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Engineering Faculty

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SIMAU

Master thesis topic:

"RECYCLING OF TEXTILE WASTE: SORTING, TREATMENT OF MIXED TEXTILES AND RELATIVE ENVIRONMENTAL IMPACT".

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Preface

This MSc. thesis is submitted as a requirement for obtaining a master's degree in Environmental Engineering at Marche Polytechnic University UNIVPM. It is written based on data analysis obtained from the laboratory work at TU Wien university in Vienna - Austria, the work is conducted by the author, Rida Jbr, under the supervision of Prof. M. Letizia Ruello, and co-supervisor of Dr. Andreas Bartl and co-supervisor Chiara Giosue'.

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Rida Jbr

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Introduction.

The Textile - Clothing - Fashion value chain (TCF) is one of the most important and strategic in the "Made in Italy" sector: both for the number of companies (45,000), employees (398,000) and overall turnover (in 2018 about 55 billion euro, equal to 30.9% of the entire European TCF industries).

In Italy there is a complete TCF supply chain, whose macro-sector of production is characterized by a strong district vocation, with a strong component of heterogeneity. Another element that characterizes the Italian textile industry is the non-direct availability of natural fibers, which are almost always imported from foreign producers.

TCF are one of the most polluting and resource-draining industries in the world, next only to oil, in terms of environmental impact [DEFRA. (2008). Sustainable Clothing Roadmap Briefing Note. December 2007; Fletcher, K. (2008). Sustainable Fashion and Textiles: Design Journeys. London: Earthscan].

Pursuing increasingly sustainable production, transformation and resource management models based on the concept of circular economy thus becomes a factor of competitiveness and innovation for the entire supply chain.

The Italian Circular Economy Stakeholder Platform (ICESP that was launched in 2018 as the mirror platform of the ECESP - European Circular Economy Stakeholder Platform) has identified, among the Italian production chains, TCF as relevant, with the aim of identifying and promoting good practices and successful cases relating to the closure of cycles in the supply chain also at an intersectoral level and identify regulatory and technical criticalities of the sector.

The analysis conducted by ICESP, recommends the need for a systematic combination of strategies that help reduce impacts and encourage the reuse of resources (material, water and energy) in the sector of origin or in a new destination (industrial symbiosis). Since it is in the design phase that much of the fate and impact of the final textile product is determined, the centrality of a circular design is emphasized (eco-design both for the extension of the useful life and to favor recyclability and disassembly of clothing) and the development of standardized tools for measuring circularity. Furthermore, investments in

research activities are necessary to develop technologies and processes for the separation, reprocessing and recycling of the various fibers that make up the materials and products of the supply chain. Furthermore, in terms of recycling and recovery, clear rules and a general simplification of procedures must be adopted authorizations for the recovery and reuse of waste and products at the end of their life: the cessation of the status of waste is essential in the textile sector (End of Waste) for the valorisation of by-products and processing waste, currently considered waste. An enabling role in the implementation and dissemination of initiatives of circular economy is carried out by the creation of web platforms as meeting points between producers and users of secondary raw materials (industrial symbiosis) and by the implementation of digital technologies for traceability. Awareness-raising actions on the issues of sustainability and the circular economy are needed, to stimulate a real change of mentality and a cultural approach and re-orientation of consumer behavior to increase market acceptability towards recycled textile products.

ICESP has analyzed the relevant aspects for the transition to the circular economy for the TCF sector, identifying obstacles and barriers, and outlining some strategic priorities in the short, medium and long term.

Short-term priorities

• Substantial modification of the legislation through the definition of clear and certain rules on the reuse and recovery of waste, and by-roducts and the development of specific criteria for the sector on the regulation of the End of Waste;

• Creation of financial instruments and tax levers to support companies, for investments in innovative and mature technologies that allow the efficient recovery of resources;

• Creation of information meeting points (platforms, web sites) between supply and demand of pre- and post-consumer production waste (platforms and networks of industrial symbiosis).

Medium-term priorities

• Development and application of systems for measuring circularity and environmental impacts: increase in the use of tools for sustainability assessments with a life cycle approach (Life Cycle Assessment and Product Environmental Footprint);

• Increased awareness of consumers and society on circular economy issues, environmental product labeling and existing systems for the reuse/recycling of textile garments or for their sharing;

• Development of a simple and controlled national system for the separate collection of the textile fraction;

• Increase in the number of existing plants in the national territory for the recycling of textile materials and development of innovative technologies for recycling, in view of the obligation of municipalities to carry out separate collection of used clothing and textile waste in general from 2025;

• Harmonization of research and innovation activities and initiatives relating to the circular economy in the TCF sector and technology transfer activities to businesses;

• Interventions for the digitization of legally valid evidence on products and processes (certificates, laboratory analyzes, etc.) with the aim of digitally supporting circular economy processes and promoting interventions for the adoption and strengthening of data exchange standards in the supply chain.

Long-term priorities

• Training of operators and development of company know-how;

• Investments in research and development activities for technological and process innovation, with particular reference to the development of systems for the recognition, separation and treatment of composite textile materials;

• Widespread dissemination among companies of a true culture of innovation with an intersectoral vision, stimulating and supporting participation in research projects.

The present thesis work focus on one of the medium-term priorities, i.e. on the development of innovative technologies for recycling ...

Collection & Sorting of textile wastes.

The core message of recent studies regarding the recycling process of textile waste is that textile waste shall ultimately be considered as a new material resource.

A circular textile system is the future vision of garments sector, where products are made to last long, from safe, recycled or sustainably sourced inputs that can recirculate multiple times.

The complexity of textiles iscoming from the fact of the used materials to deliver innovative and high-performance products to consumers and because of the highest regard of safer, cleaner, and sustainable materials[Textile Waste as a Resource: Infrastructures, Waste Shipment, and Secondary Raw Materials Markets; Amersrdam, July 2021].

Therefore, the Policy Hub – Circularity for Apparel and footwear strongly recommends the followings:

1.   To harmonise EPR and waste collection rules across the EU.

2.   To bring textile recycling solution at scale through research, development and funding opportunities.

3.   To set a definition of textile waste, harmonising end-of—waste criteria at EU level to secure a constant flow of high quality secondary raw materials.

4.   To invest in sustainable innovations that can decontaminate waste streams and increase safe recycling.

5.   To simplify and digitalise the authorisation process under the revised waste shipment regulation when post-consumer recoverable waste is shipped within the EU and globally for the purpose of sorting, preparation for reuse or recycling.

A textile is a flexible material made up of a network of natural or artificial fibers. Most textiles are formed by weaving or knitting yarn into fabric, but textiles can also be non-woven, with fibers bonded into fabric by chemical, mechanical or

heat treatment. Textile products can be classified into apparel, industrial textiles and household textiles. Apparel is the largest area of textile use by some margin, accounting for around 60% of global demand for fibers, with the share of household and industrial textiles roughly equal (accounting for around 20% each of global demand for fiber) (PCI Wood Mackenzie, 2016).
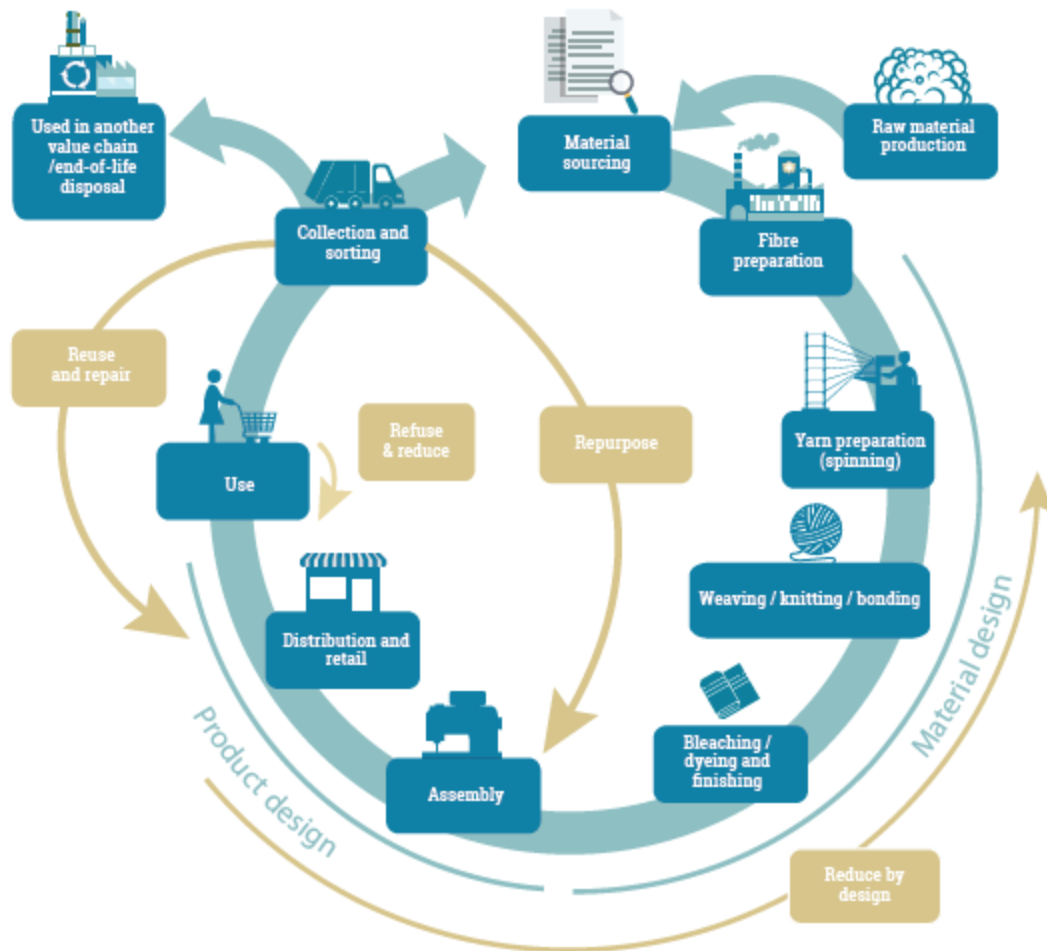
The textile value chain is comprised of all the activities that provide or receive value from designing, making, distributing, retailing and consuming a textile product (or providing the service that a textile product renders), including the extraction and supply of raw materials, as well as activities involving the textile after its useful service life has ended. In this sense, the value chain covers all stages in a product's life, from supply of raw materials through to disposal after use, and encompasses the activities linked to value creation such as business models, investments, and regulation. At all stages in the value chain, and in the transporting of intermediate and finished products between the different stages, raw materials and energy are required and emissions are released into the environment.
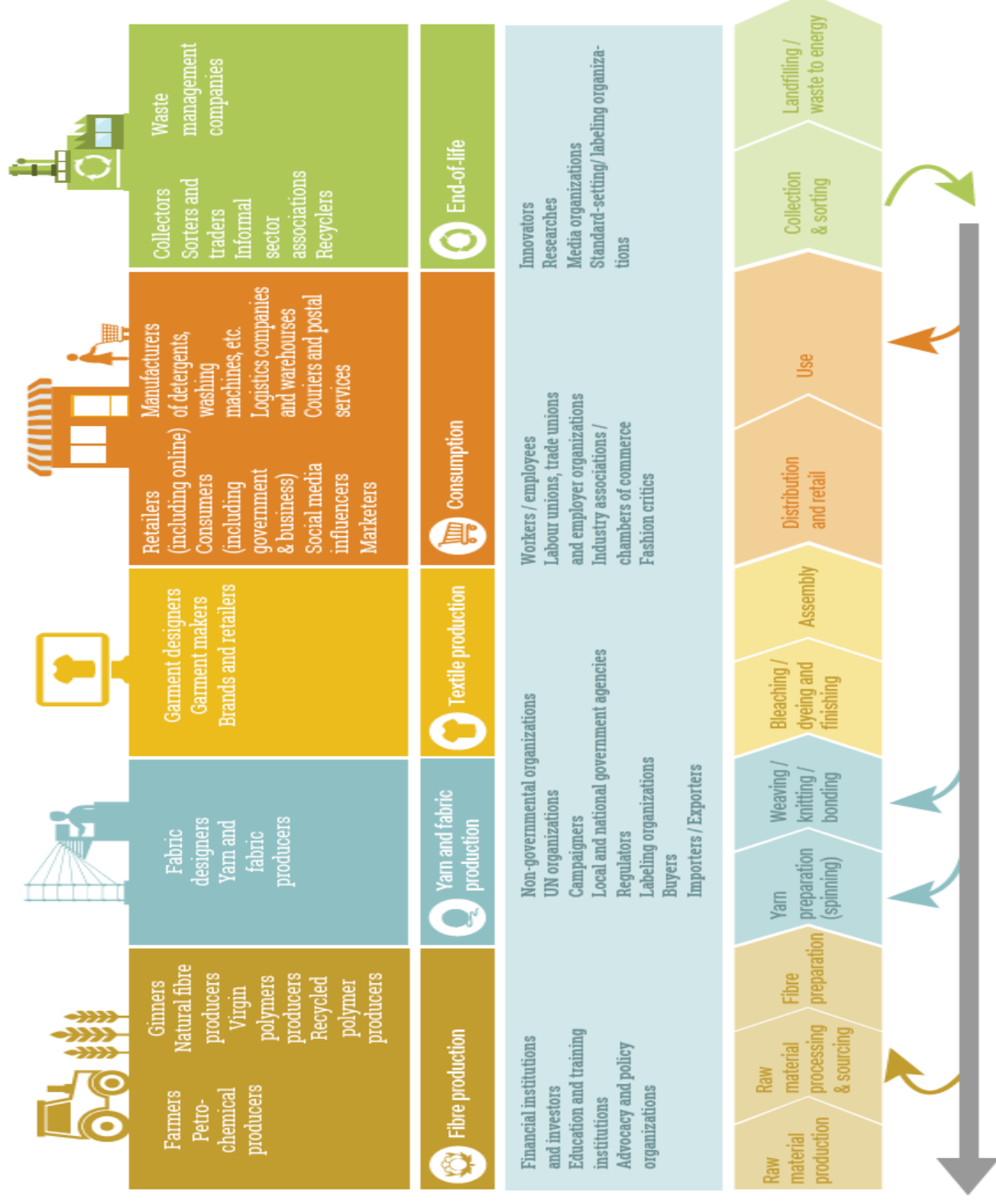
For a textile product, the value chain starts with fiber production. This can either be sourcing of natural agricultural materials and their subsequent processing to extract the fiber (e.g. cotton), or crude oil extraction and the manufacture of chemicals from which synthetic fibers are made (e.g. polyester), or a combination of both, as textiles are frequently blends of natural and synthetic fibers or involve both natural materials and chemical processing in their manufacture.

Subsequent manufacturing stages involve spinning the fibers into yarn, and knitting, weaving or bonding the fibers in some other way into fabric. The fabric is then subject to chemical and/or mechanical processing (known as finishing) to produce a textile with the desired properties (e.g. softness or water repellency). The next step in the value chain involves cutting and sewing the textile into the product, followed by getting the product to the user (distribution and retail). After its first use, the textile product may be used again, as happens with donated second-hand clothing, or it may be recycled to a different use. In the current predominantly linear textile value chain, very few textiles (<1%) are recycled back into clothing, with another 12% going into cascaded recycling, where they are used in products such as cleaning cloths, insulation material and mattress stuffing. Ultimately, after one or more uses, the textile will end up in some sort of end-of-life treatment. This is currently most likely to be a sanitary landfill or an

incinerator plant. In a circular value chain, after re-use the textile would be used in another textile product, e.g. upcycled into a new garment, or broken down to fiber level and spun into yarn. There is currently some limited recycling of cotton back to fibre, while new technologies, such as chemical recycling, offer the potential to recycle synthetic textiles back to the raw materials from which they were made. The activities associated with a value chain are often shown as a linear representation from raw material production to end-of-life treatment, albeit with the potential for the re-use, repair/repurposing and recycling of materials adding loops into the picture (such a linear representation is shown in Figure 2). The aim of circularity is to shift the "takemake- dispose" linear value chain into a circular system, where materials are not lost after use but remain in the economy, circulating as long as possible at the highest possible value. In this sense, a circular value chain such as that depicted in Figure 1 makes a more appropriate representation. Nonetheless, a linear representation of the value chain (see Figure 2) is more representative of the status quo and is convenient for indicating where stakeholders and impacts are located along the value chain.

The aim of circularity is to shift the "take-make-dispose" linear value chain into a circular system, where materials are not lost after use but remain in the economy, circulating as long as possible at the highest possible value

Textile value chain

Fibre production
- Farmers
- Petro-chemical producers
- Ginners
- Natural fibre producers
- Virgin polymers producers
- Recycled polymer producers

Yarn and fabric production
- Fabric designers
- Yarn and fabric producers

Textile production
- Garment designers
- Garment makers
- Brands and retailers

Consumption
- Retailers (including online)
- Consumers (including government & business)
- Social media influencers
- Marketers
- Manufacturers of detergents, washing machines, etc.
- Logistics companies and warehouses
- Couriers and postal services

End-of-life
- Collectors
- Sorters and traders
- Informal sector associations
- Recyclers
- Waste management companies

Cross-cutting actors (Fibre / Yarn and fabric production)
- Financial institutions and investors
- Education and training institutions
- Advocacy and policy organizations
- Non-governmental organizations
- UN organizations
- Campaigners
- Local and national government agencies
- Regulators
- Labeling organizations
- Buyers
- Importers / Exporters

Cross-cutting actors (Consumption)
- Workers / employees
- Labour unions, trade unions and employer organizations
- Industry associations / chambers of commerce
- Fashion critics

Cross-cutting actors (End-of-life)
- Innovators
- Researches
- Media organizations
- Standard-setting / labeling organizations

Process steps
Raw material production → Raw material processing & sourcing → Fibre preparation → Yarn preparation (spinning) → Weaving / knitting / bonding → Bleaching / dyeing and finishing → Assembly → Distribution and retail → Use → Collection & sorting → Landfilling / waste to energy

Practical part

1. Introduction

To accomplish the material recycling of complex materials, such as textiles, efficient methods for the separation of the components are needed. Since there are systems for the collection of textiles (Elander and Ljungkvist 2016) at least to a certain extent, a major barrier to accomplish textile recycling is the large mix of materials, coatings, dyes, and non-textile objects (Wang 2020), This diversity is especially challenging in the chemical recycling of textiles.

Due to greater awareness of the high environmental impact of textiles and the future costs of fixing damages, the interest in textile recycling has increased very much in recent years. This creates a high demand for the development of recycling technology.

Chemical recycling requires pure fractions, and thus, the development of separation processes is a central issue for the progress of textile recycling (Palme 2017).

Chemical fiber-to-fiber recycling comprises different processes where changes on the molecular level are made to the textile fibers, through chemical processing, to form recycled fibers. Textiles may also be recycled mechanically, i.e., in processes where the textiles are mechanically defibrated to fibers, which may then be spun with or without the addition of virgin fibers into yarns for textile production.

However, the mechanical recycling of most textile materials leads to fibers of inferior quality and may, thus, be regarded as downcycling (Morley et al. 2006).

There is no commercial-scale chemical fiber-to-fiber recycling of textiles existing today; however, small-scale projects are ongoing, such as Eco Circle (Teijin), Worn Again, Evrnu, Re:newcell, and Ioncell (Asaadi et al. 2015; Elander and Ljungkvist 2016).

Here is brief information about each of the organizations mentioned above:

- **Eco Circle Fibers:** they recycle the polyester fiber made of used polyester products by chemical degradation processes.
- **Worn Again:** specialists of replacing the use of virgin resources by recapturing raw materials from non-reusable products.
- **Evrnu:** they work on regenerating Cellulosics and Polyester, Recoverable Stretch and Bio Engineered Fibers.
- **Renewcell:** They work on dissolving used Cotton and other cellulose fibers and transform them into a new, biodegradable raw material.
- **Ioncell:** is a technology that turns used textiles, pulp or old newspapers into new textile fibers sustainably and without harmful chemicals.

In this practical part, a complete removal of Cotton (abbreviation: CO) and polyethylene terephthalate (abbreviation: PET or PES) fibers during acidic hydrolysis and alkaline hydrolysis, respectively, has been investigated. And the reason why those two types of fibers have been studied is that PET, and Cotton are the most common synthetic and natural fibers, respectively, used in the world today (CIRFS European Man-Made Fibres Association 2016).

The differences in their strengths and weaknesses make the two a perfect combination. Cotton contributes with softness and high-water absorbency, and PET contributes with durability, strength, and a low price (Hatch 1993). This makes mixes of PET and Cotton, in varying percentages, one of the most common textile materials, which are generally referred to as PolyCotton . PolyCotton is used in the main part of all service textiles, such as sheets, towels, and workwear. Recycling of service textiles could be an important first step to achieving textile recycling since the service sector uses large quantities of textiles with similar quality (Palme et al., 2017; Textiles and Clothing Sustainability, 2017).

The work has been aimed to completely remove one fraction using acid or alkali without any other catalyst, and this aim is to optimize a complete removal of one of the mentioned fiber types with the simplest approach.

Many studies had been done toward the same aim, to hydrolyze those two fractions. One of these studies has been done by (Palme et al., 2017; Textiles and Clothing Sustainability, 2017) using NaOH 10 to 15 wt% solution with the addition of a phase transfer catalyst (benzyltributylammonium chloride (BTBAC)) at 90 °C to depolymerize PET fibers and within the study this aim was achieved in 40 minutes.

The experiments carried out within the present study built upon these results as a starting point and included samples of pure Cotton from virgin T-shirt and pure PET from new textile fabric. Additionally, blended sheets of bed linen (composed of 55% Cotton and 45% PET) as well as blended t-shirts from private separate collections.

Sorting waste textile activity

In addition to the chemical separation of CO and PET, a large-scale sorting campaign activity was carried out as a part of the practical part of this work.

The main purposes of this activity were to classify textile waste and textile from separate collection according to a sorting matrix depending on material composition and content (mass share).
The main criteria of the matrix were:

- Level of contamination and complexity.
- Share of components such as cellulose and PET.

Proof could thus be given that a large fraction of the sorted material would contain material mixes like the material used in the lab-scale approach which was valuable for any future exploitation of collected textiles at the end of their useful life.

2. Materials and methods

2.1. Collection and preparation of waste textiles

Here is a list of all the materials used throughout the investigation for the different experiments which were conducted:

- Sulfuric Acid H_2SO_4, 95-98% wt.
- Sodium hydroxide (NaOH) solution, 50% wt.
- Deionized water (0.055 μS/cm).
- Acetic acid, 96-98% wt.
- Pure m-cresol
- 100% Cotton virgin T-shirt.
- 100% PET virgin fabric (yard ware).
- Sorted-out bed linen from hospitals / hotels from the municipality of the city of Vienna, consisted of 55% PET and 45% Cotton.
- Clothes from the private separate collection waste included 2 T-shirts, the first one consisted of 65% PET and 35% Cotton and the second one was 60% Cotton and 40% PET.

Prior the experiments, the waste textiles used in this study were checked carefully to assure the hygiene of the wastes.

Seams, zips, and buttons were removed, and the waste textiles were cut into small pieces (maximum mass per sample was 2.3 g for bed linen samples and 0.3 g for pure fiber samples).

2.2 Laboratory Equipments

Different tools were used during this work as listed below:

- Reaction bottles with different volumes, mainly 250 ml.
- Beakers (100, 250, 500 ml for containing chemicals and samples; 1000 ml volume for heating liquid).
- Magnetic stirring with hotplate.

- Thermometers.
- pH strips and pH probe.
- Aluminum sheets.
- Heating liquid: silicone oil.
- Analytical sieve (mesh size 32 μm) for filtration of reaction solutions.
- 30l heating pot for large scale experiment.

2.3 Laboratory workflow

For the complete removal of one fraction, either Cotton or PET, from the blended textiles with the optimum conditions of acid or alkaline concentrations, temperature, and time, it has been preferred to first conduct two different matrixes, one of them concerning the hydrolysis of pure Cotton fibers and the other one concerning the pure PET fibers hydrolysis.

The aim of these matrixes is to obtain the optimum conditions that can be implemented on pure Cotton or PET fibers as well as blended yarn / textiles made of Cotton and PET.

These 2 matrixes had a specific range of concentrations and temperature with a fixed time interval of 5 hours see [Figure 1].

To set up the concentrations and temperature boundaries of the two matrixes, preliminary experiments had been conducted on the basis of the mildest and harshest conditions (in terms of temperature, concentration and time) to specify the range of the matrixes.
The harshest conditions were taken from a fiber material test method developed by the American Association of Textile Chemists and Colorists (AATCC, 1977).

After obtaining the constraints and knowing the matrix's dimensions, it was possible to find the optimum conditions of each matrix and apply them on the blended textile to check whether the same parameters that worked for the pure fibers can give the same removal efficiency in case of mixed fibers.
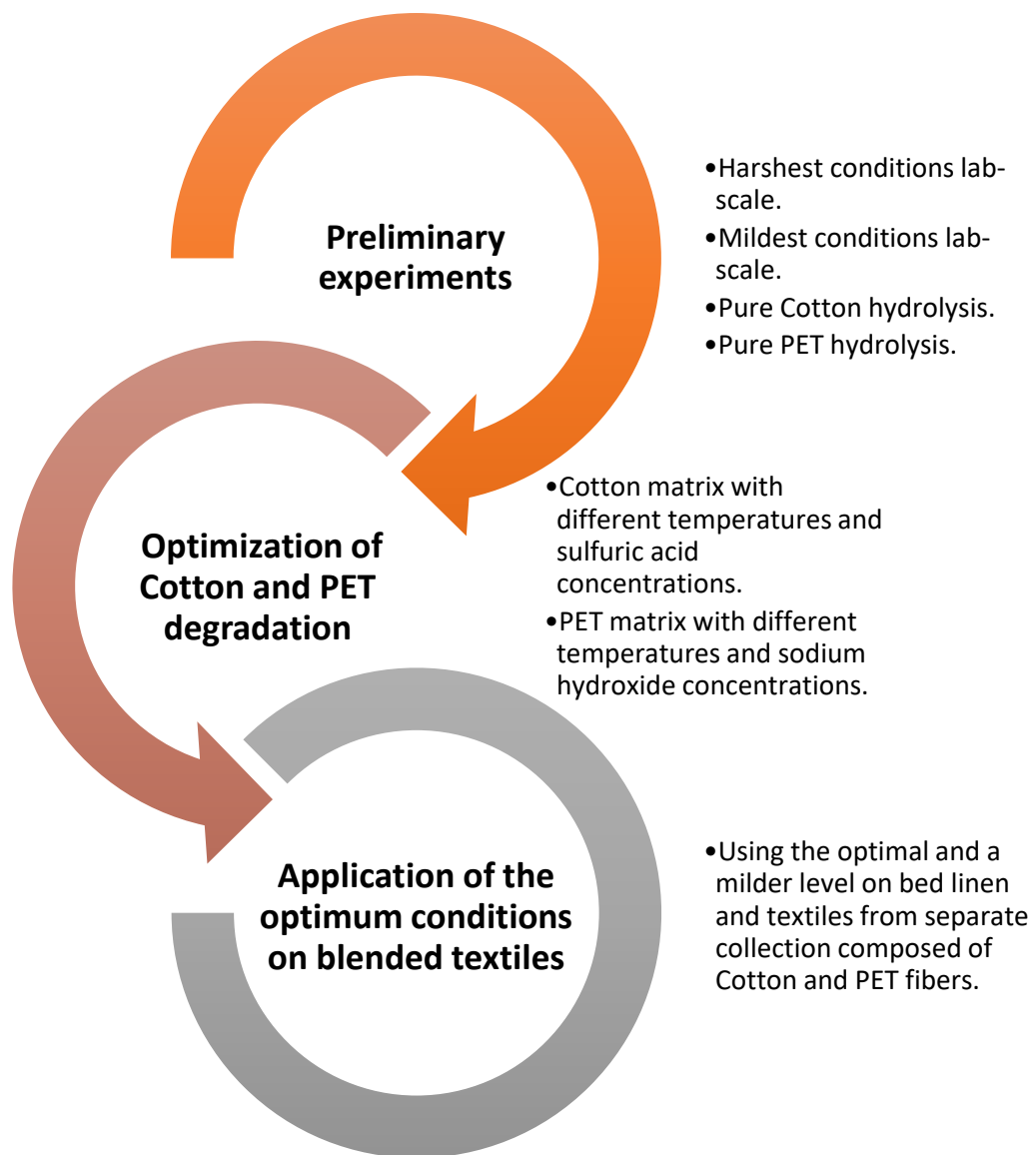
Preliminary experiments

- Harshest conditions lab-scale.
- Mildest conditions lab-scale.
- Pure Cotton hydrolysis.
- Pure PET hydrolysis.

Optimization of Cotton and PET degradation

- Cotton matrix with different temperatures and sulfuric acid concentrations.
- PET matrix with different temperatures and sodium hydroxide concentrations.

Application of the optimum conditions on blended textiles

- Using the optimal and a milder level on bed linen and textiles from separate collection composed of Cotton and PET fibers.

Figure 1. A flow chart explaining the practical phases of the lab work

2.3.1 Preliminary experiments

To accomplish these experiments, two types of analyses were conducted, the first one was the complete hydrolysis of pure dry Cotton fibers, and a 100% Cotton T-shirt was used for this purpose. The second analysis comprised the hydrolysis of PET fibers within an ordinary PET fabric (yard ware). For these experiments, it was more important to show the principal applicability on standard fabric types, and less so to know the exact single fiber dimensions within the yarns in the fabrics. The first reason for that is that a general comparison of hydrolysis conditions between CO and PET samples is not possible in the first place due to the major differences in reaction systems. The second rationale is that if fabrics are manufactured very differently from "standard types" (high weaving density, complex weaving structure, etc.) those would in any case call for a separate assessment based upon the conditions defined within this study.

For the present study, small pieces of around 0.3 g of the chosen textile fabrics were treated using different concentrations of sulfuric acid H_2SO_4 and NaOH in water, respectively.

As mentioned before, the harshest and mildest conditions were tested and for that the harshest conditions were 70 wt% of H_2SO_4 and 40 °C and the mildest conditions were 50 wt% of H_2SO_4 at room temperature without setting a time interval for both conditions, as the purpose was to monitor the samples until the complete removal of the Cotton fibers.

The concentrations were obtained by diluting 98 wt% H_2SO_4 using deionized water to the needed concentrations.

After preparing the solutions, hot-plate magnetic stirrers were used to heat up the solution and conserve continuous stirring of the samples in order to guarantee the homogeneity of the sample as well as the complete mixing of it.

The temperature was measured repeatedly using thermometers to ensure a steady temperature throughout the experiments.

Firstly, to check the relevance of stirring, two experiments were conducted on pure Cotton fibers with sulfuric acid 70% wt. and room temperature, one of them was with stirring and the other was without, and the results were as the following:

The sample with a continuous stirring had degraded after 80 minutes while the sample without stirring had exhibited no change after 150 minutes but after 24 hours it was dissolved entirely.

For all the experiments that followed those two experiments, processing was conducted with continuous stirring.

After implementing several experiments on pure PET and Cotton fibers, the constraints of the 2 matrixes were set.

It was found that the Cotton can be hydrolyzed starting from 10 wt% of H_2SO_4 at 60 °C and 70 wt% of H_2SO_4 at 40 °C as mildest and harshest conditions to represent the range of the Cotton matrix.

Following the same principal approach for PET hydrolysis in NaOH solution (instead of sulfuric acid solution for CO hydrolysis), it was found that the PET can be hydrolyzed starting from 10 wt% of NaOH at 65 °C as mildest and 40 wt% of NaOH at 65 °C as harshest conditions to represent the range of the PET matrix.

2.3.2 Cotton matrix

The purpose of implementing this matrix was to optimize the process to find best parameters viable to hydrolyze pure Cotton fibers [Table 1].

Based on the results obtained from the preliminary experiments, it was feasible to know the range of parameters where the hydrolysis of Cotton fibers is possible, thus, a set of different parameters was conducted with an increment of 20% of sulfuric acid H_2SO_4 concentration and an increment of 20 °C in temperature.
Moreover, the time of each experiment was fixed to 5 hours with 30 minutes observation frequency.

Here is the matrix [Figure 2] that was used for Cotton degradation:
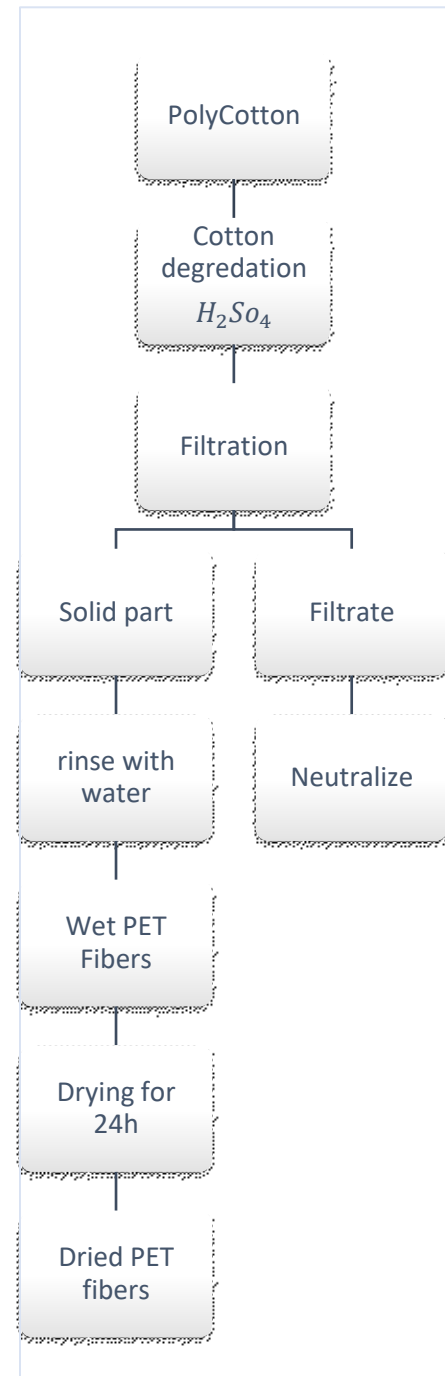
Figure 2. Cotton Matrix – principal path of the used Cotton degradation process."

Table 1. parameters used in the experiments of Cotton Matrix.

Cotton Matrix	10%	30%	50%	70%
80 C	✕	✕		
60 C	✕	✕	✕	
40 C		✕	✕	✕
20 C			✕	✕

These experiments were done using 3 hot-plate magnetic stirrers [Figure 3], and following the preliminary approach, this matrix was done, however, the additional action was putting the 250ml reaction bottles containing the textile samples in 1000 ml beakers that contained heating-oil.

Following that, the beakers were covered with aluminum sheets to maintain the temperature and avoid any external effect on it and fixing a thermometer for each sample.
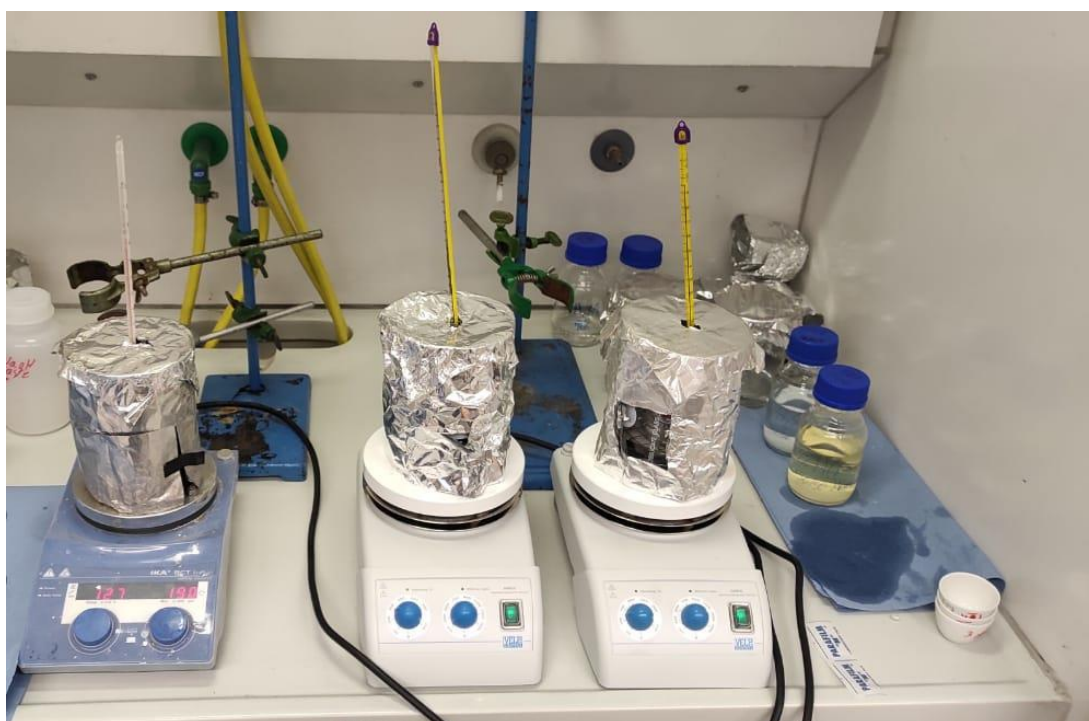
Figure 3. Lab-arrangement for Cotton and PET hydrolysis"

2.3.3 PET matrix.

The PET matrix [table 2] followed the same approach as the Cotton matrix was developed by experiment, however, treating PET fibers with NaOH solution with an increment on 10 wt% [Figure 4].
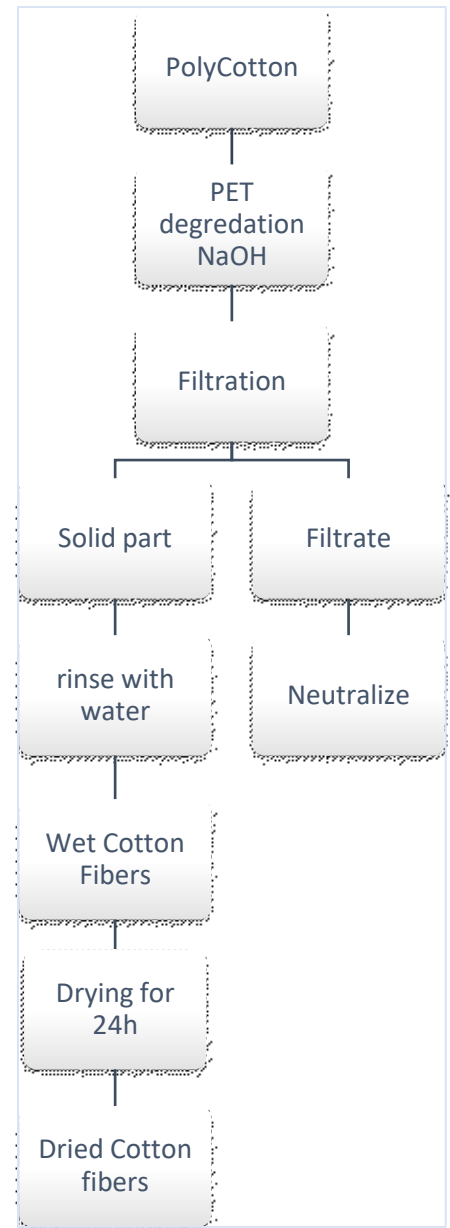
Figure 4. PET Matrix – principal path of the used PET degradation process."

Table 2. The matrix used for PET degradation:

PET Matrix	10%	20%	30%	40%
90 C	✕	✕	✕	
65 C	✕	✕	✕	✕
40 C		✕	✕	✕

2.3.4 Blended textile experiments.

After assessing best conditions to hydrolyze Cotton and PET fibers, it was important to do a trial series on blended garments that consisted of Cotton and PET fibers with known mass fraction of polymer for each material fraction and check the ability to degrade one fraction using the optimal conditions that were derived from the previous matrixes.

For that, a sequence of experiments was implemented following two patterns. The first one was to remove PET fibers out of the PolyCotton textiles using the optimal condition extracted from the PET matrix for one experiment and another experiment in parallel following a milder condition using NaOH solution for both experiments and bed linen textiles (55% PET, 45% CO) white, clean and labeled removing all the seams that may be found in it.

Small pieces of the bed linen were taken with a maximum weight of 2.5 grams.

The other pattern was to remove Cotton fibers out of the PolyCotton textiles using the optimal condition extracted from the Cotton matrix for one experiment and another experiment in parallel following a milder condition using for both experiments H_2SO_4 solution and the same bed linen textiles with same conditions.

Steps followed to conduct both patterns for Cotton and PET degradation are illustrated in the two flow charts [Figure 2, Figure 4].

After degrading one fraction, the other fiber material remaining in the fabric sample (loosened structure) was filtered out from the solution using an analytical sieve (mesh size 32 μm), dried at ambient conditions (room temperature) for 24 hours then the mass measurements were taken to check the percentage of removal in both cases.

The same patterns with same parameters were followed to degrade one fraction of mixed textiles from another origin, namely textile from private separate collection companies using 3 different colored and clean samples.

2.3.5 Medium scale experiment

In this last step, it was attempted to check the results that we found throughout the previous experiments on a bigger scale using a 25-liter heating pot [Figure 5], mechanical stirrer with a propeller stirrer mounted on the shaft (d = 100 mm), and 1300 g of the same bed linens used in the latest trials and also prepared equally.

Sodium hydroxide (NaOH) solution was again used for removing the PET fibers (one fraction) from blended textiles (consisting of PET and CO) using the previously found optimum concentration (15%), time (2h), and temperature (90 °C).

After 2h, the reaction solution was drained using the tap in the bottom of the pot, and the textile samples were neutralized using acetic acid to obtain neutral pH, then the formed salt solution was drained and the fabric fraction was washed 3 times in the sink [Figure 6] using tap water and squeezing the water out from the textiles.

Figure 5. Preparations of the pre pilot scale experiment.

Then textiles piece was separated and put in the drying cabinet at a set temperature of 105 °C for 24 hours, then the mass was measured and it was found that the expected complete removal of PET was achieved also in the large-scale approach.

[Figure 6] visualizes the neutralization and washing arrangement. The white reaction coagulate is formed as a result of the neutralization of sodium hydroxide with acetic acid (used instead of sulfuric acid due to less probability of damaging the recovered Cotton fraction), with the solution probably also containing a rest of depolymerization products from PET hydrolysis.

[figure 6]. Neutralization and washing of recovered Cotton textile fraction.

3. Results and discussion

3.1 Preliminary experiments results

Cotton and PET were treated using H_2SO_4 and NaOH respectively.
For Cotton degradation, 0.3 g of 100%-Cotton-T-shirt were used in a form of
small chunks (1 cm x 1 cm) and the results were taken depending on visual
observations of the fibers and the solution.

Table 3. illustrates all results obtained at hydrolysis of Cotton using H_2SO_4.

sample	type of Textile	weight of textile gr	type of solution	conc	Temperature C	time to dissolve (min)	Comment	Stirring
1	Co 100%	0.292	H2SO4	70%	Room T	150	not dissolved but after 24h dissolved	no
2	Co 100%	0.288	H2SO4	70%	Room T	80	Disolved completely	yes
3	Co 100%	0.297	H2SO4	70%	Room T	150	Disolved completely	yes
4	Co 100%	0.298	H2SO4	70%	40	80	Disolved completely	yes
5	Co 100% pre treated with alkali	0.337	H2SO4	70%	40	less than 15	Disolved completely	yes
6	PET 100%	0.305	H2SO4	70%	40	60	nothing changed after one hour	yes
7	Co 100%	0.317	H2SO4	50%	40	120	new weight 0,213 gr	yes
8	Co 100% pre treated with alkaline hydrolised	0.31	H2SO4	50%	40	120	new weight 0,198 gr	yes

It was observed that pure Cotton dissolved completely using H_2SO_4 with 70 wt%
concentration in 80 minutes at room temperature and in 80 minutes for 40 °C.

In addition, one experiment was conducted without a hot-plate magnetic stirrer,
and this resulted in no change of the sample in a time of 150 minutes, while after
24 hours it was dissolved completely.

Treating pure Cotton with H_2SO_4, 50 wt% and a temperature of 40 °C was able
to degrade 30 % of the original mass.

Moreover, a sample of 100% PET was treated using the same conditions to check
if H_2SO_4 is able to attack the PET fibers, and it was found that H_2SO_4 has no
effect on PET fibers, which is important and crucial in case of blended textiles
(CO and PET) assessment.

On the other hand, a set of trials were implemented to test the suitable conditions to hydrolyze PET fibers using sodium hydroxide in different concentration, temperatures, and time intervals as shown in [table 4].

Table 4. examples of experiments treating PET using NaOH.

sample	type of Textile	weight of textile gr	type of solution	concentration	Temperature C
1	PET 100%	0.307	NaOH	35%	35
2	PET 100%	0.314	NaOH	35%	50
3	PET 100%	2.401	NaOH	35%	50

The first sample was done without stirring, and after 2 hours of starting the experiment, no change was observed.

Second and third samples used the same conditions, however the second one lasted for 2 hours and the third one lasted for 5 hours.

This allowed for making an assessment of the degradation progress. For the second sample, a turbid solution was exhibited after 2 hours, retaining the fibers form. This turbidity may be linked to a partial degradation of the PET fibers but with no visual signs on the fiber chunks.

The third sample was visually stable within the reaction environment for 5 hours, where the visual appearance of the filtered-out PET chunks stayed without a change; however, their physical properties reverted to high stiffness and brittleness and thus no fiber material could be recovered after washing in tap water where the textile disintegrated.

3.2 CO matrix results

Based on the preliminary results, it was feasible to set the conditions where the Cotton hydrolysis is possible taking into account the concentration of H_2SO_4 and the temperature of the reaction media.

The time interval for all the matrix experiments was fixed with 5 hours, allowing for the assessment of other relevant parameters and their effect and to compare the best results from this parameter comparison [Table 5].

Table 5. shows the experiments conditions.

sample	type of Textile	weight of textile gr	type of solution	concentration %	Temperature C
1	Co 100%	0.237	H2SO4	10	80
2	Co 100%	0.247	H2SO4	10	60
3	Co 100%	0.204	H2SO4	50	60
4	Co 100%	0.221	H2SO4	30	40
5	Co 100%	0.25	H2SO4	30	60
6	Co 100%	0.275	H2SO4	30	80
7	Co 100%	0.332	H2SO4	50	40
8	Co 100%	0.355	H2SO4	50	20
9	Co 100%	0.342	H2SO4	70	20
10	PET 100%	0.345	H2SO4	70	40
11	PET 100%	0.346	H2SO4	50	60
12	PET 100%	0.347	H2SO4	10	80

The results revealed that H_2SO_4 has no visible effect on CO fibers when the concentration is 30 wt% and the temperature is 40 °C, this assessment included the fiber chunks' shape and the solution transparency.

Increasing the temperature showed a tangible effect on Cotton fibers hydrolysis.

10 wt% of H_2SO_4 in 80 °C gave a complete degradation of CO after 5 hours of running the test. The Cotton fibers started to disintegrate after 1.5 h and progressively until the complete hydrolysis.

50 wt% of H_2SO_4 in 60 °C gave the best degradation conditions since the fabric was all disintegrated after 30 minutes of launching the test.

Moreover, the best conditions which were obtained, were applied on 100% PET sheets to check if these optimum conditions can affect the PET fibers in the case of mixed textile consisted of Cotton and PET fibers.

The results suggested no adverse effect on PET fibers using the optimum conditions of degradation for Cotton fibers. Thus, the optimum conditions could be applied on blended textiles (CO&PET) to degrade one fraction (CO) without the risk of a possible degradation of PET fibers. This in turn is helpful to assess a complete degradation of CO in case of mixed textile (CO&PET).

3.3 PET matrix results

The same approach was followed to accomplish the PET matrix.

To degrade PET fibers NaOH solution was used in different concentrations temperatures, and fixed time interval of 5 hours.

New sheets of PET fabric (yard ware) were used in these experiments.

Table 6. Illustration of the set of experiments for the PET matrix.

sample	type of Textile	weight of textile gr	type of solution	concentration	Temperature C
1	PET 100%	0.337	NaOH	20%	40
2	PET 100%	0.383	NaOH	30%	40
3	PET 100%	0.336	NaOH	40%	40
4	PET 100%	0.367	NaOH	40%	65
5	PET 100%	0.327	NaOH	30%	65
6	PET 100%	0.331	NaOH	20%	65
7	PET 100%	0.367	NaOH	10%	90
8	PET 100%	0.381	NaOH	20%	90
9	PET 100%	0.364	NaOH	30%	90
10	Co 100%	0.335	NaOH	40%	65
11	Co 100%	0.332	NaOH	30%	90
12	Co 100%	0.321	NaOH	20%	90

The effect of temperature in PET experiments played a vital role, as visual changes were realized when using higher temperature.

Samples 1 and 2 showed no signs of PET hydrolysis at fabric level and solution level as well.

At 40 °C temperature, signs of degradation, such as solution turbidity and fine particles disintegrated from the main chunks, were observed with a concentration

equal or higher than 30 wt% of NaOH in the solution. However, the complete removal of PET was not achieved after 5 hours.

At 65 °C, a complete removal was observed after 2 hours of starting the test and using NaOH, 40 wt% with a turbid solution as a result.

Although samples 6 (NaOH, 20 wt% at 65°C) and 7 (NaOH, 10 wt% at 90 °C) showed no directly visible effects of PET hydrolysis for the fabrics within the solution at incubation, a significant mass loss was encountered after the washing step. This suggests that even though concentrations were lower than for the above-mentioned conditions, there was an attack at microscopic level, disrupting the fiber structure. This in turn can be interpreted as a sole effect by temperature rather than concentration of alkali, which is substantiated by the fact that the relative mass loss with sample 7 (90 °C incubation temperature) was even higher than with sample 6 (65 °C).

The optimal set of parameters to completely remove PET fibers were thus found at a temperature of 90 °C and of NaOH, 20 wt% after 2 hours of starting the trial.

Moreover, the best conditions which were obtained, were applied on pieces of a 100% CO T-shirt to check if these optimum conditions would affect the CO fibers in the case of mixed textile consisted of Cotton and PET fibers.

The results gave no effect on CO fibers using the optimum conditions of degradation for PET fibers, thus, the optimum conditions could be applied on blended textiles (CO&PET) to degrade on fraction (PET) without risking a possible degradation of CO fibers. This in turn is helpful to assess a complete degradation of PET in case of mixed textile (CO&PET).

3.4 Blended textile results.

Optimal conditions of both CO and PET matrixes were applied on bed linens composed of CO 42% and PET 58%.

The label of the bed linen showed a composition of 50% CO and 50 %PET, however, by following an experimental approach and applying the harshest conditions in order to remove CO or PET by using 70 wt% of H_2SO_4 to remove CO fibers or using 100 wt% of meta-cresol (AATCC Technical Manual; AATCC, 1977), it was possible to check the actual content of the fabric. The application of these conditions resulted in a 58% removal percentage of the fibers over the total mass when using 100 wt% m-cresol, which means that the PET fibers content is 58%, as m-cresol will not disintegrate the cellulose share and as it can be assumed that there were no other synthetic fibers other than from PET.

To check the accuracy of this result, another experiment was conducted to remove CO fibers using 70 wt% H_2SO_4 and by this check, it was concluded that the CO content is 42% so the assumption was correct.

To remove PET fibers from bed linens (42% CO, 58% PET), the optimal condition that was reached in the PET matrix (20 wt% NaOH, 90 °C, 2 hours) was applied.

This approach was followed by a milder approach in terms of concentration (15 wt%) to check if it is possible to obtain a complete removal adopting a slightly milder (15 wt%) and harsher (30 wt%) concentrations [Figure 7].
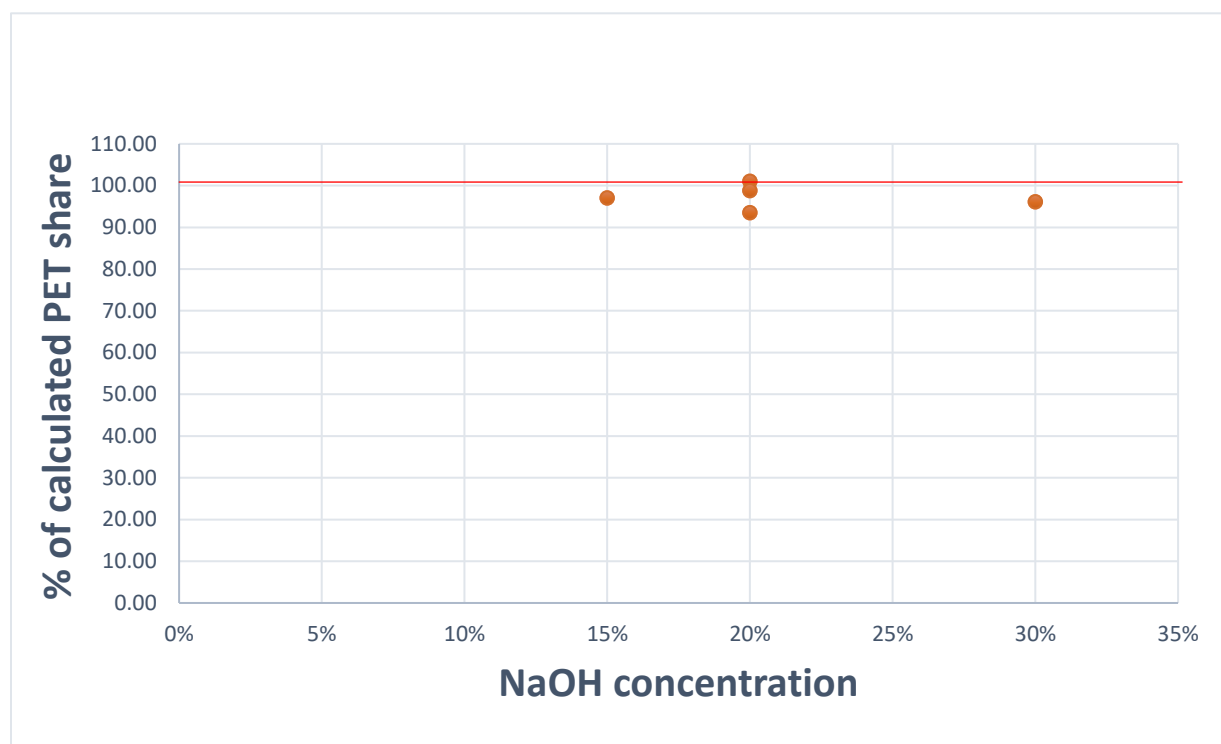
Figure 7. Removal efficiency of PET in blends using NaOH 15, 20, and 30 wt%, 90 °C, and a time interval of 2 hours.

The results showed a 100% (not considering errors due to washing) or almost 100% performance for all the concentrations that were used with a complete removal of PET fibers at 90 °C and after 2 hours, which also suggests that temperature is a crucial factor, even more than alkali concentration, as long as this concentration is within defined values.

Removal efficiency was thus calculated to 100−5 % for PET fibers, where due to possible losses of CO fibers during washing, a negative error is more likely. The slight difference of the removal percentages could be related to possible variation of temperature during the experiment or due to the washing method and agitation followed, to clean the remained fibers after stopping the tests.

On the other hand, to remove CO fibers from bed linens (42% CO, 58% PET), the optimal condition that was reached in the CO matrix (50 wt% H_2SO_4, 60 °C, 2 hours) was applied.

This approach was followed by a milder approach in terms of concentration (40 wt%) to check if it is possible to obtain a complete removal adopting a slightly milder (40 wt%) and harsher (70 wt%) concentrations.

Different durations were applied, and the results are shown in the following charts.
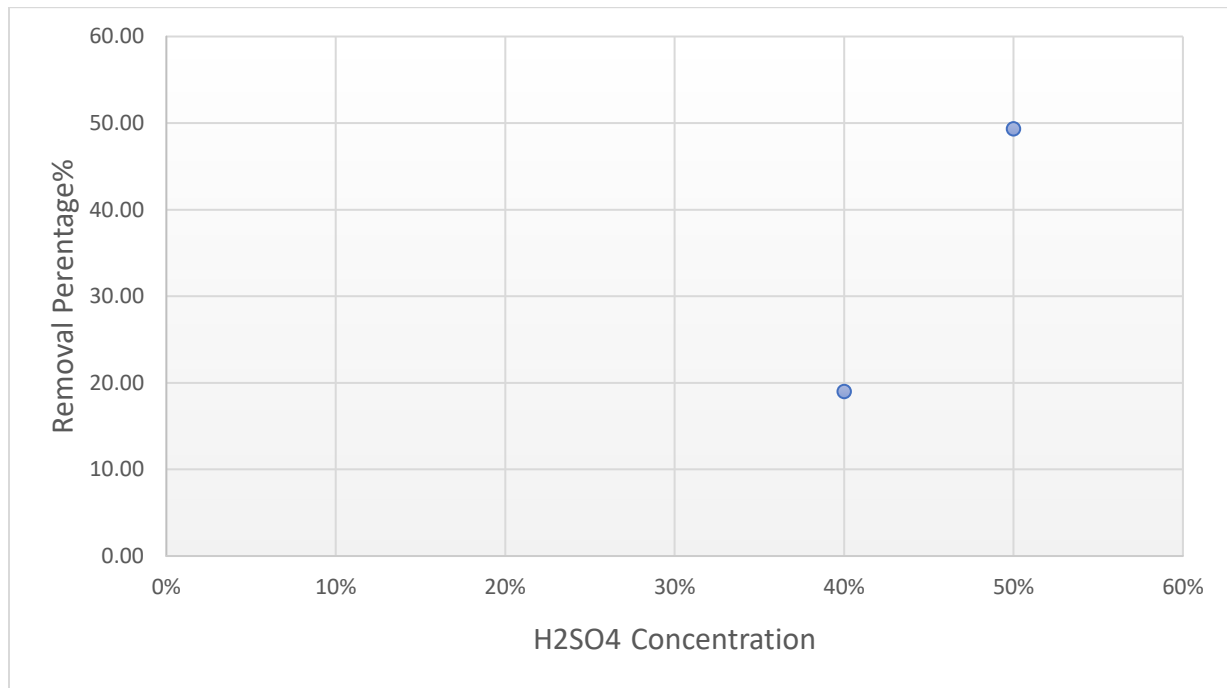
Figure 8. Removal efficiency of CO fibers using 40 and 50 wt% H_2SO_4 and 30 minutes duration.

The results obtained showed that the optimal condition that was obtained in the case of pure CO fibers were not efficient when applied to blends and were able to remove only 50% of the CO content in the blends, while for a milder concentration the removal efficiency was approximately 20% of the CO content in the blends (Figure 8). This – if no other unrecognized errors apply – may have to do with the lower overall surface accessibility of the fibers when there is a different swelling behavior in the solution due to the "stabilizing" PET content that contains the original structure more than within a pure CO fabric. Yet, it can be assumed that the Cotton share within the bed linens from the material itself should be less resistant to sulfuric acid attack, because of the fact that the textiles were frequently washed during use. However, it is not exactly clear if there were still other substances (from detergent, etc.) present on the bed linens that could also have built up a hydrophobic barrier that would also explain the overall lower conversion over time. Due to the various possibilities, it would be advisable to assess this matter in future trials.

By increasing the duration of the experiments, it was possible to observe a change in the removal efficiency of CO fibers [Figure 9].
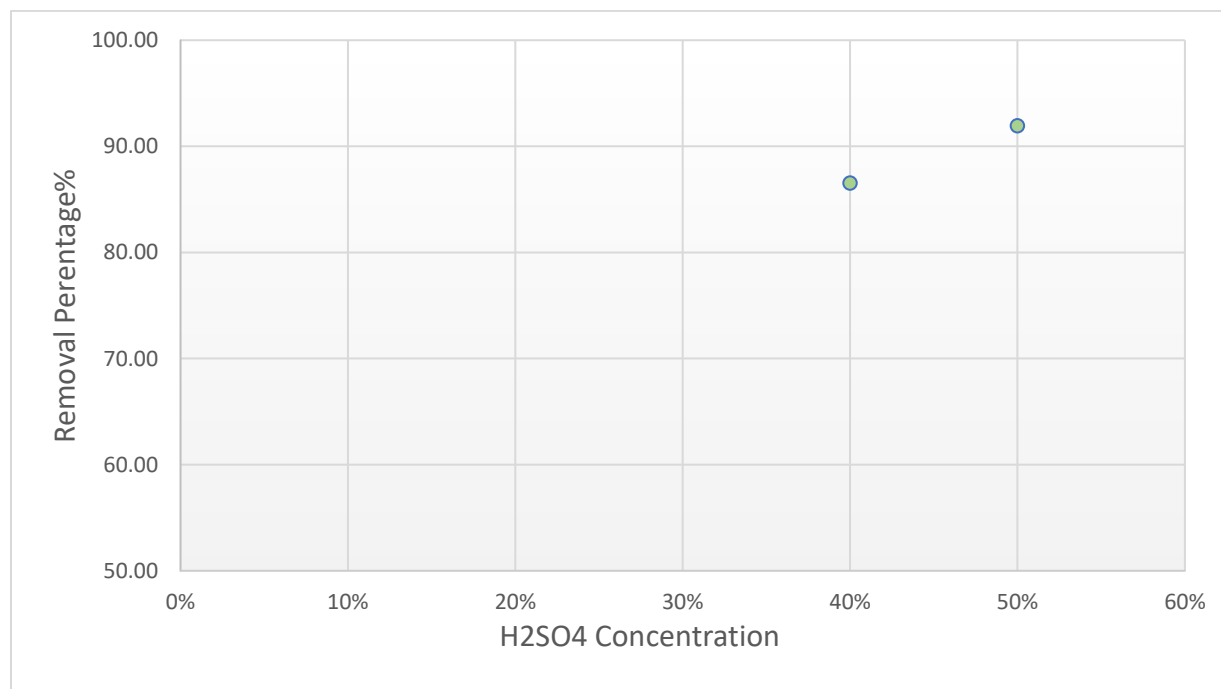
Figure 9. Removal efficiency of CO fibers using 40 and 50 wt% H_2SO_4 and 60 minutes duration.

Comparing Figure 9 and Figure 10, it was observed that the removal efficiency has drastically increased from 20% to 87% in case of 40 wt% H_2SO_4 and from 50% to 95% in case of 50 wt%. To obtain a complete removal of CO fibers it can thus be suggested to apply 2 hours duration where the results obtained [Figure 4] showed a complete removal of CO fibers with 100 +5 % removal efficiencies. Due to possible losses of PET fibers during washing, a negative error is again more likely.
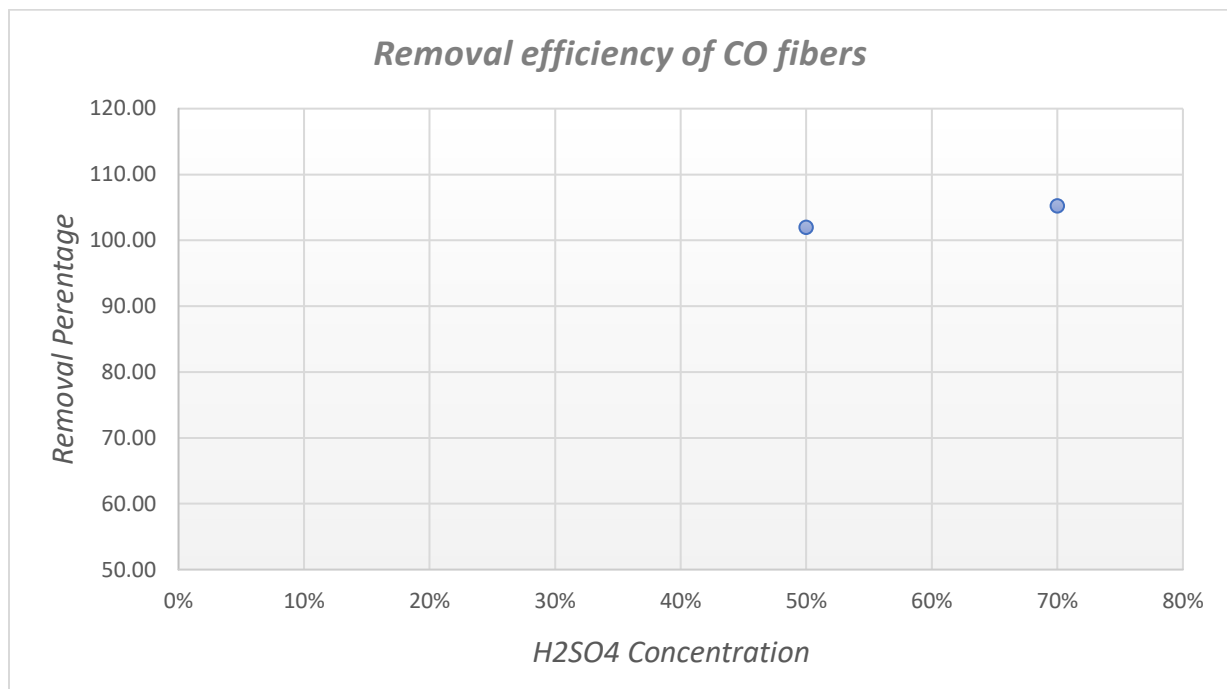
Figure 10. Removal efficiency of CO fibers using 40 and 50 wt% H_2SO_4 and 120 minutes duration.

Pre-Pilot-Scale.

Treatment of the bed linen blends was conducted in a stirred reaction vessel which has a reaction volume of 30 l in a Pre-Pilot-Scale, to depolymerize PET fibers using the determined optimal conditions.

25 kg of NaOH was used in this experiment with a concentration of 15 wt%, 90 °C, and 1300 g of blends were used.

The trial lasted for 2 hours, then the remaining fibers were washed using tap water and manual agitation, washing process was repeated 3 times to assure the neutralization state of the remaining fibers.

The following step was to dry the fibers recovered using 105 °C for 24 h, this step was followed by measuring the new mass which gave a result of 531 gr [Figure 11].
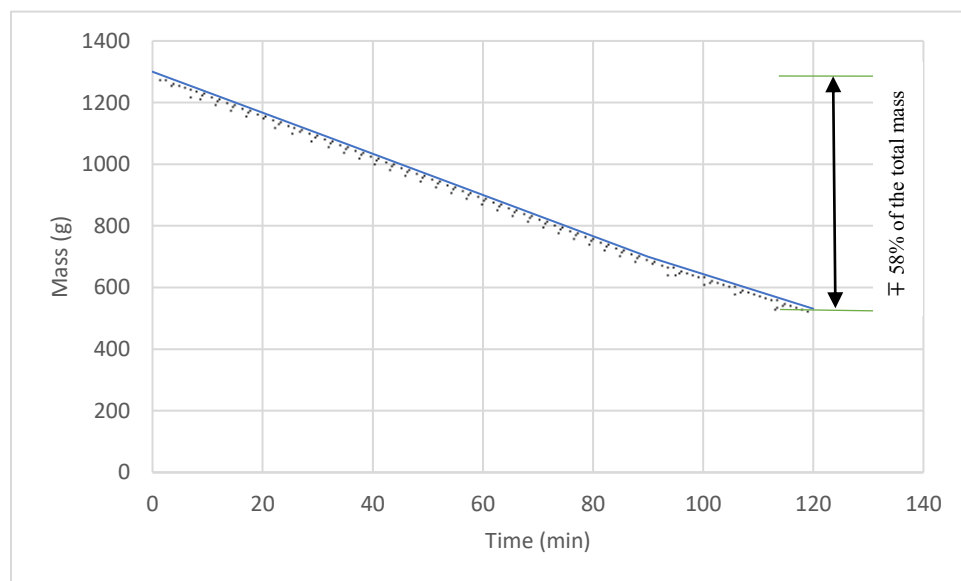
Figure 11. Reduction of the original textile mass.

The expected results from this test were reached as the graph illustrates with a removal efficiency of approximately 58% from the total mass of the blends which corresponds to 100 $\mp$5 % removal of PET fibers content.

The results from the large-scale trials show that an overall mass reduction from 1300 g of input material to 531 g of dried output material was achieved. This would reflect a reduction of PET share of 107 % (similar values from the lab-

scale trials, where full removal of the respective share was achieved, can be calculated). However, a reduction of the addressed component above 100% is not possible, which is why a loss of fibers from the loosened structure of the remaining Cotton textile fraction can be assumed. Generally, an inaccuracy of + 5% for that should be considered, yet, a negative error cannot be ruled out completely, because other measurement errors can have occurred, too. Of course, mass determination does not distinguish between polymer materials, and in principle, residues of PET could still be present. However, combined with the visual, light-microscopic assessment (see figures 16 or 17), it is obvious that only one fiber type is still present. This follows the knowledge of typical shape and surface structure of Cotton fibers.
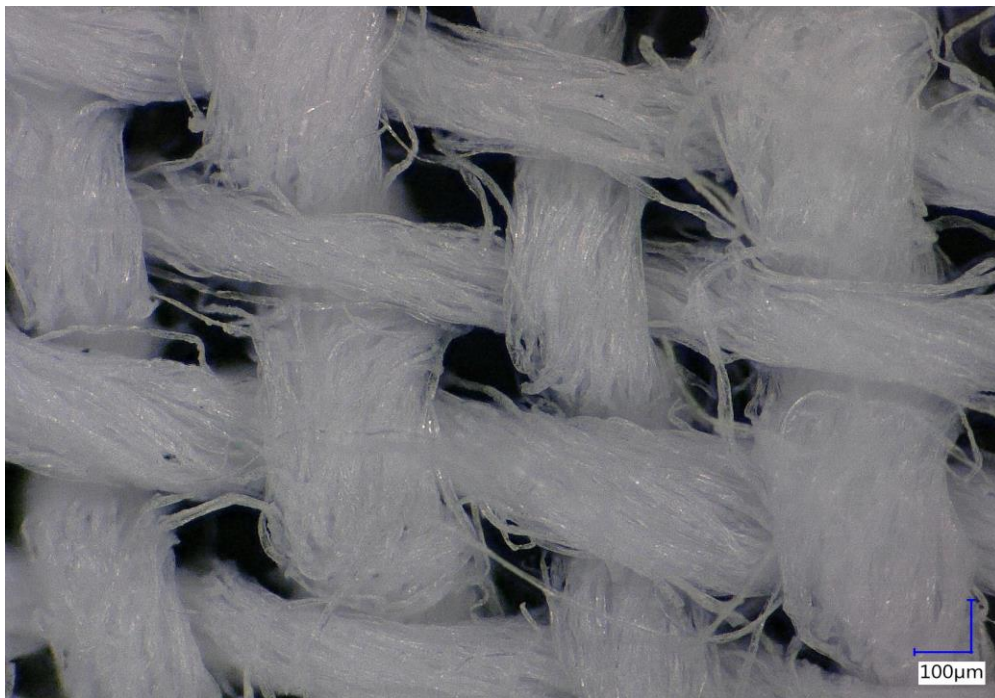
Light-microscopic analysis.

This step was implemented on the recovered textile fraction to check the impact on the integrity of the remaining fiber fraction (qualitative process assessment).
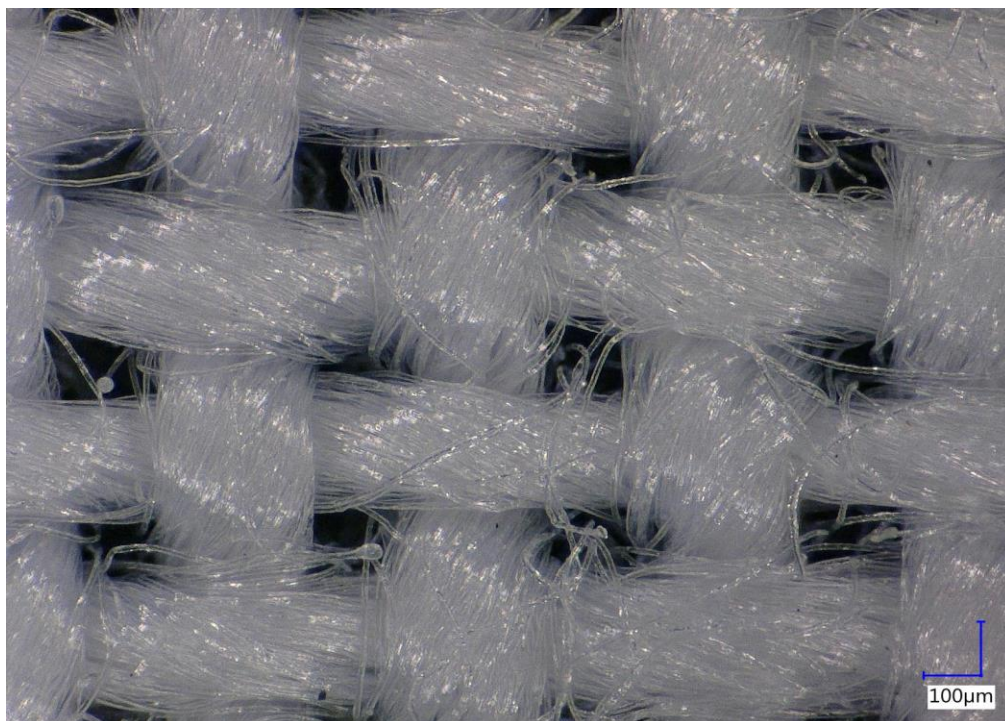
Pictures bellow show the results of the different experiments that were obtained during all the practical work.
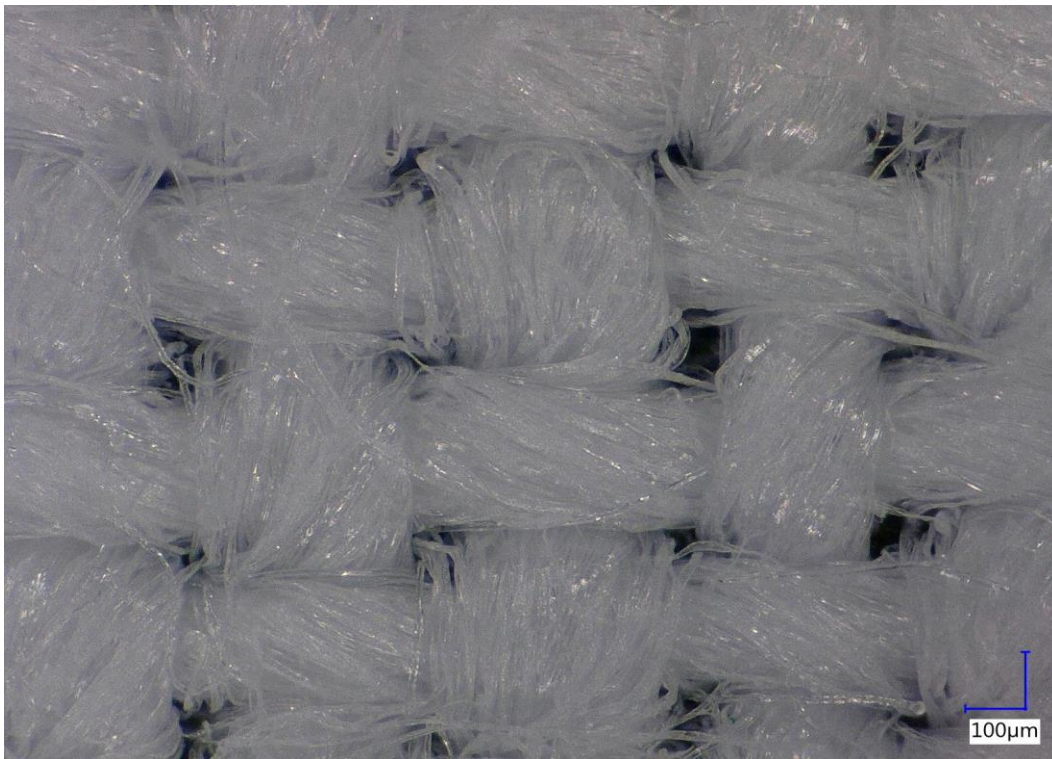
[Figure 12]. Original multi-material textile ('PolyCotton ').

[Figure 13]. Plain CO after treatment of PolyCotton with m-cresol (acc. to AATCC, 1977).

[Figure 14]. Plain PET after treatment of PolyCotton with sulfuric acid (acc. to AATCC, 1977).
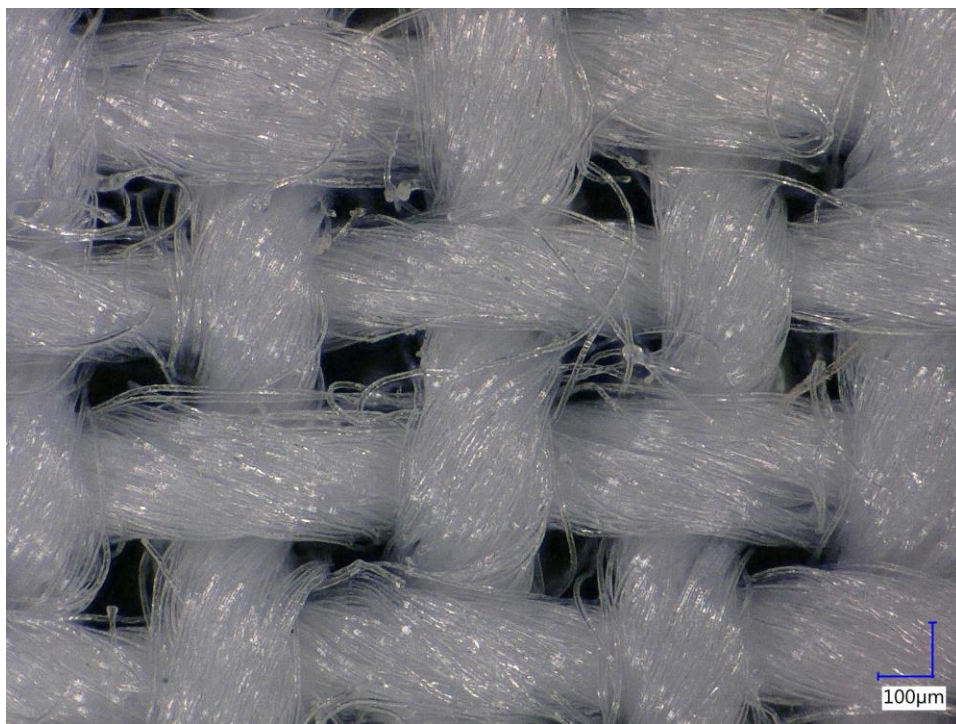

[Figure 15]. Pure Cotton treated with sodium hydroxide H_2SO_4.
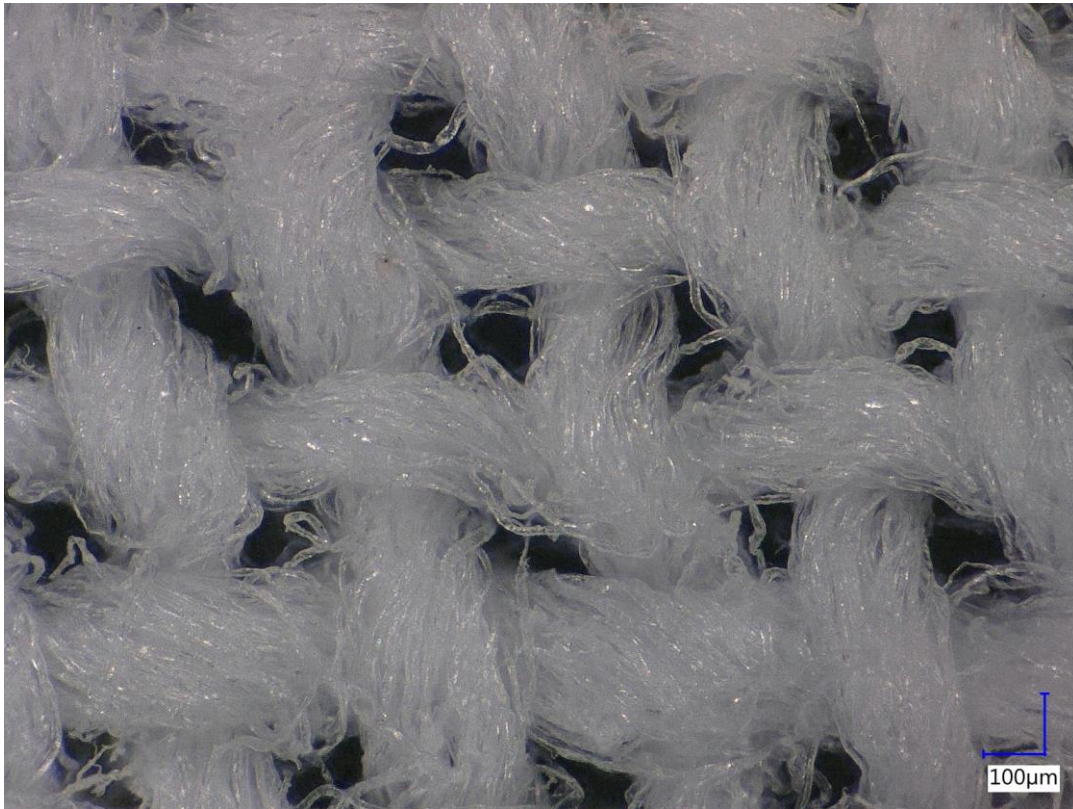
[Figure 16]. PolyCotton fiber treated with sodium hydroxide NaOH large scale.

[Figure 17]. PolyCotton fiber treated with sodium hydroxide NaOH large scale.

[Figure 18]. PolyCotton fiber treated with sulfuric acid H_2SO_4, 60 °C and 2 hours 50% lab scale.

[Figure 19]. PolyCotton treated with Sodium Hydroxide NaOH 20% 90 C and 2h lab scale.

Bibliography

1. Elander and Ljungkvist 2016
2. Wang 2020.
3. Morley et al. 2006.
4. Asaadi et al. 2015; Elander and Ljungkvist 2016
5. https://www.ctc-n.org/products/eco-circletm-fibers
6. https://wornagain.co.uk/
7. https://www.evrnu.com/
8. https://www.renewcell.com/en/
9. https://ioncell.fi/
10. Palme et al. Textiles and Clothing Sustainability (2017).
11. CIRFS European Man-Made Fibres Association 2016.
12. Hatch 1993.
13. AATCC (1977). *AATCC Test Method 20-1977 – Fibers in Textiles: Identification.* AATCC Technical Manual, Vol. 53, American Association Of Textile Chemists And Colorists, N. C., USA.