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Innovative chemical recycling systems for textile waste

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Statement of originality

I, Federico Cazzola, hereby declare that the work presented in this dissertation, titled “Innovative chemical recycling systems for textile waste", is entirely my own original work. I affirm that it has not been fully or partially submitted previously in any other Italian or foreign university for assessment purposes.

I further confirm that the content of this dissertation is the result of my own intellectual endeavours, and I have appropriately cited all sources used. This work does not infringe upon the intellectual property rights of any third party, and its contents do not constitute plagiarism.

I understand the consequences of submitting work that is not my own and affirm the honesty and integrity of this academic contribution.

Federico Cazzola

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Abstract

The textile industry is one of the most important sectors in the global economy but also one of the most impactful on our planet. Recycling of textile residue waste has been gaining attention due to the significant waste generated by this sector and to move closer to the Circular Economy goals. In contrast with mechanical recycling, chemical recycling of textiles holds the potential to yield materials of equal quality and value as products from virgin feedstock.

To address this issue, this thesis embarks on an exploration of innovative chemical recycling fibre methods, aiming to revolutionize eco-friendly practices in the textile industry. The primary objective was to research and experiment new innovative chemical recycling method on cotton-based fibres, including exploring innovative pre-treatments to remove the colour from the textile waste streams, prior to the chemical recycling. The effectiveness of the pre-treatments was evaluated, as well as its impact on cotton fibres chemical recycling.

Chapter 2 establishes the scene by giving a thorough summary of the state of the textile industry nowadays today, including information on its detrimental effects on the climate, an examination of the wide range of fibres and to conclude with an exploration of the possible type of recycling methods in the textile sector. The core of this research lies in testing new innovative methods for decolouration and greener solvent systems for dissolving cellulose-based fibres.

Chapter 3 delves into the materials and methods used for both colour removal, specifically the pretreatments utilised in the procedure consisting of alkaline, acid, reducing and ozone treatments, as well as for the dissolution of textile fibres in aqueous solvents. The chapter concludes with an explanation of the equipments used for the final analysis of the experimental data.

Chapter 4 and Chapter 5 enclose, in order, the experimental results obtained from this specific research work and analytical discussion of the experimental results obtained.

This work was carried out under the integrated Project be@t – Textile Bioeconomy, to strengthen the National Bioeconomy, financed by the Environmental Fund through Component 12 – Promotion of Sustainable Bioeconomy (Investment TC-C12-i01 – Sustainable Bioeconomy No. 02/C12- i01.01/2022), of European funds allocated to Portugal by the Recovery and Resilience Plan (RRP), within the scope of the European Union (EU) Recovery and Resilience Mechanism, framed in the Next Generation EU, for the period 2021 – 2026.

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Abbreviations	Definition
NaOH	Sodium Hydroxide
FTIR	Fourier transform infrared spectroscopy
ATR	Attenuated total reflection
Gly	Glycerin
ZnO	Zinc oxide
RT	Room temperature
HCl	Hydrochloric acid
H_2SO_4	Sulfuric acid
H_2O_2	Hydrogen peroxide
CH_2O_2	Formic acid
Wt%	Weight percentage
$\frac{w}{v}$	Weight per volume
DP	Degree of polymerization
IEA	International energy agency
USDA	U.S. department of agricolture

Chapter 1: Introduction

The clothing and textile industry is a highly resource-intensive and waste-generating industry. To achieve a transformation from linear to circular, the industry needs to pull multiple solution levers simultaneously with particular emphasis on its upstream operations. One attractive lever is to embrace fibre-to-fibre recycling. This would aid the clothing and textile industry to take an important step in moving the industry from a linear logic toward a circular system. In particular, CITEVE, The Technological Centre for the Textile and Clothing Industry of Portugal, is involved in the be@t project – Bioeconomy in textile and clothing involving a consortium of 56 entities that, in partnership, work on developing sustainable solutions for the sector.

The be@t project is structured in 4 major pillars namely Biomaterials, Circularity, Sustainability and Society covering many key points of the entire sector such as new raw materials, technologies and equipment to communication and training of stakeholders and society.

The specific case of this research dealt with an initiative within the circularity pillar, with the aim of Boost the reuse of fibres (pre- and post-consumption) for reintroduction into the natural and/or artificial fibre extrusion process, through optimised recycling processes.

This work was developed at CITEVE, The Technological Centre for the Textile and Clothing Industry of Portugal, located in Vila Nova de Famalicão, during the period between September and December 2023. CITEVE is a private non-profit organization active since 1989, being a reference organization within the national and European scene, regarding research, innovation, and technology transfer promotion for the Textile & Clothing Industry. CITEVE works for supporting the technical and technological development of the textile & clothing industry, promoting innovation and inducing new capacities and new competences as well as helping on the definition of industrial public policies. It offers technological services of the highest level in different areas: Laboratorial activities, Technological consultancy & development, R&D+Innovation, Technology Watch, Product standards and certification, Training and Fashion intelligence.

Aim of the thesis

This research work endeavours to explore different methodologies for innovative chemical recycling fibres, aiming to contribute to the evolution of eco-friendly practices within the textile industry. The primary objective is to use greener solvents for the dissolution of cotton textile fibres, followed by their regeneration, targeting innovative chemical recycling processed for cellulosic fibres. Innovative decolourisation methods will be tested on cotton fibres, this being a point strategically linked to the objective outlined earlier.

Chapter 2: Literature review

The linear economy is defined as the take-make-dispose approach. The maximization of output and supply is central to this economic model. Unnecessary resource losses resulted from the linear production model due to issues like production chain and end-of-life waste, excessive use of energy sources, and ecosystem deterioration (Ketelaars, 2019). The conventional system, known as the linear economic model, does not provide a driving force toward sustainable growth (Ghisellini and Ulgiati 2020). The only goal of this economic system is the procurement of raw material, its manufacturing, and conversion to a final product and eventually its disposal (Sharma et al. 2020). Opposite to this system, the circular economy is an innovative concept to help society change towards a more sustainable economy; maintenance, reuse, refurbishment, remanufacture, recycling, and composting are key processes where materials and products are kept in circulation perspective. The circular economy addresses climate change as well as other global issues including waste, pollution, and biodiversity loss (Ellen Mac Arthur Foundation). This paradigm shift is based on re-thinking and re-designing production and consumption patterns to avoid environmental impacts and preserve the natural resources as long as possible (Gaustad et al., 2018; Simon, 2019).

One valuable approach to accomplish the transition from a linear to a circular economy is the encouragement and practice of recycling. According to the Waste Framework Directive Art 3(17) ‘recycling’ means “any recovery operation by which waste materials are reprocessed into products, materials, or substances whether for the original or other purposes. It includes the reprocessing of organic material but does not include energy recovery and the reprocessing into materials that are to be used as fuels or for backfilling operations”. The recycling process prevents the waste from going to landfills or incineration, thereby reducing further usage of energy production, air pollution due to incineration, as well as air and water pollution. Hence, the recycling process has become crucial to waste reduction, becoming the third factor of the waste hierarchy, “Reduce, Reuse, and Recycle” (Recycling, 2019).

Textile industry and the need for sustainable recycling

The textile and fashion industry is an important part of the world manufacturing industry, playing a meaningful role in the economic and social well-being of many regions (Girneata and Mascu, 2014). Clothes are an essential asset in human life, generating in Europe about 64 billion dollars of export and 115 billion dollars in imports and hiring about 1,3 million of employers in 2022. Indirectly, the sector creates additional jobs in upstream or downstream industries such as mechanical engineering, design and logistics (Facts & key figures 2024 of the European textile and clothing industry, eurotex 2024 report).

Textile manufacturing unfolds across extensive and intricate supply networks, spanning various geographic regions. Comprising farmers and processors of raw fibres, yarns, and textiles, weavers, knitters, dyers and finishers, product makers, and distributors, are involved in the creation of textiles. While textiles have various end uses, from interiors and automotive fitouts to geo-textiles, agri-textiles and hygienic textiles, the sector is essentially fashion driven, as most global fibre production (60%) is destined for clothing (Niinimäki et al., 2020). Due to lengthy supply chains and energy-intensive production methods, it's estimated that textile industry generates 8–10% of global carbon emissions, superseding emissions from the aviation and shipping industries combined (European Parliament, 2021). It is estimated that textile purchases in the EU in 2020 generated about 270 kg of CO_2 emissions per person (Change 2018). In addition, according to the European Environment Agency, textile production is estimated to be responsible for about 20% of global clean water pollution from dyeing and finishing processes with an estimation for 35% of microplastics released into the environment due to the laundering of the synthetic clothes (EEA, 2020).

From the sourcing of raw materials to textile production, garment manufacturing, and distribution to retail stores, the textile industry generates huge amounts of waste, which occupies a large place in the municipal solid waste category (Yalcin-Enis et al. 2019).

Textile waste can generally be defined as any undesirable or discarded piece of fabric or clothing that is unfit for its original purpose (Stanescu, 2021) and it is originated from the community via number of streams including the fibres, textile or clothing manufacturing industries, consumers, commercial and service industries (Kumari, 2020).

Depending on the source textile waste can be divided into three large groups, specifically, pre-consumer waste, post-consumer waste, and post-industrial waste. Pre-consumer waste is generated throughout the first stage of the supply chain before the textile reaches the consumer so during the production, manufacturing or processing of textiles and typically comprises fabric scraps, leftover yarns or rejected defective products. Post-consumer_waste is produced when textile products have been used and are discarded before or at their end of life. Instances of this waste are clothing, bedding or curtains thrown away by households or institutions (Stanescu, 2021). Post-industrial waste is generated by other industries that use textiles as inputs or outputs, which include discarded medical textiles, automotive textiles or packaging textiles (tomovska et al 2017).

Textile waste has given rise to negative social, economic and environmental problems. Incineration and landfill of textile waste are still widely used and the lead to soil and water pollution as well as emissions of greenhouse gases (Quan zhou et al 2022). According to global fashion agenda each year, as much as 92 million tons of clothing ends up in landfills and only 20% of textiles are collected for reuse or recycling globally (Fig 7).

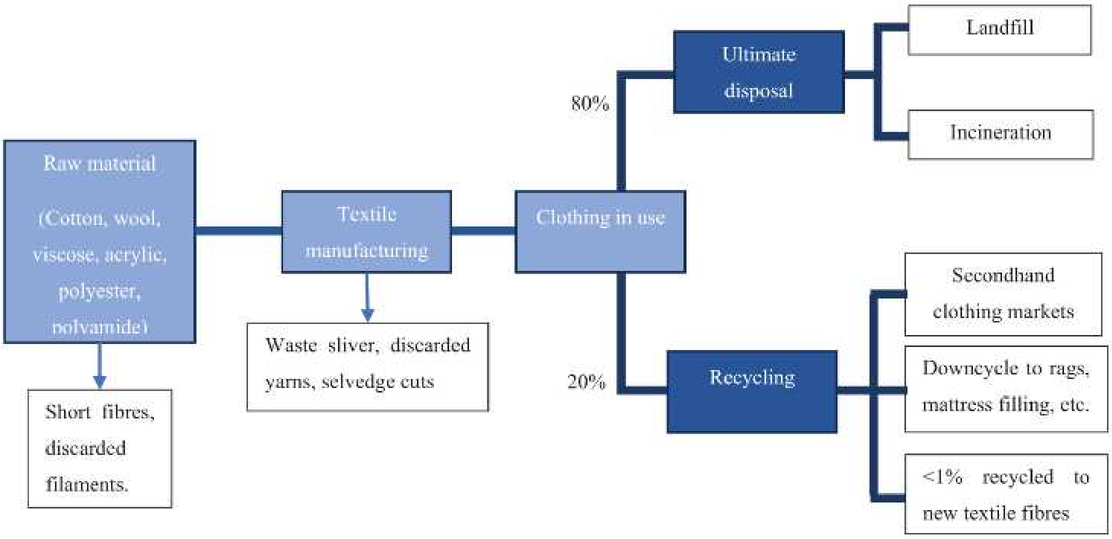

Fig 7: Textile waste flow from raw material to disposal.

Source: Baloyi R.B. et al. 2024

The toxic dyes and additive auxiliaries present in textiles are often disposed of by textile dyeing and finishing plants without appropriate effluent treatment. Consequently, these chemicals may seep into the soil and nearby water sources, ultimately entering our food and immediate surroundings, alongside microplastic particles. This situation has significant implications for the overall health of humans and other living organisms in the vicinity as well as on a global scale. (Moazzem et. al., 2021).To overcome these problems, the Sustainable and Circular Textiles Strategy sets out a vision for the textiles industry's transition. By 2030, the EU market should plan durable, recyclable, largely recycled, and eco-friendly textile products. Consumers will enjoy affordable textiles, moving away from fast fashion, with profitable reuse and repair services readily available. Producers across the value chain will take responsibility for their products, through extended producers responsibility (EPR) rules, even after they become waste. The circular textiles ecosystem will flourish with robust fibre-to-fibre recycling, minimising textile incineration and landfilling.

Textile Fibres

The global fibre production reached 116 million metric tons in 2022 (Textile exchange, report), which has doubled in the last 20 years (Shirvanimoghaddam *et al.* 2020) and according to Statista Research department, the forecast production is expected to reach 149 million metric tons by 2030 (Fig 8). This global consumption is continuously increasing because of the growth of the population, economy, and fashion cycles (Lu et al., 2022). In addition, the fast fashion trend in the clothing industry and increased fibre consumption have led to more shorter life cycles of textiles, and a huge amount of textile waste (Shirvanimoghaddam et al., 2020).

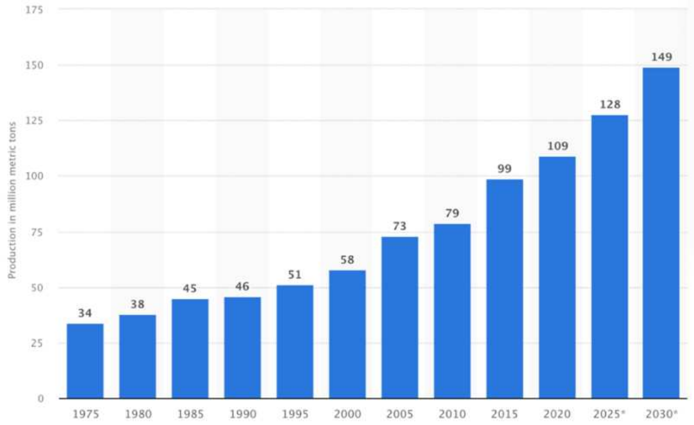

Fig 8: Production of textile fibres worldwide from 1975 to 2020, with a forecast for 2025 and 2030 (in million metric tons).

Source: Statista research department

Textile fibres are classified into two primary categories according to Elmogahzy (2009) (Fig. 9). Firstly, natural fibres which comprise materials like cotton, wool, silk, linen, hemp, and jute, sourced directly from plants, animals, or minerals.

Secondly, man-made fibres are created through the modification of natural polymers, such as viscose, acetate, lyocell, and modal, offering versatile properties for various applications. Within this category are also grouped the synthetic fibres which include a diverse range, including both organic types derived from petrochemical products such as polyester, nylon/polyamide, acrylic, and polypropylene, as well as inorganic variants like glass, metal, carbon, or ceramic, tailored to meet specific performance requirements in modern textile manufacturing.

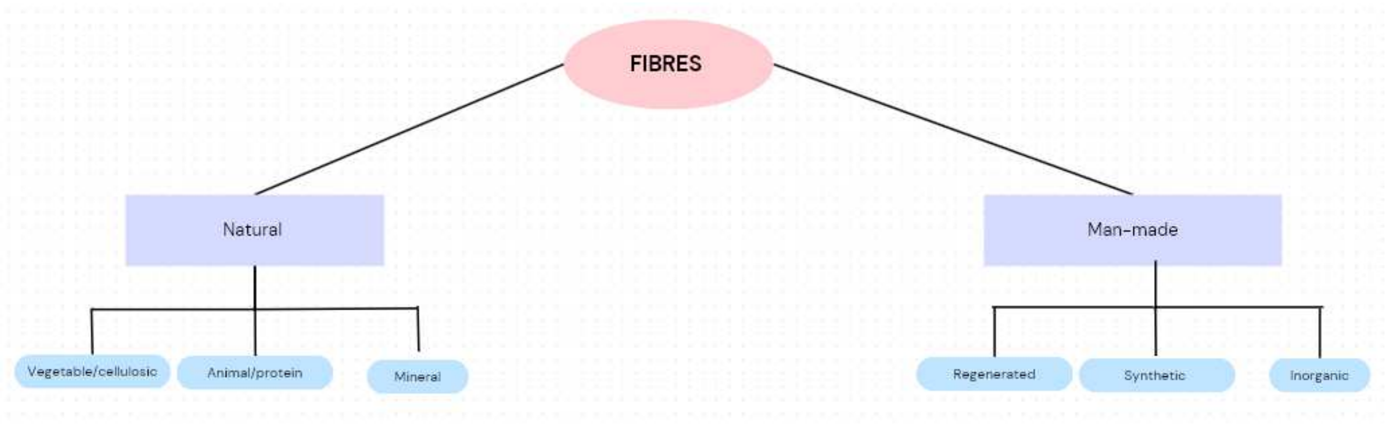

Fig. 9: Textile Fibre classification.

Source: Woodhead Publishing Series in Textiles: Number 126 Textiles and Fashion Materials, Design and Technology, edited by Rose Sinclair

Synthetic fibres have dominated the fibre market since the mid-1990s, when they overtook cotton volumes. At around 76 million tonnes, this fibre category made up approximately 65% of global fibre production in 2022 (Textile exchange, report 2023) (Fig. *10*).

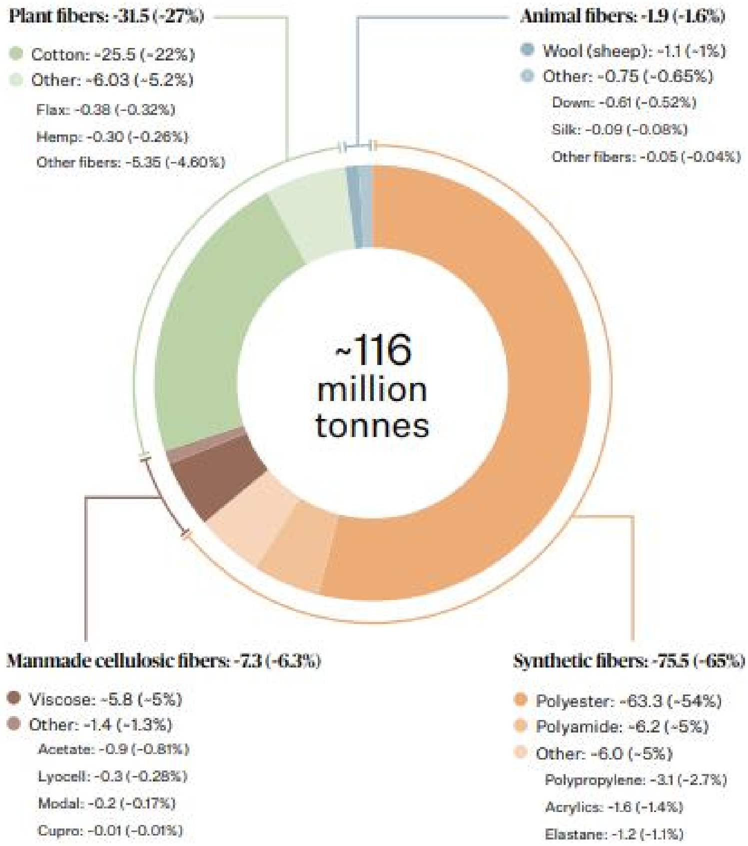

Fig. 10: Global fibre production in 2022 (in million tons and % of global fibre production).

Source: Textile Exchange based on data from CIRFS, FAO, ICAC, IVC, IWTO, Maia Research, and its own modelling

It’s estimated that less than 1% of the material used to produce clothing was effectively recycled into new clothing (Ellen Mc Arthur foundation, 2022). Increasing the uptake of textile-to-textile recycled fibres is a key strategy to help the industry achieve a 45% reduction in greenhouse emissions by 2030 (Textile exchange, 2023). Because this thesis work is centred on cotton-based fibres, special attention will be given to analysing the role of cotton within the textile industry.

Cotton cultivation has a very significant environmental impact since cotton is the largest user of water agricultural products, with 20,000 litters of water to produce one kilogram of cotton, polluting water sources with toxins and chemical substances that greatly affect the biodiversity of wildlife through direct contact and long term accumulation within the biosphere, soil and freshwaters (WWF, cotton). Due to these aspects this thesis work explores circularity solutions for cotton fibres in close collaboration with the be@t project, in the following chapters all details will be fully explained.

Cotton: from the field to the fabric

Cotton is a natural fibre obtained from the seed hairs of plants of the genus *Gossypium*. There exist about 50 species of *Gossypium* whereas only four have been domesticated for cultivation to derive textile fibres (Mehboob-ur-Rah- man *et al*., 2012). The subspecies *Gossypium hirsutum* (*Fig. 11*) accounts for 80% of the world cotton fibre production (Dochia *et al.,* 2012).

Fig. 11: Cotton specie *(Gossypium hirsutun).*

Source: Dochia et al. 2012

The cotton fibre represents the purest form of cellulose in nature with a possible content up to 96%. Table 1 shows the chemical composition of the cotton fibre (Ansell and Mwaikambo, 2009; Dochia et al., 2012; Mauersberger,1947).

Table 1: Chemical composition of cotton fibre

Source: (Ansell and Mwaikambo, 2009; Dochia et al., 2012; Mauersberger,1947)

Constituent	Value $\frac{w}{w}$%
Cellulose	82-96
Hemicellulose	2.0-6.4
Protein	1.0-1.9
Waxes	0.4-1.2
Pectin substances	0.4-1.2
Inorganics	0.7-1.6
Others	0.5-8.0

Cellulose is a linear homopolymer of β-D glucose monomers covalently linked together by 1-4 glycosidic bonds i.e. the ringed glucose monomers are joined together via polycondensation reaction between hydroxyl groups at C1 of a glucose unit and C4 of the neighbouring glucose unit. Since, every glucose unit is rotated 180° with respect to its neighbours along the fibre axis, the dimer of glucose, called cellobiose, is considered a repeating unit of cellulose polymer (Fig. 12) (Habibi Y. et al.2010). Cellulose is a long-chain molecule whose degree of polymerization (DP) varies depending on the source and extraction methods used. According to reports, the DP of cellulose in wood and cotton fibres can reach 10,000 and 15,000, respectively (Moon RJ *et al.* 2011; George J. *et al.* 2015).

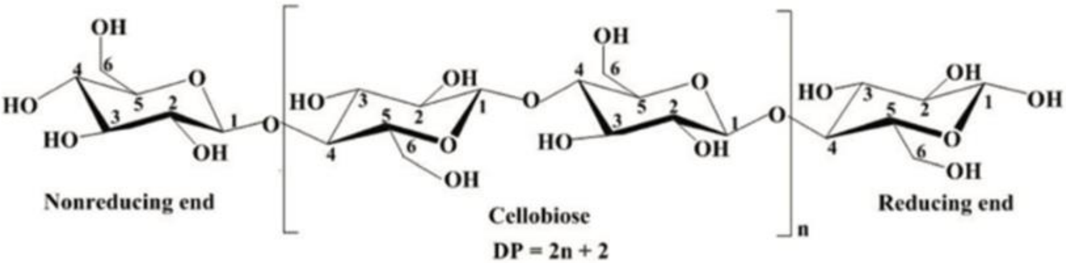

Fig. 12: Chemical structure and hydrogen bonding in cellulose.

Source: Habibi Y. et al.2010, Moon RJ et al. 2011; George J. et al. 2015

Prevalence of hydroxyl groups in cellulose (three hydroxyl groups per glucose monomer) results in extensive intra-and interchain hydrogen bonding in cellulose (Fig 13). The three hydroxyl groups are chemically reactive and they can be subjected to substitution reactions during processes aimed at altering the cellulose fibres or when crosslinking dyes and finishes are applied.

The hydroxyl groups also serve as principal sorption sites for water molecules. Directly sorbed water is firmly chemisorbed on the cellulosic hydroxyl groups by hydrogen bonding. (Parthasarathi R. *et al*. 2011).

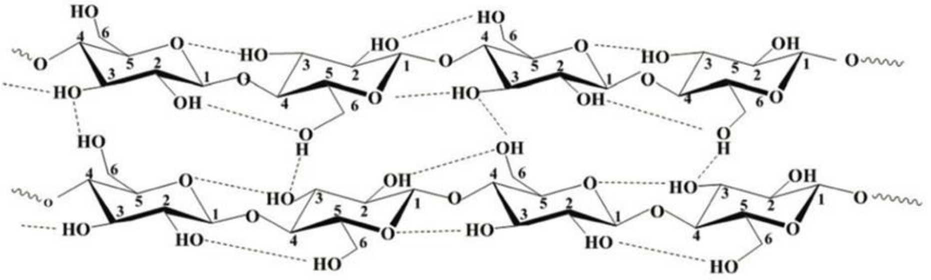

Fig 13: Hydrogen bonding in cellulose.

Source: Parthasarathi et al.2011

The Hydrogen bonds facilitate the formation of inter- and intra-molecular forces that cause a highly ordered arrangement (crystalline regions) of cellulose fibrils although there are also amorphous regions present (where the arrangement of cellulose chains is disordered) as depicted in Fig. 8 (Parthasarathi R. *et al*.2011). In general, cellulose, regardless of the source, is highly crystalline, which means that the molecules are closely packed and parallel to one another. It is a high molecular weight biopolymer and is, usually, fibrous, tough and hydrophilic but insoluble in water and other common solvents (Peresin MS. *Et al*.2010).

Cellulose from cotton fibre is more crystalline (80% crystallinity) as compared to wood cellulose (50% crystallinity). (Khan F. et al. 2013). It is usually agreed that, during biosynthesis, approximately 36 individual cellulose molecules are assembled together to form elementary fibrils, which a square cross section of 3–5 nm in size. Elementary fibrils further undergo packing into a larger entity called microfibrils with a cross section of approximately 20 nm x 8 nm. These microfibrils further assemble into macro sized cellulose fibres (e.g. wood fibre, cotton fibre) (Moon RJ et al 2011; Habibi Y et al. 2010) (Fig. 14).

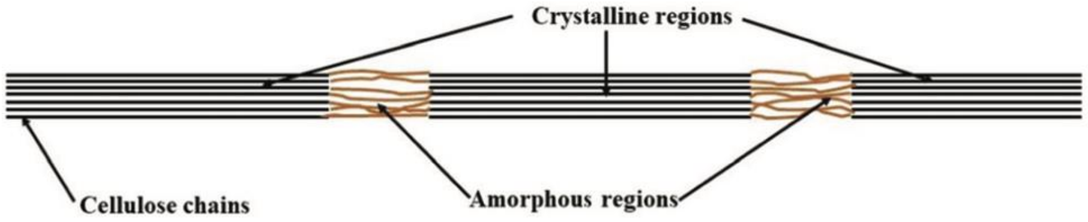

Fig. 14:: Schematic of cellulose microfibrils showing crystalline and amorphous structure.

Source: Parthasarathi *et al.*2011

The mature cotton fibre presents a longitudinal cavity in its centre, the so-called lumen. Around the lumen, cellulose walls are arranged. At the outermost layer, most of the pectin and waxes are present, and this layer is responsible for a certain hydrophobicity. The cotton fibre is not rotationally symmetric in shape, and it is contorted with about 60 convolutions cm^{-1} of fibre (Dochia *et al.*, 2012). *Fig 15* shows a schematic representation of mature cotton fibre showing in various layers.

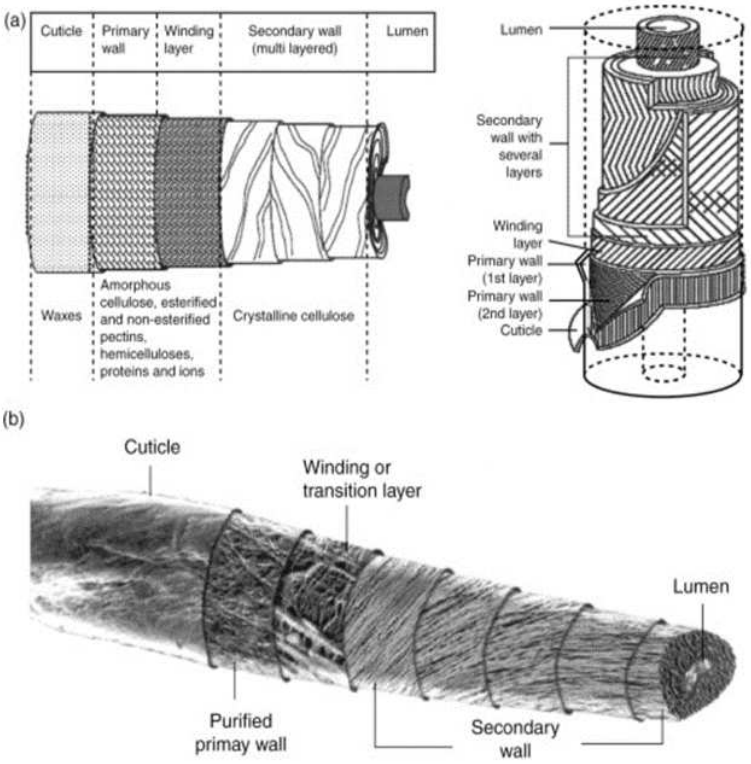

Fig 15: A schematic representation of mature cotton fibre showing its various layers: (a) Cross section of cotton fibre. Typical components in dry, mature cotton fibres and compositions of each layer. (b) Morphological model of cotton fibre.

Source: Dochia et al.2012

Cotton is one of the most common raw materials in the textile industry and is the most consumed fibre after polyester (Huang et al., 2022). The use of cotton has a long tradition in the clothing industry due to the important characteristics since these fibres are moisture-absorbent, have a good drape and are known for their long durability.

Top ten cotton- producing countries are China, India, United States, Brazil, Australia, Turkey, Pakistan, Uzbekistan, Argentina, Mali. Currently, an estimated 25 million tons of cotton is being produced worldwide (USDA, 2023) and as the largest cotton producer in the world, China harvested more than 6.684 million tons of cotton in 2022. (Fig. 16).

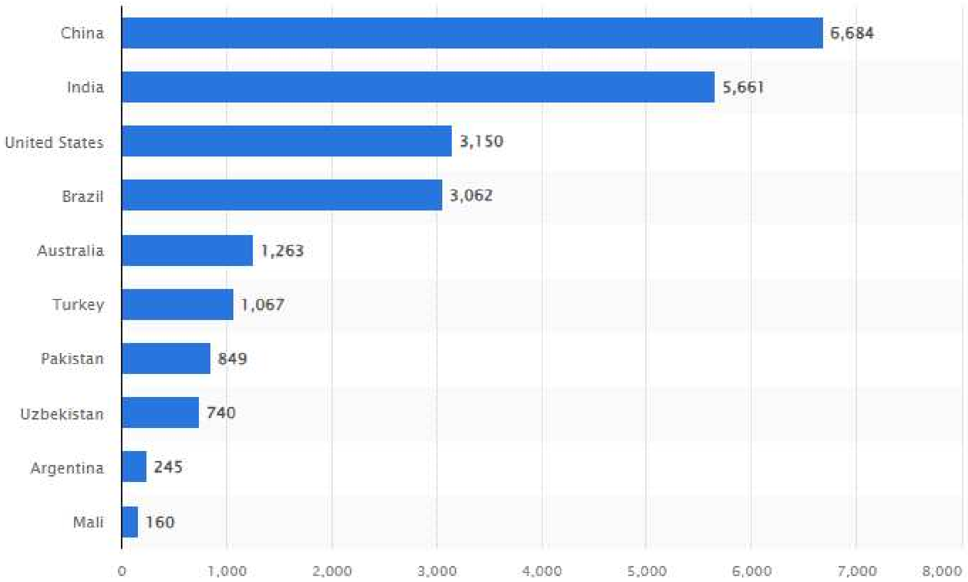

Fig. 16: Cotton producing countries worldwide 2022/2023.

Source: Statista 2023

According to the forecast, the total quantity of textile waste will reach 148 million tons by 2030, of which cotton waste accounts for about 35–40% (Lu *et. al.* 2022). Efficient utilization of waste cotton textiles and emission reduction of harmful substances have become research hotspots. (Liu et al.2022). As a result, recycling of cotton textiles has become a highly sought alternative for garments end of life (Esteve-Turrillas and de la Guardia, 2017).

Textile recycling strategies

Textile recycling routes can be classified into open-loop recycling and closed-loop recycling, based on the end-product aimed. In open-loop recycling, the quality and inherent properties of the recycled material are different from the original material and, therefore, the recycled material is used for a different product or purpose than the original. The open-loop recycling process converts waste material into a new form of material, which can be used as an input to another manufacturing process. In closed-loop recycling, recycled material is converted into a similar product as the original and it can substitute the original virgin material (Larrain et al. 2020). Therefore, closed-loop recycling is important to reduce the environmental impacts created by the textile industry, since a worn- out textile is recycled into the original fibre form, thus replacing virgin fibre (Asaadi et al. 2016).

According to the literature, textile recycling can be mainly categorized into four technologies: mechanical, thermomechanical and chemical processes, alongside emerging advancements in biochemical approaches (Dissanayake, G. et al.2021). The combination of different methods are usually involved for the recycling processes. For example, chemical recycling often involves an initial mechanical aspect of shredding the material. Biological processes might require a blend of mechanical or green chemistry methods for pretreatment (Ribul, M. et al. 2021). In some approaches the combustion of textile waste can be used for energy production when the former recycling options are not suitable (Dissanayake, G. et al. 2021). However, it stands as the least favoured option for resource recovery.

Mechanical recycling

Mechanical recycling processes are the most widely used processes for textiles. Mechanical recycling involves processing textile waste into secondary raw material without altering the polymer chemical structure of the fibres (Harmsen P. et al. 2021). In cost comparison, mechanical processes are generally more economical than chemical and bio-based alternatives. However, a significant drawback is the occurrence of inter-fibre friction, which leads to a gradual decline in the quality of recycled fibres. Consequently, to achieve the necessary strength and quality for apparel production, blending recycled fibres with virgin fibres is often required when producing new yarns (Le, 2018). Typically, fabrics produced trough mechanically recycled materials can only use 20–30% of recycled fibres before the fabric quality is significantly reduced (Aronsson J. *et al.* 2020).

The mechanical recycling of natural cellulosic fibres is applied to various waste streams within the value chain. Fibres mechanically recovered from recycled cotton could be respun into new yarns using the conventional ring or rotor spinning process or developed into non-wovens. This recycling is based on a combination of several processing steps such as collection, identification, sorting, grinding, carding, blending and respinning into new fibres (Todor M. *et* al 2019) (Fig. 17).

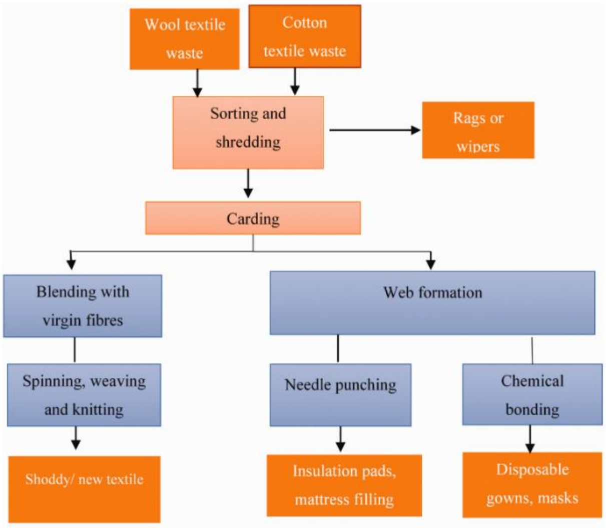

Fig. 17: Mechanical recycling technologies for natural origin fibre.

Source: Todor M. et al 2019

Chemical recycling

Chemical recycling of textile waste provides a promising alternative as it can overcome some of the shortcomings of mechanical recycling and provides substantial opportunities to maintain materials in a closed loop. Textile recycling can employ two chemical processes: monomer and polymer recycling. While chemical recycling theoretically applies to most textile fibres, monomer recycling is currently exclusively utilized for synthetic fibres (Ribul, M. 2021b).

Monomer recycling involves the process of depolymerisation followed by repolymerisation, wherein the waste material is broken down into its individual monomer units. Ideally, end-of-use materials can be recycled into virgin-quality fibres using monomers (Guo et al., 2021). In the depolymerisation process, plastic polymers such as polyester can be depolymerized into monomers or oligomers and repolymerised into new fibres or materials (Vadicherla and Saravanan 2017; Sandin and Peters 2018).

Polymer recycling involves dissolving fibres, a process achieved through mechanical methods like shredding, followed by chemical dissolution using specific solvents, often hazardous. However, cotton fibres, the focus of the work herein developed, poses a challenge in this regard due to their resistance to common solvents, attributed to the robust intra and inter-molecular hydrogen bonds among cellulose chains. This route is commonly used for cellulosic fibres such as cotton (De Silva et al. 2014; Mohd et al. 2017). The overview of the chemical recycling processes for cotton is illustrated in Fig. 18.

Cellulose is known to be insoluble in water due to the significant hydrogen bond networks (Anita E. et al.2023). According to the literature certain solvents or solvent systems can be used to dissolve the cellulose since they are able to diffuse in and disrupt the crystalline structures in addition to separating cellulose chains from one another (Ghasemi et al. 2017 a,b). The solvent when placed in contact with cellulose, permeates into the structure causing changes in volume and physical properties (Medronho and Lindman 2015). At the initial time swelling of the cellulose fibres occurs and if the interaction among cellulose and solvent are stronger than the intra and intermolecular interaction in the crystalline structure the crystalline network of cellulose is gradually destroyed increasing the possibility of conformational chain movement of individual chains (Rabideau et al. 2013).

This process can be achieved thanks to different systems such as Lyocell process, using NMMO as solvent, (Haule LV. Et al 2014), alkali/Urea (Liu W. et al 2019) or ionic liquid (IL)-based processes (Sixta H et al 2015). In the terms of researched for chemically recovering cellulosic fibres Lyocell and IL-based technologies emerge as the most established processes (Schuch AB, 2016). In the Lyocell process, cellulose undergoes physical dissolution in NMMO, followed by fibre formation through dry-jet wet spinning into an aqueous precipitation bath fibre (Klemm et al. 2005; Zhang et al. 2018). N-methyl- morpholine-N-oxide (NMMO) is used industrially by Lenzing to produce Tencel^{TM} fibres in the Lyocell process (Lyocell.info, n.d.). It is the most used solvent for the dissolution of cellulose because it can completely dissolved cellulose without any degradation (Haule et al. 2016). The challenges with this process include high thermal instability and energy consumption during spinning, as well as the fibrillation of regenerated Lyocell fibres under wet abrasion, resulting in an undesirable hairy appearance that can complicate the dyeing of Lyocell fibres (Haule et al.2016). In recent years, the recycling of cotton waste fabrics has shifted towards IL solvents, which are considered more environmentally friendly due to their ability to optimize energy usage during the process. This is achieved through complete pulp dissolution at lower temperatures and in less time compared to the Lyocell process (Baloyi RB et al 2024). However, when employing IL, it is essential to confirm the viscosity of the waste cotton before dissolution, enabling the spinning of the resulting dope into regenerated fibres (Schuch AB, 2016).

Lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) system is another possible solution in recycling cotton fabric waste. However, in this specific case, several reports say that recycled polymers have generally lower mechanical performance compared to conventional processes, so strengthening additives are required to achieve the desired properties for regenerated fibres (Biswas *et al.* 2021).

Cellulose dissolution with Alkali/urea aqueous system is a fast physical dissolution process as well as the advantages of no pollution, easy operation, low energy consumption and high efficiency.

the production cost and energy consumption are less than Lyocell process and ionic liquid process since both processes require high temperature (80-120 °C) and high pressure, and this can be linked with high energy consumption and high labour cost (Tu et al. 2020). Despite the many pros of this process, poor solubility and solution stability are among the issues that still plague the alkali/urea system, and the fibre preparation procedure is still in its pilot stage. (Hu tu et al. 2022)

In general, chemical recycling of textiles offers several key advantages. It efficiently breaks down textile materials into high-quality recycled fibres, overcoming limitations of mechanical recycling. This process supports closed-loop systems, reducing the need for virgin materials and lowering environmental. However, the contaminants like dyes and finishes can hinder the process by affecting recycled material quality (addressed in other section of this chapter). The diverse range of textile materials also poses challenges, as different fibres may require distinct chemical treatments. Moreover, the cost and complexity of chemical recycling, along with energy consumption, can prevent scalability and offset environmental benefits. Efficiency may vary based on fibre type and processing conditions. Overcoming these challenges is essential for maximizing the sustainability of chemical recycling in textile waste management.

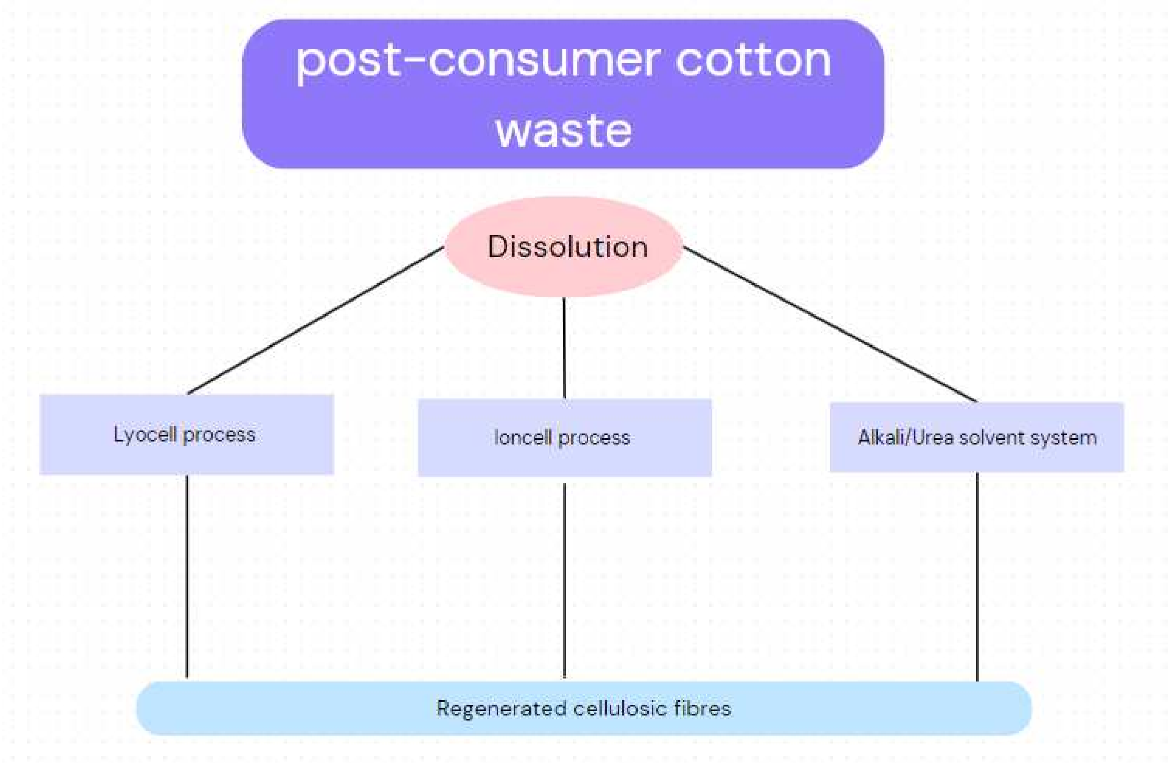

Fig. 18: Chemical recycling technologies of cotton.

Source: Le k. 2018 (adapted)

Biochemical recycling processes

The biochemical process of textile recycling is an environmentally friendly enzymatic alternative that breaks down polymers into monomers (Dissanayake et al.2021). The advantages of this technology are the low energy demand, the use of benign solvents and chemicals and a process highly selective, making them good option for separating blended textile waste (Piribauer B et al. 2019). However, this technology has some drawbacks, including its limitation to natural polymers, as well as higher costs and longer reaction times compared to chemical recycling (Baloyi RB et al 2024). Most enzymatic processes which use cellulosic biomass as a feedstock for fermentation require a chemical pretreatment before the enzymatic step converts the cellulose into sugars (Beig et al., 2020). This is because amorphous cellulose is easier to degrade compared to crystalline cellulose (Roy Choudhury A, 2014). Such pretreatments include various methods, such as size reduction, utilization of acid or alkaline solutions, ammonia treatment, application of pressure and/or high temperature, microwave processing (Yu et al., 2020), as well as the use of ILs (George et al., 2015). Acid pretreatment is the most widely used pre-treatment process for cellulose-based fibres, in which the amorphous region of cellulose is hydrolysed while crystalline region can be exposed to enzymatic degradation. Alkali pre-treatment can be used to breakdown the inter- and intra-chain bonds of the cellulose molecules through the swelling effect, creating more space for the enzymatic attack (Dissanayake et al.2021). Sodium hydroxide, potassium hydroxide, and calcium hydroxide are the commonly used chemicals for alkali pretreatment (Gholamzad et al. 2014). Despite the challenges, biochemical recycling holds promise for sustainable textile practices, provided ongoing research addresses its limitations and optimizes efficiency, thus laying the groundwork for future industrial implementation of these processes.

Chapter 3: Materials and methods

The pretreatment and dissolution of 100% cotton fibres were explored using environmentally friendly methods and reagents. Various variations of the pretreatment methods were explored, to remove any contaminants and dyes present in the fibres. Additionally, four different approaches were explored for the dissolution of the cotton.

3.1) Materials

The fibres explored in this work were 100% cotton fibres mechanically recycled from knits. The mechanical recycling was conducted at CITEVE. Fig 19 depicts the two samples studied.

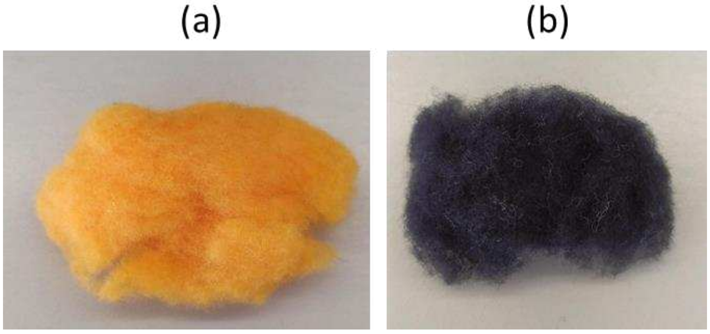

Fig 19: Cotton samples used to perform the pre-treatment and dissolution assays (a) orange fibre sample (b) black fibre sample.

3.2) Pretreatments:

The main goal for the application of pretreatments was to remove colour and other contaminants from the fibre samples, to proceed with the chemical recycling process. The pretreatment included four combinations of procedures that were explored and compared between each other:

1- Acid treatment > alkaline treatment > reducing treatment > ozone treatment;
2- Reducing treatment > ozone treatment;
3- Acid treatment > reducing treatment > ozone treatment;
4- Alkaline treatment > reducing treatment > ozone treatment.

The acid, alkaline, and reducing treatments were performed in a Mathis LABOMAT® equipment. (Fig. 20).

Fig. 20: Mathis LABOMAT® equipment.

3.2.1) Acid treatment:

For the acid treatment, a CH_2O_2 (Carlo Erba, Germany) aqueous solution of 2 ml/L was prepared. Using a bath ration of 1:100, 1g of fibre was treated at 80 ºC, for 1h.

3.2.2) Alkaline treatment

The alkaline treatment was performed using a NaOH (50%) solution (João Manuel Lopes Barros – Lda, Portugal) at 20% wt%. Using a bath ration of 1:100, 1 g of fibre was treated for 100 minutes at a temperature of 90°C.

3.2.3) Reducing treatment

For the reducing treatment a thiourea dioxide (Atusmic, Portugal) solution was used, consisting of 4 g/L of this reducing agent and 4 g/L of sodium carbonate (Solvay, Belgium). Using a bath ration of 1:100, the fibres were treated for 60 minutes at 80ºC.

3.2.4) Ozone treatment

For the ozone treatment, the fibres were impregnated in a H_2O_2 (João Manuel Lopes Barros – Lda, Portugal) solution of 20% wt% concentration and pressed twice for humidity control. The pressing phase was conducted using a W. Mathis AG® equipment (Fig. 15)

Fig. 21: W. Mathis AG®.

Subsequently, each fibre sample was subjected to an Ozone treatment for about 1,5 hours using an Ozone machine MTEX NS® equipment (Fig. 22).

Fig. 22: Ozone machine MTEX NS® equipment.

3.2.5) Softeners removal

Both fibre samples were impregnated in a solution of silicone base softener, using the Mathis LABOMAT®. The main goal of this study was to analyse whether the pre-treatments used were effective in removing softeners on cotton-based fibres.

At the end of the treatment, the cotton fibres were analysed by FTIR.

3.3) Dissolution treatments:

After contaminants and dyes removal, the samples were subjected to chemical treatments with the main goal of dissolving the cotton fibres in aqueous NaOH-based solution. In Scheme 1 is depicted the schematic overview of the procedures used. Initially, attempts were made to dissolve cellulose using NaOH/Gly and NaOH/ZnO solutions. Following this, two different strategies were tested. The first process involved using alkyl and acid hydrolysis for pre-treatment, followed by employing NaOH/Gly and NaOH/ZnO solutions as solvents. Subsequently, the approach shifted to utilizing NaOH/Gly and NaOH/ZnO solutions as pre-treatments for dissolution, while still employing alkyl and acid hydrolysis.

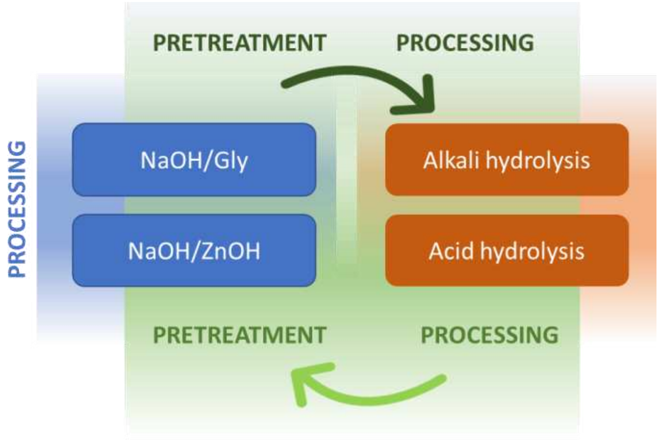

Fig 23: Schematic overview of the procedure explored for the cellulose dissolution.

3.3.1) Dissolution in Glycerine/NaOH aqueous solution

The procedure for the dissolution assay was adapted from Ke li, et al 2020. Briefly, a solution of NaOH (Fisher scientific, USA) and glycerine (Gly) (HiMedia Laboratories, Germany) was prepared by adding 9 g of NaOH and 1 g of glycerine to 90 mL of deionized water. Then, 2.0 to 3.0 g of textile sample were added to the mixture and allowed to swell for 6 hours, at room temperature (RT). After 6 h, the sample was placed at 4 ºC overnight. The following day, the sample was stirred using a homogenizer for 20 min and filtered to collect the supernatant. Afterwards 3M HCl (Fluka, Honeywell) solution was added to the cellulose solution (2:1) for 10 min, to regenerate the cellulose. The cellulose aggregates were collected by centrifugation, discarding the supernatant. The precipitate was washed twice, using deionized water, and then oven-dried at 45 ºC for 20 h. Additionally, the losses during the process were quantified by washing the undissolved cellulose/textile material was washed with 100ml of water three times in the Mathis LABOMAT® at room temperature, dried and weighted.

The dissolution yield Y(%) was determined using the following equation: (Equation 1):

$$Y(\%) = \frac{Wf}{Wi} * 100 \qquad \text{Equation 1}$$

where Wf is the final weight of the sample (the amount of regenerated cellulose), and Wi is the initial amount of textile material. The described procedure was used both as pre-treatment and as a processing strategy.

3.3.2) Dissolution in NaOH/ZnO aqueous solution

The dissolution using the NaOH/ZnO solvent systems was performed according to Määttänen M. et al. 2021, with slight adjustments. Firstly, a stock solution of NaOH 18% (w/v) and ZnO 3% (w/v) (Panreac Quimica, Spain) was prepared, which was stored at –20 °C until use. After, an aqueous NaOH/ZnO solution was prepared by diluting the stock solution to 9% w/v NaOH and 1% w/v ZnO. The prepared solution was used to treat the textile sample. For that 2 and 3 g of textile were added and allowed to swell for 6 h at RT. Afterward, the sample was placed at 4 ºC overnight. On the following day, the sample was stirred in ice water using a homogenizer for 20 min, followed by the filtration and collection of the undissolved cellulose/textile material. The cellulose was regenerated with 3M HCl (2:1) for 10 min. The resulting cellulose aggregates were collected by centrifugation and the supernatant was discarded. The precipitate was washed twice by deionized water and oven dried at 45 ºC for 20 h. The dissolution yield was determined using Equation 1, and the losses quantification during the dissolving process were determined according to the procedure described in section 3.3.1. The outlined procedure was employed both as a pre-treatment and as a processing strategy.

3.3.3) Acid hydrolysis:

The acid hydrolysis process involved the utilization of an aqueous 3 M H2SO4 (Panreac Quimica, Spain) solution, with a liquor ratio of 1g of fibre per 20 ml of aqueous acid solution (1:20). The hydrolysis was conducted at a temperature of 50 ºC for a duration of 1 hour.

3.3.4) Alkali hydrolysis:

For the alkali hydrolysis, a solution 3M of NaOH was prepared. After, the samples underwent hydrolysis at 50 ºC for 1 hour, using a liquor ratio of 1g fibre/ 20 ml alkaline solution (1:20).

3.4) Testing and analysis

3.4.1) Cielab

Several colour measurement systems have been developed in order to standardize perceived colours in terms of colour definition and communication and one of the most widely used colourimetric systems is the CIELAB colour-space, drawn up by the Commission Internationale de l'Éclairage (or 'CIE') (Bechtold & Pham, 2019).

The CIE L*a*b* system is defined on the base of physical properties of light and the physiological build of human eye. Inside this chromatic system, any colour can be specified inside the space by using the rectangular coordinates CIE L *, a *,b *. This system consists in two axes a* and b* that are perpendicular to each other and that represent the tone of colours. These are based on the fact that a colour cannot be at the same time red and green or blue and yellow, because these colours oppose each other. On the a* axis positive values indicate the sums of red, while the negative values indicate the sums of green. On the b* axis positive values indicate the sums of yellow, and negative values indicate the sums of blue. For both axes, zero is neutral gray (Insight on colours, Vol 8. NO 7). The third axis is the luminosity L* that is perpendicular to the plane made by the axes a* and b* (Figure 18) and it refers to the reflected quantity of light by the colour or, to the percentage of black in the colour. L* takes values from zero (-) for perfect black to 100 (+) for perfect white (Insight on colours, Vol 8. NO 7) (Fig 24).

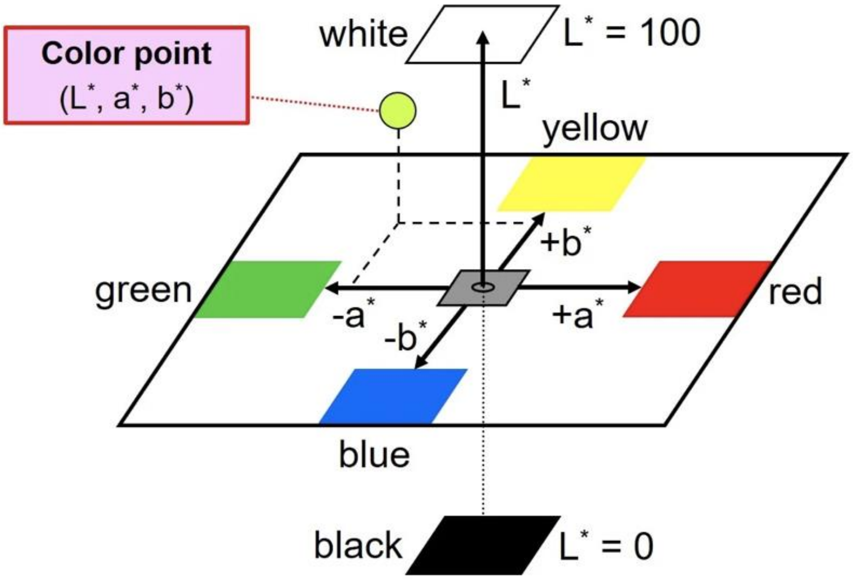

Fig 24: Three-dimensional representation of the CIELAB-color space, with characteristic coordinates.

Although the CIELAB colour coordinates enable generalized description of colour and colour differences, this system does not suffice when the colour-strength needs to be described. As a consequence, colour strength is frequently assessed by the Kubelka–Munk colour strength ‘K/S’.

K/S value is an important parameter which can indicate the depth of the colour of dyed fabric surface. (Haiyan Zhang, 2014). The Kubelka-Monk equation is useful when formulating colours for industries such as textile, paper and coating. This value is received by measuring the reflectance curve after radiation of a surface and applying the Kubelka–Munk function (Equation 2): at a given wavelength, this function calculates a value for the ratio of light that is absorbed (K) to the amount of light that is scattered (S). When more light is absorbed and less light is scattered, the K/S-value (and thus colour strength) increases (Bechtold & Pham, 2019).

Equation 2

$$\frac{K}{S} = \frac{[1 - 0.01\,R]^{\wedge}2}{2[0.01\,R]}$$

With R being the reflection at a given wavelength, with a value 0-1

In the present work, the colour coordinates from the CIELAB system, as well as the K/S values from the fibres that underwent the colour removal treatments were analysed. The equipment used was a Datacolour Spectro 750 spectrometer (Fig 25).

Fig 25: Cielab equipment.

3.4.2) FTIR

The samples and fibres were chemically characterized by Fourier Transform Infrared Spectroscopy (FTIR) (Fig 26). FTIR spectra were measured on a PerkinElmer Precisely Spectrum 100 equipped with a Bruker Platinum diamond ATR sampling accessory. To evaluate the effectiveness of the removal of softners16 scans were collected against an air background, with a resolution of 8 cm^{-1}. Additionally, for each spectrum from the samples originated from the chemical recycling processes 18 scans were collected against an air background, with a resolution of 8 cm^{-1}.

Fig 26: FT-IR equipment.

Chapter 4: results

The results for the colour removal experiments are divided between approaches, depending on the sequence of treatments applied to the fibres, as explained in the previous section. These were applied to cotton fibres after mechanical treatment, with two different colours.

For the cellulose dissolution, the results are divided between systems, depending on the aqueous solution applied to the fibres. These were applied in cotton fibres after the colour removal approaches.

4.1) Colour removal

First approach

The fibres were subjected to four different successive treatments: acid treatment, alkaline treatment, reducing treatment and ozone treatment (Fig 21). The colour coordinates and K/S values of the fibres were determined after each treatment to evaluate the efficiency of colour removal (Fig. 22 and Fig. 23).

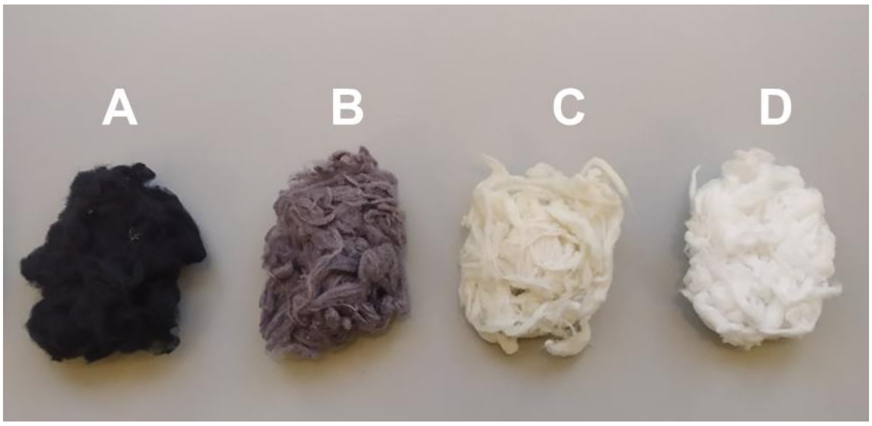

Fig. 21: Black cotton fibre after the progress of treatments.

A: acid treatment B: alkaline treatment C: reducing treatment D: ozone treatment

Fig.19 clearly shows the removal of the black colour from the fibres after each treatment, especially after the reducing treatment (C).

Fig. 20 shows the cielab values of the fibres after the four colour removal treatments. The graph shows a successive increase in the L* values after each treatment. For the a* coordinates the values do not vary greatly from the 0 axis, indicating a neutral grey following the reducing treatment. The b* coordinate demonstrates that the fibres had a blue hue before the reducing treatment, to which the values become positive, and therefore, indicate a yellow colour. However, the values are very low and close to neutral grey as well.

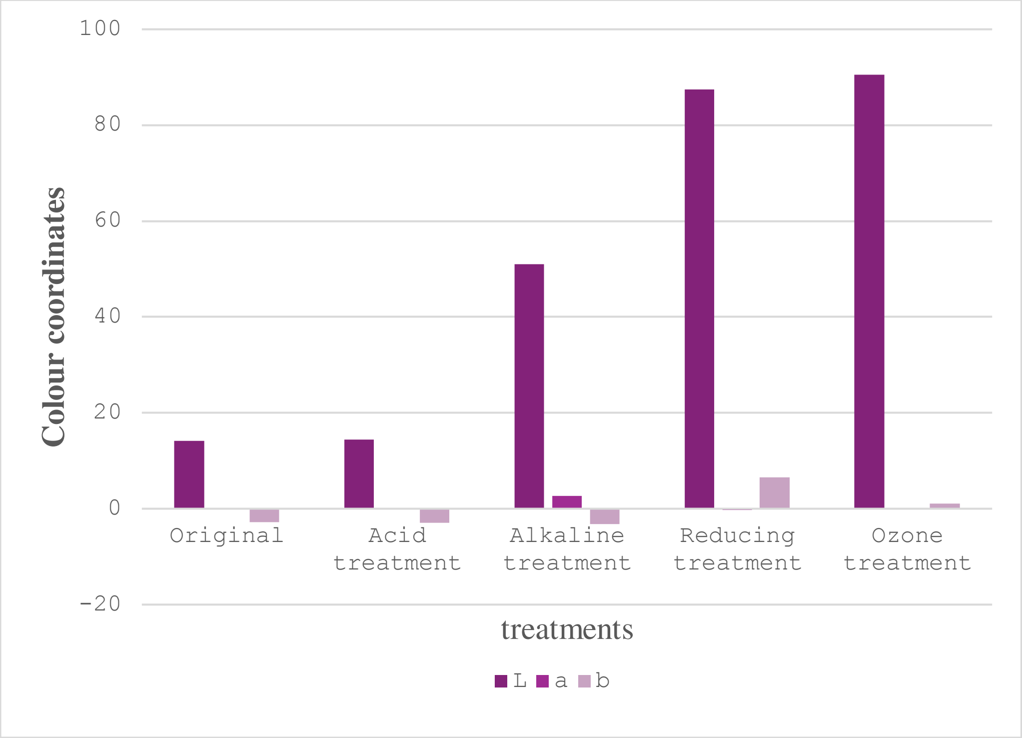

Fig. 22: Cielab values of L*, a* and b* coordinates of the black fibre after each treatment of the first approach.

Regarding the K/S parameter, the results show a decrease with each treatment applied, indicating a decrease in intensity of colour. Additionally, the alkaline treatment shows the highest decrease in the K/S values (Fig. 23).

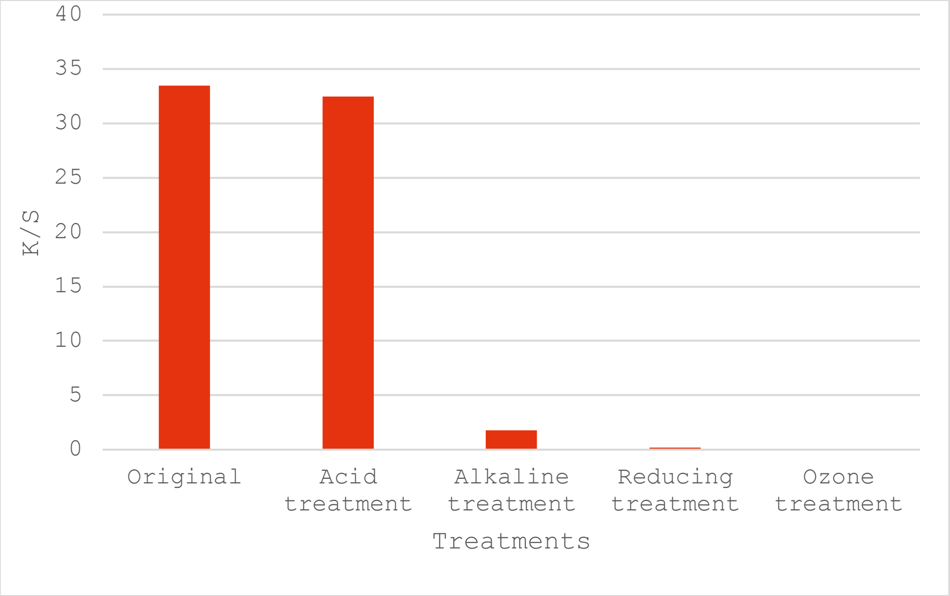

Fig. 23: K/S values of the black cotton fibres after each treatment of the first approach.

The same procedure was also studied in orange cotton fibres (Fig. 24).

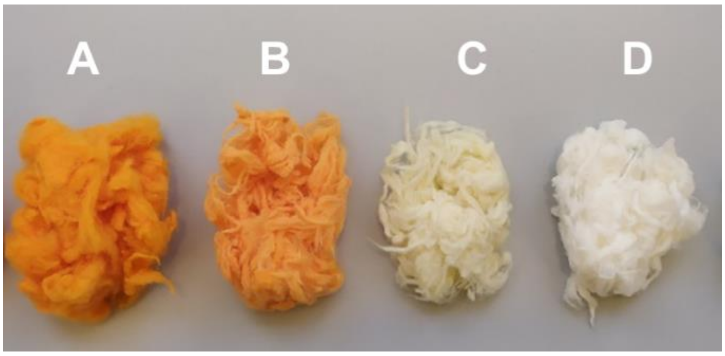

Fig. 24: Orange fibres after the different treatments.

Fig. 24 shows a clear colour removal from the orange fibres from one treatment to another. The colour coordinates and K/S values are shown in colour (Fig. 25 and Fig. 26).

The increasing L* values demonstrate the increase in luminosity, while a* coordinate approaches 0 the more treatment the fibre suffers. The same behaviour is observed for the colour coordinate b* (Fig. 25).

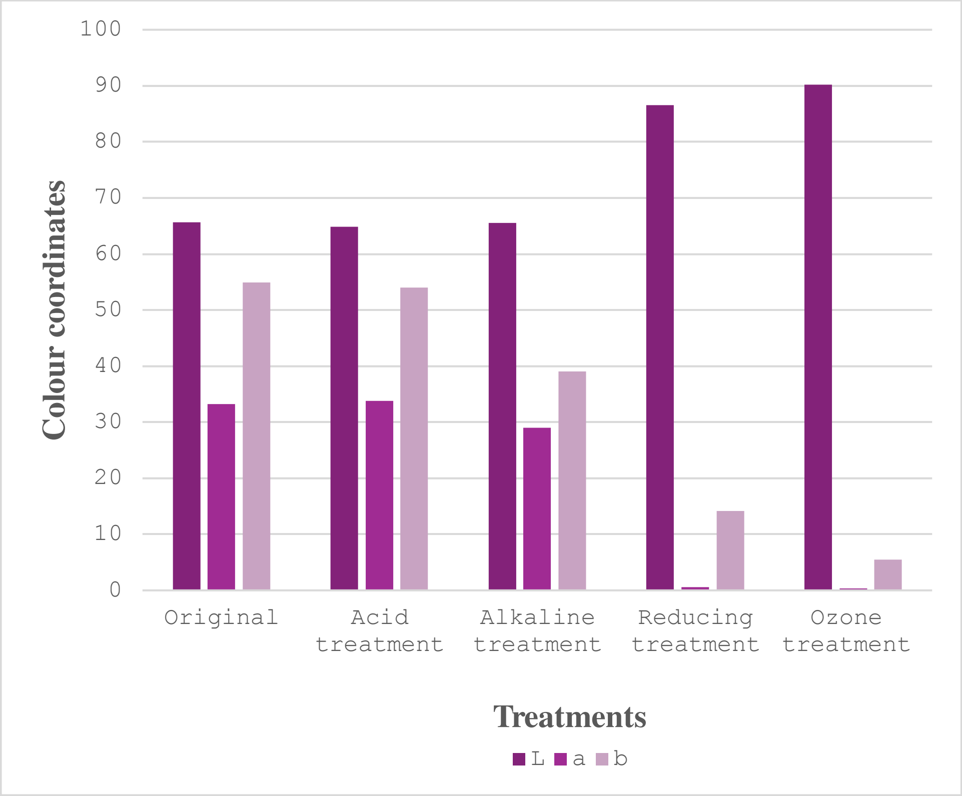

Fig. 25: Cielab values of L*, a* and b* coordinates of the orange fibre after each treatment of the first approach.

The K/S parameter (Fig. 26) for the orange fibres show a successive decrease of values, indicating the decrease in intensity of colour.

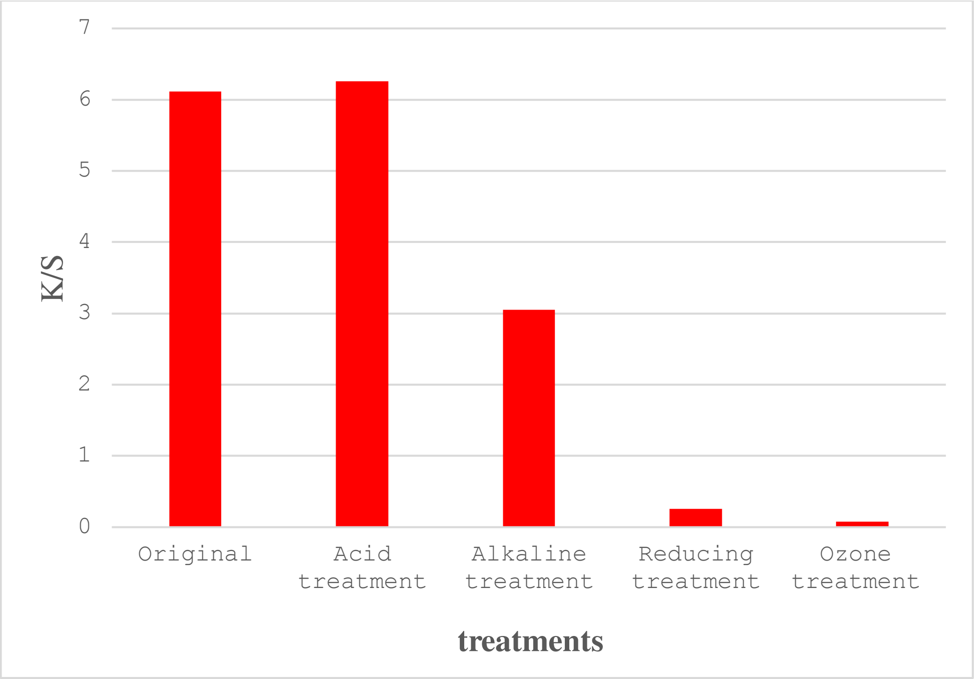

Fig. 26: K/S values in orange fibre after first approach.

Second approach

the fibres were subjected to only two different treatments, the reducing treatment and Ozone treatment. (Fig. 27).

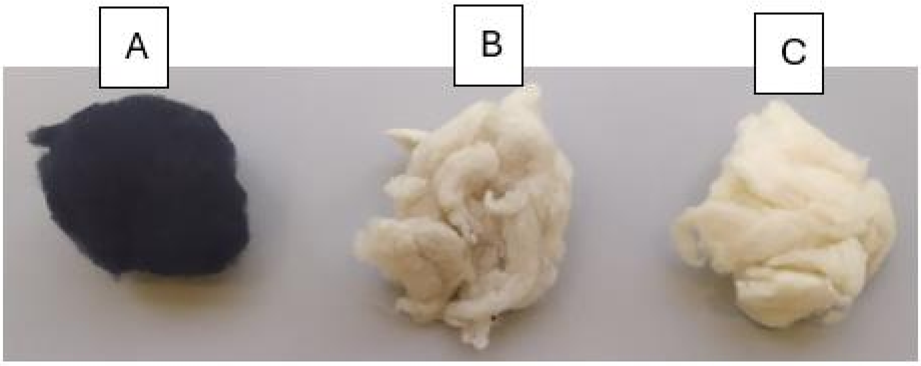

Fig. 27: Black cotton fibre after each treatments.
A: Original fibre B: Reducing treament C: Ozone treatment.

The fig. 28 shows the Cielab values of the black fibre samples after the the two treatments.
The increasing L* values do not show a considerable change between the two treatments, although it can already be considered a high-value fibre colour For the other coordinates, no notable changes are observed for the a* coordinate, and the b* compared suffers a slight increase after the ozone treatment fibre.

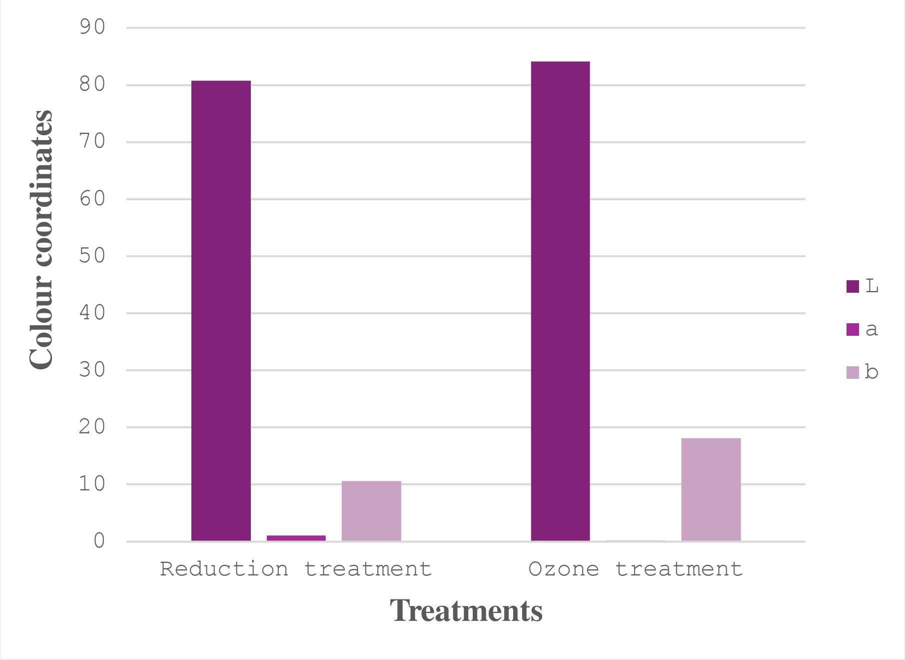

Fig. 28: Cielab values in black fibre after second approach.

This approach was also studied in orange cotton fibres (Fig. 29).

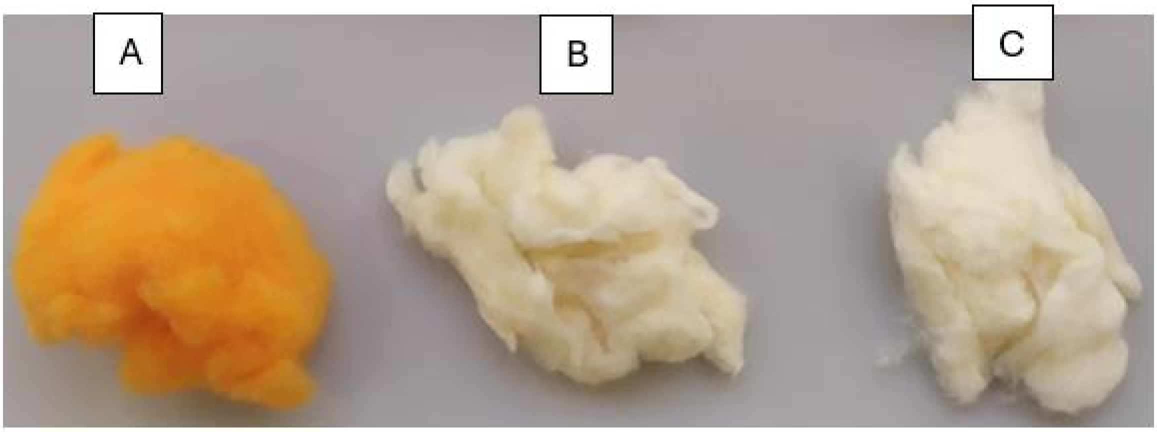

Fig. 29: Orange fibre after each treatments.

A: Original fibre B: Reducing treatment C: Ozone treatment.

For the orange fibres, there was no visible difference between the coordinates after the reduction treatment and after the ozone treatment. The same could be observed in Fig. 30, where the fibres after the reduction and ozone treatment have a similar, apparent, fibre colour.

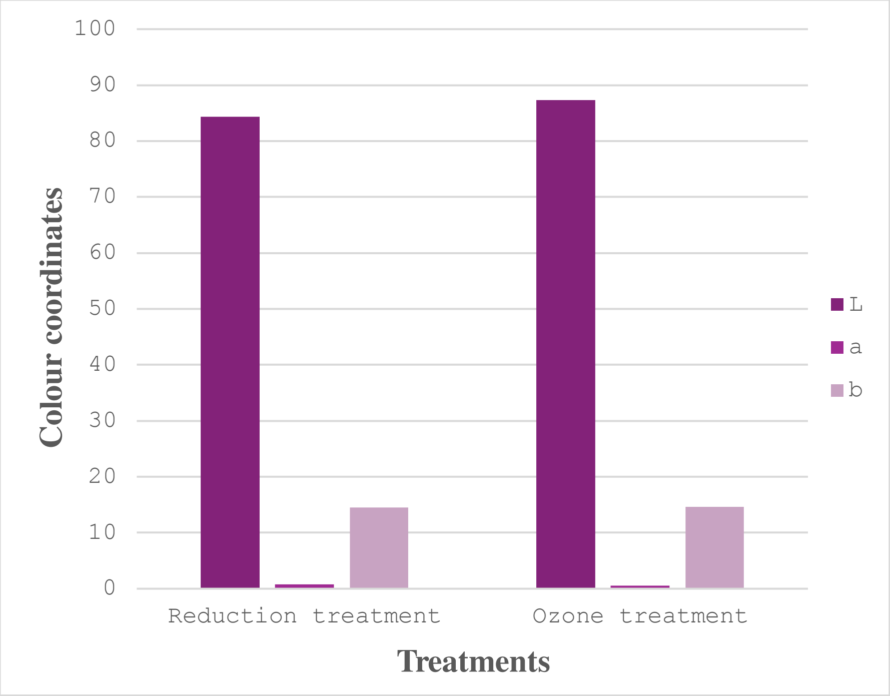

Fig. 30: Cielab values in orange fibre after second approach.

Comparing first and second approaches, fFg. 31 shows the K/S values for the black and orange fibres for both.

The results show that, for both fibres, the second approach has a higher K/S value, compared to the first approach.

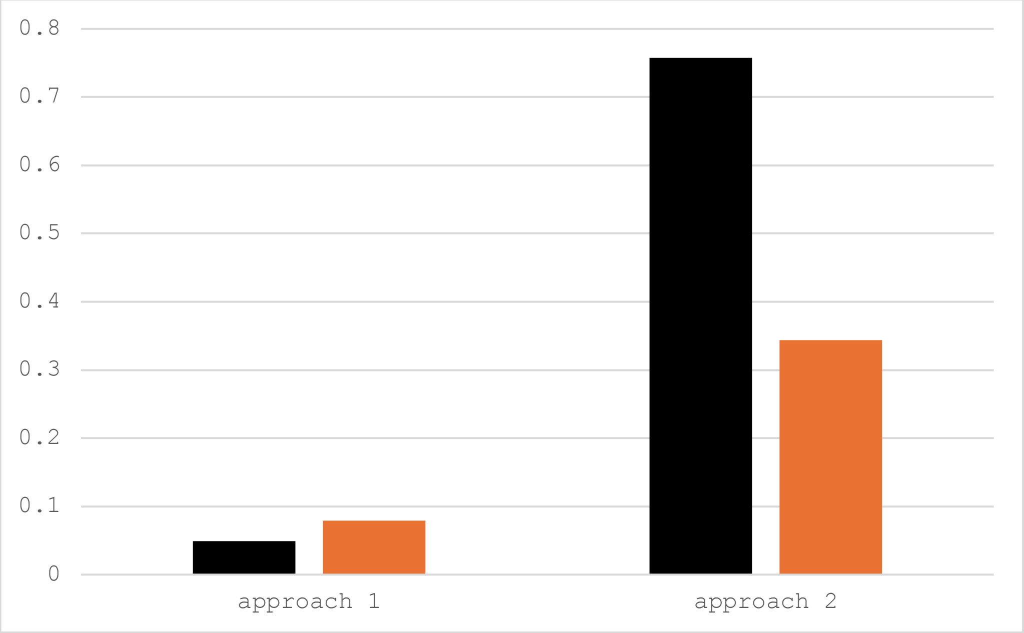

Fig. 31: K/S values for the black and orange fibres for both approaches.

Third and fourth approaches

the fibres were subjected to third approach and forth approach.

The third approach was composed by three different treatments, the acid treatment, the reducing treatment and the ozone treatment and the forth approach was composed by three different treatments, alkaline treatment, reducing treatment and ozone treatment (Fig. 32).

Fig. 32: Black cotton fibres appearance after the third and forth approach.

Both approaches were also studied in orange cotton fibres (Fig. 33).

Fig. 33: Orange cotton fibre appearance after the third and forth approach.

Comparing third and forth approaches, The fig. 34 shows the K/S values for the black and orange fibres for both.

The results show that, for both fibres, the third approach has a higher K/S value, compared to the first approach.

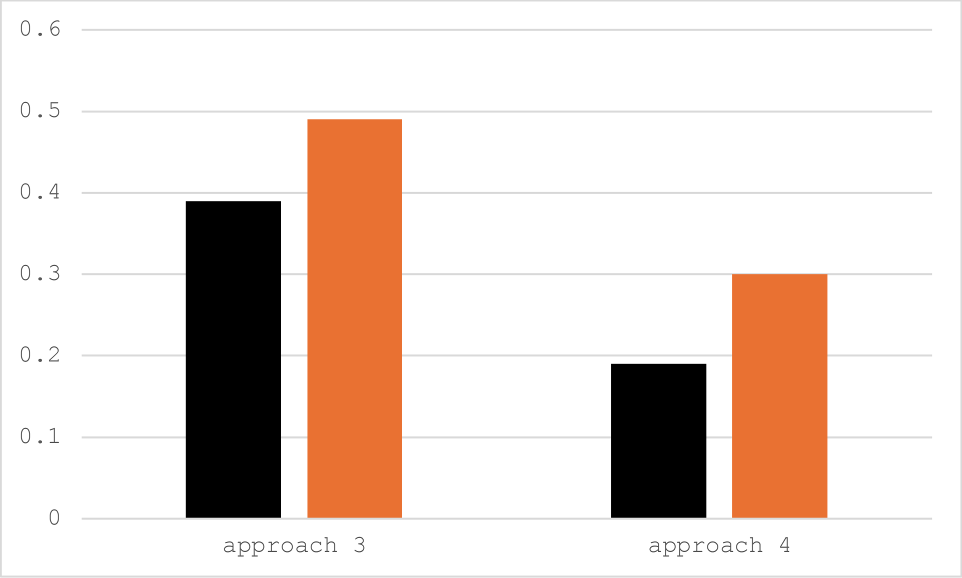

Fig.34: K/S values for the black and orange fibres for both approaches.

4.1.1) FTIR analysis

Third approach

To verify the influence of the treatments in the cotton structure, the samples from the third approach were analysed through FTIR.

Fig. 35 and Fig. 36, show the FTIR analysis of the black and orange cotton based-fibres subjected to the third approach, respectively.

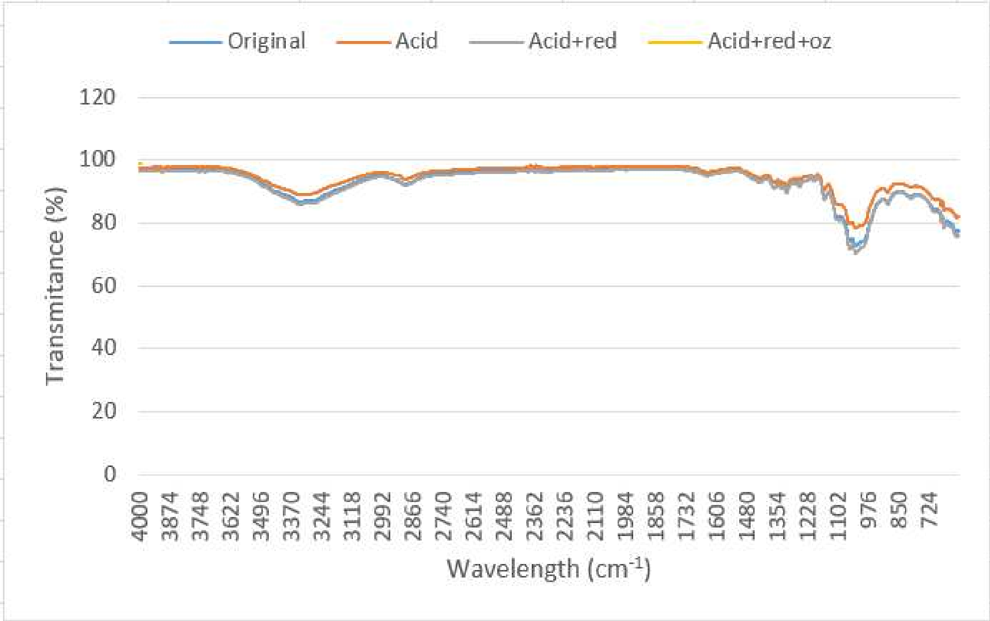

Fig. 35: FT-IR cotton spectrum of black cotton-based fibre after third approach.

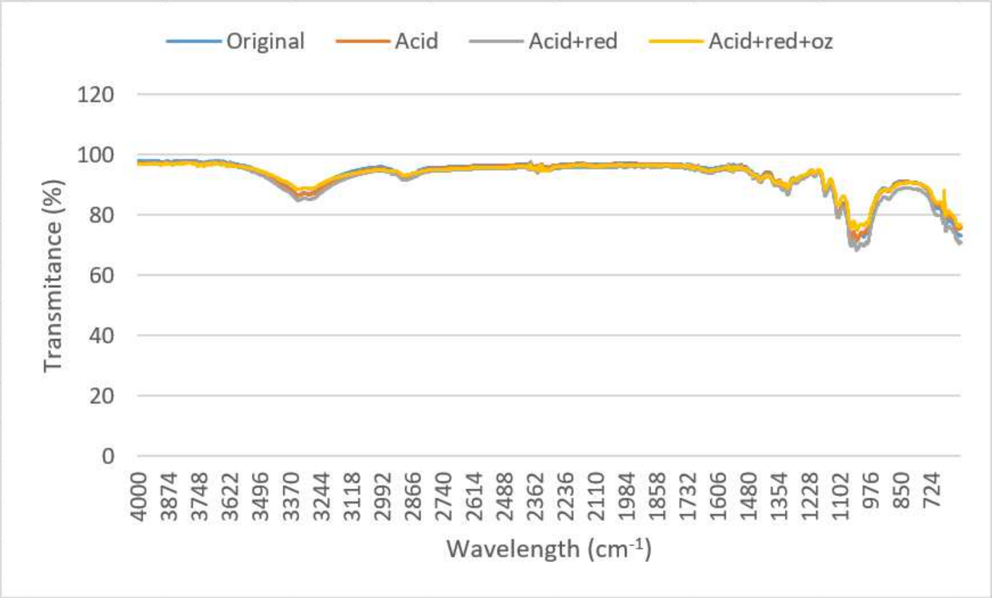

Fig. 36: FT-IR cotton spectrum of orange cotton-based fibre after third approach.

According to Table 2, all the most relevant peaks of the cotton spectrum are present in the analysed samples. Comparing the different samples with the original fibres, there are not visible differences in the FTIR spectrums, for both black and orange fibres.

Table 2. Most relevant peaks in cotton molecule spectrum

Source: Portella et al.2016

Peaks (cm^{-1})	Groups/linkages

3335	OH
2893	C-H
1414	CH_2
1344	C-H
1306	C-O
1000	(CO) and (OH)
934	B-glycosidic

Fourth approach

The same FTIR analysis was performed on the sample subjected to the fourth approach. Fig. 37 and Fig. 38 show the FTIR analysis of black and orange cotton based-fibre subjected to the fourth approach.

In both cases, the peaks representative of the cotton spectrum are present, fibre with no visible differences observed between the different curves and the one from the original fibre.

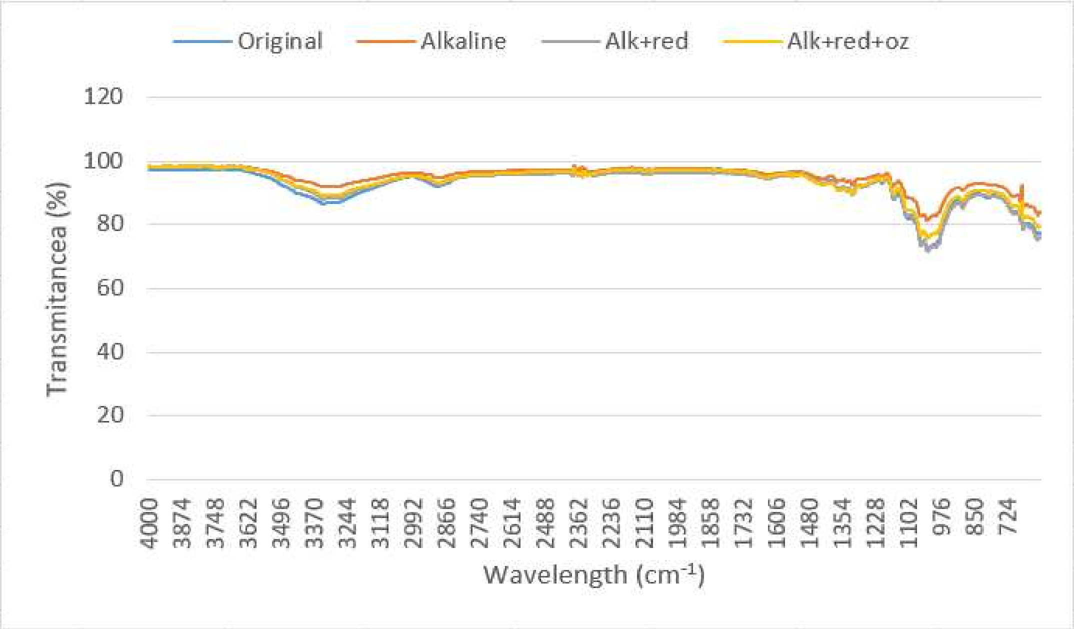

Fig. 37: FT-IR cotton spectrum of black cotton- based fibre after forth approach.

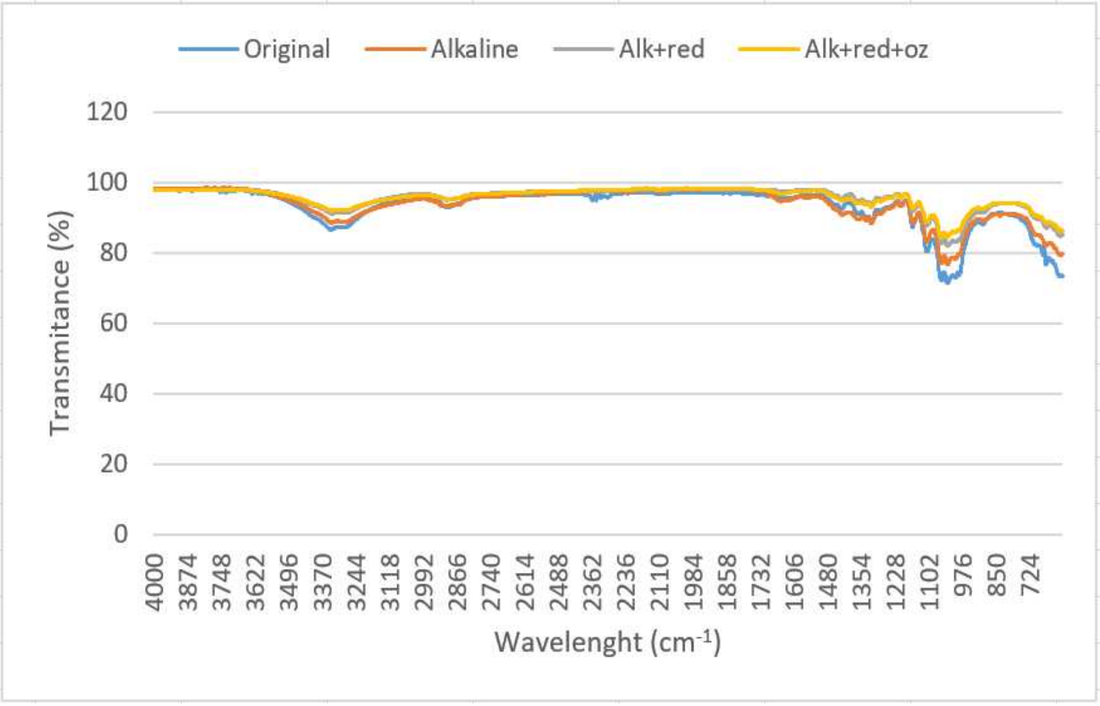

Fig. 38: Cotton spectrum of orange cotton-based fibre after forth approach.

As in the previous case, according to Table 2, all the most relevant peaks of the cotton spectrum are present in the analysed samples. Comparing the different samples with the original fibres, there are not visible differences in the FTIR spectrums, for both black and orange fibres.

4.2) Cellulose dissolution in aqueous solution

In this thesis, various methods were explored to dissolve cellulose after removing contaminants (results section 4). Initially, the cellulose dissolution was attempted using NaOH/Gly and NaOH/ZnO solutions. After, two different strategies were tested. The first process involved using alkyl and acid hydrolysis for pre-treatment, followed by employing NaOH/Gly and NaOH/ZnO solutions as solvents. Subsequently, the approach shifted to utilizing NaOH/Gly and NaOH/ZnO solutions as pre-treatments for dissolution, with alkyl and acid hydrolysis still being employed. The aim is to explore diverse methods for recycling cotton textile waste, specifically focusing on aqueous-based systems and environmentally friendly strategies.

Dissolution in NaOH/Gly solution

In a first approach, NaOH/Gly solution was used toward the dissolution of cotton fibres after colour removal, without either acid or alkali hydrolysis as pre-treatments. The process was tested using different amount of textile (3% (w/v) and 4% (w/v)). The macroscopic appearance of the samples during the process is depicted in Fig.39.

Fig. 39: Dissolution steps of the cotton-based fibre in NaOH/glycerin solution.

A: cellulose aggregates B: regenerated cellulose C: dried regenerated cellulose.

After filtering and drying, the recovered cellulose fraction was analysed by FTIR and the spectra are depicted in Fig 40.

Table 3: FTIR values of the sample

Peaks (cm^{-1})	Bands	
896	C1 frequency	Cellulose 1
1107	Ring asymmetric stretching	
1161	C-O-C asymmetric	
1430	CH_2 symmetric bending vibration	
1261	CH bending vibration	Cellulose II
1313	CH_2 wagging vibration	Cellulose II
1366	CH bending vibration	Cellulose I and II

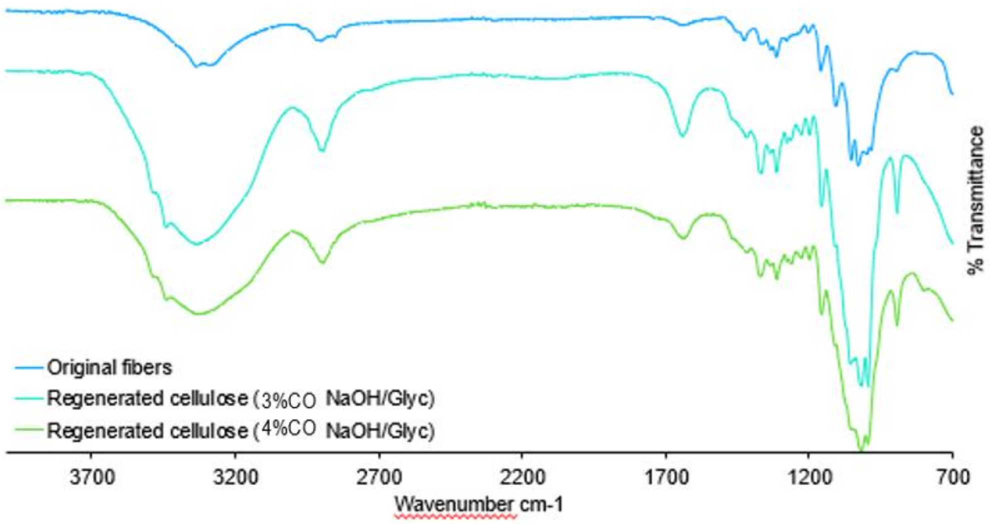

Fig. 40: FT-IR spectrum of the dried sample.

The yield from the different assays was also calculated, by weighting the samples before and after the process, and the results are presented in Fig. 41.

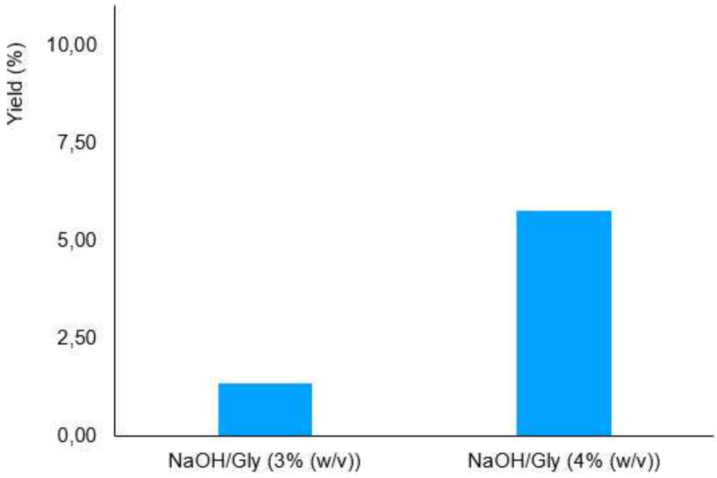

Fig. 41: Calculated yield of the dried sample.

Dissolution in NaOH/ZnO

Subsequently, the dissolution of cotton fibres post-colour removal was attempted using NaOH/ZnO solution, without employing acid or alkali hydrolysis as pre-treatments. This time, the process was evaluated using concentrations of 2% (w/v), 3% (w/v), and 4% (w/v). Fig.42 illustrates the macroscopic appearance of the samples throughout the process.

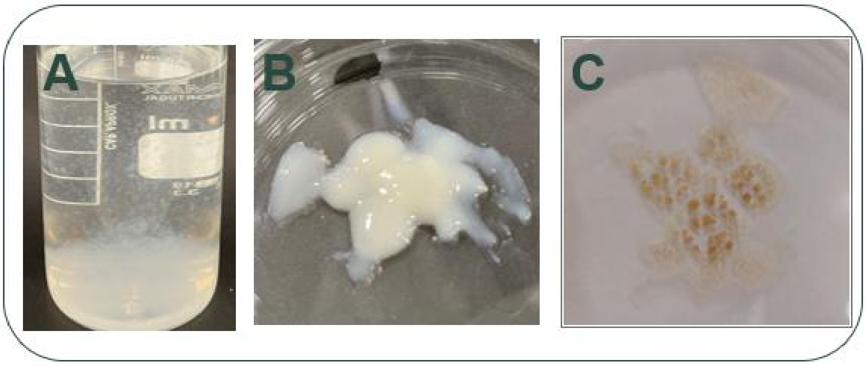

Fig. 42: Dissolution steps of the cotton-based fibre in NaOH/ZnO solution.

A: cellulose aggregates B: regenerated cellulose C: dried regenerated cellulose.

As before, to verify the effectiveness of the process, the recovered cellulose fraction was subjected to analysis by FTIR, and the spectra are depicted in Fig. 43.

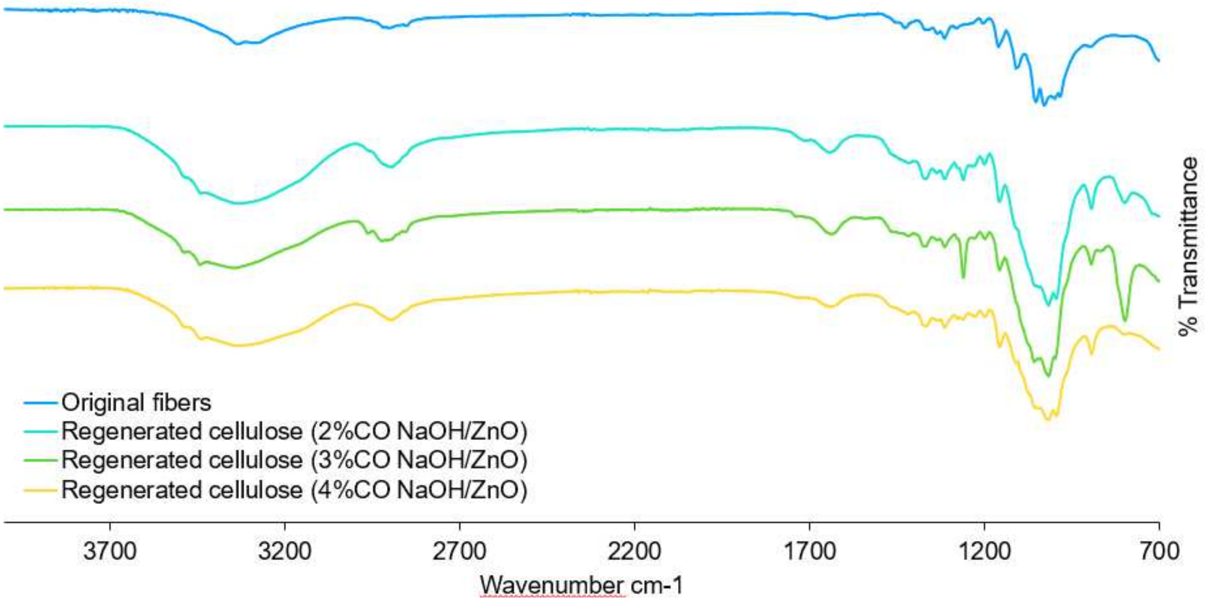

Fig. 43: FT-IR spectrum of the dried sample.

The yield from the various assays was also calculated by weighing the samples before and after the process. The results are presented in Fig. 44.

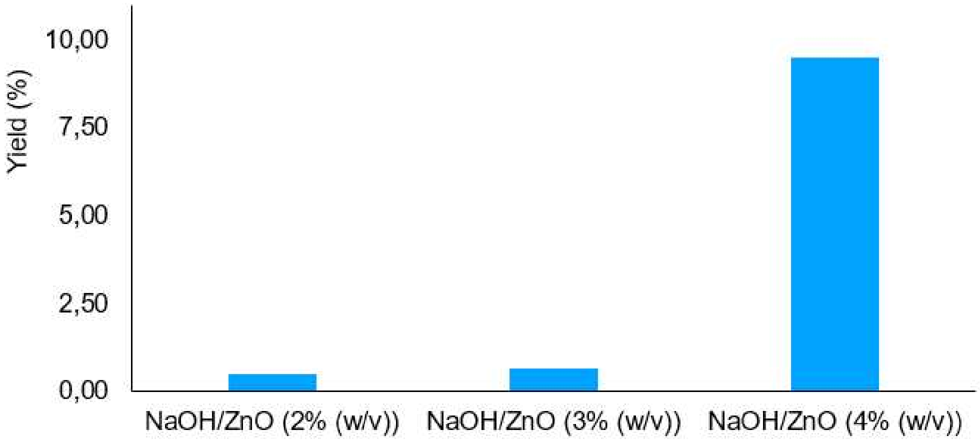

Fig. 44: Calculated yields of the dried samples.

Alkali and acid hydrolysis as pretreatment for dissolution in aqueous NaOH systems (NaOH/Gly and NaOH/ZnO)

The pretreatments were conducted due to low yields observed in previous assays. By subjecting the samples to pre-treatment processes, the aim was to enhance the efficiency of cellulose dissolution and increase the yield of recovered cellulose fraction.

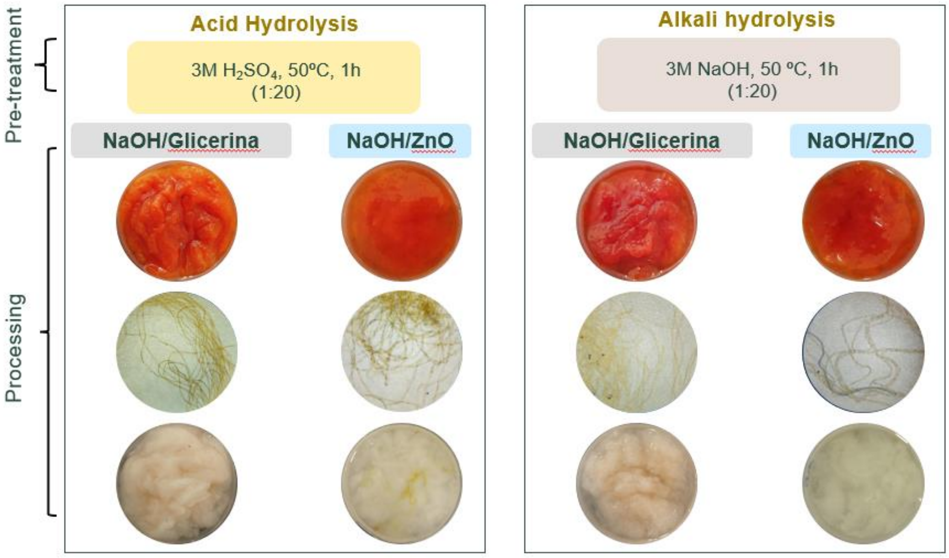

Fig. 45: Experimental scheme of the approach.

Aqueous NaOH solvent systems (NaOH/Gly and NaOH/ZnO) as pre-treatment for alkali and acid hydrolysis.

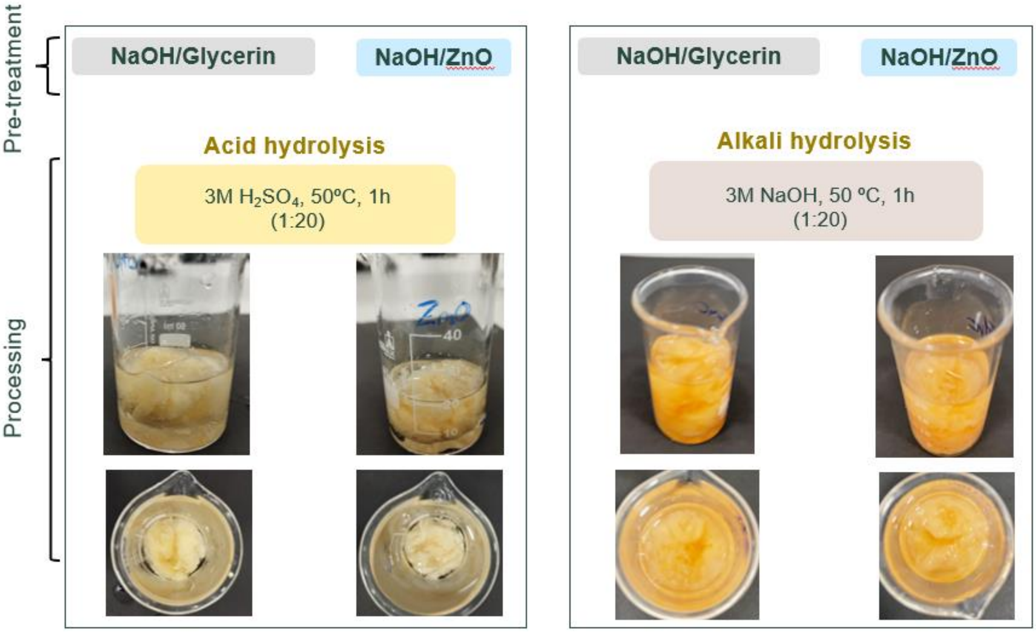

Fig. 46: Experimental scheme of the approach.

Chapter 5: Discussion

5.1) Discussion for colour removal:

In this thesis project, different innovative pretreatments, based on alkaline, acid, reducing and ozone treatments, have been evaluated for the capacity to remove the colour from the textile recycled fibres.

Four different approaches were used to evaluate which was the most effective in removing colour from the fibre. After the first two approaches, further tests were performed to optimize the treatments, and assess whether reducing the number of treatments could achieve good results in terms of efficiency in colour removal.

The first approach performed included all the four pretreatments under study.

Analysing the Fig. 21 and Fig. 24, it is possible to visibly see the good performance of the approach in removing colour in both black and orange fibres.

The analytical values given by Cielab confirm this conclusion (Fig. 22 and Fig. 25) since the increasing L* colour coordinate values indicate an increase in the fibre luminosity, which can be related to the removal of the colour from the fibres.

For the a* and b* coordinates, Fig. 22 and Fig. 25 show a tendency toward zero, thus indicating the corresponding neutral grey value.

Another important parameter for determining the success in removing colour from fibre samples is the K/S. According to the literature (Shimo S.S, 2015), the relative colour strength and K/S values increases with the increase of dye concentration in fabric samples.

Fig. 23 and Fig. 26 show that in both cases there was a significant reduction in the K/S values at the end of the pretreatments with a clear decrease in the values from treatment to treatment. This indicates the decrease in intensity of colour on both fibre samples, and therefore, it's removal.

An accentuated decrease in K/S values is observed after the alkaline pretreatment. According to the literature, the alkaline pretreatment has a more significant effect on the degradation of the cellulosic material compared to the acid pretreatment (Jankovicova et al. 2022) and this increased degradation could be linked to a higher release of chain-related substances in solution, in this specific case, of dyes.

The second approach performed included two different pretreatments understudy, reducing treatment and ozone treatment.

Fig. 27 and Fig. 29 show that even with only two treatments, the fibres colour has been efficiently removed in both orange and black fibres, results that were also confirmed by Cielab colour coordinates values.

In Fig.28 and Fig.30, L* colour coordinate values increase considerably after the reducing and ozone treatment, indicating the increase in luminosity in the samples, linked with colour removal. For the a* coordinate values, in both cases, it tends toward 0, while the b* coordinate values, unlike the first approach, undergo a slight increase after the treatments. This can be explained by the slight yellowing of the samples after being exposed to the ozone. However, none of the coordinates show visible differences between the two treatments applied.

Fig. 31 represents the K/S values for the black and orange fibres, of the first and second approaches. In both cases, it can be seen that the K/S values for the first approach are lower than those of the second approach, demonstrating that the first approach is more efficient in removing the colour of the fibres. However, the values for the second approach are already low enough to consider this an effective method, especially taking into account the reduction in the number of treatments.

In the third approach, the fibres suffered an acid, reducing and ozone treatments, while in the fourth approach, the fibres went through an alkaline, reducing and ozone treatment (Fig.32 and Fig.33).
Fig. 34 K/S values for the two treatments, and the results show that the K/S values for the fourth approach, i.e. with the alkaline treatment, are lower compared the third approach, indicating that the alkaline treatment has an effect in colour removal of the fibres, especially compared to the acid treatment.

Afterwards, the samples from both approaches were analysed by FTIR, to verify whether these different processes could affect the chemical structure of the cotton-based fibre. Fig. 35 and Fig. 36 show FT-IR spectra of the cotton-based fibre for the third approach, for both the orange and black fibres.
In terms of cotton spectrum, all the relevant peaks are visible in the curves after each treatment of this approach, which means that none of the applied treatment affected the cellulose structure of the fibres. The same was observed for the fourth approach, (Fig. 37 and Fig. 38) where the FT-IR spectra, did not show any visible differences between the original cotton fibre and the fibres after each treatment. Additionally, these treatments were also tested for the capacity to remove the softener present in the fibres. The results show that there wereno visible differences in the spectrums that could clearly indicate the efficient removal of the softener from the fibres, after the treatments.It is possible that the concentration of softeners used on the fibres was too low to be detected by FTIR equipment.

Wedin et al.2018 studied how to chemically recycle and remove reactive dyes from cotton fabric treated with a wrinkle free finish. The process developed included 3 steps to remove the dye and finish, starting with and alkaline solution, followed by an acid treatment.

It was found that in order to recycle the cotton effectively, the reactive colour and the wrinkle free finish need to be removed in a prephase, for the cotton fibre to be processed into viscose.

5.2) Discussion for cellulose dissolution in aqueous solution

Dissolution of cellulose in aqueous NaOH solutions

A mixed aqueous solution of NaOH and glycerin (Gly) was employed as a green solvent system for cellulose dissolution process. In the NaOH/Gly system, glycerin serves as a co-solvent, enhancing the solubility of NaOH and facilitating its interaction with cellulose fibres. This system is known for its ability to efficiently dissolve cellulose and has been widely studied for various applications, including in the production of regenerated cellulose materials.

In the Fig. 39 the macroscopic appearance of the different cellulose fractions throughout the entire procedure, starting from the cellulose aggregates in solution to the dried regenerated cellulose is depicted. Various concentrations were tested for textile substrates, specifically 3.0% (w/v) and 4.0% (w/v).

The highest yield was achieved when using an aqueous NaOH/Glycerin system at a concentration of 4% (w/v), resulting in a 6% yield of regenerated cellulose (Fig. 41).

Fig. 40 shows the FTIR spectrum finger print of the dried sample in the region of 4000-700 cm^{-1}. The peaks at 896, 1107, 1161, and 1430 cm^{-1} correspond to specific absorption bands in cellulose I: C1 frequency, ring asymmetric stretching, C-O-C asymmetric stretching, and CH2 symmetric bending vibration, respectively (Nelson M L et al. 1964). These bands from the crystalline cellulose I spectrum vanish from the regenerated cellulose fibre spectrum, indicating that crystalline cellulose II, which contains amorphous cellulose, makes up the majority of the material in the fibres of regenerated cellulose. Moreover, crystalline cellulose II predominates in the regenerated cellulose fibres as indicated by the absorption bands at 1261, 1313, and 1366 cm^{-1}, which are attributed to CH bending vibration in cellulose II, CH_2 wagging vibration in cellulose II, and CH bending vibration in cellulose I and cellulose II, respectively (Marchessault R.H. et al. 1960). In addition, compared with spectrum of glycerin, peak 1647 cm^{-1} (Fig. 38) in regenerated cellulose indicate the trace amount of glycerine residue (Gomez-Siurana et al. 2013). This suggests that the washing step needs to be optimized to achieve a purer regenerated cellulose fraction. In conclusion the FTIR spectrum of the analysed sample resulted in the presence of regenerated cellulose with a predominance of crystalline cellulose II in the regenerated fibres. However, the yields were low compared to the literature.

A study conducted by Li et al. 2020 was selected for discussion due to the presence of similarities with this project since the dissolution of three kinds of cellulose with an α-cellulose content more than 95% with different degree of polymerisation was carried out in cotton linter pulps using a mixed aqueous solution of NaOH and glycerin. In this study, a system consisting of 1.0 wt% glycerin and 9.0 wt% NaOH was able to dissolve cellulose effectively and form a homogeneous solution, a result not observed in the experiments conducted for this thesis. It has been hypothesised that this may be due to the degree of polymerization (DP) of the fibres used in our study (DP 2248), as they did not undergo any pre-treatment for this assay, and the values are too high. The literature describes various ideal DPs depending on the type of aqueous solution used and furthermore it is difficult to dissolve substantially all cellulose having a high degree of polymerization (DP > 300) in an alkali aqueous solution having only a single alkali composition.

It's reported that NaOH/urea solution and aqueous NaOH/thiourea solution can dissolve cellulose with relatively high DP (DP = 500–900) completely (Cai and Zhang 2005; Qi et al. 2008; Ruan et al. 2004). Although the compositions and dissolution conditions are different, all NaOH-based aqueous systems mentioned previously have similar NaOH concentrations (ranging from 6 to 10 wt%) and can only dissolve cellulose at low temperatures.

At the same time, a different strategy was studied using an aqueous system composed of NaOH/ZnO. ZnO was here used in residual concentrations, working as a catalyst. The addition of ZnO to aqueous NaOH supports the dissolution of cellulose and hinders its self-aggregation in solution (Väisänen et al. 2021). Similarly, to the previous process, in the Fig. 42 depicts the pictures of the entire procedure, starting from the cellulose aggregates in solution to the dried regenerated cellulose. Again, different concentrations have been tested of textile substrate rather including 2.0 % (w/v), 3.0 % (w/v) and 4% (w/v). As previously noted, the highest yield of regenerated cellulose (9%) was achieved at the higher textile substrate concentration of 4% (w/v).

The Fig. 43 shows the FTIR spectrum of the dried sample, as in the previous case the most relevant peaks are present in the sample (Fig. 40) confirming that the analysed sample resulted in the presence of regenerated cellulose with a predominance of crystalline cellulose II in the regenerated fibres. Similarly to the NaOH/Glycerin system the yields obtained were too low.

In a study by Väisänen et al. (2021), the complete dissolution of a 4 wt% cellulosic sample was successfully achieved using a solvent system containing 9 wt% NaOH and 1 wt% ZnO (Fig.44). This was not observed in our study, where the yields were too low. In this work the authors used as samples kraft pulp (DP 3680) and microcrystalline cellulose powder (DP 400), the first having a DP superior to the samples used in our study (DP 2248) and showing poor dissolution in the tested system.

With this in mind, it has been concluded that reducing the degree of polymerization (DP) of the fibres is necessary to achieve satisfactory cellulose dissolution. To accomplish this, various pretreatments were tested.

Alkali and acid hydrolysis as pretreatment

Considering the low yields obtained for the NaOH/Gly and NaOH/ZnO a different strategy was herein proposed. According to the literature, in the pursuit of efficient cellulose dissolution, pre-treatments play a critical role in modifying the inherent characteristics of cellulose. Firstly, these treatments increase cellulose reactivity, facilitating subsequent dissolution processes. Secondly, pre-treatments contribute to a reduction in crystallinity, a key impediment to solubility. Additionally, these processes enhance cellulose accessibility by breaking down barriers that may prevent the penetration of dissolving agents. Moreover, pretreatments often result in a decrease in cellulose molecular weight and DP, easing its dissolution. According to thermodynamics a polymer becomes more soluble when it's DP decrease as the entropy become larger with a higher number of molecules in solution, so DP has been analysed and reported as crucial factor for dissolution (Isogai and Atalla 1998; Yamashiki et al 1990; Yang et al. 2011).

Furthermore, the removal of impurities through pretreatments is critical in eliminating substances that could interfere with the dissolution process (Rasaq S. Abolore et al.2024). The chemical activation methods, which included alkaline and acid hydrolysis are usually applied to remove any dissolution limiting impurities and to optimize the cellulose molecular weight (Antti koistinen et al. 2023).

Based solutions were explored as pretreatment methods to reduce the degree of polymerization (DP) of the fibres and facilitate cellulose dissolution. Fig. 45 illustrates the entire procedure, detailing both acid and alkaline pre-treatments carried out before attempting dissolution in aqueous NaOH-based solutions. Despite these efforts, neither pre-treatment method resulted in dope formation; the fibres remained intact and did not dissolve. This indicates that the pre-treatments employed were insufficient for achieving the desired reduction in DP and subsequent cellulose dissolution. Further optimization of the pretreatment processes is necessary to achieve better results.

Several works from the literature report the use of either acid or alkali solutions as pre-treatment for cellulosic substrates extraction. A study conducted by Antti koistinen et al. 2023 examines the effect of pulp pre-hydrolysis conditions on pulp structure, subsequent dissolution in cold aqueous NaOH/ZnO solvent, and regenerated cellulose film properties. It has found that the hydrolysis and the temperature affect the cellulose degree of polymerization and the reduction of the degree of polymerization improve the pulp dissolution. The hydrolysed pulp (dry matter content ca. 20 wt%) was diluted with deionized (DI) water and NaOH/ZnO stock solution was added to achieve 7.8 wt% NaOH, 1.3 wt% ZnO and 7.0 wt% cellulose consistency dope in a glass beaker and then the dopes were placed in the freezer (–20 °C) for at least overnight.

Subsequently, the dissolved cellulose samples were precipitated into regenerated cellulose (RC) films. The study demonstrated that when DP was 500, pulps formed a heterogeneous mixture of undissolved fibres in the NaOH/ZnO solvent. The reference and samples with DP>500 sample preserved their fibrillar shape during dissolution: only heterogeneous swelling with ballooning was seen. All samples that had a DP<500 were somewhat dissolved; however, the undissolved residue was observed in all samples. Medium DP samples exhibited dissolution and loss of the fibre structure. Low DP samples were visually dissolved to nearly invisible, however, clear undissolved fragments are visible under cross-polarized light. A study conducted by Saija Vaisanen et al.2021 discusses the effect hydrolytic pretreatments on pulp dissolution in the aqueous NaOH–ZnO solvent system. The study consisted of a never-dried softwood kraft pulp that was hydrolysed under seven different conditions as well as the pulp without hydrolysis as a reference. The dissolution of the pulps in the NaOH–ZnO solvent system was evaluated both at the macro level as well as at the molecular level. The fibre properties as well as the chemical composition (hemicellulose and cellulose contents) and the viscosity of the pulps was investigated. Comparison of the pulp viscosities showed that the pulp started to dissolve when the viscosity was decreased to below ca. 400 ml/g (i.e. DP = 550). The mean period of the helical twists in the bundles is greater than the length of cellulose chains with a DP of 550. Therefore, it appears that individual cellulose chains must be sufficiently short to pass through the physical barrier created by the fibril structure's helical twists in order to separate from one another.

Aqueous NaOH solvent systems (NaOH/Gly and NaOH/ZnO) as pretreatment for alkali and acid hydrolysis

Another approach performed in this study was to use NaOH/Gly and NaOH/ZnO solvent systems as pretreatment solutions.

Fig. 45 illustrates the entire procedure, detailing both Solvent systems carried out before attempting dissolution in alkali and acid hydrolysis.

Overall, the use of aqueous NaOH solvent systems as pretreatment methods offers a promising approach to preparing cellulose for subsequent hydrolysis reactions. By modifying the cellulose structure, these systems aim to overcome barriers to dissolution, ultimately enabling the production of regenerated cellulose. These solvent systems were, for the first time, tested toward the possibility of modifying the cellulose structure, making it more amenable to subsequent hydrolysis and consequent dissolution.

As in the previous case in both cases there was no dope formation and the fibres remained intact.

Chapter 6: Conclusions

The textile industry is one of the most environmentally impactful industries in the world. In order to achieve a more environmentally responsible textile sector, there is a need for a change of perspective in the development of this sector such as using renewable materials, developing more energy-efficient

industries, using less hazardous and impactful solvents and using increasingly high-performance technologies.
The textile recycling, especially chemical recycling, can play a key role in this important ecological transaction in the textile sector both from the point of view of raw material utilisation and waste reduction.
This thesis work was marked by exploration, innovation and searching of a sustainable perspective in terms of chemical recycling of textile waste recycling in the textile industry.
The objectives of this Master thesis were twofold: as headline, to test innovative chemical recycling systems for textile waste using greener and environmentally friendly solvent systems, and secondarily to evaluate different innovative decolouration pretreatments. The various routes that brought about both challenges and success should be taken into account.

The innovative decolouration pretreatments, an important aspect for the achievement of our target in terms of chemical recycling, tested in this thesis proved to be promising, as revealed by the results obtained in which the reducing treatment played a key role in the objective in all the approaches analysed.

Turning to the primary objective, the solvent systems used for the chemical recycling of textile fibres have proven to be potentially effective for the above purpose as proven by the results obtained in which the NaOH/ZnO system performed slightly better in terms of yield.
While challenges and limitations have been encountered, such as the ability to achieve a higher yield of regenerated pulp and even the total incomplete dissolution of fibres by combining acid and basic hydrolysis with the greener solvent systems, subjects of this study, found in the final results, these results point to opportunities for further research and development.

The research's conclusions add to the greater conversation on recycling sustainable fibres. New solvent solutions are being developed by the textile industry as eco-friendly substitutes, marking a significant advancement toward a more sustainable and ecologically sensitive future.

This thesis work can be conceptualized as preliminary investigation into new innovative chemical recycling systems in the textile industry and serving as a starting point for the future advancements. The primary goal is to change the textile industry toward a more sustainable and ecologically approach. The commitment to improving sustainable practices in the textile sector going forward is still on the continuing route.

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