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ECO-DESIGNED FUNCTIONALIZATION OF POLYESTER FABRIC

Doctoral dissertation by

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ABSTRACT

There is an increased awareness of the textile dyeing and finishing sector's high impact on the environment due to high water consumption, polluted wastewater, and inefficient use of energy. To reduce environmental impacts, researchers propose the use of dyes from natural sources. The purpose of using these is to impart new attributes to textiles without compromising on environmental sustainability. The attributes given to the textile can be color and/or other characteristics. A drawback however, is that the use of bio-sourced dyes is *not* free from environmental concerns. Thus, it becomes paramount to assess the environmental impacts from using them and improve the environmental profile, but studies on this topic are generally absent.

The research presented in this thesis has included environmental impact assessment, using the life cycle assessment (LCA) tool, in the design process of a multifunctional polyester (PET) fabric using natural anthraquinones. By doing so an eco-design approach has been applied, with the intention to pave the way towards eco-sustainable bio-functionalization of textiles.

The anthraquinones were obtained from the root extracts of the madder plant (*Rubia tinctorum L.*), referred to as madder dye. The research questions were therefore formulated related to the use of madder dye. Three research questions have been answered: (I) Can madder dye serve as a multifunctional species onto a PET woven fabric? (II) How does the environmental profile of the dyeing process of PET with madder dye look like, and how can it be improved? (III) What are the main challenges in using LCA to assess the environmental impacts of textile dyeing with plant-based dyes?

It is concluded that there is a potential for the madder dye to serve as a multifunctional species onto PET. Based on the encouraging result, a recommendation for future work would be to focus on the durability of the functionalities presented and their improvement potential, both in exhaustion dyeing and pad-dyeing. LCA driven process optimization of the exhaustion dyeing enabled improvement in every impact category studied. However, several challenges have been identified which need to be overcome for the LCA to contribute to the sustainable use of multifunctional plant-based species in textile dyeing. The main challenges are the lack of available data at the research stage and the interdisciplinary nature of the research arena. It is envisaged that if these challenges are addressed, LCA can contribute towards sustainable bio-functionalization of textiles.

Keywords: Eco-design, Life cycle assessment, Madder, Anthraquinone, Bioactive, Multifunctional, Polyester

RÉSUMÉ

Le secteur de la teinture et de l'ennoblissement textile est de plus en plus conscient de son impact sur l'environnement dû principalement à la consommation élevée de l'eau et à sa pollution, et aux pertes d'énergie. Pour réduire ces impacts, les chercheurs proposent l'utilisation de molécules issues de ressources naturelles, pour traiter les textiles en limitant les impacts sur l'environnement. C'est le cas pour l'obtention de textiles colorés ou pour l'attribution de toute autre fonctionnalité. Cependant, il n'est pas évident que ces molécules bio-sourcées n'aient aucun impact sur l'environnement. On comprend l'importance d'évaluer les impacts de leur utilisation et d'améliorer leur profil environnemental. Or ce type d'étude est peu présent dans la littérature.

La recherche présentée dans cette thèse comporte l'évaluation des impacts environnementaux en utilisant l'outil d'analyse du cycle de vie (ACV) pour la conception du traitement d'un tissu de polyester (PET) multifonctionnel avec des anthraquinones naturelles. La méthodologie d'éco conception que nous avons appliquée ouvre la voie à une bio-fonctionnalisation des textiles plus respectueuse de l'environnement.

Les anthraquinones ont été obtenues par extraction des racines de plantes de garance et constituent le colorant appelé garance. Les trois questions principales abordées lors de ce travail de recherche sont formulées autour de l'utilisation de la garance : (I) Peut-on traiter les tissus de PET avec de la garance pour obtenir des propriétés multifonctionnelles ? (II) Quel est le profil environnemental du procédé de teinture du PET par la garance et comment l'améliorer ? (III) Quels sont les principaux challenges pour l'utilisation de l'ACV dans l'évaluation environnementale du traitement des textiles par des colorants naturels?

Nous avons montré que la garance peut être utilisée pour conférer des propriétés multifonctionnelles au PET. Ensuite, nous avons pu orienter notre étude pour améliorer la durabilité des traitements par les procédés de fonctionnalisation à la fois par épuisement ou par foulardage. En s'appuyant sur l'ACV, l'optimisation de la teinture que nous avons réalisée réduit tous les impacts sur l'environnement. Cette étude nous permet d'identifier les challenges qui doivent être surmontés pour que l'ACV puisse contribuer à l'utilisation de bio-molécules pour la teinture des textiles dans le respect des principes de développement durable. Ils concernent le manque de données pour ces travaux de recherche et leur nature interdisciplinaire. Ainsi, en résolvant ces questions, on peut envisager aboutir à une bio-fonctionnalisation des textiles respectueuse de l'environnement.

Mots clés: Eco-conception, Analyse du Cycle de Vie, Garance, Anthraquinone, Bioactivité, Multifonctionnel, Polyester

ABSTRAKT

Den höga miljöpåverkan från textilfärgning och efterbehandling, på grund av hög vattenförbrukning, dess förorening, och ineffektiv användning av energi, är idag välkänt. För att minska miljöpåverkan föreslår forskningsvärlden användning av färgämnen från naturliga resurser. Syftet med att använda dessa är att ge nya attribut till textilier utan att göra avkall på miljömässig hållbarhet. Attribut som ges kan vara färg och/eller andra egenskaper. En nackdel är dock att användningen av bio-baserade färgämnen är *inte* fri från att belasta miljön. Det blir därför av största betydelse att bedöma denna miljöpåverkan och förbättra miljöprofilen. Sådana studier är dock i allmänhet sällsynta.

Studien som presenteras i denna avhandling har inkluderat miljöpåverkans-bedömning, med hjälp av livscykelanalys (LCA), i designprocessen av en multifunktionell polyester (PET) väv via naturliga antrakinoner. Genom att göra så har ett eko-design tillvägagångssätt använts, med avsikt att bana väg för miljömässigt hållbar bio-funktionalisering av textil.

Antrakinonerna erhölls från rot extrakt av växten krapp (*Rubia tinctorum L.*), och hänvisas till som krapp färgämne. Frågeställningar var därför formulerade relaterat till användningen av krapp färgämne. Tre forskningsfrågor har besvarats: (I) Kan krapp färgämne verka multifunktionellt på en PET väv? (II) Hur ser miljöprofilen ut, från färgningsprocessen av PET med krapp färgämne, och hur kan den förbättras? (III) Vilka är de största utmaningarna med att använda LCA för att bedöma miljökonsekvenserna av textilfärgning med växtbaserade färgämnen?

Det kan konkluderas att det finns potential för krapp färgämne att verka multifunktionellt på PET. Baserat på uppmuntrande resultat är en rekommendation för det framtida arbetet att fokusera på kvalitén hos de attribut som presenterats och deras förbättringspotential, både i färgning via färgbad och via foulard. LCA driven processoptimering av textilfärgningen förbättrade i varje miljöpåverkans-kategori som studerats. Emellertid har flera utmaningar identifierats som måste

övervinnas för att LCA skall kunna bidra till en hållbar användning av multifunktionella växtbaserade färgämnen för textil. De största utmaningarna är bristen på tillgängliga data i forskningsstadiet och den tvärvetenskapliga forskningsarenan. Det är tänkt att om dessa utmaningar bemästras kan LCA bidra till en hållbar bio-funktionalisering av textil.

Nyckelord: Eko-design, Livscykelanalys, Krapp, Antrakinon, Bio-aktiv, Multifunktionell, Polyester

摘 要

纺织染整行业由于生产环节中会产生大量的工业废水，能源利用率较低和水耗较高等问题，给环境带来严重影响而逐渐为人们所重视。为了减轻对环境的影响，染整行业的科技工作者们试图将天然生物资源利用起来。天然生物资源的利用是在环境可持续性的前提下赋予纺织品新的特性，如颜色或其它属性。然而，天然产物的使用对自然环境也并不是毫无影响的。因此，对天然产物的使用进行环境评估并提高其环境友好性十分必要。但目前几乎尚未有诸如此类的研究和报道。

本论文主要研究了利用生命周期评价（LCA）工具对涤纶（PET）的蒽醌结构天然产物多功能整理工艺进行环境影响的评价。通过运用生态设计的方法来达到可持续性制备生物功能性纺织品的目的。

茜草染料（*Rubia tinctorum L.*）是一种蒽醌结构的天然产物, 取自茜草植物的根部。本研究课题以茜草染料的应用为主题，着力解决以下三个问题：（1）茜草染料是否能够用于涤纶织物的多功能整理？（2）茜草染料用于涤纶织物多功能整理的环境效应如何且怎样提高？（3）生命周期评价用于纺织品天然染料染色的环境影响的评价时面临的主要问题是什么？

本课题证明了茜草染料可以用于涤纶织物的多功能整理。在本课题中所获得成果的基础上，后续的研究工作将主要集中在对染色（浸染和轧染）织物功能性的耐久性进行评价并提高其耐久性。生命周期评价的研究目的在于优化每一个所研究的影响因素以改善染色工艺。然而，将生命周期评价方法运用于天然产物多功能纺织品的可持续性制备中却充满了挑战，这些挑战在于现有的科学研究资料的不足以及其为交叉学科的特点。因此，如果这些问题得以解决，那么生命周期评估的方法将有助于生物功能性纺织品的可持续性制备的研究。

关键词：生态设计，生命周期评价，茜草，蒽醌，生物活性，多功能性，涤纶

PREFACE

The work included in this thesis has been carried out at the following laboratories:

Textile Materials Technology, Department of Textile Technology, The Swedish School of Textiles, Faculty of Textiles, Engineering and Business, University of Borås, 501 90 Borås, Sweden

Laboratoire de Génie et Matériaux Textiles (GEMTEX), École Nationale Supérieure des Arts et Industries Textiles (ENSAIT), 2 allée Louise et Victor Champier, 590 56 Roubaix, France

National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, 199 Renai Road, Suzhou 215123, China

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LIST OF APPENDED PUBLICATIONS

This thesis is based on the work presented in the following publications, referred to by Roman numerals in the text:

I. Agnhage T, Perwuelz A, Behary N (2016) Eco-innovative coloration and surface modification of woven polyester fabric using bio-based materials and plasma technology. *Industrial Crops and Products,* 86:334-341

II. Agnhage T, Perwuelz A, Behary N (2016) Dyeing of polyester fabric with bio-based madder dye and assessment of environmental impacts using LCA tool. *Vlákna a textil, (Fibers and textiles),* 3:4-9

III. Agnhage T, Perwuelz A, Behary N (2017) Towards sustainable *Rubia tinctorum L.* dyeing of woven fabric: How life cycle assessment can contribute. *Journal of Cleaner Production,* 141:1221-1230

IV. Agnhage T, Zhou Y, Guan J, Chen G, Perwuelz A, Behary N, Nierstrasz V (year) Bioactive and multifunctional textile using plant-based madder dye: Characterization of UV protection ability and antibacterial activity. Accepted Aug 2017 for publication in *Fibers and Polymers*.

V. Agnhage T, Perwuelz A (2017) Call for environmental impact assessment of bio-based dyeing – an overview. In: Muthu S S (ed) Sustainable chemistry and wet processing. Detox fashion, vol 2. Springer ISBN: 978-981-10-4875-3

CONTRIBUTION TO APPENDED PUBLICATIONS

The author's contributions to the appended publications are as follows:

Publications I, II and III: Planned the experiments together with the co-authors. Conducted the experiments and wrote the text.

Publication IV: Planned and conducted the experiments together with Y. Zhou, and wrote the text.

Publication V: Publication V is a book chapter, written by the author with feedback from the co-author.

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LIST OF ABBREVIATIONS

ADEME	Environment and Energy Management Agency
BREF	Best Available Techniques Reference Document
GOTS	Global Organic Textile Standard
K/S	Color Strength
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory analysis
LCIA	Life Cycle Impact Assessment
LR	Liquor:fabric Ratio
Owf	On weight of fabric
PEF	Product Environmental Footprint
PET	Polyester (polyethylene terephthalate)
REACH	Registration, Evaluation and Authorization of Chemicals
Tg	Glass transition Temperature
UPF	Ultraviolet Protection Factor

TERMINOLOGY

Eco-design	An approach that includes environmental criteria in the design of a product. Examples of main principles of eco-design are: life cycle thinking to avoid pollution transfers to another life cycle stage and multicriterion thinking to avoid improving an environmental issue by worsening another one (Roy 2015).
Eco-sustainability	Environmental sustainability - one of the 3 key elements of sustainability (social, environmental and economic). Examples of eco-sustainability challenges include: increase energy efficiency, reduce use of toxics and reduce quantity of wastewater (UNEP 2009).
Environmental impacts	Perturbations of natural cycles by environmental interventions (Margni 2015).
Environmental interventions	Change in state of natural environment due to human activities (Margni 2015).
Functionalization	Refers to imparting attributes to the textile fabric, and supplement the inherent characteristics related to the fiber raw material and fabric structure. Herein, bio-functionalization refers to the use of bio-sourced materials for obtaining the functionalization effect.
Hotspot	Activities throughout the life cycle that are associated with higher risks of environmental impact.
Impact category	Class representing environmental issues of concern to which life cycle inventory analysis results may be assigned. Each category has its own environmental mechanism; for example, global warming (ISO 2006a).
LCA	Accounting for all environmental interventions associated with the life cycle of a product (Margni 2015).
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1 Introduction

1.1 Research context

1.1.1 The Sustainable Management and Design for Textiles program

The research presented in this thesis follows from the joint Doctorate Program in Sustainable Management and Design for Textiles, financed by the European Erasmus Mundus program and the EU Window Chinese Government Scholarship. The project belongs to the program theme on sustainable and innovative design processes and materials, and has been devoted to exploring methods to reduce the environmental impacts of textile wet-treatments. These methods include the innovative use of bio-sources to impart new attributes to textiles and the use of life cycle assessment (LCA) tool.

1.1.2 The unsustainable situation

The most accepted definition of sustainable development is the one presented in the Brundtland Commission Report (Kates et al. 2005): 'Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs' (WCED 1987).

From a holistic perspective sustainable development comprises three key elements: social development, environmental protection and economic development - also referred to as people, planet and profit (UNEP 2009).

Through several approaches however, such as the living planet index (WWF 2016), planetary boundaries (Rockström et al. 2009) and the environmental footprint (Hoekstra and Wiedmann 2014), it has been communicated that the current production and consumption pattern is more unsustainable than sustainable. For example, according to the Global footprint network, humanity today uses the equivalent of 1.6 Earths to provide the resources we use and absorb our waste.

It is clear that that the environmental pressure on the planet needs to be reduced and, as a major world industry, textiles need to respond to this rising concern.

1.1.3 The importance of resources and wastes in textiles

The textile industry is among the largest industries in the world. In 2014 not less than 92.0 million tons of textile fibers were produced (Fiber Organon 2015). Nevertheless, the industry also contributes to a significant share of the environmental burden on Earth; for example, 1 kg of textiles contributes to three times more climate pollution compared to 1 kg of metal or plastics (Lövin 2008).

The environmental impacts of textiles are related to the use of resources, and the production of waste and emissions. The resources may be either renewable or nonrenewable. Renewable recourses are those which can be replaced as they are used up, and are the product of living things in our nature. Nonrenewable resources are those with a finite supply on the planet, such as fossil fuels.

For a textile product to be produced in a sustainable way, renewable or recyclable materials should be used and as efficient as possible (Bach and Schollmeyer 2007). Nevertheless, renewable resources – bio-sourced materials cannot be regarded as being in infinite supply. The amount available will be dictated by the lifeform capable of producing it. If this not is respected, there is a risk for overexploitation. In this respect, it is important to consider sustainable production of the required resource. For cotton, for example, this would mean a production at a rate and on land types which secure long-term maintenance without any adverse environmental effects (Conell 1995).

Furthermore, for sustainable textiles, the production of waste and emissions should be kept to a minimum. The waste can either be biodegradable or nonbiodegradable, toxic or nontoxic, recyclable or nonrecyclable.

The waste is also related to the end-of-life of the textile. The textile industry has traditionally considered a linear 'take, make and waste' approach. However, increased attention is given to a circular design instead of a linear. This includes considering waste as going into a cycle where everything has a value (Aneja 2016).

1.1.4 Environmental aspects of textile wet-treatments

Textile wet-treatments, such as dyeing and finishing, generally require a great amount of water, chemicals and energy.

The amount of water varies depending on the fiber type, on average as much as 100-150 liters of water are needed to process 1 kg of textile material (Davis et al. 2015; Wong 2016).

Moreover, a considerable amount of process chemicals is needed which results in wastewater. Surfactants are one type of chemicals often used in wet-processes. These chemicals may be harmless to human but can be toxic to other species, and cause substantial loss of aquatic life if not properly treated in an effluent plant (Conell 1995). With respect to untreated wastewater, it has been estimated that 17-20 % of all industrial water pollution results from the textile dyeing and finishing process (Davis et al. 2015).

In addition to being water and chemical intense, wet-treatments are also energy intense, due to heating of water baths and drying operations.

In order to quite the criticism for its role in causing high impacts on the environment (Allwood et al. 2006; Greenpeace 2011), the textile industry attempts to apply cleaner and safer technologies (Ozturk et al. 2016). Important references here are the European BREF (Best Available Techniques Reference Document) for textile finishing (Nieminen et al. 2007), the REACH regulation for eliminating the use of hazardous chemicals, and the creation of the ZDHC group (Zero Discharge of Hazardous Chemicals). The ZDHC group is a result from the Greenpeace Detox campaign, which began in 2011 and has had a great impact on the textile chemical industry (Brigden et al. 2012). The ZDHC group has today more than 20 major global brand members. From this, the present thesis falls in line with the global interest in improving the environmental performance from this water, chemical and energy intense production phase.

1.1.5 Managing the sustainability challenge through eco-design

The eco-design approach was introduced in the 1990s, with the objective to include environmental criteria in the design of a product. Main principles of eco-design are (Bureau Veritas CODDE):

- Environmentally responsible decisions
- Reduce, Reuse and Recycle
- Life cycle thinking
- Multicriterion thinking
- Functional unit concept
- The environment should be integrated as early as possible in the decision-making process

In addition, there are different eco-design strategies. These strategies are clustered according to the stages of the life cycle of a product, and typically shown in an Eco-design strategies wheel. An example is in **Figure 1** (Bureau Veritas CODDE; UNEP).

In this thesis eco-design has been applied by using the life cycle assessment (LCA) tool. Moreover, four eco-design strategies have been included: namely, optimization of functions, low-impact materials, optimize production and optimize initial lifetime. These are shown in gray color in **Figure 1**.

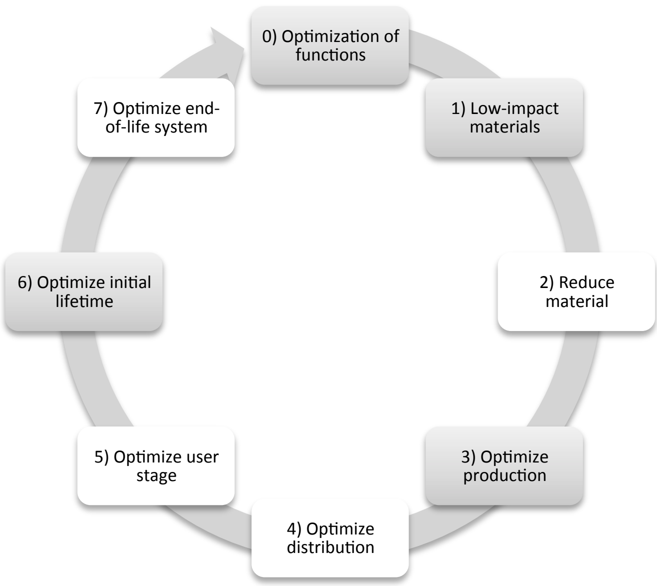


Figure 1 Eco-design strategies wheel

1.2 Justification

Many researchers today propose the application of multifunctional natural dyes in textile dyeing on account of their potential to add several value adding attributes; for example, color and antibacterial effect, and their environmentally friendly approach.

However, the use of bio-sources should not be the only parameter considered for an environmentally sound dyeing concept. By utilizing the LCA methodology, the environmental impacts of the dyeing process can be analyzed, so as to substantiate environmental claims, but studies on this topic are generally absent. As a consequence, the eco-friendliness may be misleading.

The research presented in this thesis has included environmental impact assessment, using the LCA tool, in the design process of a multifunctional PET fabric using natural anthraquinones from the madder plant. By doing so an eco-design approach has been applied, with the intention to pave the way towards eco-sustainable bio-functionalization of textiles.

1.3 Objective

The research herein has aimed to pave the way towards eco-sustainable bio-functionalization of textiles. From this, the work focused on the development of a multifunctional PET fabric using madder dye. The developed fabric then served as a prototype for environmental impact assessment using LCA. The results thereof intend to provide guidance for the development of bio-functionalized textiles with added value in terms of environmental performance.

1.3.1 Research questions

The thesis has dealt with three research questions.

Research question 1: Can madder dye serve as a multifunctional species onto a PET woven fabric?

The first research question has been formulated from the context in which bio-sourced dyes may have the ability to simultaneously obtain color and other functional effects onto textiles. To answer research question 1, an experimental study on bio-functionalization of PET with madder dye was designed, presented in Publication I and Publication IV.

Research question 2: How does the environmental profile of the dyeing process of PET with madder dye look like, and how can it be improved?

The second research question has been created in order to not have a larger than necessary impact on the environment from the dyeing process with madder dye. To answer research question 2, LCA driven process optimization of the PET dyeing with madder dye was performed and presented in Publication II and Publication III.

Research question 3: What are the main challenges in using LCA to assess the environmental impacts of textile dyeing with plant-based dyes?

The third research question dealt with the current challenges in applying the LCA tool for the eco-sustainable use of plant-based dyes in textile dyeing. What is the importance of using LCA and what are the difficulties? The study dealing with research question 3 has been presented in Publication V.

1.4 Methodology and structure of the study

The first two research questions were answered by experimental work that involved iterative development with quantitative evaluations. The third and last research question was a descriptive kind and, to a large extent, answered by literature review.

Due to its multidisciplinary nature, this work has required collaboration with expertise from diverse research fields: bio-functionalization of textiles and LCA. The structure of the study is illustrated in **Figure 2**. Three focus areas, five publications and three research questions support this thesis.

The first focus area deals with the development of a bio-functionalized PET fabric (Publications I and IV). Focus was firstly given to process optimization with respect to color as the functionality, and its durability. Two dyeing methods were used, and advantages and limitations for each method were discussed in Publication I. Secondly, once a dyed fabric with good durability performance was obtained, characterization of functional properties other than color was performed, presented in Publication IV. Together Publication I and Publication IV answered the first research question. Structure of the first focus area is presented in **Figure 3**.

The second focus area is based upon the developed fabric in Publication I, and deals with environmental impact assessment using LCA (Publications II and III). In Publication III process optimization of the dyeing process, at lab-scale, was performed with respect to environmental sustainability. From this publication the second research question could be answered. Additionally, we studied the environmental impacts from the scenario of a madder dyed PET shirt, presented in Publication II. Structure of the second focus area is presented in **Figure 4**.

The third focus area addresses a LCA perspective on bio-based dyeing in general (Publication V). A focused literature overview on technical and environmental aspects of bio-based dyeing from a LCA perspective supports Publication V, which calls for environmental impact assessment of bio-based dyeing. From this focus area, the third and last research question was answered.

Together the three focus areas pave the way towards eco-sustainable bio-functionalization of textiles, which was the aim of this thesis.

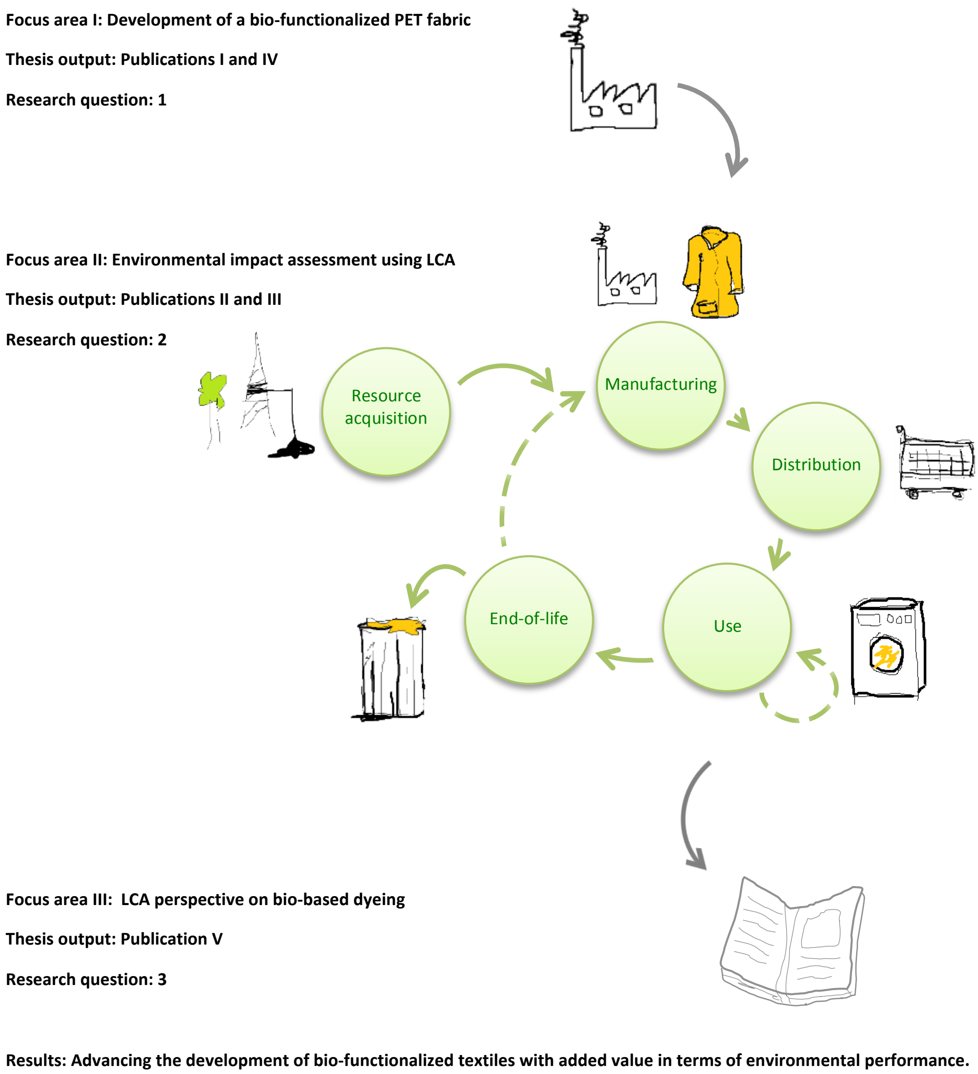


Figure 2 Resarch route to fulfill the objective

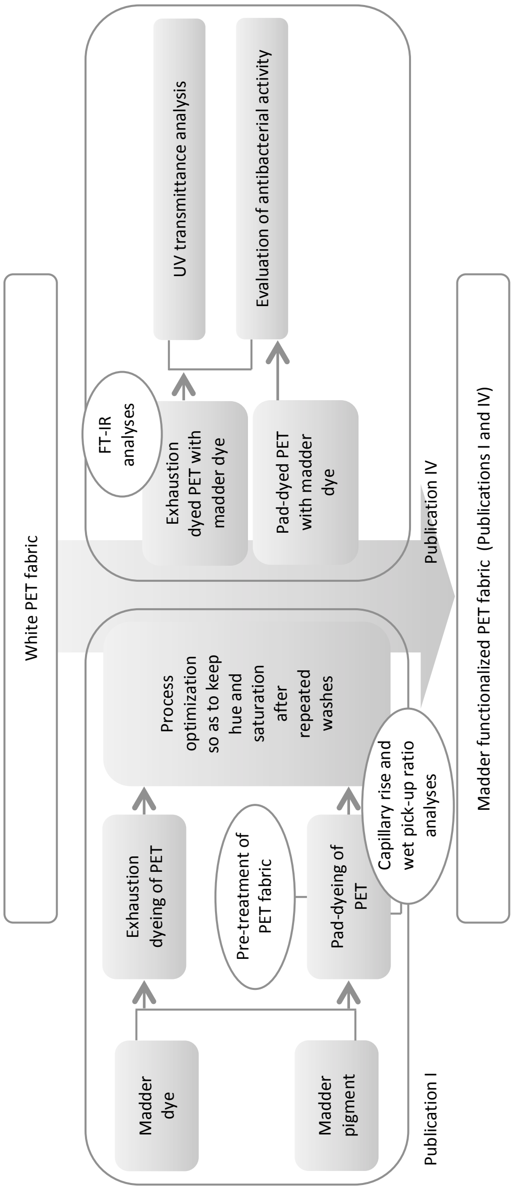


Figure 3 Structure of the thesis work in focus area I

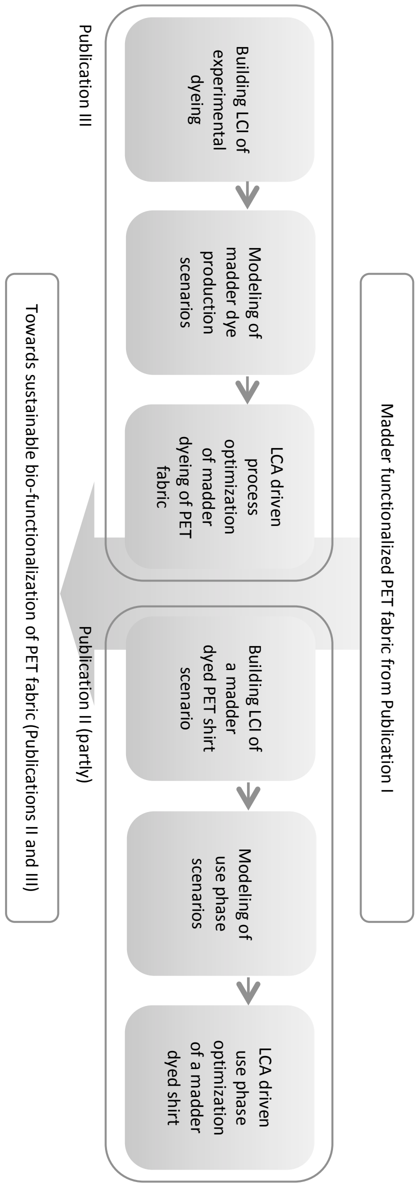


Figure 4 Structure of the thesis work in focus area II

1.5 Outline of the thesis

The thesis is divided into seven main chapters:

1. Chapter 1 provides a broad overview of the research topic by addressing sustainability and eco-design. This chapter also presents the objective, defines the research questions and moreover aims to show the research route to fulfill the object.
2. Chapter 2 presents the research background, and is divided into two parts. The first part will make the reader familiar with bio-functionalization of PET. The second part introduces the LCA methodology and the state-of-art regarding textile LCA studies. It is from this chapter the research gap has been defined.
3. Chapter 3 explains the experimental prototype making, carried out in the thesis. The subsequent LCA modeling is based upon the findings from this chapter. The chapter is described through four eco-design strategies.
4. Chapter 4 describes the experimental LCA modeling. Here the thesis enters into optimization of the prototype, with respect to environmental sustainability. Thus, this chapter links the two research areas: bio-functionalization of PET and LCA.
5. Chapter 5 addresses the LCA perspective on bio-based dyeing in general. This chapter is the result of literature studies and also based on experiences from the LCA modeling performed in the thesis.
6. Chapter 6 is the concluding chapter and discusses the answers to the research questions.
7. Chapter 7 puts forward recommendations for future work.

2 The research arena

2.1 Bio-functionalization of PET

2.1.1 The PET fiber

Until the seventeenth century natural fibers were mainly used for the production of textiles, and garments were made of for example, cotton, wool or silk. However, the situation today is different. Along with the development of synthetic fibers in the late 1930s, these fibers are now the ones predominantly used for textiles (Sinclair 2015).

Examples of synthetic fibers are the polyester fibers, which contain ester groups in their main polymeric chain (Deopura and Padaki 2015). This fiber group includes polyethylene terephthalate (PET), often referred to as polyester on garment labels.

The PET fiber is the most produced and consumed fiber in the world, with a global production of 49.1 million tons in 2014 compared to 25.4 million tons for natural fibers (cotton, wool, linen and silk) (Fiber Organon 2015).

Moreover, PET recycling is in development (Mowbray 2016a), as well as bio-based PET. The latter includes the use of sources of cellulose such as grasses and corn stover, instead of using crude oil (Mowbray 2016b). From this, this fiber type was used in the present thesis, envisaging that recyclable and bio-based PET will be available in the future.

The chemical structure of PET can be seen in **Figure 5**. The fiber is hydrophobic with limited water wetting behavior due to few polar interactions. The moisture regain value is as low as 0.4 % (Deopura and Padaki 2015). Because of its hydrophobicity textiles made of PET dry quickly, for example, as compared to cotton which takes longer to dry and has a moisture regain of 8.5 % (Yu 2015).

The fiber is considered semi crystalline with partially amorphous and crystalline regions. The glass transition temperature (Tg) of PET is about 78 °C, and increases to 120 °C when in drawn fiber form (East 2009). Due to the compactness of the fiber structure, chemicals do not easily diffuse inside the fiber. Dyeing is therefore generally performed at temperatures above the fiber Tg, around 130 °C. At this temperature the macromolecular mobility is increased, and the dye may diffuse to the interior of the fiber. However, studies have shown that the fiber Tg can be locally reduced by the plasticizing nature of certain dyes (De Clerck et al. 2005). The fiber is generally dyed with synthetic disperse dyes, designed specially for hydrophobic fibers, but some researchers have shown that there are natural dyes which possess similar structure as disperse dyes and potentially can be used to dye PET (Drivas et al. 2011).

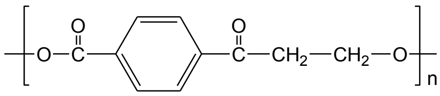


Figure 5 Chemical structure of PET

2.1.2 The functional species

2.1.2.1 Multifunctional and bio-sourced. The functional agent applied to the textile can be a man-made or bio-sourced species. In this thesis a bio-sourced dye was used. This type has been chosen for two reasons.

Firstly, bio-sourced dyes can potentially impart several attributes to the textile through one single dyeing treatment, and by doing so enable 'design for more consumer value using less material'. Textiles of today are namely, to a great extent, expected to fulfill several functional properties; for example, not only have a certain color but also show antibacterial activity (Yi and Yoo 2010) or flame retardant properties (Yasin et al. 2017).

Secondly, resource consumption can be replaced by the use of renewable materials.

2.1.2.2 Madder. One dye plant, which can be cultivated under European soil and climatic conditions, is the tinctorial plant madder (*Rubia tinctorum L.*). Moreover, with respect to plant yield and dye content, this dye plant has the potential to be used for industrial applications (Biertümpfel and Wurl 2009). Based on this, coloring species from the madder plant was used in the present thesis.

The madder, also known as European madder or the 'Queen of reds', is one of the oldest dye sources used throughout history. The plant, which is a perennial plant, was historically cultivated in Central and Western Europe and among the most important dye plants in Europe at the end of the nineteenth century. At this time in history, mills in France (Provence - one of the main regions for production) produced as much as 33 million kilograms of powdered madder during 8 months of yearly production (Cardon 2007).

However, with the invention of synthetic dyes in the late 19th century, plant-based dyes and their cultivation disappeared almost completely (Biertümpfel and Wurl 2009). The synthetic dyes were considered favorable, for example, because it was easier to reproduce shades, the dyeing process was simpler and cost of production could be reduced. Nevertheless, environmental issues such as resource shortage have led to a renaissance in research into the potential use of natural dyes as alternatives to existing synthetic ones (Drivas et al. 2011).

The madder coloring species can be found in the root of the plant, and are anthraquinone dyes. Anthraquinones constitute the largest group of natural coloring species, and around 200 different types can be found in flowering plants (Duval et al. 2016). About 36 anthraquinones have been identified in the madder root whereof 14 have been reported as important for dyeing.

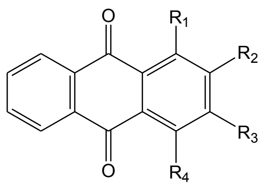
Alizarin **(1)** is well known as the main dye. Other species present are for example, purpurin **(2)**, xantho-purpurin **(3)**, rubiadin **(4)**, pseudopurpurin **(5)**, munjistin **(6)** and lucidin **(7)**, **Table 1**.

It has been shown that 1,3-dihydroxyanthraquinones which bear a methyl or hydroxymethyl group on carbon-2 are mutagenic, such as lucidin (Bechtold 2009). However, by using appropriate extraction method, lucidin may be completely eliminated (Derksen et al. 2003).

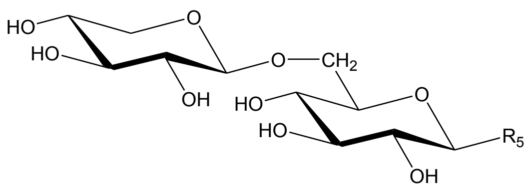
Indeed the madder dye is not a single chemical entity but a mixture of closely related compounds, and their relative content may vary according to the age of the plant and climate conditions. The dye is thus a multicomponent, and each component will have its own key features.

Table 1

Chemical composition of dyes in madder roots (Cuoco 2012; Cuoco et al. 2009; Derksen et al. 2004 & 2003 & 1998)



Anthraquinone (aglycone)



Primeveroside R_5 = O – aglycone

Common name	Structure
Alizarin **(1)**	R_1 = OH, R_2 = OH, R_3 = H, R_4 = H
Purpurin **(2)**	R_1 = OH, R_2 = OH, R_3 = H, R_4 = OH
Xanthopurpurin **(3)**	R_1 = OH, R_2 = H, R_3 = OH, R_4 = H
Rubiadin **(4)**	R_1 = OH, R_2 = CH_3, R_3 = OH, R_4 = H
Pseudopurpurin **(5)**	R_1 = OH, R_2 = COOH, R_3 = OH, R_4 = OH
Munjistin **(6)**	R_1 = OH, R_2 = COOH, R_3 = OH, R_4 = H
Lucidin **(7)**	R_1 = OH, R_2 = CH_2OH, R_3 = OH, R_4 = H
Anthragallol **(8)**	R_1 = OH, R_2 = OH, R_3 = OH, R_4 = H
Nordamnacanthal **(9)**	R_1 = OH, R_2 = COH, R_3 = OH, R_4 = H
Quinizarin **(10)**	R_1 = OH, R_2 = H, R_3 = H, R_4 = OH
Lucidin primeveroside **(11)**	R_1 = OH, R_2 = CH_2OH, R_3 = O – primeveroside, R_4 = H
Ruberythric acid **(12)**	R_1 = OH, R_2 = O – primeveroside, R_3 = H, R_4 = H
Galiosin **(13)**	R_1 = O – primeveroside, R_2 = OH, R_3 = COOH, R_4 = OH
Rubiadin primeveroside **(14)**	R_1 = OH, R_2 = CH_3, R_3 = O – primeveroside, R_4 = H

2.1.3 Functionalization methods

There are various methods for applying the functional species to the textile. It can be done either during fiber production (Ciera et al. 2014; Kim et al. 2016), or in a fiber/fabric treatment (Ferrero et al. 2015; Zhou et al. 2015). Examples of the latter include exhaustion and pad-dry-cure methods, and will be addressed here more in detail. For description of other functionalization methods, the reader is referred to Sun G (2016).

2.1.3.1 Exhaustion method. In exhaustion method the textile is immersed in a water bath containing the functional species. The functional species is firstly adsorbed on the fiber surface, and then diffuses to the interior of the fiber. The method requires a temperature above the fiber Tg, which induces segmental movements of the polymer chain. Once the polymer chains are mobile, a free volume will allow the functional species to enter the center of the fiber (Gedic et al. 2014). When the functional agent is a dye, this method is called exhaustion dyeing. After a certain dyeing duration, equilibrium will be reached between the dye concentration in the dyebath and inside the PET fiber. The dyebath is then cooled down, and the dye is trapped inside the fiber, **Figure 6**.

In addition to the Tg, dye diffusion depends on several parameters such as the size of the dye and the dyeing environment including its pH and amount of auxiliary chemicals.

2.1.3.2 Pad-dry-cure. In pad-dry-cure, the functional species is applied on the surface of the polymer. This includes dipping the fabric in a bath, containing the functional agent, before it is squeezed between rolls. This is followed by a drying and curing step. Through this method the functional species may be grafted onto the surface, with or without crosslinking agents, **Figure 6**. However, during the curing step, the species may move from the surface of the fiber to the interior. When this occurs and the functional species is a dye, this method is called pad-dyeing.

Previous research in the GEMTEX laboratory (ENSAIT, France) has shown that, through the padding method, the chitosan bio-polymer can make the textile surface cationic (Behary et al. 2012) and further enables grafting with anionic functional molecules. Grafting on PET is a challenge, since the fabric is hydrophobic. The same research laboratory has shown that air atmospheric plasma treatment is an effective way to assist the grafting by modifying the nature and the number of functional groups of the PET fiber (Ran et al. 2012).

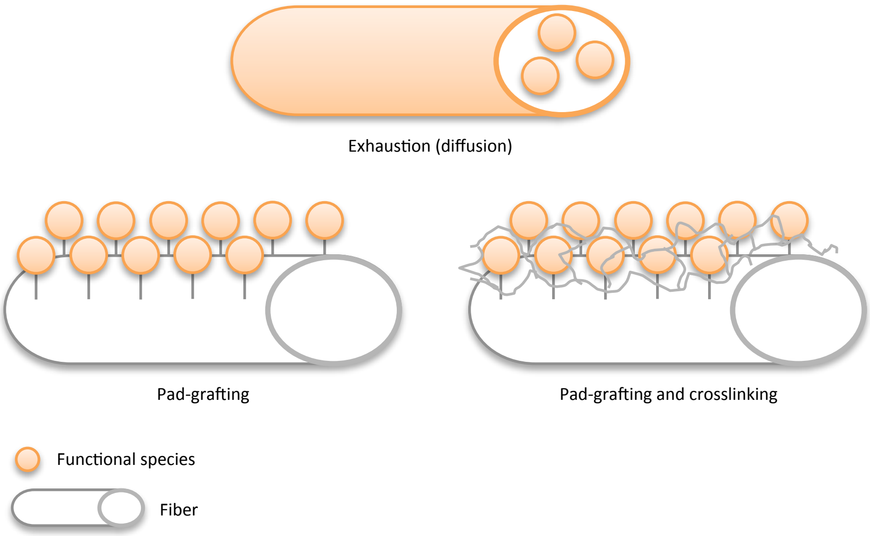


Figure 6 Functionalization methods (schematic)

2.1.4 Functional attributes through madder dyeing - in theory

2.1.4.1 Color. When looking at some of the characteristics of alizarin, the main dye in madder, it can be hypothesized that this molecule has the potential to dye PET. Namely, the molar volume is 155.9 ± 3 cm^3, indicating a finer size than several commercial anthraquinone disperse dyes. This holds also for other dyes present in madder such as purpurin and quinizarin (Gedic et al. 2014).

Halochromic behavior is another characteristic. The neutral, anionic and di-anionic forms of alizarin respectively, present different positions of their absorption maxima (Lofrumento et al. 2015; Van der Schueren and De Clerck 2010). The halochromism includes that the color of alizarin in an aqueous solution will be influenced by the pH, and that the polarity of the molecule may be reduced because the polar charge is delocalized. The less polar the dye, the more suitable for PET.

The solubility parameter has been used to explain disperse dye sorption onto hydrophobic fibers. The solubility parameter of the dye should be near that of the fiber, in our case near 21.7 $(J/cm^3)^{0.5}$. However, most anthraquinone dyes, including alizarin, have a solubility parameter greater than 26.4 $(J/cm^3)^{0.5}$, indicating a value not very near to the solubility parameter of PET. Nevertheless, when dyeing of PET is performed at high temperatures such as 130 °C, this issue seems to be of less importance (Karst and Yang 2005).

2.1.4.2 Antibacterial activity. The term 'antibacterial' refers to an agent that either destroys various bacteria or slows down their growth. More specifically, there are several ways antibacterial agents may inhibit bacterial growth; for example, by cell wall damage, inhibition of cell wall synthesis or inhibition of the synthesis of proteins and nucleic acids. Some agents act by diffusion, such as silver ions incorporated in the fiber matrix. In this case, the silver ions diffuse out from the fiber, penetrate the membrane of the bacteria and block the replication of bacterial DNA. The antibacterial agent can also act through direct contact with the bacteria from the fiber surface. Here an example is quaternary ammonium salts, which are cationic surface active agents. These can be applied to surfaces of fibers, and work by disrupting the negatively charged cell membrane of the bacteria (Hardin and Kim 2016).

Antibacterial activity of the madder dye has been reported in Kalyoncu et al. (2006), but the same study does not reveal the responsible molecule or molecules for the antibacterial effect. From other researchers however, it has been shown that alizarin, purpurin and quinizarin present antioxidant and antibacterial activities (Dzoyem et al. 2017; Lee et al. 2016; Yen et al. 2000). The antibacterial effect may be related to the redox potential of these molecules, as for quinones in general, and their ability to form complexes with amino acids. This will inhibit the synthesis of proteins and the bacterial growth (Alihosseini 2016). Lee et al. (2016) suggest that the anthraquinone backbone, which bear hydroxyl units on carbon-1 and carbon-2 such as alizarin, can affect the bacterial cell wall of *Staphylococcus aureus,* but that further studies is needed in order to better understand the mechanisms responsible for the antibacterial effects.

2.1.4.3 Ultraviolet protection ability. Ultraviolet (UV) radiation ranges between 100 and 400 nm, and is subdivided into UV-C (100-280 nm) stopped in the stratosphere, UV-B (280-315 nm) and UV-A (315-400 nm) (Sun and Tang 2011). It is known that overexposure to UV-A and UV-B can cause harmful effects such as premature aging and skin cancers. In order to avoid these effects, the UV radiation exposure needs to be reduced, for example, with textile clothing (Grifoni et al. 2014; Hupel et al. 2011).

The UV protection ability of textiles is influenced by several factors such as the fiber type, the fabric structure and its color. Dyes impart UV protective effect onto textiles to varying extent depending on their chemical nature: the conjugated systems (alternating double and single bound) and electronic transitions (electrons in the dye molecule are excited from one energy level to a higher energy level) (Sönmezoğlu et al. 2012; Zhou et al. 2015). It has been shown that that alizarin in the madder dye has an absorption not only in the visible region, with maxima around 430 nm (pH<7), but also in the UV region with an intense peak at 300 nm (De Reguardati and Lemonnier 2012). From this, it can be assumed that alizarin in the madder dye may contribute to UV protective effect when applied to textiles.

2.1.4.4 Characterization methods. From the above (Sections 2.1.4.1-2.1.4.3), it can be hypothesized that coloring species in madder dye will give color to PET, as well as impart UV protection ability and antibacterial activity. To characterize these functional performances there are, however, various methods. The ones used in this thesis will be specified here.

The color was characterized using either Datacolor Spectraflash SF600 reflectance spectrophotometer (Publication I) or HunterLab UltraScan PRO reflectance spectrophotometer (Publication IV). Regardless of the type, illuminant D65 and 10 ° standard observer were used.

The antibacterial activity was evaluated quantitatively, according to GB/T 20944.3-2008 (eq. ISO 20743-2007). Two types of bacteria were use; namely, *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*). The former Gram-positive, and the latter Gram-negative.

UV protection performance was measured and evaluated according to Australia/New Zealand Standard AS/NZS 4399:1996. This standard uses UV protection factor (UPF) ratings and, from this, the textile can be classified as insufficient, good, very good, or excellent protection.

2.2 Life cycle assessment tool

2.2.1 The methodology

The LCA methodology holistically evaluates the environmental impacts of a product by quantifying the energy and materials used (inputs), the wastes and emissions released to environment (outputs) and the environmental impacts of those inputs and outputs over the entire life cycle (Jiménez-González et al. 2000).

The holistic approach helps to avoid a narrow view of environmental concerns and reduces the risk for burden shifting; namely, shifting the environmental problem from one life cycle phase to another or one environmental issue to another (ADEME 2005; Roos et al. 2015).

According to ISO 14040 and ISO 14044 standards, a LCA comprises of four phases which are interdependent: (1) goal and scope definition, (2) life cycle inventory analysis (LCI), (3) life cycle impact assessment (LCIA) and (4) interpretation (ISO 2006a; ISO 2006b). The relationship between these phases is illustrated in **Figure 7**.

The four phases are described in Publication V. However, it is here reiterated that the goal and scope definition includes defining the functional unit (FU). The FU serves as the central element of LCA. It quantifies the function of the system studied and acts as a reference unit, by answering questions such as 'what', 'how much', 'how well' and 'how long' (Ilcd 2010). In a comparative LCA, the functional units must have the same functional performance. Otherwise a meaningful and valid comparison is not possible. However, it is not always easy to identify *the* function of the system. This is because systems can be multifunctional and differentiation between primary and the secondary functions may be indiscernible (Judl et al. 2012; Margni 2015).

LCA is an iterative process, which allows for adjustments as a result of new insights. The iterative character of LCA is described by the arrows back and forth between the phases in **Figure 7**, and also shown in **Figure 8**.

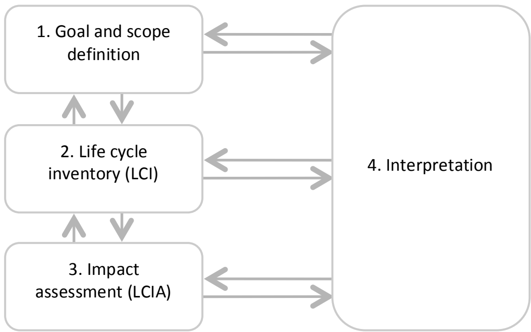


Figure 7 The four phases of a LCA and their interrelations in the LCA framework (ISO 14040)

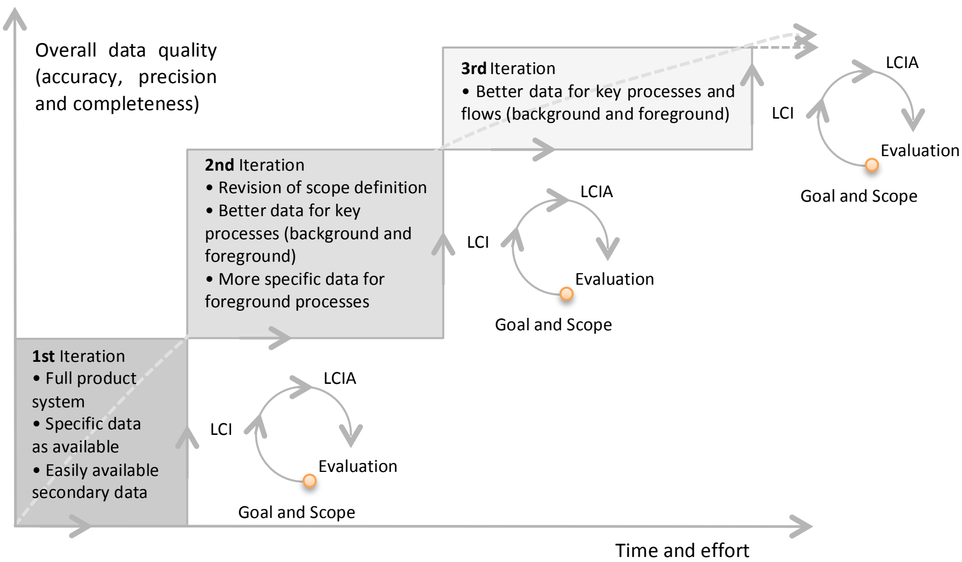


Figure 8 Iterative nature of LCA (Ilcd 2010)

2.2.2 Uncertainty and data quality

LCA tries to model the reality and, through its iterative character, aims first to be accurate (screening) and works then on precision (detail LCA). It is preferable to be imprecisely accurate than precisely inaccurate, see **Figure 9** (Humbert et al. 2015). For example, screening may include characterization of the environmental profile so as to determine the processes that contribute the most to environmental impacts (key processes/hotspots). From this one may move to detailed LCA, focused on gathering better data for key processes. Thus, screening to detailed LCA involves 'acting where it counts'. An example on moving from screening to detailed LCA is given in Section 4.1.1.

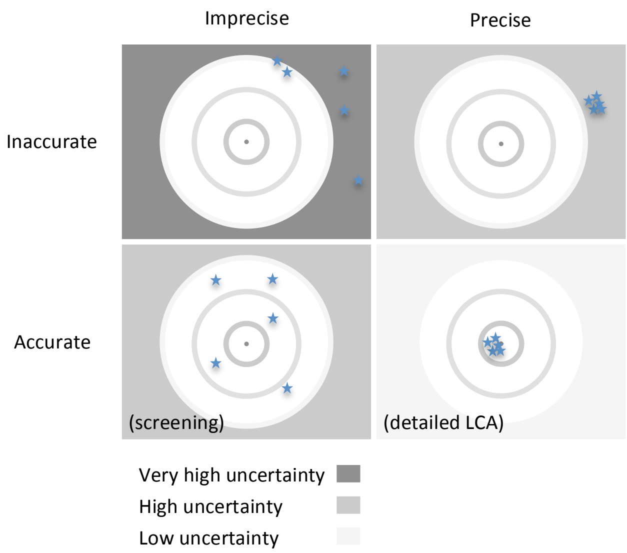


Figure 9 Uncertainty in LCA (Humbert et al. 2015)

In order to estimate results, such as evaluating how well the LCA model reflects the reality or the actual consequence of implementing the results of the investigation, an uncertainty analysis should be performed.

If the LCA database does not include results on uncertainty, another way is to use a pedigree matrix with data quality indicators. Weidema and Wesnaes (1996) have introduced five indicators to describe the data quality: reliability, completeness, temporal, geographical and technological (**Table 2**). However, it may be mentioned that the guidelines for the product environmental footprint (PEF) implementation recommend six data quality criteria by adding methodology to the other five (PEF 2012).

Table 2

Data quality matrix with 5 data quality indicators (Weidema 1998)

Data quality indicator	Score				
	1	2	3	4	5
Indicators, which are independent of the study in which the data are applied:					
Reliability of the source	Verified data based on measurements	Verified data partly based on assumptions or non-verified data based on measurements	Non-verified data partly based on assumptions	Qualified estimate (e.g. by industrial experts)	Non-qualified estimate or unknown origin
Completeness	Representative data from a sufficient sample of sites over an adequate period to even out normal fluctuations	Representative data from a smaller number of sites but for adequate periods	Representative data from an adequate number of sites but from shorter periods	Representative data but from a smaller number of sites and shorter periods or incomplete data from an adequate number of sites and periods	Representativeness unknown or incomplete data from a smaller number of sites and/or from shorter periods
Indicators relating to the technological and natural production conditions under which the data are valid, and therefore dependent of the data quality goals for the study in which the data are applied:					
Temporal correlation	Less than 3 years of difference to year of study	Less than 6 years of difference	Less than 10 years of difference	Less than 15 years of difference	Age of data unknown or more than 15 years of difference
Geographical correlation	Data from area under study	Average data from larger area in which the area under study is included	Data from area with similar production conditions	Data from area with slightly similar production conditions	Data from unknown area or area with very different production conditions
Further technological correlation	Data from enterprises, processes and materials under study	Data from processes and materials under study but from different enterprises	Data from processes and materials under study but from different technology	Data on related processes or materials but from same technology	Unknown technology or data on related processes or materials, but from different technology

This dissertation has addressed inventory data gaps and uncertainties through the use of the last three quality indicators listed in **Table 2**.

The next section will give an overview of the state-of-the-art for textile LCA studies. For further description of the LCA methodology in general, the reader is referred to ISO 1404X and the handbook produced by the European Commission (Ilcd 2010).

2.2.3 Textile LCA studies

The European Science Foundation's COST Action 628 (Nieminen et al. 2007) suggests the use of LCA to focus the development of new textile processes. By applying LCA, the environmental impacts can be analyzed and the polluting stages identified and, among the several life cycle stages that a textile product passes through, LCA has helped to show that the largest contributions to impacts on the environment arise from the manufacturing and the use phases (Chapman 2010).

LCAs have shown that the dyeing unit process is very important with respect to impacts on the environment. For instance, a LCA study of the production of dyed cotton yarn revealed that the dyeing phase was a hotspot due to the intensive use of chemicals and energy (Bevilacqua et al. 2014). Moreover, Allwood et al. (2006) acknowledge that major environmental impacts of the textile sector arise from the use of chemicals and energy. This makes conventional dyeing an eco-issue of concern as it indeed consumes chemicals and thermal/electrical energy in addition to a great amount of water, the last around 100 times the fabric weight as addressed in Section 1.1.4.

Parisi et al. (2015) performed a LCA to evaluate the environmental impacts associated with a new dyeing process in comparison to a classical dyeing process. Other LCA studies deal with spin-dyeing versus conventional dyeing (Terinte et al. 2014) as well as pad-dyeing technology (Yuan et al. 2013). These studies have one thing in common: via LCA, improvement options have been proposed so as to minimize the environmental impacts of textile dyeing.

Nevertheless, there are life cycle stages other than the dyeing stage where improvements can be made, described subsequently.

Firstly, the impacts of fiber production should be minimized. For this purpose, a LCA cradle-to-gate study of acrylic fiber manufacturing has been performed (Yacout et al. 2016). Another study has dealt with PP fibers, revealing that a recycled alternative offers environmental benefits compared to a virgin one (Yin et al. 2016). Muthu (2015) reviews that for PET fibers, the production of purified terephthalic acid is a major issue. Natural fibers for example, raw silk (Astudillo 2015), flax (Deng et al. 2016) and hemp (Van der Werf and Turunen 2008) have also been studied. These studies have one thing in common: through the use of LCA, improvement options have been identified to minimize the environmental impacts of fiber manufacturing and so help in converting the textile industry to a more environmentally sound one.

Next, regarding the spinning and weaving stage, energy consumption is inversely proportional to yarn fineness. Therefore, the LCA can only be accurate when fineness for yarn or information such as density for a fabric is specified in the functional unit (Van der Velden et al. 2014). However, Nieminen et al. (2007) point out that such definitions are generally absent, textile weight in kg is often used instead. For the LCA to be a support for product development, quality aspects need to be included in the functional unit.

While water and land use impacts of the production of wood based fibers and cotton fibers have been studied in Sandin et al. (2013), Baydar et al. (2015) performed a comparative study between an organic cotton T-shirt and a conventional alternative. The latter study revealed that the organic cotton T-shirt had lower environmental burdens for every impact category studied, compared to the conventional T-shirt. Furthermore, indeed, the use phase of the T-shirt contributed to global warming potential due to the laundry operations.

Van der Velden et al. (2014) however, showed less relative impact from the use phase than suggested by others. The same study highlights that it is extremely difficult to determine consumer's wear and care habits and that the outcome may vary substantially depending on the concrete circumstances.

In order to reduce the environmental impacts from the use phase, in particular from textile laundry, the development of 'self-cleaning' textiles has attracted attention. Through the LCA tool Busi et al. (2016) showed that an innovative easy washable textile, produced by depositing a nano crystalline layer (TiO_2 photocatalytic) onto the textile's surface, was a more eco-sustainable alterative than the conventional alterative due to reduced impacts from the laundering in the use phase. Similarly, potentially lower washing frequency in the use phase has been suggested to compensate for increased CO_2 eq. loads in manufacturing of a nano silver T-shirt (Walser et al. 2011). Furthermore, Manda et al. (2015) addressed that antibacterial textiles may enable fewer washing cycles in the use phase, thus presenting an opportunity to reduce environmental impacts.

Roos et al. (2015) pointed out that bleached cotton may contribute to lower environmental burdens than unbleached, due to an expected longer lifetime in the use phase of the bleached garment. Moreover, Roos (2016) recently presented a dissertation on advancing LCA of textile products to include textile chemicals.

From this literature review, it can be said that LCA has become an important tool for evaluating and communicating the environmental impacts of textiles.

3 Prototype making

The first experiments regarded to create a prototype, which could be used in the LCA modeling. The initial idea was to perform a comparative LCA between the two dyeing methods: exhaustion dyeing and pad-dyeing. Based on this, experiments were designed so as to create a prototype for each dyeing method. The prototype making will be described in relation to the Eco-design strategies wheel (Section 1.1.5).

3.1 Low-impact materials

According to the 2nd strategy in the UNEP Eco-strategies wheel, recycled or recyclable materials are preferred. In this thesis a recyclable PET was used, more in detail a monocomponent plain woven fabric of density 110 g/m^2.

Also choosing bio-sourced materials is part of the 2nd strategy. However, in the textile sector many products are bio-sourced, it does not mean that they are eco-designed. It depends on the production, the yield and the region. In this thesis bio-sourced GOTS and REACH certified madder (*Rubia tinctorum L.*) water soluble dye and water insoluble pigment were used, kindly supplied by Couleurs de plantes (France).

3.2 Optimization of production

Optimization of production is part of the 4th strategy. From the beginning we dealt with the question how to optimize the dyeing with respect to color and durability. Subsequently, the exhaustion dyeing and pad-dyeing will be addressed individually.

3.2.1 Exhaustion dyeing

In this thesis exhaustion dyeing was carried out in 200 mL beakers in a high pressure and high temperature/beaker dyeing machine (Labomat, Switzerland), as described in Publication I.

The first trials revealed that the dyebath pH influenced durability performance of the color and its hue and saturation. For example, with increased pH the wash fastness decreased and the color shifted from yellow/orange to purple (Publication I). Based on additional experiments, which regarded dyeing temperature and dyeing duration, an optimized dyeing condition was found. This included an acidic dyebath (pH 5) with dyeing temperature of 130 °C and dyeing duration of 45 minutes. Temperature/time profile of the most promising exhaustion dyeing condition is shown in **Figure 10**. Pre-wash was preformed so as to clean the fabric from surface impurities. After-wash was done in order to remove physio-sorbed dyes which may cause low fastness properties.

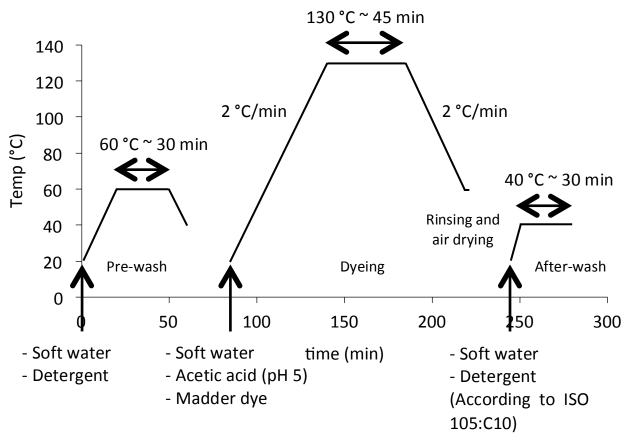


Figure 10 Temperature/time profile for the most promising exhaustion dyeing route (Publication II)

3.2.2 Pad-dyeing

In our work the pad-dyeing of PET fabric was carried out using a laboratory-scaled padder (Werner Mathis AG, Switzerland). The pressure was set to 2 bars and the rotation speed to 2.5 m/min.

We were encouraged by the first pad-dyeing results: namely, a homogenously dyed fabric with a wet-pick up of 90 % was obtained, and the process enabled a low amount of effluents. Nevertheless, the wash fastness was considered low from gray scale measurements. Because of this, different fabric pre-treatments were designed with the aim to improve the pad-dyeing route and with as little as possible impact on the environment. Specifically, air atmospheric plasma treatment and chitosan bio-polymer were used, both addressed in the BREF.

The conditions for the plasma treatment were selected based on Guo et al. (2009) and Pasquet et al. (2014), and included a treatment power of 45 kJ/m^2, and two treatments on each side. Further description can be found in Publication I. From this, the wet pick-up increased to 99 %, and the capillary uptake increased with 68 % (Publication I). The chitosan was applied in 3 g/L in the presence of formic acid (pH 3).

We found that the color strength increased the most with the procedure illustrated in **Figure 11**; namely, surface activation by plasma, padding with chitosan, drying and curing, pad-dyeing with madder dye and finally drying and curing again. This result could be explained by the increased wettability by plasma treatment and the increased Zeta-potential by chitosan application. In the GEMTEX research laboratory (ENSAIT, France) studies have namely shown that chitosan deposition results in a more positive Zeta potential compared to untreated PET (+60 mV to −10 mV at pH 5 same comparison) due to positive charges on the fabric surface (protonation of amino groups) (Behary et al. 2012; Guo et al. 2009).

Nevertheless, the production chain for the pad-dyeing route is long, compared to the exhaustion dyeing which requires three steps: pre-wash, dyeing and after-wash. Included in the 4th eco-design strategy is to apply fewer production processes. Each process step illustrated in **Figure 11** will have an impact on the environment and, for example, the twice drying and curing will require a considerable input of energy. Not presented in any publication but to overcome this limitation we tried to reduce the number of steps in the pad-dyeing route, for instance by applying the dye and chitosan in the same bath. Nevertheless, these trials were less successful with respect to obtained color strength.

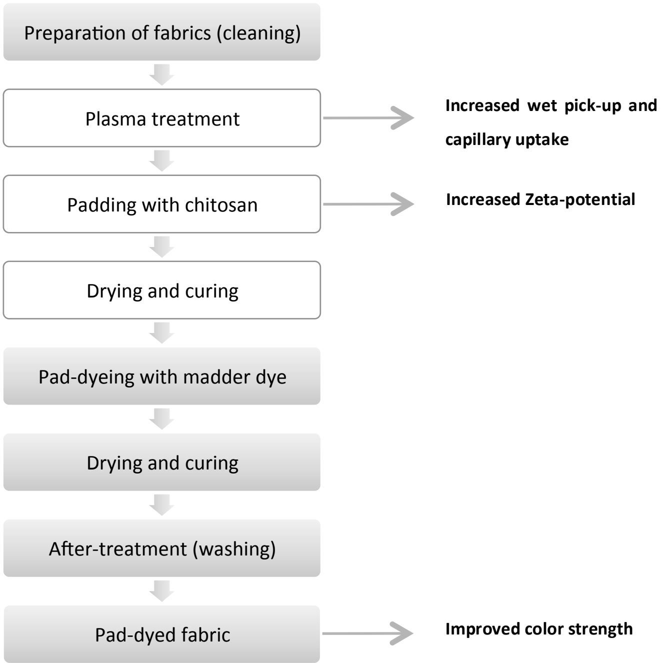


Figure 11 Schematic flowchart of the most promising pad-dyeing route (adapted from Publication I)

3.3 Optimization of initial lifetime

Optimization of the initial lifetime is part of the 7th strategy in the Eco-design strategies wheel. Moreover, as addressed in environmental management (ISO/TR 2002), in pursuing a more sustainable development, it is necessary to consider not only conservation of resources but also the functionality of the product and its durability properties. Increasing the durability/quality can reduce environmental impacts as it may delay the disposal of the product and the arrival of another one using water, energy and chemicals (Muthu et al. 2013).

Pasquet (2012) has revealed that color fading is one of the major reasons why garments are discarded. Based on this, and the previous paragraph, the dyeing process parameters were optimized so as to maintain color hue and saturation after repeated washes (Publication I). Additionally, wet and dry rub fastness properties were studied (Publication I) and fastness to light (Publication IV). The durability tests refer to ISO standard methods or equivalent, as described in the publications (I and IV).

Results showed that the optimized exhaustion dyeing enabled good to excellent wash fastness and rub fastness properties (Publication I) and moderate light fastness (Publication IV). Optimized pad-dyeing showed low to moderate durability performance overall (Publication I).

More in detail, regarding the wash fastness, dyed samples were subjected to five consecutive washing cycles. At the end of each wash, the samples were rinsed in soft water and left to dry under ambient conditions. The exhaustion dyeing was carried out using the optimized condition shown in **Figure 10**, and with three dye concentrations: 1 %, 3 % and 5 % owf. Owf represents the dye concentration 'on weight of fabric'. The color strength (K/S) reached its greatest value of 1.5 with 5 % owf. The same color strength could be reached through pad-dyeing, and more specifically, when the optimized route shown in **Figure 11** was applied with 30 g/L madder dye. Nevertheless, as seen from **Table 3**, indeed the wash fastness was different for the two dyeing methods, with exhaustion method being the favourable one.

Table 3

Color strength (K/S) values of madder dyed PET fabrics

	K/S initial[1]	K/S after 5 washes
Exhaustion dyeing	1.5	1.4
Pad-dyeing	1.5	0.4

[1] K/S initial was measured before after-wash. The after-wash was considered as the first wash.

3.4 Optimization of functions

Optimization of functions belongs to the 1st eco-design strategy, which includes integration of several functions; this said, once a dyed fabric with good durability performance was obtained, functional properties other than color were studied. This included characterizing the UV protection ability and antibacterial activity against *S. aureus* and *E. coli* (Publication IV). As our study showed that the exhaustion dyeing was more favorable than the pad-dyeing, with respect to fastness properties, exhaustion dyed samples were used for characterization of the additional functional properties. It shall be pointed out that the same samples were used in Publication I and Publication IV and, although a year had passed in between, their color appearance were unimpaired.

We found promising results. Inhibited growth of bacteria as well as UV protection performance was obtained. For the former, the 3 % owf dyed fabric showed an antibacterial activity of 86 % against both types of bacteria tested. For the latter, the undyed PET fabric showed high UV protection ability and could be classified as 'excellent' UV protection (UPF value of 65). Nevertheless, when the fabric was dyed with madder dye, the UV protective effect increased. More specifically, UPF values of 106 and 112 were found for 3 % and 5 % owf, respectively.

Finally, a multifunctional madder dyed PET fabric could be presented, and our results indicate that the theory presented in Section 2.1.4 may hold. Color was obtained; namely, the madder dyed fabric absorbed blue/green color, and a yellow/orange color appeared to the human eye. The λ_{max} of the color obtained was in agreement with the absorption peak related to the neutral form of alizarin (430 nm) (Lofrumento et al. 2015; Van der Schueren and De Clerck 2010) (Publication I). From CIELab data, the dyed fabric (3 % owf) showed a yellowness-blueness value of +24 (positive value denotes yellow) and a redness-greenness value of +14 (positive value denotes red)(Publication IV). Moreover, the madder dye improved the UV protection ability by decreasing the transmittance of UV radiation. The dye also inhibited bacterial growth, possibly by migration of alizarin molecules from the interior to the surface of the fiber. Once at the surface, alizarin can be released so as to be active and affect the bacterial cell wall.

4 Putting the prototype into the LCA tool

4.1 Life cycle assessment

Once a prototype was created for each dyeing method: exhaustion dyeing and pad-dyeing, the study proceeded towards eco-sustainable bio-functionalization of textiles. This was done by introducing the LCA tool in the design process.

The initial idea was to compare the two prototypes in LCA. It was found however, that the modeling of the pad-dyeing route included a less representative inventory compared to the one for the exhaustion method. For example, the chitosan bio-polymer had to be replaced by the module 'unspecified organic compound'. Moreover, since the durability was less good with the pad-dyeing route, a comparison was not considered meaningful. Instead we focused on LCA driven process optimization of the exhaustion dyeing.

Referring to Section 2.2.1, the LCA was performed according to ISO standards (ISO 2006a; ISO 2006b). EIME software was used (Bureau Veritas CODDE). Publication II considered a cradle-to-grave perspective, while Publication III considered a gate-to-gate perspective.

Ten impact categories were studied in the present thesis: Air Acidification (AA)[AE], Air Toxicity (AT)[m^3], Freshwater Ecotoxicity (FWE)[CTUe], Global Warming Potential (GWP)[kg CO2 eq.], Ozone Depletion Potential (ODP)[kg CFC-11 eq.], Photochemical Ozone Creation Potential (POCP)[kg NMVOC eq.], Raw Material Depletion (RMD)[person reserve], Terrestrial Ecotoxicity (TE)[kg 1,4 – DB eq.], Water Depletion (WD)[dm^3] and Water Eutrophication (WE) [kg PO_4^{3-} eq.], and the potential environmental impacts were expressed at midpoint level.

Neither Publication II nor Publication III addressed the use of the midpoint level. Conversely, it was discussed in Publication V. Publication V told that LCIA can be expressed *either* close to the environmental intervention at the midpoint level *or* further away at the endpoint level. At the midpoint level, known as the classical impact assessment method, the results are typically expressed as equivalent values for every impact category (e.g. kg CO_2 eq. for global warming potential). At the endpoint level, the impact categories are translated into damage categories for example, human health, resource depletion and ecosystem quality (UNEP/SETAC 2011) and the results are expressed as damage values (e.g. DALYs for human health).

Endpoint level indicators are considered to increase in relevance, but at the same time the uncertainty of the results increases (Bulle 2015). This is because in general an indicator defined closer to the environmental intervention will result in more certain modeling while an indicator more far away will provide more relevant information linked to society's concern and areas of protection (Georgakellos 2016; Sonnemann et al. 2004). Along with the improvement of the LCA tool, it would be relevant to assess the environmental impacts of bio-based dyeing and proceed the assessment to the endpoint level.

LCA typically includes a process flow diagram of the system studied. The process-flow diagram of the gate-to-gate system studied is shown in **Figure 12** while **Figure 13** shows the one for the cradle-to-grave. The geographical scope was France.

Referring to Section 2.2.1 and **Figure 7**, the first phase in the LCA framework includes definition of the functional unit (FU). Based on the dyeing experiments, the chosen FU for the gate-to-gate was 'dyeing of 1 kg woven polyester fabric (110 g/m^2) with 3 % owf madder dye'. The FU for the cradle-to-grave was 'one madder dyed woven polyester shirt to be worn and cleaned, twice a month, for 2.5 years'. The lifetime of the shirt was 2.5 years based on recommendations from textile quality experts (Bureau Veritas CODDE).

Subsequently, the gate-to-gate and cradle-to-grave study will be addressed individually.

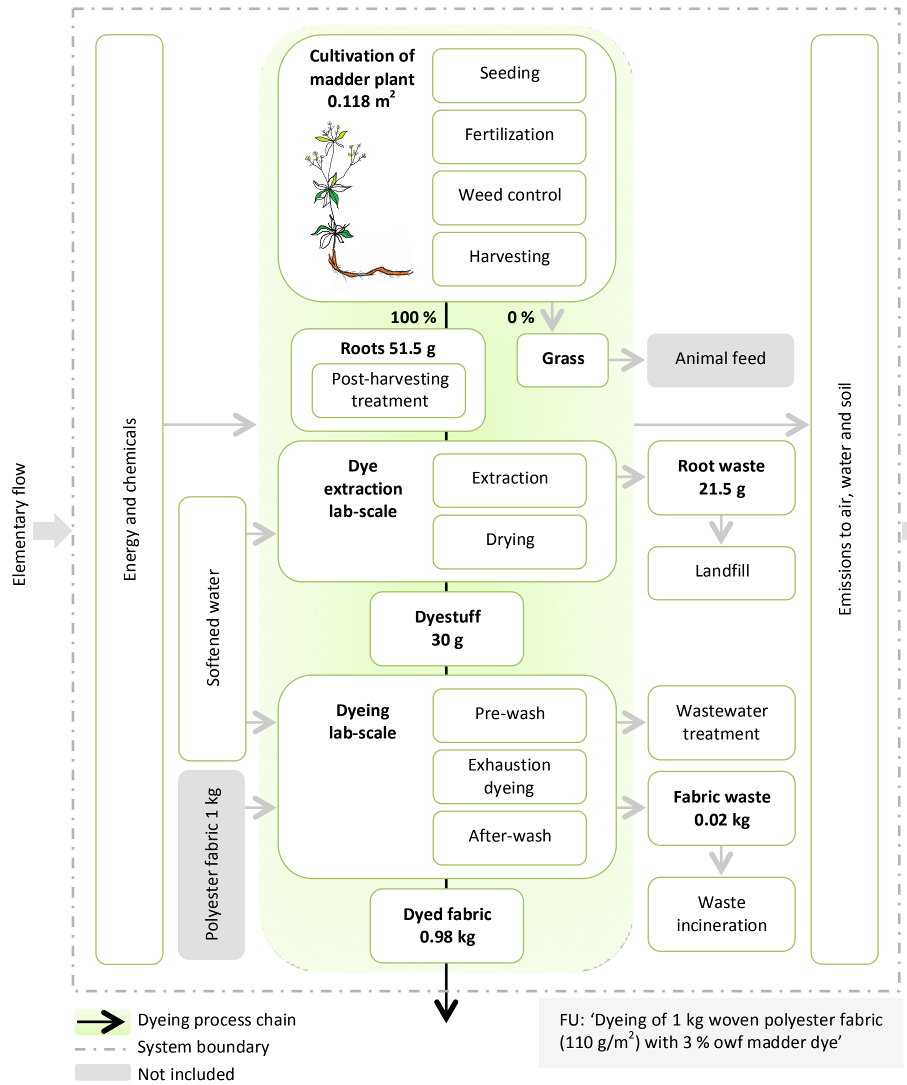


Figure 12 Process-flow diagram of the gate-to-gate system studied (gray boxes were not considered) (Publication III)

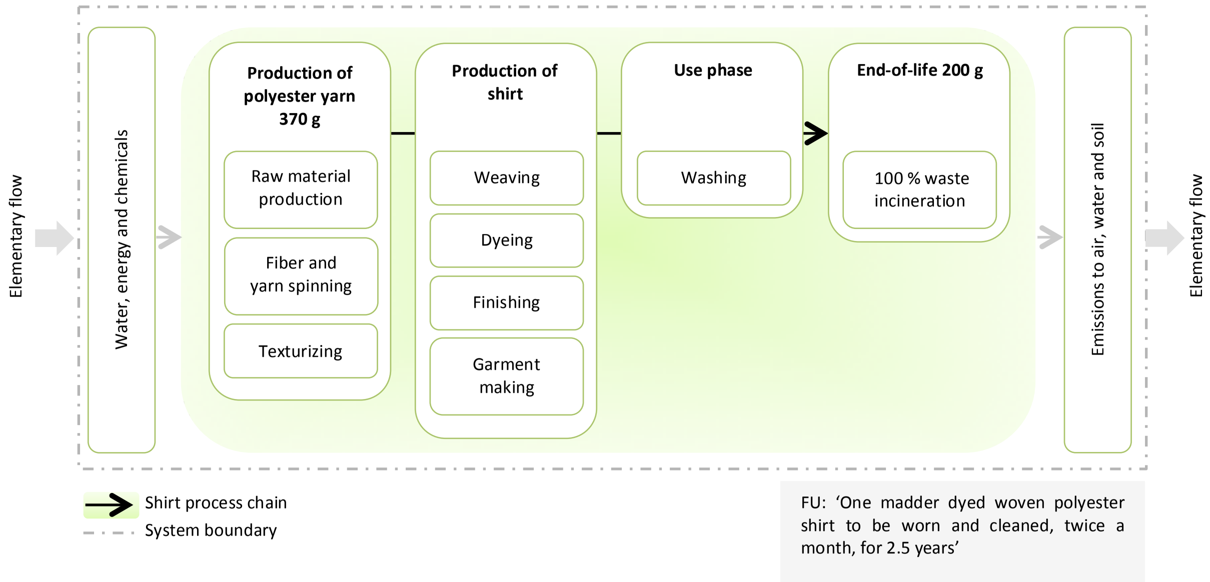


Figure 13 Process-flow diagram of the cradle-to-grave system studied

4.1.1 Gate-to-gate

The gate-to-gate study considered the three life cycle phases: agriculture (seeding to post-harvesting treatment), dye extraction (extraction and drying) and the dyeing phase (pre-wash to after-wash), as described in Publication III.

The data acquisition for the dyeing phase was based on foreground information; namely, the data from the laboratory experiments described in Publication I. The collected data regarded each step of the dyeing phase by considering the energy and water consumption and the quantities of chemicals used for the prototype. From this, primary activity data was used for the dyeing phase. For the agriculture phase and dye extraction, secondary activity data was used.

Firstly screening of the dyeing process was performed. This revealed that for 'dyeing of 1 kg woven polyester fabric (110 g/m^2) with 3 % owf madder dye' the dye extraction phase was a hotspot.

Here it needs to be told that, tinctorial plants contain coloring species and other non-coloring plant constituents, starch among others. The dyes must thus, be extracted from the plant material (separation of the coloring species from the non-coloring ones) so as to prepare dyes of high purity. In order to minimize the environmental impacts from dye extraction, unconventional extraction methods have been researched; for example, a comparison between classical reflux extraction and novel ultrasound extraction has been described in Cuoco et al. (2009). Their results pointed out higher dye yield and shorter extraction time when replacing the classical method with the novel one.

With the intention to show LCA driven process optimization of the dyeing (including madder dye production), different dye extraction scenarios were modeled in LCA; namely, classical reflux and novel ultrasound assisted. From the modeling of the two, for the production of 30 g madder dye (30 g presents the amount of dye necessary per FU), a greater amount of softened water and lesser amount of electrical energy, methanol and waste were needed when replacing the conventional method with the novel method. The precise amounts can be found in Publication III.

Moreover, also the dyeing phase was a hotspot. Because of this, after-wash scenarios were evaluated. This included studying different liquor:fabric ratio (LR) as well as the quantity of detergent. For the comparison, we confirmed that neither

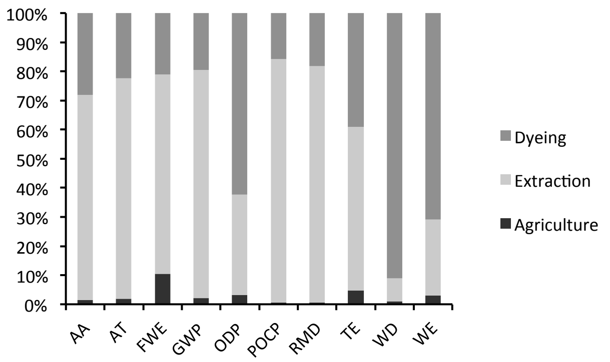
LR nor detergent quantity influenced the color performance. The color and the color's durability remained the same.

Based on the dye extraction and after-wash scenarios, we were able to show LCA driven dyeing process optimization at the research stage. This route is shown in **Figure 14**. As seen, improvement was needed in both hotspots in order to perform optimally in all impact categories studied.

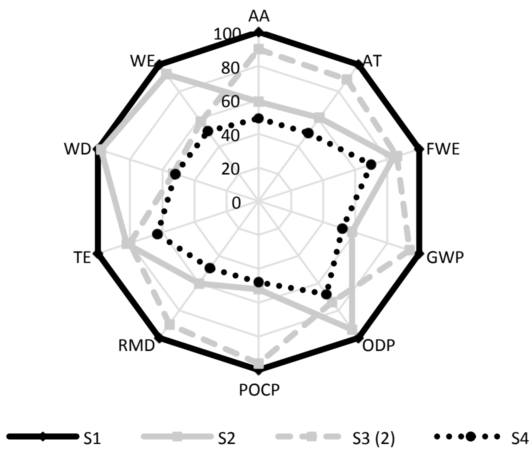
The results presented in **Figure 14** are adapted from Publication III. Publication III addressed that these results cannot be directly extrapolated to other production regions, because the amount of roots/ha varies from one country to another and one region to another; for example, around 3 ton/ha in Germany and 8 ton/ha in Italy. To increase the validity of the research results it could have been interesting to compare the situation in France (root yield of 4.35 ton/ha) with the other two production regions, for which the root yield is quoted, and the electricity mix is different (predominantly nuclear in France). However, this remains to be explored in future work.

It should be emphasized that the importance of the results presented in **Figure 14** lies in contextualizing the application of LCA to dyeing of textiles with bio-based dyes, and that it shows a method how to measure progress towards sustainable bio-functionalization of textiles.

1. Characterization of the environmental profile (reference scenario)



2. Modeling dyeing phase and extraction phase scenarios (Publication III)



3. Comparison between scenarios: S1 = reference, S2 = dye extraction scenario, S3 (2) = after-wash scenario and S4 = both S2 and S3 (2)

Note. Absolute values for the reference: AA=5.66E-02 AE, AT= 1.89E+06 m3, FWE=5.75E-01 CTUe, GWP=1.49E+01 kg CO2 eq., ODP=4.98E-06 kg CFC-11 eq., POCP=3.32E-02 kg NMVOC eq., RMD=1.76E-03 person reserve, TE=2.27E-04 kg 1.4-DB eq., WD=9.01E+01 dm3 and WE=1.05E-03 kg PO43− eq.

Figure 14 Route for LCA driven dyeing process optimization (adapted from Publication III)

4.1.2 Cradle-to-grave

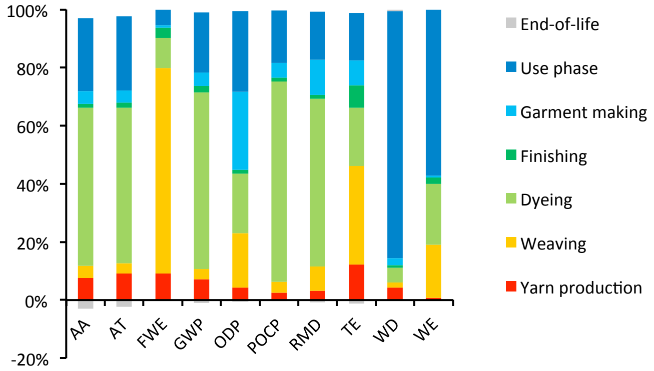
Based on the gate-to-gate study (Section 4.1.1), the system boundaries were extended to include the lifetime of a madder dyed PET shirt.

The shirt scenario considered PET from secondary raw material. The fabric was made through weaving, using a rapier loom weaving machine, to the same density as the fabric used in the experimental dyeing (110 g/m^2). The use of energy for texturizing the yarn was taken into account, since the dyed fabric's weft was texturized. The lab-scale dyeing process was extrapolated to an industrial overflow machine. This was done since laboratory dyeing machines use electrical energy for heating water baths, whereas industrial machines require steam (Van der Velden et al. 2014). An antistatic finishing was considered, because this seemed relevant for improved wear comfort. The upstream processes also included energy generation for garment making (sewing). Textile waste was considered throughout the life cycle, giving in total 170 g of waste for the production of a 200 g shirt.

The function of the shirt was assumed to be to adorn and protect the human body. According to the FU, the shirt was washed twice per month for 2.5 years. This gives a lifetime of 60 washes. Two 'wear before wash' were considered, based on the Mistra Future Fashion report (Gwozdz et al. 2000), giving 120 wears for the defined FU. Full filling load, of both textile and detergent, was assumed, and the washing temperature was 41 °C (Pesnel 2014).

For 'one madder dyed woven polyester shirt to be worn and cleaned, twice a month, for 2.5 years', the sum of the dyeing stage and the use phase stage of the shirt played the major roles in the environmental impacts for 8 out of 10 impact categories, **Figure 15**.

Publication II focused on three impact categories: GWP, WD and WE, which are the ones used in the French environmental labeling platform for clothing (ADEME 2016). The dyeing showed the greatest contribution for GWP (62 %) while the use phase was responsible for the major contributions to WD (85 %) and WE (57 %) as a result of the laundry operations.



Note. Absolute values: AA=2.30E-02 AE, AT= 7.98E+05 m³, FWE=1.23E+00 CTUe, GWP=6.03E+00 kg CO_2 eq., ODP=2.17E-06 kg CFC-11 eq., POCP=1.30E-02 kg NMVOC eq., RMD=6.04E-04 person reserve, TE=1.75E-04 kg 1.4-DB eq., WD=1.43E+02 dm³ and WE=8.49E-04 kg PO_4^{3-} eq.

Figure 15 Environmental profile of the cradle-to-grave scenario (characterization)

Not presented in any publication but addressed was that the shirt might be used for more or less days/times before it is washed and also the washing temperature and filling load depend on the user's preferences. In order to capture these variations, different number of uses before washing (1, 2 or 3 times) (Gwozdz et al. 2000), laundry temperature (30 °C, 41 °C, or 60 °C) (Pesnel 2014) and filling load were studied (full or half filling load of textile and detergent). From this, the various controlled variables could be ranked according to their influence. The first of these was the number of uses between washes, this was followed by the filling load of laundry and detergent, and then washing temperature.

With half textile filling load, the environmental impacts increased due to higher energy consumption allocated to the shirt (188 %) (Kim et al. 2015). A possible limitation is that we did not account for two times of washing operations (half filling load would need two times of laundries to wash the shirt 60 times). The present work hypothesized that for each laundry the shirt was chosen so, the number of laundry operations was the same as the reference. Furthermore, control of water was assumed.

LCA driven optimization of the use phase showed that the best alternative would be the combination of an increased number of uses before wash (3 instead of 2) and reduced washing temperature (30 °C instead of 41 °C). With this use phase, the environmental impacts from the shirt reduced 8 % in GWP, 29 % in WD and 19 % in WE.

It remains to be said that our focus has been on the use phase with respect to technical aspects such as the durability, addressed in Section 3.3. However, the user's wear and care preferences to a great extent influence the environmental profile of a textile product, and should not be neglected.

5 LCA perspective on bio-based dyeing

5.1 Holistic view on bio-based dyeing

From a LCA point of view, and its holistic approach, the environmental impacts of bio-based dyeing are not only an inherent consequence of the chemistry in the dyeing house but also depend on issues related to the acquisition of plant material, dye extraction, dyeing method and finally the quality. It is important to include all these steps in the system boundaries, as modeled in Publication II and Publication III. The LCA tool can then help to prevent pollution transfers from one life cycle phase to another.

For example, the LCA tool may ensure that a reduced impact in agriculture is not at the expense of worsening the dye extraction phase due to a lower dye yield in the plant, or that a reduced impact in dye extraction is not at the expense of worsening the dyeing phase due to low quality dyes. Furthermore, the tool can help to answer questions and resolve trade-offs within each phase such as support decision making regarding whether or not to use solvent recycling in the dye extraction phase. However, LCA at the research stage on textile dyeing with bio-based dyes brings challenges, challenges which have been discussed in Publication V and reiterated in the next section.

5.2 The importance and difficulties

In the third focus area we focused on sharing details, the importance and difficulties, regarding the application of the LCA tool to bio-based dyeing (Publication V). The main advantage addressed was value creation. A value creation based on reducing the environmental impacts in each life cycle phase from plant material acquisition to dyed fabric, while at the same time preventing pollution transfers between the stages or environmental issues. However, LCA at the research stage on textile dyeing with bio-based dyes brings challenges.

One difficult issue raised was the FU definition; namely, when using bio-based dyes there are, as we have seen, many properties that can be attributed to the textile. Not only can color be obtained but also, for example, antibacterial activity. Hence, it may not be obvious how to distinguish the primary function from secondary ones. The LCA methodology has a subjective component in several aspects, such as the FU defining (Pieragostini et al. 2012), and in order to get a more complete understanding of the environmental impacts, it may be relevant to use different functional units so as to reflect various viewpoints (Cerutti et al. 2013). The use of different FUs may be an option for bio-based functionalized textiles. Not only for reflecting several functional attributes, but also for addressing different points of view - the one from the dyer as well as the one from the agronomist and the chemist.

Another difficult issue is the data gaps. In Publication V it was discussed that contributions from agro-researchers, among others, would help to build a creditable inventory, by answering questions concerning land use, efficiency and yield, as well as what to do with the wastes that originate from the cultivation and acquisition of tinctorial plant-material. Furthermore, the need for resource efficient dye extraction techniques was brought up and that input and output data from chemists should be shared to the LCI.

In this focus area we also pointed out that the environmental impacts from the dyeing phase can be reduced through optimization of process parameters. However, in the end, it is the consumer who decides if the attributes brought through the bio-based dyeing are acceptable or not. Based on this, it was addressed in Publication V that contribution from the sociology and fashion research arena would improve the inventory.

Overall, the third and last focus area called for environmental impact assessment of bio-based dyeing of textiles, and interdisciplinary collaboration so as to improve the creditability of the inventory and to the largest extent possible reflect the actual consequences of implementing the results.

6 Conclusions

The thesis has been able to answer the three research questions that were formulated:

1. Can madder dye serve as a multifunctional species onto a PET woven fabric?
2. How does the environmental profile of the dyeing process of PET with madder dye look like, and how can it be improved?
3. What are the main challenges in using LCA to assess the environmental impacts of textile dyeing with plant-based dyes?

The answer to the first research question was positive, meaning that it was possible to obtain a colored PET fabric with good durability performance. However, this was the case for exhaustion dyeing only. Pad-dyeing, which also was explored, gave less good color durability though the combination of plasma and chitosan pre-treatment gave a more suitable PET surface for madder dye sorption. Regarding functionalities other than color, both UV protective performance and antibacterial activity were obtained.

The second research question identified the following hotspots: the solvent and energy use for madder dye extraction and the liquor:fabric ratio in the dyeing phase. An improved environmental profile was obtained thanks to the use of a more resource efficient dye extraction method and a reduced amount of water in the after-wash of the dyed fabric. It needs to be remembered, however, that this study used primary activity data for the dyeing phase. Secondary activity data were used for madder dye production, which contribute to the uncertainty level of the results.

For the third research question, several challenges have been identified which need to be overcome before the LCA can contribute to the eco-sustainable use of plant-based dyes in textile dyeing. Identified challenges were, among others, to close inventory data gaps, and resolve trade-offs; for example, plant yield versus the use of chemicals and fertilizers in agriculture, and dyestuff yield versus the use of organic solvent and its recycling in dye extraction. There is also the question of consumer acceptance of the color, and the functional performance. To overcome these challenges, this thesis has called for interdisciplinary collaboration so as to build creditable inventories in the future.

7 Perspectives

This work can be continued in several directions. Some suggestions are given below.

Fill data gaps: Priorities should be given to improve the LCA inventory by collecting primary activity data for madder cultivation and dye extraction.

Uncertainties: In future work the use of the pedigree matrix needs to be evaluated. For an efficient move towards sustainable use of the madder dye, it will be paramount to clearly communicate the uncertainties. This will point out the next step forward.

Upscaling implications: The environmental impacts at the lab-scale and its use for comparison at the product level will bring upscaling implications. This issue needs to be addressed in future work.

Innovative dyeing methods: It is encouraged to explore low LR dyeing as well as waterless techniques. For this, it is recommended to characterize the chemical constitution of the dye and determine which type of coloring species that contributes to the functional effects on the PET fiber.

Improvement potential of the functional properties: Durability of the functionalities presented, other than color, and their improvement potential remain to be explored.

Apply the methodology beyond madder and PET: With this study being the first of its kind, one needs to look beyond madder and PET. Research on other natural dyes and fabric types may include LCA in the design process, and contribute towards sustainable use of bio-sources applied to textile functionalization.

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Soochow 2017

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The publications are not appended in the digital version of the thesis due to copyright limitations. References to the publications can be found on the following pages. Each publication has been peer reviewed.

PUBLICATION I

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