Advantages of Green Technology in Textile Finishing Using Supercritical Carbon Dioxide

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Review

This paper encompasses the application of supercritical carbon dioxide (scCO$_2$) primarily in textile finishing as one of the high-efficiency and green processes offering significant environmental and economic benefits. The scCO$_2$ technology reduces water consumption, waste, greenhouse gas emissions and promotes recycling and reuse, thereby representing a sustainable alternative to traditional textile finishing processes. The paper presents numerous advantages of this process but also considers challenges that still pose barriers to its widespread implementation, such as high equipment costs and technical difficulties encountered during certain treatments. The application of this process is broad and continuous further research will undoubtedly result in even wider implementation of this green technology in the industry. Textile finishing in supercritical carbon dioxide plays a significant role in promoting a circular economy, which focuses on reducing waste and increasing resource efficiency. Supercritical CO$_2$ can be efficiently recycled and reused in processes, not only reducing waste but also cutting waste management costs. The ability to recycle and reuse CO$_2$ ensures better resource management, adding value to this sustainable technology.

Keywords: *supercritical carbon dioxide; textile finishing; sustainability; green technology; recycling*

Pregled

Prednosti zelene tehnologije oplemenjivanja tekstila u superkritičnom ugljikovom dioksidu

Ovaj rad obuhvaća primjenu superkritičnog ugljikovog dioksida (scCO$_2$) prvenstveno u oplemenjivanju tekstila kao jedan od visokoučinkovitih i zelenih postupaka koji nude značajne ekološke i ekonomske prednosti. Tehnologija scCO$_2$ smanjuje potrošnju vode, otpad i emisije stakleničkih plinova te potiče recikliranje i ponovnu upotrebu, čime predstavlja održivu alternativu tradicionalnim postupcima oplemenjivanja tekstila. U radu su prikazane brojne prednosti ovog postupka, ali su razmotreni i izazovi koji još uvijek predstavljaju prepreku široj primjeni, poput visokih troškova opreme i tehničkih poteškoća do kojih dolazi prilikom pojedinih obrada. Primjena ovog postupka je široka, a kontinuirano provođenje daljnjih istraživanja zasigurno će rezultirati još širom implementacijom ove zelene tehnologije u industriji. Oplemenjivanje tekstila u superkritičnom ugljikovom dioksidu ima značajnu ulogu u promicanju kružnog gospodarstva, koje se usredotočuje na smanjenje otpada i povećanje iskoristivosti resursa. Superkritični CO$_2$ se može učinkovito reciklirati i ponovno upotrijebiti u procesima, čime se ne samo smanjuje otpad već i troškovi upravljanja otpadom. Sposobnost recikliranja i ponovne upotrebe CO$_2$ osigurava bolje upravljanje resursima, dodajući vrijednost ovoj održivoj tehnologiji.

Ključne riječi: *superkritični ugljikov dioksid; oplemenjivanje tekstila; održivost; zelena tehnologija; recikliranje*

1. Introduction

The textile industry represents one of the largest global industrial sectors and at the same time is one of the leading sources of environmental pollution [1]. Wet finishing processes require large amounts of water and chemicals, resulting in significant water consumption, water pollution, and greenhouse gas emissions [2]. Traditional wet finishing processes in textiles are major energy consumers, which further increases their ecological footprint [3].

Wet finishing processes might lead to the release of harmful chemicals such as phthalates, formaldehydes, heavy metals, and azo dyes into the environment or can also cause serious health issues among workers in the industry and within local communities, including dermatological problems and respiratory diseases [1]. New opportunities to reduce the negative impact of the textile industry on the environment are opening up with the development of green chemistry [2], which aims to reduce or eliminate the use of hazardous substances in the design, production, and use of chemical products and processes [3]. Initiatives such as replacing hazardous chemicals with less harmful alternatives, recycling wastewater, and energy efficiency are becoming increasingly prevalent. One of the significant innovations that green chemistry brings to the textile industry is the use of supercritical carbon dioxide ($scCO_2$) in dyeing and finishing processes, offering an alternative to traditional water-based treatments [4,5].

2. Supercritical Carbon Dioxide ($scCO_2$)

Supercritical carbon dioxide ($scCO_2$) is the state of carbon dioxide when exposed to temperature and pressure above its critical point, that is, above 31.1°C (critical temperature) and 7.38 MPa (critical pressure), Fig.1. This state of matter is neither solid, liquid, nor gaseous, but possesses properties of all three phases [6]. Supercritical carbon dioxide is characterized by properties of low viscosity and high diffusion capacity (Tab.1) which makes it exceptionally efficient for various applications [5,8].

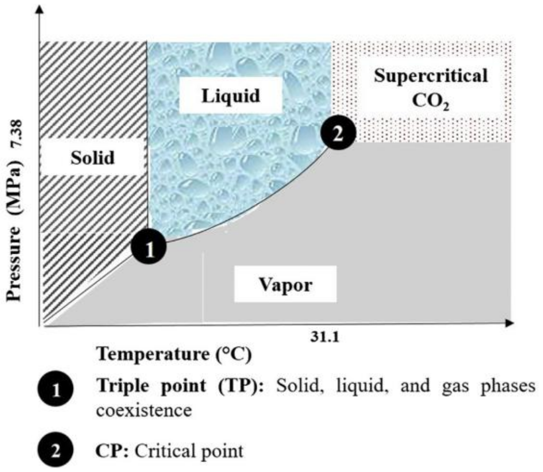

Fig.1 Phase diagram of carbon dioxide [7]

Tab.1 Comparison of density, viscosity, and diffusion for typical liquids, gases, and supercritical fluid phases [9]

Typical Properties of Supercritical Systems				
	Unit	Gas	Liquid	Supercritical Fluid Phase
Density	kg m^{-3}	1	100	100-1000
Viscosity	cp	0.01	0.5-1.0	0.05-0.1
Diffusion	mm^2 s^{-1}	1-10	0.001	0.01–0.1

Using supercritical carbon dioxide can reduce water and energy consumption, minimize the emission of harmful substances into the environment, and improve the safety and health of workers in the textile industry [2,9,10]. Thanks to its low surface tension, $scCO_2$ can penetrate the microstructures of textiles, making it particularly suitable for processes such as dyeing and final textile finishing [5,7]. Furthermore, the development of green chemistry opens up new opportunities to reduce the negative impact of the textile industry on the environment [11]. Green chemistry aims to reduce or eliminate the use of hazardous substances in all stages, starting from design, production, textile care, all the way to their recycling [12]. One of the significant innovations that green chemistry brings to the textile industry is the use of supercritical carbon dioxide ($scCO_2$) in textile finishing processes, offering an alternative to traditional water-based treatments [4,5].

3. Finishing Processes in Supercritical Carbon Dioxide

Due to its unique properties, supercritical carbon dioxide finds application in numerous industrial sectors, including the textile industry. In the textile industry, $scCO_2$ offers several key advantages over traditional processes:

- *Excellent Penetration Ability:* Thanks to its low viscosity and high diffusion capacity, $scCO_2$ can efficiently penetrate the pores and fibers of materials, allowing for thorough finishing and dyeing of fabrics.
- *Environmental Efficiency:* Processes using $scCO_2$ do not require the use of water or heavy chemicals,

significantly reducing the ecological footprint of the industry.

- *Solvent Selectivity*: $scCO_2$ is a highly selective solvent, meaning it can efficiently dissolve certain substances while leaving others untouched. These properties make it ideal for processes like dyeing and cleaning textiles without the risk of damage or alterations to the materials [13].

The most important processes using $scCO_2$ include prewashing, bleaching, degumming, cleaning, and final finishing of natural and synthetic materials. This textile finishing technology has already found application in various areas, starting from pretreatment [14], dyeing [6,15,16,17], final finishing [18], dry cleaning [19,20], all the way to recycling [21-25].

3.1. Textile Pretreatment Processes

A significant step in textile finishing, which serves to remove impurities, natural waxes, and other unwanted substances from the surface of fibers, is prewashing. Traditional methods use water and textile auxiliaries and are considered energy-intensive processes that produce large quantities of wastewater. Using $scCO_2$ produces no wastewater, thus reducing energy costs, while simultaneously preserving the mechanical properties of the fibers due to the selectivity of the applied medium [1,4,8].

Research of Ghanayem H. and Okubayashi S. has proven that $scCO_2$ can be applied to remove waxes from cotton materials in the pretreatment phase [26]. The aim of the research was to develop an environmentally friendly process for removing wax from cotton fabric using $scCO_2$ as a solvent. In the study, various concentrations of co-solvents and surfactants were used in combination with $scCO_2$, with acetone, ethanol, methanol, and tetrahydrofuran being used as co-solvents. The addition of polyoxyethylene laurel ether as a surfactant in combination with acetone significantly improved the hydrophilicity of the fabric. Fabric samples were treated under different conditions of temperature and pressure, and one of the methods of confirming effectiveness is microscopic surface analysis, using FE-SEM (Field Emission Scanning Electron Microscopy), Fig.2.

SEM images of cotton fabric treated with different $scCO_2$ mixtures indicate that ridges and indentations are visible on the surface of the untreated material (Fig.2a), which partially disappear after alkali treatment (Fig.2b). Treatment in $scCO_2$ caused no significant change on the fiber surface (Fig.2c). A slightly smoother fiber surface is visible after treatment with a mixture of $scCO_2$ and methanol as a co-solvent (Fig.2d). The most significant morphological change occurred after treatment with $scCO_2$ in the presence of a surfactant (Figs 2e and 2f), as the parallel ridges

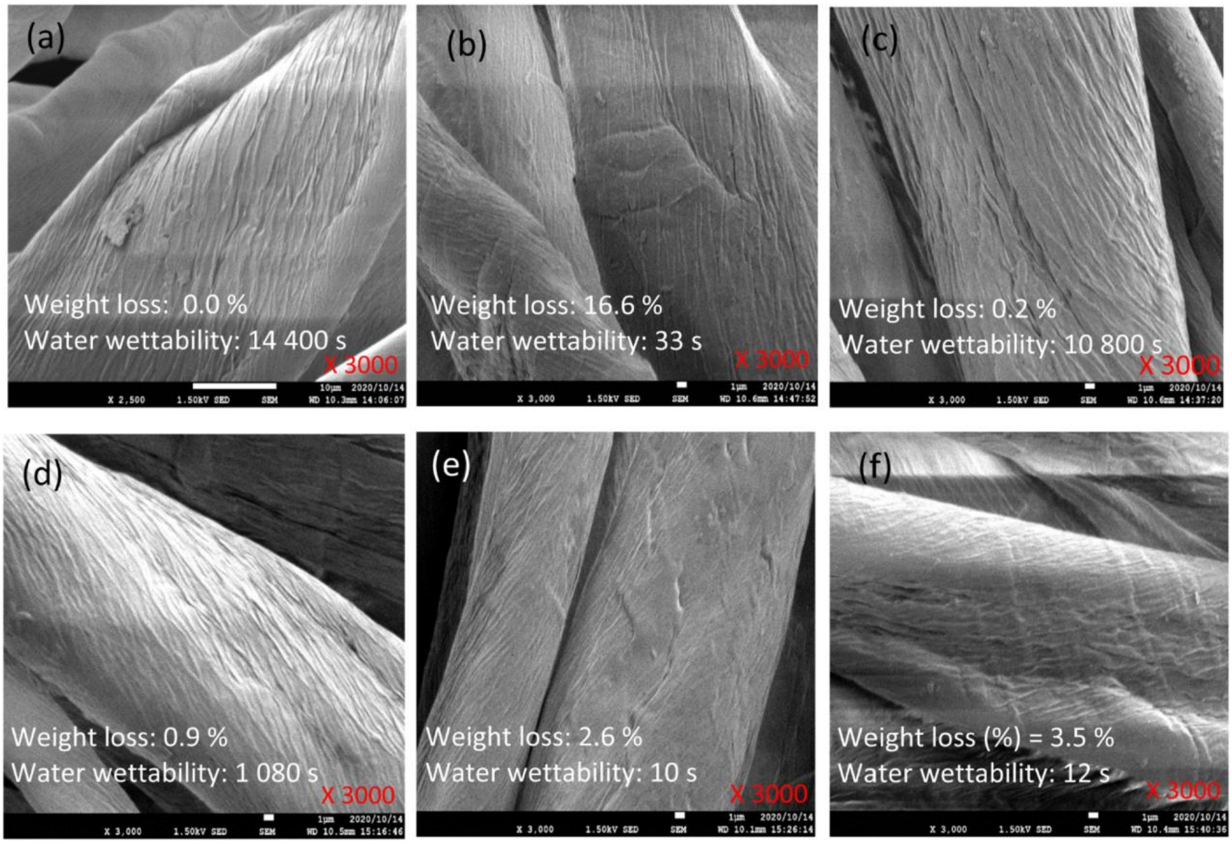

Fig.2 FE-SEM images: (a) untreated cotton plush fabrics, (b) treated with alkali, (c) treated in scCO2, (d) with the addition of methanol, (e) with the addition of surfactant, (f) with the addition of methanol/surfactant [26]

and indentations almost disappeared and the fiber surface became flatter and smoother.

Analyses have shown that the removal of waxes with $scCO_2$ is very effective because a significant increase in hydrophilicity is achieved, even if mass loss occurs. Furthermore, a mixture of methanol or tetrahydrofuran in $scCO_2$ unexpectedly removes pectin very well, suggesting that this system can be used for developing a new $scCO_2$-based extraction method. To remove impurities in cotton and improve the fabric's hydrophilicity, it is recommended to use a combination of surfactant and co-solvent, as it increases fiber swelling as well as the solubility of both the surfactant and the impurities. As a result, the fabric becomes more hydrophilic compared to the traditional scouring process using alkali solutions [26].

3.1.1. Bleaching of Cotton Material

Supercritical carbon dioxide has proven effective in bleaching of textiles, reducing the need for conventional bleaching agents such as sodium hypochlorite, which can be harmful to the environment [14]. $scCO_2$ transforms this process with its ability to remove impurities without the use of water and additional chemicals, thereby reducing water consumption and the amount of harmful substances in wastewater. Studies show that $scCO_2$ can achieve a similar level of whiteness as traditional methods but with a lesser environmental impact [2,3,9,14].

In the study by Eren *et al*. [14], knitted cotton fabric was successfully bleached using supercritical carbon dioxide, and it was further found that this led to improvements in fabric softness and strength, thereby enhancing the characteristics of the final product.

3.1.2. Degumming of Silk

Traditionally, silk degumming was performed using hot soap solutions to remove sericin. Supercritical CO_2 effectively removes sericin without the need for water and soap, allowing the isolation of pure sericin, which has applications in medicine and the cosmetic industry. This method not only saves resources but also adds commercial value by utilizing all by-products. Silk degumming using supercritical carbon dioxide was demonstrated in the study by Lo, C.L. [17], which confirmed that $scCO_2$ can be very effective in removing sericin from silk without damaging the delicate silk fibers. Silk degummed in this way showed improved affinity for indigo dyes, indicating that $scCO_2$ can also enhance dye depth. A key aspect of this research is the consideration of environmentally sustainable alternatives for reducing agents currently used in the industry. The purpose of reducing agents is to lessen oxidative processes and stabilize various chemical reactions, crucial for maintaining product quality and durability. Researchers used banana peels as a potential source of bioactive compounds, such as phenolic compounds and flavonoids, which can act as environmentally friendly reducing agents [17].

3.1.3. Washing of Sheep's Wool

Sheep's wool is a highly valued material in the textile industry, used for clothing production as well as in various technical applications. Traditional methods of processing sheep's wool, which include cleaning, scouring (washing), bleaching, and drying, are both environmentally and economically problematic due to high water and chemical consumption, and wastewater pollution.

As an alternative to these processes, supercritical carbon dioxide technology has emerged. A series of studies confirm the effectiveness of this technology in removing wax and other impurities from sheep's wool. For example, research conducted by Jones et al. in 1997 showed that $scCO_2$ could efficiently extract about 98% of the wax from sheep's wool. A study by Lopez-Mesas et al. in 2005 used $scCO_2$ to extract wax from waste produced during wool cleaning, where the process was significantly shorter compared to the conventional Soxhlet method [15]. Long et al. in 2013 investigated how $scCO_2$ affects the chemical and crystalline structure of wool fibers, discovering that this treatment can further improve the thermal properties of wool fibers [27]. Given the aforementioned advantages, including reducing the environmental impact, increasing the speed of processing, and lowering resource costs with the possibility of extracting lanolin for cosmetic purposes, optimizing the wool dyeing process, and reducing the number of steps required in the processing, significant time and energy savings are achieved. However, there are some limitations. The most important is the high cost of equipment needed to operate under high pressure and temperature. Additionally, there is an issue with the lower solubility of polar and high molecular weight compounds in $scCO_2$, which may require the addition of co-solvents such as ethanol or hydrogen peroxide. Another challenge is the need for regular cleaning of equipment due to clogging of valves and other components [15].

3.2. Biomass Pretreatment

In recent research led by teams from the University of Paraná, Brazil, and the University of Toulouse, France, innovative methods using supercritical fluids for biomass pretreatment have been introduced. This approach offers significant advantages in terms of efficiency and sustainability, which could impact the future of biorefineries and the production of new eco-friendly materials [28,29]. Lignocellulosic biomass, which includes materials such as wood, straw, and agricultural waste, is rich in cellulose, hemicellulose, and lignin, making it resistant to degradation [30]. Traditional pretreatment methods often require extreme conditions, which are energy-intensive and environmentally harmful due to the production of toxic byproducts. In contrast, supercritical fluids, such as carbon dioxide and water under high pressure and temperature, allow for biomass pretreatment under mild conditions, avoiding sugar degradation and the production of fermentation inhibitors. Supercritical fluids offer several advantages, including high sugar yields and low production of fermentation inhibitors, significantly enhancing the efficiency of ethanol and other biochemical productions. Due to their unique properties, supercritical fluids can penetrate the complex structure of biomass, improving the accessibility of cellulose and hemicellulose for enzymatic breakdown. Moreover, combining supercritical fluids with other solvents, such as green solvents and acids, further optimizes the pretreatment process [28].

3.3. Dyeing

During the dyeing process using $scCO_2$, textile fabrics are evenly dyed without significant damage, resulting in high-quality dyeing [17,31]. The method has proven effective in dyeing various types of textile materials, primarily synthetic, but there is also potential for processing cotton, wool, and silk [6, 16].

3.3.1. Dyeing of Synthetic Materials

Supercritical CO_2 is particularly effective in dyeing synthetic fibers such as polyester, where it facilitates dye penetration due to its ability to swell and plasticize the fiber. The small CO_2 molecules enhance the mobility of polymer chains, allowing better dye diffusion and leaving the dye within the fiber structure after the process is complete [5,6]. In synthetic fibers dyeing, disperse dyes are commonly used. These can be modified for use in $scCO_2$ [6]. The dyeing mechanism for PET fibers has been well clarified since its introduction in the 1980s. The success of the technology lies in the increased solubility of disperse dyes in supercritical carbon dioxide, as well as the solvent's ability to plasticize the fibers. For polyamide fibers like PA6, research is limited but has shown that it is less capable of dyeing in $scCO_2$ than PET. Recent research focuses on new disperse dyes that enable dyeing of nylon without the use of co-solvents. Meta-aramid fibers are challenging to dye due to their high glass transition temperature and crystallinity. However, experiments have shown that good dyeing can also be achieved in this case using non-toxic carriers. Ultra-high molecular weight polyethylene (UHMWPE) and polypropylene are also challenging to dye due to their crystalline structure, but progress has been made using special dyes and co-solvents. Results suggest that this process will soon be applicable for dyeing nylon and polypropylene as well [5, 6, 32].

3.3.2. Dyeing of Natural Materials

Natural fibers such as cotton and wool present a challenge in the context of $scCO_2$ due to their hydrophilic properties. Hydrophilic fibers tend to absorb water, while the $scCO_2$ molecule is less polar than water, making it difficult for the dye to be absorbed into the fibers. Due to the lower polarity of $scCO_2$, the chemical interactions that are crucial for successful dye fixation on fibers become less efficient [5,6,32]. Moreover, most traditional dyes used for dyeing natural fibers are not soluble in $scCO_2$, further complicating the dyeing process and necessitating the development of specialized dyes that can effectively function in these conditions [5,6].

New methods such as the application of reverse micelles and the synthesis of reactive disperse dyes have been developed to overcome these challenges. Reverse micelles are microemulsions that can dissolve polar dyes but are environmentally unacceptable due to the use of fluorocarbon surfactants [4]. Reactive disperse dyes can be synthesized by functionalizing dyes soluble in supercritical carbon dioxide by adding appropriate reactive groups. This process allows for the chemical fixation of dyes on hydrophilic fibers. Many different reactive functional groups have been proposed over the years, but vinyl sulfone and triazine have been recognized as the most successful. Depending on their chromophore, reactive disperse dyes can be divided into two groups: anthraquinone and azo dyes. Both types of dyes have advantages and disadvantages in dyeing different types of fibers. Anthraquinone dyes have proven particularly effective on wool and silk. Additional solvents are often needed in the dyeing process, resulting in an extra step and diminishing the environmental advantage of using $scCO_2$. Chlorotriazine dyes are especially effective on cotton, and other reactive groups, such as vinyl sulfone, also have potential but are primarily used on wool and silk. Fixing these dyes on cotton requires additional steps and catalysts, as shown in studies that used perfluoroalkylsulfonil-quaternary ammonium iodides (FC-134) for phase transfer catalysis [6]. Although rarely used in traditional dyeing processes, pigment dyes can be effective in $scCO_2$ due to their stability and resistance to process conditions [33]. Dyeing natural fibers with $scCO_2$ is a complex and challenging process that continues to be researched and has not yet been widely implemented.

Abou Elmaaty *et al*. made significant progress in the first pilot project for dyeing cotton fabrics in $scCO_2$. The methodology was designed for dyeing two types of unmodified 100% cotton material (fabric and knit) using the dye N,N-diethyl-4-((4-vinylsulfonil) phenyl)diazinylaniline under laboratory conditions. Optimal results were achieved at 130°C, a pressure of 28 MPa, a dye concentration of 2%, and a duration of 120 minutes [34]. The addition of disodium EDTA significantly improved the solubility of the dye, resulting in a noticeable improvement in the K/S values of the dyed cotton with vinyl sulfone dye. The color intensity significantly increased by adding disodium EDTA to the $scCO_2$ dyeing medium. The proposed methodology was applied at a pilot level using optimal conditions, and the results showed higher K/S values and excellent colorfastness. However, it is necessary to synthesize and apply more dyes of various shades on 100% cotton at both pilot and industrial scales to fully test and introduce the technology into practice [33].

3.4. Textile Finishing

Textile finishing (functionalization) denotes the last step of wet operations, in which additional functional and aesthetic properties are imparted to textiles. Using supercritical carbon dioxide ($scCO_2$) has proven extremely successful in enhancing various materials, as confirmed by numerous studies [9, 15, 17, 30, 34]. Impregnation with $scCO_2$ has become a popular method for developing new functional products, as traditional impregnation methods involve not only the use of hazardous solvents but also significant energy consumption and the drawback of exceedingly slow diffusion. As a result, a long contact time is required, and the low efficiency of the process necessitates the use of a significant amount of chemicals and solvents. Due to its unique characteristics and environmental acceptability, impregnation using $scCO_2$ is a sustainable solution to these issues, and $scCO_2$ impregnation has a wide range of applications, mainly for embedding various active substances into the polymer matrix, such as drugs, functional finishing agents, dyes, and other agents. The demand for functional and smart textiles has increased in recent years as people's lifestyles have changed.

The impregnation process in $scCO_2$ consists of three steps: (1) dissolution of additives, (2) absorption of the mixture ($scCO_2$ and additives) into the polymer matrix, and (3) pressure reduction and system stabilization. In most cases, the dissolution of additives and the absorption of the solvent mixture occur simultaneously. During the dissolution process, complete or partial dissolution can occur, depending on the properties of the additives and/or processing conditions. The final step of system stabilization eliminates CO_2 and is also one of the methods used for embedding additive molecules into specific polymer matrices of $scCO_2$ [18].

The most common agents used for textile functionalization using $scCO_2$ are silicones, fluoropolymers, natural extracts, and organometallic-based agents. Abou Elmaaty *et al*. produced new hydrazone-propanonitrile dyes and used $scCO_2$ to apply new types to polyester fabric with additional antibacterial protection. Using the $scCO_2$ dyeing technique, effective dyeing was achieved with simultaneously excellent antibacterial properties and durability. The same research group also developed a series of disperse azo dyes with potential antimicrobial activity, which were applied to PA 6 by impregnation using $scCO_2$. Improvements in antibacterial properties and dye durability were obtained compared to traditionally dyed samples [35,36].

Many researchers have explored the impregnation of organometallic compounds into polymer matrices using supercritical fluids. Silver in various forms is widely used to develop different functionalities in fibers. Using $scCO_2$, silver nanoparticles were used to modify woolen fabrics, and the results showed good catalytic, antistatic, and antibacterial properties. Two different silver-based precursors were applied to cotton fabric using $scCO_2$. Cotton fabrics treated with silver precursors demonstrated excellent antibacterial activity [18].

For the production of antimicrobial material, a silicone sol containing quaternary ammonium salt (QAS) was also synthesized and applied to cotton treated in $scCO_2$. The treated fabric showed strong antibacterial activity, resistance to washing, and UV radiation. Additionally, silicone 2,2,6,6-tetramethyl-4-piperidinol (TMP) N-chloramine was applied in the $scCO_2$ treatment process of polyethylene (PE) fiber. Using a pressure of 28×10^6 Pa, a homogeneous coating of TMP-N-chloramine with a thickness of 70×10-9 m was achieved. This treated PE has strong and long-lasting biocidal action. The same research group applied biocidal fluorinated pyridinium silicone, which was applied to cotton yarn using scCO2. At 24×10^6 Pa and 50°C, the biocidal layer with pyridinium groups on the top surface could reach a thickness of 50×10^{-9} m, and the resulting material had even better biocidal effectiveness [37].

According to Orhan *et al*., using $scCO_2$ with N-halamine could be an alternative option for obtaining antibacterial functionality on the surface of polyester. First, N-(2-methyl-1-(4-methyl-2,5-dioxo-imidazolidin-4-yl)propan-2-yl) acrylamide was produced and applied to polyester treated in $scCO_2$ at 120°C and 30 MPa over various processing times. Adding N-halamine to the surface resulted in significant antibacterial activity against *E. coli* [38].

Mohamed *et al*. introduced silicone compounds in the $scCO_2$ treatment of cellulosic materials. They applied silicone polymers with terminal silanol groups, adding catalysts 3-isocyanatopropyltriethoxysilane (IPES) and tetraethyl orthosilicate (TEOS) to create covalent bonds with cellulose. Studies showed that a three-dimensional network of silicone compound and catalyst was formed, creating a layer just below the surface of the fabric. Compared to treatment in a conventional aqueous medium where deposition primarily occurs on the surface, $scCO_2$ treatment allows deeper penetration of the agent into the fibers and its more uniform distribution through the fabric structure [39].

Furthermore, various natural substances, including thymol, carvacrol, eugenol, and pyrethrum extract, were used for $scCO_2$ treatment to modify the characteristics of various polymers and create new functions [39]. Milovanović et al. conducted extensive research on the application of thymol to various textile substrates in $scCO_2$ to produce various functional materials. They investigated the solubility of thymol in $scCO_2$ and its impregnation on cotton gauze. The impregnated gauze showed significant antibacterial activity against a variety of bacteria and fungi - *Escherichia coli, Staphylococcus aureus, Bacillus subtilis, Enterococcus faecalis*, and *Candida albicans*, providing maximum antimicrobial protection (99.9%) for all tested microorganisms. FT-IR analysis results confirmed the presence of thymol on the surface of cotton fibers. According to the results of this study, the impregnation of cotton gauze intended for wound dressings with thymol using supercritical carbon dioxide showed significant antimicrobial effectiveness [40].

Studies on the application of chitosan and its derivatives in an $scCO_2$ bath for antimicrobial treatment of polyester showed that low molecular weight chitosan and chitosan lactate were successfully impregnated. Low molecular weight chitosan and chitosan lactate were successfully integrated into polyester fabric using the $scCO_2$ dyeing process, resulting in high antibacterial activity. Overall, the application of natural and sustainable substances by impregnation in $scCO_2$ has shown great potential for the production of various functional materials [41].

Sechin Chang *et al*. explored the use of $scCO_2$ to enhance the flame retardancy of cotton materials. The study describes the preparation of new piperazine derivatives, such as tetraethyl piperazine-1,4-diyldiphosphonate (PDP) and tetramethyl piperazine-1,4-diyldiphosphonothioate (PDTP), containing phosphorus and nitrogen. Thermogravimetric analysis (TGA) and flammability testing showed promising results in improved resistance to burning. Furthermore, the Limiting Oxygen Index (LOI) indicated that the treated fabrics require a higher oxygen concentration to sustain combustion, further confirming their enhanced flame resistance. An interesting aspect of the research is the use of $scCO_2$, which is not only environmentally friendly but also enhances the penetration of flame retardants into the fabric, increasing the efficiency of FR treatment. SEM analysis confirmed that the treatment with $scCO_2$ allows for a uniform application of FR agents on cotton fibers, resulting in the formation of a protective layer [42].

Cotton can also be treated with $scCO_2$ using palladium (II) hexafluoroacetylacetonate to produce conductive textiles. The research by Iwai and colleagues studies the method of copper deposition using $scCO_2$ to obtain conductive cotton using an electroless method. The paper describes the impregnation process of cotton with palladium(II) hexafluoroacetonate, followed by electroless copper deposition to obtain a conductive fabric resistant to electromagnetic interference. The use of $scCO_2$ was chosen for its excellent properties such as high solubility, diffusivity, absence of surface tension, and low risk of thermal deformation of materials. The analytical part of the research included scanning electron microscopy (SEM) and transmission electron microscopy (TEM), which examined the structures and surface morphologies of the treated cotton. This study is significant as it represents advancement in the production of conductive textiles that can find wide application in protecting electronic equipment and medical devices from electromagnetic interference [43].

Furthermore, Peng *et al*. coated woolen textiles in $scCO_2$ with silver nanoparticles, and the impregnated fabric exhibited good catalytic, antistatic, and antibacterial properties [44].

Bilalov T.R. *et al.* explore the use of ammonium palmitate in $scCO_2$ for treating cotton fabrics to achieve hydrophobicity. The study shows how this method can effectively change the properties of the fabrics, making them ultra-hydrophobic and superhydrophobic. In the experimental part of the paper, the solubility of ammonium palmitate in $scCO_2$, modified with acetone and dimethyl sulfoxide, at temperatures from 35.0°C to 60.0°C and pressures from 10.0 to 32.5 MPa is described. The impregnation process was conducted under static conditions, where the treated samples showed significant improvement in hydrophobicity, with contact angle values ≥120°, and in some cases even ≥150° [45].

Another possible application of $scCO_2$ treatment is shown in the work by Pajnik J. *et al*., where pyrethrum extract was used for tick treatment [46]. This agent was chosen for its good insecticidal properties and relatively low toxicity to mammals. The treated fabrics showed good effectiveness against ticks, which is of great importance due to the health risks posed by ticks transmitting various pathogens.

The possibility of using $scCO_2$ for multifunctional treatments (for water resistance, oil resistance, and dirt resistance) of polyester is shown in the work by Guan, L.Y. and colleagues. The results indicate that the method is effective as it is possible to achieve a water and dirt resistance rating of ≥4, and oil resistance of 5-6 [47].

The cited papers demonstrate that during the final finishing process using $scCO_2$, there is excellent penetration of the applied active substances into the microstructure of the textiles, which allows for their deep and uniform application, thus achieving effective functionalization of textile materials, such as antimicrobial, flame retardant, and UV protection. From the various examples of effective functionalization mentioned above, it is clear that there is a possibility for successfully replacing traditional treatments with these green and sustainable processes.

4. Textile Care

Supercritical carbon dioxide technology is also used for dry cleaning textiles. This method represents an environmentally friendlier alternative to traditional cleaning that uses perchloroethylene, a chemical known for its toxicity and potential harm to the environment [20, 48, 49]. Textile care is extremely important for the maintenance and longevity of textile products. This process involves removing dirt, stains, and other impurities from the fabric. Traditionally, the process requires a large amount of water and often uses aggressive chemicals. $scCO_2$ acts as a cleaning agent, solvent, or carrier of other chemicals [4, 49]. The cleaning method using $scCO_2$ has proven successful in numerous studies. Sutanto *et al.* investigated dry cleaning of textiles using $scCO_2$ [20, 48]. Previous studies showed that dirt removal was weaker compared to that with PER, due to the low amount of mechanical action in $scCO_2$. The average Cleaning Performance Index (CPI) of $scCO_2$ for all impurities using the best combination of commercial machine and process is still 25% lower than the results obtained using PER and 18% lower than the results with water. The index is 11% higher compared to the K4 solvent, also known as SOLVONK4, which is produced by the German company Kreussler Textile Chemistry. K4 solvent, whose main component is dihydrotridecylpropanoate (D5), offers high cleaning efficiency, lower toxicity, higher biodegradability, and non-flammability, making it a safer and more environmentally friendly alternative to traditional solvents such as perchloroethylene (PER). Additionally, the process with $scCO_2$ does not require drying because CO_2 evaporates from the fabric during the pressure reduction phase, with lower levels of redeposition of impurities [48].

5. Application of $scCO_2$ in Recycling Textiles and Other Materials

In today's world, we are faced with challenges of sustainable resource management and reducing the environmental footprint. Recycling is a key component in strategies for environmental conservation, and among the innovative methods that stand out for their efficiency and environmental acceptability is recycling using supercritical carbon dioxide ($scCO_2$). The use of $scCO_2$ in recycling offers a range of advantages. The first is environmental acceptability because the process does not require the use of toxic chemicals and can easily be removed from the process by simply lowering the pressure. Furthermore, processes that use $scCO_2$ typically consume less energy compared to traditional methods, reducing operational costs and greenhouse gas emissions. This chapter aims to present the potential of $scCO_2$ as a key factor in the transition to a circular economy and a more sustainable society.

5.1. Recycling Polyethylene (PE)

Polyethylene is a widely used synthetic material, utilized in a broad range of products, often for various types of packaging. Recycling polyethylene with the help of $scCO_2$ has proven to be very effective. Experiments have shown that thermal oxidation of polyethylene in the presence of oxygen and $scCO_2$ leads to significant decomposition of polymer chains, creating low molecular weight products such as acetic, formic, and propionic acids (Fig.4). This process is more efficient at lower O_2 ratios, allowing for better decomposition in the presence of $scCO_2$. This has been demonstrated by analyses using GPC (Gel Permeation Chromatography) chromatography and NMR (Nuclear Magnetic Resonance Spectroscopy) [21].

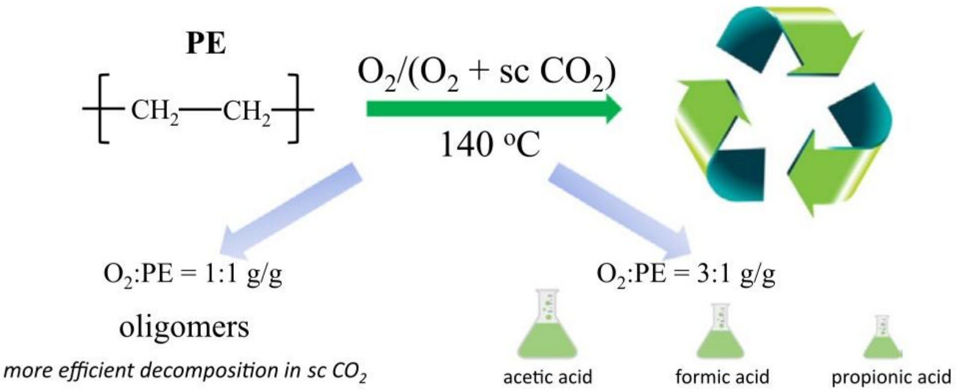

Fig.4. Thermal oxidation of polyethylene [21]

Thermal oxidation of polyethylene has been studied in pure oxygen and in an oxygen/ $scCO_2$ mixture. The process was conducted at 140°C and 14 bar for pure O_2 and at 215 bar for the $O_2/scCO_2$ mixture. At an oxygen to polymer ratio of 1:1 g/g, $scCO_2$ enhances thermal oxidation. At an oxygen to polymer ratio of 3:1 g/g, 40% mass of volatile products is formed. One example of successful application of $scCO_2$ technology is for extracting various contaminants from HDPE (high-density polyethylene) containers. The use of $scCO_2$ in this case proved very efficient and without polymer degradation. Studies have shown that supercritical extraction can effectively remove a wide range of contaminants, which was confirmed by spectroscopic analyses such as NIR (Near-Infrared Spectroscopy) and GC-MS (Gas Chromatography–Mass Spectrometry) [22].

5.2. Recycling Polypropylene (PP)

In the modern context of the circular economy, recycling plastic packaging like polypropylene (PP) presents a key challenge due to its propensity for thermal degradation, which complicates the effective removal of contaminants using traditional methods. In search of innovative solutions, Singha *et al*. explore the use of $scCO_2$ as a means for extracting contaminants from polypropylene [23]. The method is based on using $scCO_2$ which allows decontamination at lower temperatures (60-80°C) under constant pressure. This avoids thermal degradation of PP, preserving its physical properties and suitability for reuse in food contact packaging. Research conducted on PP cups showed high decontamination efficiency, especially in removing easily volatile organic compounds such as ethylbenzene and chlorobenzene, as well as semi-volatile compounds like phenylcyclohexane. One of the main advantages of the $scCO_2$ method is that it does not compromise the physical or sensory characteristics of the material. Additionally, the method does not affect the overall migration of substances from plastic into food, which is particularly important for materials that come into contact with food. The study also shows that $scCO_2$ has a significantly smaller environmental impact compared to conventional chemical solvents, aligning with the principles of sustainable development. The results of this research suggest that $scCO_2$ could be a key technology for enhancing the recycling process of PP, allowing not only for more environmentally friendly recycling but also the production of recycled plastic materials that meet increasingly stringent standards for food contact. This opens new doors for the plastic recycling industry and represents a step towards closing the cycle of the circular economy.

5.3. Recycling Polyvinyl Chloride (PVC)

PVC is widely used in the construction industry, medical devices, and many other applications. The use of $scCO_2$ for recycling PVC allows for the breakdown of polymer chains into smaller units, facilitating recycling. Additionally, this process can remove additives and other contaminants, improving the purity and quality of the recycled PVC [24, 25]. In general, the use of $scCO_2$ for recycling synthetic materials offers a sustainable and efficient alternative to traditional methods and represents the future of sustainable waste management, significantly contributing to environmental protection and the conservation of natural resources.

5.4. Recycling Lithium-Ion Batteries

The application of $scCO_2$ for processing end-of-life lithium-ion batteries (LIBs) is extremely interesting. This technology can play a key role in the development of a circular economy due to its ability to recover critical raw materials and reuse non-metal components. LIBs are widely used in consumer electronics, electric vehicles, and stationary energy storage systems, which also leads to a great need for recycling their components. LIB recycling has recently moved into a new phase focused on developing advanced pretreatment processes and more sustainable metallurgical methods. The extraction of electrolytes from lithium-ion batteries using $scCO_2$ is a crucial step in recycling processes, enabling the recovery of fluorinated compounds from the electrolytes, which could disrupt or even damage recycling processes. The first use of $scCO_2$ for electrolyte extraction from LIBs was recorded in 2014. The extraction is fast, selective, and efficient, and the results show high recovery rates. Compared to liquid solvents, subcritical and $scCO_2$ offer unique advantages without the need for additional concentration or purification steps.

Successful electrolyte recovery procedures using $scCO_2$ are being considered along with innovative research on extracting critical metals from the cathode, showing promising recovery rates for Li, Co, Mn, and Ni. Special focus has been placed on the innovative potential of $scCO_2$ for separating and reusing the fluorinated binder from the electrode, providing an environmentally friendly alternative to traditional methods that lead to the emission of hazardous fluorinated gases. The role of CO_2 as an extraction medium is important for future applications in recycling LIB cells, enabling quantitative extraction without loss of information due to dilution factors or compounds that cannot be extracted [50,51]. This innovative approach not only addresses environmental issues associated with traditional methods but also offers a valuable opportunity for material recovery and reuse, contributing to the circular economy and enhancing the sustainability of lithium-ion batteries as key components of future energy storage solutions. Given the growing number of used LIBs and strict recycling laws, this technique will increasingly gain importance in the near future.

6. Challenges and Future Directions

Although the processes of textile finishing in supercritical carbon dioxide ($scCO_2$) have the potential to significantly transform the textile industry in terms of sustainability, further research is needed to successfully implement this technology at an industrial scale. Challenges include controlling process parameters, managing equipment, safety measures, and economic aspects [13,52,53].

The first challenge is the high cost of initial investment for equipment capable of using $scCO_2$. Such equipment must be constructed to withstand the high pressures needed to maintain CO_2 in a supercritical state, which can be expensive and unattainable for smaller textile producers [7,13]. There is also the challenge of significant investment required to transition from traditional technologies to new technology, and the question of the profitability of such investments and the disposal of old machinery.

A second challenge is the technical difficulties in managing $scCO_2$, including maintaining a stable state and recycling and reusing CO_2 [5]. Additionally, a detailed study of the interactions between CO_2, the treatment agent, and textile fibers is necessary to optimize the process and ensure high-quality results [10,54].

Although research on dyeing and processing cellulose fibers with supercritical carbon dioxide has not yet led to widespread industrial use, the development of new techniques and fixing mechanisms continues, and preliminary tests show that significant improvements in results are possible [9]. The Dutch company DyeCoo is a leader in commercializing this technology for companies like Nike, Adidas, and IKEA. Nike's "ColorDry process" significantly reduces energy and water consumption, demonstrating the great potential of this technology [9]. The technology also has the potential to positively impact environmental challenges in the textile industry, especially in countries like India and China. DyeCoo aims to expand this sustainable technology in India, which would undoubtedly contribute to a significant reduction in industrial pollution. In collaboration with Huntsman Textile Effects, specialized products and dyes adapted for use in $scCO_2$ are being developed, opening up new possibilities for the industry [9].

Textile finishing technology in $scCO_2$ represents a promising direction in the sustainable development of the textile industry. This technology offers numerous environmental and economic benefits, including significant reductions in water consumption, waste, and greenhouse gas emissions. The ability to recycle and reuse $scCO_2$ makes this technology a more sustainable and economically viable alternative compared to traditional methods [10,14].

This technology has great potential for growth and innovation. There are numerous opportunities for further research and development, including creating new dyes and additives that are compatible with $scCO_2$, improving the quality of dyeing, and optimizing the process to reduce energy consumption [4,14,19].

One of the key future directions is the creation of new materials and dyes specifically designed for use with $scCO_2$. Such materials could improve the efficiency of dyeing and allow for more precise process control. Additionally, new materials could expand the applications of $scCO_2$ in the textile industry, enabling the development of advanced textile products with enhanced properties [12,16,53].

There are also opportunities for process optimization with the aim of reducing energy consumption. Advances in technology and a better understanding of process dynamics could lead to significant improvements, making the technology of $scCO_2$ even more attractive for industrial application [4,19].

Overall, despite the challenges it faces, $scCO_2$ finishing technology has enormous potential for further development and widespread application in the textile industry. Its potential lies not only in the ability to environmentally friendly finish and dye, but also in creating advanced textile products with improved properties. Further research and development could make $scCO_2$ a key high-efficiency technology in the future of the textile industry [9,25,55].

7. Conclusion

Based on existing research, it becomes clear that the technology of textile finishing using $scCO_2$ is one of the more promising directions for an environmentally friendly future of the textile industry. Unlike conventional processes that rely on large amounts of water, textile finishing technology using $scCO_2$ enables a water-free finishing process. This feature makes the technology particularly attractive in the context of sustainability, considering the increasing global challenges related to water. Additionally, the elimination of the need for water can also result in a reduction in the amount of wastewater generated during the textile finishing process, contributing to environmental protection. Furthermore, this textile finishing technology can also help reduce energy and chemical consumption, thereby reducing overall production costs as well as greenhouse gas emissions and the discharge of chemical residues into the environment.

However, despite these advantages, the use of $scCO_2$ also brings certain challenges. The equipment required for the process is expensive, and the process requires conditions of high temperature and pressure. Also, although it can be recycled, there is a need for constant monitoring and control to ensure that the carbon dioxide does not escape into the atmosphere. Moreover, while $scCO_2$ can replace many traditional textile processing methods, some types of processing still require the use of water, as is the case with wool where although $scCO_2$ is excellent as a solvent for nonpolar compounds, its low dielectric constant makes it difficult to extract ionic and polar compounds, and since sheep's wool contains organic potassium salts, it requires the addition of polar organic solvents such as ethanol, hydrogen peroxide, and ether as co-solvent, or chemical additives to improve solubility. Despite the challenges presented, the future of textile finishing technology using $scCO_2$ represents an extremely promising alternative to traditional textile processing methods.

In conclusion, the use of supercritical carbon dioxide demonstrates significant potential for transforming the textile industry into a circular and sustainable one. This technology offers effective and sustainable alternatives for textile finishing, while simultaneously reducing negative environmental and human health impacts. Textile finishing and processing in $scCO_2$ play a key role in promoting the circular economy, which focuses on minimizing waste and maximizing resource utilization. Supercritical CO_2 can be efficiently recycled and reused in processes, not only reducing waste but also waste management costs. This ability to recycle and reuse ensures better resource management, adding value to this sustainable technology.

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Literatura:

[1] Singha, K.; Pandit, P.; Maity, S.; Sharma, S. R. Harmful Environmental Effects for Textile Chemical Dyeing Practice. In *Green Chemistry for Sustainable Textiles*. Elsevier, **2021**, 153-164. https://doi.org/10.1016/B978-0-323-85204-3.00005-1.

[2] Arif, R.; Jadoun, S.; Verma, A. Green Chemistry in Textile Industry and Their Positive Impact of Implementation. In *Green Chemistry for Sustainable Textiles*. Elsevier, **2021**, 113–119. https://doi.org/10.1016/B978-0-323-85204-3.00023-3.

[3] Choudhury, A. K. R. Green Chemistry and Textile Industry. *JTEFT* **2017**, 2 (3). https://doi.org/10.15406/jteft.2017.02.00056.

[4] Abou Elmaaty, T. Recent Advances in Textile Wet Processing Using Supercritical Carbon Dioxide. In Green Chemistry for Sustainable Textiles; Elsevier, **2021**, 279–299. https://doi.org/10.1016/B978-0-323-85204-3.00011-7.

[5] Abou Elmaaty, T.; Abd El-Aziz, E. Supercritical Carbon Dioxide as a Green Media in Textile Dyeing: A Review. *Textile Research Journal* **2018**, 88 (10), 1184–1212. https://doi.org/10.1177/0040517517697639.

[6] Banchero, M. Recent Advances in Supercritical Fluid Dyeing. *Coloration Technology* **2020**, 136 (4), 317–335. https://doi.org/10.1111/cote.12469.

[7] Haji, A.; Bahtiyari, M. İ. Natural Compounds in Sustainable Dyeing and Functional Finishing of Textiles. In *Green Chemistry for Sustainable Textiles*. Elsevier, **2021**, 191–203. https://doi.org/10.1016/B978-0-323-85204-3.00004-X.

[8] Amenaghawon, A.N.; Anyalewechi, C.L.; Kusuma, H.S.; Mahfud, M. Applications of Supercritical Carbon Dioxide in Textile Industry. In *Green Sustainable Process for Chemical and Environmental Engineering and Science*. Elsevier, **2020**, 329–346. https://doi.org/10.1016/B978-0-12-817388-6.00013-1.

[9] Eren, H.A.; Yiğit, İ.; Eren, S.; Avinc, O. Sustainable Textile Processing with Zero Water Utilization Using Super Critical Carbon Dioxide Technology. In *Sustainability in the Textile and Apparel Industries*; Muthu, S.S., Gardetti, M.A., Eds.; Springer International Publishing, Cham, **2020**, 179–196. https://doi.org/10.1007/978-3-030-38545-3_8.

[10] Kiran, S.; Rafique, M.A.; Ashraf, A.; Ahmad, I.; Naz, S.; Afzal, G. New Emerging Green Technologies for Sustainable Textiles. In *Green Chemistry for Sustainable Textiles*. Elsevier, **2021**; pp 239–251. https://doi.org/10.1016/B978-0-323-85204-3.00014-2.

[11] Pandit, P.; Maiti, S.; Maity, S.; Singha, K. Green Chemistry in Textile Processes. In *Green Chemistry for Sustainable Textiles*. Elsevier, **2021**, 353–374. https://doi.org/10.1016/B978-0-323-85204-3.00025-7.

[12] Brune, D.; Krauch, H. Ima li CO_2 ekološku prednost?, *Tekstil* **2006**, 55 (12), 648-650.

[13] Ramsey, E.; Sun, Q.; Zhang, Z.; Zhang, C.; Gou, W. Mini-Review: Green Sustainable Processes Using Supercritical Fluid Carbon Dioxide. *Journal of Environmental Sciences* **2009**, 21 (6), 720–726. https://doi.org/10.1016/S1001-0742(08)62330-X.

[14] Eren, S.; Avinc, O.; Saka, Z.; Eren, H.A. Waterless Bleaching of Knitted Cotton Fabric Using Supercritical Carbon Dioxide Fluid Technology. *Cellulose* **2018**, 25 (10), 6247–6267. https://doi.org/10.1007/s10570-018-2004-z.

[15] Salem Allafi, F.A.; Hossain, M. S.; Ab Kadir, M. O.; Hakim Shaah, M. A.; Lalung, J.; Ahmad, M. I. Waterless Processing of Sheep Wool Fiber in Textile Industry with Supercritical CO_2: Potential and Challenges. *Journal of Cleaner Production* **2021**, 285, 124819. https://doi.org/10.1016/j.jclepro.2020.124819.

[16] Broadbent, P.J.; Carr, C.M.; Lewis, D.M.; Rigout, M.L.; Siewers, E.J.; Shojai Kaveh, N. Supercritical Carbon Dioxide (SC-CO_2) Dyeing of Cellulose Acetate: An Opportunity for a "Greener" Circular Textile Economy. *Coloration Technology* 2023, 139 (4), 475–488. https://doi.org/10.1111/cote.12690.

[17] Lo, C.H. Degumming Silk by CO_2 Supercritical Fluid and Their Dyeing Ability with Plant Indigo. *IJCST* **2021**, 33 (3), 465–476. https://doi.org/10.1108/IJCST-06-2019-0072.

[18] Hassabo, A.; Zayed, M.; Bakr, M.; Abd El-Aziz, E.; Othman, H. Applications of Supercritical Carbon Dioxide in Textile Finishing: A Review. *J. Text. Color. Pol. Sci.* **2022**. https://doi.org/10.21608/jtcps.2022.140947.1120.

[19] Aslanidou, D.; Tsioptsias, C.; Panayiotou, C. A Novel Approach for Textile Cleaning Based on Supercritical CO_2 and Pickering Emulsions. *The Journal of Supercritical Fluids* **2013**, 76, 83–93. https://doi.org/10.1016/j.supflu.2013.02.005.

[20] Sutanto, S. Textile Dry Cleaning Using Carbon Dioxide: Process, Apparatus and Mechanical Action, Delft University of Technology, **2014**. https://doi.org/10.4233/UUID:75CBFE8E-561E-4809-93CC-6D1C20E30555.

[21] Elmanovich, I.V.; Stakhanov, A.I.; Kravchenko, E.I.; Stakhanova, S.V.; Pavlov, A.A.; Ilyin, M. M.; Kharitonova, E.P.; Gallyamov, M.O.; Khokhlov, A.R. Chemical Recycling of Poly-ethylene in Oxygen-Enriched Supercritical CO_2. *The Journal of Supercritical Fluids* **2022**, 181, 105503. https://doi.org/10.1016/j.supflu.2021.105503.

[22] Alassali, A.; Aboud, N.; Kuchta, K.; Jaeger, P.; Zeinolebadi, A. Assessment of Supercritical CO_2 Extraction as a Method for Plastic Waste Decontamination. *Polymers* **2020**, 12 (6), 1347. https://doi.org/10.3390/polym12061347.

[23] Singh, S.; Pereira, J.; Brandão, T.; Oliveira, A. L.; Poças, F. Recycling of Polypropylene by Supercritical Carbon Dioxide for Extraction of Contaminants from Beverage Cups. A Comparison with Polyethylene Terephthalate and Polylactic Acid. *J Sci Food Agric* **2023**, 103 (3), 1127–1138. https://doi.org/10.1002/jsfa.12213.

[24] Ait-Touchente, Z.; Khellaf, M.; Raffin, G.; Lebaz, N.; Elaissari, A. Recent Advances in Polyvinyl Chloride (PVC) Recycling. *Polymers for Advanced Techs* **2024**, 35 (1), e6228. https://doi.org/10.1002/pat.6228.

[25] Safe and Efficient Recycling of Soft PVC from Medical Devices by Sustainable Supercritical Carbon Dioxide ($scCO_2$) Technology; Environmental Protection Agency, **2023**. Available at: https://mst.dk/publikationer/2023/marts/safe-and-efficient-recycling-of-soft-pvc-from-medical-devices-by-sustainable-supercritical-carbon-dioxide-scco2-technology (Accessed 2/5/2024)

[26] Ghanayem, H.; Okubayashi, S. Water-Free Dewaxing of Grey Cotton Fabric Using Supercritical Carbon Dioxide. *The Journal of Supercritical Fluids* **2021**, 174, 105264. https://doi.org/10.1016/j.supflu.2021.105264.

[27] Long, J.-J.; Cui, C.-L.; Wang, L.; Xu, H.-M.; Yu, Z.-J.; Bi, X.-P. Effect of Treatment Pressure on Wool Fiber in Supercritical Carbon Dioxide Fluid. *Journal of Cleaner Production* **2013**, 43, 52–58. https://doi.org/10.1016/j.jclepro.2013.01.002.

[28] Escobar, E. L. N.; Da Silva, T. A.; Pirich, C. L.; Corazza, M. L.; Pereira Ramos, L. Supercritical Fluids: A Promising Technique for Biomass Pretreatment and Fractionation. *Front. Bioeng. Biotechnol.* **2020**, 8, 252. https://doi.org/10.3389/fbioe.2020.00252.

[29] Villamil Jiménez, J. A.; Sabir, S.; Sauceau, M.; Sescousse, R.; Espitalier, F.; Le Moigne, N.; Bénézet, J.-C.; Fages, J. Supercritical CO_2 Assisted Extrusion Foaming of PLA-Cellulose Fibre Composites: Effect of Fibre on Foam Processing and Morphology. *The Journal of Supercritical Fluids* **2024**, 207, 106190. https://doi.org/10.1016/j.supflu.2024.106190.

[30] Kovačević, Z.; Bischof, S.; Bilandžija, N.; Krička, T. Conversion of Waste Agricultural Biomass from Straw into Useful Bioproducts—Wheat Fibers and Biofuels. *Sustainability* **2024**, 16 (11), 4739. https://doi.org/10.3390/su16114739.

[31] Lara, L.; Cabral, I.; Cunha, J. Ecological Approaches to Textile Dyeing: A Review. *Sustainability* **2022**, 14 (14), 8353. https://doi.org/10.3390/su14148353.

[32] Zheng, H.; Zheng, L. Dyeing of Meta-Aramid Fibers with Disperse Dyes in Supercritical Carbon Dioxide. *Fibers Polym* **2014**, 15 (8), 1627–1634. https://doi.org/10.1007/s12221-014-1627-4.

[33] Sanchez-Sanchez, J.; Fernández-Ponce, M.T.; Casas, L.; Mantell, C.; De La Ossa, E.J.M. Impregnation of Mango Leaf Extract into a Polyester Textile Using Supercritical Carbon Dioxide. *The Journal of Supercritical Fluids* **2017**, 128, 208–217. https://doi.org/10.1016/j.supflu.2017.05.033.

[34] Elmaaty, T.A.; Kazumasa, H.; Elsisi, H.; Mousa, A.; Sorour, H.; Gaffer, H.; Hori, T.; Hebeish, A.; Tabata, I.; Farouk, R. Pilot Scale Water Free Dyeing of Pure Cotton under Supercritical Carbon Dioxide. *Carbohydrate Polymer Technologies and Applications* **2020**, 1, 100010. https://doi.org/10.1016/j.carpta.2020.100010.

[35] Elmaaty, T.; El-Aziz, E.; Ma, J.; El-Taweel, F.; Okubayashi, S. Eco-Friendly Disperse Dyeing and Functional Finishing of Nylon 6 Using Supercritical Carbon Dioxide. *Fibers* **2015**, 3 (3), 309–322. https://doi.org/10.3390/fib3030309.

[36] AbouElmaaty, T.; Abdeldayem, S.; Ramadan, S.; Sayed-Ahmed, K.; Plutino, M. Coloration and Multi-Functionalization of Polypropylene Fabrics with Selenium Nanoparticles. *Polymers* **2021**, 13 (15), 2483. https://doi.org/10.3390/polym13152483.

[37] Chen, Y.; Zhang, Q.; Ma, Y.; Han, Q. Surface-Oriented Fluorinated Pyridinium Silicone with Enhanced Antibacterial Activity on Cotton via Supercritical Impregnation. *Cellulose* **2018**, 25 (2), 1499–1511. https://doi.org/10.1007/s10570-018-1657-y.

[38] Orhan, M.; Demirci, F.; Kocer, H. B.; Nierstrasz, V. Supercritical Carbon Dioxide Application Using Hydantoin Acrylamide for Biocidal Functionalization of Polyester. *The Journal of Supercritical Fluids* **2020**, 165, 104986. https://doi.org/10.1016/j.supflu.2020.104986.

[39] Mohamed, A. L.; Er-Rafik, M.; Moller, M. Supercritical Carbon Dioxide Assisted Silicon Based Finishing of Cellulosic Fabric: A Novel Approach. *Carbohydrate Polymers* **2013**, 98 (1), 1095–1107. https://doi.org/10.1016/j.carbpol.2013.06.027.

[40] Milovanovic, S.; Stamenic, M.; Markovic, D.; Radetic, M.; Zizovic, I. Solubility of Thymol in Supercritical Carbon Dioxide and Its Impregnation on Cotton Gauze. *The Journal of Supercritical Fluids* **2013**, 84, 173–181. https://doi.org/10.1016/j.supflu.2013.10.003.

[41] Abate, M.T.; Ferri, A.; Guan, J.; Chen, G.; Ferreira, J.A.; Nierstrasz, V. Single-Step Disperse Dyeing and Antimicrobial Functionalization of Polyester Fabric with Chitosan and Derivative in Supercritical Carbon Dioxide. *The Journal of Supercritical Fluids* **2019**, 147, 231–240. https://doi.org/10.1016/j.supflu.2018.11.002.

[42] Chang, S. Preparation of FR Cotton Fabric Using Environmental Friendly Supercritical Carbon Dioxide. *IJMSA* **2017**, 6 (6), 269. https://doi.org/10.11648/j.ijmsa.20170606.11.

[43] Iwai, Y.; Sameshima, S.; Yonezawa, S.; Katayama, S. Fabrication of Conductive Cotton by Electroless Plating Method with Supercritical Carbon Dioxide. *The Journal of Supercritical Fluids* **2015**, 100, 46–51. https://doi.org/10.1016/j.supflu.2015.02.027.

[44] Peng, L.; Guo, R.; Lan, J.; Jiang, S.; Li, C.; Zhang, Z. Synthesis of Silver Nanoparticles on Wool Fabric in Supercritical Carbon Dioxide. *mat express* **2017**, 7 (5), 405–410. https://doi.org/10.1166/mex.2017.1386.

[45] Bilalov, T.R.; Zakharov, A.A.; Jaddoa, A.A.; Gumerov, F.M.; Neindre, B.L. Treatment of Different Types of Cotton Fabrics by Ammonium Palmitate in a Supercritical CO_2 Environment. *The Journal of Supercritical Fluids* **2017**, 130, 47–55. https://doi.org/10.1016/j.supflu.2017.07.036.

[46] Pajnik, J.; Stamenić, M.; Radetić, M.; Tomanović, S.; Sukara, R.; Mihaljica, D.; Zizovic, I. Impregnation of Cotton Fabric with Pyrethrum Extract in Supercritical Carbon Dioxide. *The Journal of Supercritical Fluids* **2017**, 128, 66-72 https://doi.org/10.1016/j.supflu.2017.05.006.

[47] Guan, L.-Y.; Shi, M.-W.; Long, J.-J. One-Step Method for Stain Proofing Finishing of Polyester Fabric in Supercritical Carbon Dioxide. *Journal of CO_2 Utilization* **2023**, 67, 102316. https://doi.org/10.1016/j.jcou.2022.102316.

[48] Sutanto, S.; Van Roosmalen, M.J.E.; Witkamp, G.J. Mechanical Action in CO_2 Dry Cleaning. *The Journal of Supercritical Fluids* **2014**, 93, 138–143. https://doi.org/10.1016/j.supflu.2013.09.019.

[49] Soljačić, I.; Ćavara, L. O suhom pranju tekstilnog materijala pomoću tekućeg CO_2. *Tekstil* **1997**, 46 (11), 651-653. https://tekstil.hist.hr/index.php/tekstil/article/view/1848/1848

[50] Cattaneo, P.; D'Aprile, F.; Kapelyushko, V.; Mustarelli, P.; Quartarone, E. Supercritical CO_2 Technology for the Treatment of End-of-Life Lithium-Ion Batteries. *RSC Sustain.* **2024**, 2 (6), 1692–1707. https://doi.org/10.1039/D4SU00044G.

[51] Nowak, S.; Winter, M. The Role of Sub- and Supercritical CO_2 as "Processing Solvent" for the Recycling and Sample Preparation of Lithium Ion Battery Electrolytes. *Molecules* **2017**, 22 (3), 403. https://doi.org/10.3390/molecules22030403.

[52] Burkinshaw, S.M. *Physico-Chemical Aspects of Textile Coloration*. John Wiley & Sons / Society of Dyers and Colorists, Chichester, West Sussex, UK, **2016**, 575-592.

[53] Eren, H.A.; Avinc, O.; Eren, S. Supercritical Carbon Dioxide for Textile Applications and Recent Developments. *IOP Conf. Ser.: Mater. Sci. Eng.* **2017**, 254 (8), 082011. https://doi.org/10.1088/1757-899X/254/8/082011.

[54] Antony, A.; Raj, A.; Ramachandran, J.P.; Ramakrishnan, R.M.; Wallen, S.L.; Raveendran, P. Sizing and Desizing of Cotton and Polyester Yarns Using Liquid and Supercritical Carbon Dioxide with Nonfluorous CO_2-Philes as Size Compounds. *ACS Sustainable Chem. Eng.* **2018**, 6 (9), 12275–12280. https://doi.org/10.1021/acssuschemeng.8b02699.

[55] Agrawal B.J. Supercritical Carbon-dioxide Assisted Dyeing of Textiles: An Environmental Benign Waterless Dyeing Process, *IJIRCT* **2015**, 1 (2), 201-206. Available at: https://www.ijirct.org/viewPaper.php?paperId=IJIRCT1201043 (Accessed 2/5/2024).