Impact of Dyes and Finishes on the Aquatic Biodegradability of Cotton Textile Fibers and Microfibers Released on Laundering Clothes

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1. Abstract

The presence, compatibility and biodegradability in the environment of pervasive textile materials microfibers shed during laundering or use has been increasingly recognized as an important environmental issue. Textile materials that biodegrade are greatly advantageous relative to those that are not. In this research, the influence of typical textile finishes on the persistence of cotton fibers in aquatic environment has been assessed in aerobic conditions using an RSA PF-8000 respirometer (ISO 14851) using an inoculum of activated sludge at low concentration (30 ppm of total suspended solids). The presence of the finishes alters the surface chemistry of the fibers and their biodegradation rate in aquatic environments. Fibers and fragments of the same cotton knitted fabrics (interlock) without a finish and with different finishes such as durable press, silicone softener, C6 based fluorinated (Non-PFOA) water repellent, and a dye (blue 19) were tracked and fit to kinetic biodegradation models. relative to cotton fabrics without treatments. The biodegradation of fabrics with some levels of crosslinking in the finishing treatment was more affected than other finishes. Cotton fibers with water repellent finish have the longest lag-phase (λ) in which the biodegradation is delayed initially, whereas cotton fabrics with durable press finish had the lowest degradation rate (R) and degraded the least among the samples. Despite the differences in rate, all the cotton samples reached more than 60% biodegradation in 102 days; in fact, the cotton fibers with silicone softener degraded by 90%. The biodegradation rates extents with respect to the different samples are in agreement with the observed trends of the same samples for cellulase hydrolysis and cellulase adsorption experiments (Cellulclast, a cellulase mixture from Trichoderma reesi). This indicates that the finishes decrease the adsorption of enzymes excreted by the microorganisms and the initial rates of biodegradation relative to untreated cotton but that the cellulosic material maintains its biodegradability.

1. Introduction

Microplastics are synthetic solid particles or polymer matrix with size ranging between 1 μm to 5 mm, of either primary or secondary manufacturing origin [1]. The International Union for Conservation of Nature (IUCN) estimated that between 0.8-2.5 Mt per year of primary microplastics are released into the ocean, in which the micro-size fibers generated for the abrasion of textiles during laundering represents the most significant portion (35%) [2].

It is believed that these microfibers enter the wastewater treatment plants (WWTPs) with the effluents of the washing machines [3–5]. Even though WWTPs have an excellent microplastics removal capacity (>98%), there are large volumes of effluents with low concentrations of microplastics discharged daily to freshwater and marine environments [6–11]. These microplastics are found mainly in the fiber-like form, predominantly from polyethylene terephthalate (PET) [6–8,11–15]. Nonetheless, cellulose-based fibers, such as those found in tissue paper and textiles, have also been observed in the wastewater effluents [6,8,11,14]. The environmental science community calls these micro-sized fibers microfibers regardless of their origin, synthetic or natural [16]. The fate and role of natural fibers in the anthropogenic pollution issue in aquatic environments is not well-known in published literature [17–20]. Natural fibers are not considered plastics; nevertheless, functional finishes are usually applied to improve their properties. Natural fibers such as cotton represent a large volume of the textile industry, it represents the second greatest portion of the global fiber production after polyester [21].

The shedding capacity of different fabrics from synthetic and cellulose-based fibers have been tested during laundering [4,16,22–28]. In our previous study, the generation of microfibers per gram of textile laundered was significantly higher in cellulose-based fabrics compared to polyester, which also was shown by Sillanpää and Sainio (2017) [27]. We also observed that under aerobic aquatic biodegradation conditions using activated sludge from a wastewater treatment plant at low concentration, seawater, and lake water as inoculum, cellulosic fibers such as cotton and rayon were degraded while polyester fibers were not [16,29]. Bacterial communities related to the assimilation and mineralization of complex carbohydrates were promoted with the cellulosic, cotton and rayon, samples during biodegradation [29]. Nevertheless, it is important to mention that these studies were done using fabrics and yarns without finishing agents.

For cotton fabrics, the most common functional finishes are durable press for wrinkle resistance and dimensional stability, softening agents for hand feel, water repellents, and antimicrobials [30,31]. In general, around 5% of the labeled apparel cotton products in the US have a wrinkle resistance or durable press finish, most of the products use softeners and dyes, and in terms of water repellents, some niche products apply these chemistries for outdoor clothing [32].

Softness is related to comfort and a soft hand feel, one of the most important aspects for the customers [33]. This property is the result of a combination of measurable properties such as elasticity, compressibility and smoothness [33]. The softening of textile fabrics is generally achieved by reducing the coefficient of friction between the fibers, filaments, and yarn, basically lubricating the area [30]. Although natural fibers contain natural softeners such as oils and waxes, these are removed during desizing, scouring and bleaching, making cotton less soft or sometimes harsh and brittle [33,34]. For that reason, softeners are added during textile manufacturing as finish agent to improve the handle and have a pleasant touch [30]. There are different types of softeners such as cationic, anionic, non-ionic, and silicone softeners [30,34,35].

For textiles containing cotton or other cellulosic fibers, it is essential to maintain their dimensional stability, image, and performance [36]. This is achieved by the easy-care, durable press or wrinkle-free finishes [36]. Durable press finishes provide resistance against shrinkage and improve wet and dry wrinkle recovery to cellulosic textiles by the inhibition of easy movement of the cellulose chains by crosslinking with resins or polymers [30,37]. There are two types of finishes, formaldehyde-based and formaldehyde-free compounds [37]. For most fabrics, the conventional formaldehyde-based dimethylol dihydroxy ethylene urea (DMDHEU) is used [30,37,38].

Water repellents are applied to textiles for water, and depending on the chemicals, oil and stain resistance [39]. The liquid repellent fabric is achieved by a combination of the fabric surface roughness and the hydrophobic character of the finishing agent [39]. The most common and effective water repellent chemistries are based on polymeric per and polyfluoroalkyl substances (PFASs) that have a high level of washing and dry cleaning durability and water, dirt, and oil resistance [39]. PFASs are highly persistent, potentially bioaccumulative, and toxic [40]; for that reason, long-chain PFASs have been replaced with short-chain PFASs or non-fluorinated alternatives which include paraffin, waxes, silicones, and other chemistries [39–41]. In the US, fluorochemicals are commonly applied for water repellency of cotton fabrics because of their durability and efficiency in preventing water from wetting the fabric and excellent oil and stain repellency without compromising the natural feel of cotton [42].

There is evidence that some treatments applied on textiles to improve their final properties affect their biodegradability. Antimicrobial agents such as silver (Ag) and titanium dioxide (TiO_2) nanoparticles have been probed to decrease the biodeterioration of the finished cellulose fibers and fabrics; these additives are applied to protect textiles against the attack of the microbial organisms [43–46]. Lazic et al. (2015) showed a decrease in weight loss during soil burial test up to 33% due to the presence of Ag and TiO2 nanoparticles in cellulose fabrics [45]. Besides, Li et al. (2010) showed that the biodegradation of cotton fabrics in soil and composting facilities depends on the chemical treatments of the fabrics [47]. The treatment with DMDHEU resin hindered biodegradation by 6.5 % while the presence of an amino-functional silicone softener promoted biodegradability by 5.5 % compared to cotton fabrics that were only scoured and bleached [47]. Nevertheless, these studies were limited to soil and composting environments did not cover the effect of dyes and water repellents and did not provide details on how the physical and chemical changes on the surface of the fibers related to their biodegradation.

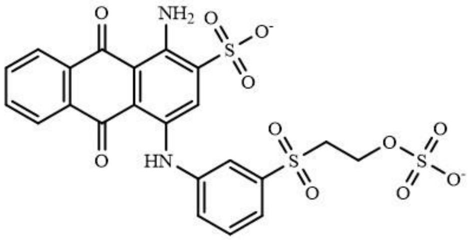
This research aims to determine whether and to what degree, the chemical treatments during textile manufacturing on natural fibers such as cotton affect the biodegradation in aquatic environments. This is of great importance as major trends to develop natural or biobased or renewable materials in order to replace synthetic petroleum based materials. In order to approach some properties that synthetics have (water resistance, wrinkle resistance, solvent and stain resistance) these natural materials may require considerable derivatization or blending or coatings with additives, thus necessitating the understanding the final products end-of-life behavior when in the environment.

The effect of typical textile finishes on the aquatic biodegradation of fibers released from cotton during laundering was studied. Cotton knitted fabrics (interlock) with different finishes such as durable press, silicone softener, C6 based fluorinated (Non-PFOA) water repellent, and dye (blue 19) were evaluated relative to samples without treatments.

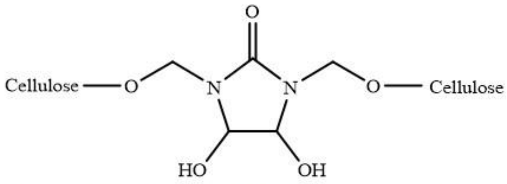
2. Materials and Methods

2.1 Fabrics

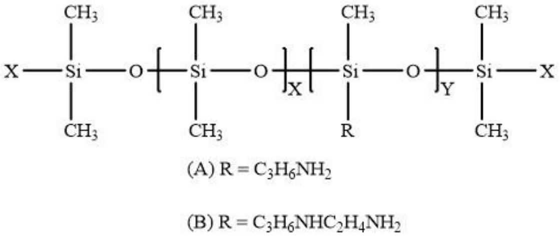
Cotton knitted fabrics (interlock) with different finishes such as durable press, silicone softener, C6 based fluorinated (Non-PFOA) water repellent, and dye (blue 19) were evaluated relative to samples without treatments (Table 1 and Figure 1). The knitted fabrics (Figure 2) were deconstructed to micro-size <5 mm for the biodegradation experiments (Table 2). These materials were compared with microcrystalline cellulose (MCC) which is readily biodegradable and oak leaves (12.5 % cellulose, 11.7% hemicellulose, 38% Klason lignin, and 11.6% ashes, Appendix A, Table 11) that commonly percolate into aquatic bodies.



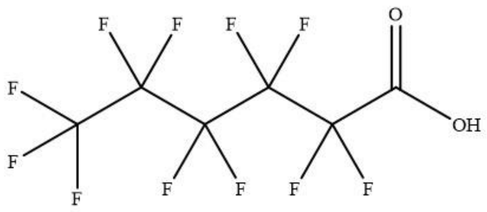
Dye – Reactive Blue 19



Durable Press - DMDHEU & Catalyst



Softener - Modified amino-functional silicone



Water Repellent - C6 & PBI
Non-PFOA fluorochemical
Polyfunctional blocked isocyanate crosslinker

Figure 1. Textile finishes commonly applied to cotton.

Table 1. Specifications of knitted cotton fabrics.

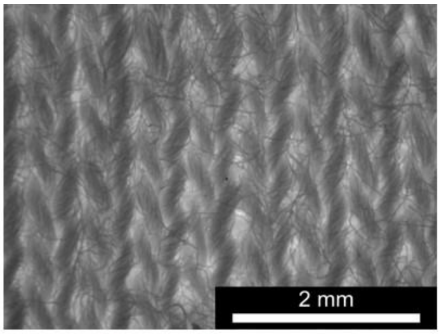
Treatment	Finishes % on weight of the bath (owb)	Fabric Construction	Weight (g/cm^2)	Yarn Type	Yarn Size
No Finish	N/A	Weft Knitted Fabric 24 Cut Interlock	240	Ring-Spun	40/1 Ne **
Dye (Blue 19) *	Dye - 2.00 %				
Durable Press†¥	Resin - 5.00 % Catalyst - 2.75 %				
Softener†	Softener - 5.00%				
Water Repellent†#	Fluorochemical - 8.00% Crosslinker - 1.60%				

*Warm wet processing at 60 °C and 18 rpm
†Pad-apply at 40 psi, 0.7 m/min, 1 dip & 1 nip; and dry at 121°C for 90 seconds
¥ Cure at 171°C for 45 seconds
Cure at 177°C for 60 seconds

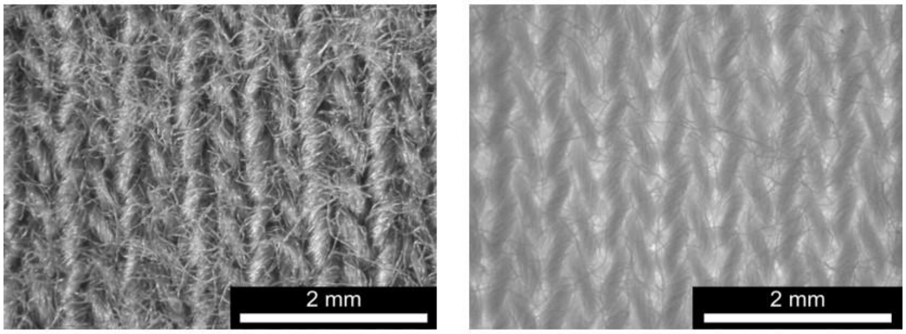
**Ne (English Cotton Count) – 40/1 Ne = 40 x 840 yards of one single yarn weigh 1 pound.

Table 2. Size of cotton fabrics and oak leaves fragments.

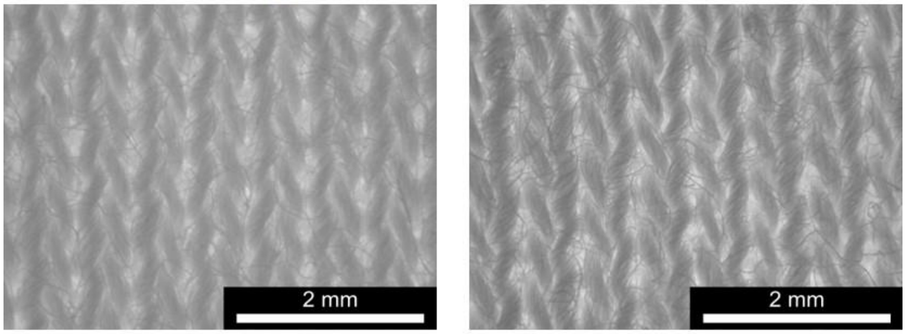
Samples	Length (mm)	Width (mm)
Cotton - No Finish	3.97 ± 0.29	2.2 ± 0.14
Cotton - Dyed	3.66 ± 0.19	1.78 ± 0.15
Cotton - Durable Press	4.07 ± 0.39	2.22 ± 0.11
Cotton - Softener	3.54 ± 0.26	1.82 ± 0.14
Cotton - Water Repellent	3.55 ± 0.32	2.04 ± 0.16
Oak Leaves	4.52 ± 0.28	3.07 ± 0.19



Cotton – No Finish



Cotton – Dye **Cotton – Durable Press**



Cotton – Softener **Cotton – Water Repellent**

Figure 2. Cotton knitted fabrics with different finishing treatments.

2.2 Fabrics Characterization

Elemental Analysis

The elemental analysis (carbon, hydrogen, and nitrogen) measurements for the fabrics and residual solids were performed at the Environmental and Agricultural Testing Service Laboratory (EATS), Department of Crop and Soil Sciences, at NC State University (Raleigh, NC) by total combustion with the Perkin Elmer 2400 CHNS Analyzer (Massachusetts, USA). The amount of organic carbon obtained was used to determine the ThOD.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of the fabrics were acquired using a Frontier FT-IR Spectrometer brand Perkin Elmer with a Perkin Elmer Universal attenuated total reflectance (ATR) sampling accessory (Massachusetts, USA). The FTIR parameters used were resolution 1 cm^{-1}, spectral range 650 cm^{-1} to 4000 cm^{-1}, and 4 scans.

Crystallinity

The crystallinity of the yarns was measured by X-Ray Diffraction (XRD) using a PANalytical Empyrean X-ray diffractometer (Royston, United Kingdom) in the Analytical Instrumentation Facility, NC State University (Raleigh, NC). The Cu Kα radiation source (λ = 0.15418 nm) was generated at 40kV and 44 mA. The diffraction scans were obtained from 5 to 50 degrees for 2θ in 0.026-degree steps at 116 seconds per step. The crystallinity of the samples was obtained using the peak deconvolution method [48] and the peak fitting features of CasaXPS version 2.3.19.

Morphology

The influence of the finishes and biodegradation on the morphology of the fibers was observed. SEM images of the fabrics were taken with a Variable Pressure Scanning Electron Microscope Hitachi S3200N (Krefeld, Germany) in the Analytical Instrumentation Facility, NC State University (Raleigh, NC). The samples were coated with gold for 5 minutes to increase their conductivity.

Thermo-Gravimetrical Analysis (TGA)

A Q500 thermogravimetric analyzer (TGA, TA Instruments, New Castle, DE) was used to determine the degradation temperature of the fabrics. Dry nitrogen gas was used to sweep out the volatiles from the sample. The gas flow rate was 40 ml/min for balance gas and 60 ml/min for sample gas. The gas was not pre-heated before entering the furnace. The samples of approximately 5.0 to 11.0 mg were loaded into a Platinum sample pans (Part #952018.906, TA Instruments) were used and had dimensions of 2 mm height and 10 mm diameter. The equipment was equilibrated at 30 °C and heated to 800 °C at a heating rate of 10 °C/min. For this measurement, the fabric pieces were equilibrated at 21 °C and 65% relative humidity for 24 hours.

Differential Scanning Calorimetry (DSC)

A differential scanning calorimeter (Q100 DSC, TA Instruments, New Castle, DE) equipped with a cooling unit (RCS, Refrigerated Cooling System) was used to measure the glass transition temperature of the fabrics. The samples of approximately 2.0 to 5.0 mg were sealed into a DSC aluminum pan (TA Instruments, Part #901683.901 for the bottom and Part #901671.901 for the lid). The equipment was equilibrated at 30 °C and heated just below the degradation temperature (from TGA) of each sample at a heating rate of 10 °C/min. An empty pan was used as a reference. For this measurement, the fabric pieces were equilibrated at 21 °C and 65% relative humidity for 24 hours.

X-Ray Photoelectron Spectroscopy (XPS)

The chemical composition of the fabric surface was performed with a SPECS FlexMod XPS photospectrometer with a Hemispherical analyzer PHOIBIS 150 (Berlin, Germany). The X-ray source was Mg (kα excitation, 1254 eV). The takeoff angle was normal to the surface, the X-Ray incidence angle was ~30° from surface, and the angle of the X-ray source to the analyzer ~60°. The base pressure in the analysis chamber was in the 10−10 mbar range.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF SIMS)

ToF-SIMS analyses were conducted in the Analytical Instrumentation Facility in NC State University using a TOF SIMS V (ION TOF, Inc. Chestnut Ridge, NY) instrument equipped with a Bi_n^{m+} (n = 1 - 5, m = 1, 2) liquid metal ion gun, Cs^+ sputtering gun and electron flood gun for charge compensation. Both the Bi and Cs ion columns are oriented at 45° with respect to the sample surface normal. The instrument vacuum system consists of a load lock for rapid sample loading and an analysis chamber, separated by the gate valve. The analysis chamber pressure is maintained below 5.0 x 10-9 mbar to avoid contamination of the surfaces to be analyzed. For high lateral resolution mass spectral images acquired in this study, a Burst Alignment setting of 25 keV Bi^{3+} ion beam was used to raster the area.

Water Contact Angle

A surface electro-optics (SEO) contact angle analyzer (Phoenix 300; Surface Electro Optics Co., Ltd., Suwon City, Gyeonggi-do, Korea) was used to determine the influence of the finishes on the water contact angle. The angle was measured immediately after the drop touched the surface in three different places. To control the formation speed of the drop, the fast speed was set at 47 and the slow speed at 32. An industrial needle with a gauge of 27 was used for all tests. For this measurement, the fabric pieces were equilibrated at 21 °C and 65% relative humidity for 24 hours.

Moisture Regain

The fabric pieces were equilibrated at 21 °C and 65% relative humidity for 24 hours. Then, the samples were weighed before and after drying at 105 °C until constant weight.

Water Absorbency of Textiles

A drop of deionized water was allowed to fall from a 10-mm height onto the cotton fabric surface, and the time required for the water droplet to be absorbed by the fabric was measured as the wet-out time [49]. The averages of wet-out times at five different places on the sample surface were recorded. For this measurement, the fabric pieces were equilibrated at 21 °C and 65% relative humidity for 24 hours.

2.3 Compositional Analysis

The chemical compositional analysis of the oak leaves and the control cotton fabric (no finish) was performed by acid hydrolysis as described by Sluiter et al. (2012) [50], the extractives of the oak leaves were not removed previously. The sugars from the hydrolysis were measured by High Performance Liquid Chromatography, HPLC (Agilent Technologies 1200 Series, California, USA) using a Shodex column (sugar SP0810, New York, USA). Besides, the ash content of the samples was measured after ignition for 6 hours at 525 °C in a muffle furnace (TAPPI, 2202). The samples were oven-dried overnight at 105 °C before these procedures.

2.4 Aquatic biodegradability in aerobic conditions

For this experiment, aquatic aerobic environments were simulated within an RSA PF-8000 respirometer (Figure 3) using the standard method ISO 14851 [51]. The aerobic biodegradation of the pieces of fabric was assessed using as inoculum activated sludge at low concentration (30 ppm of total suspended solids, TSS) from the Neuse River wastewater treatment plant (Raleigh, North Carolina USA). In this experiment, 100 mg of material was added in the corresponding bottles except in the blank where only the inoculum and the nutrients were added, 400 ml of test medium were used to ensure good stirring (500 rpm) and enough headspace for oxygen transfer (aerobic). The theoretical oxygen demand (ThDO) is calculated (Appendix A, Table 10) based on the TOC, and the percentage of biodegradation is based on the oxygen uptake versus the ThOD.

The reaction vessels were prepared within 24 hours after the inoculum collection. In total, 24 flasks were prepared for each experiment, three replicates of each sample and a blank that contained only the inoculum and the nutrients (Table 3). The standard nutrient solutions (Table 4) recommended by the method 51 were used. After adding the test medium, a carbon dioxide absorption tube filled with 4 ml of 30% potassium hydroxide (KOH) solution was inserted in each bottle, and these were closed tightly before connecting each vessel to an RSA Pulse-Flow 8000 Respirometer System (Arkansas, USA) in aerobic mode [52]. These flasks were incubated in a dark room at a constant temperature (25 °C) and under stirring with magnetic bars. After one week of incubation, the materials were added to the flasks, and the respirometer was reinitiated to record the oxygen uptake data. The CO_2 absorption (KOH) solution was changed every week, and the pH of the system was measured and adjusted to 7 if needed with 1 N sodium hydroxide and hydrochloric acid solutions [29].

Table 3. Flasks prepared for the aquatic biodegradation test of textile yarns [53].

Flasks	Purpose	# Flasks	Test Material (100 mg per Flask)	Reference Material (100 mg per Flask)	Inoculum	Samples	# Flasks
F_T Test Material	Measure the oxygen consumption of the test material and reagents in the test medium.	3/per sample	+	-	+	Cotton Fabrics: • No Finish • Dye • Durable Press • Softener • Water Repellent Oak Leaves	18
F_B Blank	Measure the oxygen consumption of the reagents in the test medium.	3	-	-	+	1	3
F_C Inoculum Check	Check the inoculum activity.	3	-	+	+	1	3
Total Flasks Prepared							**24**

Table 4. Standard test medium preparation [53].

Test Medium Components	Volume needed to prepare 1 L of test medium	Solution Preparation
Water	Initially add 500 ml of water, and the end of the test medium preparation make up until have 1 L of solution.	N/A
Solution A	10 ml	For 1 L of solution dissolve the following substances in water and make up until 1000 ml with water. 8.5 g of KH_2PO_4 (Fisher Chemicals) 21.75 g of K_2HPO_4 (Fisher Chemicals) 33.4 g of $Na_2HPO_4 \cdot 2H_2O$ (Fisher Chemicals) 3-1.5 g of NH_4Cl (Acros Organics)
Solution B	1 ml	Dissolve 22.5 g of $MgSO_4 \cdot 7H_2O$ (Acros Organic) in water and make up until 1000 ml.
Solution C	1 ml	Dissolve 36.4 g of $CaCl_2 \cdot 2H_2O$ (Sigma-Aldrich) in water and make up until 1000 ml.
Solution D	1 ml	Dissolve 0.25 g of $FeCl_3 \cdot 6H_2O$ (Fisher Chemicals) in water and make up until 1000 ml. This solution must be prepared freshly or add a drop of concentrated HCl or EDTA (0.4 g/l) to avoid precipitation.

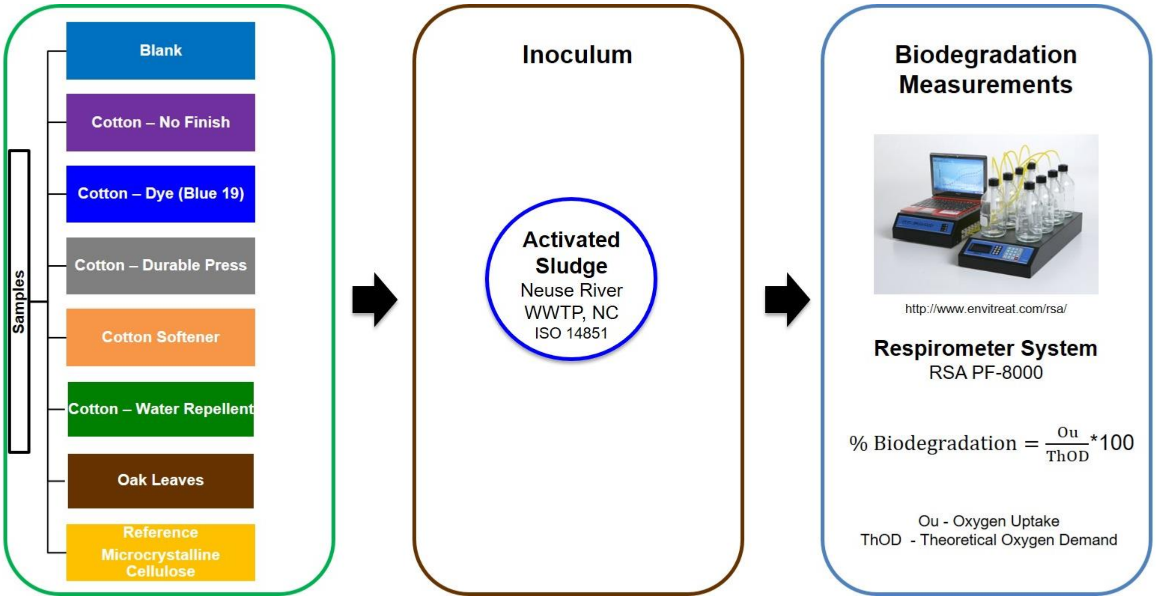


Figure 3. Experimental plan to study the effect of finishes on cotton biodegradation in aquatic environments.

At the end of the experiment, the nitrification interferences were measured by quantification of the dissolved nitrites (NO_3-N) and nitrates (NO_2-N) in the liquid test media formed during the biodegradation process. The oxygen consumption due to this process was subtracted from the results. The measurements were done in the Environmental Analysis Laboratory in the Department of Biological Agricultural Engineering (BAE) at NC State University (Raleigh, NC). The Cadmium reduction method for automated analysis was used with slight modifications, including dialysis [54]. The analysis was conducted on a Bran & Luebbe Digital Autoanalyzer III system (Norderstedt, Germany).

Statistics

For the statistical analysis, SAS 9.4 and Excel 2016 software versions were used to assess the differences in biodegradation between the fabrics using the data from the plateau phase in the biodegradation curve. Multiple comparisons were made using a non-parametric model for One-Way ANOVA (proc NPAR1WAY, Wilcoxon Model, Median One-Way Analysis). The kinetic models were fitted using a non-linear function (proc nlin) in SAS 9.4 and the oxygen uptake data.

2.5 *Cellulase* Interactions

Enzymatic hydrolysis

The enzymatic hydrolysis of the cotton fabrics with the different finishes was performed using Celluclast from Novozymes, a cellulase mixture from Trichoderma reesi. The fabrics were cut in pieces of 200 mg, and three replicates were made per fabric type per day of analysis. The enzymatic hydrolysis was performed in 10 ml of sodium acetate buffer (0.1 M, pH 5) at 50 °C at 110 rpm with an enzyme loading of 2ml of enzyme per liter of sodium acetate buffer. The enzymatic hydrolysis was performed for three days, taking samples every day for glucose determination by HPLC (Agilent Technologies 1200 Series, California, USA) using a Shodex column (sugar SP0810, New York, USA). The fabric samples were weighed before and after hydrolysis, drying at 65 °C until achieving a constant weight [45,46].

Enzymatic Adsorption

The effect on surface chemistry on enzyme adsorption on the surface of the fabrics was studied using Celluclast from Novozymes, a cellulase from Trichoderma reesi, as a model enzyme. The fabrics were cut in pieces of 20 mg, and three replicates were made per fabric type. The fabric samples and three blanks (no fabric) were incubated for 4 hours at 4 °C without stirring in 600 µl of an enzyme solution containing 245 µg of enzyme per ml of sodium acetate buffer (0.1 M, pH 5) [55]. The enzyme concentration before and after incubation was determined using the Pierce Rapid Gold BCA Protein Assay Kit [56] and the Genesys 50 UV-Visible spectrophotometer (Waltham, MA, USA).

3. Results and discussion

3.1 Fabric Characterization

In Table 5, the characteristic FTIR peaks obtained from the spectra (Appendix A, Figure 11) are presented. The functional groups of the crosslinking agents in DMDHEU for the durable press (1710 cm^{-1}, C=O) and PBI (1740 cm^{-1}, ester groups) for the water repellent were present, all of the other fabrics showed no significant differences compared to the non-treated control fabric (Table 5).

In terms of crystallinity, there were no significant differences among the fabrics; they have around 85%-detected crystallinity, with the cotton fabric treated with water repellent and durable press showing a slightly higher crystallinity (~88%) (Appendix A, Figure 10). Similarly, there were no significant differences in the thermal properties of the fabrics. It was observed from TGA results that all the cotton fabrics degraded between 355℃ to 365℃, only the fabric treated with durable press showed a second peak at 253℃ (Appendix A, Figure 12). In the DSC curves, no significant changes were observed due to the presence of the finishes (Appendix A, Figure 13).

Table 5. Characteristic FTIR peaks of cotton fabrics with different finishes: water repellent, softener, durable press, a dye (blue 19), and as control a non-treated fabric (no finish).

Sample	Characteristic Peak (cm $^{-1}$)	Functional Group
Cellulose I – Cotton No Finish Softener Dyed (Blue 19)	3341 cm^{-1}	OH stretching
	2916 cm^{-1} and 2853 cm^{-1}	C-H alkane stretching
	1629 cm^{-1}	OH bending
	1437 cm^{-1}	C-H bending
	1316 cm^{-1}	OH in plane bending
	1164 cm^{-1}, 1114 cm^{-1}, and 1029 cm^{-1}	C-O stretching corresponding to alkyl aryl ethers and alcohols
Water Repellent	1740 cm^{-1}	Ester groups in PBI
	1210 cm^{-1}	C-F stretching
Durable Press	1710 cm^{-1}	C=O in DMDHEU

The most significant influence was observed in the surface properties of the fabrics. The XPS spectra of the cotton fabrics (Appendix A, Figure 14) showed that the chemical composition of the surface changes considerably with the treatments (Table 6). The cotton fabric with softener had a 9% Silicon (Si) content on the surface and the cotton fabric with the durable press finish showed 2% nitrogen (N) surface content; these two compounds were absent in the control fabric (no finish). In the case of the water repellent finish, 50% surface content of this fabric was fluorine (F). Residues of silicon (2%) were observed in the dyed fabric.

Similarly, the ToF SIMS spectra of the fabrics showed the distribution of these finishes on their surface; the negative ion fragments are shown in Figure 4, whereas the positive ions are presented in Figure 17 (Appendix A). The cellulose ion fragments are shown in red and the characteristic ions of the finishes are presented in green on top of the fibers. The control fabrics showed residues of CN^- ions (Figure 4) and silicone fragments (Appendix A, Figure 17) that could be attached to the fabric structure during their manipulation; however, these compounds were not observed by XPS (Table 6). The cotton fabric treated by durable press showed ion fragments containing nitrogen related to the structure of DMDHEU (dimethylol dihydroxy ethylene urea) whereas the fabric with softener showed on its surface silicone ion fragments representative from the modified amino-functional silicone used as the softener agent. In the case of the water repellent cotton fabric, the surface is highly covered by fluorine fragments in agreement with the XPS results. These images indicate that there was not a homogenous and complete coverage of the fibers; instead the surface displays much area that is covered by cellulose and exposed directly to the inoculum. This suggests that there are parallel paths for enzymes towards the fibers; it is hypothesized that the cellulose-exposed areas would be a quick pathway to hydrolyze the cellulose whereas the coated areas would mainly present a more resistant path to the fiber.

Hydrophilicity is a key parameter in biodegradation, with substrates that can favorably interact with the aqueous inoculum with respect to adsorption and absorption in order to obtain surface interactions between substrate and enzymatic species. In terms of hydrophilicity (Table 7), only the cotton fabrics treated with softener and the water repellent additive showed an increase in their water contact angle. Similarly, the water absorbency occurred immediately in all the fabrics except in the one treated with softener in which the droplet of water stayed on the surface for around 3 seconds and in the water repellent cotton fabric where the fabric did not absorb the droplet even after hours. Despite this, no significant differences were observed in terms of moisture regain at 65% relative humidity and 21°C (Table 7).

Table 6. Surface chemical composition of the cotton fabrics obtained by XPS.

Samples	**C 1s (%)**	**O 1s (%)**	**Si 2p (%)**	**F 1s (%)**	**N 1s (%)**	**Cl 2p (%)**
Cotton – No Finish	66	34	0	0	0	0
Cotton – Softener	54	37	9	0	0	0
Cotton – Dyed (Blue 19)	63	35	2	0	0	0
Cotton – Water Repellent	42	8	0	50	0	0
Cotton – Durable Press	64	33	0	0	2	1

Table 7. Water absorbency of the cotton fabrics (wet-out time), water contact angle, and moisture regain of cotton fabrics conditioned at 65% relative humidity and 21°C.

Samples	**Wet-out Time** N=5	**Water Contact Angle** N=3	**Moisture regain (%)** N=3
Cotton – No Finish	Zero	NA	5.36±0.25
Cotton – Softener	3.5 ± 0.6 s	127° ± 1°	5.26±0.1
Cotton – Dyed (Blue 19)	Zero	NA	6.19±0.34
Cotton – Water Repellent	60 + s	134° ± 1°	5.07±0.13
Cotton – Durable Press	Zero	NA	5.20±0.30

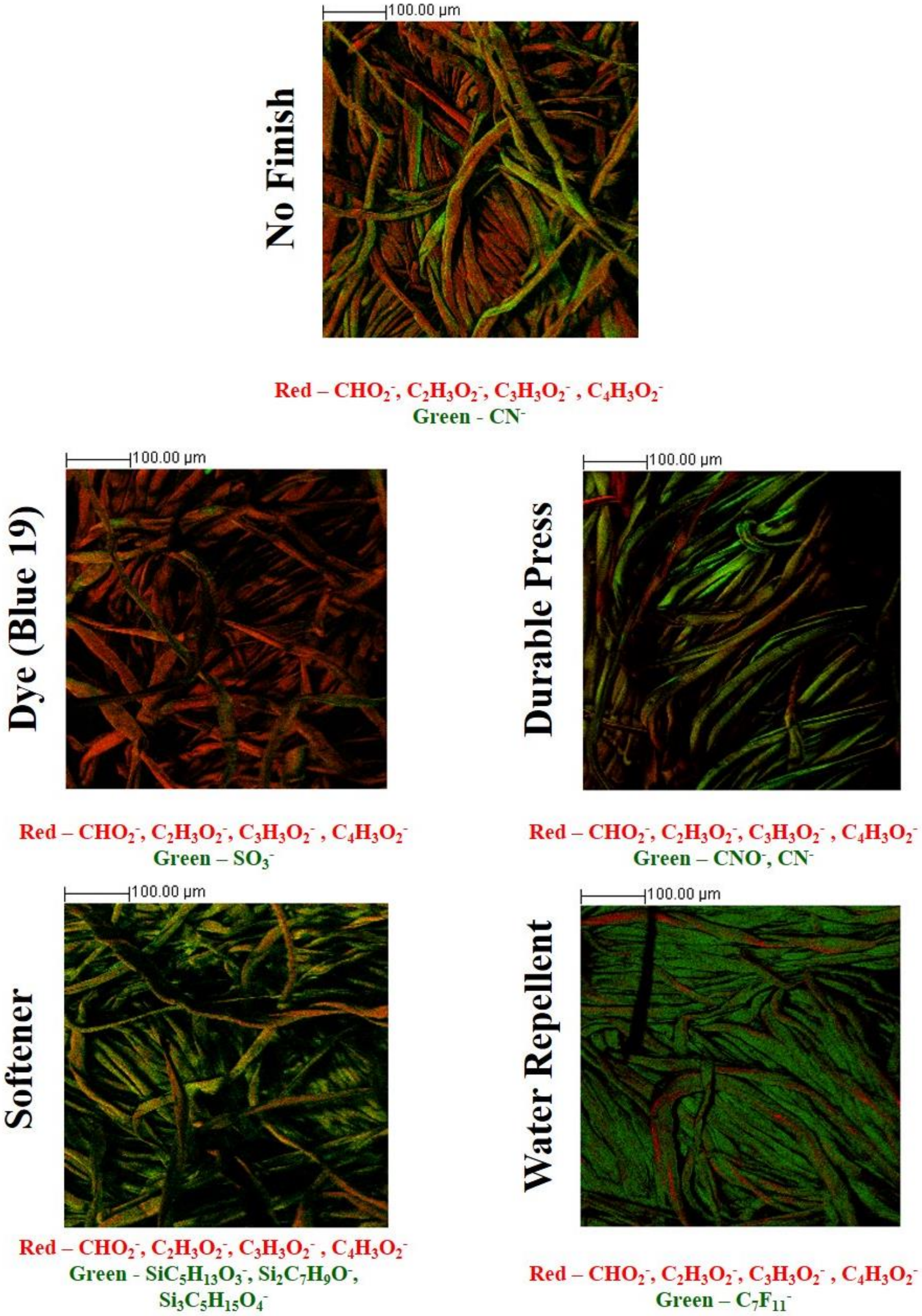


Figure 4. Distribution of finishes of the surface of cotton fabrics by ToF SIMS (negative ions), red color reflects cellulose groups and the green color indicates groups from the finishing treatment.

3.2 Aquatic biodegradability in aerobic conditions

The aquatic biodegradability of the finished fabrics was studied following the ISO standard method for ultimate aerobic biodegradability of plastic materials in aqueous media [53]. The percentage of biodegradation was measured comparing the oxygen uptake of the system with the theoretical oxygen demand ThOD calculated according to the elemental composition in each sample (Appendix A, Table 10). The inoculum used for the biodegradation experiments was collected from the aerobic bioreactors of Neuse River WWTP in Raleigh NC, the activated sludge was diluted to have 30 ppm TSS in the incubation bottles (Appendix A, Table 12 and Table 13

). The nitrification interferences during the experiment were not significant compared to the oxygen consumption due to biodegradation of the polymeric materials studied (Appendix A, Table 14).

The finishes applied during textile processing on cotton fabrics affect their surface chemistry and hydrophilicity and their biodegradation in aquatic environments, Figure 5. The Reference Material (Microcrystalline Cellulose) reached 87.7 ± 5.4 % of degradation in 102 days. The percentage of biodegradability in the materials tested at the end of the experiment is shown in Table 8.

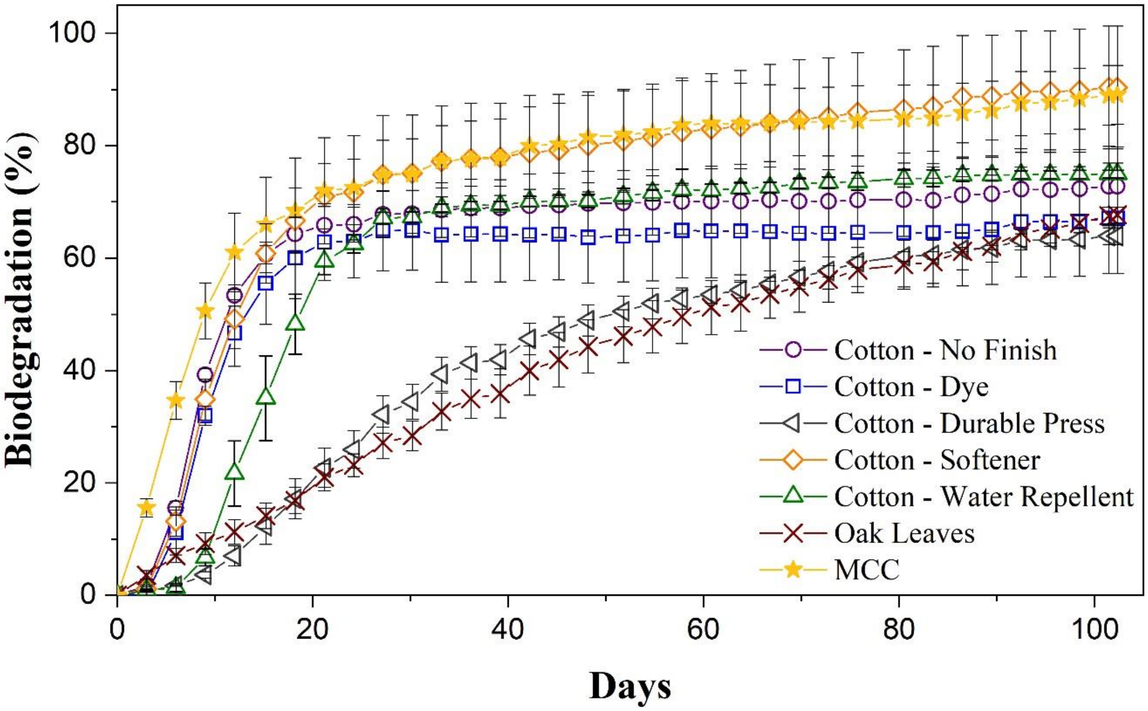


Figure 5. Effect of finishes on the biodegradation of the cotton microfibers. Biodegradation curves based on the standard method ISO 14851:1999 for the determination of the ultimate

aerobic biodegradability of plastic materials in an aqueous medium* [51]*. As inoculum 30 ppm TSS of activated sludge from Neuse River WWTP was used. The percentage of biodegradation was based on the oxygen uptake of the system versus the theoretical oxygen demand calculated for each yarn. The error bars represent the standard error of the mean (N=3), for oak leaves N=2.

Table 8. Summary – Effect of finishes on cotton biodegradation

Samples	**% Biodegradation**
Cotton – Softener	89.6 ± 10.9 %
Reference Material (MCC)	87.7 ± 5.4 %
Cotton – Water Repellent	74.9 ± 0.7 %
Cotton – No Finish	72.2 ± 7.0 %
Cotton – Dye (Blue 19)	66.2 ± 9.8 %
Oak Leaves	64.9 ± 2.3 %
Cotton – Durable Press	63.0 ± 1.0 %

According to the results shown in Figure 5, the finishes applied during textile processing on cotton fabrics affect their biodegradation in aquatic environments within the period of the experiment (102 days). The biodegradability of cotton with different finishes within the 102-day time frame is as follow: Softener > MCC > Water Repellent ~ No Finish > Dye (Blue 19) > Oak Leaves > Durable Press. It appears that the durable press and the oak leaves did not achieve their plateau phase, both still showing a slow rate of biodegradation at the end of the experiment.

In terms of the final extent of biodegradation, there is no significant difference between the samples (pvalue=0.1812, α=0.05, Appendix A, Table 16). However, the rate of biodegradation is significantly affected by the presence of the finishes. The first-order hydrolysis model is used when the samples start consuming oxygen very quickly; MCC and the oak leaves followed this behavior (Appendix A, Table 17 and Figure 24).

In contrast, the Gompertz model is used when there is a long lag phase, the incubation time before the degradation starts and all the cotton samples behave according to this model (

Table ***9***, and Figure 6).

The first order hydrolysis model was fitted to the data based on Equation 1 and the Gompertz model was fitted to the data based on Equation 2 [57–59].

$$\frac{B}{Bo} = 1 - e^{-K_h * t} \qquad (1)$$

Where,
B = cumulative oxygen consumption (mg O_2/ g initial material)
Bo = Ultimate oxygen consumption (mg O_2/ g initial material)
K_h = First order hydrolysis constant (1/day)
t = time (days)

$$M = P * exp\left\{-exp\left[\frac{\mathrm{R*e}}{P}(\lambda - t) + 1\right]\right\} \tag{2}$$

Where,
M = cumulative oxygen consumption (mg O_2/ g initial material)
P = Ultimate oxygen consumption (mg O_2/ g initial material)
R = Oxygen Consumption Rate (mg O_2/ g initial material*day)
λ = lag-phase period (days)
t = time (days)
e=2.718282

The degradation rate was significantly lower for the oak leaves than for the microcrystalline cellulose (MCC) based on the first hydrolysis kinetic model, 0.013 day^{-1} vs 0.099 day^{-1} respectively (Appendix A, Table 17). This difference is attributed to the high content of lignin and ash of the oak leaves compared to the MCC, which is essentially pure cellulose (Appendix A, Table 11).

The results for the Gompertz kinetic model are shown in

Table ***9***. The rate of biodegradation based on oxygen consumed by the mass of the initial material added to the reactors was higher for the non-treated cotton fabric (no finish), followed by cotton dyed (blue 19), cotton with water repellent, cotton with softener, and cotton with durable press finish (lowest rate). In contrast, the lag phase was smaller for cotton with softener followed by the control cotton sample (no finish), cotton dyed (blue 19), cotton with durable press finish, and cotton with water repellent.

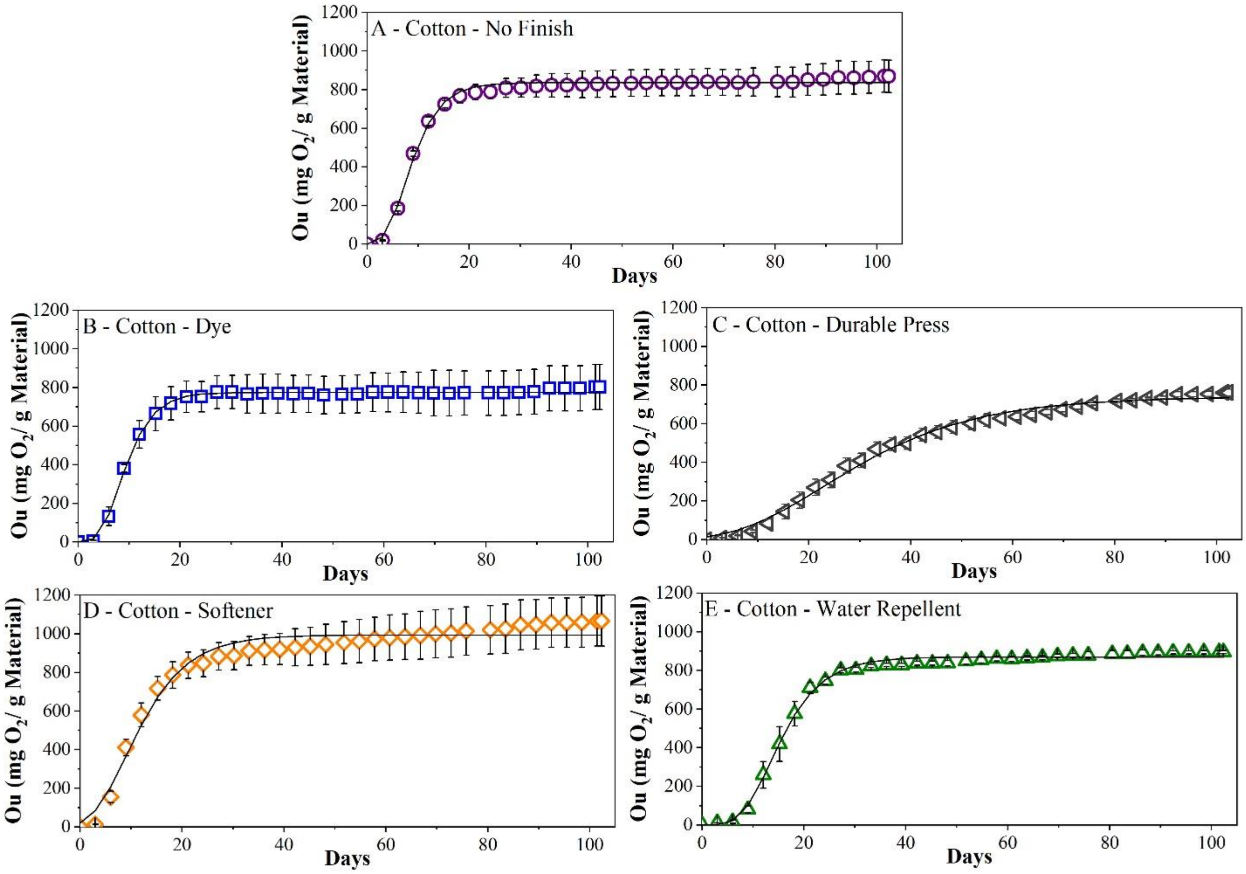


Figure 6. Oxygen uptake (Ou) curves - Effect of finishes on the biodegradation of the cotton microfibers. Gompertz kinetic model fitted to the oxygen uptake data obtained during aquatic aerobic biodegradation of cotton microfibers from fabrics with different finishing treatments: A – No Finish, B – Dye, C – Durable Press, D – Softener, and E – Water Repellent. The error bars represent the standard error of the mean, for MCC N=3 and for oak leaves N=2.

Table 9. Gompertz kinetic model parameters fitted to the oxygen uptake data obtained during aquatic aerobic biodegradation of cotton microfibers from fabrics with different finishing treatments

Treatment	**P** (mg O_2 / g initial material)	**R** (mg O_2 / g initial material*day)	**λ** (days)	**R^2**
Cotton – No Finish	836.2 ± 10.2	81.0 ± 11.7	3.5 ± 0.8	0.86
Cotton – Dye (Blue 19)	775.2 ± 15.6	77.4 ± 18.7	4.3 ± 1.3	0.70
Cotton – Durable Press	740.0 ± 8.8	16.2 ± 0.7	5.9 ± 0.9	0.97
Cotton – Softener	993.9 ± 18.3	55.1 ± 8.5	2.3 ± 1.5	0.77
Cotton – Water Repellent	869.4 ± 4.9	56.7 ± 2.9	7.7 ± 0.4	0.98

In summary, the biodegradation of fabrics with some levels of crosslinking in the finishing treatment was more affected. Cotton fabrics with durable press finish degraded the least among the samples and had the lowest degradation rate (R). Likewise, the cotton fabric with water repellent finish has the longest lag-phase (λ); nevertheless this is not only due to the crosslinking treatment but also due to the high hydrophobicity of the fabric.

In the case of the softener, it has been reported that the presence of softeners favors the biodegradation of cotton fabrics in soil and composting systems [47]. In this study, the tendency is similar; the cotton fabrics with softener achieved the highest biodegradation (90%), at an average rate, and short lag phase.

These results are also in agreement with the changes in morphology observed on the fabrics during the biodegradation process by SEM (Figure 7). After 13 days, the non-treated cotton fabric and the dyed fabric were disintegrated completely. Nevertheless, the fibers of the cotton fabrics treated with the durable press, softener, and water repellent finishes were still present and intact due to their low degradation rate and long lag phase. At the end of the experiment (102 days), only cotton fibers treated with the durable press additive were observed. It is essential to mention that this fabric showed the lowest degradation and rate, an absence of the plateau phase at the end of the experiment, and the second-highest lag-phase during this experiment.

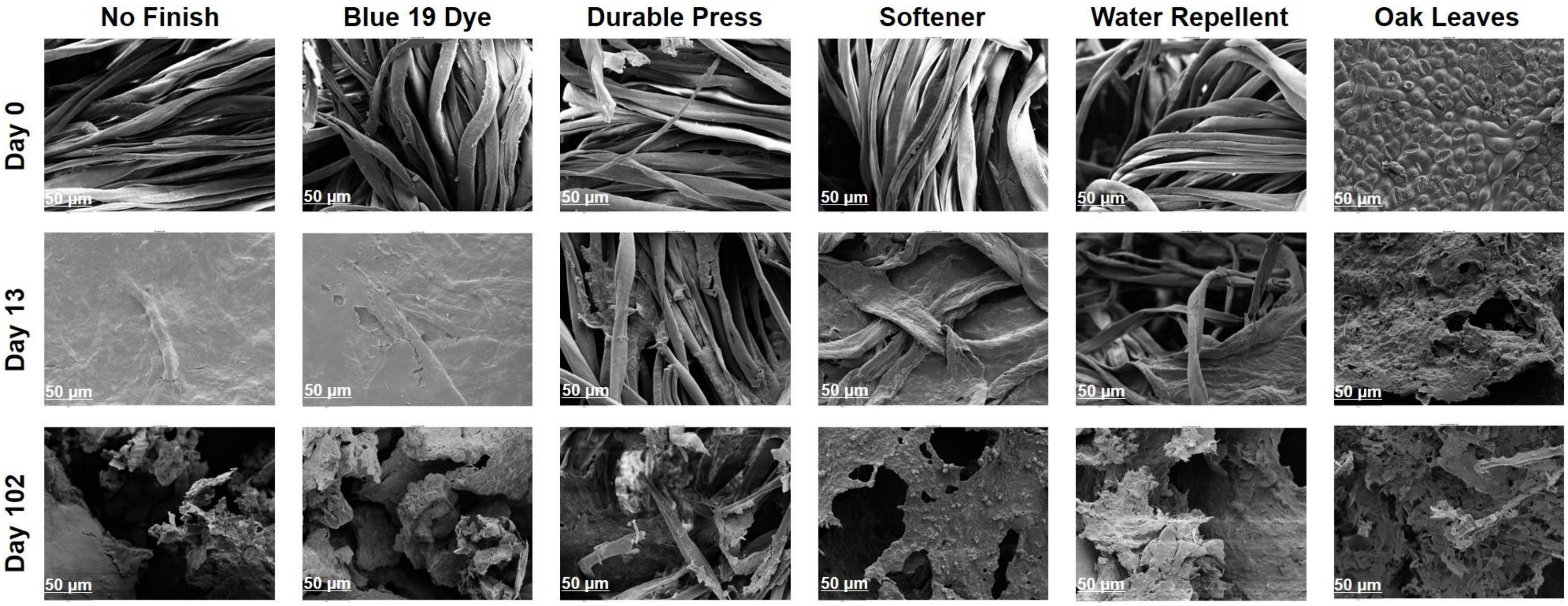


Figure 7. SEM images of the fibers during aerobic biodegradation using as inoculum 30 ppm of TSS of Activated Sludge solids from the Neuse River WWTP.

3.3 *Cellulase* Interactions

The finishes applied during textile processing on cotton fabrics affect their ability to be hydrolyzed by *Cellulase*. Similarly to the aerobic biodegradability results, the fabrics that have crosslinking treatments (durable press and water repellent) and high hydrophobicity (water repellent) on the surface delay the penetration of enzymes within the polymeric matrix. In general, the glucose released of the fabrics after three days (Figure 8) was as follows: No Finish > Softener ~ Dyed (Blue 19) >> Water Repellent ~ Durable Press.

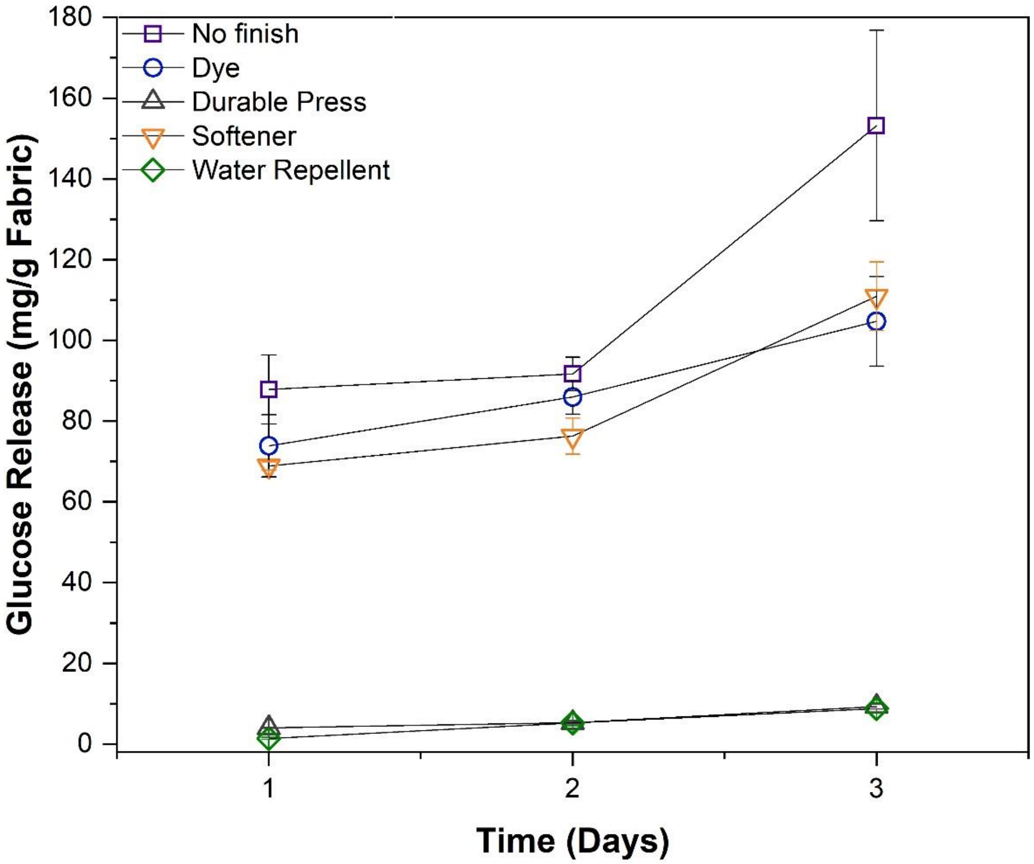


Figure 8. Effect of Finishes on Cotton Enzymatic Hydrolysis by Cellulase – Glucose release. Error bars denote the standard error (N=3).

Besides, it also seems that the crosslinking of the surface and the high hydrophobicity of the water repellent treatment reduces the availability of *cellulase*-binding sites on the cotton structure (Figure 9). The finishes applied during textile processing on cotton fabrics affect the binding ability of *Cellulase* to the surface of the fabric as follows: No Finish ~ Dye (Blue 19) ~ Softener >> Durable Press > Water Repellent. In general, it can be said that until the enzymes and microorganisms do not pass the layer of finishes, the biodegradation will not occur. However, based on Figure 4 the coverage of the treatment is not 100% complete, thus the overall biodegradation rate may be a complex function of finish coverage, the ability of enzymes to diffuse through the finish, non-productive binding to the treated surface, and the rate that the finish deteriorates and detaches from the cellulose in aquatic media.

The modified amino-functional silicone finishing applied to the cotton fabric in this study shows a tendency to promote the biodegradability of cotton as in accordance with previous observations by Li et al. (2010) [47]. In terms of *cellulases* interactions, no differences were observed in comparison to the dyed and control cotton fabrics. Nevertheless, it has been reported that polydimethylsiloxane polymers tend to adsorb non-specific proteins from the surrounding environment due to their hydrophobicity triggering microbial adhesion and biofilm formation [60,61]. The surface hydrophobicity of the silicon-coated cotton fabric is not high enough to delay the penetration of water and enzymes within the fabric and fiber structure but it seems is somehow promoting biodegradation (Table 7).

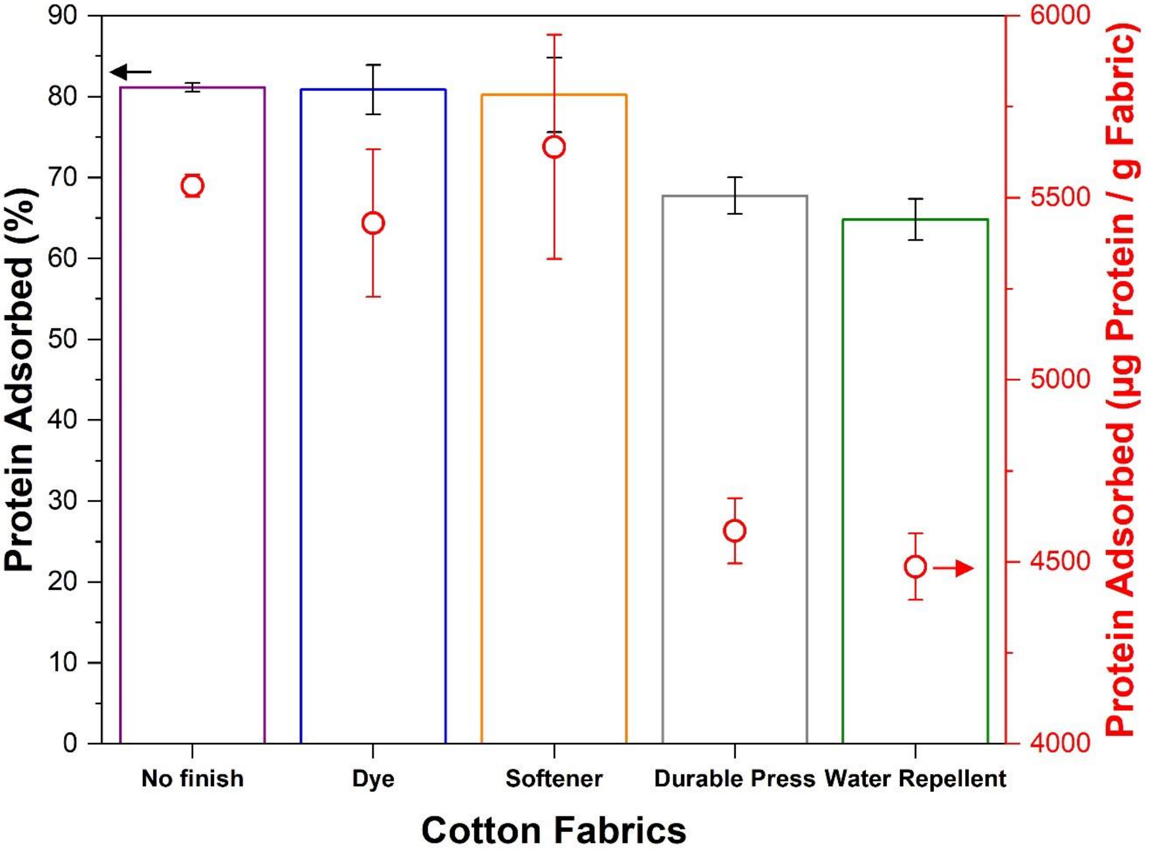


Figure 9. Effect of Finishes on the Adsorption of Cellulase Enzyme on Cotton Fabrics. Error bars denote the standard error (N=3).

3.4 Environmental Implications

Even though the cotton fabrics degraded significantly under the conditions of this study, and are expected to biodegrade in fresh and seawater as demonstrated in our previous study for cotton yarns [29], the active compounds of the finishing formulations are, in most cases, not biodegradable, and there are concerns about their environmental effects and toxicity. These finishes were applied in a wet state with a concentration ranging from 2 to 8 % owb (on weight of the bath) in the fabrics (Table 1). Textile finishes are in the range of several µg per m^2 of fabric or some mg per Kg of fabric [62].

Fabric finishing has an enormous impact on the environment due to the use of large volumes of water and energy, and the amount and great variety of chemicals used during the process [62,63]. Most of the hazardous chemicals in easy-care products, fluorocarbons for water- and oil-repellent properties, dyes, softeners, anti-static agents, flame retardants (halogen or phosphor-based), plasticizers and solvents in the formulations have already been proposed for or are already restricted or banned [62,63]. These substances could be carcinogenic, mutagenic, toxic for reproduction, allergenic, and present several environmental hazards [62]. These substances are not limited to the treatment of cellulosic fabrics; synthetic fabrics also used a vast extent of chemicals for finishing.

In general, for cellulosic, wool, and acetate fabrics the finishes are used to improve wrinkle resistance, water repellency, soil resistance, fire resistance, hand feel, shrinkage control, abrasion resistance, and colorfastness [64]. Synthetic fabrics such as polyester are hydrophobic and finishes are required to overcome some problems such as the generation of static electricity, poor heat resistance, yarn slippage, and uncomfortable feel to the skin [64].

The most common functional finishes for cellulosic fabrics are durable press resins for wrinkle resistance and dimensional stability, softening agents for hand feel, water/soil repellents, and antimicrobials [30,31,64,65].

The main concern with durable press finishes is the release of free-formaldehyde that can irritate mucous membranes, cause teary eyes, coughing, headaches, difficulties in breathing, and skin irritation and allergies [37,63,65–69]. Formaldehyde is a volatile organic compound that has been reported to be highly toxic and human carcinogenic [63,66–70]. Fabrics treated with DMDHEU are susceptible to formaldehyde release, DMDHEU is the final product of the reaction between urea, glyoxal, and formaldehyde [37,69].

The formaldehyde released from DMDHEU finished fabrics tends to be higher at high temperatures and pH, and it decreases in sweat solution compared to pure water [69,71–74]. Nevertheless, the level of formaldehyde release can be reduced by increasing the catalyst concentration and curing temperature during the crosslinking of DMDHEU in the cotton fabric [69,71–74].

The early versions of durable press finishes contained large amounts of free formaldehyde, but in the last decades, the conditions of finishing have improved, and the formaldehyde release is likely below the threshold for the elicitation of dermatitis [75]. The threshold level for formaldehyde in clothes that may cause allergic contact dermatitis (ACD) is unknown [76]. In the US, it has been reported that levels < 200 ppm are safe for ACD and textiles usually do not contain higher amounts, there is no definite proof that ACD from formaldehyde in the USA is caused by textiles [76].

In this study, a short-chain PFAS (C6) was used as a water repellent agent who is possibly derived from a fluorotelomer-based product containing perfluorohexanoic acid (PFHxA) as side chain [39,40,77]. The lack of sulfur in the XPS analysis (Table 6) suggests that the presence of perfluorohexane sulfonic acid (PFHxS) is unlikely.

In general, PFASs-based water repellents will form and release persistent perfluoroalkyl acids (PFAAs) or precursors for persistent PFAAs [41,78,79]. A recent study showed that the fluorinated compounds applied to synthetic textiles for water repellency are most likely chemically bonded to the microfibers released during laundering and not free in the laundering water [79]. These compounds are applied to natural, cellulosic, and synthetic fabrics for water and oil repellency and soil resistance [63,80,81]. The fluorinated side chains will be slowly cleaved from the coated fibers in the environment or the wastewater treatment plants and then transformed into shorter perfluoroalkyl acids (PFAAs) [79]. The polymeric C6 fluorinated compound used as a water repellent in this study to impart water repellency to cotton will ultimately degrade to form highly stable perfluorohexanoic acid (PFHxA) [39,78]. Short-chain PFAAs are equally persistent as their long-chain counterparts; nevertheless, they have low bioaccumulation potential, short-chain PFAAs have a higher elimination rate except for PFHxS (C6) which has a longer half-life in humans than perfluorooctanoic acid (PFOA, C8) and perfluorooctanesulfonic acid (PFOS, C8) [39,40]. In animals, the acute toxicity of short-chain PFASs is low, but repeated exposure could cause damage to the liver and kidneys [82]. Nevertheless, the relatively high concentrations of short-chain PFAS in human tissues indicate that these chemicals behave differently in humans than in laboratory animals, there are studies showing associations between PFHxS and effects on lipid metabolism, fertility, thyroid hormones, asthma, and children’s behavior [82]. In general, the toxicity of PFAS increases with increasing fluorocarbon chain length, however, the toxicity of short-chain PFAS has not been thoroughly studied or well described, and there are exceptions [82].

An alternative for short-chain PFAS is silicone compounds similar to the softener used in this study that does not affect the biodegradation of the cotton fibers significantly. Nevertheless, silicone-based water repellents for synthetic, natural, and cellulosic fabrics have moderate durability to laundering and do not offer oil repellency [39,80] There is no alternative matching the performance of the PFAS-based repellents [41].

The siloxanes present in the softener structure are persistent and widespread in the environment, mainly in urban areas and in aquatic ecosystems; apparently, they are inert and generally have no adverse effects [41]. Nevertheless, there is uncertainty about the potential release and hazard of persistent siloxanes during the lifecycle of silicone-based additives [39,41]. The potential degradation products from silicone-based textile finishes are short-chain silanols, dimethylsilanediol (DMSD), and tetramethylsilane (TMS); cyclic siloxanes (D4 and D5) may also remain in the fabrics as impurities [39,41]. For short-chain silanols, DMSD, and TMS, there is a huge data gap in terms of toxicity and effects on human health [39]. These compounds can degrade slowly in the environment; therefore, there are still considered persistent [39]. In the case of the cyclic siloxanes impurities, these compounds are very persistent and bioaccumulative, have high acute toxicity for humans and aquatic environments [39].

Likewise, textile dyes applied to synthetic and natural fabrics not only represent an aesthetic problem to water bodies, but their lack of biodegradability can also cause significant effects in human health and the ecology of aquatic environments [83–88]. Eutrophication, oxygen depletion, photosynthesis impairment, inhibition of plant growth, persistence, bioaccumulation, toxicity, mutagenicity, and carcinogenicity are some of the problems caused by textile dyes [83–88].

The reactive blue 19 dye used to finish the fabrics of this study leached to the water during this biodegradation study, as was observed visually as the water became blue (Figure 22). Blue 19 contains an anthraquinone nucleus as a chromophore group that makes this type of dyes extremely resistant to biodegradation due to their fused aromatic structures [83,84,89]. Anthraquinone-based reactive dyes have acute toxicity and mutagenicity on exposed aquatic organisms [90]. The half-life of the hydrolyzed and the vinyl sulfone form of the reactive blue 19 dye is about 46 years at pH 7 and 25 °C [85,91]. Blue 19 derivatives have been observed during the degradation of cotton fabrics in soil [92,93]. The degradation products were formed losing the $-SO_{3-}$ groups from the hydrolyzed form of the dye creating desulphonated hydrophobic biodegraded products that are difficult to degrade further [93].

It is important to note that as society strives to replace synthetics with biobased materials that the manufacturing techniques, derivatization, blending and coating to improve their performance in use, have implications on the environmental fate and impact of the overall product.

4. Conclusions

The finishes applied during textile processing on cotton fabrics influence the dynamics of biodegradation in aquatic environments, specifically the rate at which this process occurs. In general, the biodegradation extent decreases as follows: Softener > MCC > Water Repellent ~ No Finish > Dyed (Blue 19) ~ Oak Leaves > Durable Press. Nevertheless, the cotton fabrics evaluated in this study degraded significantly (>60%). The biodegradation of fabrics with some levels of crosslinking in the finishing treatment was more affected. Cotton fabrics with water repellent finish have the longest lag-phase (λ), while cotton fabrics with durable press finish had the lowest degradation rate (R) and degraded the least among the samples. Likewise, the fabrics that have some levels of crosslinking (durable press and water repellent) and high hydrophobicity (water repellent) on the surface slow down the initial adsorption of enzymes excreted by the microorganisms in the inoculum and delay the penetration of *Cellulases* within the polymeric matrix that result in a decrease in the cellulose hydrolysis to glucose. The active compounds of these finishing formulations are, in most cases, not biodegradable, and they will ultimately be released to the water.

5. Accomplishments in 2019

- The manuscript "*Aquatic Biodegradability of Cotton, Polyester, and Rayon Yarns*" won the second place in the Herman and Myrtle Goldstein Graduate Student Paper Competition, American Association of Textiles Chemist and Colorist (AATCC) 2019 International Conference (April 2019).
- The poster "*Aerobic Biodegradation in Freshwater and Marine Environments of Textile Microfibers Generated in Clothes Laundering: Effects of Cellulose and Polyester-based Microfibers on the Microbiome*" won the third place in the Molecular Biotechnology Symposium Poster Competition (3rd Place Winner), NC State University, Raleigh, USA (November 2019).
- The manuscript "*Aerobic biodegradation in freshwater and marine environments of textile microfibers generated in clothes laundering: Effects of cellulose and polyester-based microfibers on the microbiome*" was accepted for publication in Marine Pollution Bulletin.
- Several presentations at national and international conferences were performed: AATCC, ACS, BEPS, Textile Exchange, RISE, ICAC, University of Sydney, Textile Exchange Sustainability Conference TExcrusion, etc.

6. Next Steps

- Perform anaerobic biodegradation experiments of the finished cotton fabrics using mesophilic digestion sludge from OWASA (Orange Water And Sewer Authority) in Chapel Hill following the ISO method 14853:2016 "Determination of the ultimate anaerobic biodegradation of plastic materials in an aqueous system — Method by measurement of biogas production" using the Echo Respirometer

- Perform aerobic lake water and seawater biodegradation experiments of the finished cotton fabrics using the RSA PF-8000 Respirometer.
- Submit water samples of biodegradation experiments of cotton with dyes/finishes to Dr. Nelson Vinueza in the Textiles Department at NCSU to characterize the dye, finishes and their degradation products using low and high-resolution mass spectrometry. The samples are currently being stored at -20°C in the Forest Biomaterials Department.

7. Appendix A

7.1 Fabrics characterization

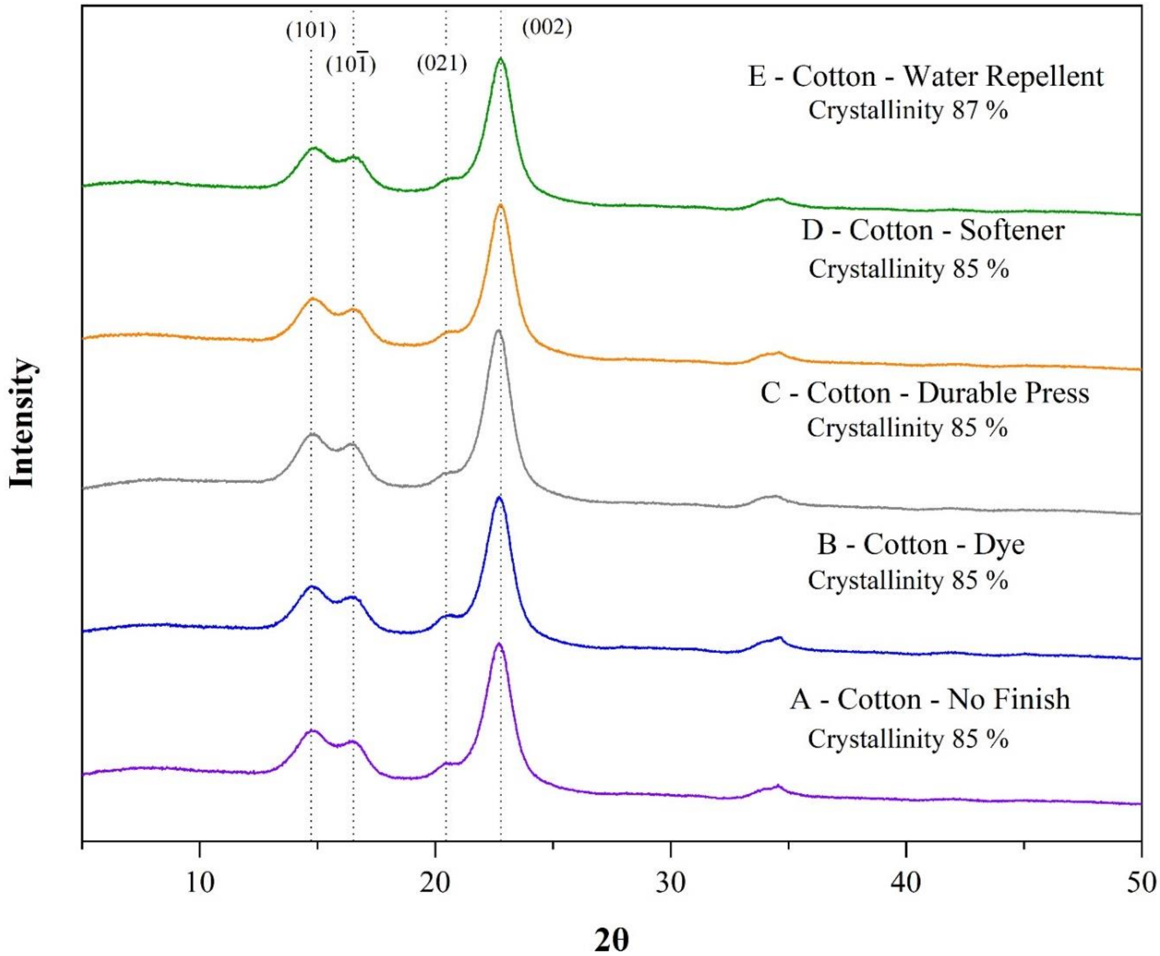


Figure 10. X-Ray diffraction spectra, characteristic peaks, and crystallinity of cotton fabrics with different finishes: water repellent, softener, durable press, a dye (blue 19), and as control a non-treated fabric (no finish).

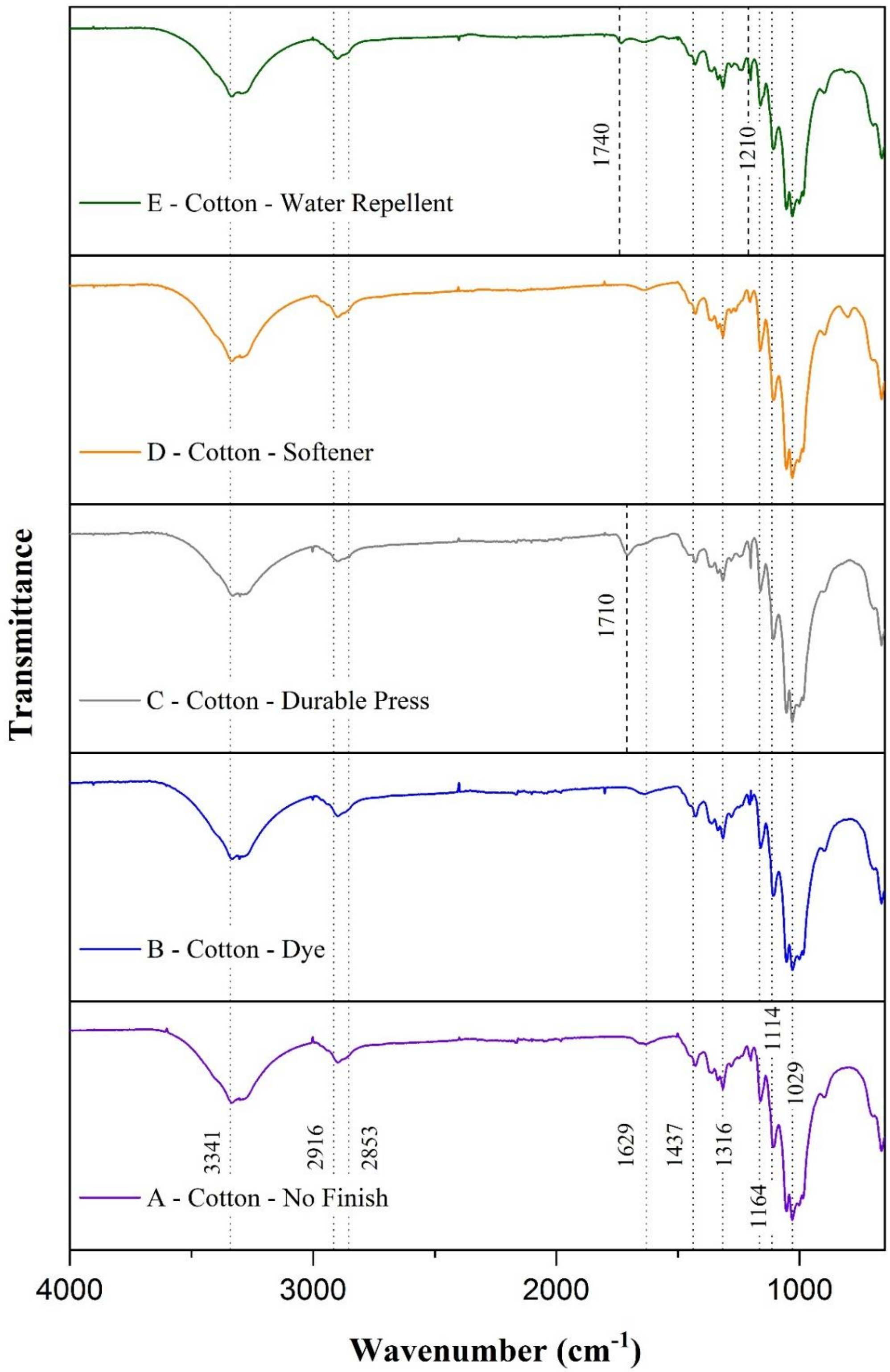


Figure 11. FTIR spectrum of cotton fabrics with different finishes: water repellent, softener, durable press, a dye (blue 19), and as control a non-treated fabric (no finish).

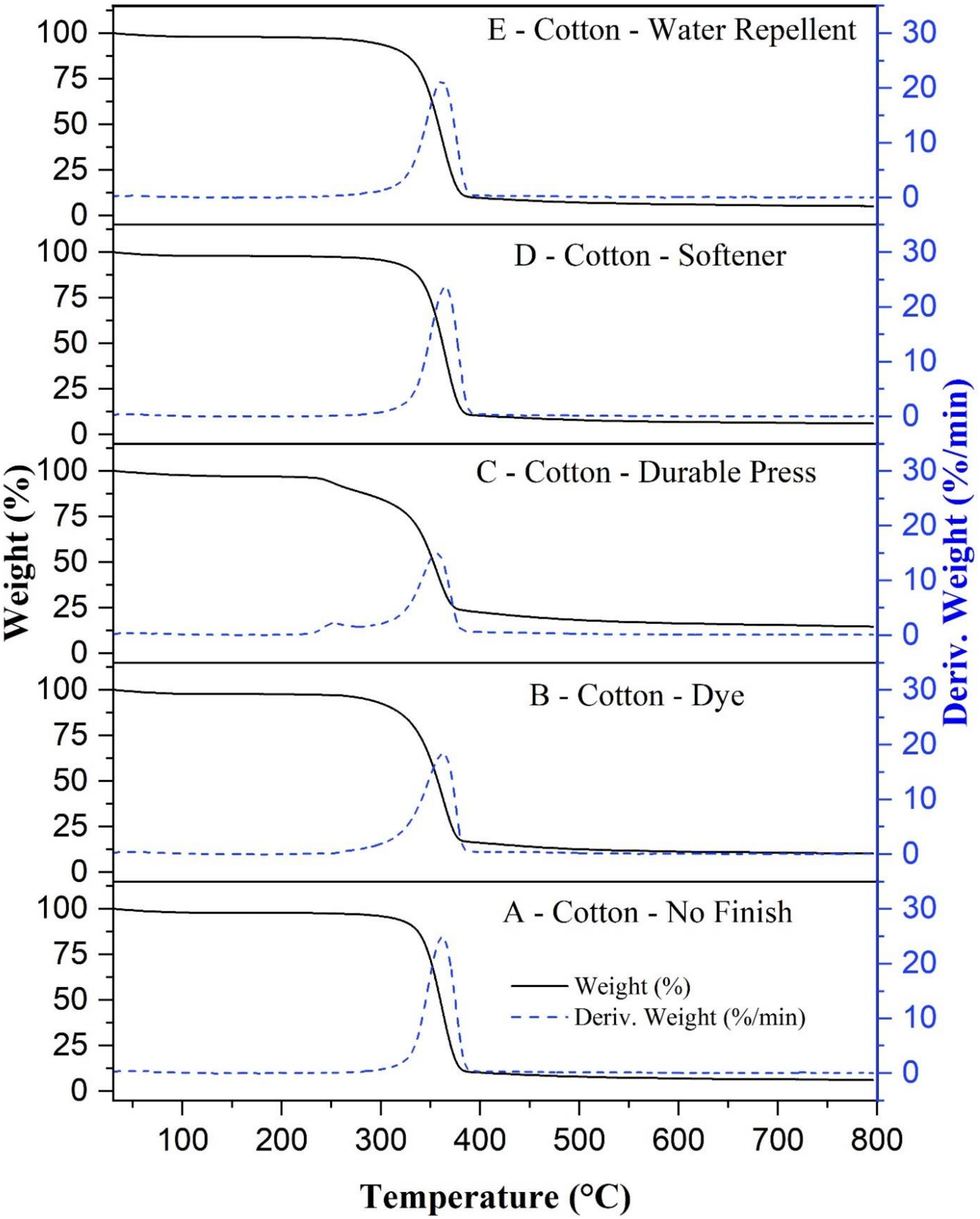


Figure 12. Thermo-Gravimetrical Analysis of cotton fabrics with different finishes: water repellent, softener, durable press, a dye (blue 19), and as control a non-treated fabric (no finish). Weight Loss and Deriv. of Weight Loss vs. Temperature. Samples conditioned at 65% relative humidity and 21°C.

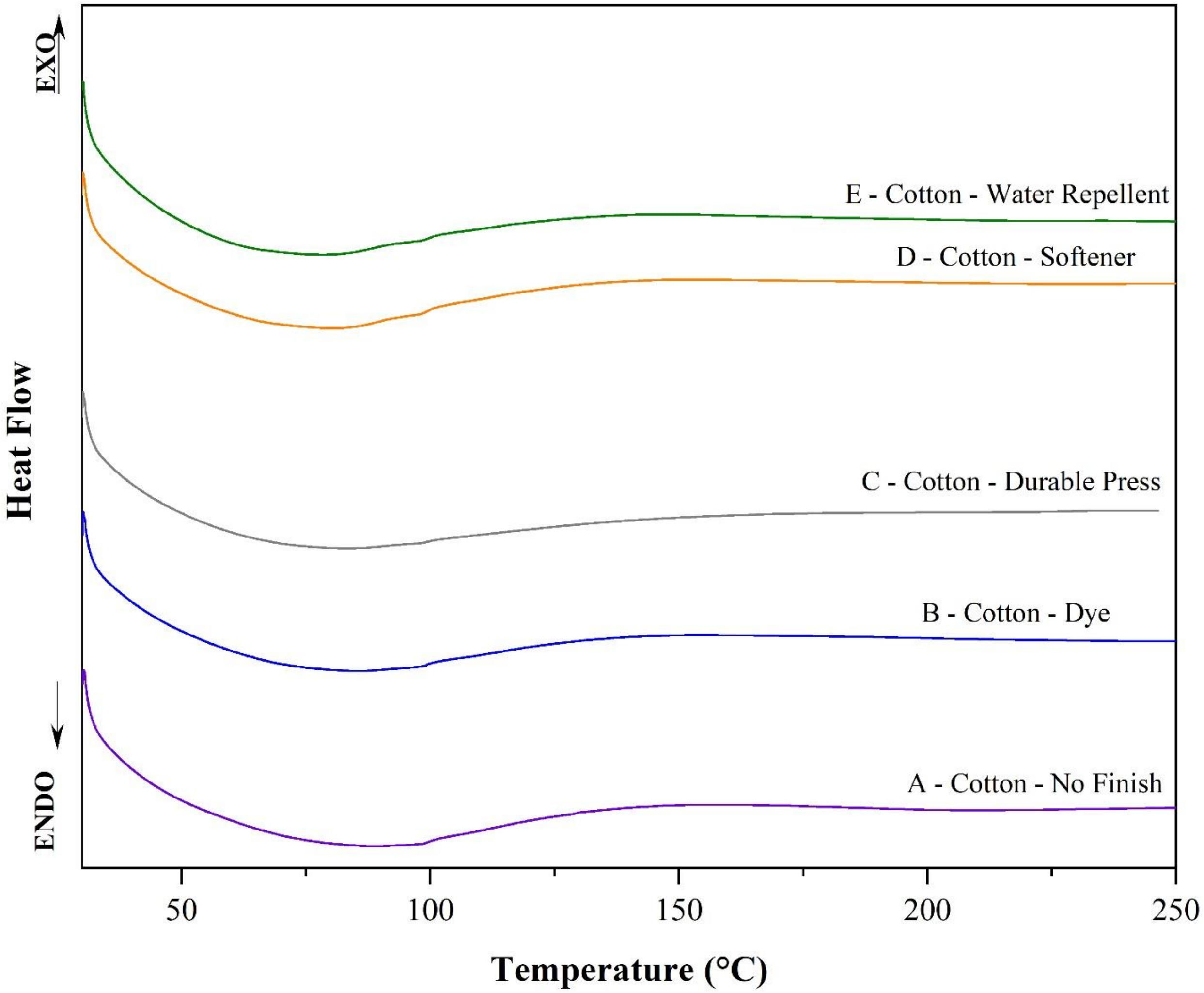


Figure 13. Differential Scanning Calorimetry Curves of cotton fabrics with different finishes: water repellent, softener, durable press, a dye (blue 19), and as control a non-treated fabric (no finish). Heat flow vs Temperature. Samples conditioned at 65% relative humidity and 21°C.

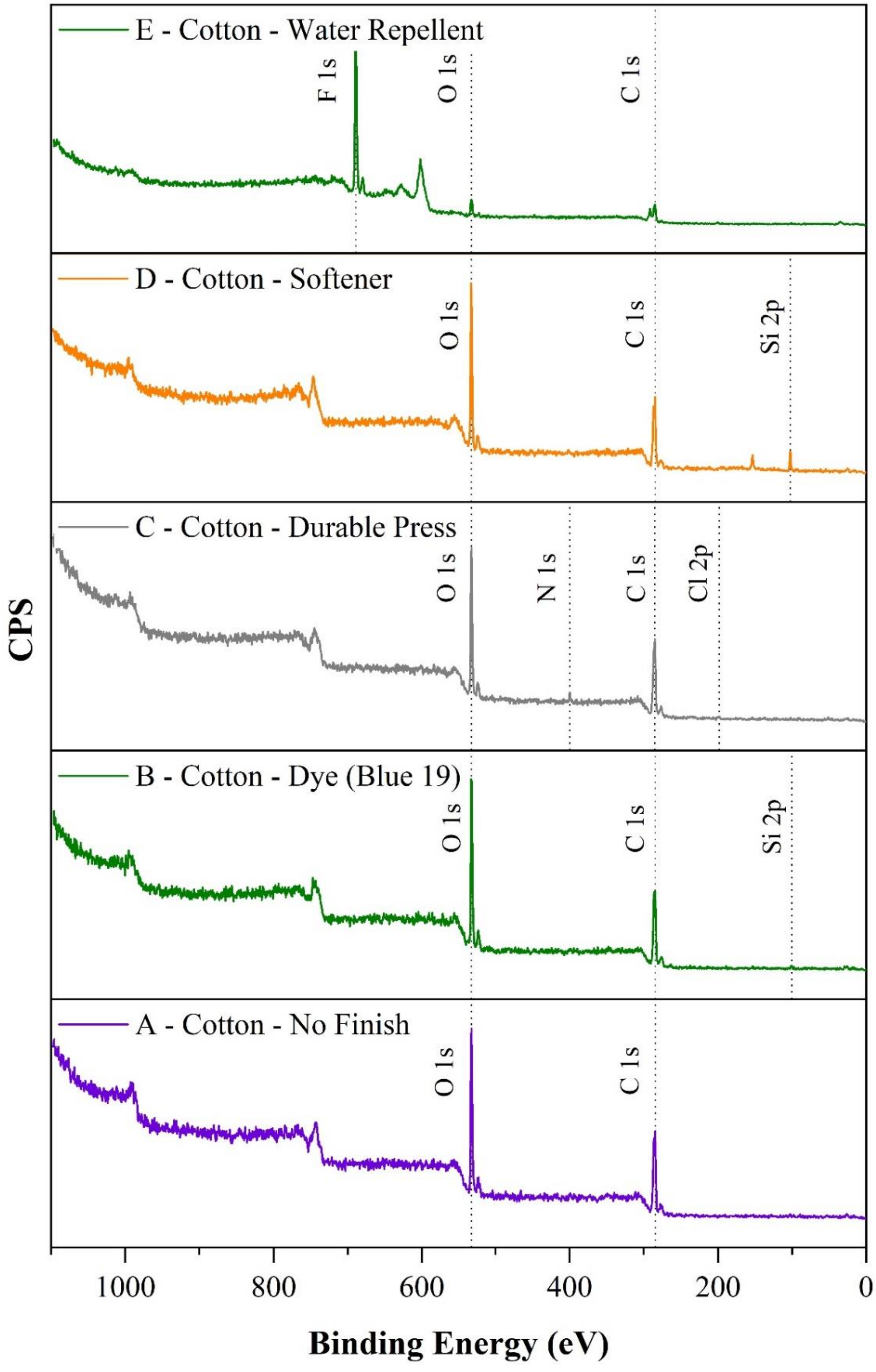


Figure 14. XPS spectra of cotton fabrics with different finishes: water repellent, softener, durable press, a dye (blue 19), and as control a non-treated fabric (no finish).

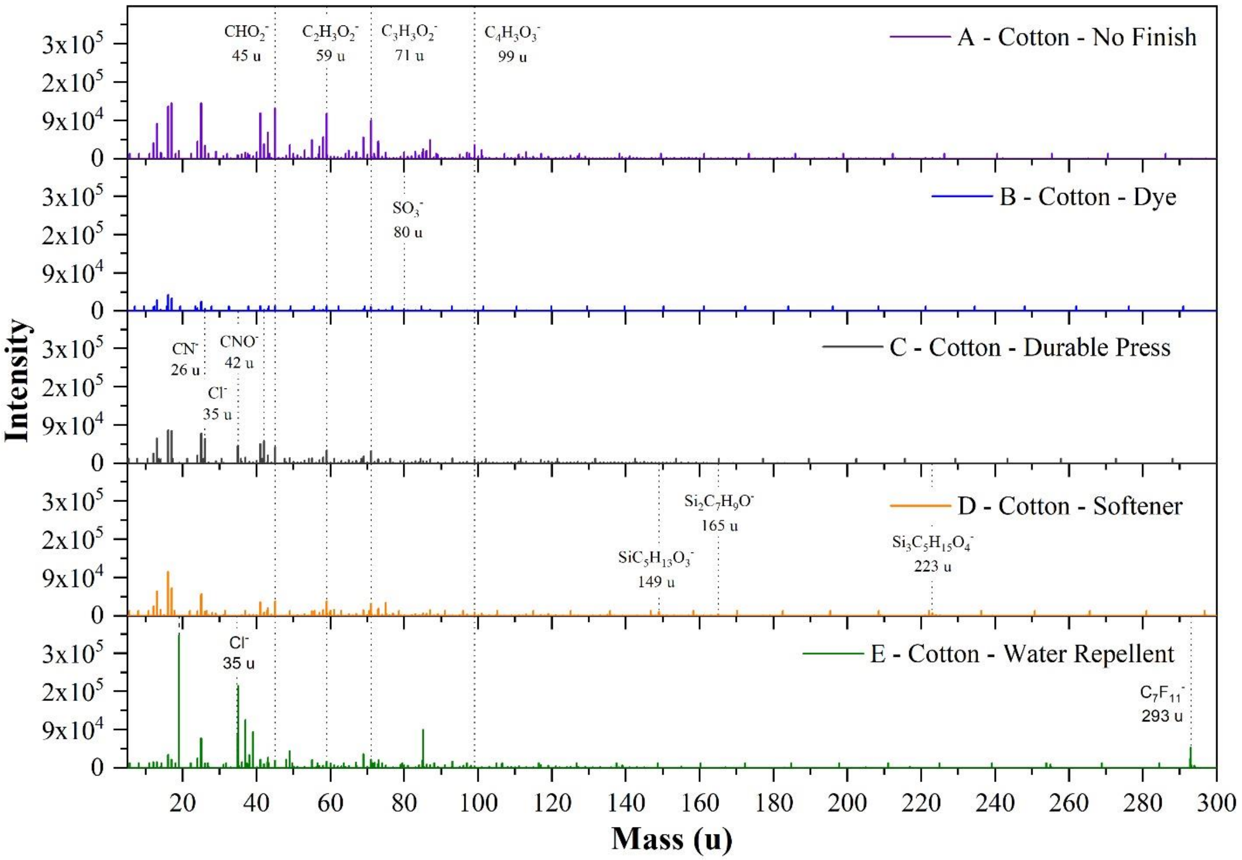


Figure 15. Negative ToF SIMS spectra of of cotton fabrics with different finishes: water repellent, softener, durable press, a dye (blue 19), and as control a non-treated fabric (no finish).

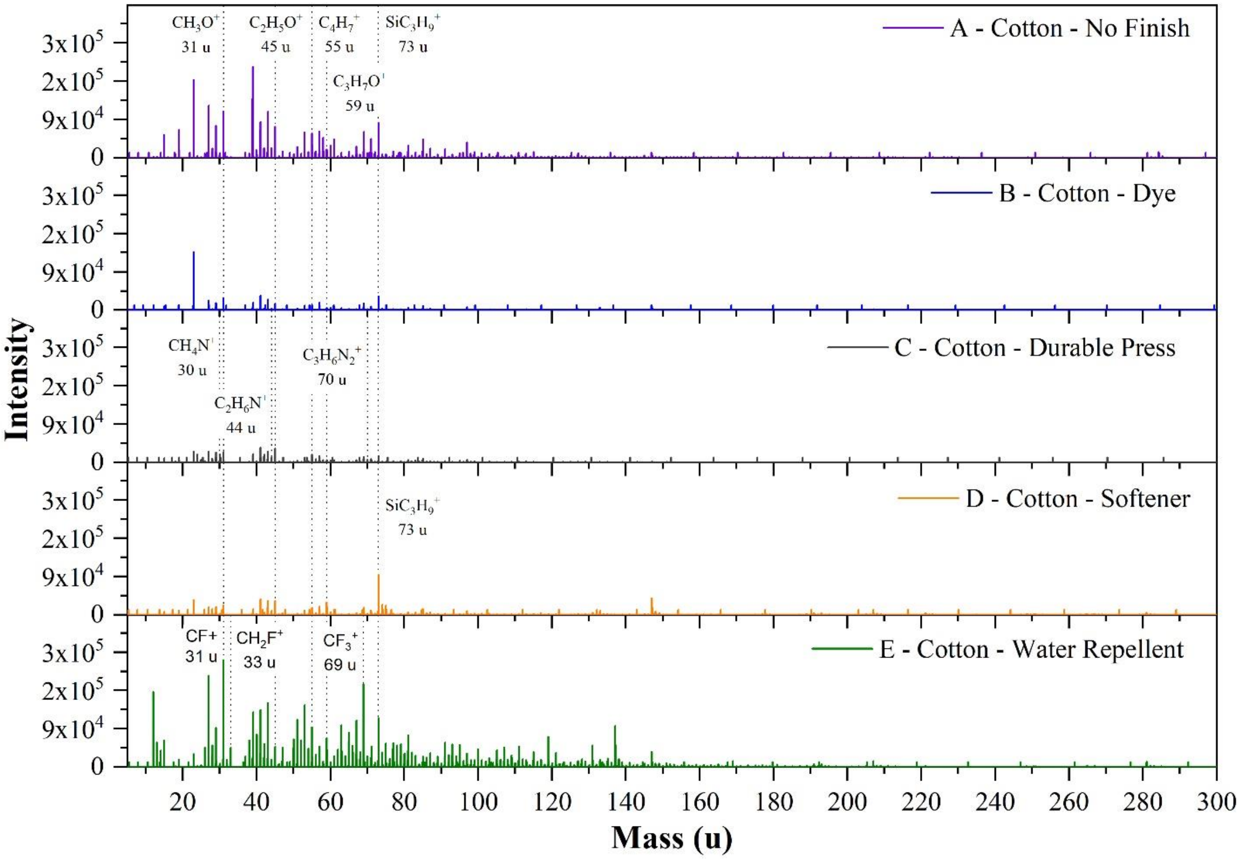


Figure 16. Positive ToF SIMS spectra of of cotton fabrics with different finishes: water repellent, softener, durable press, a dye (blue 19), and as control a non-treated fabric (no finish).

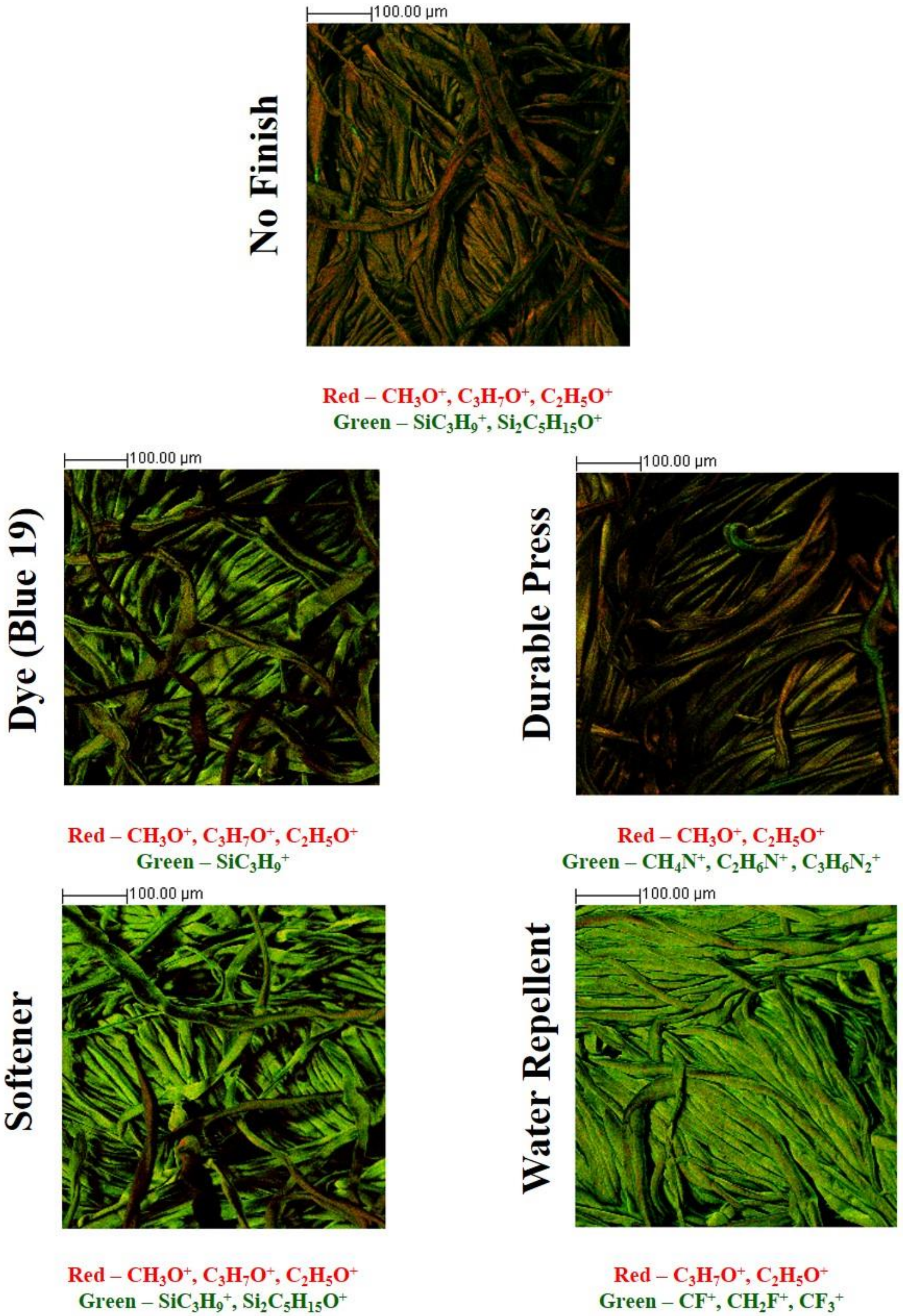


Figure 17. Distribution of finishes of the surface of cotton fabrics by ToF SIMS (positive ions), red color reflects cellulose groups and the green color indicates groups from the finishing treatment.

7.2 Aquatic biodegradability in aerobic conditions

Table 10. Elemental Analysis and theoretical oxygen demand of cotton fabrics, oak leaves, and MCC.

Sample	**Carbon**	**Hydrogen**	**Nitrogen**	**ThOD**
Name	**-wt. %-**	**-wt. %-**	**-wt. %-**	**mg O_2/g Fabric**
Cotton - No Finish	43.54	6.62	0.14	1193.67
Cotton – Dye (Blue 19)	43.66	6.57	0.32	1195.37
Cotton – Durable Press	43.13	6.71	0.50	1190.33
Cotton - Softener	43.17	6.63	0.06	1180.20
Cotton – Water Repellent	43.57	6.61	0.10	1193.47
Oak Leaves	44.23	5.27	0.91	1104.83
Reference Material (Microcrystalline Cellulose)	44.44	6.17	0.00	1185.19

Table 11. Compositional Analysis fabrics (control, no finish) and oak leaves.

Component	**Samples**	
	Oak Leaves	**Cotton**
Glucose (%)	12.54±0.25	88.24±2.62
Xylose (%)	4.79±0.03	0.2±0.02
Galactose (%)	3.22±0.03	0.92±0.07
Arabinose + Mannose (%)	3.68±0.07	0.97±0.07
Klason Lignin (%)	38.03±1.73	0.61±0.15
Ash (%)	11.62±0.39	0.32±0.08
Others (%)*	26.12±1.74	8.74±3.02

* Acid Soluble Lignin (ASL) and Extractives

Table 12. Inoculum collection.

Inoculum	Activated Sludge
Collection Site	Neuse River WWTP
GPS Coordinates	35°43'08.7"N 78°29'08.8"W
Date	March 18, 2019
Time	10:30 am
Temperature	17.7 °C
Dissolved Oxygen	0.99 mg/L

Table 13. Inoculum characteristics*.

Characteristics	**Mean**	**SD**

Total Kjeldahl Nitrogen TKN (mg/L)	255.75	6.24
Ammonium Nitrogen NH$_4$ N (mg/L)	29.23	1.41
NO$_3$ N (mg/L)	0.08	0.04
Total Nitrogen (mg/L)		
Total Phosphorus (mg/L)	131.00	4.59
Orthophosphate (mg/L)	29.50	0.97
Total Suspended Solids TSS (mg/L)	2986.67	76.88
Conductivity (uMHOS/cm)	683.33	16.67
Total Organic Carbon TOC (mg/L)	143.98	2.03
Total Carbon TC (mg/L)	159.83	7.34
C/N	6.24	0.02
pH	6.06	0.03
Na	8.93	0.09
K	28.20	1.73
Ca	9.02	0.15
Mg	18.13	0.27
Cu	0.57	0.04
Zn	1.27	0.07
Fe	79.40	4.28
Mn	1.34	0.08
Cd	0.017	0.003
Pb	0.24	0.06
Ni	0	0
Cr	0	0

*Analyses performed at the Environmental Analysis Laboratory in the Department of Biological Agricultural Engineering (BAE), North Carolina State University (American Public Health Association et al., 2012; U.S. EPA, 1993).

SD – Standard Deviation

Table 14. Nitrification interferences (N=4).

Sample	**BOD N NO_3/NO_2**	
	mg/L	**SD**
Cotton - No Finish	8.67	1.10
Cotton – Dye (Blue 19)	7.29	0.79
Cotton – Durable Press	7.78	0.51
Cotton - Softener	7.84	0.38
Cotton – Water Repellent	7.79	0.45
Oak Leaves*	8.74	0.18
Reference Material (Microcrystalline Cellulose)	7.61	0.15

SD – Standard Deviation

Table 15. CNH analysis of the materials after biodegradation.

Sample	**C**		**H**		**N**	
	Wt.%	**SD**	**Wt.%**	**SD**	**Wt.%**	**SD**
Cotton - No Finish	10.68	2.66	2.66	0.55	1.57	0.29
Cotton – Dye (Blue 19)	9.63	1.24	1.92	0.35	1.00	0.40
Cotton – Durable Press	22.77	1.59	3.41	0.12	1.47	0.09
Cotton - Softener	6.03	1.98	1.84	0.17	0.84	0.17
Cotton – Water Repellent	15.12	4.33	2.53	0.47	1.35	0.20
Oak Leaves*	23.15	5.35	3.38	0.68	1.59	0.35
Reference Material (Microcrystalline Cellulose)	10.80	2.03	3.08	0.51	1.56	0.26

* N =2, the rest of samples N=3, SD – Standard Deviation

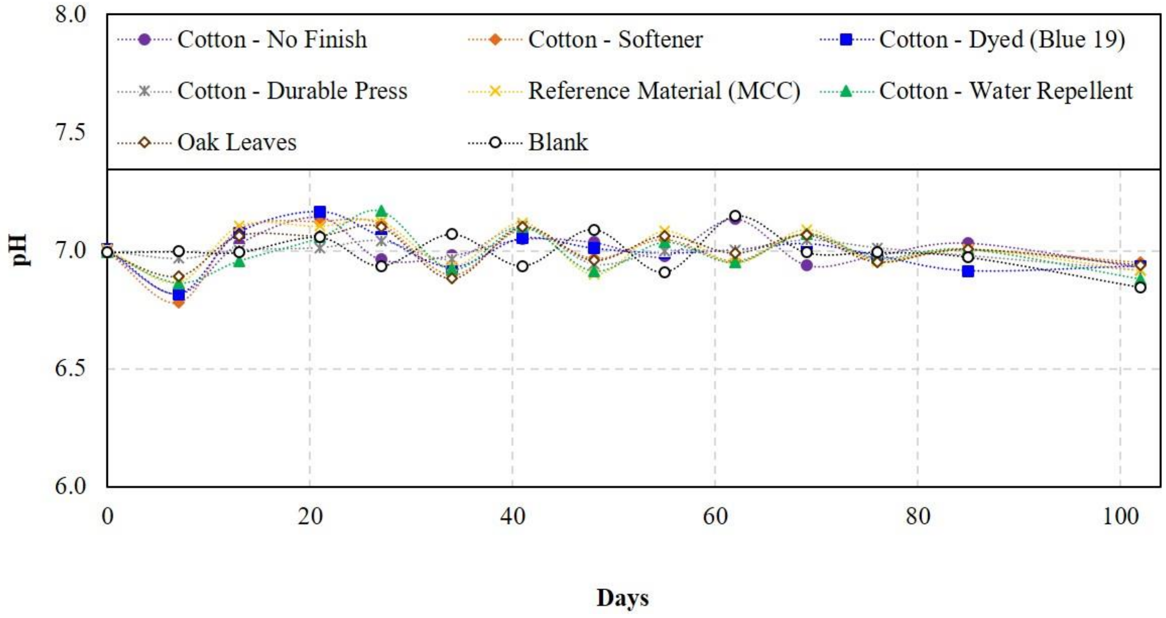


Figure 18. Effect of finishes on the biodegradation of the cotton microfibers, pH profile during the biodegradation.

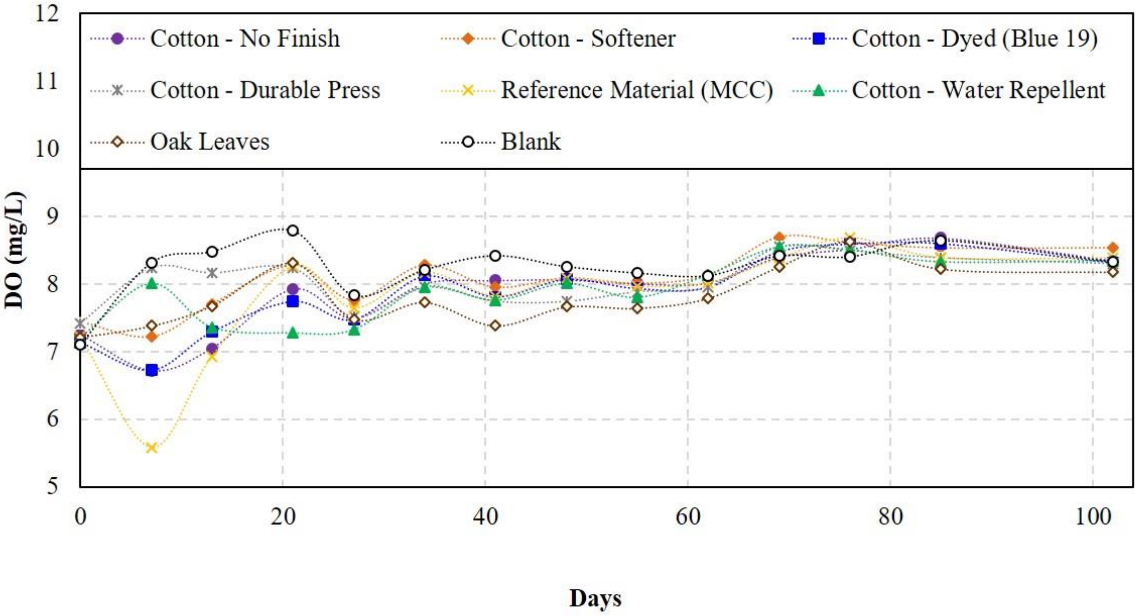


Figure 19. Effect of finishes on the biodegradation of the cotton microfibers, dissolved oxygen profile during the biodegradation.

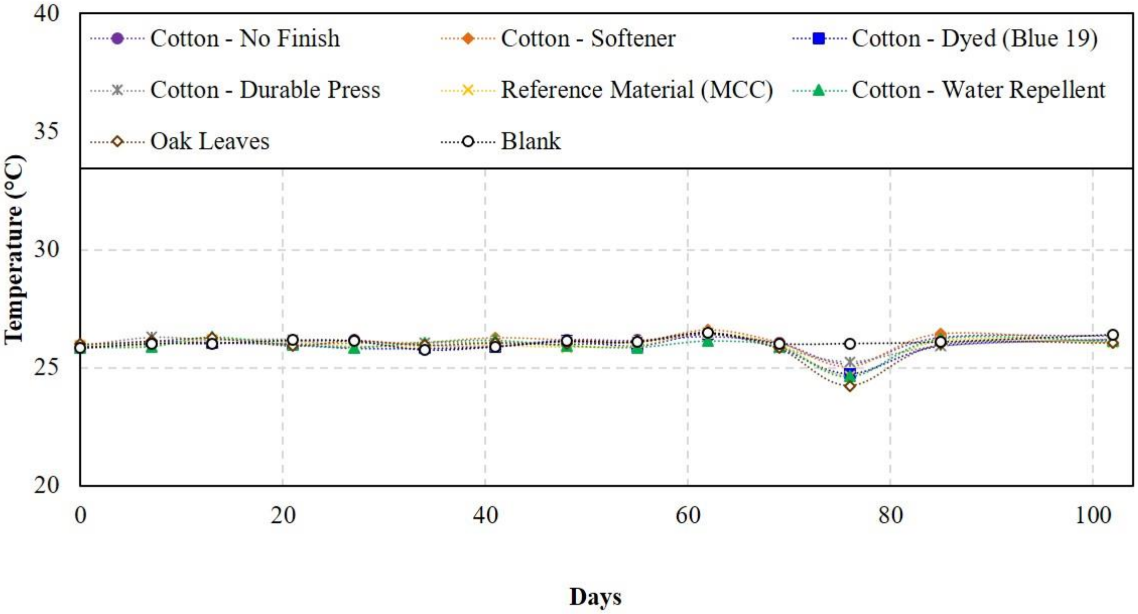


Figure 20. Effect of finishes on the biodegradation of the cotton microfibers, temperature profile during the biodegradation.

Table 16. Effect of finishes on the biodegradation of the cotton microfibers in aquatic environemnts using activated sludge from Neuse River wastewater treatment plant at low concentration (30 ppm TSS) – NPAR1WAY (Wilcoxon model, Kruskal-Wallis test) at a 95% confidence interval (=0.05).

Median One-Way Analysis	
Chi-Square	8.8667
DF	6
Pr > Chi-Square	0.1812

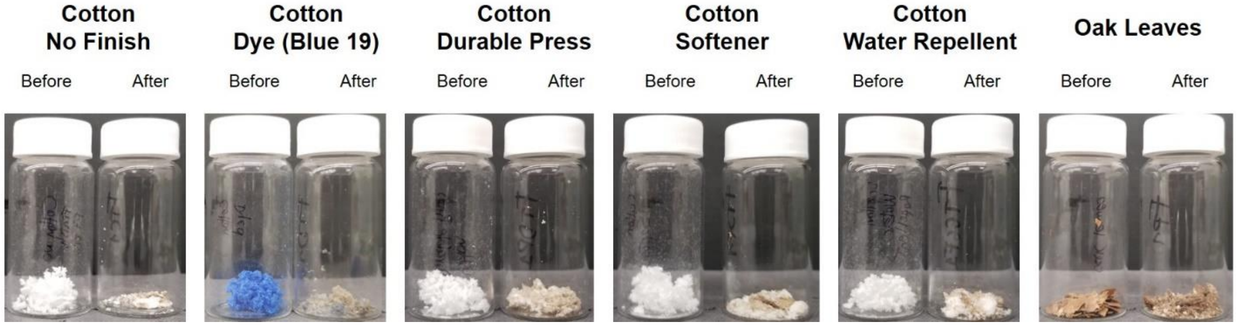


Figure 21. Fabrics before aerobic biodegradation (left, initial) and residual solids after biodegradation (right, final). In this experiment, activated sludge from the Neuse River WWTP was used as inoculum at low concentration

Figure 22. Water collected from the incubation bottles after aerobic biodegradation of cotton without finishes (left) and cotton dyed with Blue 19 (right). In this experiment, activated sludge from the Neuse River WWTP was used as inoculum at low concentration.

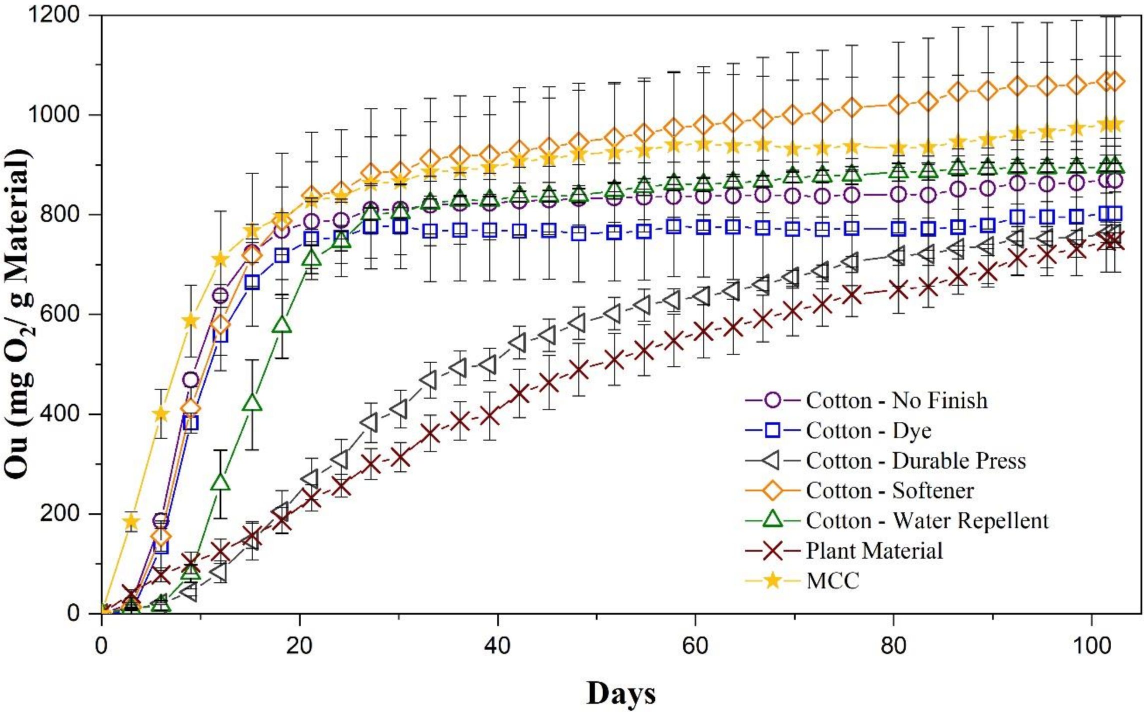


Figure 23. Oxygen uptake (Ou) curves - Effect of finishes on the biodegradation of the cotton microfibers. The error bars represent the standard error of the mean (N=3), for oak leaves N=2.

Table 17. First hydrolysis kinetic model parameters for the oxygen uptake data obtained during aquatic aerobic biodegradation of oak leaves and microcrystalline cellulose (MCC).

Sample	**Bo** (mg O_2/g initial material)	**K_h** (1/day)	**R^2**
Oak Leaves	1024.9 ± 57.4	0.013 ± 0.001	0.97
MCC	940.9 ± 23.2	0.099 ± 0.015	0.57

± Standard Error

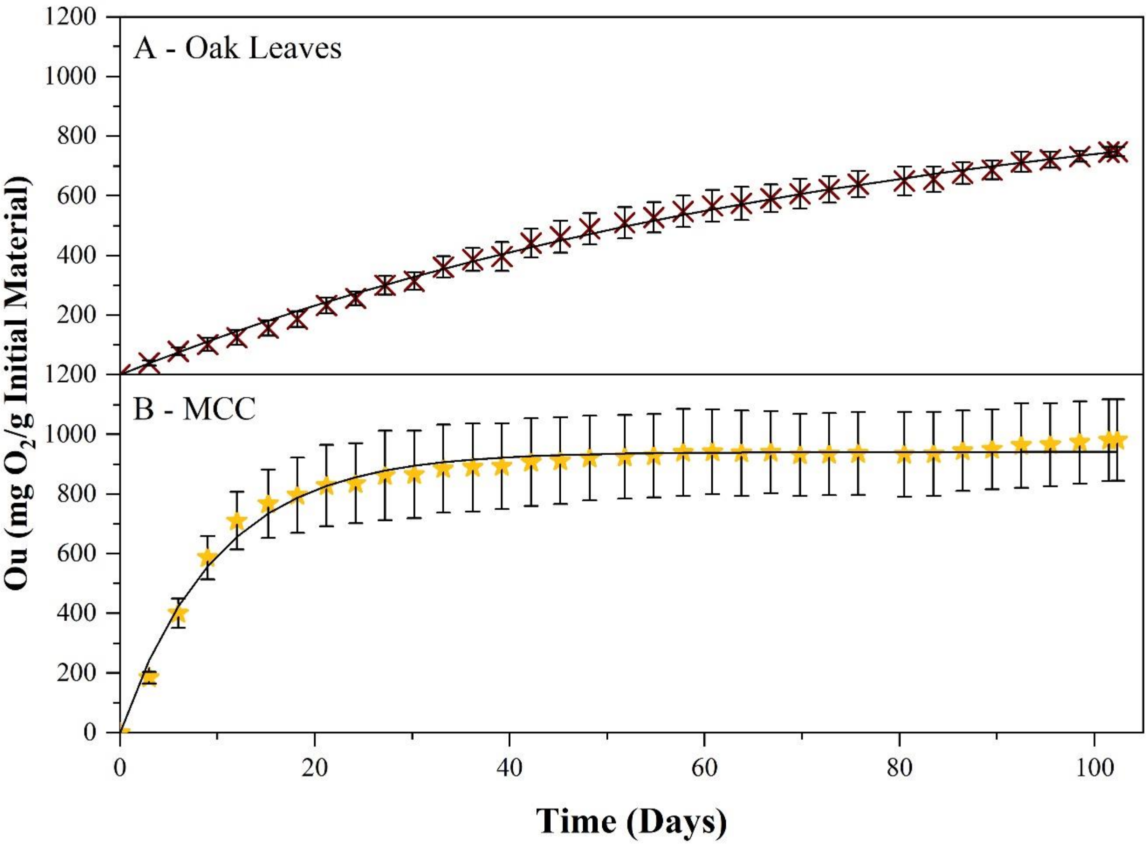


Figure 24. Oxygen uptake (Ou) curves - Effect of finishes on the biodegradation of the cotton microfibers. First hydrolysis kinetic model fitted to the oxygen uptake data obtained during aquatic aerobic biodegradation of oak leaves and microcrystalline cellulose (MCC). The error bars represent the standard error of the mean, for MCC N=3 and for oak leaves N=2.

7.3 *Cellulase* interactions

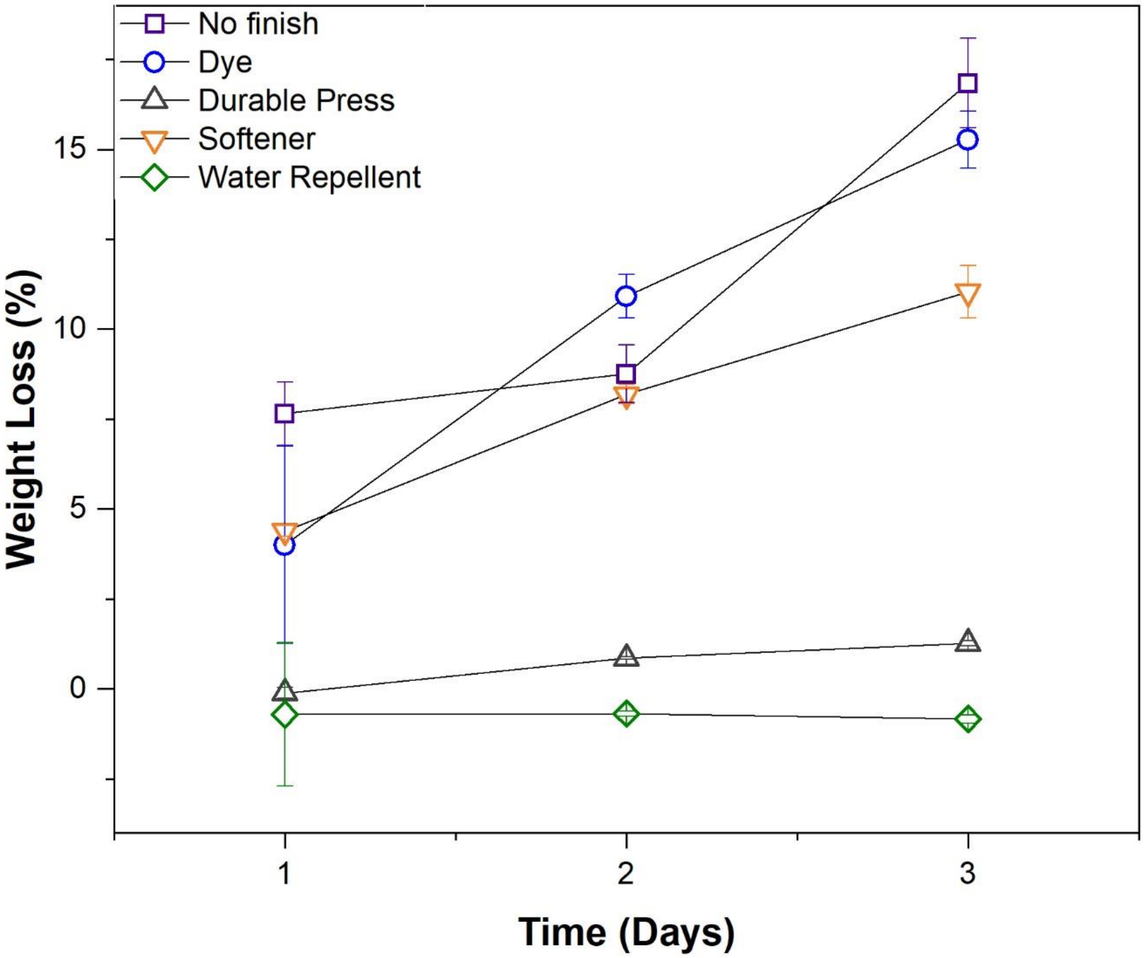


Figure 25. Effect of Finishes on Cotton Enzymatic Hydrolysis by Cellulase – Weight Loss. Error bars denote the standard error (N=3).

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