6 shows that the relative color strength (%) of the dyed samples decreased with increasing cellulose concentration for each shade % of the dye. These results further indicate that the cellulose coating decreased the dye uptake by the coated cotton fabric. The Commission Internationale de l'Eclairage (CIE) Lab system was used to determine the color parameters and color variation, where L* indicates the darkness–lightness value with 0 to 100 representing black to white, the a* value goes from negative (green) to positive (red), and the b* value goes from negative (blue) to positive (yellow); ΔE gives the total color difference. High L* values indicate that the dyed coated sample was lighter than the uncoated sample. Reactive Blue 49 dye showed lower L* values (Table 6) than Reactive Red 240 or Reactive Yellow 95. However, the L* value increased with increasing cellulose concentration, meaning that all the coated samples were brighter compared with uncoated cotton fabric.

The color difference values (ΔE) are presented in Table 6, showing that there was a significant color difference between the uncoated and coated cotton fabric samples with different cellulose concentrations, even though both samples were dyed with the same dye concentration. The ΔE values for the samples dyed with Reactive Blue 49 were better than for the other two dyes used for dyeing. Hence, Reactive Blue 49 showed better dyeability of coated cotton fabric compared with Reactive Red 240 or Reactive Yellow 95. ΔE for Reactive

Blue 49 dyed samples are better than other two dyes which was used for dyeing. Hence the Reactive Blue 49 has better dyeability to coated cotton fabric as compare to Reactive Red 240 and Reactive Yellow 95.

5.12 Evaluation of fastness properties

During the use of textiles, they are frequently put through washing, rubbing & perspiration, therefore durability of coated cotton fabric to these conditions is very important and that's why it was evaluated and given in Table 7. Washing and rubbing fastness was evaluated for all the three types of dyed fabric. Washing fastness of cellulose coated cotton fabric for staining with adjacent fabrics (wool and cotton) for all dyed fabrics are excellent (4–5) & for change in color are also fine (2-3). Ratings against rubbing for cellulose coated cotton fabrics are good, 4 at dry rubbing and 3 at wet rubbing conditions. Thus, there is no significant impact of cellulose coating on washing and rubbing fastness properties of cotton fabric. Perspiration fastness at acidic & alkaline condition in terms of gray scale ratings for cellulose coated and uncoated samples are given in Table 8. The gray scale ratings in the case of cellulose coated dyed samples for change in color are 2-3 at both acidic and alkaline, that means dyed samples are sensitive towards pH. Rating 4-5 for staining with wool as adjacent fabrics are excellent and with cotton as adjacent fabric are also good. Perspiration fastness was observed for all three kind of dyed samples and almost ratings are similar to all dyed samples. Hence the perspiration fastness after coating cellulose on the surface of cotton fabric remain good.

Table 7. Washing and Rubbing Fastness properties assessment of dyed samples

Dye Content [% owf]	**Dye**	**Cellulose Content [%]**	**Wash Fastness**			**Rubbing Fastness**	
			Evaluation of change in color	Evaluation of staining		Evaluation of staining	
				Cotton	Wool	Dry	Wet
3	Reactive Red 240	Control	2-3	4-5	4-5	4-5	3-4
		1	2-3	4-5	4-5	4-5	3-4
		3	2-3	4-5	4-5	4-5	3-4
		5	2-3	4-5	4-5	4-5	3
	Reactive Yellow 95	Control	2-3	4-5	4-5	4-5	3-4
		1	2-3	4-5	4-5	4-5	3-4
		3	2-3	4-5	4-5	4-5	3-4
		5	2-3	4-5	4-5	4-5	3
	Reactive Blue 49	Control	2-3	4-5	4-5	4-5	3-4
		1	2-3	4-5	4-5	4-5	3-4
		3	2-3	4-5	4-5	4-5	3-4
		5	2-3	4-5	4-5	4-5	3
9	Reactive Red 240	Control	2-3	4-5	4-5	4-5	3-4
		1	2-3	4-5	4-5	4-5	3-4
		3	2-3	4-5	4-5	4-5	3-4
		5	2	4-5	4-5	4-5	3
	Reactive Yellow 95	Control	2-3	4-5	4-5	4-5	3-4
		1	2-3	4-5	4-5	4-5	3-4
		3	2-3	4-5	4-5	4-5	3-4
		5	2	4-5	4-5	4-5	3
	Reactive Blue 49	Control	2-3	4-5	4-5	4-5	3-4
		1	2-3	4-5	4-5	4-5	3-4
		3	2-3	4-5	4-5	4-5	3-4
		5	2	4-5	4-5	4-5	3
15	Reactive Red 240	Control	2-3	4-5	4-5	4	3-4
		1	2-3	4-5	4-5	4	3-4
		3	2	4-5	4-5	4	3
		5	2	4-5	4-5	3-4	3
	Reactive Yellow 95	Control	2-3	4-5	4-5	4	3-4
		1	2-3	4-5	4-5	4	3-4
		3	2-3	4-5	4-5	4	3
		5	2	4-5	4-5	3-4	3
	Reactive Blue 49	Control	2-3	4-5	4-5	4	3-4
		1	2-3	4-5	4-5	4	3-4
		3	2-3	4-5	4-5	4	3
		5	2	4-5	4-5	3-4	3

Table 8. Perspiration Fastness assessment of dyed samples

Dye Content [% owf]	Dye	Cellulose Content [%]	Perspiration Fastness					
			Evaluation of change in color		Evaluation of staining			
					Acidic		Alkaline	
			Acidic	Alkaline	With wool	With cotton	With wool	With cotton
3	Reactive Red 240	Control	2-3	2-3	4-5	4-5	4-5	3-4
		1	2-3	2-3	4-5	4-5	4-5	3-4
		3	2-3	2-3	4-5	4-5	4-5	3-4
		5	2-3	2-3	4-5	4-5	4-5	3-4
	Reactive Yellow 95	Control	2-3	2-3	4-5	4-5	4-5	3-4
		1	2-3	2-3	4-5	4-5	4-5	3-4
		3	2-3	2-3	4-5	4-5	4-5	3-4
		5	2-3	2-3	4-5	4-5	4-5	3-4
	Reactive Blue 49	Control	2-3	2-3	4-5	4-5	4-5	3-4
		1	2-3	2-3	4-5	4-5	4-5	3-4
		3	2-3	2-3	4-5	4-5	4-5	3-4
		5	2-3	2-3	4-5	4-5	4-5	3-4
9	Reactive Red 240	Control	2-3	2-3	4-5	3-4	4-5	3-4
		1	2-3	2-3	4-5	3-4	4-5	3-4
		3	2-3	2-3	4-5	3-4	4-5	3-4
		5	2-3	2-3	4-5	3-4	4-5	3-4
	Reactive Yellow 95	Control	2-3	2-3	4-5	3-4	4-5	3-4
		1	2-3	2-3	4-5	3-4	4-5	3-4
		3	2-3	2-3	4-5	3-4	4-5	3-4
		5	2-3	2-3	4-5	3-4	4-5	3-4
	Reactive Blue 49	Control	2-3	2-3	4-5	3-4	4-5	3-4
		1	2-3	2-3	4-5	3-4	4-5	3-4
		3	2-3	2-3	4-5	3-4	4-5	3-4
		5	2-3	2-3	4-5	3-4	4-5	3
15	Reactive Red 240	Control	2-3	2-3	4-5	3-4	4-5	3-4
		1	2-3	2-3	4-5	3-4	4-5	3-4
		3	2-3	2-3	4-5	3-4	4-5	3-4
		5	2-3	2-3	4-5	3-4	4-5	3
	Reactive Yellow 95	Control	2-3	2-3	4-5	3-4	4-5	3-4
		1	2-3	2-3	4-5	3-4	4-5	3-4
		3	2-3	2-3	4-5	3-4	4-5	3
		5	2-3	2-3	4-5	3-4	4-5	3
	Reactive Blue 49	Control	2-3	2-3	4-5	3-4	4-5	3-4
		1	2-3	2-3	4-5	3-4	4-5	3-4
		3	2-3	2-3	4-5	3-4	4-5	3
		5	2-3	2-3	4-5	3-4	4	3

5.13 Mechanical properties

Breaking strength of cotton and cellulose-TiO_2 coated fabric was measured on Testometric M250 - 2.5 instrument. Breaking strength of coated and the uncoated cotton fabric is shown in figure 31. It is clear from figure 31 that the tensile strength increased after coating of cellulose-TiO_2 on the surface of the cotton fabric. The breaking strength of cellulose-TiO_2 coated fabric is increased by 65-83 N. The strength of coated fabric was increased because coated cellulose attaches on the surface in the form of thin layer and this attached cellulose provides additional strength to cotton fabric.

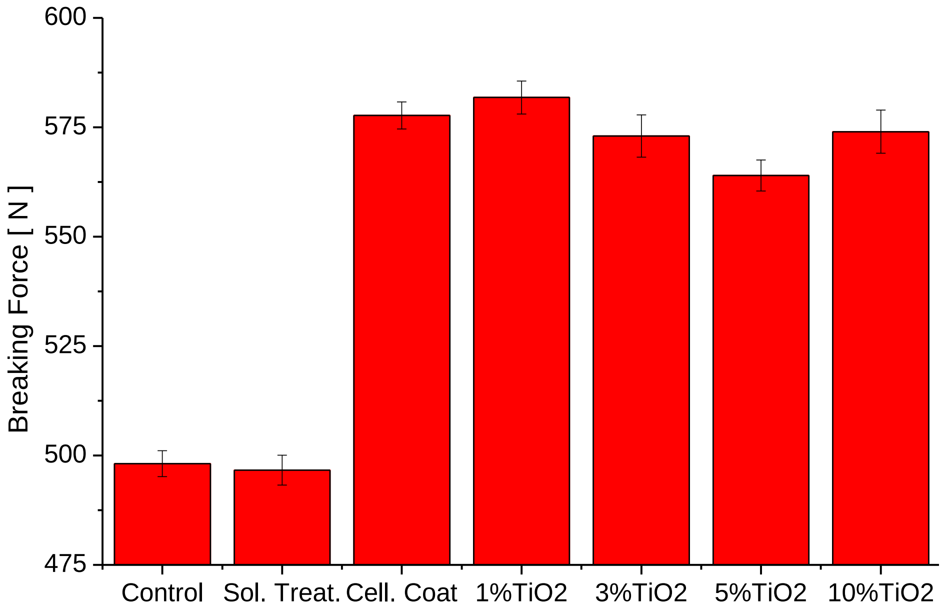


Figure 31. Breaking strength of control, Solvent treated (Sol. Treat.) and coated cotton fabrics.

Table 9. Mechanical properties

Sample description	Modulus (E) [Mpa]	Elongation [%]
Control	121.73	6.23
Solvent treated	121.37	7.33
Only cellulose coated	141.18	8.19
1% TiO_2 coated	142.17	8.23
3% TiO_2 coated	140.03	7.99
5% TiO_2 coated	137.83	7.40
10 % TiO_2 coated	140.27	8.39

Tensile strength was not decreased even though strong solvent was used for coating because while coating solvent does not interact strongly with cotton cellulose and was confirmed by analyzing X-ray diffraction patterns of solvent treated cotton fabric. Table 9 shows modulus and % elogation of coated and uncoated cotton fabric. Rresults show that modulus and elongation increases after cellulose coating. It also confirms that only cellulose coating increases the strength, elongation and modulus of cotton fabric. Hence the added strength due to cellulose made the fibrous material withstand more load with increase in elongation.

5.14 Air and water vapor permeability

Air and water vapor permeability are the important comfort properties of textiles. It is necessary to analyze the effect of coating on comfort properties of textiles. Figure 32 and 33 shows the effect of cellulose coating on air (figure 32) and water vapor permeability (figure 33) of the cotton fabric.

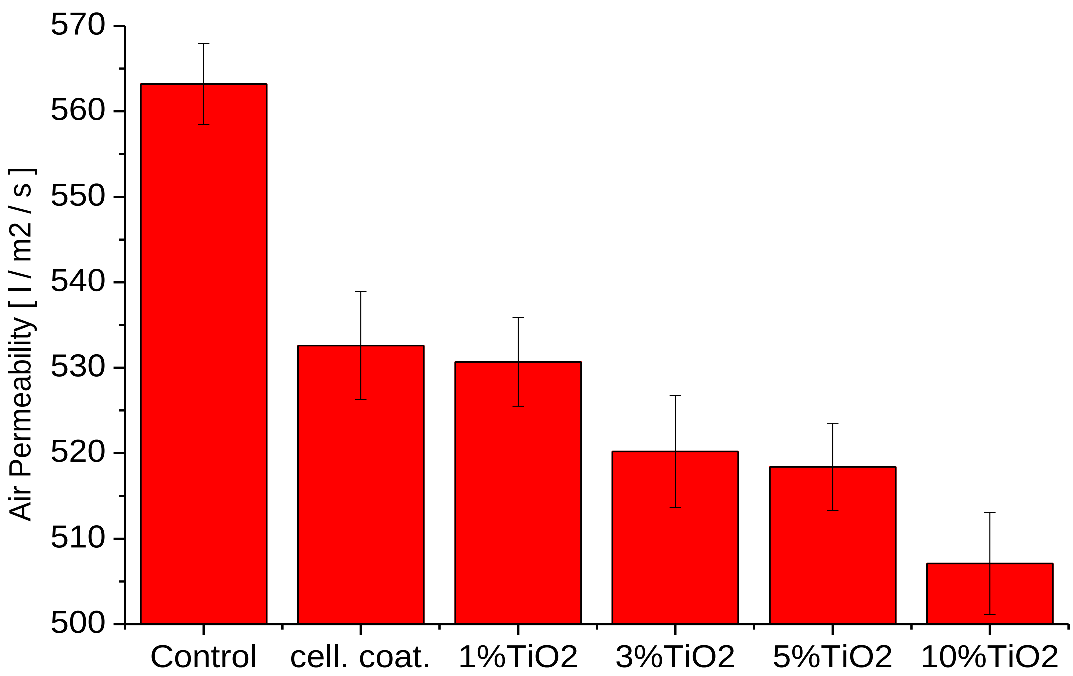


Figure 32. Effect of cellulose-TiO_2 coating on air permeability of cotton fabric

Air permeability of cotton fabric was decreased by 32.5 to 56.1 $l/m^2/s$. However, there was no significant deterioration of air permeability. Water vapor permeability was also slightly decreased (3.94 %) but is acceptable. 10% TiO_2 showed lower air and water vapor permeability as compared to other samples. Cellulose forms a thin film on the surface of the cotton fabric and covers the space between two yarns, which is the main cause that permeability was decreased slightly after cellulose coating. From the results, it can be concluded that there is no significant drop in both air and water vapor permeability after cellulose-TiO_2 coating on the surface of the cotton fabric.

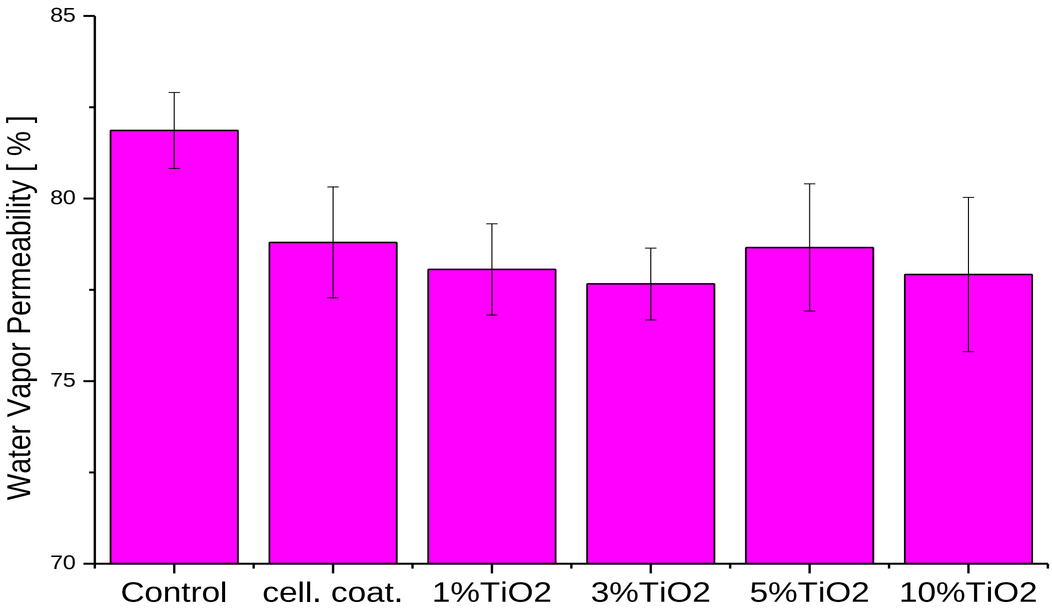


Figure 33. Effect of cellulose coating on water vapor permeability of cotton fabric

6 Evaluation of results and new finding

This study has produced new route to make cotton fabric self-cleaning, antibacterial and stiff. Cellulose-TiO_2 nanoparticles were coated on the surface of cotton fabric by using roller padding. Novel method was developed for quantification of cellulose II by X-ray diffraction patterns. Degradation of Orange II dye under UV light was evaluated by using "Image J" software. Effect of cellulose coating on dyeing, color fastness, perspiration fasness, rubbing fastness and washing fastness was studied by using three reactive dyes. Staphylococcus aureus and Methicillin-resistant Staphylococcus aureus bacterias were used for evaluation of antibacterial activity. The following findings were drawn from the results;

- Surface morphology showed that coated cellulose is attached to cotton fibres and this is due to interchain linkage between coated cellulose molecules and cotton fabric cellulose molecules of cotton fabric by intermolecular hydrogen bonding. Since both the molecules are same and both have hydrogen bonding, it is difficult to prove by using spectroscopic measurements. However, SEM pictures and washing study confirms that coated cellulose is strongly attached to cotton fabric. Coated cellulose forms thin film on the surface of cotton fabric and it holds the TiO_2 nanoparticles.

- Presence of characteristic peak of TiO_2 at 25.4° in x-ray diffraction pattern of cellulose-TiO_2 coated cotton fabric confirms successful coating process. Since strong solvent is used for this study, the effect of solvent on cotton fabric has been studied by developing simulation model on the basis of X-ray diffraction patterns. According to simulation amount of cellulose II was increased slightly after solvent treatment.

- Tensile strength increased significantly after cellulose coating without affecting comfort properties like air and water vapour permeability significantly.

- Reactive Blue 49 dye showed better dyeability towards the coated cotton fabric compared with Reactive Red 240 or Reactive Yellow 95 dye. However, the decrease in the *K/S* values indicates that cellulose coating decreased the dye uptake by the fabric. The L^* value increased in the case of cellulose-coated samples, meaning that cellulose coating increased the lightness of the cotton fabric. The fastness properties of both control and coated cotton fabrics against washing, rubbing, and perspiration were similar and good.

- Stiffness increased of cotton fabric significantly after cellulose coating. This new route has potential to replace traditional starching method to stiffen the clothes. The main drawback of starching is that it needs to reply after each laundering but in cellulose coating no need to reapply cellulose after each washing unlike starch and that has been proved by washing study.

- 5 % TiO_2 coated cotton fabric showed excellent self-cleaning ability and was stable against washing up to 10 cycles. Durability is the key in self-cleaning, stiffness etc. and this issue is solved by this method.

- Samples coated TiO_2 shows significant reduction of Staphylococcus aureus and Methicillin-resistant Staphylococcus aureus bacteria under UV light. Degradation of orange II and reduction in bacteria were increased with increasing TiO_2 concentration.

After the success of this coating method, it has opened new doors to incorporate nanoparticles on cotton fabric for various applications like flame retardant, thermoregulatory, antifungal, antibacterial, self-cleaning etc. This coating method can be commercialised to make cotton fabric self-cleaning, antibacterial and stiff permanently. Materials used for this method are not very expensive and method is quite feasible and easy to commercialise.

7 References

1. Ali, S., et al., *Cationic starch (Q-TAC) pre-treatment of cotton fabric: influence on dyeing with reactive dye.* Carbohydr Polym, 2015. **117**: p. 271-8.
2. Abidi, N., L. Cabrales, and E. Hequet, *Functionalization of a cotton fabric surface with titania nanosols: applications for self-cleaning and UV-protection properties.* ACS Appl Mater Interfaces, 2009. **1**(10): p. 2141-6.
3. Bae, G.Y., et al., *Superhydrophobicity of cotton fabrics treated with silica nanoparticles and water-repellent agent.* J Colloid Interface Sci, 2009. **337**(1): p. 170-5.
4. Boxun Leng, et al., *Superoleophobic Cotton Textiles.* Langmuir, 2009. **25**: p. 2456-2460.
5. Gupta, D. and M.L. Gulrajani, *Self cleaning finishes for textiles.* 2015: p. 257-281.
6. Meilert, K.T., D. Laub, and J. Kiwi, *Photocatalytic self-cleaning of modified cotton textiles by TiO2 clusters attached by chemical spacers.* Journal of Molecular Catalysis A: Chemical, 2005. **237**(1-2): p. 101-108.
7. Daoud, W.A., J.H. Xin, and Y.-H. Zhang, *Surface functionalization of cellulose fibers with titanium dioxide nanoparticles and their combined bactericidal activities.* Surface Science, 2005. **599**(1-3): p. 69-75.
8. Wu, D. and M. Long, *Realizing visible-light-induced self-cleaning property of cotton through coating N-TiO2 film and loading AgI particles.* ACS Appl Mater Interfaces, 2011. **3**(12): p. 4770-4.

9. Xu, F., et al., *A self-stiffness finishing for cotton fabric with N-methylmorpholine-N-oxide.* Cellulose, 2015. **22**(4): p. 2837-2844.
10. Nazari, A., et al., *Self-cleaning properties of bleached and cationized cotton using nanoTiO2: A statistical approach.* Carbohydrate Polymers, 2011. **83**(3): p. 1119-1127.
11. Xu, B., et al., *Self-cleaning cotton fabrics via combination of photocatalytic TiO2 and superhydrophobic SiO2.* Surface and Coatings Technology, 2015. **262**: p. 70-76.
12. El-Rafie, H.M., et al., *Antibacterial and anti-inflammatory finishing of cotton by microencapsulation using three marine organisms.* International Journal of Biological Macromolecules, 2016. **86**: p. 59-64.
13. Shaheen, T.I., et al., *Durable antibacterial and UV protections of in situ synthesized zinc oxide nanoparticles onto cotton fabrics.* International Journal of Biological Macromolecules, 2016. **83**: p. 426-432.
14. Borkow, G. and J. Gabbay, *Biocidal textiles can help fight nosocomial infections.* Med Hypotheses, 2008. **70**(5): p. 990-4.
15. Kang, C.K., et al., *Antibacterial cotton fibers treated with silver nanoparticles and quaternary ammonium salts.* Carbohydr Polym, 2016. **151**: p. 1012-8.
16. Joost, U., et al., *Photocatalytic antibacterial activity of nano-TiO2 (anatase)-based thin films: effects on Escherichia coli cells and fatty acids.* J Photochem Photobiol B, 2015. **142**: p. 178-85.
17. Banerjee, S., D.D. Dionysiou, and S.C. Pillai, *Self-cleaning applications of TiO2 by photo-induced hydrophilicity and photocatalysis.* Applied Catalysis B: Environmental, 2015. **176-177**: p. 396-428.
18. Saif, M., et al., *Synthesis of highly active thin film based on TiO2 nanomaterial for self-cleaning application.* Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2013. **112**: p. 46-51.
19. Shan, A.Y., T.I.M. Ghazi, and S.A. Rashid, *Immobilisation of titanium dioxide onto supporting materials in heterogeneous photocatalysis: A review.* Applied Catalysis A: General, 2010. **389**(1-2): p. 1-8.
20. Afzal, S., W.A. Daoud, and S.J. Langford, *Photostable self-cleaning cotton by a copper(II) porphyrin/TiO2 visible-light photocatalytic system.* ACS Appl Mater Interfaces, 2013. **5**(11): p. 4753-9.
21. Stylidi, M., *Visible light-induced photocatalytic degradation of Acid Orange 7 in aqueous TiO2 suspensions.* Applied Catalysis B: Environmental, 2004. **47**(3): p. 189-201.
22. Ryu, J., et al., *Photocatalytic nanocomposite thin films of TiO2-β-calcium phosphate by aerosol-deposition.* Catalysis Communications, 2009. **10**(5): p. 596-599.
23. Khataee, A.R., V. Vatanpour, and A.R. Amani Ghadim, *Decolorization of C.I. Acid Blue 9 solution by UV/Nano-TiO(2), Fenton, Fenton-like, electro-Fenton and electrocoagulation processes: a comparative study.* J Hazard Mater, 2009. **161**(2-3): p. 1225-33.
24. Andronic, L. and A. Duta, *The influence of TiO2 powder and film on the photodegradation of methyl orange.* Materials Chemistry and Physics, 2008. **112**(3): p. 1078-1082.
25. He, H.Y., *Comparison Study of Photocatalytic Properties of* $SrTiO_3$ *and* TiO_2 *Powders in Decomposition of Methyl Orange.* International Journal of Environmental Research 2009. **3**(1): p. 57-60.

26. Mai, F.D., et al., *Fabrication of porous TiO2 film on Ti foil by hydrothermal process and its photocatalytic efficiency and mechanisms with ethyl violet dye.* J Hazard Mater, 2010. **177**(1-3): p. 864-75.
27. Wu, C.H., *Photodegradation of C.I. Reactive Red 2 in UV/TiO2-based systems: effects of ultrasound irradiation.* J Hazard Mater, 2009. **167**(1-3): p. 434-9.
28. Cappelletti, G., et al., *Photodegradation of Pollutants in Air: Enhanced Properties of Nano-TiO(2) Prepared by Ultrasound.* Nanoscale Res Lett, 2008. **4**(2): p. 97-105.
29. Jiang, X., et al., *Cotton fabric coated with nano TiO2-acrylate copolymer for photocatalytic self-cleaning by in-situ suspension polymerization.* Applied Surface Science, 2011. **257**(20): p. 8451-8456.
30. Doganli, G., et al., *Functionalization of cotton fabric with nanosized TiO2 coating for self-cleaning and antibacterial property enhancement.* Journal of Coatings Technology and Research, 2015.
31. Peterson, E. and T. Dantzig, *Stiffness in fabrics produced by different starches and starch mixtures, and a quantitative method for evaluating stiffness*, in *Technical Bulletin*
No. 108. 1929. p. 33.
32. Chen, Y., W.H. Kampen, and B.J. Collier, *Evaluation of CPI Starch for Laundry Application.* Textile Chemist & Colorist, 1998. **30**(11): p. 25-30.
33. Mukerjea, R., G. Slocum, and J.F. Robyt, *Determination of the maximum water solubility of eight native starches and the solubility of their acidic-methanol and -ethanol modified analogues.* Carbohydr Res, 2007. **342**(1): p. 103-10.
34. Yuan, Z., et al., *Fabrication of cellulose self-assemblies and high-strength ordered cellulose films.* Carbohydr Polym, 2015. **117**: p. 414-21.
35. Feese, E., et al., *Photobactericidal Porphyrin-Cellulose Nanocrystals: Synthesis, Characterization, and Antimicrobial Properties.* Biomacromolecules, 2011. **12**(10): p. 3528-3539.
36. Hashemikia, S., et al., *A novel cotton fabric with anti-bacterial and drug delivery properties using SBA-15-NH2/polysiloxane hybrid containing tetracycline.* Materials Science and Engineering: C, 2016. **59**: p. 429-437.
37. Wang, C., et al., *Cotton fabric with plasma pretreatment and ZnO/Carboxymethyl chitosan composite finishing for durable UV resistance and antibacterial property.* Carbohydrate Polymers, 2016. **138**: p. 106-113.
38. Khajavi, R. and A. Berendjchi, *Effect of dicarboxylic acid chain length on the self-cleaning property of Nano-TiO2-coated cotton fabrics.* ACS Appl Mater Interfaces, 2014. **6**(21): p. 18795-9.
39. Wu, D., et al., *Photocatalytic self-cleaning properties of cotton fabrics functionalized with p-BiOI/n-TiO2 heterojunction.* Surface and Coatings Technology, 2014. **258**: p. 672-676.
40. Molgaard, S.L., et al., *Cellulose-nanofiber/polygalacturonic acid coatings with high oxygen barrier and targeted release properties.* Carbohydr Polym, 2014. **114**: p. 179-82.
41. Raeisi, M., et al., *Effect of carboxymethyl cellulose-based coatings incorporated with Zataria multiflora Boiss. essential oil and grape seed extract on the shelf life of rainbow trout fillets.* LWT - Food Science and Technology, 2015. **64**(2): p. 898-904.
42. Imran, M., et al., *Cellulose derivative based active coatings: Effects of nisin and plasticizer on physico-chemical and antimicrobial properties of hydroxypropyl methylcellulose films.* Carbohydrate Polymers, 2010. **81**(2): p. 219-225.

43. Grüneberger, F., et al., *Nanofibrillated cellulose in wood coatings: Dispersion and stabilization of ZnO as UV absorber.* Progress in Organic Coatings, 2015. **87**: p. 112-121.
44. Lavoine, N., I. Desloges, and J. Bras, *Microfibrillated cellulose coatings as new release systems for active packaging.* Carbohydr Polym, 2014. **103**: p. 528-37.
45. Klemm, D., et al., *Cellulose: fascinating biopolymer and sustainable raw material.* Angew Chem Int Ed Engl, 2005. **44**(22): p. 3358-93.
46. Ioelovich, M., *Study of Cellulose Interaction with Concentrated Solutions of Sulfuric Acid.* ISRN Chemical Engineering, 2012. **2012**: p. 1-7.
47. Gupta, K.M. and J. Jiang, *Cellulose dissolution and regeneration in ionic liquids: A computational perspective.* Chemical Engineering Science, 2015. **121**: p. 180-189.
48. Kimura, A., N. Nagasawa, and M. Taguchi, *Cellulose gels produced in room temperature ionic liquids by ionizing radiation.* Radiation Physics and Chemistry, 2014. **103**: p. 216-221.
49. Gao, Q., X. Shen, and X. Lu, *Regenerated bacterial cellulose fibers prepared by the NMMO·H2O process.* Carbohydrate Polymers, 2011. **83**(3): p. 1253-1256.
50. Shen, L., E. Worrell, and M.K. Patel, *Environmental impact assessment of man-made cellulose fibres.* Resources, Conservation and Recycling, 2010. **55**(2): p. 260-274.
51. Dupont, A.-L., *Cellulose in lithium chloride/N,N-dimethylacetamide, optimisation of a dissolution method using paper substrates and stability of the solutions.* Polymer, 2003. **44**(15): p. 4117-4126.
52. Jin, H., C. Zha, and L. Gu, *Direct dissolution of cellulose in NaOH/thiourea/urea aqueous solution.* Carbohydr Res, 2007. **342**(6): p. 851-8.
53. Ingvar, V.J., *Method of starching fabrics*. 1954, Google Patents.
54. Tang, X.N., et al., *Digitally quantifying cerebral hemorrhage using Photoshop and Image J.* J Neurosci Methods, 2010. **190**(2): p. 240-3.
55. Schneider, C.A., W.S. Rasband, and K.W. Eliceiri, *NIH Image to ImageJ: 25 years of image analysis.* Nat Meth, 2012. **9**(7): p. 671-675.
56. https://imagej.nih.gov/ij/docs/index.html.
57. Fridrichová, L., *A new method of measuring the bending rigidity of fabrics and its application to the determination of the their anisotropy.* Textile Research Journal, 2013. **83**(9): p. 883-892.
58. Naujokaityteˇ L, Strazdieneˇ E, and F. L, *Comparative Analysis of Fabrics' Bending Behavior Testing Methods.* Journal Textile Clothing and Technology 2007. **6**: p. 343-349.
59. Wiegand, C., et al., *In vitro assessment of the antimicrobial activity of wound dressings: influence of the test method selected and impact of the pH.* J Mater Sci Mater Med, 2015. **26**(1): p. 5343.
60. ISO, *Testing of textiles. Evaluation of the action of microfungi*. 2003.
61. Xu, M., et al., *How to decrease the viscosity of suspension with the second fluid and nanoparticles?* Sci Rep, 2013. **3**: p. 3137.
62. French, A.D., *Idealized powder diffraction patterns for cellulose polymorphs.* Cellulose, 2013. **21**(2): p. 885-896.
63. Nam, S., et al., *Segal crystallinity index revisited by the simulation of X-ray diffraction patterns of cotton cellulose Ibeta and cellulose II.* Carbohydr Polym, 2016. **135**: p. 1-9.
64. Yue, Y., et al., *Characterization of cellulose I/II hybrid fibers isolated from energycane bagasse during the delignification process: Morphology, crystallinity and percentage estimation.* Carbohydr Polym, 2015. **133**: p. 438-47.

65. Cook, J.G., *Handbook of Textile Fibres, Natural fibers*. 1984, Merrow, Cambridge: Woodhead Publishing. 240.

8 List of paper publisheFd by author

8.1 Publications in journals

1. **Kale B.M**., Wiener J., Militky J., Rwawiire S., Mishra R., Jacob I.K., Wang Y. Coating of Cellulose-TiO_2 nanoparticles on cotton fabric for Photo-catalytic self-cleaning and permanent stiffness, Carbohydrate polymers,2016, 150:107–113.
[Impact factor = 4.21]
2. **Kale B.M**., Wiener J., Militky J., Mishra R., Rwawiire S., Jabbar A. Dyeing and stiffness characteristics of cellulose coated cotton Fabric, Cellulose, 2016, 23:981-992.
[Impact factor = 3.19]
3. **Kale B.M**., Wiener J., Militky J., Maqsood S.H. Effect of Cellulose Coating on Properties of Cotton Fabric, Materials Science Forum, 2016, 860:81-84.
[Impact factor = 0.28]
4. **Kale B.M**., Wiener J., Rwawiire S., Militky J., Development of Photocatalytic Self-Cleaning Cotton Fabric, Material Science Forum, 2016, 866:171-175.
[Impact factor = 0.28]
5. **Kale B.M**., Wiener J., Militky J., Rwawiire S., Jabbar A., Multifunctional cotton fabric with Nano TiO_2 loaded cellulose, Carbohydrate polymers, under review- CARBPOL-D-16-03418.
[Impact factor = 4.21]

8.2 Contribution in conference proceeding

1. **Kale B.M**., Wiener J., Rwawiire S., Militky J. Development of Photocatalytic Self-Cleaning Cotton Fabric, ICCEMS 2016, Singapore.
2. **Kale B. M**., Wiener J., Rwawiire S., Militky J. Antibacterial and Self-cleaning Cotton Fabric by Nano TiO_2-cellulose Coating, Nanocon, 2016, Brno, Czech Republic
3. **Kale B. M**., Vijay B., Wiener J., Militky J., Ludmilla F. Novel method to improve stiffness of cotton fabric permanently, ICNF, 2015, Azores, Portugal.
4. **Kale B.M**., Wiener J., Militky J. Use of celllose solution as a stiffener for cotton fabric, ICTN, 2014, IIT Delhi, India.
5. **Kale B.M**., Wiener J., Militky J. Novel method to produce high stiffness cotton fabric, Strutex, 2014, Liberec, Czech Republic.

8.3 Citations

Article: Kale B.M., Wiener J., Militky J., Rwawiire S., Mishra R., Jacob I.K., Wang Y. Coating of Cellulose-TiO2 nanoparticles on cotton fabric for Photo-catalytic self-cleaning and permanent stiffness, Carbohydrate polymers,2016, 150:107−113.

(Cited in)

1. Hanggara, et al., " A new, cost-effective solar photoactive system N-ZnO@polyester fabric for degradation of recalcitrant compound in a continuous flow reactor," Materials Research Bulletin, Vol. 83, pp. 369-378, 2016

2. Jabbar, et al., "Nanocellulose coated woven jute/green epoxy composites:Characterization of mechanical and dynamic mechanical behavior," Composite Structures, vol. 161, pp. 340-349, 2017.

3. Rwawiire, et al., " Short-term creep of barkcloth reinforced laminar epoxy composites," Composites Part B: Engineering, Vol. 103, pp. 131-138, 2016.

Article: Kale B.M., Wiener J., Militky J., Mishra R., Rwawiire S., Jabbar A. Dyeing and stiffness characteristics of cellulose coated cotton Fabric, Cellulose, 2016, 23:981-992.

(Cited in)

1. Jabbar, et al., "Nanocellulose coated woven jute/green epoxy composites:Characterization of mechanical and dynamic mechanical behavior," Composite Structures, vol. 161, pp. 340-349, 2017.
2. Kale, et al., "Effect of cellulose coating on properties of cotton fabric, " Materials Science Forum, vol. 860, pp. 81-84, 2016

Curriculum Vitae

BANDU MADHUKAR KALE

17. Listopadu 587/8
Liberec 460 15, Czech Republic.
bmkale41@gmail.com
+420774653273

EDUCATION

Ph. D., Material Engineering- Technical University of Liberec (2013- Present)

Thesis: Coating of Cellulose-TiO_2 nanoparticles on the surface of cotton fabric for self-cleaning, antibacterial properties and permanent stiffness.

Visiting Research Scholar –Georgia Institute of Technology, Atlanta, USA. (2015-2016)

Topic: Development of simulation method to quantify amount of cellulose II by x-ray diffraction technique.

M.Sc. Organic Chemistry – University of Pune, MS, India (2009)

B.Sc. Chemistry– University of Pune, MS, India (2007).

PROFESSIONAL EXPERIENCE

ADITYA BIRLA GROUP– Mumbai, India

Research Associates *(2010-2013)*

An Indian multinational, $40B manufacturing and services conglomerate. Worked on multiple projects - synthesis of nano silica, modification of starch for its use as a filler, high luster and low cost acrylic fiber using sodium thiocyanate technology, wet spinning of cellulose fiber using ionic liquid, value added acrylic, and cellulose fiber like thermoregulatory, antibacterial and fire retardant. Developed innovative experimental procedure and data collection method to achieve desired goals with new revenue stream by reducing cost 3% of acrylic fiber production which has capacity of 120,000 TPA

S A PHARMACHEM PVT. LTD– Mumbai, India

Research Associates *(2009-2010)*

Worked on synthesis and characterization of Active pharmaceutical ingredients like Ascorbyl Palmitate (Vita.C) and 3- hydroxyl sulpholane.

SKILLS AND TRAINING

- A creative thinker of innovation and a passion for learning, teaching and mentoring
- Extensive research experience using a multidisciplinary approach by applying the principles of basic science and engineering
- Organic transformation and polymerization of acrylic co-polymers.

- Wet spinning process consisting of acrylic and cellulose fiber spinning technology
- Experience in synthesis of heterocyclic transformation.
- Strong knowledge of analytical techniques like IR, NMR (1H & 13C-NMR), Mass spectrometry, XRD, GC, HPLC, DSC, GPC, TGA and elemental analysis.
- Synthesis of antioxidants for Ascorbyl palmitate.
- Purification techniques using reprocessing, re-crystallization and column chromatography
- Lab scale fiber spinning, firefighting training, First-aid, Basic Lab Safety.
- Excellent computer, oral, written communication and interpersonal skills
- Eager to optimize global resources, develop novel First of a Kind material, generate significant cost savings and promote innovative solutions in complex environments.

PUBLICATIONS

PATENTS

1. Sahoo A, Lodha P, Karuppasamy P, **Kale B.M**, Acrylonitrile polymer composite using modified starch and a method of preparation thereof : Indian patent WO2014132266 A2.
2. Mohite L, Lodha P, Saha S, **Kale B.M**, Makwana R, Process for manufacturing non-fibrillating cellulosic fiber: Indian Patent, 1553/MUM/2013 (2015).

JOURNAL PUBLICATIONS

1. **Kale B.M**., Wiener J., Militky J., Mishra R., Rwawiire S., Jabbar A. Dyeing and stiffness characteristics of cellulose coated cotton Fabric, *Cellulose, 2016,* 23:981-992.
2. **Kale B.M**., Wiener J., Militky J., Rwawiire S., Mishra R., Jacob I.K., Wang Y. Coating of Cellulose-TiO_2 nanoparticles on cotton fabric for Photo-catalytic self-cleaning and permanent stiffness, *Carbohydrate polymers,2016,* 150:107–113.
3. Jabbar A., Militky J., **Kale B.M**., Rwawiire S., Yasir N., Baheti V. Modeling and analysis of the creep behavior of jute/green epoxy composites incorporated with chemically treated pulverized nano/micro jute fibers, *Industrial Crops and Products, 2016, 84:*230-240.
4. Rwawiire S, Tomkova B, Militky J, Jabbar A, **Kale B.M**. Development of a biocomposite based on green epoxy polymer and natural cellulose fabric (bark cloth) for automotive instrument panel applications, *Composites Part B 2015,* 81:149-157.
5. Kale B.M., Wiener J., Militky J., Maqsood S.H. Effect of Cellulose Coating on Properties of Cotton Fabric, *Materials Science Forum, 2016,* 860:81-84 ISSN: 1662-9752.
6. **Kale B.M**., Wiener J., Rwawiire S., Militky J., Development of Photocatalytic Self-Cleaning Cotton Fabric, Material Science Forum, 2016, 866:171-175 ISSN: 1662-9752.
7. Samson R., Tomkova B., Militky J., **Kale B. M**. Effect of layering pattern on the mechanical properties of Bark Cloth (Ficus Natalensis) Epoxy composites.*International Journal of Polymer Analysis and Characterization,* 2014, 20(2), 160-171 .
8. Mishra R., Militky J., Baheti V., **Kale B.M**., Huang J., Veerakumar A., Bele V.S., The production, characterization and applications of nanoparticles in the Textile industry, *Textile Progress, Vol 46, Iss. 2,* 2014.

9. Samson R., Tomkova B., Militky J., Kasedde A., **Kale B. M**., Jabbar A., Short-term creep of barkcloth reinforced laminar epoxy composites, Composite Part B 2016, Just accepted.
10. **Kale B.M**., Wiener J., Militky J., Rwawiire S., Jabbar A., Antibacterial and self-cleaning cotton fabric by TiO_2-cellulose coating, RSC Advances, under review- RA-ART-08-2016-020997.
11. **Kale B.M**. Davoud S., Wiener J., Militky J., Jacob K.I., Garmestani H., Wang Y., Oomman T., PLA Composites Containing Acetylated Microcrystalline Cellulose at Varying degrees of Acetate Substitution, Composite part B under review- JCOMB-2016-1340
12. **Kale B.M**., Wiener J., Rwawiire S., Militky J., Development of Photocatalytic Self-Cleaning Cotton Fabric, *Material Science Forum, 2016,* 866:171-175 ISSN: 1662-9752.
13. **Kale B.M**., Wiener J., Militky J., Effect of cellulose coating on stiffness of cotton fabric, *Fibers and polymers,* under review- FIPO-D-14-00900.

CONFERENCE PUBLICATIONS

1. **Kale B.M**., Wiener J., Rwawiire S., Militky J. Development of Photocatalytic Self-Cleaning Cotton Fabric, ICCEMS 2016.
2. **Kale B.M**., Wiener J., Militky J., Maqsood S.H. Effect of Cellulose Coating on Properties of Cotton Fabric, ICCMME, 2016.
3. **Kale B.M**., Wiener J., Militky J., Self-cleaning and stiffness characteristics of TiO_2-cellulose coated cotton fabric, PhD student workshop, Technical University of Liberec, *Svetlanka*, 2016.
4. **Kale B. M**., Vijay B., Wiener J., Militky J., Ludmilla F. Novel method to improve stiffness of cotton fabric permanently, ICNF international conference- 2015
5. **Kale B.M**., Wiener J., Militky J., Cellulose solution to increase stiffness of cotton fabric permanently, PhD student workshop, Technical University of Liberec, *Svetlanka,* 2015.
6. **Kale B.M**., Wiener J., Militky J. Use of celllose solution as a stiffener for cotton fabric, *ICTN international conference* - 2014.
7. **Kale B.M**., Wiener J., Militky J. Novel method to produce high stiffness cotton fabric, *Strutex* international conference 2014.
8. **Kale B.M**., Wiener J., Militky J., Acetylation of Microcrystalline cellulose, PhD student workshop, Technical University of Liberec, *Svetlanka*, 2014.

PROJECT HANDLED

1. Student grant scheme project (SGS - 30162) was successfully handled as a leader in 2015-16.

2. Was part of “DRDO project” and helped for testing and analysis in 2014-15.

Brief description of the current expertise, research and scientific activities

Doctoral Studies:	Full-time student at the Faculty of Textile Engineering, Department of Material Engineering Specialization: Textile Technics and Material Engineering
List of Exams Passed:	[1]. Heat and Mass Transfer in Porous Media [2]. Structure and Properties of Textile Fibers [3]. Textile Metrology [4]. Mathematical Statistics and Data Analysis [5]. Experimental Technique of Textile
State Doctoral Examination:	Passed
Research Projects:	[1] Student grant scheme project (SGS - 30162) was successfully handled as a leader in 2015-16. [2] Was part of "DRDO project" and helped for testing and analysis in 2014-15.

Record of the state doctoral exam

TECHNICKÁ UNIVERZITA V LIBERCI
Fakulta textilní

ZÁPIS O VYKONÁNÍ STÁTNÍ DOKTORSKÉ ZKOUŠKY (SDZ)

Jméno a příjmení doktoranda:	**Bandu Madhukar Kale**
Datum narození:	**1. 6. 1986**
Doktorský studijní program:	**Textilní inženýrství**
Studijní obor:	**Textile Technics and Material Engineering**
Termín konání SDZ:	**1. 12. 2016**

prospěl ~~**neprospěl**~~

Komise pro SDZ:

		Podpis
Předseda:	prof. Ing. Jakub Wiener, Ph.D.	
Místopředseda:	doc. Ing. Maroš Tunák, Ph.D.	
Členové:	doc. Ing. Ladislav Burgert, CSc.	
	doc. Ing. Petr Exnar, CSc.	
	doc. Ing. Antonín Potěšil, CSc.	
	doc. Mgr. I. Lovětinská-Šlamborová, Ph.D.	
	Ing. Miroslava Pechočiaková, Ph.D.	Pechočiaková

V Liberci dne 1. 12. 2016

O průběhu SDZ je veden protokol.

Recommendation of the supervizor

Supervisor's opinion on PhD thesis of Mr. Bandu Madhukar Kale M.Sc.

Date: 30.03.2017

Thesis title: Multifunctional cotton fabric with nano TiO_2 loaded cellulose

The PhD thesis titled "Multifunctional cotton fabric with nano TiO_2 loaded cellulose" is quite comprehensive and fulfills the objectives outlined in his thesis. The candidate has done all his work quite systematically, on required scientific level, with specific objectives. Discussion of the results is comprehensive and logical with citations of previous work where necessary. The quality of figures and tables is good and understandable. The language level of the thesis is good and meets the PhD standard.

His publication activities are in very good level. During his research work in TUL on the PhD theme, he has published 5 papers in impact factor journals, 1 book chapter and 5 paper presented at international conferences.

He has introduced new route to make cotton fabric self-cleaning, antibacterial, antifungal and permanently stiff by coating cellulose-TiO_2 nanoparticles on the surface. From results, it is concluded that functional properties are durable against repeated washing, tensile strength increases after cellulose coating and comfort properties are hardly affected. He has developed novel method from X-ray diffraction patterns to quantify amount of cellulose I, II and amorphous fractions. The conclusions of the thesis are interesting and novel. I therefore recommend the thesis for final defense.

Liberec 30/03/2017

Prof. Ing. Jiří Militký, CSc. EURING

Supervisor

Opponents's reviews

Opponent's review

This opponent's review was elaborated based on Ing. Jana Drašarová, PhD. (dean of Faculty of Textile, Technical University in Liberec) assignment for review Ph.D. dissertation thesis (ref. no. TUL-17/4814/025833, dated 26. 6. 2017) of **Bandu Madhukar Kale "Multifunctional Cotton fabric with Nano TiO_2 Loaded Cellulose"**. Tutor of the Ph.D. student was Prof. Ing. Jiří Militký, CSc.

Thesis presented was studying new route to make cotton fabric self-cleaning, antimicrobial, antifungal and highly stiff.

The main objective was the preparation of cellulose – TiO_2 coated cotton fabric and its characterization for organic stain removal, inhibition efficiency against bacteria's, and disinfection of cotton fabric from fungal colonization.

Major results of this thesis was focused on developed of novel method for quantification of cellulose fractions by simulating X-ray diffraction patterns, degradation of orange II dye under UV light, effect of cellulose coating on dyeing, color fastness, perspiration fastness, rubbing and washing fastness. Antimicrobial and antifungal activity was tested as well. Durability was the major concern with those methods.

The multifunctional cotton fabric was prepared with cellulose - TiO_2 solution on the surface by roller padding machine at time 20 s with same time using of sulfuric acid (60 %) for treat fabric. The coated fabrics were evaluated for their perspiration fastness using the test method ISO 105-E04. Furthermore, there were applied methods of X-ray analysis, SEM morphology and colorimetry analysis for optimization of amount surfactants. The chosen methods fully characterize studied cotton surface for given purposes. Mechanical and photocatalytic properties were tested as well.

Stiffness of treated fabric was affected by cellulose concentration, there was no effect of TiO_2 presence, and thus this procedure can replace traditional starching method. In opposite, antimicrobial and antifungal properties were affected by TiO_2 under 3 %.

Applied methods used by the applicant were modern up to date measuring techniques and give exhaustive information about the studied material and its use.

Proposed application of multifunctional cotton fabric can be commercialized to make self-cleaning suiting, shirting and women wear etc.

From the formal point of view, results of the theses and the thesis itself were well written, results were presented in the form of tables and graphs. Thesis represent typical material science oriented study focused on treatment cotton fabrics as a self-cleaning material for textile industry.

Thesis were written in English language in the form of the monograph. Total number of references cited in the thesis was 152. There were cited fundamental research articles as well as the latest publications. However the format of the reference list was not fulfilling requirements of the citation standard CSN ISO 690.

Results of the thesis of the applicant **Kale B. M.** were published in 5 scientific papers in impacted international journals where applicant was first author in all cases. He was attending several scientific conferences at home as well as abroad.

Questions to be answered during thesis defense:

1) How many washing cycles will keep modification functional on a fabric?
2) Which mechanism of the attachment of the pigments do you expect to be acting at the particle solid surface interface?

Based on the latter mentioned facts and by the course of law (Higher Education Law No. 111/1998. Sb.) §47 I recommend to accept the PhD. dissertation thesis of Bandu Madhukar Kale, for defense.

In Zlin, August 1, 2017

Doc. Mgr. Barbora Lapčíková, Ph.D.

Associated professor for materials science and engineering
Tomas Bata University in Zlin

Referee´s report on PhD. thesis of

Bandu Madhukar Kale

„ Multifunctional Cotton Fabric with TiO2 Loaded Cellulose“

Professor Miroslav Černík

The presented thesis consists of 90 pages divided into 7 major chapters plus References and List of publications. The thesis deals with cotton fabrics loaded with cellulose - nano TiO_2.

Abstract summarizes content of the thesis with major results.

Chapter 1 (Introduction) is about background of the topic – cotton fibres, application on ZnO and TiO_2 for self-cleaning of the fibres and antibacterial activity of the fibres. There is also definition of the problem to be solved – coating of cellulose for use as self-cleaning, antibacterial, antifungal and stiffness fabric.

Chapter 2 (Aim and objectives) defines objectives of the thesis – investigation of different properties of cellulose- TiO_2 cotton fabric.

Chapter 3 (Literature review) is a very illustrative introduction into the topic, cotton, self-cleaning materials (e.g. example of well-known lotus effect), antibacterial fabric, antifungal fabric, stiff fabric, functional nanoparticles and fabric materials.

Chapter 4 (Experimental) deals with methods used for preparation of fabrics and characterization. Major part is a description of measurement of different properties of the fabrics, e.g. mechanical, photocatalytic, antibacterial and antifungal properties, dyeing properties.

Chapter 5 (Results and discussion) Besides other characteristics of the fabrics with different loading of titanium oxide, degradation of Orange II and red wine stain under UV light are the most interesting.

Chapter 6 (Conclusions) summarizes the determined results of the thesis. The thesis shows new route to make self-cleaning, antibacterial, antifungal and highly stiff cotton fabric. Cellulose - TiO_2 nanoparticles were coated to the surface of cotton by roller padding. All these properties were evaluated and compared for different content of TiO_2. Surface morphology showed attachment of cellulose to cotton fibres by hydrogen binding. This theory was not fully confirmed and it is based on strong attachment and resistance against washing out. Also titanium oxide nanoparticles are hold in a thin coated film on the surface of the cotton fabric. These theories are not so strong and I am not convinced on these types of binding together.
The samples have strong resistance against washing, author said, but the results are disputable. Why the sample with 10% of TiO_2 lost its blue color intensity strongly than 3 and

5% solution and after 10 time washing it is below value for these two concentrations (Figure 29). Even in blue color intensity at different TiO_2 additions are different on Figure 28 and 29.

There was no effect of TiO_2 on stiffness of the cellulose fabric. Table 1 which shows amount of added cellulose-TiO_2 per gram of cotton fabric shows the same added amount for all TiO_2 concentrations. If this is true, the effect of added TiO_2 on fabric properties cannot be evaluated.

Other presented results are confirmed by experiments and they are likely right.

Chapter 7 (Applications and future works) contains examples of products which can be later developed based on tested technology.

Referee remarks, question and conclusions

The thesis is logically divided into chapters, the content is explained illustratively, and all determined results are simply described.

QUESTIONS

1. I do understand the weight of fabric after coating in cellulose-TiO_2 solution as it is described in Table 1 (p.31). Why the weight after coating in more TiO_2 concentrated solution is lower? And what is the content of TiO_2 on fabric for different TiO_2 solution?
2. Who made the antibacterial and antifungal experiments? Could you describe results on Figures 37, which are not readable in the presented form? Is the reduction of *Staphylococcus Aureus* for 3% TiO_2 really 96.7%? Figure 37a) shows different results, or at least from bad quality of the picture it looks like?
3. Are the SEM photographs on Figure 24 really representatives? Why figure b) and f) are similar and the others different?
4. Why Figures 28 and 29 differed. Figure 29 w/o washing should correspond to Figure 28 or not?

Imperfections and recommendations

Language of the thesis is very good and thesis is nicely written. I did not find many errors and mistypes. Some examples:

1. soltion (p.30), wrong equation (4) (p.18), TiO2 without subscript in whole Abstract.
2. Titanium (Ti^{4+}) atoms (and similarly) are not atoms but ions (cations).
3. Some sources of pictures are missing and I do not expect they are drawn by the author (e.g. Fig. 4, 12)
4. Symbols in eq.10 (p.31) are wrong (what are the indexes?)
5. Figure 27 caption is wrong - e, f are missing.

Referee´s conclusion

The presented thesis is logic, has all necessary parts and show the author understand his work and he is able to put results logically into appropriate parts. The above mentioned recommendations and questions are not so significant, that they decrease the scientific merit of the thesis. There are no significant recommendations for next author´s work. The language is good and fully understandable.

<u>The thesis is good and meets all criteria to be taken to the defence.</u>

In Liberec (Czech R.) on October 30, 2017 **Prof. Dr. Ing. Miroslav Černík, CSc.**