Study on Decolorization of Reactive-dyed Cotton through Fenton-oxidation as a Pre-treatment for Textile Recycling

Elise Meurs
Student number: 02006997

Supervisors: Dr. Mohammad Neaz Morshed, Dr. May Kahoush, Prof. Dr. Satoko Okubayashi
Examiner: Prof. Dr. Nawar Kadi

Thesis submitted under the framework of WE-TEAM: World Textile Engineering Advanced Master, in order to obtain the academic degree of

- International Master of Science in Textile Engineering from Ghent University, Belgium
- Master of Science in Textile Engineering from Universitat Politècnica de Valencia, Spain
- Master of Science in Electrical and Electronic Engineering by Research from University of West Attica, Greece
- Master of Engineering from Kyoto Institute of Technology, Japan

Academic year 2022-2023
Date: 2023-06-01

Acknowledgements

Firstly, I would like to express my gratitude to my supervisors Dr. Mohammad Neaz Morshed and Dr. May Kahoush, who provided me with support and guidance throughout the project and without whom this thesis work would not have been possible. I would also like to thank my examiner Prof. Nawar Kadi and Prof. Satoko Okubayashi for their time reviewing my thesis and giving valuable comments.

Secondly, I want to thank the lab-technicians at the Swedish school of Textile for their help and advisory I received during the experimental section of my thesis project.

I would also like to express my appreciation to the organization of WE-Team for giving me the opportunity to experience this International Master in Textile Engineering, in which I got to learn and grow as an engineer and as a person.

Lastly, I would like to express my deepest gratitude to my family and friends for the unconditional support and encouragement during this thesis-semester and the rest of my studies.

Permission for use on loan: The author gives permission to make this master dissertation available for consultation and to copy parts of this master dissertation for personal use. In all cases of other use, the copyright terms have to be respected, in particular with regard to the obligation to state explicitly the source when quoting results from this master dissertation.

(2023-06-01)

Remark on master’s dissertation and oral presentation: This master's dissertation is part of an exam. Any comments formulated by the assessment committee during the oral presentation of the master's dissertation are not included in this text.

Abstract

In this master thesis, the feasibility of Fenton-oxidation for the decolorization of reactive dyed cotton is investigated as a potentially environmental-friendly preparatory treatment for mechanical/chemical recycling. Raw, knitted cotton is dyed with a black and a blue dye, whereafter preliminary tests are performed to investigate the influence of increasing Fenton-solution concentrations and different iron-sources on the efficiency of the discoloration, without carrying out complete optimization of the process-parameters. Based on the preliminary test-results, Fenton-treatments of the reactive-dyed cotton are upscaled, with discoloration efficiencies of 62 and 73% (for the black- and blue-dyed cotton respectively). Analytical characterization (by means of microscopy, TGA, DSC and FTIR) and mechanical analysis (tensile tests and shredding of the fabric) of the upscaled treated samples are performed, and the results indicate no major alterations of the main cellulosic structure of the cotton fibers. However, besides the degradation of the dye-molecules, also some oxidation (and therefore damage) of the cellulose-chains of the cotton fibers occurs, leading to reduced mechanical properties. Although this facilitates the mechanical recycling process, it possibly also reduces the quality of the re-spun yarns. Nevertheless, the Fenton-oxidation in the context of decolorization of reactive-dyed cotton forms an interesting future research-topic with many opportunities and prospects for increasing the efficiency and sustainability of the recycling process, and therefore increasing the sustainability of the textile industry in general.

Keywords: Fenton-oxidation, advanced oxidation processes, decolorization, textile recycling, cotton, reactive dye

Popular Abstract

The annual production of the textile industry has increased immensely due to changes in our consumption-behavior and the development of fast fashion. Due to the industry's high energy- and water-demand and the generation of a substantial amount of landfill which increases more and more every year, the textile sector has become one of the most polluting industries. In 2018, only 15% of the yearly produced textiles was recycled, while 66% of the produced textiles was disposed as landfill. Therefore, in order to increase the overall sustainability of the textile industry, the amount of landfill should be reduced by reusing disposed textiles after recycling (either mechanically or chemically). However, for efficient recycling, foreign substances such as dye-molecules should be removed before the recycling process. Therefore, color removal is an important preparatory treatment for efficient recycling of waste-textiles.

One of the most common materials used in the textile industry is cotton, which is mostly dyed with reactive dyes, which chemically bind to the fabric and are therefore difficult to remove from the textile material. Consequently, decolorization of reactive dyed cotton usually consists of highly energy- and water-consuming processes, which also require substantial amounts of oxidizing/reducing agents (for example potassium permanganate or sodium-hypochlorite) which are often toxic for the environment and harmful for the textile material. Consequently, alternative, less harmful decolorization processes of reactive-dyed cotton have become sought-after research-topics in the past decades. One example of a group of more ecological processes which can be used in the oxidation of dye-molecules is called 'advanced oxidation processes'. This group consists of three types of mechanisms, which all generate highly oxidative hydroxyl-radicals which will attack unsaturated bonds in organic substances, such as the conjugated chromophore groups in dye-molecules. The three different types of advanced oxidation processes are: 'ozone-assisted degradation', 'photocatalytic degradation' and 'Fenton-oxidation processes' (which consists of an iron-catalyst in the presence of hydrogen peroxide).

All three types of AOP's have been successfully used in the decolorization of dye-solutions. However, only the ozone-assisted and photocatalytic oxidation processes have been efficiently used for color removal from waste fabric. Therefore, decolorization of textiles by means of Fenton-oxidation currently still forms a gap in research which is yet to be tackled. For this reason, this master thesis investigates the feasibility of the Fenton-oxidation for the decolorization of reactive-dyed cotton, and the influence of this process on the fabric and its thermal and mechanical properties.

Complete optimization of the process-parameters is not performed, however, preliminary discoloration experiments of black- and blue-dyed cotton are carried out to investigate the influence of increasing Fenton-solution concentrations and the use of different iron-sources. The results of these tests are used for determining the conditions for further upscaled Fenton-oxidation based discoloration treatments. Hereafter, the upscaled discoloration allows analytical tests by means of microscopy, thermal gravimetric analysis, differential scanning calorimetry, Fourier-transform infrared spectroscopy, tensile tests of the unraveled yarn and shredding of the dyed and discolored fabric. Results of the upscaled Fenton-treatment and the analytical experiments indicate a decrease in color strength (62% discoloration of the black-dyed cotton, 73% discoloration of the blue-dyed cotton), but also reduced mechanical properties due to occurring oxidation of the cellulose-chain (and therefore damage to the cotton fibers) besides the oxidation of the dye-molecules. However, since complete optimization of all process-parameters via experimental design is yet to be performed in future research, milder conditions achieving acceptable discoloration-efficiencies – which cause less damage to the fibers – might be allowed.

In comparison to the activated hydrogen-peroxide decolorization used in industry, only 30-60% of the required amount of H_2O_2 and half of the required temperature is needed for the Fenton-oxidation based discoloration applied in this thesis-project, which already indicates a more ecological characteristic of the Fenton-mechanism due to lower chemical- and energy demand. Moreover, the Fenton-treatment still has many aspects which offer opportunities for improved sustainability of the process. Therefore, the Fenton-mechanism would be feasible for discoloration of reactive-dyed cotton, and forms a future research-topic with many opportunities for increasing the efficiency and sustainability of the recycling process, and therefore increasing the sustainability of the textile industry in general.

List of Abbreviations

AOP:	advanced oxidation process
COD:	chemical oxygen demand
DSC:	differential scanning calorimetry
Fe:	iron atom
Fe^{2+} or Fe(II):	two-valent iron cation
Fe^{3+} or Fe(III):	three-valent iron cation
FTIR:	Fourier-transform infrared
GOx:	Glucose oxidase
H_2O_2:	hydrogen peroxide
K/S:	Kubelka–Munk color strength
n:	sample size used in statistical tests
OH-:	hydroxyl functional group
omf:	on mass of fabric
rpm:	revolutions per minute
TGA:	thermogravimetric analysis
wt%:	weight percentage
X^*:	radical of substance X
α:	significance level used in statistical tests
λ:	wavelength

Table of Contents

1. Introduction

1.1 Recycling in the Textile Industry

The annual global production of textile has increased immensely (Figure 1.1) due to changes in consumption-behavior and development of fast-fashion. In 2018, a total amount of 17 million US tons (which corresponds to around 15,4 billion kilograms) of textile-products was generated. At the end-of-life stage of these textiles, only 14,7% was recycled and 18,9% was combusted for energy-recovery. The rest of these waste-textiles (66,4%) was deposited as landfill (United states Environmental Protection Agency, 2022).

Considering the significant amount of generated landfill, together with the high energy- and water-demand for the manufacturing of these textile-products, the textile-industry has become one of the most polluting industries on earth. In order to decrease this pollution, the waste-stream in the shape of landfill needs to be diminished. For that reason, textile recycling processes have to be taken to a higher level.

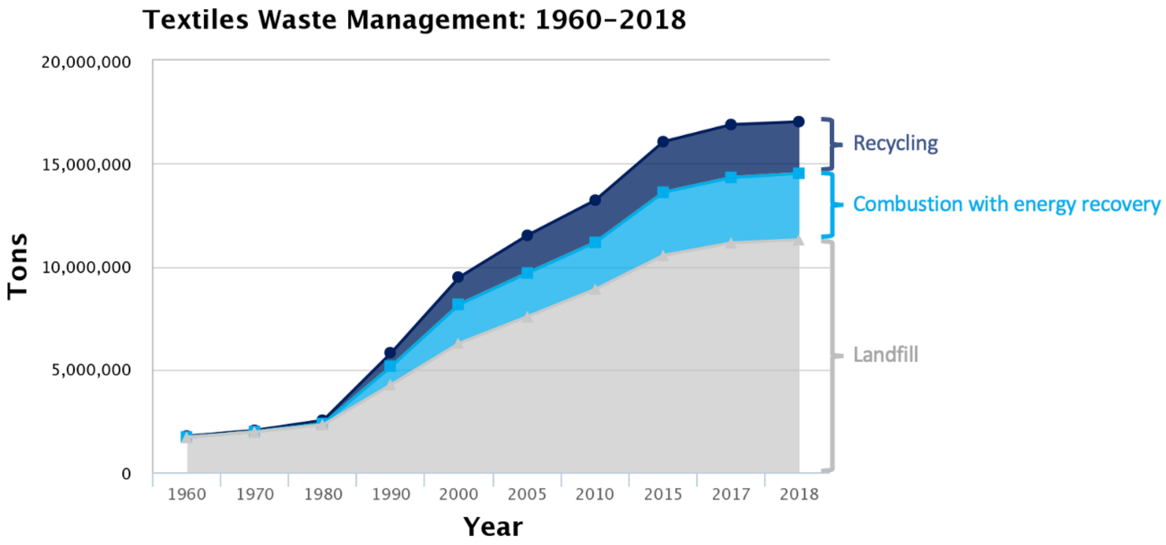


Figure 1.1: Trend in the textile-production per year (in US tons) and the different types of waste management from 1960 up to 2018 (United states Environmental Protection Agency, 2022).

1.2 Decolorization in the Textile Industry: Pretreatment for Textile Recycling

In order for textile to be efficiently recycled, aiming to regain as much of the initial quality of the fibers as possible, foreign substances such as finishing-components and dyestuff should be removed from the fabric before the chemical or mechanical recycling. Decolorization is therefore a crucial preparation-step for efficient recycling of textile-products.

Current industrial decolorization processes are usually based on alkaline reductive processes, which require high concentrations of various oxidizing and/or reducing agents which cleave the chemical bonds of chromophore groups (Li et al., 2022). Common agents used for this treatment are potassium permanganate ($KMnO_4$), sodium-hypochlorite ($NaClO$), sodium-hydrosulphite ($Na_2S_2O_4$), hydrogen peroxide (H_2O_2)… which are known for their efficient decolorization, nonetheless also known to be toxic and damaging to the textile (Powar et al., 2021a). In addition, the decolorization processes require high temperature and liquor consumption, and are therefore not ecological regarding waste-discharge, toxicity and chemical- and energy-consumption (Powar et al., 2021a).

Since decolorization is an essential step towards efficient recycling in order to decrease waste-disposal and increase sustainability of the textile industry, the search for efficient decolorization of waste-fabric by means of alternative processes with a lower environmental impact has become a popular research-topic during the past years.

A group of processes called 'advanced oxidation processes' (AOP) is one example of a recently growing field in research aiming towards more environmental-friendly decolorization processes. These processes all involve the generation of hydroxyl-radicals, which contain a high oxidation potential and are therefore suitable for oxidizing unsaturated bonds of organic substrates such as chromophore-groups in dye-molecules (Powar et al., 2021a).

This group of AOP's consists of 3 different mechanisms, which all generate the highly-oxidative OH-radicals: Fenton-oxidation (an iron-catalyzed mechanism), photocatalytic degradation (UV-initiated) and ozone-assisted degradation. All three of these mechanisms have been successfully used in decolorization of wastewater streams. Regarding the decolorization of fabric, ozone-assisted and photocatalytic degradation have already been researched in recent years, with varying color-stripping efficiencies depending on the process conditions. However, to the best of my knowledge, the use of Fenton-oxidation for decolorization of fabric has not yet been studied.

1.3 Research Gaps and Research Questions

Although the Fenton-oxidation mechanism has already been known for many years, the use of this process for discoloration of waste-fabric as a pre-treatment for efficient textile recycling currently still forms a gap in research. Therefore, the purpose of this master-thesis is to investigate the feasibility of the Fenton-oxidation as an efficient tool for discoloration of reactive dyed cotton fabric and investigate the influence of the treatment on the mechanical and thermal properties of the decolored textile-material. The feasibility of mechanical recycling of the Fenton-discolored textile material will also be studied. Based on that, following research questions will be answered through this thesis-project:

a) ‘How does the Fenton oxidation affect the color removal of reactive-dyed cotton?’
b) ‘How does the Fenton-oxidation affect the thermal and mechanical properties of the cotton?’
c) ‘How does the Fenton oxidation influence the mechanical recycling process of the fabric?

2. Literature Review

2.1 What is Color?

Perception of color by the human eye is the result of interactions between electromagnetic radiation and molecules present in the material. Electromagnetic radiation can be described as a set of waves with a broad range of wavelengths, and therefore containing a broad range of amounts of energy. Only a small part of this electromagnetic radiation (namely the wavelength-range of around 400 – 700 nm) is visible to the naked eye and is also known as 'visible light' (Lee, 2021).

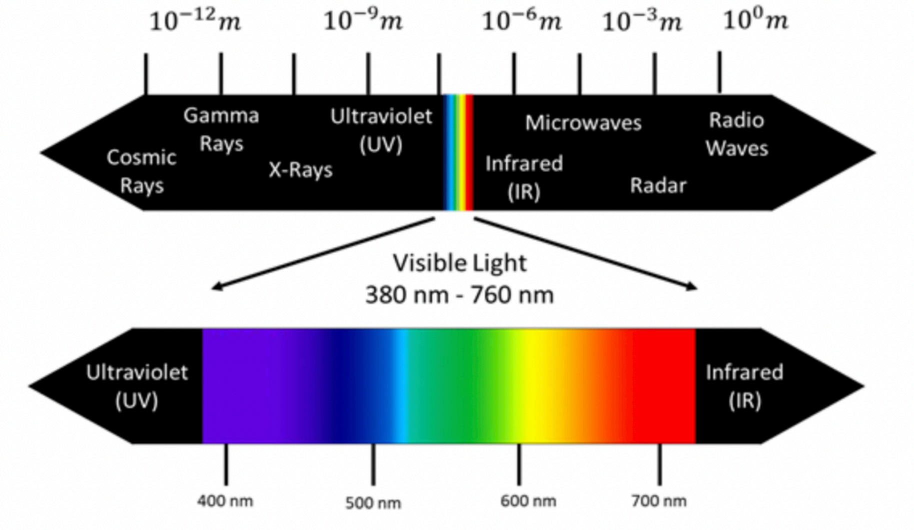


Figure 2.1: Total range of electromagnetic radiation with the visible light consisting of wavelengths between 400-700 nm (Lee, 2021).

When a substance is radiated by electromagnetic radiation, multiple phenomena can occur: the electromagnetic waves can be reflected or scattered, transmitted, absorbed or a combination of these phenomena (Bechtold & Pham, 2019).

A color of a substance is the result of the interaction between visible light and the substance radiated by this light: when the radiated material contains molecules which (partly) absorb a range of wavelengths within the visible range, the appearance of this material will be colored. When absorbing the energy of the light-waves, electrons of the molecule will be excited to orbitals of higher energy levels, whereafter the extra energy can be released again (by non-light-emitting ways such as vibration or rotation within the molecule) and the electron will go back to the initial energy-state. Therefore, a part of the initial electromagnetic range radiating the material is absorbed and will not be returned to the observing eye, while the other wavelengths are reflected at the surface (Figure 2.2). This will lead to a change in intensity of the reflected and scattered light which reaches the eye, and consequently the substance will be visible as colored material (Bechtold & Pham, 2019; Datacolor, 2023).

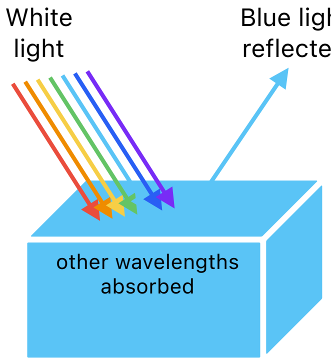


Figure 2.2: illustration of physics of light and color: white light (spectrum of wavelengths from 400 – 700 nm) falls into substance which absorbs part of the spectrum, and only reflects specific range of the visible spectrum (cyan blue in this case), which gives the substance a blue color.

2.1.1 Molecular Structure of Dyes

Not all molecules have the ability to absorb light (within the visible range). The ones which do, usually consist of large, conjugated electron groups such as conjugated double bonds and aromatic rings. These types of molecules are usually called ‘dyes’, and the conjugated groups responsible for the color of the dye-molecules are called ‘chromophores’. Most chromophores of textile-dyes contain one or more azo-bonds (-N=N-) or anthraquinoid structures (Figure 2.3). Therefore, those dyes are respectively called ‘azo-dyes’ and ‘anthraquinone dyes’ (Bechtold & Pham, 2019).

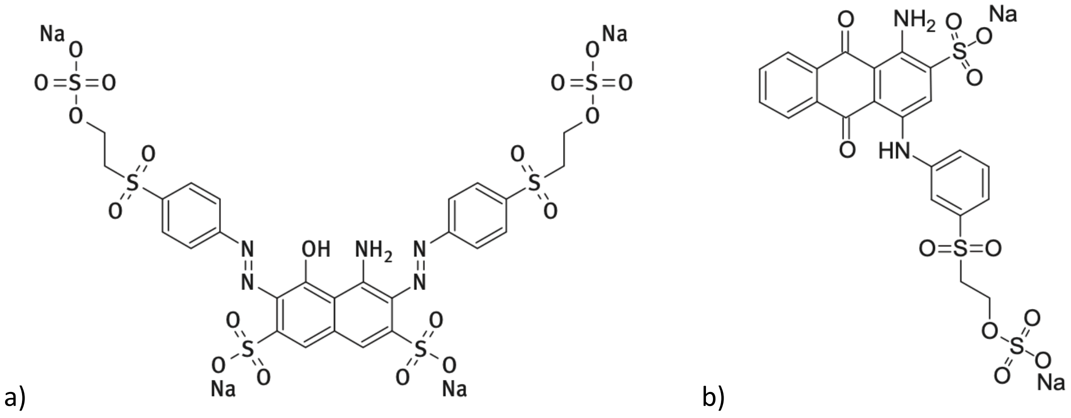


Figure 2.3: structure of a) di-azo-dye (C.I. Reactive Black 5) and b) anthraquinone dye (reactive blue 19) (Bechtold & Pham, 2019).

The aromatic groups of the chromophores also usually contain multiple substituents, such as -OH, $-NH_2$, -COOH, $-NO_2$… These substituents affect the absorbed wavelength-range due to their mesomeric- and inductive-effects on the conjugated systems, and therefore also have an impact on the color of the substance (Bechtold & Pham, 2019).

Since most of the dye-molecules consist of big conjugates systems, they are usually rather hydrophobic. In order to allow dissolution in the dye-bath and diffusion from the dye-solution to the fabric, the dye-molecules also usually contain some solubilizing groups, for example sulphonated groups ($-SO3^-$) (Bechtold & Pham, 2019), as is also visible in Figure 2.3

2.1.2 Reactive Dyes

Multiple types of dye exist, with different properties and applicable for different kinds of materials. Reactive dyes are a group of dye-molecules which form a covalent bond with a substrate in a chemical reaction (nucleophilic substitution or nucleophilic addition). Therefore, reactive dyes are only compatible with fabrics containing a substantial amount of nucleophilic functional groups, such as hydroxyl-groups (-OH) and amino-groups (-NH2). As a consequence, reactive dyes are mainly used for cellulosic fibers such as cotton (containing hydroxyl-groups on the glucopyranose-rings), and protein fibers such as wool and silk (containing hydroxyl- and amino-groups on the amino-acids which form the basis of the protein-fibers) (Bechtold & Pham, 2019).

Reactive dyes usually consist of a chromophore system with its substituents, some solubilizing groups and a reactive binding group which will make the reaction with the fabric surface possible. Various types of binding groups exist, such as vinyl-sulphone groups (visible in both dyes in Figure 2.3), dichloro-triazine groups, monofluoro-triazine and many more. For reactive dyes with vinyl-sulphone binding groups in the presence of alkali, an addition-reaction $(2.1 \& 2.2)$ is initiated by the nucleophilic groups of the fabric (for example OH-groups in cellulosic fibers) which attack the carbon double-bond (-C=C-) in the vinyl-binding-group of the dye (Bechtold & Pham, 2019).

$$Dye - SO_2 - CH_2 - CH_2 - O - SO_3^- \ Na \xrightarrow{alkali} Dye - SO_2 - CH_2 = CH_2 + NaHSO_4 \qquad (2.1)$$

$$Dye - SO_2 - CH_2 = CH_2 + cellulose \longrightarrow Dye - SO_2 - CH_2 - CH_2 - O - cellulose \qquad (2.2)$$

2.1.3 Color Measurement

When electromagnetic radiation reaches the human eye, it is transformed into a physiological signal. As a consequence, many physiological and psychological factors influence our individual perception of color, and difference in individual color-perception will therefore always hinder a generalized description of color-observation-systems by the naked eye (Bechtold & Pham, 2019).

For that reason, several color measurement systems have been developed in an attempt to transfer the physiological color-properties of materials into objective and measurable units with accompanying values, in order to standardize perceived colors in terms of color-definition and -communication. Multiple color-measurement systems exist, but one of the most widely used colorimetric systems is the CIELAB color-space, drawn up by the *Commission Internationale de l'Éclairage* (or 'CIE') (Bechtold & Pham, 2019).

This CIELAB color-space was developed to obtain a generalized and uniform description of color by means of its characteristic coordinates (L*, a*, b*) in the three-dimensional color-space (Figure 2.4). The coordinate L* gives a value for the lightness of a color (L*=100 for white substance, L=0 for black substance). The a*-coordinate represents the position of the measured color along the red-green axis and the b*-coordinate represents the position along the yellow-blue axis. The position of the color in the a*,b*-plane can also be described by polar C*,h*-coordinate-system, in which vector C* represents the chromaticity or saturation of the color, while the hue or color angle h* defines the color quality (Bechtold & Pham, 2019).

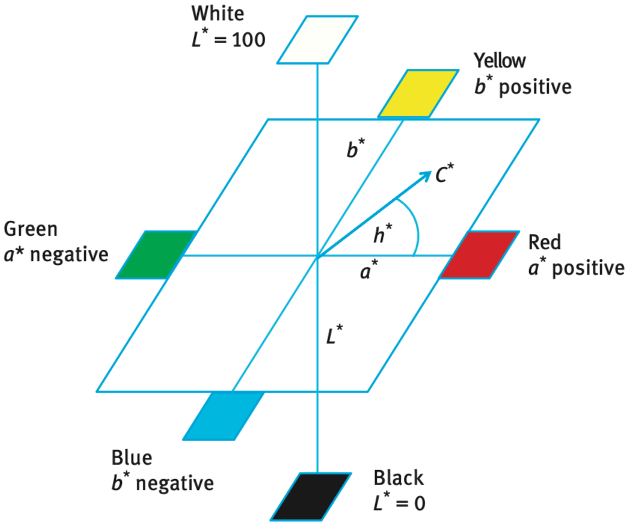


Figure 2.4: Three-dimensional representation of the CIELAB-color space, with characteristic coordinates (Bechtold & Pham, 2019).

Although the CIELAB color-coordinates enable generalized description of color and color differences, this system does not suffice when the color-strength needs to be described. As a consequence, color strength is frequently assessed by the Kubelka–Munk color strength 'K/S'. This value is received by measuring the reflectance curve after radiation of a surface and applying the Kubelka–Munk function $(eq. 1)$: 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 color strength) increases (Bechtold & Pham, 2019).

$$\text{Kubelka–Munk function:} \qquad K/S = (1-\beta)^2/2\beta \qquad (eq. 1)$$

With β the reflection at a given wavelength, with a value between 0 – 1.

2.2 Decolorization of Textiles as a Pre-treatment for Textile Recycling

As was discussed in the introduction, the decolorization of textiles is regarded as an important preparation-step for efficient recycling of textile-products.

Cotton is one of the most common materials in the textile industry and more than 50% of cotton textiles are reactive-dyed (Li et al., 2022). As a consequence, effective removal of this reactive dyestuff is of importance for efficient recycling. However, since reactive dyes bind covalently to the cotton-substrate, the removal of these dye-molecules usually require high concentrations of various oxidizing and/or reducing agents which cleave the chemical bonds of chromophore groups (Li et al., 2022). Current industrial decolorization is based on alkaline reductive processes, using agents such as hydrogen-peroxide (H_2O_2), potassium permanganate ($KMnO_4$), sodium-hypochlorite (NaClO) and sodium-hydrosulphite ($Na_2S_2O_4$). However, these components are known to be toxic and damaging to the textile. In addition, these decolorization processes require high temperature and liquor consumption, and are therefore not very sustainable regarding waste-discharge, toxicity and chemical- and energy-consumption (Powar et al., 2021).

For example, for activated alkaline hydrogen peroxide decolorization, temperatures of 70-90°C and bleaching-solutions with 0,5-1M H_2O_2 at pH ≈ 10 with a fabric-to-liquor-ratio of around 1:30 for 60 to 180 minutes are required in order to obtain discoloration percentages of around 50 to 96% (Li et al., 2021; Määttänen et al., 2019; Walger et al., 2015). Therefore, high temperatures, big volumes and high concentrations of H_2O_2 are required.

2.2.1 Alternative Decolorization Processes: Advanced Oxidation Processes

Recently, multiple alternative oxidation processes are being researched, aiming to decrease the environmental impact of decolorization processes compared to the currently used alkaline reductive processes.

'Advanced Oxidation Processes' have recently become a frequently studied research-topic aiming towards more environmental-friendly decolorization processes. These processes all involve the generation of hydroxyl-radicals, which have a high oxidation potential and are therefore suitable for oxidizing unsaturated bonds of organic substrates (A. Powar, Perwuelz, Behary, Hoang, et al., 2021). OH-radicals can potentially fully mineralize the organic substrate (R) into carbon dioxide (CO_2) and water (H_2O), for example through hydrogen abstraction:

$$R + OH^* \rightarrow R_{oxidized} + H_2O \qquad (2.3)$$

The AOP-group consists of three different types of mechanisms, which are described in the sections below.

2.2.1.1 Ozone

In an ozonation treatment, ozone (O_3) is generated and reacts with the substrate in a reactor. This generated ozone is a strong and selective oxidant, which can react directly with the substrate (2.4) or indirectly via secondary oxidants, namely OH-radicals (2.5 & 2.3). The ozone or secondary oxidant attacks conjugated double bonds of the chromophore group of the dye-molecules, making it an efficient decolorization treatment for wastewater or textile-substrates (Powar et al., 2021a).

Direct reaction: $$O_3 + R \rightarrow R_{oxidized} \qquad (2.4)$$

Indirect reaction: $$O_3 + H_2O \rightarrow 2OH^* + O_2 \qquad (2.5)$$

$$R + OH^* \rightarrow R_{oxidized} + H_2O \qquad (2.3)$$

Plenty of research articles investigate the ozone-assisted decolorization of water and textiles, with varying color-stripping percentages depending on the applications and reaction-conditions. An overview of the state of the art of ozone-assisted degradation of dye-molecules in solution and on fabric is given below, and other detailed studies can be found in Atav et al. (2022), Chen et al. (2009), He et al. (2019), Song et al. (2007), Wang et al (2022), Zainal et al., (2012), Zhou et al. (2013) and Zulfiqar et al. (2023).

Table 2.1: overview of state of the art of ozone-assisted degradation of dye in solution and on fabric.

Reference	Process description	Color stripping
Rekhate & Srivastava, 2020	Ozone-based (O_3, O_3/UV and O_3/Fe(II)) decolorization of azo-dye in solution	49 – 98 %
Powar et al., 2020	Ozone-based decolorization of reactive dyed cotton	33 – 98 %
Powar et al., 2021b	Ozone-based decolorization of pigment-printed cotton	23 – 95 %
Lou et al., 2022	Ozone-based decolorization of disperse dyed polyester	10 – 51 %

2.2.1.2 Photocatalysis

Photocatalytic stripping involves solar- or UV-initiation and semiconductor nanoparticles – such as TiO_2 – catalyzing the production of OH-radicals which will then cause the oxidation and degradation of organic compounds such as dye molecules (Ajmal et al., 2014). The mechanism is illustrated in Figure 2.5.

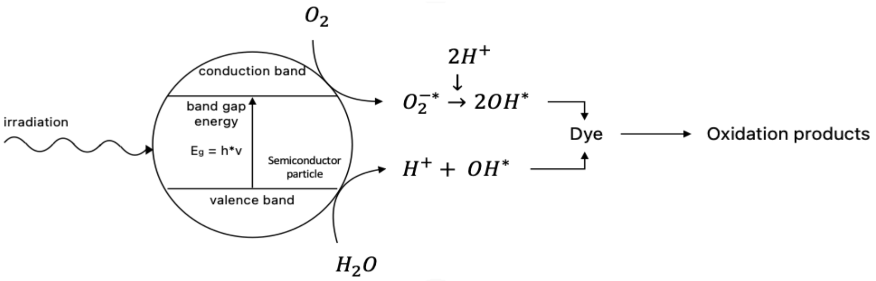


Figure 2.5: mechanisms occurring in photocatalytic dye-degradation: catalyzed by a semiconductor particle and initiated by irradiation of a light-energy source, based on Ajmal et al. (2014).

The photocatalytic degradation of dyes in wastewater has already being investigated, and recently photocatalytic color fading of textiles is being researched as well. An overview of the state of the art of photocatalytic degradation of dye-molecules in solution and on fabric is given below, and other detailed studies or reviews can be found in Ajmal et al. (2014), Eren (2019), Qutub et al. (2022), Rafiq et al. (2021), Shah et al. (2021) and Soutsas et al. (2010).

Table 2.2: overview of state of the art of photocatalytic degradation of dye in solution and on fabric.

Reference	Process description	Color stripping
Neppolian et al., 2002	Photocatalytic degradation of reactive dye in solution	10 – 100 %
Long et al., 2017	Photocatalytic decolorization of reactive dyed cotton with TiO_2	79 – 98 %
He et al., 2021	Photocatalytic decolorization of reactive dyed cotton with $K_2S_2O_8$	23 – 95 %

2.2.1.3 Fenton-oxidation

The essence of the Fenton-mechanism is an Fe(II/III)-catalyzed oxidation of organic substrates in the presence of H_2O_2. Hereby, OH-radicals are generated from the reduction of the H_2O_2 by the iron-catalyst (2.6), which will then attack unsaturated bonds (2.3) in the chromophore group of the dye-molecule (Swaminathan et al., 2003).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^* \tag{2.6}$$

$$R + OH^* \rightarrow R_{oxidized} + H_2O \tag{2.3}$$

Alternatives to this chemical Fenton-process have been developed, aiming to improve the efficiency. For example electro-Fenton uses electrochemical reduction of O_2 into extra H_2O_2, which leads to higher yield of OH-radicals and thus higher oxidation efficiency of the mechanism (Ozcan & Özcan, 2018). Sono-Fenton reactions on the other hand, are carried out in an ultrasound sono-reactor, giving extra energy to the reaction-medium and therefore increasing the amount of generated OH-radicals in the medium. Photo-Fenton reactions work similarly, however with extra energy delivered by a UV-source in a photoreactor (Sundararaman et al., 2009). Lastly, bio-Fenton reactions utilize enzymatic activity for in-situ generation of H_2O_2, which makes the additions of H_2O_2 to the reaction mechanism unnecessary (Karimi et al., 2012).

Fenton-oxidation has only been researched in the context of decolorization of dye-solution. An overview of the state of the art of Fenton-oxidation for the degradation of dye-molecules in solution is summarized below, and other detailed studies or reviews can be found in Barros et al. (2006), Ghoneim et al. (2011), Huang et al. (2008), Kahoush et al. (2018), Kim et al. (2004), Ramos et al. (2021), Soon & Hameed (2011), Sun et al. (2009) and Yu et al. (2005).

Table 2.3: overview of state of the art of Fenton-oxidation of dye in solution.

Reference	Process description	COD removal
Swaminathan et al., 2003	Fenton decolorization of azo dye-solution	5 – 82 %
Özcan & Özcan, 2018	Electro-Fenton decolorization of azo dye-solution	82 – 98 %
Sundararaman et al., 2009	Fenton, photo-Fenton and sono-Fenton decolorization of azo dye-solution	80 – 98 %
Karimi et al., 2012	Bio-Fenton decolorization of azo dye-solution	55 – 90 %
Morshed, 2021	bio-Fenton decolorization by immobilized GOx and inorganic (Fe^0) catalysts on non-woven polyester	32 – 78 %

2.2.2 Progress and Prospects of Color Removal Processes using AOP's

When doing a search on 'advanced oxidation processes' on Web Of Science, 95 search-results written in the past 10 years turn up. When entering both 'advanced oxidation processes' and 'color removal', only 10 search-results written in the past 10 years can be found. Therefore, it is clear that the use of advanced oxidation processes in the context of decolorization is in its early stages. Other applications of advanced oxidation processes are for example in treatment of waste-water streams from pharmaceutical activity (Kaur et al., 2019), agricultural activity and livestock farming (S. Ameta, 2018).

As a consequence, interest in the use of AOP's in decolorization-processes is rather recent. Nonetheless, the search towards an accessible and more environmental-friendly decolorization process is an important step towards extended and more efficient recycling processes, and therefore increased sustainability in the textile industry.

Although the Fenton mechanism has been used in the oxidation of organic compounds for many years, the first research articles focusing on the removal of color from wastewater effluents only appeared around 1990 (for example in Kuo (1992), Lin & Peng (1995), Park et al. (1999)) Furthermore, despite the trend of ozone- and photocatalytic degradation being researched in the context of decolorization of textiles, Fenton-oxidation has barely been researched for decolorization of textile as a pretreatment for recycling. Therefore, the use of Fenton-mechanisms for color-stripping treatments of fabric still forms a gap in research.

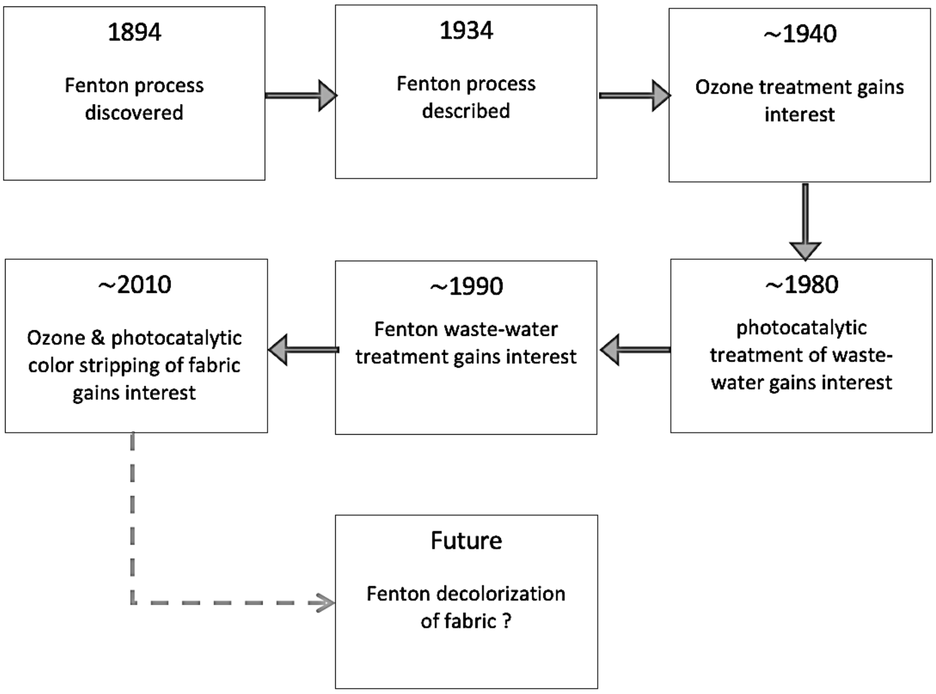


Figure 2.6: timeline of progress in research of the advanced oxidation processes and its use in color removal-treatments.

2.3 Fenton-oxidation: Mechanism and Influencing Factors

2.3.1 Mechanism

The reaction-mechanism of Fenton-oxidation requires ferrous (Fe^{2+}) or ferric (Fe^{3+}) cations and H_2O_2, in order to oxidate unsaturated bonds of the organic substrate present in the reaction-solution. The reactions occurring in the mechanism are:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \ OH^- + OH^* \qquad k = 40 - 80\ L/mol * s \qquad (2.6)$$

$$R + OH^* \rightarrow R_{oxidized} + H_2O \qquad (2.3)$$

$$R_{oxidized} + OH^* \rightarrow CO_2 + H_2O \qquad (2.7)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2{}^* \qquad k = 9 * 10^{-7} L/mol * s \qquad (2.8)$$

$$Fe^{3+} + HO_2{}^* \rightarrow Fe^{2+} + \ O_2 + H^+ \qquad k = 0{,}3 - 2 * 10^6 L/mol * s \qquad (2.9)$$

In reaction 2.6, Fe^{2+} is oxidized to Fe^{3+} while generating hydroxyl-radicals, which will act as the main oxidizing-agents in the degradation of organic compounds (Vasquez-Medrano et al., 2018): the highly oxidative OH-radicals will attack unsaturated bonds of the organic molecules (R) present in the medium (2.3). In theory, the organic substances can be completely degraded into CO_2 and H_2O (2.7) (Morshed, 2021).

The Fe^{3+} generated in reaction 2.6 will also react with H_2O_2 in order to regenerate the Fe-catalyst for continuation of the oxidation (2.8 & 2.9), however, at a much lower speed than the first reaction. Therefore, the regeneration of the Fe-catalyst is the rate-determining step, however crucial for not depleting the iron available for the hydroxyl-radical production (Vasquez-Medrano et al., 2018).

The performance of Fenton-reactions depends on several process parameters. The most obvious process-parameters are pH, Fe^{2+}-concentration, H_2O_2-concentration, temperature and reaction time. Naturally, more parameters influence the reaction-efficiency (such as organic substance concentrations and others), but the sections below will describe the most important influences on the process.

2.3.2 Influence of pH

The pH plays an important role in the ability to regenerate the ferrous cation: when the pH increases (starting from pH ≈ 4), Fe^{3+} will form a brown-colored precipitate iron(III)hydroxide (2.10). As a solid, the iron will not be able to contribute to the oxidation of the organic molecules, and therefore will lead to lower efficiencies of the Fenton-treatment. Consequently, the Fenton-oxidation works most efficient in a low pH (Vasquez-Medrano et al., 2018). However, at too low pH (≤ 2), the hydroxyl radicals can react with the protons (2.11), which will also lead to a decreased efficiency (Giwa et al., 2020). An optimal pH for Fenton-reactions hence lies between pH = 2,5 – 4.

$$Fe^{3+} \leftrightarrow Fe(OH)^{2+} \leftrightarrow Fe(OH)_2^+ \leftrightarrow Fe(OH)_3\,(s) \tag{2.10}$$

$$OH^* + H^+ + e^- \rightarrow H_2O \tag{2.11}$$

2.3.3 Influence of Fe^{2+}-concentration

An increasing concentration of Fe^{2+} will increase the oxidation-performance up to a certain level, whereafter the performance of the reaction will stagnate with increasing iron-source. This is caused by the increasing concentration of Fe^{3+} – due to the slow conversion back to the reactive ferrous form – and consequently more chance at undesired precipitation-reactions (2.10) (Kahoush et al., 2018) .

2.3.4 Influence of H_2O_2-concentration

Similar to the influence of Fe^{2+}-concentration, an increasing amount of hydrogen peroxide will increase the efficiency of the Fenton-performance up to a certain level. Since H_2O_2 is a rather unstable molecule, too high amounts will lead to consumption of the formed hydroxyl-radicals, with production of hydroperoxyl-radicals with lower oxidation potentials (2.12) and possibly even consumption in recombination reactions (2.13) which will lead to reduced decolorization performance.

$$H_2O_2 + OH^* \rightarrow HO_2^* + H_2O \tag{2.12}$$

$$HO_2^* + HO_2^* \rightarrow H_2O_2 + O_2 \tag{2.13}$$

2.3.5 Influence of Temperature

The Fenton-oxidation is an endothermic mechanism, and therefore increased temperatures give higher conversion percentages. In Giwa et al. (2020), temperatures from 25-45°C are tested, showing increasing efficiencies with increasing temperature. In theory, even higher efficiencies can be achieved with even higher temperatures. However, with an eye on sustainability, too high energy-consumptions due to high temperatures should be avoided.

2.3.6 Influence of Reaction Time

Oxidation-efficiencies increase with longer reaction-duration. However, at a certain point, most of the hydrogen-peroxide will be consumed and the reaction will slow down. For example, in Swaminathan et al. (2003), this stagnation occurs after a duration of 120 minutes.

2.3.7 Optimal Conditions for Fenton-decolorization of Dye-solutions

As mentioned above, only optimizing studies on treatments of dye-solutions can be found in literature. Optimal conditions for this treatment - based on research articles and reviews found in literature - are presented in Table 2.4.

However, the conditions presented in the table below are optimal for dye in solution, with a concentration of around 20-25mg/L. When treating dyed cotton, the dye is bound to the fabric and is present in higher concentrations than 20mg/L. Therefore, optimal conditions for the chemical Fenton-oxidation of dye in solution will still be different than for discoloration of dyed fabric.

Table 2.4: summary of optimal conditions for Fenton-discoloration of dye in solution (~20mg/L dye), based on Giwa et al. (2020), Kahoush et al. (2018) and Swaminathan et al. (2003).

Parameter	pH	T (°C)	$[H_2O_2]$ (mM)	$[Fe^{2+}]/[H_2O_2]$	Time (min)
Optimal value	3 - 4	35 - 45	40 - 70	0.05	30 - 120

2.3.8 Fenton-like Mechanisms

'Fenton-like' mechanisms follow similar mechanisms as mentioned above, but instead of adding Fe^{2+}, other types of iron-sources (Fe^{3+} or Fe^0) are added to the reaction-medium.

For example, when Fe^{3+} is added, the reaction-medium starts with the much slower Fe^{2+}-catalyst-generation reactions $(2.8 \& 2.9)$, before production of the hydroxyl-radicals is possible. Therefore, the Fenton-like mechanisms using an Fe^{3+}-source are usually much slower in the first stages of the reaction. Moreover, the pH should stay low enough ($pH \approx 3$) for this mechanism to avoid unwanted precipitation reactions of the Fe^{3+} (2.10) (Wang, 2008).

Besides the slower reaction-mechanism of Fe(III)-sources, ferric ions (Fe^{3+}) are also known to be good coagulant-flocculants for negatively charged organic substances, leading to destabilization of the charged molecules by means of charge neutralization. Since most dye-molecules contain negatively charged sulfonated-groups for increased solubility of the dye-molecule, they are susceptible to coagulation with the ferric ions, which consequently also leads to a discoloration-effect (Kim et al., 2004).

Therefore, using Fe(III)-sources will also lead to discoloration, however possibly due to an accumulative effect of the Fenton-mechanism and coagulation of the ferric-ions with the dye-molecules as in Kim et al (2004).

2.3.9 Environmental Challenges of Fenton-oxidation

The Fenton-oxidation mechanism has promising qualities for a more sustainable version of decolorizing treatment of waste fabric. However, the actual effect of the process on the environment is not yet known. For example, the mechanism might require lower amounts of toxic and flammable chemicals (such as H_2O_2), but still some of this chemical is needed for the reaction to occur. Moreover, Fe-cations are used in the mechanism, which can possibly also contribute to pollution of effluents due to the formation of hydroxo-complexes with certain reactive species causing them to deactivate (Kahoush et al., 2018). Furthermore, the reaction-mechanism works optimally at a low pH (2,5 – 4), which also influences the impact of the process on the textile-material and on the environment. Therefore, the Fenton-mechanism might have promising prospects for sustainable decolorization, but the exact impact of the Fenton-solution on the textile-material and on the environment is yet to be investigated.

2.3.10 Bio-Fenton: Mechanism and Influencing Factors

Alternatives to the chemical Fenton-process – developed for increasing the efficiency and/or sustainability – were introduced in section 2.2.1.3: electro-Fenton, photo-Fenton, sono-Fenton and bio-Fenton. The latter (bio-Fenton) is considered as an environmental-friendly version of the chemical Fenton-mechanism, which uses enzymatic glucose oxidase (GOx) for in situ production of H_2O_2 and D-glucono-1,5-lactone ($C_6H_{12}O_7$) from the substrate β-D-glucose ($C_6H_{12}O_6$). This mechanism avoids the need to store, transport and add the toxic and flammable H_2O_2 to the reaction medium (Kahoush et al., 2018). Moreover, the bio-Fenton mechanism requests a lower energy-consumption and uses natural, bio-sourced catalysts which can perform under milder conditions (Karimi et al., 2012; Morshed, 2021). Because this thesis-project has the aim to focus on sustainability, also the mechanism and influencing factors of the bio-Fenton process will be discussed in the section below.

As mentioned above, the H_2O_2 is in situ-produced by enzymatic activity (2.14). The rest of the mechanism is similar to the mechanism described for the chemical Fenton-mechanism $(2.6, 2.3, 2.7, 2.8$ & $2.9)$ in section 2.3.1.

$$C_6H_{12}O_6 + H_2O + O_2 \xrightarrow{GO_X} C_6H_{12}O_7 + H_2O_2 \tag{2.14}$$

The enzymes used in the bio-Fenton process (glucose oxidase) are more sensitive to changes in parameters and can even denaturate when the conditions become too extreme. Therefore, the optimal reaction-conditions for bio-Fenton will be different than for the chemical Fenton-treatment. The factors influencing the efficiency of the bio-Fenton treatment are: pH, Fe^{2+}-concentration, enzyme-concentration, glucose-concentration, temperature and reaction time.

The pH of the mechanism should now not only be beneficial for the Fenton-reaction, but also for the enzyme. However, these two mechanisms have different optimal pH-values: Fenton-oxidation works best in pH = 2,5 - 4 (see section 2.3.2) while the enzyme is active in a pH-range from 4 – 8, with an optimum activity at pH = 5,5 (Zia et al., 2007). Furthermore, at a pH below 2 or above 8, the bonds within the enzyme can be disrupted, which leads to unfolding of the active sites, and therefore inactivates the enzyme. Consequently, a middle ground achieving acceptable productivity for both mechanisms should be found. Multiple research-articles maintain a compromising pH of 4,5 - 5 (Kahoush, 2019; Karimi et al., 2012; Morshed, 2021).

Considering the iron-concentration, similar phenomena as to what is described in chapter 2.3.3 will occur: too high concentrations of Fe^{2+} will make the efficiency of the oxidation stagnate, due to undesired precipitation-reactions of the Fe^{3+} cation (2.10).

An increase of the substrate of the enzyme (glucose) will increase the efficiency of the bio-Fenton mechanism up to a certain point, whereafter the active sites of the enzymes are saturated and the reaction-rate cannot increase any further. However, if both the glucose- and enzyme-concentrations increase, an increase in enzyme-activity can be achieved while avoiding saturation (Karmali et al., 2004).

The activity of enzymes is sensitive to the reaction-temperature, and denaturation can occur when the temperature gets too high. The optimal temperature for GOx lies between 30-35°C (Singh & Verma, 2013), whereafter the enzymatic activity will decrease due to decreased stability, and even drop down to zero once a temperature of around 55-60°C is reached due irreversible denaturation of the enzyme (Zoldák et al., 2004).

The bio-Fenton reaction works slower than the chemical Fenton oxidation, because the enzyme first has to produce the hydrogen peroxide before it can be used as a reagent in the Fenton-reaction. Therefore, longer reaction times are more beneficial for bio-Fenton mechanisms.

2.3.9.1 Optimal conditions for bio-Fenton-decolorization of dye-solutions

Based on research articles and reviews found in literature (Kahoush, 2019; Karimi et al., 2012 and Morshed 2021), optimal conditions for bio-Fenton decolorization of dye-solutions are presented in Table 2.5. However, the conditions presented are optimal for dye in solution, with a concentration of around 20 mg/L. When treating dyed cotton, the dye is bound to the fabric, and in higher concentrations than 20mg/L. Therefore, the optimal conditions for bio-Fenton-treatment of dye in solution will still be different than for discoloration of dyed fabric.

Table 2.5: summary of optimal conditions for bio-Fenton-discoloration of dye in solution (~20mg/L dye), based on Kahoush (2019), Karimi et al. (2012) and Morshed (2021).

Parameter	pH	T (°C)	[Fe^{2+}] (mM)	Glucose (g/L)	GOx (U/L)	Time (min)
Optimal value	4 - 5.5	30 - 35	0.4 - 10	1.5 - 4	2000 - 3000	120 - 250

3. Experimental

3.1 Materials

For this thesis, raw cotton yarn was purchased from Stiafilco. Two different reactive dyes; Reaktivfärg Blå 43 (reactive blue 19) and Remazol Black B (C.I. Reactive Black 5) were purchased from Zenit and DyStar respectively. Sodium chloride (NaCl), sodium carbonate (Na_2CO_3) were purchased from Sigma Aldrich and used as its original form without further purifications.

For the Fenton-processes, iron(II)sulfate hepta-hydrate ($FeSO_4x7H_2O$, ≥99.0% purity) and hydrogen peroxide solution (H_2O_2, 35 wt%) were purchased from Sigma Aldrich and Merck respectively. Also iron(III)chloride ($FeCl_3$, 98% purity) purchased from Fisher Scientific and citric acid ($C_6H_8O_7$, 99% purity) purchased from Sigma Aldrich are used.

For the bio-Fenton treatment, the enzyme Glucose-Oxidase from *Aspergillus niger* (type X-S, 148176 units/g), its nutrimental substrate glucose (D-(+)-Glucose, 99,5% purity) and sodium hydroxide (NaOH, ≥ 97,0% purity) were purchased from Sigma Aldrich.

3.2 Methods

3.2.1 Method of Fabric Preparation

For this thesis-project, raw combed cotton yarn with a yarn count of 24Nm (or 41,7 tex) is knitted with a TK-83 circular knitting machine (Lucas-Elha), with a gauge of 20 needles per inch. A knitted structure was chosen due to its more open structure compared to woven structures, which might facilitate diffusion in water-based reaction-solutions.

3.2.2 Method of Dyeing

Samples of the knitted fabric were cut and dyed in a Pyrotec MB2-machine. Two different reactive dyes were used in this dyeing process: half of the samples were dyed with a blue dye and the other half with a black dye. For both dyes, a quantity of 6% omf dyestuff, electrolyte-concentration (NaCl) of 80 g/l and an alkaline-concentration (Na_2CO_3) of 20 g/l was added. For the blue dye, a liquor ratio of 1:25 was used, while for the black dye, a liquor ratio of 1:10 was used – as recommended by the technical data-sheets of the companies. Both dye-processes were performed by a two-step process with a temperature rise from 30°C up to 60°C (Figure 3.1).

After dyeing, the samples are rinsed in cold water, washed in warm water with detergent, and rinsed in cold water again. Afterwards, non-bound dye is removed as much as possible by washing the fabric in glass flasks filled with water in an ultrasound cleaning bath (VWR® USC-TH) for 10 minutes at 40°C. This step is repeated with new water until the added water stays clear (a total of 6 times).

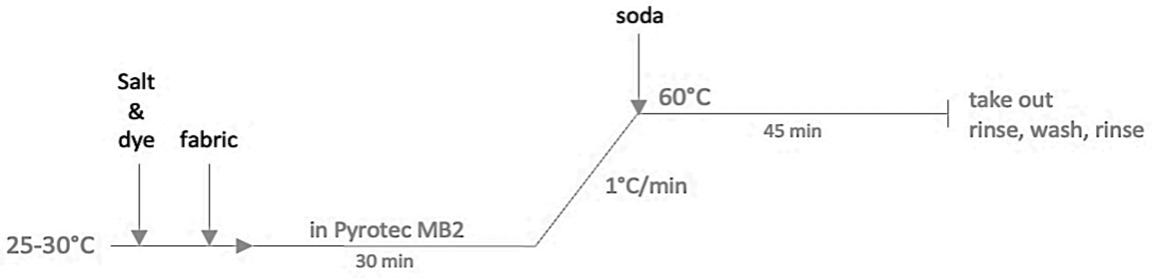


Figure 3.1: graphical representation of the applied dyeing process.

3.2.3 Method of Preliminary Studies on Fenton-oxidation based Discoloration of Cotton

A detailed description of the method of preliminary studies can be found in Section A.2 of Annex A. As discussed earlier in Chapter 2, Fenton-oxidation has only been researched in the context of decolorization of dye-solutions. Therefore, only optimal conditions for Fenton-decolorization of dye in solution can be found in literature and is summarized in Table 2.4. However, these conditions are optimal for dye in solution with a concentration of around 20mg/L. When dyed cotton is treated, the dye is bound to the fabric, and in higher concentrations: in the case of the dyeing-process described above (6% omf dyestuff) and when treating 25 cm^2 (or ~0,4g) in 100 ml solution, a maximum dye-concentration (assuming complete exhaustion) of around 240 mg/L is bound to the fabric. This concentration is 12 times higher than the 20mg/L for which the optimal concentrations in Table 2.4 are given. Due to this big difference in dye-concentration, the optimal conditions for the removal of dyes in solution are not likely to be compatible for the removal of color from fabric. Therefore, a preliminary study to investigate the influence of certain parameters on the efficiency of the discoloration of fabric was necessary.

Preliminary tests were performed to investigate the influence increasing Fenton-solution concentrations: four different Fenton-solutions with increasing concentrations were tested and are listed in Table A.1, starting with the optimal conditions for discoloration of dye in solution in Table 2.4 (referred to as ‘Fenton 1’) and multiplying these concentrations by 2 (‘Fenton 2), by 4 (‘Fenton 3’) and by 8 (‘Fenton 4’) for the other three conditions.

Since Fenton-like mechanisms (with an Fe(III)-source) can also be used in discoloration-treatments, the efficiency of an Fe^{3+}-source ($FeCl_3$) was compared to an Fe^{2+}-source ($FeSO_4$).

During Fenton or Fenton-like mechanisms, part of the iron will be present in the form of Fe^{3+}. However, these ferric-ions are known to be good coagulants for organic substances such as dye-molecules, which might cause an accumulative effect on the discoloration of the fabric (Kahoush, 2019; Kim et al., 2004). In practice, this would be beneficial for the discoloration of cotton. However, since this thesis-project focusses on the discoloration due to Fenton-oxidation, the accumulative discoloring effect of coagulation should be avoided. For this reason, the effect of a solution with only the iron-source (no H_2O_2) was investigated. This experiment is performed for both iron-sources ($FeSO_4$ and $FeCl_3$).

3.2.4 Method of Upscaled Fenton-oxidation based Discoloration of Cotton

Based on the results from preliminary studies (annex A), 'Fenton 3' (as presented in table 3.1) was chosen for further Fenton-oxidation based discoloration of textile as per the visual representation provided in Figure 3.2.

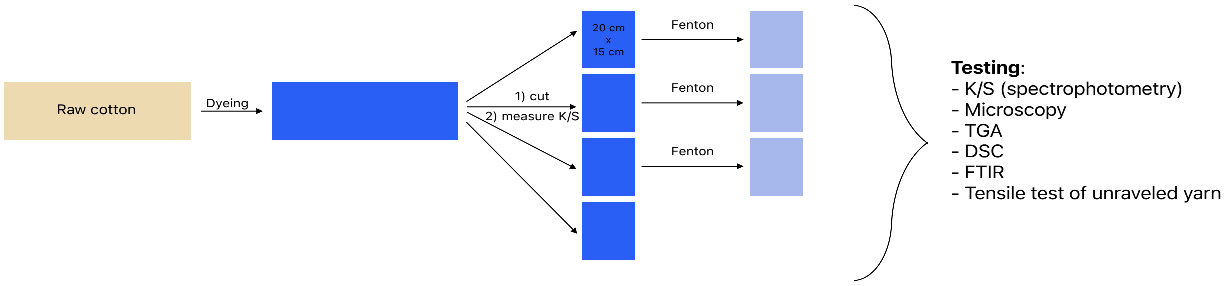


Figure 3.2: visual representation of the plan for Fenton-upscaling and further analysis.

According to the method, 3 fabric-samples of $300cm^2$ are treated for both dyes (each in 1200 ml Fenton-solution) according to the Fenton-conditions given in table 3.1. The fabrics are treated for 60 minutes, the temperature is kept at 40°C by means of a warm water bath and the solution is stirred by magnetic stirring at 400 rpm. Upscaling is performed in order to allow further analysis of the fabric before and after the treatment.

Before the start of the treatment, the fabrics are pre-wetted (in de-ionized water in an ultrasound cleaning bath (VWR® USC-TH) for 10 minutes at 40°C) in an attempt to impede the reaction in solution, since the raw dyed cotton tends to be rather hydrophobic.

Table 3.1: conditions for Fenton-solution in upscaled tests.

Parameter	$[Fe^{2+}]$ (mM)	$[H_2O_2]$ (mM)	T (°C)	$pH_{t=0\ (non\text{-}altered)}$
Value	14	280	40	~2,5

The color strength (K/S-values) is measured before and after the Fenton-treatment (see section 3.2.5). For each sample, the color-measurement is performed on 3 different parts of the sample, whereafter a mean value is calculated, which is then used in further analysis.

3.2.5 Method of Color Measurements - Spectrophotometry

Color measurements are performed by a UV-VIS-spectrophotometer (Datacolor 500) illuminating the sample with a D65/10 light-source, containing a FL40-UV filter (0%UV), and calibrated by comparison of a sample diagnostic tile to a reference diagnostic tile.

The reflectance-curve, absorbance-curve, color strength (K/S at λ_{max}) and CIELAB-coordination's are measured/calculated before and after treatments. The measurements are performed on a double folded fabric (4 layers), in order to avoid contributions from the background material placed behind the sample due to transparency of the knitted fabric.

From the K/S-values, the discoloration percentage is calculated as follows:

$$discoloration\% \qquad (eq.2)$$

$$= \frac{color\ added\ by\ dyeing - color\ removed\ by\ Fenton\ treatment}{color\ added\ by\ dyeing} x\ 100$$

$$= \frac{((K/S_{at\ \lambda_{max},dyed} - K/S_{at\ \lambda_{max},raw\ cotton}) - K/S_{at\ \lambda_{max},Fenton-treated})}{(K/S_{at\ \lambda_{max},dyed} - K/S_{at\ \lambda_{max},raw\ cotton})} x\ 100$$

3.2.6 Methods of Analytical Characterizations

3.2.6.1 Digital Optical Microscopy

Images of the knitted structure and the yarns of the raw cotton, dyed cotton and Fenton-treated fabrics are captured with a reflection-microscope Inskam 315-W 5MP Dual Lens Digital Microscope (Inskam) with magnification of 250x.

Images of the cotton fibers of the raw, dyed and Fenton-treated fabrics are captured by means of a transmission-microscope Eclipse Ei Microscope (Nikon), with a 10x binocular set and a 40x magnification objective (and thus a total magnification of 400x).

3.2.6.2 Thermogravimetric analysis

The thermogravimetric analysis is performed by a TGA Q500 (TA Instruments). Samples of around 10 mg of the dyed and discolored cotton in a platinum pan are heated in an inert N_2-atmosphere from 30°C up to 500°C, with a heating rate of 20°C/min. This test is repeated 3 times.

3.2.6.3 Differential scanning calorimetry

The differential scanning calorimetry was performed by a DSC Q2000 (TA Instruments). Samples of around 5 mg of the dyed and discolored cotton were cooled and heated in three cycles: heating from -25°C degrees up to 250°C, cooled back down to -25°C and lastly heated again to 250°C. The heating rate used is 10 °C/min and the DSC was performed in an inert N_2-atmosphere. The samples were measured against an empty reference pan. This test is repeated 3 times.

3.2.6.4 Fourier-transform infrared spectroscopy

FTIR-spectra of the raw, dyed and Fenton-treated cotton are captured by the FTIR-instrument Nicolet iS10 (Thermo Scientific), with a resolution of 4 cm^{-1} and 64 scans for each sample. To calibrate the measurements, the spectrum of the background (ambient air) was made and deducted from following measurements of the fabric-samples. This test is repeated 3 times.

3.2.7 Methods of Testing of Mechanical Properties of Samples

3.2.7.1 Tensile testing of the unraveled yarn

The strength, elongation and tenacity of unraveled yarn of the dyed cotton and Fenton-treated cotton are measured during stretching with a Tensolab 2512A (Mesdan-Lab), according to standard EN ISO 2062: the length of the yarn between the clamps is 500 mm, and the yarns are stretched at a constant rate of 500mm/min ± 10mm/min. The textured yarn was attached between the clamps while being stretched to remove most of the crimp, while making sure to keep the pre-tension below 0,5 cN/tex. For each treatment (dyed and discolored), this test was repeated for 10 samples.

The samples were conditioned in a standard atmosphere for a minimum of 4 hours before the testing, according to standard EN ISO 139: in a standard atmosphere with a temperature of 20°C and a humidity of 65%.

3.2.7.2 Mechanical shredding of the cotton fabric

Samples of around 15cmx20cm of the raw cotton, dyed- and Fenton-treated cotton are shredded with a Trim Fabric Opening Machine (Kingtech Machinery), while collecting the opened fabric for qualitative analysis.

3.2.8 Concept study of Bio-Fenton Oxidation based Discoloration of blue-dyed Cotton

A first attempt at replacing the H_2O_2 by its in-situ producing enzyme is based on upscaling the optimal conditions for bio-Fenton oxidation of dye in solution (Table 2.5): using the same amount of Fe^{2+} as for the upscaled chemical Fenton treatments, and scaling the other chemicals while maintaining the ratios as in Table 2.5. The actual conditions used for the bio-Fenton trial are given in Table 3.2. Since only D-glucose (a mixture of α- and β-D-glucose) was available, a correction was made in the calculation of the required amount of substrate, considering that D-glucose in solution consists of around 60% β-D-glucose (Tao et al., 2009).

Table 3.2: conditions for bio-Fenton-solution in concept study.

	$[Fe^{2+}]$ (mM)	Glucose (g/L)	GOx (U/L)	T (°C)
bio-Fenton conditions	14	18	5400	35

Practically, the enzyme and the glucose are mixed together in 100 ml of de-ionized water for 5 minutes at pH = 5 and 35°C. After these 5 minutes, the iron is added and the pH is adapted back to pH = 5 by adding some drops of 0,1M NaOH-solution, whereafter pre-wetted blue dyed cotton of 5x5 cm (wetted in de-ionized water in an ultrasound cleaning bath for 10 minutes at 35°C) is added to the mixture. This mixture is kept at 35°C in a warm water bath, while mixing with a magnetic stirrer at 400 rpm for 60 minutes. To be able to see the natural trend of the pH during the reaction, the pH is monitored - but not adapted - during the reaction by measuring every 10 minutes. This treatment is performed for 3 separate fabric samples of the blue dyed cotton (the blue dye turned out to be more sensitive to the oxidation mechanism, see results). Since a higher pH reduces the possibility of Fe^{3+} reducing back to Fe^{2+}, the probability of Fe^{3+} coagulating with the dye and contributing to the discoloration of the fabric also increases. Therefore, a control treatment containing only the iron and glucose (no enzyme), following a similar trend in pH (adapted by adding some drops of 0,1M-solution of citric acid), is performed for 3 separate samples (of 5x5 cm) of the blue dyed cotton.

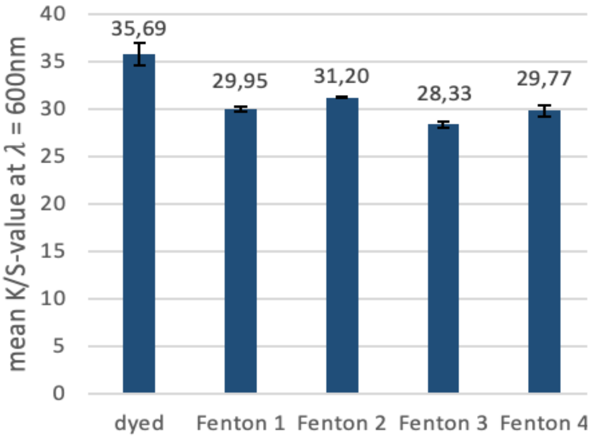
3.2.9 Method of Statistical Analysis

Investigating whether test-results before and after a treatment are significantly different is tested by two-sided paired t-tests using Excel. Investigating whether certain treatments give significantly different results is tested by two-sided t-tests using Excel. All t-tests are performed with a confidence interval CI = 95% (or α = 0,05). For obtained p-values < α = 0,05, the difference in results can be assumed 'significant'.

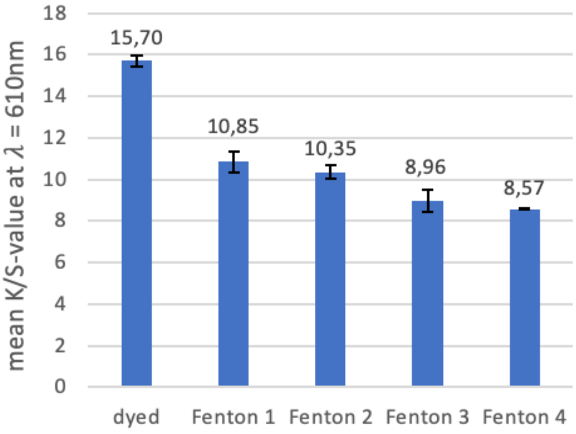
4. Results and Discussions

4.1 Analysis of Results from Preliminary Studies

According to results presented in Section A.3 of annex A, it can be seen that all 4 different concentrations lead to significant discoloration (between 12,39% and 20,46% for the black-dyed cotton and 30,62% and 45,15% for the blue-dyed cotton) as observed from the measurements of K/S-values (Graph 4.1 and 4.2) and paired t-tests between the values before and after the Fenton-treatments with increasing solution-concentrations.



Graph 4.1: mean K/S-values of the black-dyed cotton before and after Fenton treatments with increasing concentrations according to Table A.1



Graph 4.2: mean K/S-values of the blue-dyed cotton before and after Fenton treatments with increasing concentrations according to Table A.1

From t-tests between the K/S-values after the treatments, the conditions with the 2 highest concentrations (Fenton 3 and Fenton 4: solutions with respectively 4 and 8 times the recommended concentrations for discoloration of dye in solution in Table 2.4) do not indicate significantly different results for both dyes. Keeping sustainability in mind, it is decided to work with the conditions which request a lower amount of chemicals (Fenton 3) in further parts of the preliminary tests (in annex A), obtaining a 20,46% discoloration of the black-dyed cotton and a 42,71% discoloration of the blue-dyed cotton. Opting for homogeneous conditions for both dyes will also facilitate better comparison of the sensitivity of the different dyestuff to the treatment later on. Measurements of the pH (as shown in Graph A.3) indicate that increased concentrations of the Fenton-solution lead to decreased values of pH (from $pH_{t=0} \approx 3,0$ for Fenton 1 to $pH_{t=0} \approx 2,4$ for Fenton 4) since both the ferric-sulphate and hydrogen peroxide are acidic. The pH-curves also show a decrease in pH during the Fenton-reaction, which is likely to be caused by the production of hydroxyl-ions during the reaction-mechanism (reaction 2.6).

An Fe(III)-source ($FeCl_3$) also leads to significant discoloration percentages (13,16% discoloration of the black-dyed cotton and 59,65% discoloration of the blue-dyed cotton). For the black-dyed cotton, this discoloration is significantly lower than for the treatment with $FeSO_4$ (achieving 20,46% discoloration). For the blue-dyed cotton, $FeCl_3$ achieves significantly higher discoloration than $FeSO_4$ (59,65% compared to 42,71% discoloration respectively). Measurements of the pH show a lower pH during the reaction when $FeCl_3$ is used (starting from $pH_{t=0} \approx 2,1$ to $pH_{t=60} \approx 1,9$), which is already below the optimal pH-range for the Fenton-mechanism.

When investigating the contribution of coagulation of Fe^{3+}-cations with the dye-molecules by only adding the iron-sources (no H_2O_2) to the solution, the $FeSO_4$ leads to non-significant percentages of discoloration (2-3%) for both dyes. However, the $FeCl_3$ alone achieves significant discolorations of 14,03% for the black-dyed cotton and 59,08% for the blue-dyed cotton, which are similar to the percentages achieved when $FeCl_3$ is used in the Fenton-solution (with H_2O_2). Therefore, it is likely that coagulation of the ferric-ions with the dye-molecules contributes to the discoloration of the cotton when an Fe(III)-source is used. Consequently, only the $FeSO_4$ will be used as an iron-source for further treatments.

4.2 Results of Upscaled Fenton-oxidation based Discoloration

4.2.1 Analysis of Discoloration of Black-dyed Cotton

Digital Image Analysis

Pictures of the black-dyed cotton before and after the Fenton-oxidation based discoloration treatment (Figure 4.3) show that color was removed but complete decolorization did not occur, and the tone of the color changed from a dark black-blue to grey. Further analysis was carried out below for quantification of the discoloration.

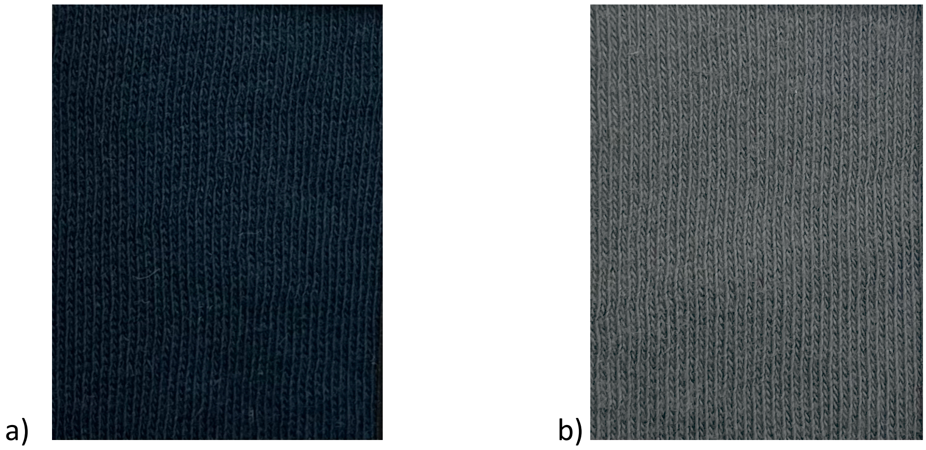


Figure 4.3: pictures of the black-dyed knitted cotton before (a) and after (b) Fenton-treatment.

K/S Analysis

Spectrophotometry of the black-dyed cotton before and after the upscaled Fenton-oxidation based discoloration treatment (Figure 4.4) shows reduced color strength with an accompanying mean discoloration percentage of 61,54% at $\lambda_{max} = 600$ nm. A paired t-test of the K/S-values before and after the treatment (with α = 0,05 and n = 3) indicates a significant discoloration (p = 0,003) due to the Fenton-oxidation.

However, the spectrum still shows remaining color strength after the oxidation-treatment which is evened out over the full visible-range, indicating incomplete degradation of the dyestuff and altered chromophore groups of the remaining dye-molecules. The spread-out color strength over the full range of visible wavelengths would lead to the grey-colored treated sample as is visible in Figure 4.3.

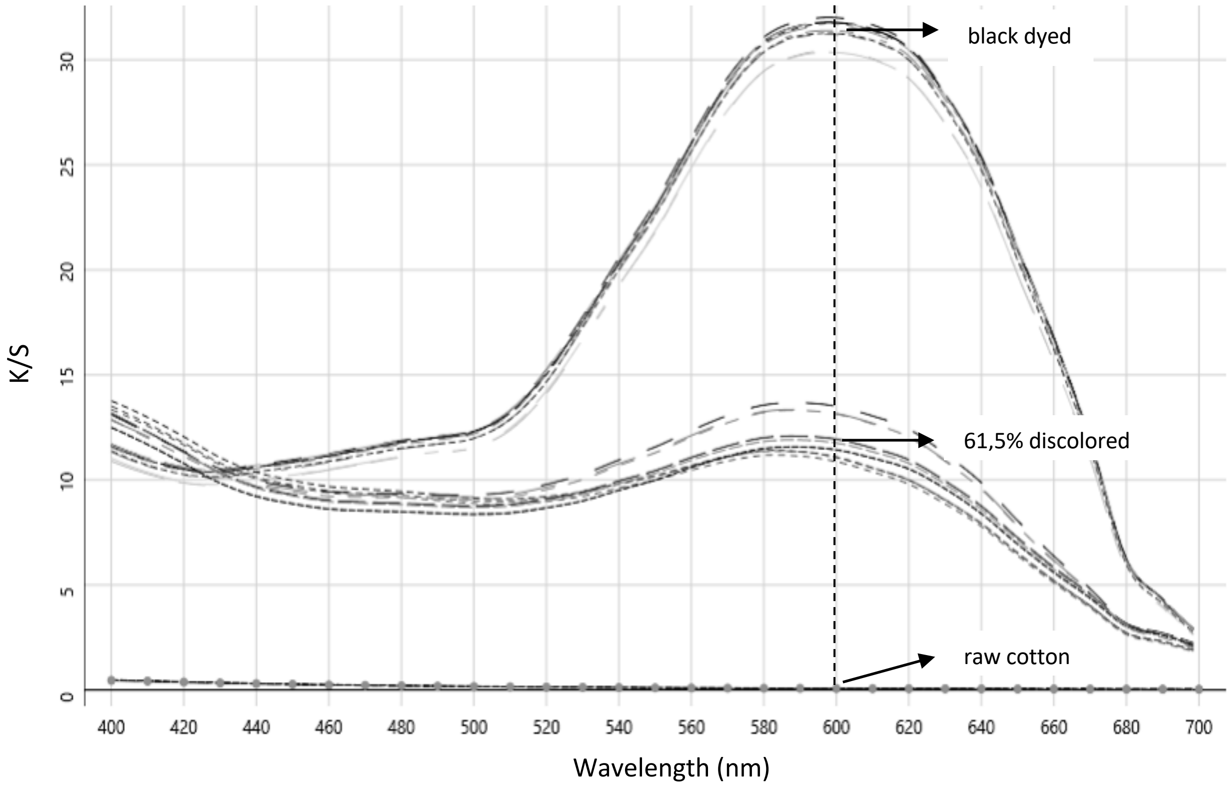


Figure 4.4: plot of measured K/S-values of black cotton before and after Fenton-treatment.

Optical Microscopic analysis

Microscopy-images of the knitted structure, the yarn and the fiber of the black-dyed cotton before and after the Fenton-oxidation based discoloration treatment are given in Figure 4.5, Figure 4.6 and Figure 4.7.

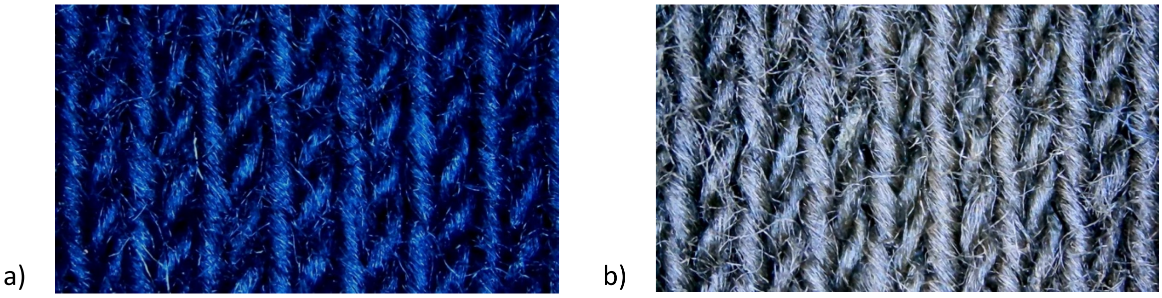


Figure 4.5: microscope-images of knitted structure of black-dyed cotton before (a) and after (b) Fenton-treatment.

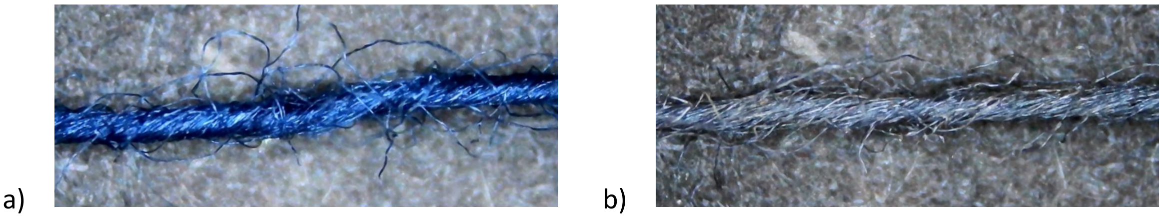


Figure 4.6: microscope-images of black-dyed cotton yarns before (a) and after (b) Fenton-treatment.

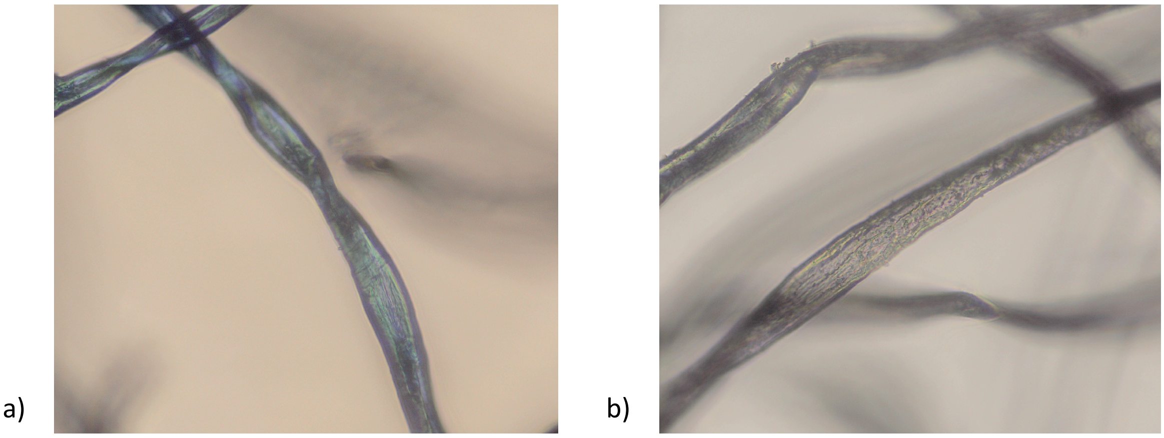
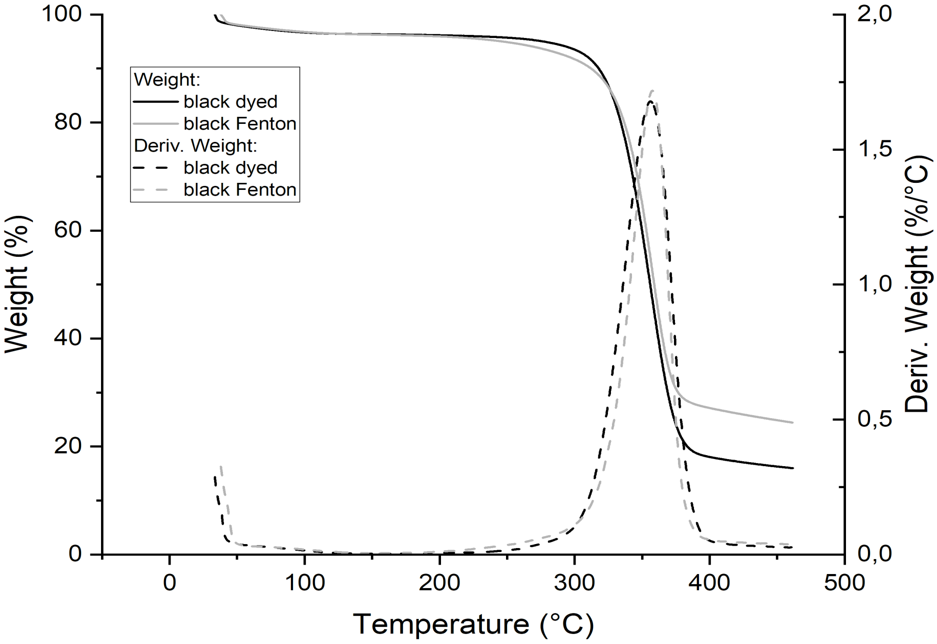


Figure 4.7: microscope-images of black-dyed cotton fibers before (a) and after (b) Fenton-treatment.

From the microscopy images of the black dyed cotton before and after the Fenton-treatment, it is visible that color was removed, but complete decolorization did not occur (still more pigmented spots are visible compared to the raw cotton in Annex B). When looking at the yarn and the knitted structure of the dyed cotton before and after Fenton-treatment, it is visible that most of the remaining color is situated in the center of the yarn, where the fiber density is high which makes it difficult for the discoloring reagents to reach the dye-molecules. On fiber-scale, the black-dyed fibers turn out lighter and more grey-colored after treatment. Looking at the shape of the cotton fibers (twisted, with a kidney-bean intersection), no remarkable differences are to be found before and after treatment.

Thermogravimetric Analysis (TGA)

A plot of the weight percentage versus temperature and its derivative measured during TGA-tests of the black-dyed cotton and the discolored cotton are given in Graph 4.8.



Graph 4.8: plot of relative weight percentage in relation to temperature during TGA-testing of the black-dyed cotton before and after Fenton-treatment.

The mean decomposition temperatures and weight residue at 450°C with accompanying standard deviations are given in Table 4.1.

Table 4.1: mean decomposition temperatures and weight residues of the black-dyed and Fenton-treated cotton, measured during thermogravimetric analysis.

	black dyed	black Fenton
Decomposition temperature (°C)	356,82 $\pm$ 2,55	358,14 $\pm$ 0,47
Weight residue at T = 450°C (%)	16,70 $\pm$ 0,38	25,10 $\pm$ 0,62

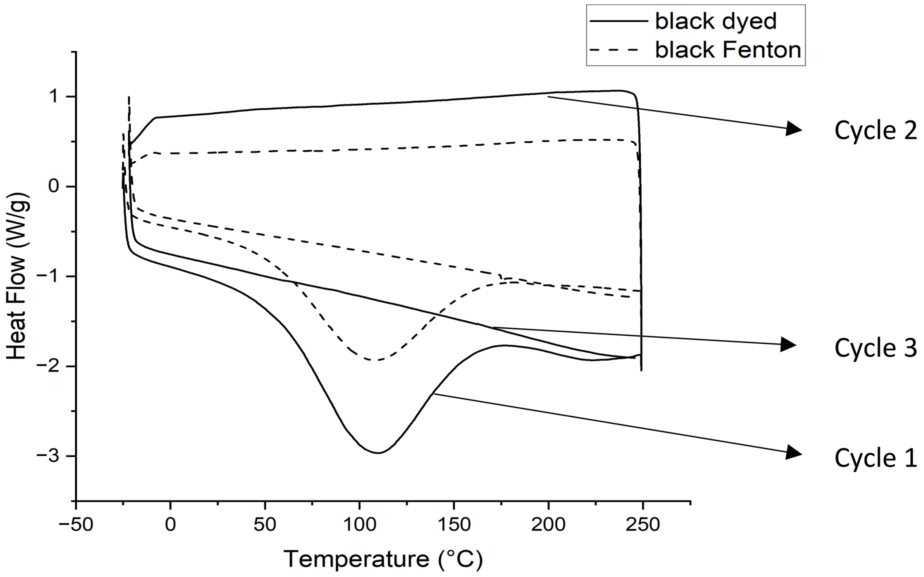
A t-test (α = 0,05 and n = 3) between the values of the decomposition temperatures from dyed- and discolored cotton indicates a non-significant difference (p = 0,43). However, the mean weight-residue increased significantly after Fenton treatment (p < 0,001).

In the TGA-plot, a small initial weight loss between 30 and 110°C is visible, which is attributed to the vaporization and loss of water physically bound to the fibers (Trivedi, 2015). The big second weight loss (between 220 and 450°C) is due to the decomposition of the cellulosic structure of the fiber (Portella et al., 2016), with a decomposition temperature (T at maximum decomposition rate) of around 357°C for the black-dyed cotton.

Significantly more residue after the Fenton treatment is visible compared to the dyed fabric. In literature, the reactive-dyeing process of cotton increases the amount of residue during TGA-tests by enhancing a low-energy reaction of transforming the cellulose into char residue instead of volatilizing the cellulose into flammable gasses in high-energy reactions, which also leads to a decrease in decomposition-temperature (Badri, 2008). The achieved TGA-results indicate that the Fenton-treatment increases the char-formation and therefore the remaining weight residue even further.

Differential Scanning Calorimetry (DSC) Analysis

A plot of the heat flow versus temperature measured during DSC-tests of the black-dyed cotton and black Fenton-treated cotton is given in Graph 4.9, and the separate cycles during DSC are indicated: cycle 1 (heating from -25°C degrees up to 250°C), cycle 2 (cooling back down to -25°C) and cycle 3 (heating back to 250°C).



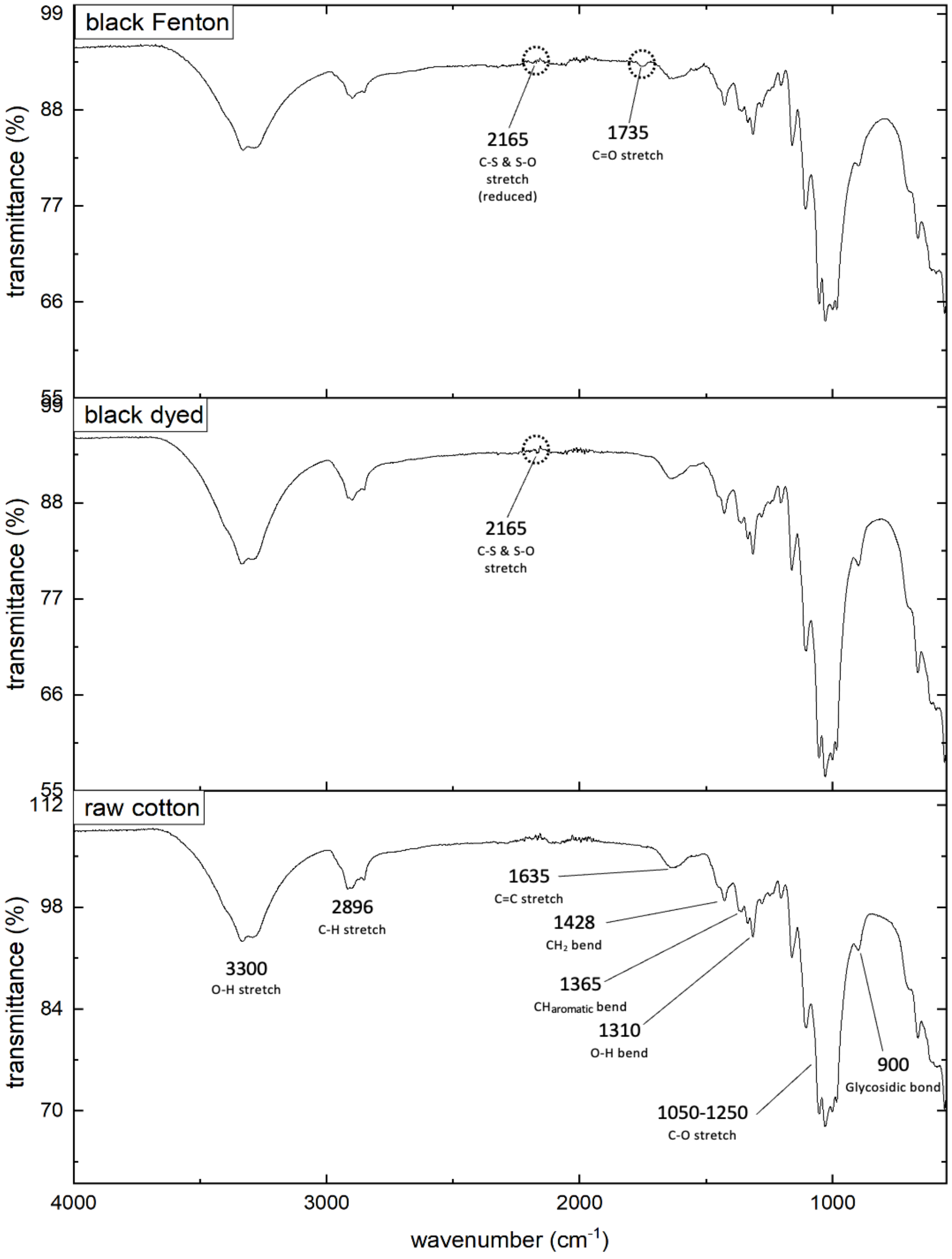
Graph 4.9: heat flow in relation to temperature measured during DSC-testing of the black cotton.

In cycle 1, an endotherm peak between 50 and 150°C due to the elimination of physically bound water (Trivedi et al., 2015) can be observed. The peak is spread over a broad range of temperatures because the water bound to the yarn-surface evaporates easily, while water bound by strong hydrogen bonding in the internal amorphous parts (or nanopores) of the cellulose requires more heat in order to be removed (Igarashi et al., 2020). Since the water is being removed in the first cycle, this endotherm peak is not visible anymore in the cycle 3.

It is also visible that the DSC-curves of the dyed and discolored cotton are shifted relative to each other, indicating that the Fenton-treated sample requires less heat for the same increase in temperature as for the dyed samples. In other words, the heat capacity of the cotton has changed due to the treatment. Because the heat capacity is linearly correlated to the crystallinity index (Blokhin et al., 2011), this reduction in heat capacity visible in the DSC-plots could be due to reduced crystallinity after the oxidative treatment.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Stacked plots of the transmission-spectra measured during FTIR-spectroscopy of the raw cotton, black dyed cotton and black Fenton-treated cotton are given below.



Graph 4.10: Stacked FTIR -spectra (transmittance % versus wavenumber) of raw cotton, black-dyed cotton and black Fenton-discolored cotton.

Based on information found in literature (Nikonenko et al., 2000; Portella et al., 2016), the most characteristic peaks of cotton are marked in the spectrum of raw cotton in Graph 4.10. The spectra of the dyed and Fenton-treated cotton show the same peaks, indicating that the main structure of the cotton is not altered due to the treatments.

However, there are some small additional peaks present in the spectra of the dyed cotton and Fenton-treated cotton which are not visible for raw cotton. Firstly, two small peaks around 2165-2170 cm^{-1} are visible in the spectrum of the dyed cotton, and also reduced but still visible in the spectrum of the Fenton-treated samples. These small peaks may be due to low amounts of C-S and S-O bonds present in the dye-molecules. The reduction of these peaks in the spectra of the Fenton-treated samples may indicate the degradation of the dye-molecules due to the treatment.

Another peak which is not appearing in the spectrum of raw cotton, is the peak around 1735-1740 cm^{-1}, which may be attributed to C=O bonds (Sigma Aldrich, 2023). This bond is not present in the black dye (Figure 2.3) and therefore not visible in the black-dyed cotton spectrum. However, this peak is visible after treatment, which could indicate that not only the dye-molecules are being oxidized in the Fenton-reaction, but also the chain-structure of the cellulosic fiber is attacked by the hydroxyl-radicals. Figure 4.11 shows the bonds in the cellulose structure which are most sensitive to oxidation: the C=C bonds in the aromatic structures (which would lead to opening of the ring-structure) and hydroxyl- or ether-groups which can be oxidized into carbonyl groups, which could lead to higher C=O signals in the infrared spectra (Hellström et al., 2014).

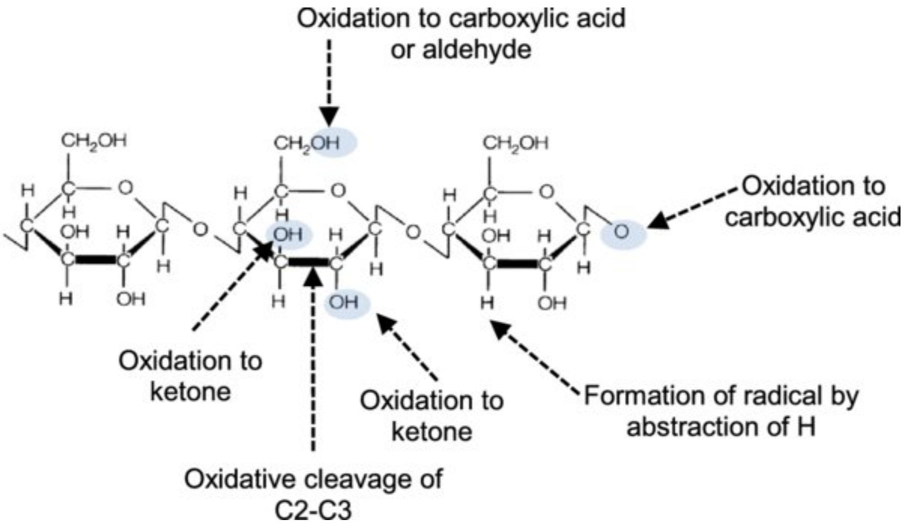
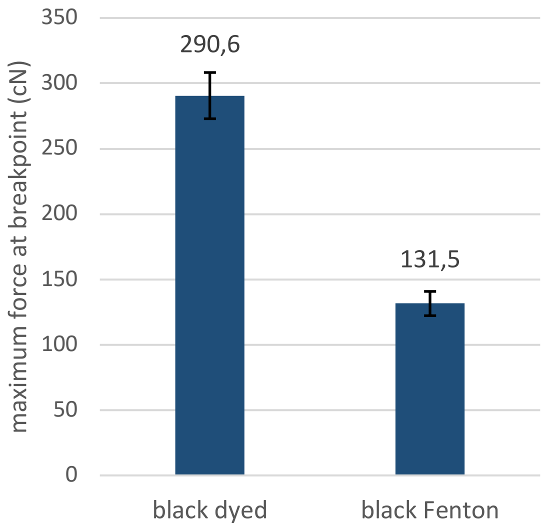


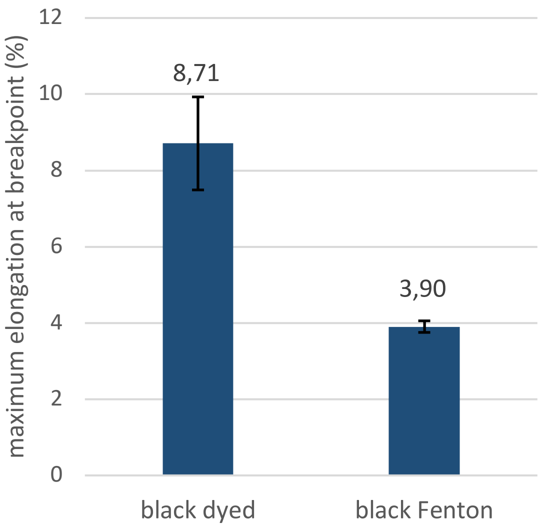
Figure 4.11: Positions in the cellulose chain sensitive to oxidation reactions (Hellström et al., 2014).

Tensile Testing Analysis

Mean values of the force and elongation at breakpoint (measured during tensile-tests) of the black-dyed cotton before and after Fenton-treatment are given below. For the black-dyed cotton, the Fenton-treatment causes a decrease in maximum force (of 54,7%) and maximum elongation (of 55,2%) compared to the dyed cotton. T-tests (with $\alpha = 0{,}05$ and $n = 10$) between the obtained values of the dyed cotton and Fenton-treated cotton indicate significant differences (with $p < 0{,}001$ for both units).



Graph 4.12: mean values of maximum force at breakpoint of the raw cotton, black-dyed cotton and Fenton-treated cotton, measured during tensile testing of the unraveled yarn.



Graph 4.13: mean values of maximum elongation at breakpoint of the raw cotton, black-dyed cotton and Fenton-treated cotton, measured during tensile testing of the unraveled yarn.

These reductions in tensile strength and elongation could indicate distortion of the cellulosic fiber-structure by the oxidative treatment, since the hydroxyl-radicals might also attack unsaturated bonds (such as C=C in the aromatic structures, leading to opening of the ring-structures) or oxygen-atoms from hydroxyl- or ether-groups in the cellulosic chain. The oxidation leading to opened ring-structures would distort the ordered crystalline regions of the cotton fibers and the intermolecular hydrogen-bonds, leading to reduced tensile strength (Balani et al., 2015). This is in line with the results from the thermal analysis, indicating the oxidation of the cellulosic structure and accompanying decrease in crystallinity.

4.2.2 Analysis of Discoloration of Blue-dyed Cotton

Digital Image Analysis

Pictures of the blue-dyed cotton before and after the Fenton-oxidation based discoloration treatment (Figure 4.14) show that color was removed but complete decolorization did not occur, and the tone of the color changed from blue to green. Further analysis was carried out below for quantification of the discoloration.

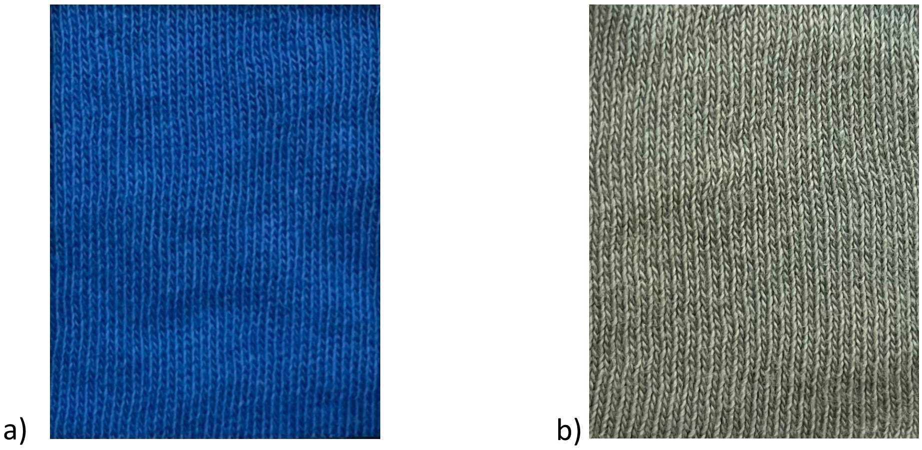


Figure 4.14: pictures of the blue-dyed knitted cotton before (a) and after (b) Fenton-treatment.

K/S Analysis

Spectrophotometry of the blue-dyed cotton before and after the upscaled Fenton-oxidation based discoloration treatment (Figure 4.15) shows reduced color strength with an accompanying mean discoloration percentage of 72,90% at $\lambda_{max} = 610$ nm. A paired t-test of the K/S-values before and after the treatment (with α = 0,05 and n = 3) indicates a significant discoloration ($p < 0,001$) due to the Fenton-oxidation.

For both the black- and blue-dyed cotton, the discoloration percentages achieved in these upscaled treatments (61,54% for the black-dyed cotton, 72,90% for the blue-dyed cotton) are much higher than the efficiencies achieved during pre-treatment (20,46% and 42,71% respectively). This increased efficiency could be due to two reasons. First of all, the pre-wetting step which is added in the upscaled treatment enhances the reaction with the rather hydrophobic raw dyed cotton in the water-based Fenton-solution. Secondly, a rather old batch of H_2O_2-solution was used during the preliminary tests, while a new batch was used for the upscaled treatments. Since H_2O_2-solutions are relatively unstable, the old batch probably did not contain the initial amount of active H_2O_2 as is present in a newly ordered batch.

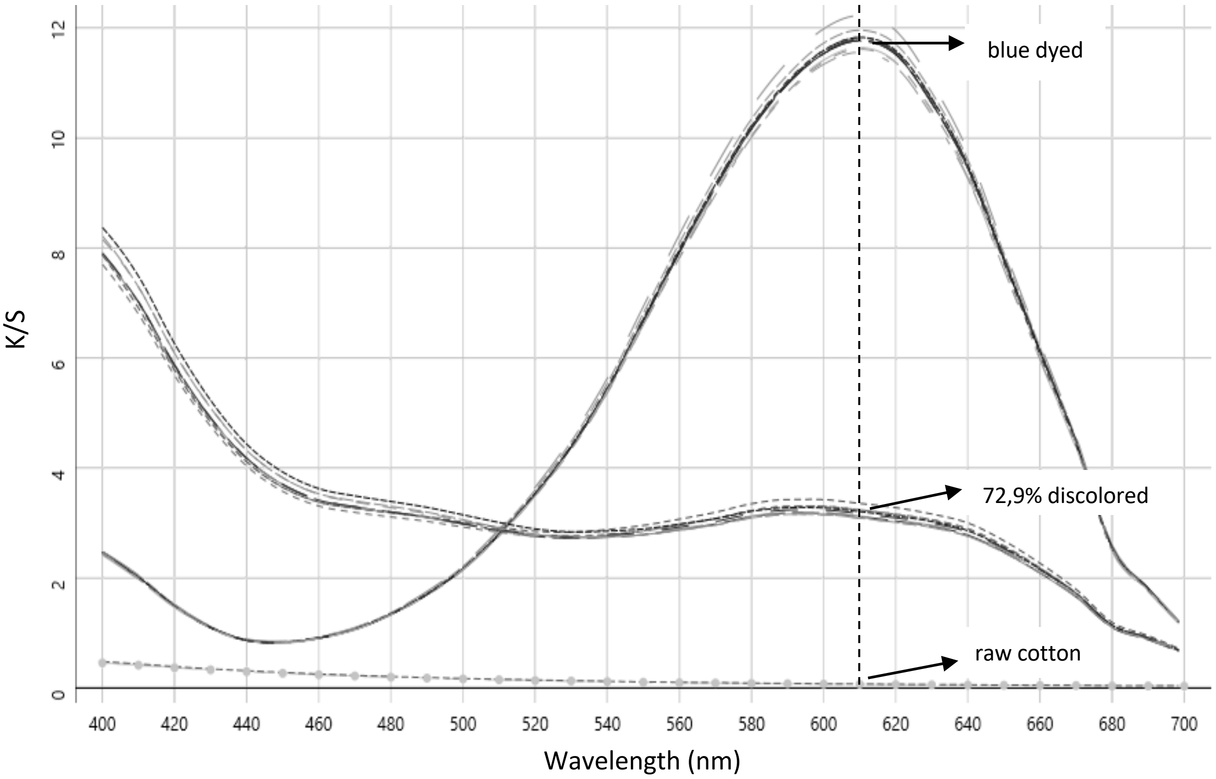


Figure 4.15: plot of measured K/S-values of blue cotton before and after Fenton-treatment.

For the Fenton-treated black-dyed cotton (Figure 4.4), the color strength is more or less evened out over the full visible-range, which leads to a grey-colored treated sample (also visible in Figure 4.3). For the blue dye however, a shift towards absorption of shorter wavelengths is visible (Figure 4.15), leading to a green appearance of the treated sample (also visible in Figure 4.14). This change in chromaticity indicates that the chromophore groups of the dye-molecules bound to the fabric are not fully degraded, yet the molecular structure of the dye is changed leading to modification of the absorption behaviour (Bechtold & Pham, 2019).

A difference in sensitivity to the oxidation-mechanism is indicated by the difference in discoloration-percentages for both dyes. This might be caused by the chemical structure of the dyes (Figure 2.3): the less substituted anthraquinone ring in the blue dye-molecule (Reactive Blue 19) is more easily distorted than a di-azo-chromophore group attached to several aromatic structures in the black dye (C.I. Reactive Black 5) (Tang & Chen, 1996). Moreover, the black dye contains two binding groups, making it more securely bound to the cotton fibers and therefore more stable.

Optical Microscopic Analysis

Microscopy-images of the knitted structure, the yarn and the fiber of the blue-dyed cotton before and after the Fenton-oxidation based discoloration treatment are given below.

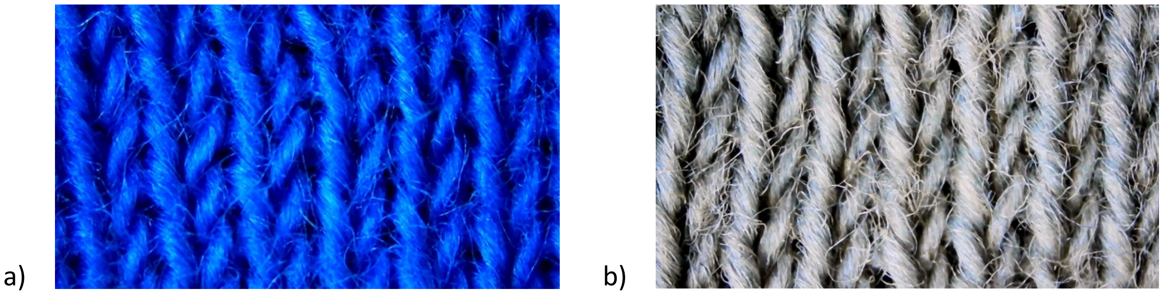


Figure 4.16: microscope-images of knitted structure of blue-dyed cotton before (a) and after (b) Fenton-treatment.

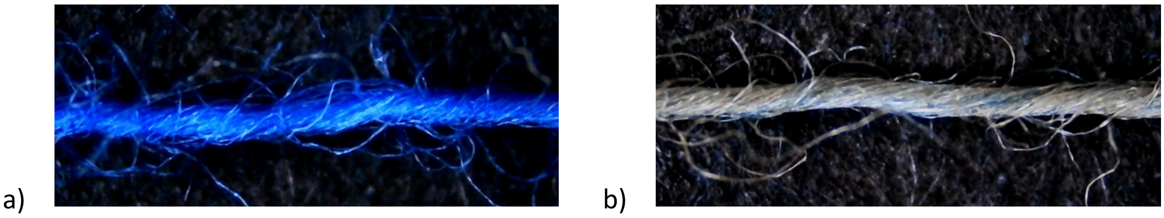


Figure 4.17: microscope-images of blue-dyed cotton yarns before (a) and after (b) Fenton-treatment.

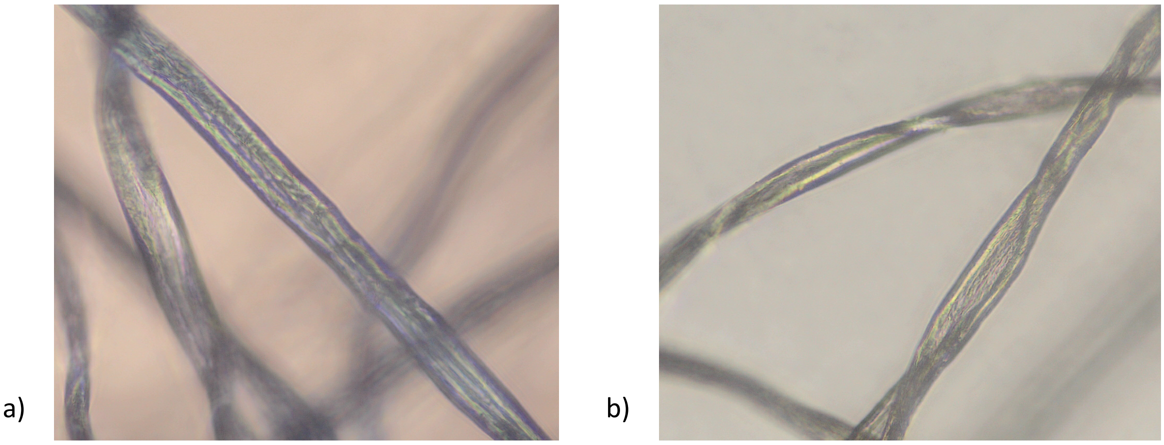
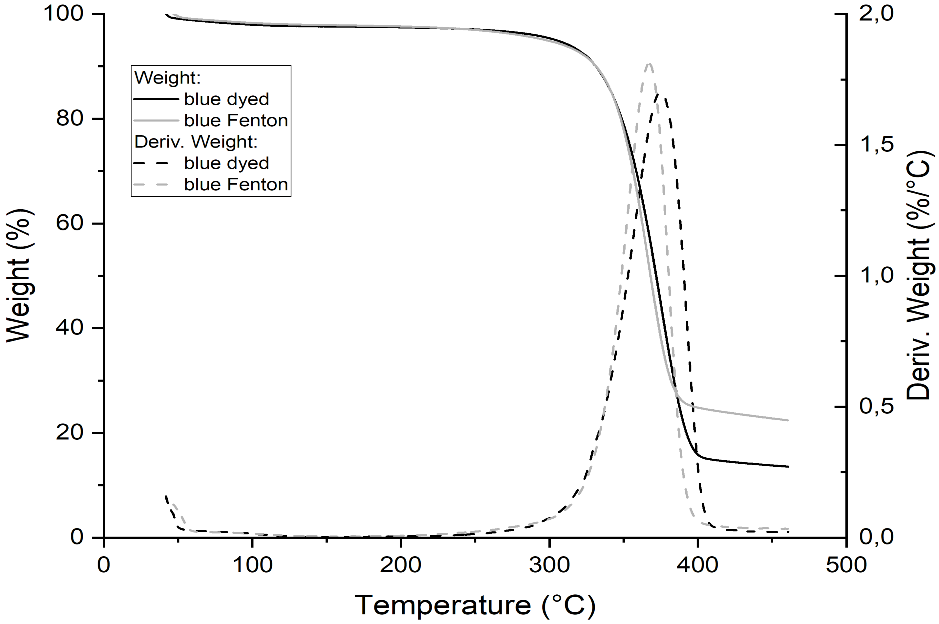


Figure 4.18: microscope-images of blue-dyed cotton fibers before (a) and after (b) Fenton-treatment.

Also for the blue-dyed cotton, it is visible that color was removed, but complete decolorization did not occur (still more pigmented spots are visible compared to the raw cotton in Annex B), and most of the remaining color is situated in the center of the yarn. On fiber-scale, the blue-dyed cotton fibers show a green tone after treatment. When looking at the shape of the cotton fibers, no remarkable differences are to be found before and after treatment.

Thermogravimetric Analysis (TGA)

A plot of the weight percentage versus temperature and its derivative measured during TGA-tests of the blue-dyed cotton are given in Graph 4.19.



Graph 4.19: plot of relative weight percentage in relation to temperature during TGA-testing of the blue-dyed cotton before and after Fenton-treatment.

The mean decomposition temperatures and weight residue at 450°C with accompanying standard deviations are given in Table 4.2.

Table 4.2: mean decomposition temperatures and weight residues of the blue-dyed and Fenton-treated cotton, measured during thermogravimetric analysis.

	blue dyed	blue Fenton
Decomposition temperature (°C)	373,77 ± 1,10	365,36 ± 1,48
Weight residue at T = 450°C (%)	13,28 ± 0,48	23,04 ± 0,42

Figure 4.19 shows a slight but significant ($p = 0,001$) decrease in decomposition temperature after Fenton-treatment and a significant ($p < 0,001$) increase in mean weight-residue after Fenton treatment.

Similar to the TGA-plots of the black-dyed cotton, a small initial weight loss between 30 and 110°C due to vaporization and loss of water is visible (Trivedi, 2015), and a big weight loss between 250 and 450°C due to the decomposition of the cellulosic structure of the fiber (Portella et al., 2016), with a decomposition temperature around 374°C. This higher decomposition temperature compared to the black-dyed cotton (357°C) might be attributed to the bigger molecular structure of the black dye compared to the blue dye (Figure 2.3), which would distort the crystalline regions of the cotton more due to distorting the intermolecular hydrogen bonds between the cellulose chains responsible for ordered crystalline zones in the cellulose fibers (Figure 4.20). Lower crystallinity can accelerate the degradation process and therefore reduce the thermal stability of the fiber (Poletto et al., 2014).

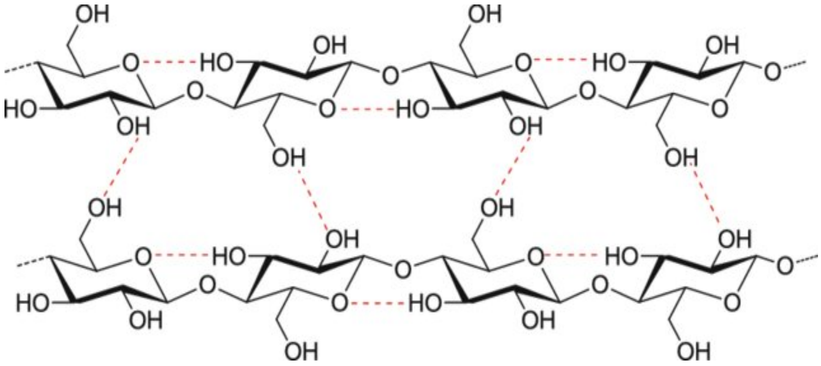


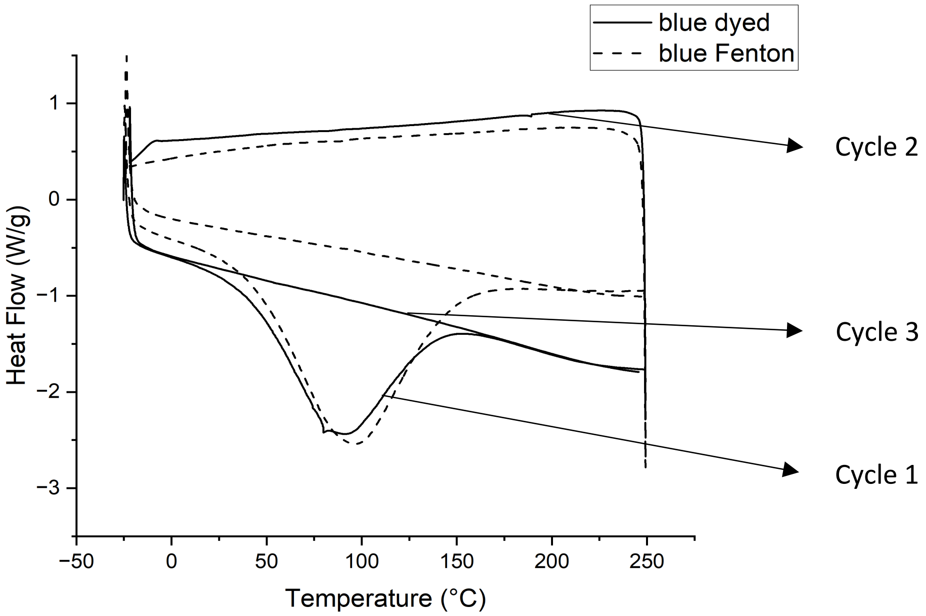
Figure 4.20: Schematic drawing of the molecular structure of cellulose chains and the hydrogen bonding network within the chains ('intramolecular') and between the chains ('intermolecular') (Li & Liu, 2015).

Unlike the black-dyed cotton, the decomposition temperature of the blue-dyed cotton is significantly influenced by the treatment (decreases to around 365°C). This might possibly indicate a bigger decrease in crystallinity after the Fenton-treatment for the blue-dyed cotton due to the same reason as was mentioned above: the crystalline zones of the black-dyed cotton are already more distorted after the dyeing-process due to the bigger molecular structure of the black dye (Figure 2.3). However, further investigation of the crystallinity of the fibers is necessary to make any decisive conclusions on this matter.

Also here, significantly more residue after the Fenton treatment is visible compared to the dyed fabric, indicating enhanced low-energy reactions of transforming the cellulose into char residue instead of volatilizing the cellulose into flammable gasses in high-energy reactions (Badri, 2008).

Differential Scanning Calorimetry (DSC) Analysis

A plot of the heat flow versus temperature measured during DSC-tests of the blue-dyed cotton and black Fenton-treated cotton is given in Graph 4.21, and the separate cycles during DSC are indicated.



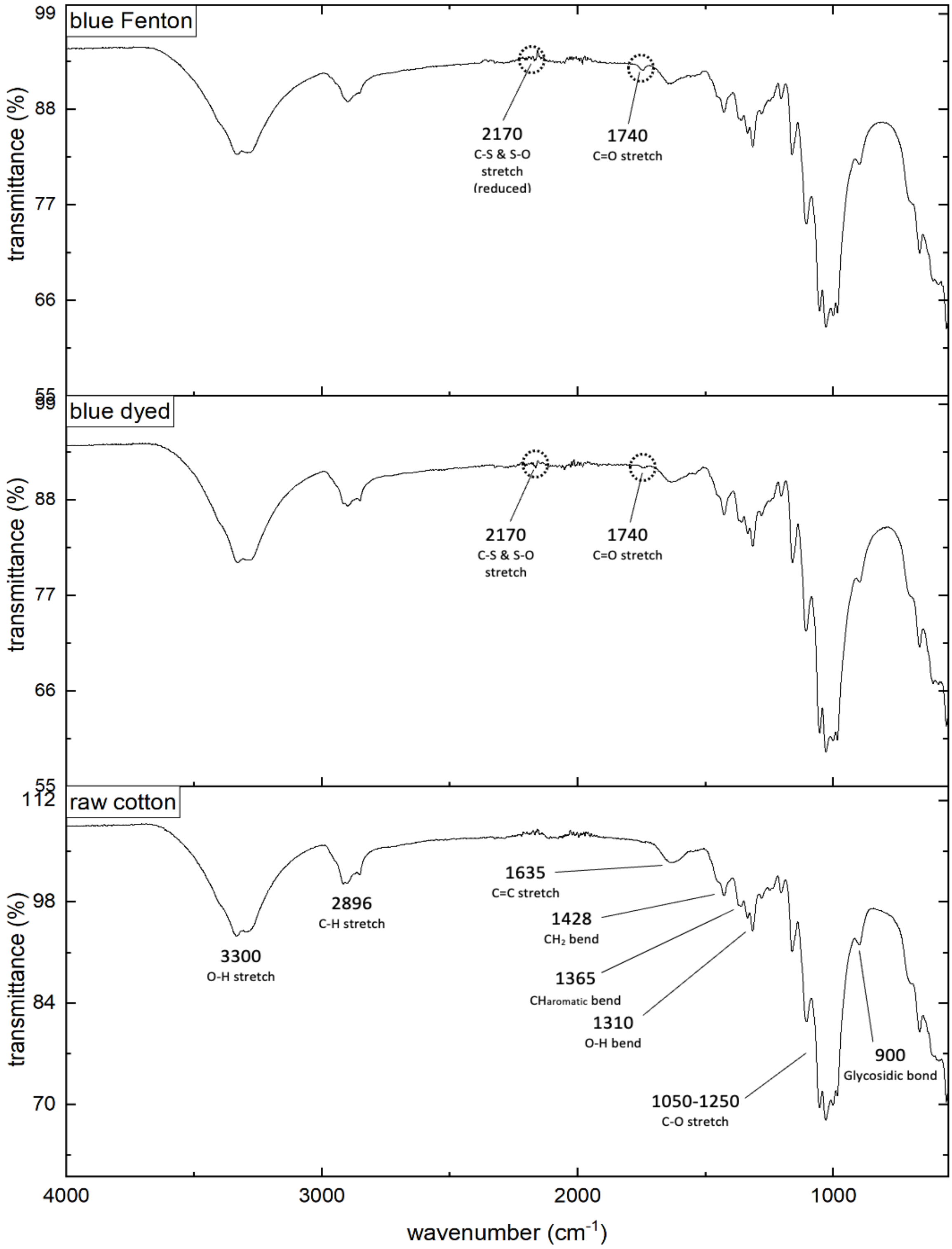
Graph 4.21: curves of heat flow in relation to the temperature during the 3 cycles of the DSC-testing of the blue-dyed cotton before and after Fenton-treatment.

Similar to the black-dyed cotton, an endotherm peak between 50 and 150°C due to the elimination of physically bound water can be observed in cycle 1 (Trivedi et al., 2015). Since the water is being removed in the first cycle, this endotherm peak is not visible anymore in the cycle 3.

Also here, the curves are shifted relative to each other, indicating that the Fenton-treatment might decrease the heat capacity of the cotton. As was already mentioned for the black-dyed cotton, this reduction in heat capacity could be caused by reduced crystallinity after the oxidative treatment due to a linear correlation between the heat capacity and the crystallinity index (Blokhin et al., 2011).

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Stacked plots of the transmission-spectra measured during FTIR-spectroscopy of the raw cotton, blue dyed cotton and blue Fenton-treated cotton are given below.



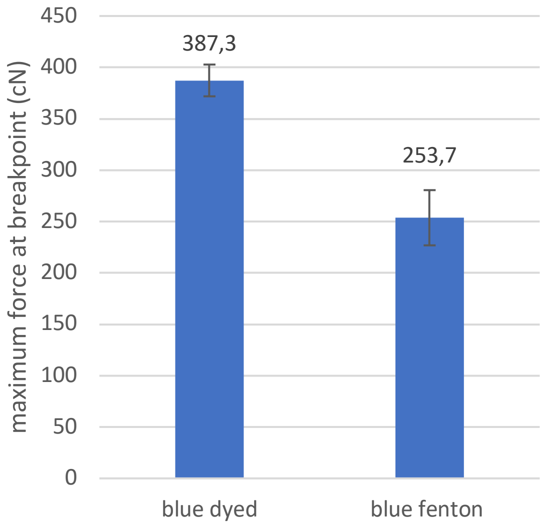
Graph 4.22: Stacked FTIR -spectra (transmittance % versus wavenumber) of raw cotton, blue-dyed cotton and blue Fenton-discolored cotton.

The spectra of the dyed and Fenton-treated cotton show the same characteristic peaks as indicated in the spectrum of raw cotton in Figure 4.22 (based on Nikonenko et al. (2000) and Portella et al. (2016)), indicating that the main structure of the cotton is not altered due to the treatment.

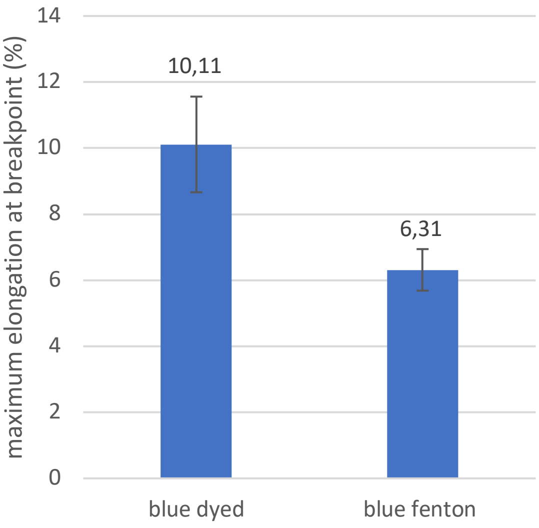
However, also for the blue-dyed cotton, some small additional peaks are present in the spectra of the dyed cotton and Fenton-treated cotton which are not visible for the raw cotton: the two small peaks around 2165-2170 cm^{-1} visible in the spectrum of the dyed cotton and reduced but still visible in the spectrum of the Fenton-treated samples, which may be due to low amounts of C-S and S-O bonds present in the dye-molecules. The reduction of these peaks in the spectra of the Fenton-treated samples may indicate the degradation of the dye-molecules due to the treatment. Also the peak around 1735-1740 cm^{-1}, which may be attributed to C=O bonds (Sigma Aldrich, 2023), is visible in the spectrum of the blue-dyed cotton (blue dye contains C=O bonds, see Figure 2.3) and has increased slightly in intensity after treatment. Similar to the discussion of the black-dyed cotton, this might indicate the oxidation of the cellulosic chain-structure of the cotton fibers besides the degradation of the dye-molecules.

Tensile Testing Analysis

Mean values of the force and elongation at breakpoint of the blue-dyed cotton and blue discolored cotton are given in Graph 4.23 and 4.24.



Graph 4.23: mean values of maximum force at breakpoint of the raw cotton, blue-dyed cotton and black Fenton-treated cotton, measured during tensile testing of the unraveled yarn.



Graph 4.24: mean values of maximum elongation at breakpoint of the raw cotton, blue-dyed cotton and blue Fenton-treated cotton, measured during tensile testing of the unraveled yarn.

For the blue-dyed cotton, the Fenton-treatment causes a decrease in maximum force (of 34,5%) and maximum elongation (of 35,3%) compared to the dyed cotton. T-tests (with α = 0,05 and n = 10) between the obtained values of the dyed cotton and Fenton-treated cotton indicate significant differences (with p < 0,001 for both units).

Similar to the black-dyed cotton, these reductions in tensile strength and elongation could indicate distortion of the cellulosic fiber-structure by the oxidative treatment, leading to distorted crystalline regions of the cotton fibers and the intermolecular hydrogen-bonds, and consequently to reduced tensile strength, which is in line with the results from the thermal analysis, indicating the oxidation of the cellulosic structure and a decrease in crystallinity (Balani et al., 2015).

When comparing the Fenton-oxidation to industrial decolorization treatments, only one article which mentions the reduction in tensile strength due to several types of industrial decolorization agents can be found in literature. In Li et al. (2021), $KMnO_4$ causes a reduction in tensile strength of 50% for a decolorization 99,4% of cotton dyed with a dark blue reactive dye, and activated H_2O_2 causes a reduction in tensile strength of 32% for a decolorization of 96,4%.

The reduction percentages in tensile strength caused by industrial decolorization agents are in line with the reduction in tensile strength obtained for the Fenton-treated cotton. However, since results of only one source in literature are available for comparison, it is too early to make decisive conclusions about whether the Fenton-oxidation would be more or less harming for the fabric compared to current industrial decolorization agents. In order to gain more insight on this topic, a comparative study on the influence of industrial decolorization agents and Fenton-treatments on the physiological properties of the cotton should be performed.

4.2.3 Analysis of the Shredded Fabric

No quantitative measurements were made in this part of the mechanical testing. However, a qualitative description concerning the amount of opened fabric and the length of the remaining non-opened yarns and opened fibers of the raw cotton, dyed cotton and Fenton-treated cotton in relation to each other is given in Table 4.3. Accompanying images of these shredded residues can be found in Annex C.

Table 4.3: Description of the residue after shredding of the raw-, dyed- and Fenton-treated cotton.

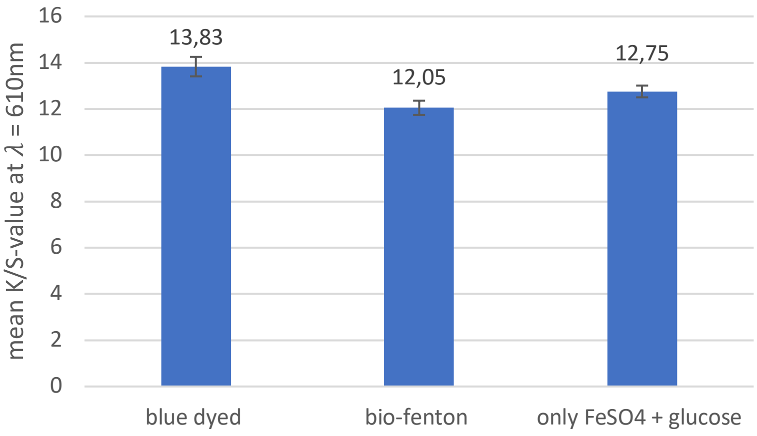
	Qualitative description of residue after shredding
Raw cotton	- Low amount of opened yarns - Non-opened yarns still rather long - Fibers from opened yarns still rather long
Black dyed cotton	- Low amount of opened yarns - Non-opened yarns shorter than raw cotton - Fibers from opened yarns still rather long
Blue dyed cotton	- Low amount of opened yarns - Non-opened yarns shorter than raw cotton - Fibers from opened yarns still rather long
Black discolored cotton	- highest amount of opened yarns - Non-opened yarns very short compared to black cotton - Fibers from opened yarns very short compared to black cotton
Blue discolored cotton	- high amount of opened yarns - Non-opened yarns shorter than blue dyed cotton - Fibers from opened yarns shorter than blue dyed cotton

The purpose of shredding is to open the fabric and yarns into fibers in order to re-spin the fibers during mechanical recycling. Bigger amount of opened fabric and longer remaining fibers is expected to enhance the mechanical recycling and the quality of the recycled yarns.

The dyeing-process does not seem to affect the amount of opened fabric. The Fenton-oxidation, however, enhances the opening of the fabric notably (see images in Annex C), which is expected to facilitate re-spinning in mechanical recycling. Nevertheless, the opened yarns of the Fenton-treated cotton also contain much shorter fibers than the dyed cotton, which could affect the quality of the mechanically recycled fiber after re-spinning negatively.

4.3 Analysis of Concept Study of Bio-Fenton Oxidation based Discoloration of Blue-dyed Cotton Fabric

The measured K/S-values of the blue-dyed cotton, the bio-Fenton treated cotton and the sample treated with only the iron-source and glucose are given in Graph 4.25. The bio-Fenton solution leads to a significant discoloration (p = 0,01) of 10,76% of the blue-dyed cotton, while the control-solution with only the iron-source and the glucose also already leads to a significant discoloration (p = 0,02) of 8,92%. The treatment of the blue-dyed cotton with a bio-Fenton solution gives a much lower discoloration percentage (10,76%) compared to what is achieved with chemical Fenton-solutions (72,90%). However, since the control-solution with only the iron-source and glucose also already leads to a discoloration of 8,92%, it is not possible to make any decisive conclusions about the efficiency of the bio-Fenton, since part of the discoloration could be caused by coagulation of the Fe^{3+} with the dye-molecules.

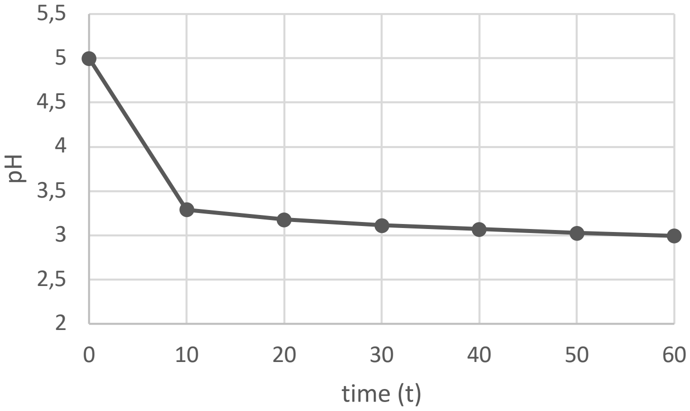


Graph 4.25: mean K/S-values of the blue-dyed cotton before and after treatment with the bio-Fenton solution in Table 3.2 and control treatment without enzyme.

The pH during the bio-Fenton treatments was monitored to be able to see the natural trend of the pH during the reaction. As mentioned in chapter 2, the performance of the enzyme is sensitive to external parameters such as pH. The enzyme is active within a pH-range of 4 – 8, and is optimally active at a pH of 5,5. However, the Fenton-mechanism works optimally at a much lower pH (2,5 – 4), and therefore a compatible pH which achieves acceptable activity for both mechanisms should be maintained. Therefore, the pH was altered to pH = 5 after adding the iron-source, and measured throughout the bio-Fenton reaction. A plot of the mean measured pH-values is given in Graph 4.26.

The increased discoloration-percentage caused by coagulation might be caused by the increased pH in which the reaction occurs (Graph 4.26: starts at pH ≈ 5, drops to pH ≈ 3) since a higher pH reduces the possibility of Fe^{3+} reducing back to Fe^{2+}, and increases the possibility of Fe^{3+} coagulating with the dye and contributing to the discoloration of the fabric.

Since the adaption of the pH (to pH = 5) is made after adding the iron-source, the bigger drop in pH in the first 10 minutes of the reaction might possibly be due the activity of the enzyme: producing the weak acids H_2O_2 and D-glucono-1,5-lactone. However, after this increase in acidity, the pH becomes too low for the enzyme to show much activity. Therefore, the pH still decreases a bit after the first 10 minutes of the reaction, but with a smaller relative decrease due to the decreased activity of the enzyme.



Graph 4.26: trend in pH during the initial trial of the bio-Fenton treatment.

In order to increase the activity of the enzyme during the full duration of the reaction, the pH should be kept at a higher value (between 4,5 – 5,5) during the reaction. However, this also increases the chance of Fe^{3+} coagulating with the dye, and therefore accumulative discoloration effects. In practice, accumulative discoloration has a positive effect on the decolorization efficiency of waste fabric, but in theory (where the purpose is to investigate the efficiency of the bio-Fenton mechanism compared to the chemical mechanism) this accumulative effect of coagulation should be avoided. A suggestion to avoid this issue in future research is to perform the bio-Fenton reaction in a 2-step reaction, where the enzyme first produces the H_2O_2 needed for the second step (Fenton-mechanism).

5. Conclusion

Although the sample size in this feasibility study is limited, the first applications of the chemical Fenton-oxidation for the color removal of reactive-dyed cotton already indicate promising discoloration percentages (61,54% for the black-dyed cotton and 72,90% for the blue-dyed cotton), even without complete optimization of all the parameters influencing the reaction-mechanism (such as pH, temperature, time, reagent concentrations, liquor ratio's…). Complete optimization of all these parameters via experimental design would lead to even better decolorization-results.

The analytical and mechanical tests of the treated fabrics indicate that the main structure of the cellulosic fibers is not altered. Nonetheless, besides oxidation of the dye-molecules, also some oxidation of the aromatic structure and hydroxyl- or ester-groups of the cellulosic chain occurs. This possibly also causes a reduction of the crystallinity of the cotton fibers, which might lead to the obtained decreased mechanical properties. However, this also leads to enhanced opening of the fabric into fibers during shredding, which facilitates mechanical recycling. Despite the enhanced opening, the fibers after shredding also turn out to be much shorter compared to the fibers before the discoloration-treatment, which is expected to lead to decreased quality of the res-pun fibers after mechanical recycling.

When comparing the amount of chemicals and the temperature required for activated hydrogen peroxide decolorization, where 0,5 – 1M H_2O_2 at 70-90°C and pH $\approx$ 10 for 60 to 180 minutes leads to discoloration percentages of 50 – 96% (see chapter 2.2), the Fenton-treatments in this thesis-project only require 0,28M H_2O_2, at a temperature of 40°C for 60 minutes while achieving discoloration percentages of 62 – 73%. Therefore, already much lower amounts of the toxic and flammable chemicals and lower temperatures are required. Moreover, when complete optimization of the process-parameters is performed, even higher decolorization efficiencies will be achieved, and milder conditions (lower temperature, lower concentrations, higher pH) might possibly be allowed while still achieving acceptable decolorization efficiencies.

An initial concept study of the bio-Fenton mechanism, aiming to increase the sustainability of the process by eliminating the toxic and flammable reagent H_2O_2, did not lead to any conclusive results about the efficiency of the bio-Fenton mechanism due to increased contribution of coagulation of Fe^{3+} with the dye-molecules to the discoloration of the fabric caused by the higher pH in which the bio-Fenton occurs. However, it can be concluded that the pH at which the bio-Fenton occurred in this thesis-project was too low for the enzyme to have acceptable activity, and should be increased for future experiments. However, increasing the pH also increases the chance of accumulative effect of coagulation of the Fe^{3+}. This might be avoided by trying to perform the bio-Fenton in a two-step reaction, with a first step of producing the H_2O_2 which is needed for the second step with the Fenton-mechanism.

An attempt to answer the research questions reads as follows: the use of Fenton-oxidation is a feasible mechanism for the discoloration of reactive dyed cotton. However, besides the degradation of the dye-molecules, also some oxidation of the cellulosic chain occurs, leading to decreased crystallinity which significantly influences the mechanical and thermal properties of the cotton. Nonetheless, these reduced mechanical properties also facilitate the mechanical recycling process, but possibly decrease the quality of the re-spun yarns after recycling. In order to gain more knowledge about the effect of the treatment on the fiber-length and mechanical recyclability of the cotton fibers after shredding, further research is suggested. Nevertheless, the Fenton-treatment as a more sustainable decolorizing pre-treatment for recycling remains a research subject with potential and interesting prospects for further investigation.

6. Sustainability and Environmental Concerns

6.1. Scientific Relevance

Until now, the discoloration of reactive dyed cotton by means of Fenton-oxidation still formed a gap in research. Therefore, this thesis is a first step in providing insight into whether or not the Fenton-oxidation is feasible for discoloration of waste fabric, and how interesting this mechanism might be for further research. The conclusions drawn from this master-thesis indicate that Fenton-oxidation based discoloration of waste fabric is indeed an interesting research-topic which can be elaborately researched in the future by other academic or industrial research-teams looking to increase the sustainability of the preparatory discoloring treatment for textile recycling. After thorough investigation of this discoloration process and investigation of the applicability on industrial scale, the Fenton-oxidation based color removal from waste cotton can possibly be applied for recycling-companies aiming to reduce their environmental impact.

6.2. Societal Relevance

As was mentioned in the previous chapters, decolorization of textiles is an important preparatory treatment for efficient recycling. Current industrial treatments decolorize the fabric efficiently but request high temperatures and concentrations of chemical agents which are harmful for the fabric and for the environment. Increasing the efficiency and the scale of the recycling process would reduce the amount of landfill and increase the circularity of materials. This would reduce the required amount of water and land and minimize the pollution accompanied with the production of new material. Increasing the sustainability of the recycling process would reduce the amount of energy, chemicals and water needed in order to make circularity of the materials possible. For these reasons, the search for efficient, environmental friendly decolorizing processes plays an important role in the reduction of pollution caused by the textile industry (which is currently one of the most polluting industries). Reducing the environmental impact of the textile industry would enhance life on earth by reducing the contribution to climate change. This research-topic tackles UN's Sustainable Development Goals number 9 ('Industry, Innovation and Infrastructure'), number 12 ('Responsible Consumption and Production'), number 13 ('Climate Action') and number 17 ('Partnership for the Goals').

7. Suggestions for Future Work

This master thesis has shown that the Fenton-oxidation is a promising mechanism for discoloration of waste fabric; already 62-73% discoloration was achieved without a completely optimized process. Further increase of this discoloration-efficiency could be achieved by Design of Experiment to optimize all process-parameters in additional research. Also the use of dyed fibers in nonwovens instead of twisted into yarns in a fabric-structure could lead to better results, since the solution will be able to reach all the dye-molecules more easily. This might allow better understanding of the mechanism in future concept-studies.

Concerning the environmental impact of the mechanism, the process also has to be non-toxic towards the environment and life on earth besides the reduction of the required amount of chemicals and energy. Therefore, future research should investigate the toxicity of the residues remaining in the Fenton-solution and on the fabric. Moreover, also iron is added to the Fenton-solution, which contributes to pollution of the effluents as well. Therefore, collecting and regenerating the Fe-catalysts, for example by fixation on magnetic particles, could be interesting to investigate for further increase of the sustainability of the Fenton-oxidation of waste fabric. Furthermore, to be able to officially claim that Fenton-oxidation is a more sustainable decolorization process, a thorough comparative study on the influence of the treatments on the environment and the textile-materials between the current industrial decolorization processes and the Fenton-oxidation should also be performed.

Efficient use of the Bio-Fenton process would further increase the sustainability of the Fenton-decolorization process, by avoiding the need to store, transport and add toxic and flammable hydrogen peroxide (Kahoush et al., 2018). However, the concept study on bio-Fenton-oxidation in this thesis project indicated that the pH at which the mechanism occurred was too low for the enzyme to have acceptable activity, and should be increased in future experiments. However, increasing the pH also increases the chance of accumulative effect of coagulation of the Fe^{3+}. In future research, this might be avoided by attempting to perform the bio-Fenton in a two-step reaction, with the production of the H_2O_2 as a first step, and the Fenton-mechanism as a second step. Furthermore, the enzymes used for the bio-Fenton-oxidation are expensive, and when used in a free state, additional steps for denaturation after the reaction (and consequently loss of the enzyme) further increase the cost of the complete operation. As a result, investigating the fixation of the enzymes in order to achieve reusability of the bio-catalyst is of interest for further increase in the sustainability in case of bio-Fenton.

To conclude, the Fenton-oxidation based discoloration of waste fabric has many more prospects for further increase of sustainability of the decolorization process, but this research is still in its infancy. Therefore, elaborate and thorough future research on this topic will have to be performed, in order know more about the impact of the treatment on the sustainability of the recycling process and gain insight on the applicability of this process in industry.

References

Aaron Lee. (2021). The EM Spectrum. In *Basic Lighting for Electricians: Level 1*. British Columbia/Yukon Open Authoring Platform.

Ajmal, A., Majeed, I., Malik, R. N., Idriss, H., & Nadeem, M. A. (2014). Principles and mechanisms of photocatalytic dye degradation on TiO2 based photocatalysts: a comparative overview. *RSC Adv.*, *4*(70), 37003–37026. https://doi.org/10.1039/C4RA06658H

Ameta, S. (2018). Chapter 1 - Introduction. In S. Ameta & R. Ameta (Eds.), *Oxidation Processes for Waste Water Treatment - Emerging Green Chemical Technology* (pp. 1–12). Academic Press.

Atav, R., Yüksel, M. F., Özkaya, S., & Buğdaycı, B. (2022). The Use of Ozone Technology for Color Stripping and Obtaining Vintage Effect on Reactive Dyed Cotton Fabrics. *Journal of Natural Fibers*, *19*(13), 6648–6658. https://doi.org/10.1080/15440478.2021.1929653

Badri, B. (2008). The influence of reactive dyes on the pyrolysis of cotton. *Journal of Analytical and Applied Pyrolysis*, *81*(2), 162–166. https://doi.org/10.1016/j.jaap.2007.10.001

Balani, K., Verma, V., Agarwal, A., & Narayan, R. (2015). Physical, Thermal, and Mechanical Properties of Polymers. In *Biosurfaces* (pp. 329–344). John Wiley & Sons, Inc. https://doi.org/10.1002/9781118950623.app1

Barros, A. L., Pizzolato, T. M., Carissimi, E., & Schneider, I. A. H. (2006). Decolorizing dye wastewater from the agate industry with Fenton oxidation process. *Minerals Engineering*, *19*(1), 87–90. https://doi.org/10.1016/j.mineng.2005.04.004

Bechtold, T., & Pham, T. (2019). *Textile Chemistry*. De Gruyter.

Blokhin, A. V., Voitkevich, O. V., Kabo, G. J., Paulechka, Y. U., Shishonok, M. V., Kabo, A. G., & Simirsky, V. V. (2011). Thermodynamic Properties of Plant Biomass Components. Heat Capacity, Combustion Energy, and Gasification Equilibria of Cellulose. *Journal of Chemical & Engineering Data*, *56*(9), 3523–3531. https://doi.org/10.1021/je200270t

Chen, T. Y., Kao, C. M., Hong, A., Lin, C. E., & Liang, S. H. (2009). Application of ozone on the decolorization of reactive dyes — Orange-13 and Blue-19. *Desalination*, *249*(3), 1238–1242. https://doi.org/10.1016/j.desal.2008.10.032

datacolor. (2023). *The Science of How We See Color—And Why We Need Spectrophotometers*. https://www.datacolor.com/blog/why-we-cant-agree-color-perception/

Eren, S. (2019). Photocatalytic Clearing of Disperse Dyed Polyester. *AATCC Journal of Research*, *6*(5), 10–15. https://doi.org/10.14504/ajr.6.5.2

Ghoneim, M. M., El-Desoky, H. S., & Zidan, N. M. (2011). Electro-Fenton oxidation of Sunset Yellow FCF azo-dye in aqueous solutions. *Desalination*, *274*(1–3), 22–30. https://doi.org/10.1016/j.desal.2011.01.062

Giwa, A.-R. A., Bello, I. A., Olabintan, A. B., Bello, O. S., & Saleh, T. A. (2020). Kinetic and thermodynamic studies of fenton oxidative decolorization of methylene blue. *Heliyon*, *6*(8). https://doi.org/10.1016/j.heliyon.2020.e04454

He, J.-M., Xie, C.-F., & Long, J.-J. (2021). Sustainable color stripping of cotton substrate dyed with reactive dyes in a developed UV/K2S2O8 photocatalytic system. *Journal of the Taiwan Institute of Chemical Engineers*, *121*, 241–256. https://doi.org/10.1016/j.jtice.2021.04.023

He, Z., Li, M., Zuo, D., & Yi, C. (2019). Color fading of reactive-dyed cotton using UV-assisted ozonation. *Ozone: Science & Engineering*, *41*(1), 60–68. https://doi.org/10.1080/01919512.2018.1483817

Hellström, P., Heijnesson-Hultén, A., Paulsson, M., Håkansson, H., & Germgård, U. (2014). The effect of Fenton chemistry on the properties of microfibrillated cellulose. *Cellulose*, *21*(3), 1489–1503. https://doi.org/10.1007/s10570-014-0243-1

Huang, Y.-H., Huang, Y.-F., Chang, P.-S., & Chen, C.-Y. (2008). Comparative study of oxidation of dye-Reactive Black B by different advanced oxidation processes: Fenton, electro-Fenton and photo-Fenton. *Journal of Hazardous Materials*, *154*(1–3), 655–662. https://doi.org/10.1016/j.jhazmat.2007.10.077

Igarashi, T., Hoshi, M., Nakamura, K., Kaharu, T., & Murata, K. I. (2020). Direct Observation of Bound Water on Cotton Surfaces by Atomic Force Microscopy and Atomic Force Microscopy-Infrared Spectroscopy. *Journal of Physical Chemistry C*, *124*(7), 4196–4201. https://doi.org/10.1021/acs.jpcc.0c00423

Kahoush, M. (2019). *Eco-Technologies for Immobilizing Redox Enzymes on Conductive Textiles, for Sustainable Development* . University of Borås.

Kahoush, M., Behary, N., Cayla, A., & Nierstrasz, V. (2018). Bio-Fenton and Bio-electro-Fenton as sustainable methods for degrading organic pollutants in wastewater. *Process Biochemistry*, *64*, 237–247. https://doi.org/10.1016/j.procbio.2017.10.003

Karimi, A., Aghbolaghy, M., Khataee, A., & Shoa Bargh, S. (2012). Use of Enzymatic Bio-Fenton as a New Approach in Decolorization of Malachite Green. *The Scientific World Journal*, *2012*, 1–5. https://doi.org/10.1100/2012/691569

Karmali, K., Karmali, A., Teixeira, A., & Curto, M. J. M. (2004). Assay for glucose oxidase from Aspergillus niger and Penicillium amagasakiense by Fourier transform infrared spectroscopy. *Analytical Biochemistry*, *333*(2), 320–327. https://doi.org/10.1016/j.ab.2004.06.025

Kaur, H., Hippargi, G., Pophali, G. R., & Bansiwal, A. K. (2019). Treatment methods for removal of pharmaceuticals and personal care products from domestic wastewater. In

Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology Emerging Contaminants and Micro Pollutants (pp. 129–150). Elsevier. https://doi.org/10.1016/B978-0-12-816189-0.00006-8

Kim, T.-H., Park, C., Shinb, E.-B., & Kim"’, S. (2004). Decolorization of disperse and reactive dye solutions using ferric chloride. In *Desalination* (Vol. 161).

Kim, T.-H., Park, C., Yang, J., & Kim, S. (2004). Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation. *Journal of Hazardous Materials*, *112*(1–2), 95–103. https://doi.org/10.1016/j.jhazmat.2004.04.008

Kuo, W. G. (1992). Decolorizing dye wastewater with Fenton’s reagent. *Water Research*, *26*(7), 881–886. https://doi.org/10.1016/0043-1354(92)90192-7

Li, R., Yang, J., Hu, J., Zhang, G., & Zhu, P. (2021). *Effects of Various Decolorizing Agents on Waste Cotton Fabric Dyed with Reactive Dyes*. https://doi.org/10.21203/rs.3.rs-825378/v1

Li, R., Yang, J., Zhang, G., & Zhu, P. (2022). Decolorization of dark-colored waste cotton fabric using redox decoloring agents. *RSC Advances*, *12*(28), 17689–17700. https://doi.org/10.1039/d2ra02071h

Lin, S. H., & Peng, C. F. (1995). Treatment of textile wastewater by Fenton’s reagent. *Journal of Environmental Science and Health . Part A: Environmental Science and Engineering and Toxicology*, *30*(1), 89–98. https://doi.org/10.1080/10934529509376187

Long, J.-J., Liu, B., Wang, G.-F., & Shi, W. (2017). Photocatalitic stripping of fixed Reactive Red X-3B dye from cotton with nano-TiO 2 /UV system. *Journal of Cleaner Production*, *165*, 788–800. https://doi.org/10.1016/j.jclepro.2017.07.149

Lou, J., Ren, L., Yuan, J., Xu, J., Gu, Z., & Fan, X. (2022). Mechanism and application of ozone fading: Oxidative decolorisation of disperse dyes and waste-dyed polyester fabrics. *Coloration Technology*. https://doi.org/10.1111/cote.12654

Määttänen, M., Asikainen, S., Kamppuri, T., Ilen, E., Niinimäki, K., Tanttu, M., & Harlin, A. (2019). Colour management in circular economy: decolourization of cotton waste. *Research Journal of Textile and Apparel*, *23*(2), 134–152. https://doi.org/10.1108/RJTA-10-2018-0058

Morshed, M. N. (2021). *Immobilizing catalysts on textiles- case of zerovalent iron and glucose oxidase enzyme* [Doctoral Thesis, University of Borås]. https://hb.diva-portal.org/smash/get/diva2:1553741/FULLTEXT01.pdf

Neppolian, B., Choi, H. C., Sakthivel, S., Arabindoo, B., & Murugesan, V. (2002). Solar/UV-induced photocatalytic degradation of three commercial textile dyes. In *Journal of Hazardous Materials* (Vol. 89).

Nikonenko, N. A., Buslov, D. K., Sushko, N. I., & Zhbankov, R. G. (2000). Investigation of stretching vibrations of glycosidic linkages in disaccharides and polysaccarides with use of IR spectra deconvolution. *Biopolymers*, *57*(4), 257–262. https://doi.org/10.1002/1097-0282(2000)57:4<257::AID-BIP7>3.0.CO;2-3

Özcan, A. A., & Özcan, A. (2018). Investigation of applicability of Electro-Fenton method for the mineralization of naphthol blue black in water. *Chemosphere*, *202*, 618–625. https://doi.org/10.1016/j.chemosphere.2018.03.125

Park, T. J., Lee, K. H., Jung, E. J., & Kim, C. W. (1999). Removal of refractory organics and color in pigment wastewater with fenton oxidation. *Water Science and Technology*, *39*(10–11). https://doi.org/10.1016/S0273-1223(99)00274-7

Poletto, M., Ornaghi, H., & Zattera, A. (2014). Native Cellulose: Structure, Characterization and Thermal Properties. *Materials*, *7*(9), 6105–6119. https://doi.org/10.3390/ma7096105

Portella, E. H., Romanzini, D., Angrizani, C. C., Amico, S. C., & Zattera, A. J. (2016). Influence of stacking sequence on the mechanical and dynamic mechanical properties of cotton/glass fiber reinforced polyester composites. *Materials Research*, *19*(3), 542–547. https://doi.org/10.1590/1980-5373-MR-2016-0058

Powar, A., Perwuelz, A., Behary, N., Hoang, L. V., Aussenac, T., Loghin, C., Maier, S. S., Guan, J., & Chen, G. (2021). Environmental profile study of ozone decolorization of reactive dyed cotton textiles by utilizing life cycle assessment. *Sustainability (Switzerland)*, *13*(3), 1–12. https://doi.org/10.3390/su13031225

Powar, A., Perwuelz, A., Behary, N., vinh Hoang, L., Aussenac, T., Loghin, C., Sergiu Maier, S., Guan, J., & Chen, G. (2021). Investigation into the color stripping of the pigment printed cotton fabric using the ozone assisted process: A study on the decolorization and characterization. *Journal of Engineered Fibers and Fabrics*, *16*, 155892502199275. https://doi.org/10.1177/1558925021992757

Powar, A. S., Perwuelz, A., Behary, N., Hoang, L., & Aussenac, T. (2020). Application of Ozone Treatment for the Decolorization of the Reactive-Dyed Fabrics in a Pilot-Scale Process—Optimization through Response Surface Methodology. *Sustainability*, *12*(2), 471. https://doi.org/10.3390/su12020471

Qutub, N., Singh, P., Sabir, S., Sagadevan, S., & Oh, W. C. (2022). Enhanced photocatalytic degradation of Acid Blue dye using CdS/TiO2 nanocomposite. *Scientific Reports*, *12*(1). https://doi.org/10.1038/s41598-022-09479-0

Rafiq, A., Ikram, M., Ali, S., Niaz, F., Khan, M., Khan, Q., & Maqbool, M. (2021). Photocatalytic degradation of dyes using semiconductor photocatalysts to clean industrial water pollution. *Journal of Industrial and Engineering Chemistry*, *97*, 111–128. https://doi.org/10.1016/j.jiec.2021.02.017

Ramos, M. D. N., Santana, C. S., Velloso, C. C. V., da Silva, A. H. M., Magalhães, F., & Aguiar, A. (2021). A review on the treatment of textile industry effluents through Fenton processes. *Process Safety and Environmental Protection*, *155*, 366–386. https://doi.org/10.1016/j.psep.2021.09.029

Rekhate, C. V., & Srivastava, J. K. (2020). Recent advances in ozone-based advanced oxidation processes for treatment of wastewater- A review. In *Chemical Engineering Journal Advances* (Vol. 3). Elsevier B.V. https://doi.org/10.1016/j.ceja.2020.100031

Shah, M., Dave, S., & Das, J. (2021). *Photocatalytic Degradation of Dyes - Current Trends and Future Perspectives*. Elsevier. https://doi.org/10.1016/C2020-0-00551-7

Sigma Aldrich. (2023). *IR Spectrum Table & Chart*. https://www.sigmaaldrich.com/SE/en/technical-documents/technical-article/analytical-chemistry/photometry-and-reflectometry/ir-spectrum-table

Singh, J., & Verma, N. (2013). Glucose oxidase from Aspergillus niger: Production, characterization and immobilization for glucose oxidation. *Pelagia Research Library Advances in Applied Science Research*, *4*(3), 250–257. www.pelagiaresearchlibrary.com

Song, S., He, Z., Qiu, J., Xu, L., & Chen, J. (2007). Ozone assisted electrocoagulation for decolorization of C.I. Reactive Black 5 in aqueous solution: An investigation of the effect of operational parameters. *Separation and Purification Technology*, *55*(2), 238–245. https://doi.org/10.1016/j.seppur.2006.12.013

Soon, A. N., & Hameed, B. H. (2011). Heterogeneous catalytic treatment of synthetic dyes in aqueous media using Fenton and photo-assisted Fenton process. *Desalination*, *269*(1–3), 1–16. https://doi.org/10.1016/j.desal.2010.11.002

Soutsas, K., Karayannis, V., Poulios, I., Riga, A., Ntampegliotis, K., Spiliotis, X., & Papapolymerou, G. (2010). Decolorization and degradation of reactive azo dyes via heterogeneous photocatalytic processes. *Desalination*, *250*(1), 345–350. https://doi.org/10.1016/j.desal.2009.09.054

Sun, S.-P., Li, C.-J., Sun, J.-H., Shi, S.-H., Fan, M.-H., & Zhou, Q. (2009). Decolorization of an azo dye Orange G in aqueous solution by Fenton oxidation process: Effect of system parameters and kinetic study. *Journal of Hazardous Materials*, *161*(2–3), 1052–1057. https://doi.org/10.1016/j.jhazmat.2008.04.080

Sundararaman, T. R., Ramamurthi, V., & Partha, N. (2009). Decolorization and COD Removal of Reactive Yellow 16 by Fenton Oxidation and Comparison of Dye Removal with Photo Fenton and Sono Fenton Process. *Modern Applied Science*, *3*(8). https://doi.org/10.5539/mas.v3n8p15

Swaminathan, K., Sandhya, S., Carmalin Sophia, A., Pachhade, K., & Subrahmanyam, Y. V. (2003). Decolorization and degradation of H-acid and other dyes using ferrous–hydrogen peroxide system. *Chemosphere*, *50*(5), 619–625. https://doi.org/10.1016/S0045-6535(02)00615-X

Swaminathan, K., Sandhya, S., Sophia, A. C., Pachhade, K., & Subrahmanyam, Y. V. (2003). Decolorization and degradation of H-acid and other dyes using ferrous-hydrogen peroxide system. *Chemosphere*, 619–625. www.elsevier.com/locate/chemosphere

Tang, W. Z., & Chen, R. Z. (1996). Decolorization Kinetics and Mechanisms of Commercial Dyes by H20~flron Powder System. In *Chemosphere* (Vol. 32, Issue 5).

Tao, Z., Raffel, R. A., Souid, A.-K., & Goodisman, J. (2009). Kinetic Studies on Enzyme-Catalyzed Reactions: Oxidation of Glucose, Decomposition of Hydrogen Peroxide and Their Combination. *Biophysical Journal*, *96*(7), 2977–2988. https://doi.org/10.1016/j.bpj.2008.11.071

Trivedi, K. M., Tallapragada, R. M., Branton, A., Trivedi, D., Nayak, G., Mishra, R. K., & Jana, S. (2015). Spectral and Thermal Properties of Biofield Energy Treated Cotton. *American Journal of Energy Engineering*, *3*(6), 86. https://doi.org/10.11648/j.ajee.20150306.12

United states Environmental Protection Agency. (2022, December 3). *Facts and Figures about Materials, Waste and Recycling*. United States Environmental Protection Agency. https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/textiles-material-specific-data

Vasquez-Medrano, R., Prato-Garcia, D., & Vedrenne, M. (2018). Ferrioxalate-Mediated Processes. In S. C. Ameta & R. Ameta (Eds.), *Advanced Oxidation Processes for Waste Water Treatment - Emerging Green Chemical Technology* (pp. 89–113). Elsevier. https://doi.org/10.1016/B978-0-12-810499-6.00004-8

Walger, E., Rivollier, C., Marlin, N., & Mortha, G. (2015). Activated hydrogen peroxide decolorization of a model azo dye-colored pulp. *Holzforschung*, *69*(6), 677–683. https://doi.org/10.1515/hf-2014-0294

Wang, S. (2008). A Comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater. *Dyes and Pigments*, *76*(3), 714–720. https://doi.org/10.1016/j.dyepig.2007.01.012

Wang, T., Le, T., Hu, J., Ravindra, A. V., Xv, H., Zhang, L., Wang, S., & Yin, S. (2022). Ultrasonic-assisted ozone degradation of organic pollutants in industrial sulfuric acid. *Ultrasonics Sonochemistry*, *86*, 106043. https://doi.org/10.1016/j.ultsonch.2022.106043

Yu, F.-Y., Li, C.-W., & Kang, S.-F. (2005). Color, Dye and DOC Removal, and Acid Generation During Fenton Oxidation of Dyes. *Environmental Technology*, *26*(5), 537–544. https://doi.org/10.1080/09593332608618535

Zainal, Z., Halim Abdullah, A., & Aqilah Mohd Fadzil, N. (2012). Ozone-assisted Decolorization of Methyl Orange via Homogeneous and Heterogeneous Photocatalysis Electrochemical Synthesis and Properties. In *Int. J. Electrochem. Sci* (Vol. 7). https://www.researchgate.net/publication/286098734

Zhou, X.-J., Guo, W.-Q., Yang, S.-S., Zheng, H.-S., & Ren, N.-Q. (2013). Ultrasonic-assisted ozone oxidation process of triphenylmethane dye degradation: Evidence for the promotion effects of ultrasonic on malachite green decolorization and degradation mechanism. *Bioresource Technology*, *128*, 827–830. https://doi.org/10.1016/j.biortech.2012.10.086

Zia, M. A., Rahman, K.-, Saeed, M. K., Andaleeb, F., Rajoka, M. I., Sheikh, M. A., Khan, I. A., & Khan, A. I. (2007). Thermal Characterization of Purified Glucose Oxidase from A Newly Isolated Aspergillus Niger UAF-1. *Journal of Clinical Biochemistry and Nutrition*, *41*(2), 132–138. https://doi.org/10.3164/jcbn.2007018

Zoldák, G., Zubrik, A., Musatov, A., Stupák, M., & Sedlák, E. (2004). Irreversible Thermal Denaturation of Glucose Oxidase from Aspergillus niger Is the Transition to the Denatured State with Residual Structure. *Journal of Biological Chemistry*, *279*(46), 47601–47609. https://doi.org/10.1074/jbc.M406883200

Zulfiqar, A., Arooj, F., Aftab, M., Rashid, M., Luqman, M., Kashif, S. ur R., & Naseer, R. (2023). A Sustainable Approach to Dyed Cotton Fabric Stripping Using Ozone. *Sustainability*, *15*(9), 7467. https://doi.org/10.3390/su15097467

Annex A – Preliminary Tests on Fenton-oxidation based Discoloration of Reactive-dyed Cotton Fabric

A.1 Materials

For the Fenton-processes, Fe^{2+} from iron(II)sulfate hepta-hydrate ($FeSO_4x7H_2O$, ≥99.0% purity, SIGMA-ALDRICH) and hydrogen peroxide (H_2O_2, 35 wt%, Merck) are used to make a Fenton-solution with de-ionized water. Also Fe^{3+} from iron(III)chloride ($FeCl_3$, 98% purity, Fisher Scientific) and 0,1M-solution of citric acid ($C_6H_8O_7$, 99% purity, SIGMA-ALDRICH) are used in several parts of the preliminary-tests.

A.2 Methods

A.2.1 Influence of Increased Solution-concentration on Discoloration Efficiency

Four different concentrations are tested: the first treatment will be according to the optimal concentrations for Fenton-discoloration of dye-solution (Table 2.4), while the concentrations for the other three treatments are found by multiplying the optimal concentrations in Table 2.4 by 2, 4 and 8. The conditions used in these four treatments are presented in Table A.1

Cotton fabric-samples of 5x5cm are treated in 100 ml solution, according to the conditions in Table A.1, for both the black- and the blue-dyed fabric. For each dye, these pre-tests are repeated 4 times. The temperature is kept at 40°C by a warm-water-bath and the diffusion is ensured by magnetic mixing bars (stirring at 400 rpm). After the 60 minutes, the fabric-samples are rinsed and left to dry.

Table A.1: Four different conditions used in pre-tests, for a fabric of 5x5cm in 100 ml solution.

	$[Fe^{2+}]$ (mM)	$[H_2O_2]$ (mM)	T (°C)
Fenton 1	3,5	70	40
Fenton 2	7	140	40
Fenton 3	14	280	40
Fenton 4	28	560	40

During the reaction, the pH is not altered by addition of extra buffer and/or acids or bases. However, the trend in pH during the reaction will be monitored by measuring the pH with a pH-sensor (FiveEasy Standard pH Meter Line, Mettler Toledo) every 20 minutes.

A.2.2 Influence of Fe-source on Discoloration Efficiency

The optimal conditions from the previous part of the pre-tests (Fenton 3; see results in section A.3.1) is repeated, but now with $FeCl_3$ as the iron source.

During this reaction, the pH is not altered by addition of extra buffer and/or acids or bases. However, the trend in pH during the reaction will be monitored by measuring the pH with a pH-sensor (FiveEasy Standard pH Meter Line, Mettler Toledo) every 20 minutes.

A.2.3 Contribution of Coagulation to Discoloration

The optimal conditions from the previous part of the pre-tests (Fenton 3; see results) will be repeated, but now without H_2O_2 (only with the Fe-source). This test is performed for both dyes, with both Fe-sources ($FeSO_4x7H_2O$ and $FeCl_3$).

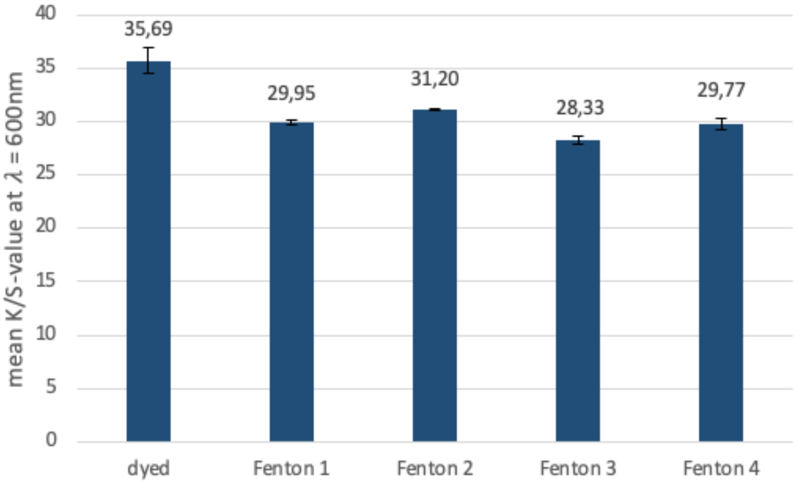
The pH is altered to the pH in which Fenton 3 occurs ($pH \approx 2{,}5$ for $FeSO_4$, $pH \approx 2$ for $FeCl_3$, see results in section A.3.1 and A.3.2), by adding some drops of 0,1M-solution of citric acid.

A.3 Results and Discussions

A.3.1 Influence of Solution-concentration on Discoloration

Black-dyed Cotton

A plot with mean K/S-values of the black-dyed cotton and the samples discolored with increasing Fenton-solution concentrations (Fenton 1 – Fenton 4) are given in graph A.1. From these K/S-values, the associated discoloration percentages of the black-dyed fabric can be calculated according to $eq. 2$, and are given in Table A.2.



Graph A.1: mean K/S-values of the black-dyed cotton before and after Fenton treatments with increasing concentrations according to Table A.1.

Table A.2: mean discoloration percentages of the black-dyed cotton for Fenton-treatments with increasing concentrations according to Table A.1.

	Fenton 1	Fenton 2	Fenton 3	Fenton 4
Discoloration %	15,89	12,39	20,46	16,40

Statistical T-tests are performed to compare the K/S-results before and after the Fenton-treatments. The seemingly optimal Fenton-condition for discoloration of the black-dyed cotton (Fenton 3) is also compared to the other treatments, to verify whether it gives statistically significant results than the other treatments. The p-values of the performed t-tests are respectively given in Table A.3.

Table A.3: p-values of t-tests between measured K/S-values of the black-dyed cotton before and after Fenton-treatments and p-values of t-tests between K/S-values of the seemingly optimal treatment (Fenton 3) and other Fenton-treatments, with all t-tests with α = 0,05 and n = 4.

	Fenton 1	Fenton 2	Fenton 3	Fenton 4
Black-dyed fabric	0,003	0,005	0,001	0,003
Fenton 3	0,033	0,008	/	**0,092**

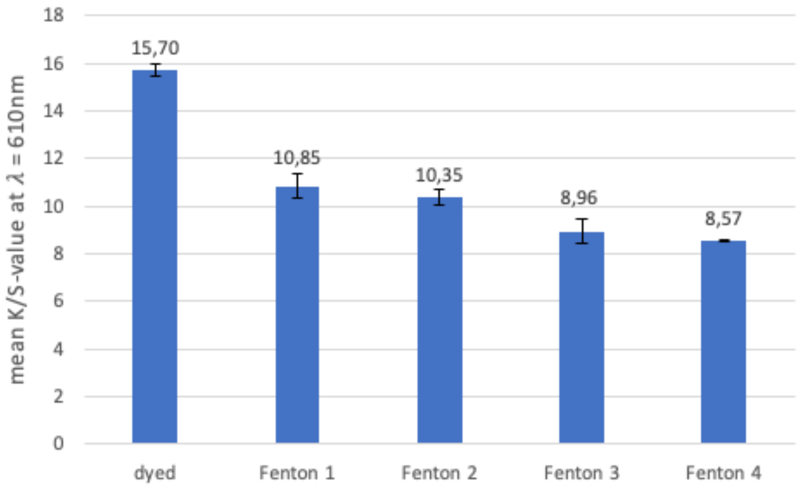
These p-values indicate that the results of all treatments differ significantly from the color strength of the black-dyed fabric (before treatment). Therefore, all Fenton-solutions from Table A.1 result in significant discoloration of the black-dyed-cotton.

From Graph A.1, Fenton 3 (with a Fenton-solution with 4 times the recommended concentrations for discoloration of dye-solution) seems to obtain the lowest color strength after treatment (K/S-value decreases from 35,69 to 28,33) and thus the highest discoloration percentage (20,46%).

When comparing the seemingly optimal treatment (Fenton 3) to the other treatments by t-tests in Table A.3, only the results from Fenton 4 cannot be assumed significantly different from Fenton 3. However, with an eye on sustainability, it is more beneficial to consume a lower amount of chemicals. Since Fenton 4 requires double the amount of chemicals compared to treatment 3, further Fenton-treatments of the black-dyed fabric will be performed with the conditions of Fenton 3.

Blue-dyed Cotton

A plot with mean K/S-values of the blue-dyed cotton and the samples discolored with increasing Fenton-solution concentrations (Fenton 1 – Fenton 4) are given in graph A.2. From these K/S-values, the associated discoloration percentages of the blue-dyed fabric can be calculated according to $eq. 2$, and are given in Table A.4.



Graph A.2: mean K/S-values of the blue-dyed cotton before and after Fenton treatments with increasing concentrations according to Table A.1.

Table A.4: mean discoloration percentages of the blue-dyed cotton for Fenton-treatments with increasing concentrations according to Table A.1.

	Fenton 1	Fenton 2	Fenton 3	Fenton 4
Discoloration %	30,62	33,76	42,71	45,15

Statistical T-tests are performed to compare the K/S-results before and after the Fenton-treatments. The seemingly optimal Fenton-condition for discoloration of the blue-dyed cotton (Fenton 4) is also compared to the other treatments, to verify whether it gives statistically significant results than the other treatments. The p-values of the performed t-tests are respectively given in Table A.5.

Table A.5: p-values of t-tests between measured K/S-values of the black-dyed cotton before and after Fenton-treatments and p-values of t-tests between K/S-values of the seemingly optimal treatment (Fenton 4) and other Fenton-treatments, with all t-tests with α = 0,05 and n = 4.

	Fenton 1	Fenton 2	Fenton 3	Fenton 4
Blue-dyed fabric	< 0,001	< 0,001	< 0,001	< 0,001
Fenton 4	0,025	0,017	**0,411**	/

These p-values also indicate that the results of all treatments differ significantly from the color strength of the blue-dyed fabric (before treatment). Therefore, all Fenton-treatments from Table 3.1 result in significant discoloration of the blue-dyed-cotton.

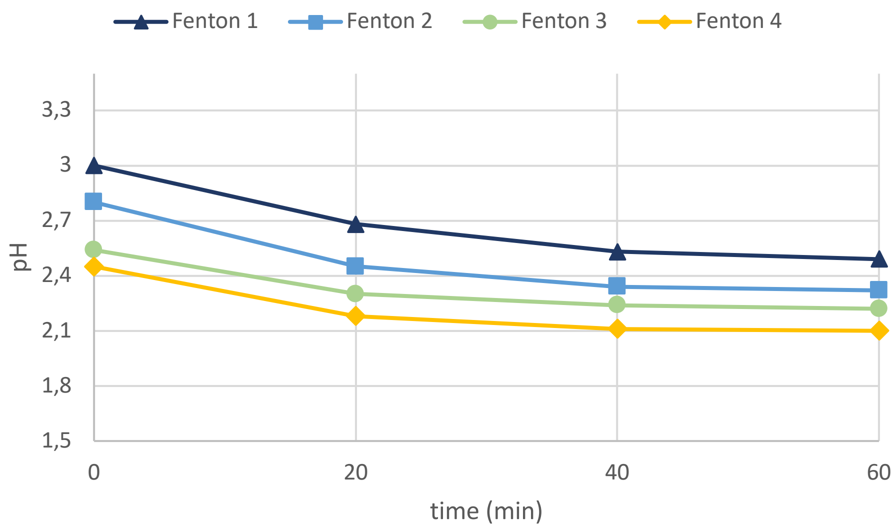
From Graph A.2, Fenton 4 (with a Fenton-solution with 8 times the recommended concentrations for discoloration of dye-solution) seems to obtain the lowest color strength after treatment (K/S-value decreases from 15,70 to 8,57) and thus the highest discoloration percentage (45,51%).

When comparing the seemingly optimal treatment (Fenton 4) to the other treatments by t-tests in Table A.5, only the results from Fenton 3 cannot be assumed significantly different from treatment 4. However, with an eye on sustainability, it is more beneficial to consume less chemicals. Since Fenton 4 requires double the amount of chemicals compared to treatment 3, and the results of Fenton 3 and 4 do not differ significantly, further Fenton-treatments of the blue-dyed fabric will be performed with the conditions of Fenton 3.

The decision to treat both the black- and blue-dyed fabric with the same Fenton-conditions for further experiments will also allow better comparison of the results of both fabrics.

Trend in pH during Fenton-treatments

For both the black- and blue-dyed cotton, the pH during the Fenton-discoloration treatments follows a similar trend. The mean values of the measured pH-values at specific time-intervals during the reaction are given in Graph A.3.



Graph A.3: trend in pH during Fenton-treatments with increasing solution-concentrations according to Table A.1.

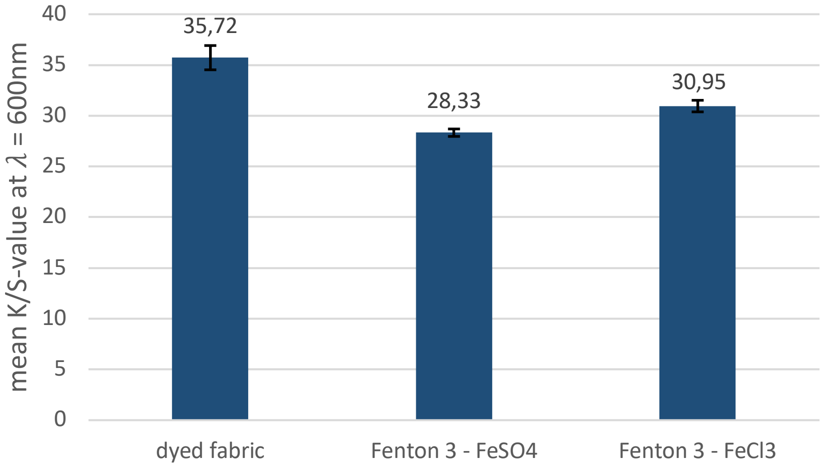
It is visible that increasing concentrations of the Fenton-solution are accompanied by decreased pH-values during the treatment, due to the acidic characteristic of both ferric-sulphate and hydrogen peroxide.

For Fenton 3, a drop in pH from pH ≈ 2,5 to pH ≈ 2,2 is visible. The drop in pH during the reaction is caused by the production of hydroxyl-ions in reaction 2.6.

The pH-range in which Fenton 3 occurs is already rather low compared to optimal conditions for Fenton-oxidations (pH ≈ 2,5 – 4) . However, since the purpose of this thesis-project is not to fully optimize the Fenton-discoloration, but rather to investigate whether the use of Fenton-mechanisms can be used for discoloration of textiles and whether this mechanism would be interesting for further research, the pH will not be adapted in further upscaled experiments to avoid overcomplicating the analysis section.

A.3.2 Influence of Fe-source on Discoloration Efficiency

Black-dyed Cotton



Graph A.4: mean K/S-values of the black-dyed cotton before and after Fenton treatments with different iron-sources ($FeSO_4x7H_2O$ and $FeCl_3$).

From the K/S-values obtained by the different iron-sources (Graph A.4), the associated discoloration percentages can be calculated according to $eq. 2$ and are given in Table A.6. Pictures of the cotton fabric before and after treatment are given in Figure A.5.

Table A.6: mean discoloration percentages of the black-dyed cotton for Fenton treatments with different iron-sources.

	Fenton 3 – $FeSO_4$ x $7H_2O$	Fenton 3 – $FeCl_3$
Discoloration (%)	20,46	13,16

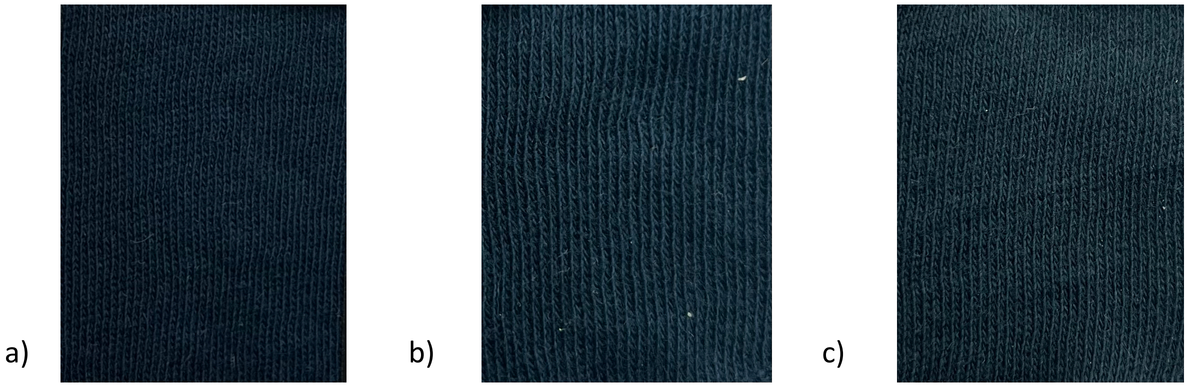


Figure A.5: black-dyed cotton before (a) and after Fenton-treatment with $FeSO_4$ (b) and $FeCl_3$ (c).

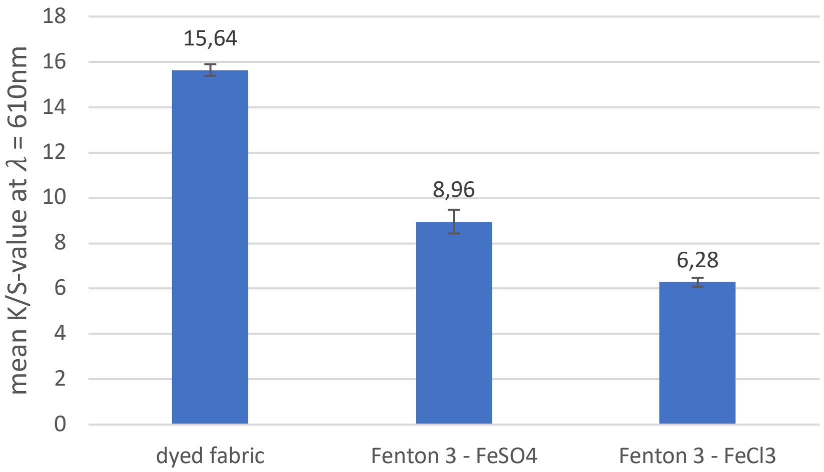
A statistical t-tests between the K/S-results of the dyed-fabric and the Fenton-treatment with the Fe(III)-source ($FeCl_3$) is performed to investigate whether this iron-source leads to a significant discoloration. Statistical t-tests between the Fenton-treatments with the different iron-sources is also performed, to determine whether the iron-source achieves a significantly different discoloration. The p-values of these statistical tests for the black-dyed cotton are listed in Table A.7.

Table A.7: p-values of t-test between measured K/S-values of black-dyed cotton before and after Fenton-treatment with an Fe(III)-source and of t-test between K/S-values of Fenton-treatments with different iron-sources (Fe(II) and Fe(III)),with α = 0,05 and n = 4.

	Black-dyed cotton	Fenton 3 – $FeSO_4$ x $7H_2O$
Fenton 3 – $FeCl_3$	< 0,001	0,005

Therefore, for the black dyed cotton, using an Fe(III)-source ($FeCl_3$) also results in a significant discoloration (13,16%), however, achieving a lower discoloration percentage than for the Fe(II)-source $FeSO_4$ (20,46%).

Blue-dyed Cotton



Graph A.6: mean K/S-values of the blue-dyed cotton before and after Fenton treatments with different iron-sources ($FeSO_4x7H_2O$ and $FeCl_3$).

From the K/S-values obtained by the different iron-sources (Graph A.6), the associated discoloration percentages can be calculated according to $eq.2$ and are given in Table A.8. Pictures of the cotton fabric before and after treatment are given in Figure A.7.

Table A.8: mean discoloration percentages of the blue-dyed cotton for Fenton treatments with different iron-sources.

	Fenton 3 – $FeSO_4 \times 7H_2O$	Fenton 3 – $FeCl_3$
Discoloration (%)	42,71	59,65

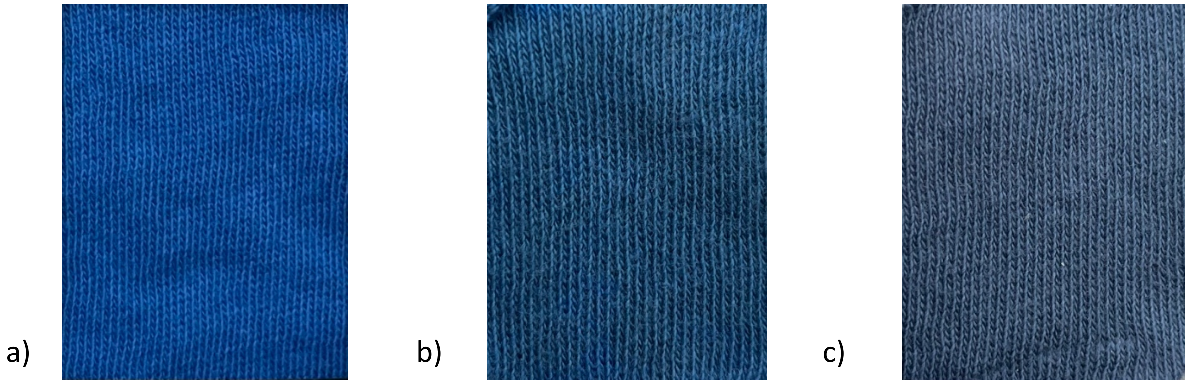


Figure A.7: black-dyed cotton before (a) and after Fenton-treatment with $FeSO_4$ (b) and $FeCl_3$ (c).

A statistical t-test between the K/S-results of the dyed-fabric and the Fenton-treatment with the Fe(III)-source ($FeCl_3$) is performed to investigate whether this iron-source leads to a significant discoloration. Statistical t-tests between the Fenton-treatments with the different iron-sources is also performed, to determine whether the iron-source achieves a significantly different discoloration. The p-values of these statistical tests for the black-dyed cotton are listed in Table A.9.

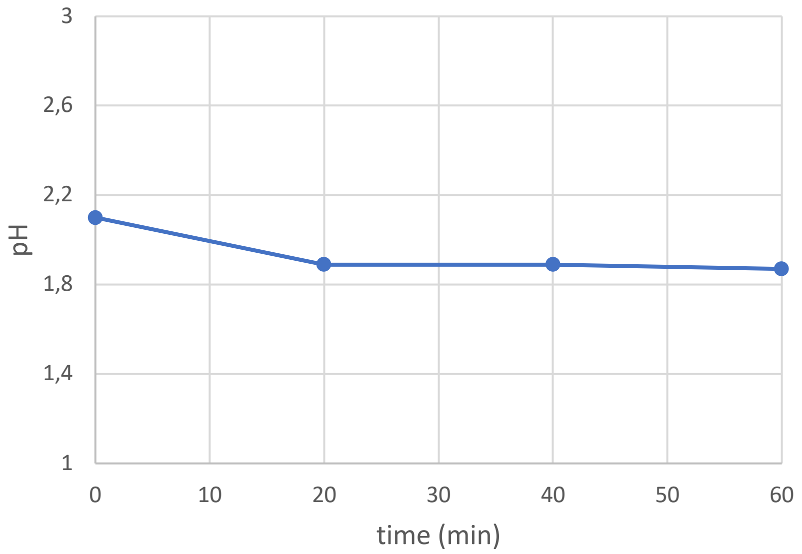
Table A.9: p-values of t-test between measured K/S-values of blue-dyed cotton before and after Fenton-treatment with an Fe(III)-source and of t-test between K/S-values of Fenton-treatments with different iron-sources (Fe(II) and Fe(III)), with α = 0,05 and n = 4.

	Blue-dyed cotton	Fenton 3 – $FeSO_4 \times 7H_2O$
Fenton 3 – $FeCl_3$	< 0,001	0,021

Therefore, for the blue-dyed cotton, the Fe(III)-source also leads to significant discoloration, which is even higher than for the Fe(II)-source (59,65% compared to 42,71%).

Trend in pH during Fenton-treatment with FeCl3

For both the black- and blue-dyed cotton, the pH during the Fenton-treatment with $FeCl_3$ follows a similar trend. The mean values of the measured pH-values at specific time-intervals during the reaction are given in Graph A.8.



Graph A.8: Trend in pH during Fenton-treatment with $FeCl_3$.

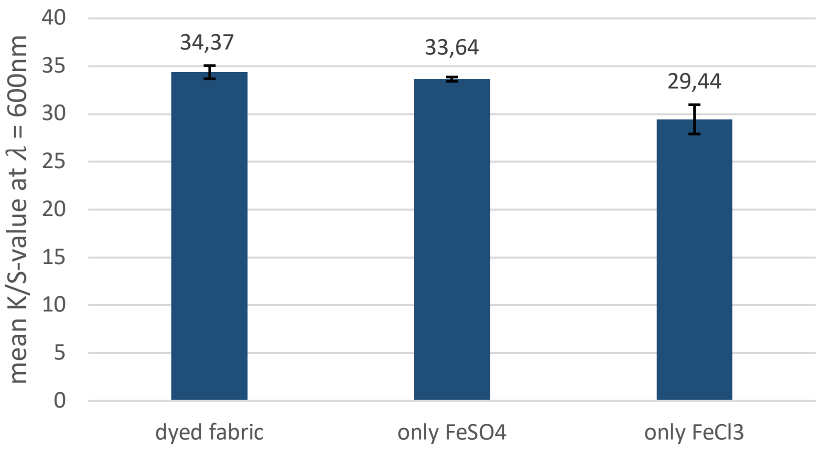
The pH during the Fenton-discoloration with $FeCl_3$ is lower than for $FeSO_4$ (pH ≈ 2 compared to pH ≈ 2,5). This is due to hydrolysis of the salt in water with generation of HCl, which is a strong acid. However, this pH is already below the lower limit for efficient Fenton-mechanism. Therefore, it is suspected that not the only the Fenton-mechanism, but also some other mechanism might be responsible for the 13,16% and 59,65% discoloration of the respective black- and blue-dyed cotton.

Since part of the iron-cations will be present as Fe^{3+} during the Fenton-mechanism, it is possible that ferric-ions will coagulate with the negatively charged dye-molecules. Therefore, the discoloration might be due to an accumulative effect of the Fenton-mechanism and coagulation of the iron with the dye-molecules. However, since this thesis-project intends to investigate the Fenton-process, accumulative discoloration results due to coagulation should be avoided.

For this reason, an experiment to examine the contribution of Fe^{3+}-coagulation to the discoloration is performed by adding the cotton-samples to a solution with only the Fe-source (no H_2O_2).

A.3.3 Contribution of Coagulation to Discoloration

Black-dyed cotton



Graph A.9: mean K/S-values of the black-dyed cotton before and after treatments with only the iron-sources $FeSO_4x7H_2O$ and $FeCl_3$ (without H_2O_2).

From the K/S-values obtained by the treatments with only the iron-sources (Graph A.9), the associated discoloration percentages can be calculated according to $eq.2$, and are given in Table A.10.

Table A.10: mean discoloration percentages of the black-dyed cotton for Fenton treatments with different iron-sources.

	Only $FeSO_4$ x $7H_2O$	Only $FeCl_3$
Discoloration of black-dyed cotton %	2,03	14,03

Statistical t-tests between the K/S-values of the dyed fabric before and after treatment with only the iron-sources are performed to investigate whether coagulation by Fe-hydroxides present in the Fenton-solution contributes significantly to the discoloration of the cotton. The p-values of these statistical tests for the black- and blue-dyed cotton are respectively listed in Table A.11.

Table A.11: p-values of t-test between measured K/S-values of the black-dyed cotton before and after treatment with only the iron-sources $FeSO_4$ x $7H_2O$ and $FeCl_3$ (no H_2O_2), with α = 0,05 and n = 4.

	Only $FeSO_4$ x $7H_2O$	Only $FeCl_3$
Black-dyed cotton	**0,292**	< 0,001

Blue-dyed cotton

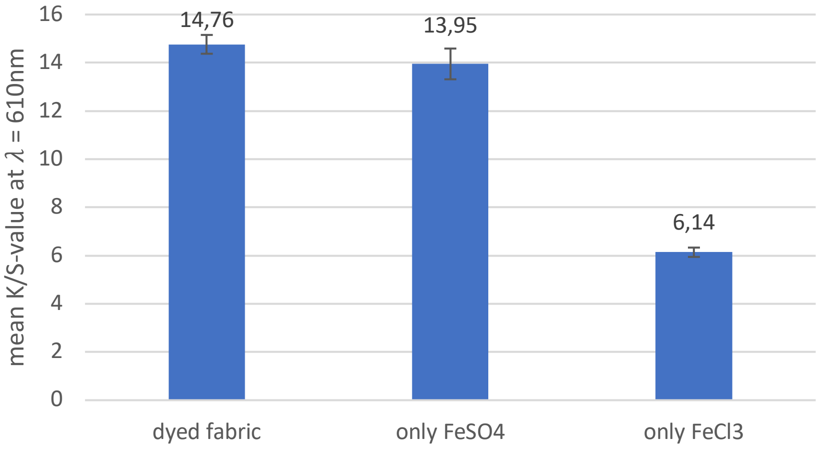


Figure A.10: mean K/S-values of the blue-dyed cotton before and after treatments with only the iron-sources $FeSO_4x7H_2O$ and $FeCl_3$ (without H_2O_2).

From the K/S-values obtained by the treatments with only the iron-sources (Graph A.10), the associated discoloration percentages can be calculated according to $eq. 2$, and are given in Table A.12.

Table A.12: mean discoloration percentages of the blue-dyed cotton for Fenton treatments with different iron-sources.

	Only $FeSO_4$ x $7H_2O$	Only $FeCl_3$
Discoloration of blue-dyed cotton %	3,03	59,08

Statistical t-tests between the K/S-values of the dyed fabric before and after treatment with only the iron-sources are performed to investigate whether coagulation by Fe-hydroxides present in the Fenton-solution contributes significantly to the discoloration of the cotton. The p-values of these statistical tests for the black- and blue-dyed cotton are respectively listed in Table A.13.

Table A.13: p-values of t-test between measured K/S-values of the blue-dyed cotton before and after treatment with only the iron-sources $FeSO_4$ x $7H_2O$ and $FeCl_3$ (no H_2O_2), with α = 0,05 and n = 4.

	Only $FeSO_4$ x $7H_2O$	Only $FeCl_3$
Blue-dyed cotton	**0,415**	< 0,001

When only the Fe(II)-source is added to de-ionized water (at pH $\approx$ 2,5), a non-significant discoloration of 2-3% is achieved for both dyes. However, a solution with only the Fe(III)-source (at pH $\approx$ 2) leads to significant discoloration of the black- (14,03%) and the blue-dyed cotton (59,08%). Since the Fenton-reactions with $FeCl_3$ lead to similar discoloration percentages (in Table 4.5 and 4.6), it cannot be concluded whether the discoloration is due to the Fenton-mechanism or due to an accumulative effect of Fenton-mechanism and coagulation of the Fe^{3+}-hydroxides with the organic dye-molecules.

Since only a non-significant percentage of the discoloration was achieved by adding the Fe(II)-source, it can be concluded that the main discoloration when using this source is caused by the Fenton-mechanism. Therefore, only this iron-source will be used in upscaled experiments in order maintain the objective of this thesis-project, namely investigating the feasibility of the Fenton-oxidation for discoloration of reactive-dyed cotton.

Annex B – Microscopy Images of Raw Cotton

Microscopy-images of the knitted structure, the yarn and the fiber of the raw cotton are given below.

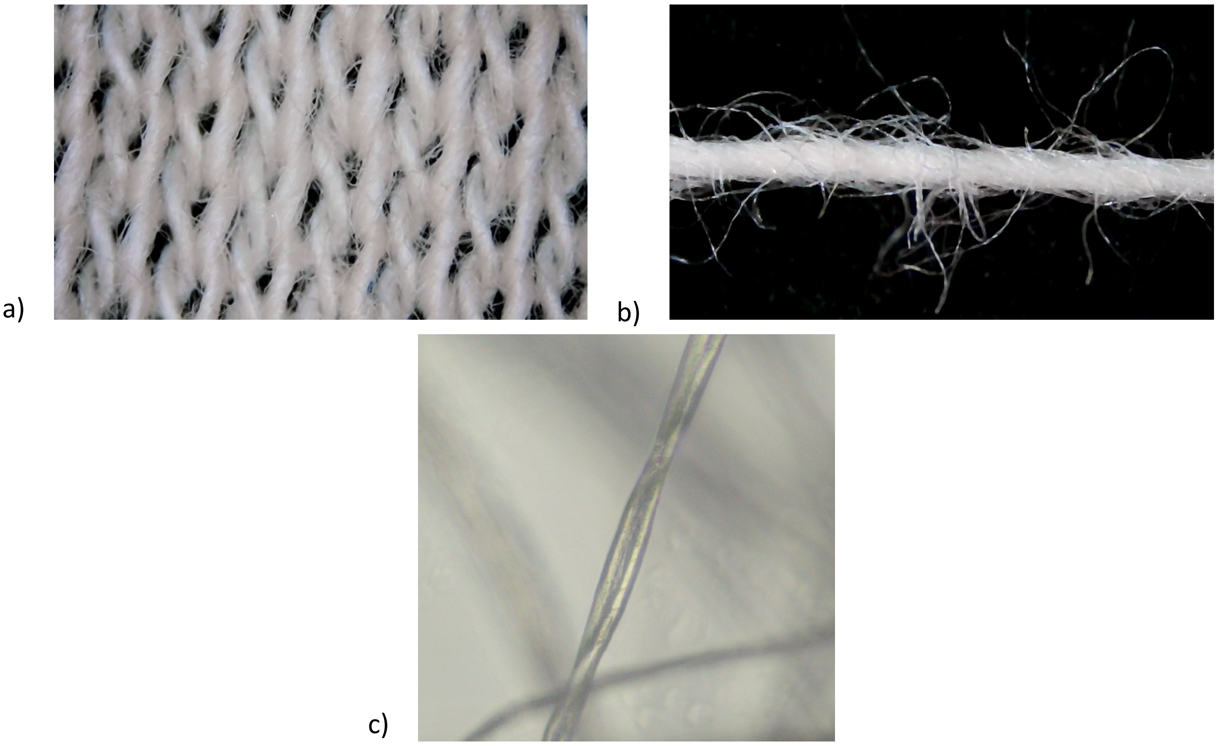


Figure B.1: microscopy-images of the knitted structure (a), spun yarn (b) and fiber (c) of the raw cotton.

Annex C – Images of Mechanically Shredded Fabric

Pictures of the residue after shredding of the raw cotton, dyed fabrics and Fenton-treated fabrics are given below.

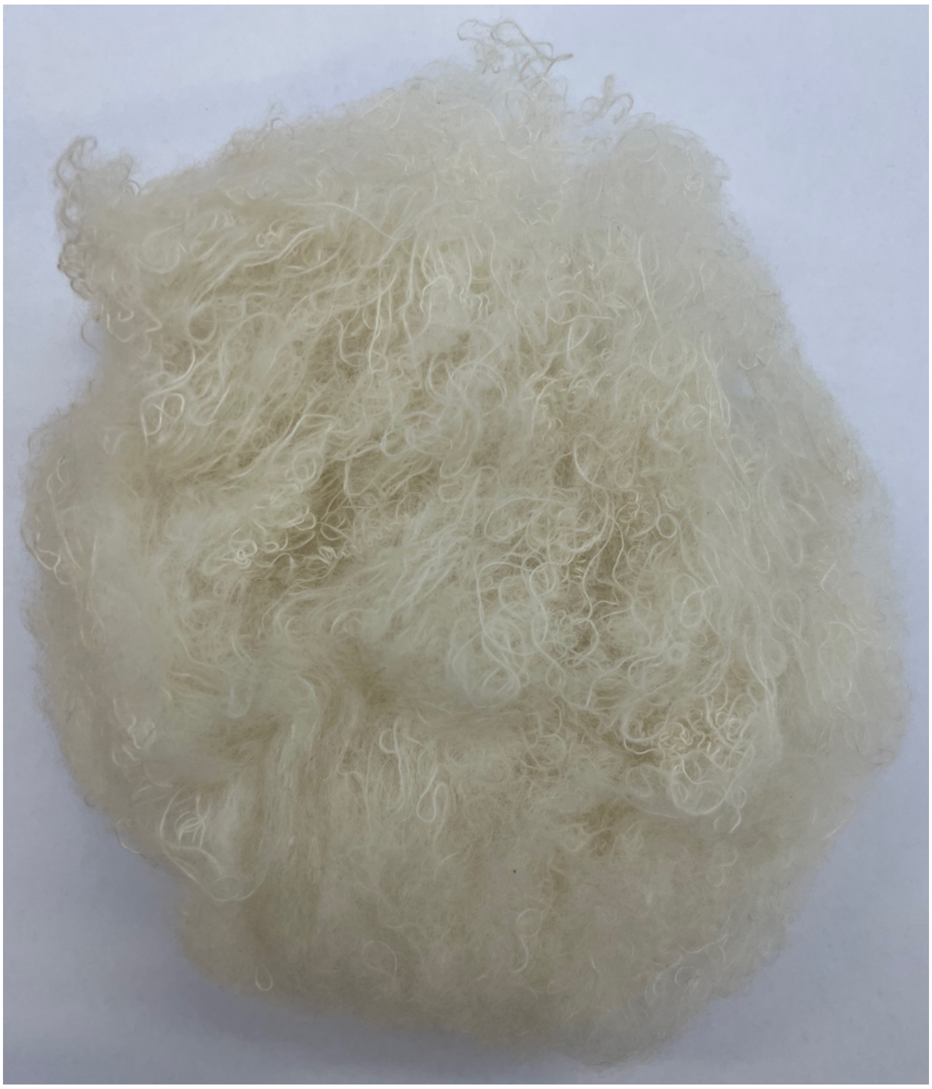


Figure C.1: picture of residue (fibers and non-opened yarns) of raw cotton after shredding.

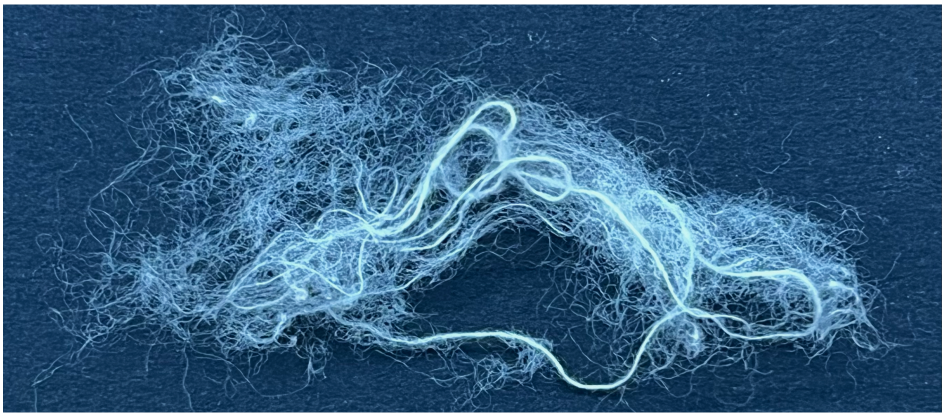


Figure C.2: detailed picture of fibers and non-opened yarns of raw cotton after shredding.

Figure C.3: picture of residue (fibers and non-opened yarns) of black-dyed cotton after shredding.

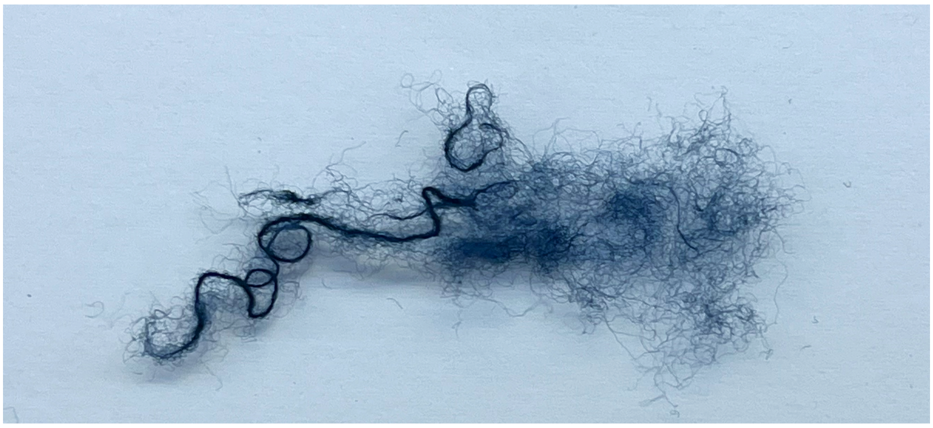


Figure C.4: detailed picture of fibers and non-opened yarns of black-dyed cotton after shredding.

Figure C.5: picture of residue (fibers and non-opened yarns) of blue-dyed cotton after shredding.

Figure C.6: detailed picture of fibers and non-opened yarns of blue-dyed cotton after shredding.

Figure C.7: picture of residue (fibers and non-opened yarns) of discolored black cotton after shredding.

Figure C.8: detailed picture of fibers and non-opened yarns of discolored black cotton after shredding.

Figure C.9: picture of residue (fibers and non-opened yarns) of discolored blue cotton after shredding.

Figure C.8: detailed picture of fibers and non-opened yarns of discolored blue cotton after shredding.