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ACV et éco-conception dans le domaine de l'élimination des produits chimiques des déchets textiles pour le recyclage des textiles

LCA and Eco-design in the field of Chemicals Removal from Textile Waste for Textile Recycling

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Declaration

I hereby declare that, the contents and organization of this dissertation constitute my own original work and does not compromise in any way the rights of third parties, including those relating to the security of personal data.

Ajinkya Sudhir Powar

I would like to dedicate this thesis to my beloved grandfather Late Shri. Dnyandeo Ganpati POWAR (Anna), Late Shri. Prabhakar Gaikwad, Late Shri.Chandrashekhar Burji (Mama) and all my family members.

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IASI, Romania

Sincerely

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Abstract

Almost everyone uses textile products around the world, and they meet basic human requirements like providing warmth and contributing to our social status. Textile and garment consumption is increasing as the world's population grows and living standards rise. Each year, the global textile sector introduces up to 100 million metric tons of new items to the market. The amount of products also indicates the extent of the textile industry's environmental impact.

The global community is facing huge challenges due to waste generation. Waste management is an important step towards the circular economy. Large amounts of waste textiles are generated each year, however currently only a small portion of it is recycled. There is an increased awareness and research potential to study on the recycling method of waste textiles.

The textile industry is evolving rapidly, and is also constantly changing. It is constantly developing new techniques for the recycling of the textiles and further research is vital for the future needs. The capability to recycle a textile material is a step towards a more green and sustainable industry. However, there are various challenges and difficulties associated with the recycling of textiles. Colorants and other impurities present on the textiles pose a big challenge to the continuity of the chemical recycling. The purpose of our study is to find out methods for the removal of the dyes or colorants from the cotton textiles for the end of life scenarios like recycling. The removal process of the chemical additives in an ecological way would add value to the recycling of textiles, which would help to obtain a recycled textile with the upgraded quality. To examine this subject, a literature study with respect to the chemicals and the removal process along with the recycling methods was done.

In general, alkaline reductive treatment is performed using sodium hydroxide and reducing agent like sodium hydrosulphite for the color stripping of the reactive dyed textiles. Bibliographic survey on the various color stripping process, their drawbacks, viability for industrial scale-up etc was also performed. In this study, we have proposed the application of the ozone assisted process for the color stripping of the reactive dyed textiles using the pilot scale setup. The quality of the color stripped fabrics was determined in terms of the color stripping %, mechanical properties and the colorimetric analysis. Response surface methodology tools like the Box–Behnken design was utilized to examine the effects of three parameters like pH of the treatment (3–7), the reaction time (10–50 min) and the ozone concentration (5–85 g/m3 of ozone). With the ozonation process, color stripping of almost 98 % was achieved. The ozonation process is done at room temperature and also can be performed without any harsh chemicals. The other advantage of the ozone based process is the pilot scale viability in our study. The drawback associated with the ozone assisted process is the damage to the mechanical properties of the treated fabric. Additionally, we have also studied the other color stripping methods like the glucose based process. The results demonstrate that the glucose assisted process can emerge as an ecological alternative to the conventional process. Glucose can act as a green alternative reducing agent to the conventional reducing agent like sodium hydrosulphite. The damage to the mechanical properties are less as compared to the conventional and the ozone based process. However, the glucose assisted process utilized high temperatures for efficient color stripping. Finally, the study has highlighted the need of developing novel methods with minimum damage to the quality of the fibers. Amongst all the impact indicators, “Water resource depletion” is the highest for all the ozonation processes since it has the greatest relative value after normalization. It was found that the major contributors to the environmental impacts were Electricity and Oxygen formation. To optimize the impacts, new experimental conditions have been studied.

Color stripping of the pigment printed textiles was studied with the ozone assisted process. It showed that the complete color removal of the pigment is difficult to be achieved even with the strong process conditions. This suggests the need to develop

alternative process for the removal of these strongly binded pigments and colorants. This study also highlights the need to study presence of contaminants like coatings present on the textiles during their end of life.

Color stripping of the pigment printed textiles was studied with the ozone assisted process. It showed that the complete color removal of the pigment is difficult to be achieved even with the strong process conditions. This suggests the need to develop alternative process for the removal of these strongly binded pigments and colorants.

It is concluded that, this thesis presents a framework methodology to study process for the removal of reactive colorants and pigments for the recycling of the waste textiles. with reactive colorants and pigments.

Keywords: Textile recycling, Waste textiles, Life cycle assessment, Color Stripping, Ozonation process, Box-Behnken design, Chemicals, Glucose, Cotton.

ACV et éco-conception dans le domaine de l'élimination des produits chimiques des déchets textiles pour le recyclage des textiles

Résumé

Presque tout le monde utilise des produits textiles dans le monde entier, et ceux-ci répondent à des besoins humains fondamentaux, comme fournir de la chaleur et contribuer à notre statut social. La consommation de textiles et de vêtements augmente à mesure que la population mondiale s'accroît et que le niveau de vie s'élève. Chaque année, le secteur mondial du textile introduit jusqu'à 100 millions de tonnes de nouveaux articles sur le marché. La quantité de produits indique également l'ampleur de l'impact environnemental de l'industrie textile.

La communauté mondiale est confrontée à d'énormes défis liés à la production de déchets. La gestion des déchets est une étape importante vers l'économie circulaire. De grandes quantités de déchets textiles sont générées chaque année, mais actuellement seule une petite partie est recyclée. Il y a une prise de conscience accrue et un potentiel de recherche pour étudier la méthode de recyclage des déchets textiles.

L'industrie textile évolue rapidement et est également en constante mutation. Elle développe constamment de nouvelles techniques pour le recyclage des textiles et la poursuite des recherches est vitale pour les besoins futurs. La capacité de recycler un matériau textile est un pas vers une industrie plus verte et durable. Cependant, le recyclage des textiles pose de nombreux défis et difficultés. Les colorants et autres impuretés présents sur les textiles posent un gros problème lors du recyclage chimique. L'objectif de notre étude est de trouver des méthodes pour éliminer les teintures ou les colorants des textiles en coton pour les scénarios de fin de vie comme le recyclage. Le processus d'élimination des additifs chimiques de manière écologique ajouterait de la valeur au recyclage des textiles, ce qui permettrait d'obtenir un textile recyclé de meilleure qualité. Pour examiner ce sujet, une étude de la littérature

concernant les produits chimiques et le processus d'élimination ainsi que les méthodes de recyclage a été réalisée.

En général, le traitement réducteur alcalin est effectué à l'aide d'hydroxyde de sodium et d'un agent réducteur comme l'hydrosulfite de sodium pour le décapage de la couleur des textiles à teinture réactive. Une étude bibliographique sur les différents procédés de décoloration, leurs inconvénients, leur viabilité à l'échelle industrielle, etc. a également été réalisée. Dans cette étude, nous avons proposé l'application d'un procédé assisté par l'ozone pour la décoloration de textile teints avec des colorants réactifs en utilisant une installation à l'échelle pilote. La qualité des tissus décolorés a été déterminée en termes de pourcentage de décoloration, de propriétés mécaniques et d'analyse colorimétrique. La méthode des surfaces de réponses de Box-Behnken a été utilisée pour examiner les effets des trois paramètres : pH du traitement (3-7), temps de réaction (10-50 min) et concentration d'ozone (5-85 g/m3 d'ozone). Le processus d'ozonation a permis d'obtenir une décoloration de près de 98 %. Ce procédé se fait à température ambiante et peut également être réalisé sans produits chimiques agressifs. L'inconvénient associé au traitement par l'ozone est l'endommagement des propriétés mécaniques du tissu traité.

Nous avons également étudié d'autres méthodes de décoloration comme le procédé à base de glucose. Les résultats démontrent que ce procédé peut apparaître comme une alternative écologique au procédé conventionnel. Le glucose peut agir comme un agent réducteur écologique alternatif à l'agent réducteur conventionnel comme l'hydrosulfite de sodium. Les dommages aux propriétés mécaniques sont moindres par rapport au procédé conventionnel et au procédé à l'ozone. Cependant, le processus assisté par le glucose utilise des températures élevées pour une décoloration efficace. Enfin, l'étude a souligné la nécessité de développer de nouvelles méthodes avec un minimum de dommages à la qualité des fibres.

Parmi tous les indicateurs d'impact, "l'épuisement des ressources en eau" est le plus élevé pour tous les procédés d'ozonation car il a la plus grande valeur relative après normalisation. Il a été constaté que les principaux contributeurs aux impacts

environnementaux étaient l'électricité et la formation d'oxygène. Pour optimiser les impacts, de nouvelles conditions expérimentales ont été étudiées.

La décoloration des textiles imprimés avec des pigments a aussi été étudiée avec le procédé assisté par l'ozone. Il s'est avéré que l'élimination complète de la couleur du pigment est difficile à réaliser, même avec les conditions de traitement les plus strictes. Cela suggère la nécessité de développer un processus alternatif pour l'élimination de ces pigments et colorants fortement liés. Cette étude souligne également la nécessité d'étudier la présence de contaminants tels que les revêtements présents sur les textiles en fin de vie.

En conclusion, cette thèse présente un cadre méthodologique pour étudier le processus d'élimination des colorants et pigments réactifs pour le recyclage des déchets textiles.

Mots-clés : Recyclage des textiles, Déchets textiles, Analyse du cycle de vie, Décapage des couleurs, Processus d'ozonation, Conception de Box-Behnken, Produits chimiques, Glucose, Coton.

Aplicarea tehnicilor LCA și de design ecologic în domeniul eliminării substanțelor chimice din deșeurile textile în scopul reciclării

Rezumat

Aproape toată lumea folosește produse textile care îndeplinesc cerințele umane de bază, cum ar fi izolarea termică și asigurarea unei imagini corespunzătoare statutului social. Consumul de produse textile și articole de îmbrăcăminte crește pe măsură ce populația lumii și nivelul de trai al acesteia crește. În fiecare an, sectorul textil global introduce pe piață până la 100 de milioane de tone de articole noi. Cantitatea de produse indică, de asemenea, amploarea impactului asupra mediului al industriei textile și de confecții.

Comunitatea mondială se confruntă cu provocări uriașe datorită generării de deșeuri ale industriei textile. Gestionarea deșeurilor este un pas important către economia circulară. În fiecare an sunt generate cantități mari de deșeuri textile, însă în prezent doar o mică parte din acestea sunt reciclate. Se identifică astfel potențialul de cercetare al domeniului reciclării deșeurilor textile și conștientizarea consumatorilor în acest sens.

Industria textilă evoluează rapid și, de asemenea, este în continuă schimbare. Ea dezvoltă în mod constant noi tehnici de reciclare a textilelor și cercetările desfășurate sunt vitale pentru direcțiile viitoare. Capacitatea de a recicla un material textil este un pas către o industrie mai ecologică și mai durabilă. Cu toate acestea, există diverse provocări și dificultăți asociate cu reciclarea textilelor. Coloranții și alți aditivi prezenți în structura materialelor textile reprezintă o mare provocare pentru eficiența reciclării chimice. Scopul studiului desfășurat în această teză de doctorat este de a identifica metode de înlăturare a coloranților sau a altor substanțe însoțitoare din textilele cu conținut de bumbac pentru scenarii de finalizare a ciclului de viață precum reciclarea. Procesul de îndepărtare a aditivilor chimici într-un mod ecologic poate adăuga valoare procesului de reciclare a materialelor textile, ceea ce ar ajuta la obținerea unor

materiale textile reciclate cu o calitate îmbunătăţită. Pentru a aborda acest subiect, a fost realizat un studiu de literatură cu privire la substanţele chimice şi procesul de îndepărtare precum şi referitor la metodele de reciclare adecvate.

În general, tratamentul reductiv alcalin se realizează folosind hidroxid de sodiu şi agent reducător precum hidrosulfitul de sodiu pentru decolorarea textilelor vopsite cu coloranţi reactivi. De asemenea, a fost efectuat un studiu bibliografic asupra diferitelor procese de îndepărtare a coloranţilor, dezavantajele acestora, viabilitatea pentru extinderea industrială etc. În acest studiu, s-a propus aplicarea procesului de ozonare pentru îndepărtarea culorii textilelor vopsite cu coloranţi reactivi folosind o instalaţie la scară pilot. Calitatea ţesăturilor tratate pentru îndepărtarea coloranţilor a fost apreciată din punct de vedere al procentului de decolorare, proprietăţilor mecanice şi al analizei colorimetrice. Au fost utilizate instrumente de apreciere a suprafeţei de răspuns, cum ar fi designul Box–Behnken, pentru a examina efectele a trei parametri precum pH-ul (3–7), timpul de reacţie (10–50 min) şi concentraţia de ozon (5–85 g/m3 de ozon). Prin procesul de ozonare, s-a realizat o îndepărtare a culorii de aproximativ 98 %. Procesul de ozonare se face la temperatura camerei şi, de asemenea, poate fi efectuat fără substanţe chimice toxice sau periculoase. Alt avantaj al procesului bazat pe ozon este viabilitatea la scară pilot demonstrate în teză. Dezavantajul asociat procesului asistat de ozon este deteriorarea proprietăţilor mecanice ale ţesăturii tratate. În plus, s-au studiat şi alte metode de eliminare a culorii, cum ar fi procesul pe bază de glucoză. Rezultatele demonstrează că procesul asistat de glucoză poate apărea ca o alternativă ecologică la procesul convenţional. Glucoza poate acţiona ca un agent reducător alternativ ecologic la agentul reducător convenţional, cum ar fi hidrosulfitul de sodiu. Reducerea proprietăţilor mecanice este mai mare]n cazul procesului de ozonizare]n comparaíe cu cu procesul conventional. Cu toate acestea, procesul bazat pe glucoză a folosit temperaturi ridicate pentru o îndepărtare eficientă a culorii. În cele din urmă, studiul a evidenţiat necesitatea dezvoltării unor metode noi cu deteriorare minimă a calităţii fibrelor. Dintre toţi indicatorii de impact, „Epuizarea resurselor de apă” este cel mai inportant pentru toate procesele de ozonare, deoarece are cea mai mare valoare relativă după normalizare.

S-a constatat că cei mai importanţi contributori la impactul asupra mediului au fost energia electrică şi formarea oxigenului. Pentru optimizarea impactului au fost studiate noi condiţii experimentale.

}ndep[rtarea coloranţilor de pe materialele textile imprimate cu pigment a fost realizată cu ajutorul procesului de ozonare. S-a arătat că îndepărtarea completă a pigmentului este dificil de realizat chiar şi în condiţiile intense ale procesului. Acest lucru sugerează necesitatea dezvoltării unui proces alternativ pentru îndepărtarea acestor pigmenţi şi coloranţi puternic legaţi la structura fibrelor. Acest studiu subliniază, de asemenea, necesitatea de a studia prezenţa contaminanţilor, cum ar fi acoperirile, prezente pe materialele textile la sfîrşitul ciclului de viaţă.

Se concluzionează că această teză prezintă o metodologie cadru pentru studierea procesului de îndepărtare a coloranţilor şi pigmenţilor reactivi utilizaţi pentru finisarea materialelor textile, în scopul reciclării deşeurilor rezultate din prelucrare sau la sfîrşitul ciclului de viaţă al produselor.

Cuvinte cheie: reciclarea textilelor, deşeuri textile, evaluare ciclului de viaţă, decolorare, proces de ozonare, design Box-Behnken, produse chimice, glucoză, bumbac.

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List of Abbreviations

LCA	Life Cycle Assessment
K/S	Colour Strength
GHG	Greenhouse Gas
AOP	advanced oxidation process
FU	functional unit
HH	human health
SFS	Sodium formaldehyde sulfoxylate
CV	Coefficient of Variation
CTUh	Comparative Toxic unit for humans
CTUe	Comparative Toxic Unit for ecosystems
ILCD	International Reference Life Cycle Data System
CS	Color Stripping
TSL	Tensile Strength Loss
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
PET	Polyester
BBD	Box-Behnken design
ISO	International standard organization
SEM	Scanning Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy
UV	Ultraviolet
CIE	Commission Internationale de l'Eclairage
DMDHEU	dimethyloldihydroxyethyleneurea

NTP	Normal Temperature and Pressure
ANOVA	Analysis of variance
RFD	ready for dyeing
CRA	crease recovery angle
RSM	Response surface methodology
MLR	material to liquor ratio
GPL or g/L	Grams Per Liter
CED	Cumulative Energy Demand
IPCC	Intergovernmental Panel on Climate Change
CTU	comparative toxic units
PLA	Polylactic Acid
RER	Europe
C.I.	Colour Index
PEeq	person year equivalent
DP	degree of polymerization
GSM	Grams per Square Meter

Chapter 1: Introduction and General Scenario

1.1 Background of the topic and aim

1.1.1 The current situation: Need of Sustainability in the textile industry

Ecologically, the textile industry (TI) is considered to be one of the most polluting industries across the world. (A. K. Roy Choudhury, 2014).Globally, it is also one of the biggest industries accounting for almost around 60 million employees in 2015.(Malik Abdul, Elisabeth Grohmann, 2014). Competitiveness and the constant need to update the clothes to the demands of the consumers are the characteristics of today's fashion market. This 'fast fashion' based business model has resulted in a continuous cycle of manufacturing the clothes and tempting the customers to visit stores often based on the idea of 'Here Today, Gone Tomorrow'. The shorter life-cycle and the higher profit margins reflect the business model of these fashion retailers. (Bhardwaj & Fairhurst, 2010). Hence, the textile production is increasing; the apparel and footwear industry throughout their life cycles have been estimated to contribute as much as 8 percent of the global greenhouse gas emissions (Quantis, 2018). In 2015, the greenhouse gas emissions resulting from the textile manufacturing amounted to 1.2 billion tonnes of carbon dioxide equivalent (CO_2-eq), much more as compared to the international flights and shipping combined. (MacArthur, 2017). The textile production process uses various harmful substances and a significant amount of water. For example, to produce one pair of jeans it costs about 7,000 liters of water. (Snoek, 2017). One can imagine the environmental pressure of the textile industry and this signifies the need of sustainable actions.

1.1.2 Significance of the resources and waste in the textile industry

The textile industry is one of the largest in the world. Every year, the global textile sector produces over 100 million metric tons of new products. (The Fiber Year, 2014). Nonetheless, the textile sector is responsible for a considerable portion of the planet's

environmental burden; for instance, 1 kg of textiles produces three times the amount of climate pollution as 1 kg of metal or plastics. (Lövin, 2008).

Textiles have environmental impacts due to resource consumption, waste creation, and emissions. It's possible that the resources are either renewable or nonrenewable. Renewable resources are the ones which will replenish as per their use and non-renewable sources are those with finite supply. e.g. fossil fuels.(Agnhage, 2017).

Renewable or recyclable resources should be used as efficiently as possible to manufacture a textile product in a sustainable manner. Though the renewable sources - bio-sourced materials can be regarded as being in finite supply. The volume available will be governed by the lifeform ability of producing it. There is overexploitation risk, if this is not respected. In this regard, considering sustainable manufacturing of the required resource is vital. In case of cotton, for e.g. it would imply production at a rate and on land types that ensure long-term upkeep with no negative environmental consequences. (Agnhage, 2017; Bach & Schollmeyer, 2007).

1.1.3 Environmental aspects of the textile supply chain

Every product manufactured begins its life cycle from raw material extraction and passes through various steps like, manufacturing, distribution and use, and finally ends up with disposal of the product. All of the stages of the manufactured products have a range of variety of environmental impacts depending on the industry and its supply chain. Textiles being one of the most vital consumable products and the textile products have significant environmental impacts due to wide range of its use such as in apparels, fashion, geotextiles, agro textiles, industrial textiles and hygienic textiles. (S. S. Muthu, 2014). Hence it is interesting to study the environmental aspects of this industry.

The textiles industry contributes substantially to the environmental impacts though the various stages like manufacturing, processing, use and end of life phase of the garments. (Wiedemann et al., 2020). Recent LCA (Life cycle assessment) case studies on the three apparels consumed in Australia have demonstrated that consumer use

stage is the main contributor for the environmental impacts through its life cycle in case of cotton and polyester apparels while production stage contributes for more impacts in case of the woolen apparel. This LCA assessment study also suggests that significant improvements could be achieved by encouraging use phase activities with less environmental impacts. This study suggested another activity related to consumer use phase, which states that great environmental impacts could be achieved if consumers donate their apparels used for reuse and recycling purpose instead of disposal option, thus preventing or minimizing the production of new apparels from virgin raw materials. (Moazzem, Daver, Crossin, & Wang, 2018). From this, the present work in the thesis also co-ordinates to study the challenges associated with end of life scenarios like recycling method to reduce the environmental impacts.

1.1.4 End of life scenarios for textiles

As discussed previously in the textile supply chain, the textiles or apparels once ready move into the use phase. After a certain time period the consumer decides to dispose the apparel/product and this is the end of life phase for the textiles. At the end of life for a product, there are various destinations or fates. These include: reuse for primary and secondary purposes; recycling (open- and closed-loop types); landfilling; and incineration.(Subramanian Senthilkannan Muthu, 2014).

Concerning the environmental impact assessment or the life cycle assessment, two terms like 'benefit' or 'credit' and 'impact' can be applied for the end of life options.

In terms of gaining only the environmental credits with nil impacts, the first and best option is reuse. In this hierarchy, the next best option is recycling which has benefits as well as certain impacts. Down the hierarchy, follows the incineration. Incineration can be carried out with or without energy recovery. Incineration with energy recovery is preferred option (as it brings credits or benefits even while generating impacts). Disposal at landfill, is the final and most undesirable option as it creates only the environmental impacts. However, the perceived degree of the credits or benefits and the impacts cannot be generalized and is quite subjective, since it is influenced by multiple factors.(Subramanian Senthilkannan Muthu, 2014).

As per the definition by the 2008 European Union (EU) Waste Framework Directive (European Council, 2008),to summarize, the best choice of the waste management is the prevention of waste, followed by the other options in the hierarchy of reuse– recycle– energy recovery–disposal at landfill. (Refer fig 1).(European Commission, 2008).

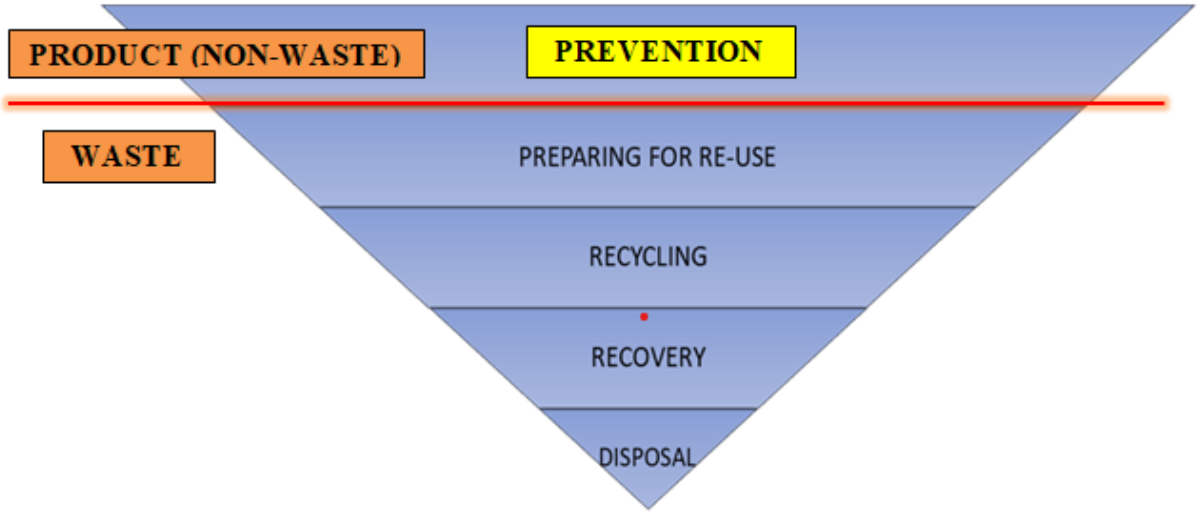


Figure 1 European Union (EU) Waste Framework Directive (European Council, 2008).

1.1.5 Importance of recycling in the textiles.

From the perspective of creating sustainability, textile recycling is an effective way, although it is facing challenges with respect to the cost, time and technology. As sustainability is gaining prime importance, a lot of efforts have been made by both the apparel and clothing producers and sector organizations to help in the improvement of the recycling outputs. As a result, there is a rapid growth in the enterprises on the recycling for textiles and the clothing industry. (Lu & Hamouda, 2014).

Economists and environmentalists conducted studies on the technical and economic needs for sustainability report that it is important to reduce the generation of the waste and increase the recycling. Below are a few reasons which convey the importance of recycling (Burçin Ütebay, 2020):

- Economic reasons: The cost of the recycling programs is less compared to the waste disposal programs. The need of high energy, water and manufacturing consumption makes this option much cheaper than producing some new textile products.
- Social reasons: Recycling helps in job creation. For every one job in the waste disposal industry, recycling centers create four jobs. Recycling method can create job opportunities for small businesses also.

Environmental reasons: Recycling method helps in the conservation of natural resources like water, oil and natural gas; saving of energy since it uses less energy compared to the manufacturing of the brand new goods; produces less greenhouse gases; and prevents natural habitat destruction.(Burçin Ütebay, 2020). Hence, recycling has gained a lot of attention these days.

1.1.6 Textile recycling

Fiber-to-fiber textile recycling may be done mechanically or chemically. The traditional mechanical process involves mechanically shredding the textiles into fibers, which can subsequently be spun into recycled yarns and textiles with or without the inclusion of new virgin fibers. When it comes to textile fibers like wool or cashmere, mechanical recycling can produce excellent results, but in case of most other fibers it leads to recycled fibers of the inferior quality. As a result, mechanical recycling is often referred to as downcycling. (Slater, 2006). Fiber-to-fiber recycling of textiles using a chemical approach entails a number of steps in which molecular changes are made to textile fibers via chemical processing to produce recycled fibers, yarns, and textiles. There are a number of small active projects in the chemical fiber-to-fiber recycling of textiles, including Eco Circle (Teijin), Worn Again, Evrnu, Re:newcell, and Ioncell, (Palme, 2017) and one commercial-scale set up exists today where recycled PET fibers are obtained is Capilene® from Patagonia.(Patagonia, 2021). Hence, Textile recycling is complicated as it consists of wide number of different materials and chemical additives. As a result, it is vital to investigate the recycling

issue. However, the scope of this thesis is restricted to study the challenges associated with the cotton textiles recycling.

1.1.7 Environmental assessment using Life Cycle Assessment (LCA)

Recently, a lot of attention has been gained across the globe with regards to the environment and to improve the sustainability. LCA is an environmental tool that assesses the environmental impacts of a product, process or activity during its entire life time, which comprises steps like extraction and raw materials processing, manufacturing, transport, distribution, use phase and end of life – accounting for emissions into air, water and soil, consumption of energy and material and waste disposal. A variety of environmental impacts like climate change, human toxicity, land use, resources depletion etc. and many others can be usually analysed using the LCA. (Albino Andre Moreira Cardoso, 2013). More detailed study on LCA will be discussed in the chapter with literature review. In our work, we have tried to assess the environmental impacts of the color stripping process adopting the gate-to-gate LCA.

1.2 Problem Statement and purpose

This study is aimed at addressing the problem of color removal from cotton based textiles before recycling. Additionally, it helped to develop methods for the color removal from textiles before recycling and also assess the environmental profile of these processes using Life cycle assessment. The obtained results will help to create new aspects with regards to the recycling process of decoloring textile waste. End of life scenarios like reuse, mechanical recycling and /or chemical recycling of the old cotton has not been studied.

1.3 Objectives of the Study

Main objectives of the study are:

1. To investigate and study the effects of ozonation process parameters like pH, ozone dose and ozone treatment time on the efficiency of the color removal from reactive dyed and pigment printed fabric using a pilot scale set up.
2. To analyze the environmental aspects of the color stripping process using pilot scale ozonation.
3. To study the glucose assisted process for the color removal from the reactive dyed textiles.
4. To determine the quality of color stripped fabric in terms of color stripping %, mechanical properties etc and comparison with the conventional methods.
5. To evaluate the quality of ozone assisted color stripped fabric, glucose based and conventional treated fabric in terms of colour fastness, colour difference with regard to reference.

1.4 Structure of the thesis

This Ph.D. thesis is divided into six different chapters.

Chapter 1 begins with the background and challenges associated with the recycling of textiles in order to get the general view of the topic and begin the research work.

Chapter 2 describes the research background, and consists of the general overview of research theme. It also consists of the literature work on the recycling scenarios and the reactive and the pigment dyed/printed goods, on the ozonation and the color stripping methods as well as the LCA and the environmental approaches.

Chapter 3 provides information related to all the raw materials utilized while studying the decolorization process, the experimental prototype making (box Behnken design matrix) used, detailed description of the various decolorization processes carried out, the operating process conditions, optimization parameters related to the decolorization process. This chapter also describes comprehensive information regarding the materials and the analysis techniques performed which were used to analyze the decolorization process. This chapter also describes the LCA modeling and the methodology used.

Chapter 4 explains the development of new color stripping processes while understanding the advantages and limitations of the process. This chapter majorly covers the results and general discussions on all the experiments, on the decolorization experiments and the proposed process.

Chapter 5 addresses the perspectives of the LCA study in general as well as with regards to the decolorization process. It also discusses the environmental profile of the various proposed processes.

Chapter 6 is the concluding chapter and discusses the outcomes of our research work and also puts forward the recommendations for the future work.

Chapter 2 State of the art

This chapter begins with a systematic review of the literature which will introduce and discuss about the cotton garments and the waste scenario associated with it. It will also include the chemical issues associated with the recycling of the cotton textiles while focusing on the chemical additives present in the waste garments. A bibliographic research on the main removal processes associated with the removal of each kind of chemicals has also been discussed. At last, it also highlights the LCA of the garment life cycle scenarios with main focus on the chemical removal process performed prior to the recycling process.

2.1 Clothing consumption and waste scenario

2.1.1 Clothing market consumption and cotton garments

Clothing is a very important industry in the European Union. According to the European Environment Agency, clothing comes to the eighth position in the household expenditure items list, yet 'in terms of the environmental impacts it is the fourth most significant consumption category, after housing, mobility and food'. Over the last decade the clothing prices however have remained fairly static, which has helped to increase the sales volume, thus supporting the fast fashion trend. Hence, there is a high price to be paid in terms of the impacts. As per the Eurostat trade statistics, in the European union (EU), greater quantities of the clothing are imported than the exports, and into each individual country. (Gray, 2017).

In EU, a large amount of clothing is consumed. The consumption was estimated to be 6.4 million tonnes of clothing in the year before (European Clothing Action Plan) ECAP was launched. The clothing consumption estimated are taken from the 'European Textiles & Workwear Market' report (European Clothing Action Plan, 2017) using PRODCOM data (Eurostat, 2015b),which compiles the statistics on goods manufactured which consists of the production, exports and imports.

Considering the clothing consumption total of 6.4 million tonnes, along with the average fibre split for clothing, (Beton et al., 2014) calculated the total quantities of range of the main textile fibres. The cotton fibre accounted for approximately, 2.8 million tonnes of the EU fibre consumption in clothing textiles (2015).

Amongst the natural fibers, cotton is the world's most widely used and accounts for about 30% of all fiber used in the textile industry. Cotton is used widely in various range of clothing, most notably in the T-shirts, shirts, and denims. Additionally, it is also used in the coats, jackets, underwear and foundation garments. (CBI, 2020).

2.1.2 Clothing waste scenario.

It is important and critical to know the amount of textile clothing in the residual waste in order to understand the potential to divert the clothing from the landfill and the incineration. Across the European countries WRAP commissioned the Resource Futures to establish a baseline estimate for the amount of clothing waste disposed. This project focused on nine EU countries of interest as per the ECAP project namely, Denmark, Germany, Italy, Netherlands, The UK, as well as Belgium, Sweden, Spain and France.

According to the estimates for clothing in ECAP countries in the residual waste, Italy had the largest clothing quantity in the household residual waste as well as higher per capita estimate of the discarded clothing amounting to 7.2 kg per capita. Italy has also the highest per capita spending on the clothing. (Almut Reichel, Lars Fogh Mortensen, Jasmina Bogdanovic, 2014). The UK, Spain, and Germany follow the list, by the total volume of the discarded textile clothing in the residual waste. Considering the per capita volumes, Spain throws away 6.6 kg as compared to the UK which discards 4.7 kg. The report findings suggest that Denmark, Belgium, France, and Sweden discard the least clothing per person in their household residual waste.

In terms of the market recovery, clothing is a high value material and the huge quantity of the clothing appearing in the residual waste streams represents a

significant opportunity in the market. Countries with the highest per capita clothing in household residual wastes like Italy, the UK, and Spain are top in the levels of clothing consumption. Hence, especially the figures of higher per capita clothing waste arising are problematic. Clothing which ends up as the household residual waste is likely to become spoiled e.g. torned, damaged or stained etc. in other way if it was not already. Once it lands up in bin, there are few opportunities related to its recycling or reuse. (Gray, 2017).

2.1.3 Classification of the textile waste

The broad classification of the textile waste is as per below:

a. Pre-consumer textile waste: It is also known as manufacturing waste and are discharged from the first stage of the textile supply chain. It includes the materials manufactured during the industrial textile processing which never reaches to the consumers. Generally, it comprises damaged or defective materials pieces, scraps, fabric selvages and the leftover fabric obtained from the cutting operation. The pre-consumer textile waste category consists of on an average about 15% of fabric used in garment manufacturing. (S Aishwariya, 2020). Often it is cut, disposed and wasted. Textiles produced from the natural fibers like cotton, silk, linen and hemp is a rich resource which can be upcycled in a value added product or recycled into compost. On the other hand the synthetic textiles can be upcycled to building blocks and composites for its use in sound proofing or construction.

b. Post-consumer textile waste: This category consists of garment or household articles that the consumer no longer uses and decides to dispose. In this section, damaged, clothing with fitting issues and out of fashion textiles are categorized. In the traditional way, the old textiles are recycled for use into various household activities like wash cloth or mop, but with the recent incursion of disposable textiles, the popular approach is use and throw, thus making the old textiles to be thrown away. Depressing fact is that, most of the people have missing approach with the repair or mending of the clothing and accessories,

and hence this psychology of consumers has developed a treacherous situation in the universe. (S Aishwariya, 2020).

c. Industrial textile waste: It is produced from the industrial applications and consists of filters, wiping rags, conveyor belts and geotextiles etc. The waste parts are thrown upon the wear and tear of the particular component. In most scenarios it is unavoidable and open for upcycling, downcycling and recycling options. Separately, a company works on these wastes and attempts to integrate the waste into a service, thus incorporating the circular economy.

2.1.4. Downcycling, Recycling and Upcycling

When a material cannot be reused it turns out into waste, but it still possesses some value. In such instances the goods are reprocessed into the same, lower or higher value as compared to the original. Generally, the reprocessing involves three major operations- upcycle, recycle and downcycle.(Vats & Rissanen, 2016).

a. Recycle

Any recovery operation due to which partly or fully an object or a material or a substance has evolved into waste but cannot be reused is reprocessed into raw materials of the same value or purpose like that of the original. The principal proposition of recycle is that the final product value is equivalent to the original or the base product. The product which is recycled can be available in other forms than the main material. In the exact words, reusing of a material would generate a new inventory/supply of the same material for example, utilized office paper would be transformed into new office paper or used frothed polystyrene into new polystyrene. (Baechler & Pearce, 2013).

b. Downcycle

Any recovery operation due to which partly or fully an object or a material or a substance that has become waste but cannot be reused is reprocessed into raw materials of the lesser/lower value/purpose as compared to the original. The value/quality of the reprocessed material is less as compared to the original material

in the same form or the other. As compared to the original product, the properties of the reprocessed products are measured as inferior. This can be connected to many reasons, the main being the degradation. During their life time some materials tend to gather undesirable elements, thus contributing to the down cycling. Downcycling aims to prevent squandering possibly helpful materials, curtail the use of new crude materials, water contamination, air contamination and vitality use. It is said that the contamination of the biosphere is increased due to the downcycling. (Mcdonough & Braungart, 2002).

c. Upcycle

Any recovery operation due to which partly or fully an object or a material or a substance that has become waste but cannot be reused is reprocessed into raw materials of the higher value/purpose as compared to the original. As the value of the reprocessed materials is more as compared to the base or the original material, this operation of the waste management is most encouraged. (Gharfalkar, Court, Campbell, Ali, & Hillier, 2015). The upcycled products can simply be logical, creative, or anything basically helpful. In other words, upcycling is also known as the productive change of the waste combining the money saving merits and also waste reduction. (Martin & Parsapour, 2012; Pol, 2010).

2.2 End of life options and recycling of cotton textiles.

2.2.1 Study on the challenges with respect to end of life options

Apart from the problems associated with the manufacturing of the textiles, another problem the world is facing is the safe disposal of the used clothes. Discarded clothes usually end up landfills. The textile dyes and the associated speciality chemicals are designed in such a way that almost 90% of them remain on the fabric and the remaining 10% is discharged into the the effluent during the manufacturing. While being concerned about the 10% chemicals from entering in the water bodies, we also need to have a look at the bigger part i.e. 90% of the textile dyes and speciality chemicals that stay on the fabrics when they end up in landfills. These dyestuffs and

chemicals will degrade over a period of time and will leach out to the same water bodies which we are trying to preserve. Currently, this major issue is not being addressed adequately. (Nimkar, 2017).

Previously, it has been seen in the studies that Flame Retardant (FR) textiles have various environmental impacts at the life cycle stages like production, the use phase and the end of life. Some flame retardants during their use phase, have been displaying to leach or in another way escape from the textile products over a period of time and assemble in indoor as well as outdoor environments, understanding the fears of potential health effects and the human exposure. In their end of life phase, which generally consists of the reuse, landfill disposal or the incineration, the FR products pose a great concern. Environmental concerns like ecotoxicity arise out of leaching of the FR products in the landfill. While, on the other side, the incineration of the discarded textiles is another fuel energy source, the existence of the FR products on the disposed textiles decreases the energy yield and thus generates toxic gas emissions. (Yasin, Behary, Giraud, & Perwuelz, 2016).

Hence, there is a need to study the techniques for the removal or degradation or elimination of the durable flame retardant products which are present on the textiles that are discarded (for instance like geotextiles) and to increase the energy yield during the incineration step. At the same time, another valorization, for the FR cotton fabrics can be their reuse prior to their end of life in the incineration step, if the mechanical properties still remain intact. Otherwise, the heat recovery while incineration can be an appropriate way for the disposed flame retardant cotton fabrics.(Yasin et al., 2016).

(Wallander, 2012)discussed the need for textiles to be banned from the landfills. Textiles once end up their life in landfills, cause many harmful effects. Textiles in landfills decompose releasing methane, a harmful greenhouse gas, which is a major contributor to the global warming. In addition to this, the dyes and other chemicals present on the textiles can leach into the soil, hence contaminating the surface and groundwater — further causing harm to the human and wildlife. (Wallander, 2012).

While discussing of the harmful effects of textile waste, (S Aishwariya, 2020) concluded in her study that, during the last century, it was common that all the textile waste generated in all the phases ended up in landfill, but currently, upcycling, redesigning, recycling, repair and reuse, restoring, reducing and downcycling are some of the ways adopted by the industry moving forward. (S Aishwariya, 2020). Hence, recycling of textiles has gained significant attention as an end of life alternative.

2.2.2 Textile Recycling:

Generally, textile recycling is mostly referred to the reprocessing of the pre- or post-consumer textile waste for use in new textile or products with non-textile base. (Sandin & Peters, 2018). For textiles, the principal material recycling routes are chemical recycling (figure 2.1: monomer, oligomer and polymer recycling) and mechanical recycling (figure 2.2: fibre and fabric recycling). Recycling process can provide different outputs with the same input material which is demonstrated for instance with cotton in figure 2.1 and 2.2.

While studying the recycling phenomenon it's also crucial to understand the difference between an open loop and a closed loop system.

The process of breaking down textile materials (deconstruction, shredding, etc.) into lower-grade input products or using them in products for different purposes (such as low-grade blankets, insulation, industrial rags, fill, etc.). is known as an open-loop recycling system. Whereas, the Closed-loop recycling system consists multiple loop processes by which the textile material is recycled and utilized in an equivalent product. (Katherine Le, 2018).

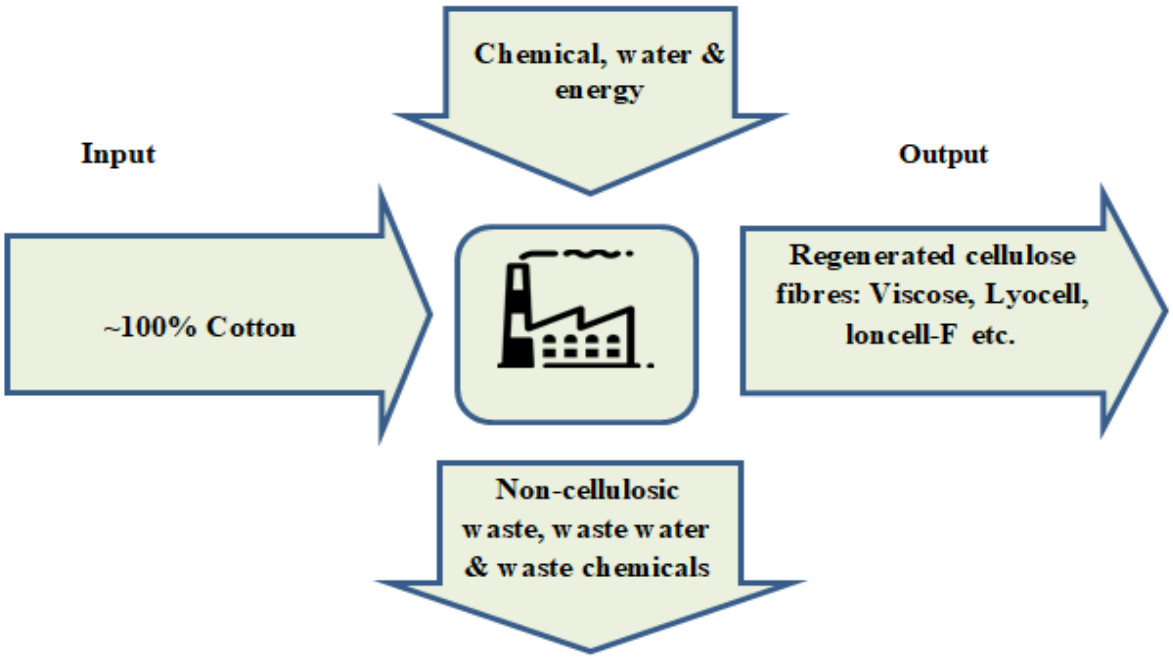
2.2.3 Chemical recycling:

This method of recycling is applicable for Open-loop system (in case of cotton materials) and Open-loop system or closed-loop system(in case of pure PET and Nylon 6 materials).

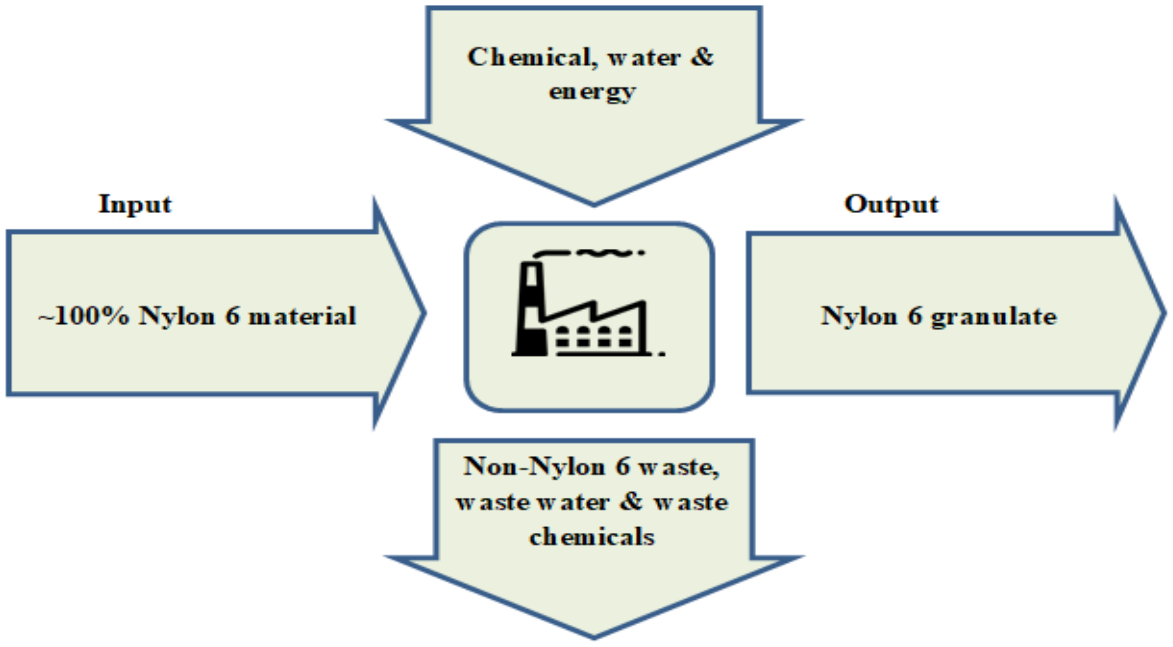
In case of a few synthetic fibres, the feasible route is chemical recycling by depolymerisation. The polymeric chains are broken down into monomers, which are further separated and purified prior to their rejoining into new polymers. All along the purification process (usually distillation) the additives are removed. Currently, Nylon 6 and polyester (PET) are chemically recycled at commercial scale (still limited).The input material used in case of the polyester (PET) is mainly the post-consumer polyester coming from the materials of food packaging and (pre-consumer) industrial textile waste. In case of the nylon, the input material commonly is post-consumer nylon coming from industrial waste, fish farm nets and carpets. In principle, the recycled fibres have the same properties like that of the virgin synthetic fibres. In theory, nearly all the polymers can be depolymerized, still an effective, realistic process has not been developed yet for all the polymers, for instance in case of nylon 6.6. (Roos, 2019).

A few cellulosic fibres like cotton can be recycled chemically via a pulping process followed by solution spinning in order to produce regenerated fibres. Currently, this is not a feasible route in case of lyocell and viscose fibres which already are regenerated fibres. Figure 2.1 represents the schematic figure of process in case of chemical recycling of cotton (2.1 a) and nylon (2.1 b) respectively while the mechanical recycling method of cellulose is displayed in figure 2.2. During the process additives are partly removed. In principle, regenerated cellulosic fibres from cotton recycling have the same properties like the other regenerated cellulose fibres. Currently, in terms of commercial availability, the only such fibre is (REFIBRA™) from LENZING, a fibre blend composed of 80 % regenerated fibres derived from virgin forest fibres and the remaining 20% recycled lyocell fibres derived from cotton.

A familiar aspect of cellulose and synthetic fibres is higher the purity of the input material, the chemical recycling process acquires higher efficiency. Presence of any content apart from the intended fibre for recycling is termed as a contamination, which decreases the produce or adds up additional separation/purification steps and eventually increases the cost both in economic and environmental terms.



2.1 (a)



2.1 (b)

Figure 2. 1 Chemical recycling of cotton (2.1 a) gives regenerated cellulose fibres that in principle have the same properties as other regenerated cellulose fibres from forest- or plant-based resources. Chemical recycling of Nylon 6 (2.1 b) gives PA6

2.2.4 Mechanical recycling:

This recycling method is applicable for Open-loop system (in case of all textile materials) or closed-loop system.

Recycling by the mechanical method is carried out either by 1) melting the synthetic fibres to produce granules which are used further for spinning new fibres. It is also known as thermomechanical recycling, or 2) shredding fabrics so as to recover the fibres and known as mechanical processing. The remelting method does not allow any form of contamination like dust, dirt or certain surface treatments. Fibre blends such as nylon 6 and Nylon 6.6 and polymers which are difficult to melt like elastane cannot be recycled using this method.

In all case, metal and plastic parts like zippers and buttons are separated from the textile material. After this, the textile material is cut into tinier pieces which are further fed into a textile shredding machine that opens up the structure of the textile and the fibres are released. When recycled to yarn, the fibre mass (textile) is carded and additionally may pass through extra steps in order to eliminate the short fibres. Thus, a sliver is produced which is further processed to form a yarn by for instance rotor (open-end spinning) or ring spinning. In the mechanical method of recycling by tearing, the fibre properties are maintained with the exception of fibre length.(Roos et al., 2019) By sorting the feedstock based on the colour, re-dyeing can be prevented, thus decreasing the environmental impact of the manufacturing process of a textile product. Figure 5 depicts the schematic diagram of the mechanical recycling process of cotton, however, this process can be used fundamentally for any textile material. This recycling method is very vital route in case of blended fibre qualities in reality. (Roos et al., 2019).

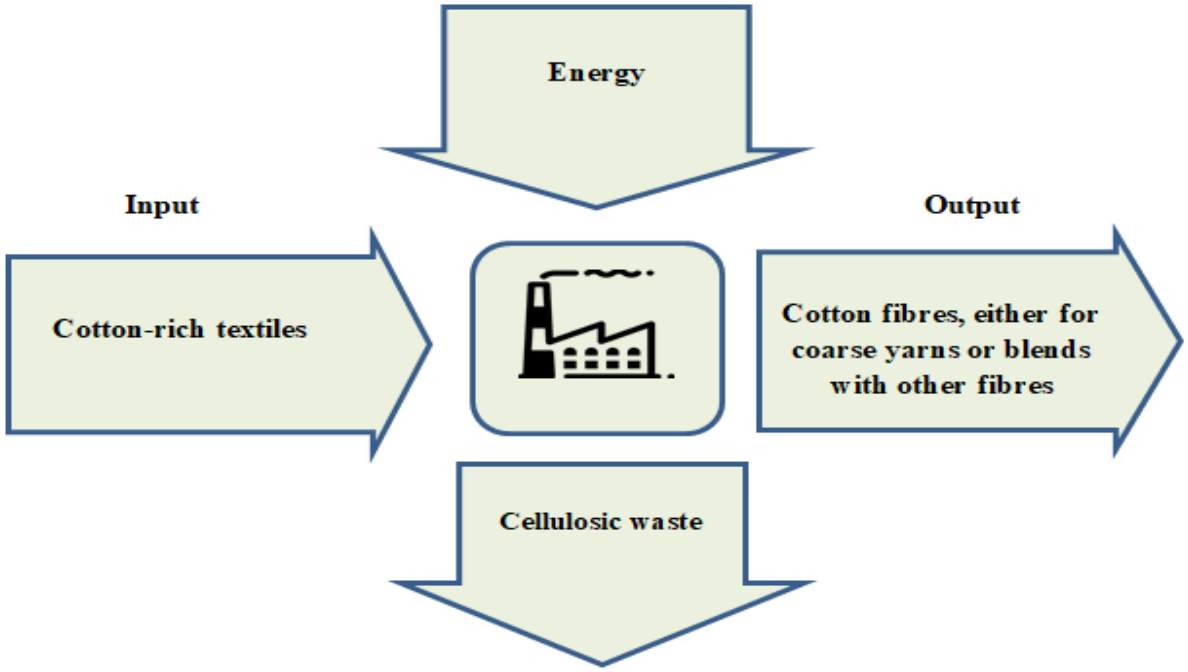


Figure 2. 2 Mechanical recycling of cotton produces cotton fibres with shorter-fibre lengths, making end-uses such as coarse yarns or blends with other fibres feasible. The figure shows the cotton case, but the same process can be applied for basically any textile

2.3 Chemical issues/challenges associated with recycling of textiles: Need of chemical removal

Generally, the current studies from the industry and literature have not discussed in deep about the potential chemicals or substances that may pose a challenge to the recycling of the textiles; hence it is necessary to carry out a literature review of the challenges or issues for the textile recycling.

(Sugai, 2003) reported that one of the drawbacks of recycling textiles through the regeneration of "first life" textiles into new fibres is the existence of different fibre blends and finishes which can hamper the regeneration process and degrade the regenerated fiber properties.

Generally in order to impart the garments with functionalities like crease resistance, crease recovery properties and dimensional stability, easy care finishes are applied to the cellulosic fabrics. Previous research studies have established that waste cotton

garments consists of the residual dimethyloldihydroxyethylene (DMDHEU); resin finish even at the garments end of life step. (L. V. Haule, M. Rigout, C. M. Carr, 2012) and the presence of this residual DMDHEU decreased the solubility of the waste cotton garments in the solutions used for the dissolution and the regeneration of cellulosic fibres. (L. V. Haule, C. M. Carr, 2014).

Still fibre-to-fibre recycling route is challenging in case of both the natural and synthetic fibres, and to accomplish a feasible business models by utilizing the regenerated fibers as the raw materials, it is critical that the fibers be of virgin quality. The usage of garment during its service phase, in particular, might change the fibres at a molecular level and reduce the DP (degree of polymerization) of the cellulose polymer, limiting mechanical recycling choices. (Palme, Idstro, Nordstierna, & Brelid, 2014).

To recycle cotton, one method could be regenerating the cellulosic cotton into man-made cellulosic fibres by the chemical recycling route (Wedin et al., 2018). As compared to the mechanical recycling of cotton which is common nowadays, a potential benefit of the chemical recycling of cellulose into manmade fibres, has the ability to eliminate impurities and separate other fibres in parallel, and resulting in a quality comparable to virgin regenerated fibres. This is significant because impurities in cotton fabric, like additives, colorants, and other finishing agents, can pose substantial technical issues in chemical recycling, as well as transfer potentially hazardous compounds existing in the raw material. Increasing recycling creates a toxin-free environment, allowing for a more effective and integrated approach to tackling potential concerns. Textile pulp must have the same impurity content as commercial dissolving pulps in order to meet the regeneration process's requirements. Decolorizing dyed cotton before dissolving is therefore necessary to lower the impurity content. (Wedin et al., 2018).

Presently, the recycling of waste cotton by the chemical way is limited, as one of the technical challenges being the existence of the crosslinks due to the modification of the cellulose hydroxyls with the reactive colorants and the finishing chemicals.

(Bigambo et al., 2019). The presence of these crosslinking colorants and wrinkle free finishes inside the cellulosic structure might diminish cellulose feedstock dissolution, the consecutive recycled cotton material spinning efficiency, and eventually impact the final qualities of the "new" regenerated cellulosic fibres. (Bigambo et al., 2019). It's also important to know that additional contaminants, like heavy metals, can make the N-Methylmorpholine N-oxide (NMMO) solvent, which is utilized for Lyocell fibre regeneration, unsafe. (Thomas Rosenaua, Antje Potthasta, Herbert Sixta, 2001; Wolfram Kalt, Johann Manner, 1996) and has potential to adulterate the solvent and as a result, the rate of recycling has decreased. As a result, any colorants, crosslinking agents, or other contaminants must be removed from waste garments before they can be turned into new fibers using the Lyocell method. Besides, reducing the dissolution of the solvent, the covalently bonded colorants also may unfavorably affect the feedstock colour and the final regenerated fibres. Hence for the new fibre regeneration, it is necessary to ensure the removal of crosslinks derived from dyes and easy care resin finishes prior to the chemical recycling of the waste cotton.

While studying about the color management in circular economy, the authors discussed that, when man-made fibre are produced from the waste cellulosic cotton textiles, the material should be subjected to the refining steps prior to the dissolution in order to fulfill the quality requirements and the regenerated fibre processes tolerance limits, as well as to provide appropriate fiber characteristics. These refining steps adjust cellulose viscosity, increase the reactivity of the cellulose and also remove unwanted impurities. (Määttänen et al., 2019). Additionally, with respect to the coloration of textiles, like the direct, reactive and vat dyeing, the pigment printing which is also utilized by digital printing or either by the traditional screen printing is a very common method and hence there is a need to study the decolorization and the refining ability of such colorants further. (Määttänen et al., 2019).

A study analyzed 15 critical features for the (fiber-to-fiber) textile recycling pertaining to the various aspects of the input material to the recycling i.e the waste textile that has been categorized and taken up for the recycling. Out of the 15 critical aspects, 9 of them are related to the design features of the textile products which perplex the

sorting and the textile recycling ; e.g. use of mixed fibers and various fibers for outer materials and lining in addition to the presence of the spandex, inlays, plastic prints, metals and plastics. Three of these aspects are closely associated with the manufacturing process namely, presence of dyes/colors, presence of chemicals and hazardous chemicals, and to the use of threads in various materials as compared to the fabric in the textile products.(Maria Elander, 2016).

Due to the modest effects of the process on the molecular level, chemicals are thought to persist in the outgoing material created during mechanical recycling, (Anders Schmidt, David Watson, Sandra Roos, 2016; Östlund Åsa, Helena Wedin, Lisa Bolin, Johanna Berlin, Christina Jönsson, Stefan Posner, Lena Smuk, Magnus Eriksson, 2015) Where chemical substances that are a source of concern are present, they may cause health and environmental problems during the product's use phase. Because a large proportion of chemical constituents in textile materials are expected to be eliminated by leaching, degradation, or related distillation and separation processes in the chemical recycling (such as depolymerization), the risk of hazardous substances carrying-over to outgoing recycled product is low. While some components may stay in the material, technical concerns such as diminished dyeability or the requirement for an additional purification process step are possible due to a lack of understanding of the interactions of specific chemicals in recycling processes. (Katherine Le, 2018).

Problems in elimination of the chemical finishing agents used for the flame retardency and the water repellency, have been mentioned as issues experienced while performing chemical recycling as well as processing of manmade textiles at a research. (Katherine Le, 2018). The chemical link between dye and fibres is expected to offer a barrier during textile recovery and recycling; nonetheless, removal techniques for several dye classes have been developed. Colorants and other impurities have been seen to coagulate or form insoluble impurities, posing a difficulty in recycling systems during spinning processes. (A.B.Schuch, 2016).

Another study presents and summarizes potential chemical compounds and product kinds of concern by (Östlund Åsa, Helena Wedin, Lisa Bolin, Johanna Berlin, Christina Jönsson, Stefan Posner, Lena Smuk, Magnus Eriksson, 2015) et al. in Table 2.1.

Table 2. 1 Potential CS of concern used in the consumer textile products(Östlund Åsa, Helena Wedin, Lisa Bolin, Johanna Berlin, Christina Jönsson, Stefan Posner, Lena Smuk, Magnus Eriksson, 2015)

Chemical Substance	Product type, uses
Biocides	Sportswear and underwear with/without odour prevention Workwear used in hygiene applications (cleanrooms, healthcare sector)
Flame retardants	Workwear, upholstery, floor covering, curtains/drapes, cotton and polycotton materials for home textiles
Fluorinated and Perfluorinated substances (short and long chain)	Workwear Outdoor textiles (water repellent coatings on clothing, equipment,tents)
Phthalates, SCCPs, heavy metals	Coated textile products Textiles with prints

2.4 Review on the bibliographic research of the main chemical removal processes associated with each individual chemical

As studied in the previous part regarding the challenges due to the chemical contaminants for the textile recycling, in this part we will review the chemical removal processes associated with each chemical.

2.4.1 Removal of the crosslinking finishes:

Several studies have been conducted in the past to test the stability of the crease resistant finishes and to develop strategies for removing them from fabrics. (N. B. Prashant Abhyankar, Keith Beck, Christine Ladisch, 1987; Prashant Abhyankar, Keith Beck, 1985, 1986). (Prashant Abhyankar, Keith Beck, 1985) stated that after immersing dimethyloldihydroxyethyleneurea DMDHEU-treated cotton fabric in a 23 percent sodium hydroxide solution for 10 minutes at boiling temperature, and discovered that while the stripped fabric's crease recovery angle (CRA) was reduced to that of the blank untreated fabric, a few traces of nitrogen attributed to the DMDHEU remained. The stripped fabric did not dissolve in the solution of ethyl acetate, according to the findings. Deprotonation of the nitrogen in the urea component or the oxygen in the ether link were the ways to remove DMDHEU.(J. F. Prashant Abhyankar, Keith Beck, Christine Ladisch, 1986; Prashant Abhyankar, Keith Beck, 1986). The use of urea-phosphoric acid solutions to eliminate DMDHEU crosslinks in the crease resistant resin-finished cotton fabric has also been investigated and recommended as a corrective therapy for easy-care finish application faults. (H. Z. Jung, R. J. Berni, 1976; H. Z. Jung, R. R. Benerito, E. J. Gonzales, 1972, 1974; Leon Segal, 1973). Urea phosphoric acid hydrolysis has the advantage of being administered at lower temperatures as compared to that of the alkaline hydrolysis. Even though the CRA performance of the cotton substrate was decreased to that of the untreated fabric, the stripping of easy-care finishes with urea phosphoric acid followed by alkali treatment left residual nitrogen in the cotton and an associated insolubility of the ethyl acetate solution. (N. B. Prashant Abhyankar, Keith Beck, Christine Ladisch, 1987). (Y. K. Kamath, R. U. Weber, S. B. Hornby, 1985) stated that the stability of the crease resistant finishes to the hydrolysis is dependent on chemical as well as the physical equilibrium conditions. The DMDHEU is largely hydrolyzed by scission of the ether bond under very acidic conditions, and this alone can hydrolyze up to 75% of the ether bonds in cellulose-DMDHEU crosslinks. The hydrolysis is favored by scission of the C–N bond under alkaline circumstances, and this could eliminate up to 25% of the crosslinks.

This shows that both acidic and alkaline conditions are required for complete removal of the DMDHEU easy-care finish from crosslinked cellulose.

(L. V. Haule, C. M. Carr, 2014) reported a sequential acid/alkali treatment for the removal of DMDHEU crease resistant finish from the cotton fabric using sulphuric acid/NaOH hydrolysis. The use of this sequential method was successful in removing the crosslinking resin finish from the cotton fabrics, resulting in a commercially viable cellulose yield.

In a related study, (Wedin et al., 2018) presented a novel alkaline/acid bleaching sequence for removing reactive dyes and the wrinkle-free finish of dimethyloldihydroxyethyleneurea (DMDHEU) from cotton textiles. Cotton pulps stripped of reactive pigment and finished wrinkle-free might then be spun into regenerated cellulosic (viscose) fibres. The mechanical qualities of these spun fibres, on the other hand, were inferior to those of commercial viscose fibres. The findings in this study reveal that reactive colorants and the DMDHEU crosslinking finishes affect the dope quality as well as the regeneration performance of the viscose. These results might lead to advancements in beating the challenges related to the quality in the chemical recycling of the cellulose.

In another study related to the chemical removal, (Bigambo et al., 2019) established a sequential acid hydrolysis/dithionite reduction/oxidative treatment (peroxide based) for the stripping of all types of the reactive colorants and postconsumer denim fabric. All the reactive colorants were removed using this technique including the anthraquinone-based dyes which are chemically resistant and the C. I. Reactive Blue 19 dye which were decolorized and a white cellulosic feedstock was obtained which could be used to produce new cellulosic fibres via the regeneration process of the Lyocell fibre. The cellulosic feedstock was utilized to make new fibres, one of which was made entirely of cotton pulp and the other of which was made partly of recycled cotton pulp (20%) and partly of wood pulp (80 percent). The qualities of the regenerated fibers were equivalent to the properties of lyocell fibers.

2.4.2 Removal of the flame retardant finishes:

(Yasin, S et.al, 2015) successfully removed the flame retardant finish (FR ammonium phosphate dibasic) from cotton fabrics using IR radiation. The degradation of finish is accelerated by reducing the distance between the sample and the IR emitter, according to the author. In addition to this, a 15 minutes IR radiation treatment was enough for the degradation of FR from the cotton placed at certain distance from the emitter. The proposed method could be used to minimize the drop in the energy yield along the gasification or the incineration process of the FR textiles.

In a study pertaining to the removal of the FR finish from the flame retardant textiles, (Yasin et al., 2016) studied Fenton reaction, an advanced oxidation process (AOP) for the removal of an durable organophosphorous FR finish N-methylol dimethyl phosphonopropionamide (MDPA) from the FR treated cellulosic textiles. The results demonstrated that the Fentons reaction could be used efficiently for the degradation of organophosphorus FRs (MDPA and TMM) in the aqueous medium as well as from the FR treated textiles. The mechanical properties remained unchanged even after the removal of FR finish using the highly oxidative fentons reagent. The FR finish degraded textile could potentially decrease the environmental impacts for the end of life options and possibly during the reuse phase.

2.4.3 Removal (Color stripping) of the reactive dyes:

Alkaline reducing process using the sodium hydroxide (alkali) and the reducing agent (Sodium hydrosulphite) is the conventional process for the color stripping. It was performed by (Uddin, Islam, & Islam, 2015) on three (Novacron Red TS-3B, Novacron Yellow TS-3R and Novacron Blue TS-3G) reactive dyed cotton fabrics. In this study, the maximum color stripping was obtained at higher temperatures like 80 and 100 deg and also with high concentration of the chemicals. The process has an impact on the quality of the fabric (Uddin et al., 2015). Similar study for the photocatalytic color stripping of Reactive Red X-3B dyed substrate was developed by employing the nano-TiO2/UV system. The results displayed that the fixed dye could be decolorized

efficiently or photocatalytically stripped. Also no any harsh chemicals were added in the decolorization process. (Long, Liu, Wang, & Shi, 2017).

(Chatha, Asgher, Ali, & Hussain, 2012) carried out color stripping of the Reactive black B dyed cotton fabric using White rot fungus Ganoderma lucidum IBL-05. The results showed that the biological method has good potential for decolorization and is superior in terms of the fabric quality and the percent color removal from the dyed cotton fabric as compared to the chemical assisted stripping.

2.4.4 Removal of patterns on printed cotton fabrics

In a novel study related to the mechanical properties of decolored cotton, (Tengblad, 2019) demonstrated a de-coloration technique with a pH responsive polymer of the Pigment Violet 23 and the pigments Heliogen Blue 15:3. The technique consisted of mechanical and chemical treatments (cationization, sonication and acidification) that caused a change in the cottons mechanical properties. With the comparative studies it was shown that the hydrophobic character, size and the pigment's charge were significantly important that influenced the color removal. Comparing the decolorization of the two pigments with the different charges it was found that, in the case of pigments with the positive charge it was easy to decolorize them. The study also stated that the smaller pigment were difficult to be removed.

Removal of the phthalocyanine pigments from the textiles is difficult because these pigments are deposited on the textiles with the resins and binders which fix them firmly and to some extent protect these pigments from the chemicals attack. In a patent related to removal of phthalocyanine pigments, the author (Alton A Cook, 1952), demonstrated a two-step process for the satisfactory removal of phthalocyanine pigments. The removal of these pigments in a substantial complete manner from the textiles was achieved by treating them in a formulation consisting of an aliphatic quaternary compound along with caustic soda and sodium hydrosulfite. The process involved the use of high temperature and treatment time.

2.4.5 Removal (Color stripping) of the disperse dyed goods:

(Fei, 2015) used Sodium formaldehyde sulfoxylate (SFS) for decolorizarion of the disperse dyed PET in water/acetone media. This method was found to provide sufficient decolorization for a wide range of the disperse dyes and the optimized conditions found were water to acetone ratio (1:2), SFS concentration (10g/L), treatment time (30 min), liquor ratio (1:50) and treatment time (30 min). This decolorization technique using SFS was used for different PET dyed samples with various chromophoric groups. Amongst them, it was difficult to decolorize the quinoline dye while the other classes of dyes like anthraquinone, methane, azo and nitro were decolorized thoroughly. No adverse effects were found wrt mechanical properties of the decolorized disperse dyed PET samples. (Fei, 2015).

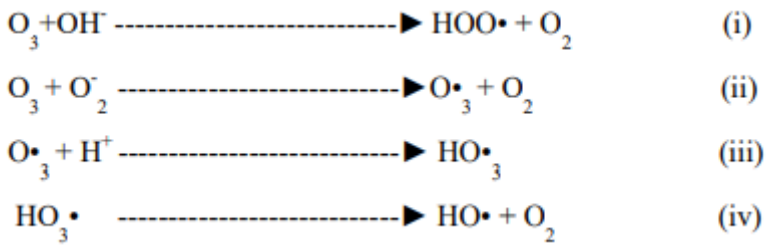
2.5 Ozonation process:

2.5.1 Ozone gas and its reaction mechanism:

Ozone is a highly reactive gas, heavier as compared to the air, an irritating pale blue gas and unstable chemically for the storage and transportation and can only be “in situ generated”. As compared to the other oxidants, ozone has a higher oxidation potential. (Arooj, 2014). The comparison of the oxidation potential of ozone with various other oxidizing agents is given in table 2.2. The ozone is produced generally utilizing the ozone generator, under the principle of the corona discharge, with the passage of dry air or oxygen over a very strong electric field , that splits the diatomic oxygen molecule (O_2) into 2 highly excited atoms of oxygen (O-) that combine with the other molecules of oxygen thus forming the ozone. (Manning et al., 2002).

In the case of non-aqueous medium, the reaction of ozone with the organic substrates takes place via ozonolysis, i.e. ionic cycloaddition of ozone to alkene double bonds which leads to ozonide formation that decomposes to produce a carbonyl compound. (Eriksson & Gierer, 2007; Hidenobu Kaneko, Shuji Hosoya, 2007). The ozonolysis process is explained in figure 2.3.

While in the aqueous media, the mechanism of the ozone reaction becomes more complex and it reacts with the substrate either in the molecular form or by the forming of hydroxyl radicals relying on the different parameters like the temperature, pH and the chemical composition of the water. Ozone may detach an electron from the organic substrates which are easily oxidized. (Reitberger, T., T. Eriksson, 1995). This electron transfer is responsible for the generation of the hydroxyl radical consisting of the following reactions:



By the reaction between hydroxide ions and ozone, superoxide anion radicals O_2 and hydroperoxyl radicals HOO• are formed directly. (Christiane Gottschalk, Judy Ann Libra, 2009). The hydroxyl radicals are easily transformed into the superoxide and vice versa under the ozone bleaching conditions. (Martin Ragnar, 2000).

Table 2. 2 Oxidation potential of ozone and other oxidative chemicals (S Contreras Iglesias, 2002)

Oxidizing agents	Oxidation potential (eV)
Fluorine	3.06
Hydroxyl radical	2.08
Nascent oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.77
Per hydroxyl radical	1.70
Permanganate	1.67
Chlorine dioxide	1.50
Chlorine gas	1.36

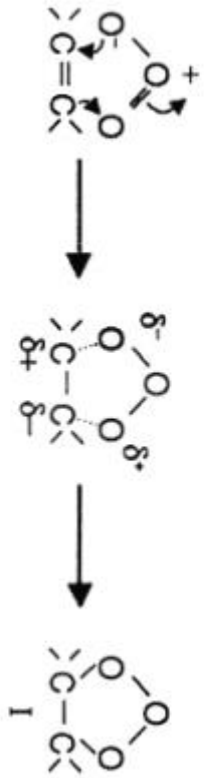


Figure 2. 3 Dipolar cyclo addition (Gunten, 2003)

2.5.2 Applications of the ozone:

Currently, scientific research and studies related to the usage of ozone in textile production sector are very popular. But in practice, the ozone use in the textile manufacturing sector is not that common. In commercial scale the use of ozone is generally in the denims and the garment washing.

Companies like Jeanologia, have developed first ozone based process treatment for continuous fabric. The name of this technology is G2 Dynamic. With this technology, the fabric finishing using the ozone has become a reality. This G2 Dynamic technology the fabric finishing process is simplified, with increased productivity and thus reducing costs. The results with this technology are comparable with those obtained in the traditional desizing, caustification and elimination of backstaining

processes, adjusting only the ozone concentration and the speed, for the fabric widths upto 2.35 m. This G2 Dynamic technology has been certified as safe and ecofriendly. (Jeanologia, 2014)

Another innovation by Jeanologia is the G2 technology which is the latest and most eco efficient ozone based textile technology. G2 cube technology permits for industrial scale production with wet or dry garments. In the dry based process, the garment is effectively cleaned by the ozone, thus improving the whiteness of the used area and removing the backstaining. In case of the wet garments, bleaching effect is accomplished using the ozone in just one step without any chemicals. This sustainable process can be utilized to achieve color fading in both the knits and denims.(Jeanologia, 2014). Various applications of ozone have been discussed here.

As previously seen, since ozone is highly oxidative agent, various application of ozone were reported in case of textile wet processing like, treatment of soybean fibre, wool fibres, polylactic acid fibres and also in the clearing of the disperse dyed polyester. (Eren, Gümüs, & Eren, 2016). Researchers have stated the efficiency of the ozone for bleaching of materials apart from cotton such as silk fabric, jute fabric and angora rabbit fibre and noticed that these substrates were effectively bleached by the ozone. (Perincek, Seher; Bahtiyari, Muhammed İ.; Körlü, Ayşegül E.; Duran, 2007; S. Perincek, Bahtiyari, Körlü, & Duran, 2008)(Sargunamani & Selvakumar, 2006). While, on the other hand utilization of the ozone for the color stripping of the reactive dyed cotton fabric is a new approach and very less studies have been reported in the literature. No studies have reported this technique in terms of the process development of stripping of the dyes or crosslinking colorants prior to the recycling of textiles to obtain regenerated fibres.

Ozone has also gained a lot of attention in the waste water decolorization. It is very effective for the textiles effluent decolorization since it readily breaks the chromophoric part (–C=C– or –N=N–) of the synthetic dyes. However, The ozonation process efficiency is dependent on several process parameters such as pH,

temperature, dye concentration, treatment time and the applied ozone dose. (Arooj, 2014).

2.6. General Framework for the LCA Methodology

This section of the thesis is aimed at providing an overview of the Life cycle assessment method and its study pertaining to the textiles, processing and recycling of the garments.

2.6.1 Life cycle assessment (LCA) and the environmental terminologies

The LCA technique assesses a product's environmental impact across its entire life cycle by quantifying the inputs (energy and materials utilized), the outputs (the wastes and emissions discharged into the environment, and the environmental repercussions of those inputs and outputs.(Jacquemin, Pontalier, & Sablayrolles, 2012). An LCA approach consists of four interdependent phases, according to the principles of the International Organization for Standardization (ISO) both 14040 and 14044 series of standards: Goal and Scope Definition, Inventory Analysis, Impact Assessment and Interpretation.(Walter Klöpffer, 2015). Figure 2.4 illustrates the descriptive LCA framework. Mainly, the LCA of any product, activity or service is inventory based, where the energy, raw materials and the environmental emissions are distinguished later.(Erica Ison, 2000). It must be noted that an enormous multidimensional set of input data, output data which are difficult to illustrate and assimilate are provided by the LCA analysis. In the LCA product system, to avoid uncertainties in impact analysis generally additional precautions are recommended while relating input to output data. (Hermann, Kroeze, & Jawjit, 2007). Hence, for a better understanding of the environmental profile of the color stripping process, LCA with comparison of the process parameters was chosen.

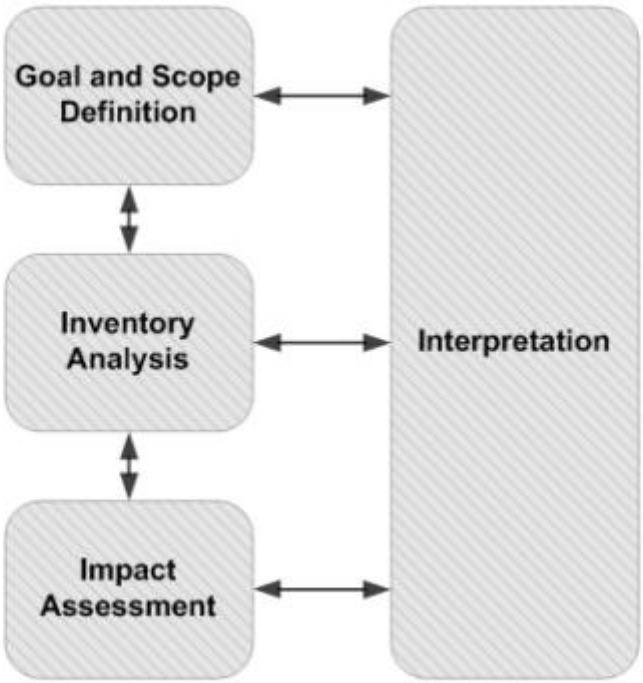


Figure 2. 4 Illustrative diagram of the four phases of LCA in the framework.

2.6.1.1 Phases of LCA

Four interdependent components or phases are carried out for a standard LCA. The four components of LCA are;

Goal Definition and Scope: The first part of LCA is the Goal and Scope Definition, which establishes the study's framework and the intended use of its findings. Factors such as functional unit (FU), system boundaries, assumption and restrictions, allocation techniques, and effect categories chosen establish technical aspects and the level of detail addressed. The aim and scope of an LCA must be clearly defined and consistent, according to ISO standards.

Life cycle inventory: Following the definition of the study's purpose and scope, the LCI is created, which is a comprehensive inventory of all relevant inputs (energy and materials) and outputs (environmental releases or emissions) associated to the functional unit defined.

Life cycle Impact Assessment (LCIA): When the quantified LCI flows are linked to their potential environmental impacts using a chosen method, the Impact Assessment

(LCIA) is performed. The technique includes a number of environmental impact categories, as well as characterization, normalization, and weighting elements. This stage is carried out using a systematic approach based on an ISO-defined series of steps (some of which are mandatory, while others are optional):

- Classification (obligatory): inventory flows are categorised according to the sort of environmental impact they have (e.g., CH_4 emissions are linked to climate change) using the method chosen.

- Characterization (obligatory): once the substance flow has been classified, it must be characterized; this means that all flows with the same environmental impact must be translated to the same representative unit (e.g. conversion of CH_4 to CO_2-eq). (Albino Andre Moreira Cardoso, 2013).

- Normalization (optional): This step consists of a reference situation (region, country or world) of pressure on the environment for each impact category analysed. (Wegener, Oers, Guinée, Struijs, & Huijbregts, 2007).

- Grouping (optional): Sorting and perhaps ranking the impact categories are part of this step.

- Weighting (optional): This step is a subjective outcome in which the impact categories are weighted in relation to one another so that a single final score may be generated.

Interpretation: This is the final stage of the LCA. The purpose of the interpretation is to summarize and discuss the outcomes that have been accomplished in a systematic manner, as well as to verify that the findings are in compliance with the established goal and scope. The study's final results are drawn, and improvements and recommendations are proposed.

Nonetheless, it can be restated that, defining the functional unit (FU) is included in the defining goal and scope. The FU is the most important part of the LCA. It answers queries like "what," "how much," "how well," and "how long" by quantifying the function

of the system under study and serving as a reference unit. (European Commission, 2010). The functional units in a comparative LCA must have the same functional performance; otherwise it is not possible to have a meaningful and valid comparison. However, identifying the function of the system is not always easy. This is owing to the multifunctional systems and separation between the primary and secondary functions can be indiscernible. (Jáchym Judl; Tuomas Mattila; Jyri Seppälä; Sirkka Koskela; Petrus Kautto, 2012; Walter Klöpffer, 2015).

2.6.1.2 LCA variants: Cradle to grave or cradle to cradle.

Cradle-to-grave and cradle-to-gate are the main variants involved in the LCA. Cradle-to-grave analysis considers a complete assessment of all the upstream and downstream inputs and interprets the associated environmental emissions from production to disposal of any item. While, in cradle-to-gate LCA analysis, the use and the disposal phases are excluded. Nonetheless, an LCA can be costly and time consuming, therefore used with limitations for its use as investigation method.

2.7 LCA studies on the textiles.

2.7.1 End-of-life textiles scenarios: Reuse and recycling.

In the UK, the clothes/textiles make up in between 4 and 5% of the municipal solid waste stream. Companies like Salvation Army Trading Company Limited (SATCOL) are responsible for the recycling of approximately 25 % of these. These companies provide a collection and distribution framework for donated shoes and clothing. In a research study conducted in the UK to quantify the energy used by a recycling / reuse operation and to assess the energy benefit, a streamlined LCA was used. The results have shown that for every 1 kg of virgin cotton replaced by used clothing, 65 kWh energy is saved approximately and for every 1 kg of virgin polyester around 90 kWh is saved. Hence, in another terms, reuse of 1 tonne of PET clothing consumes only 1.8% of the energy required to produce these goods by using virgin materials. In case of reuse of 1 tonne of cotton garments requires only 2.6% of the energy needed to manufacture from virgin materials. Thus, recycling and resue of the donated

clothes results in cutting the environmental burden as compared to buying new garments made from virgin materials.(Woolridge, Ward, Phillips, Collins, & Gandy, 2006).

(A. Bartl, 2009) described the potential for savings in energy and material for the textile recycling. Due to the high energy and the resource demands of fiber production, the author contends that the recycling process are useful. However, the paper argues that, the best option is reuse when suitable, owing to the negligible energy requirement for the collection and sorting as compared to the energy intensive apparel manufacturing.

Downcycling refers to the waste recycling into lower value products than the original products. The collected textiles which are not suited for reuse, maybe downcycled into products displayed towards the bitumen industry was proposed by (A. Bartl, 2009). Nonetheless the author has argued that as compared to the reuse of the waste derived fibers, downcycling saves much less energy. However, this study does not take into consideration for the recently emerging high value recycling technologies and also does not take into account the business loss for collectors as a result of downcycling.

(Pesnel & Perwuelz, 2013) carried out a study on the cotton bedsheets with three different recycling processes. They found a reduction in the water consumption and eutrophication potential of the bed sheet life cycle as compared to the virgin production. This decrease was owing to the prevention of the cotton cultivation. In the same study, with regards to the global warming impact category, the results indicated that mechanical recycling has lower impact than chemical recycling and energy recovery. Various steps like life cycle stage of waste collection, recycling location, manufacturing location of virgin material and other external parameters were excluded. The parameters that affected the environmental impact the most were location of the production of virgin material and the energy mix of the particular nation.

2.7.2 LCA study on various waste disposal options concerning the textile waste.

In 2007, Aitex, a textile industry research association in Spain performed a study which compared the environmental impacts of the recycled cotton yarns with the conventional cotton yarns. LCA comparison was done between recycled yarn of 80-20 % cotton – polyester fibre composition and 100 % virgin cotton. The results showed savings of over 17 % in greenhouse gas emissions (AITEX, 2007). Much higher savings in water use, as the recycled yarns used up almost 8 times less water as compared to the virgin yarns and led to almost 5 times less effluent waste water.The recycled yarns, finally averted all the impacts from the fertilizers, due to eluding the cotton production and didn't require dyeing. However, when it comes for apparel use, in terms of quality, it needs to be specified that, yarns manufactured from 100 % recycled material cannot be compared in function with the 100 % virgin material. (AITEX, 2007). Due to these reasons, for various fashion brands like H&M and G-Star Raw, in recycled collections, the recycled content rarely exceeds 20 %, as recycled yarn is not considered to be of comparable quality by the brands.

In a report on the LCA study of recycling cotton, (Miljögiraff, 2016) reported that that collecting clothes and mechanical recycling of cotton has a substantial potential to lessen the overall environmental impact on the most significant effect categories (although not for all).

(Y. Liu et al., 2020) performed a comparative LCA study to evaluate the environmental impacts of spun yarn from the recycled cotton yarns and the virgin cotton yarns. The results reveal that the recycled cotton yarns is a feasible option to relieve the pressure on the environment and the resources. Using 1 tonne of recycled cotton yarns can help save 0.5 ha of agricultural land, 2783 m3 irrigation water and reduce the 6600 kg CO2 eq. Hence, it can be summarized that, a substitute to the virgin cotton fibers can be served by the recycled cotton fibers to reduce the agricultural land and avert the environmental impacts created from the cotton plantation.

2.7.3 Life Cycle Assessments for recycling textile waste scenarios.

(Zamani, Peters, & Rydberg, 2014) carried out an LCA study on various types of recycling textile waste, which included material reuse of acceptable quality, chemical recycling of polyester and cotton polyester separation using NMMO. The impacts from the collection of the textile waste were excluded from this study. The authors summarized that, the emergent textile recycling technologies had less impacts for the global warming potential as compared to the incineration, which is a prominent waste management option in Sweden. Moreover, the energy intensity associated with the separation of the cellulose/polyester and cellulose/polyester fibres production from primary resources exerted a significant impact on the potential savings using these techniques. (Zamani et al., 2014).

A comparative LCA based on the cradle to grave carbon footprint and energy demand for man-made cellulosics (cellulose fibre produced from wood pulp), bio-based polyester, recycled polyester and PLA (polylactic acid, a bio-based polyester) was performed by (Shen, Worrell, & Patel, 2010). In this comparative LCA study, use phase was excluded. The study demonstrated that virgin polyester (petrochemical) has the highest impacts, followed by the partially bio-based polyester, the third is recycled polyester and the recycled (partially) bio-based polyester has the lowest impacts. As compared to the biobased polyester and petrochemical polyester, PLA and man-made cellulose fibres were found to have lower environmental impacts. The study recommended that for open-loop recycling, the preference of allocation method plays a vital role in the recycled products impacts. (Shen et al., 2010). The outcomes of the study point out that "both recycling and bio-based alternatives are important ways of reducing the energy requirements and GHG emissions". (Shen et al., 2010).

2.8 Literature review Summary. (regards to the textile recycling)

As per the discussion of literature in the previous paragraphs of this thesis ((AITEX, 2007; Pesnel & Perwuelz, 2013; Shen et al., 2010; Zamani et al., 2014)) points out that in the textile supply chain by avoiding the production of the virgin fibre and

substituting it with recycled fibres can help in achieving several environmental benefits. These benefits include a restricted decline in the CO2 emissions, significant reduction in the water consumption and decrease in eutrophication and acidification.

The result outcomes made by (Pesnel & Perwuelz, 2013) presented that mechanical method of recycling has less impact on environmental impact category like climate change as compared to the energy recovery and chemical recycling. (Zamani et al., 2014) demonstrated that emergent textile recycling techniques like chemical recycling of the polyester and the separation of the cotton/polyester using the NMMO were less carbon intensive as compared to the incineration and that recycling chemically strongly determines the potential savings of these technologies. (Zamani et al., 2014). Hence, both the studies correspond that chemical and mechanical recycling techniques are better alternatives than incineration.

Although (AITEX, 2007; Pesnel & Perwuelz, 2013) considered losses during the recycling processes, none of these studies took into account the distinctions in the function of the final product. As the fibres of shorter length are produced by the mechanical recycling, hence as of now, these fibres are used in very small proportion of the total fibre mass utilized in the quality apparel produce. On the other hand, chemical recycling assures to displace the production of virgin fibre even additionally, as the recycled fibres are of virgin quality and can be utilized at much higher percentages. The latter can be the case, except that there is molecular level deterioration that is carried from the previous use to the next (Palme et al., 2014).

In summary the main literature is discussed along with the research gaps associated. Apart from the literature and publications related to the textile recycling, little literature exists on the study of the environmental impacts of textile recycling technologies like chemical recycling and the mechanical recycling. The primary research study shows the potential of environmental impact reduction through the textile waste recycling. However, more detailed study needs to be done to study the chemical removal process prior to the recycling technologies as very limited studies

are available. Part of our study in the thesis is related to the discussion of these issues and studying the environmental profile of such processes.

2.9 LCA study with the unit processes:

The European Science Foundation's COST Action 628 recommends the LCA adoption to focus on developing the new textile processes. [(Nieminen, Linke, Tobler, & Beke, 2007)]. By implementing the LCA, impacts related to the environment can be analyzed, and also pollution stages can be found out and among the various stages of the life cycle a textile product passes thorough LCA has helped to demonstrate that the manufacturing and usage stages contribute the most to environmental impacts (D. A. Chapman, 2010).

LCAs have revealed that the dyeing unit process has a significant influence on the environment. For example, in case of the production of the dyed cotton yarn, an LCA study has reported that dyeing phase was an hotspot due to the usage of chemicals and energy intensively.(Bevilacqua, Ciarapica, Mazzuto, & Paciarotti, 2014). In addition to this, (Advisor & Bocken, 2006) acknowledge that in the textile sector, use of energy and chemicals gives rise to the major environmental impacts.

To assess the environmental impacts of a new dyeing technique as compared to a traditional dyeing process, an LCA was implemented by (Laura, Fatarella, Spinelli, Pogni, & Basosi, 2015). Some other LCA studies are associated with comparing spin dyeing and conventional dyeing. (Terinte, Manda, Taylor, Schuster, & Patel, 2014) and also the pad dyeing technology.(Yuan, Zhu, Shi, & Liu, 2013). All these studies have been associated with one common thing: by means of an LCA, betterment options have been suggested to minimize the environmental impacts of the textile dyeing operation.

However, there are various life cycle phases apart from the dyeing phase where improvements can be made, which we have discussed in the following part.

Basically, fiber production impacts should be lessened. A cradle-to-gate LCA analysis of acrylic fiber manufacturing was conducted for this reason. (Yacout, El-kawi, & Hassouna, 2016). Another research conducted on PP fibers and found that a recycled alternative is better for the environment than a virgin one.(Tuladhar & Yin, 2019). The production of terephthalic acid (purified one) is a major concern in case of PET fibers was reviewed by (S S Muthu, Services, & Kong, 2015). For instance, natural fibers like flax (Deng et al., 2016), hemp (Werf & Turunen, 2007) and raw silk (Astudillo, Thalwitz, & Vollrath, 2014) etc. also have been studied. These studies report one common thing ie; by the LCA application, enhancement options are identified to lessen the impacts due to fibre manufacturing and facilitating the textile industry to sound more environmental friendly.

Next, energy usage is inversely related to yarn fineness during the spinning and weaving stages. As a result, the LCA can only be accurate if the functional unit specifies yarn fineness or information like as fabric density.(Velden & Patel, 2014). Nonetheless, according to (Nieminen et al., 2007) such definitions are rarely utilized, and textile weight in kilograms is frequently employed instead. Quality considerations must be incorporated in the functional unit for the LCA to be useful for product development.

(Sandin, Peters, & Svanström, 2013) examined the water and land use impacts of the manufacturing of wood-based fibers and cotton fibers. A comparison study was conducted by (Baydar, Ciliz, & Mammadov, 2015) between an organic cotton T-shirt and a traditional one. For the every environmental impacts studied, the organic cotton Tshirt had lower environmental burdens as compared to the conventional one. In addition, because of the laundry operations, the T- shirt's use phase contributed to the global warming potential.

Nevertheless, (Velden & Patel, 2014) demonstrated less impact relatively from the use phase as compared to other suggestions. In the same study, it has been highlighted that, it is highly difficult to conclude on the wear and care habits of the consumers and the outcomes may vary to a large extent depending on the actual circumstances.

In an attempt to decrease the environmental impacts due to the use phase, particularly from the textile laundry, the self-cleaning textiles and their development has drawn attention. With the application of the LCA tool, (Busi, Maranghi, Corsi, & Basosi, 2016) demonstrated that an easy washable innovative textile, functionalized by depositing on the textile surface a nano-crystalline (photocatalytic TiO2) layer, was a more eco-sustainable alternative as compared to the traditional alternative due to lower impacts from laundering during the use phase. Likewise, in the production of a nano silver T-shirt, to compensate for increased CO_2 eq. loads, a decreased washing frequency in the usage phase has been proposed. (Walser, Demou, Lang, & Hellweg, 2011). In addition, (Manda, Worrell, & Patel, 2015) also pointed out that antibacterial textiles may allow for fewer washing cycles throughout the use phase, potentially lowering environmental impacts.

Another study has mentioned that bleached cotton may share lower environmental burdens as compared to the unbleached cotton (Roos, Posner, Peters, & Jo, 2015), the reason is due to the longer life cycle expected in the use stage of the bleached apparel.

From this review of literature study, it can be clearly said that the LCA has become a vital technique for the assessment and disseminating the environmental impacts of the textiles.

Textile recycling solutions are now undergoing extensive research and development and commercialization. Chemical recycling methods are gaining popularity as a result of their capacity to separate complicated blends while retaining or improving the original fiber's value. Cotton must be pre-treated to lower the degree of polymerization before it may be chemically recycled (DP). The environmental footprints of two distinct pre-treatment procedures, sodium hydroxide pre-treatment and sulphuric acid pre-treatment, were investigated using LCA in this study. (Rosson & Byrne, 2020). Across all impact categories, the authors found that acid pre-treatment has a much lower environmental footprint. This can be linked to the shorter treatment periods and lower material and energy requirements for chemicals production.

In a similar study, with regards to color removal from the reactive dyed cotton textiles prior to recycling, (A. S. Powar, Perwuelz, Behary, Hoang, & Aussenac, 2020) studied the environmental profile of the ozone based decolorization process and also the hotspots associated with it using “gate to gate” LCA tool. (A. S. Powar et al., 2020) reported that the oxygen formation for ozone generation and electricity were the major contributors for the environmental impacts. Additionally, the environmental impacts can be further reduced by decreasing the treatment time, decreasing the ozone input, and by simultaneously decreasing both the treatment time and the ozone input.

However, very little focus has been on the chemical removal process prior to the recycling from the LCA perspective. In the future, more emphasis needs to be given on the development of the chemical removal technologies from the textiles in order to ease recycling. Also their simultaneous evaluation needs to be done to analyse the environmental profile of the designed process.

Chapter 3 Materials and Methods

In this chapter, the materials, methods, experimental set up, analytical tests and operational procedures and optimization techniques used are described.

3.1 Chemicals: Dyes and pigments.

3.1.1 Reactive dyed product and additives.

Reactive dyes are the most commonly used colorants for the cotton textiles and also each class of reactive dyes has a different chromophoric group. Also, there are varieties of reactive dyes available. Hence, we carefully chose the most commonly used azo dye CI Reactive black 5 for our initial study to produce the reactive dyed fabric. The same reactive dyed fabric was used for the comparison of various color stripping methods.

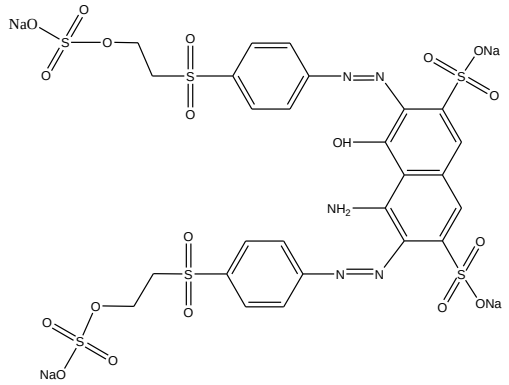


Figure 3. 1 Structure of C.I. Reactive Black 5 dye

3.1.1.1 Preparation of the reactive dyed product.

For dyeing purpose, a 100 % cotton ready for dyeing (RFD) woven fabric was chosen. The woven fabric was procured and the fabric grammage was 150 g/m2. As previously said, we used a commonly used azo based reactive dye Noir Everzol B, C.I. Reactive Black 5 dye provided by the Achitex Minerva, France. (figure 3.1).

Reactive dyeing was performed on a Jigger dyeing machine. The woven cotton fabric samples were dyed with 1% o.w.f of Reactive Black 5 dye with the standard dyeing recipe of reactive dye (C.I. Reactive Black 5). The hue colour developed by 1% o.w.f of Reactive Black 5 dyed cotton fabric is shown in Figure 3.2.

Figure 3. 2 Reactive dyed cotton fabric 1% o.w.f (C.I. Reactive Black 5)

3.1.2 Pigment printed product and additives.

Pigment printing constitutes one of the oldest and easiest printing methods, because of the ease of its application. Also, pigment printing shares more than 80 % of the print based goods due to several benefits. (El-Molla & Schneider, 2006; Yaman, Ozdogan, & Seventekin, 2012). Recently, researchers have also stressed the need to study the color removal from the pigment printed textiles (A. Powar et al., 2021). Hence, we chose the pigment printed textiles for the decolorization study. Also, we have chosen the phthalocyanine pigment azo dye CI Pigment Blue 15 for our initial study.(Figure 3.3).

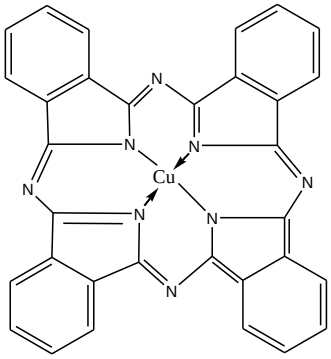


Figure 3. 3 Structure of C.I. Pigment Blue 15

3.1.2.1 Preparation of the pigment printed product.

For the pigment printing, same cotton woven fabric as used in the earlier study was chosen. We have used the following chemicals: UNISPERSE BLUE G pigment

(Huntsman); APPRETAN N 9210, an acrylic ester copolymeric binder from Archroma; and LYOPRINT® PT-RV NEW (Huntsman) a thickener were of commercial grade. All of other chemicals used were namely, sodium hydroxide, phosphoric acid used and were of the reagent grade.

Pigment printing was performed on a Johannes Zimmer Type Magnetic System Laboratory machine available in ENSAIT, France. The speed of the printing was 4 m/min. Mathis Laboratory finishing line was used for the drying and curing of the samples. The printed samples were dried and then cured at 160 º C for 03 minutes. For the printing, a sample and rectangular bar design pattern was selected. Pigment printing was done with the following pigment paste formulation (table 3.1):

Table 3. 1 Pigment paste formulation

Printing paste components	**g/kg**
Pigment colorant	30
Binder	80
Thickener	40
Water	850
Total	1000

The hue colour and the print pattern developed by pigment printing on the cotton fabric is shown in Figure 3.4.

Figure 3. 4 Pigment printed cotton fabric

3.2 Removal process: Ozonation, conventional and glucose aided process.

3.2.1 Removal of the color from the reactive dyed product

The decolorization of the reactive dyed cotton textiles consisted of the process employed.

3.2.1.1 Color stripping using conventional method:

Color stripping using the conventional method was performed using sodium hydrosulphite and alkali like sodium hydroxide. This process was carried out in a lab scale rota dyer machine set up with 10 g/l sodium hydrosulphite and 10 g/l NaOH at 100^{o}C for 30 minutes. A 40 g of the blue reactive dyed fabric sample was treated in a color stripping liquor of 1200 ml. The after treatment included the cold washing of the fabric and then the subsequent drying. (A. Powar, Perwuelz, Behary, & Hoang, 2019).

3.2.1.2 Ozonation process

The color removal from the reactive dyed cotton fabric was carried out with the help of ozonation process in situ on a pilot scale reactor.

As the aim of our study was to see the color removal from the reactive dyed textile, various parameters were considered using the Box Behnken statistical tool to find the optimum conditions for color removal with low mechanical loss to the fabric. For the in-situ color removal from the reactive dyed fabric using ozonation, three different ozone concentrations 5,45 and, 85 g/m^3 NTP ozone; three different pH values (3, 5 and 7) and three treatment times (10, 30 and 50 min) were used.

3.2.1.3 In-situ color removal from the reactive dyed cotton textiles

The color removal from reactive dyed cotton textiles was carried out using ozonation process performed in a pilot scale reactor. Previous studies have demonstrated the color stripping of reactive dyed cotton textiles using ozonation yielded the best color stripping results with 45 min ozonation treatment time. (Eren et al., 2016). However, in our study we tried to understand the effect of three variables like pH, treatment time and ozone concentration on the color stripping of the textiles as well as the tensile strength properties. The important aspect of the study is it was conducted at a pilot scale.

Secondly, box Behnken statistical model was used to study the optimum conditions required to achieve good coloration results with minimal strength loss. All the experiments were performed at room temperature and reverse osmosis (RO) water was used in the ozone based reactor with 60 litres of liquor volume.

After the ozonation treatment, all the treated fabric samples were washed with normal tap water to remove any residual ozone and some of the byproducts of oxidation on the fabric. Finally, the treated samples were dried for further characterization.

3.2.1.4 Experimental set up.

The experimental set up was consisted of pilot scale ozonation reactor.

The pilot scale reactor, as shown in figure 3.5 was used to perform the decolorization study of the reactive dyed textiles. The reactor is built of 316L stainless steel having 80 L volume, used mostly for treating the food grains. The design and construction of reactor are allowed to work at around ozone concentration of 200 g/m^3 ozone NTP and 1.2 bar gauge pressure. The ozone can be produced in the ozone generator with high purity oxygen (e.g. the help of liquid oxygen, 99.5 % purity) as well as the atmospheric oxygen. But the ozone generated with higher purity of oxygen can produce higher concentrations of ozone than the ozone generated by the dry air with the same ozonator.

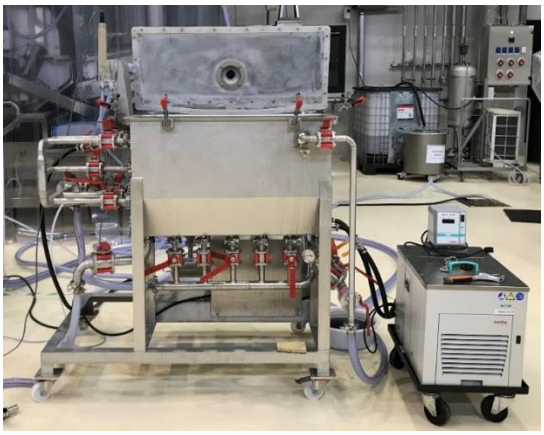


Figure 3. 5 Actual reactor setup of the ozonation

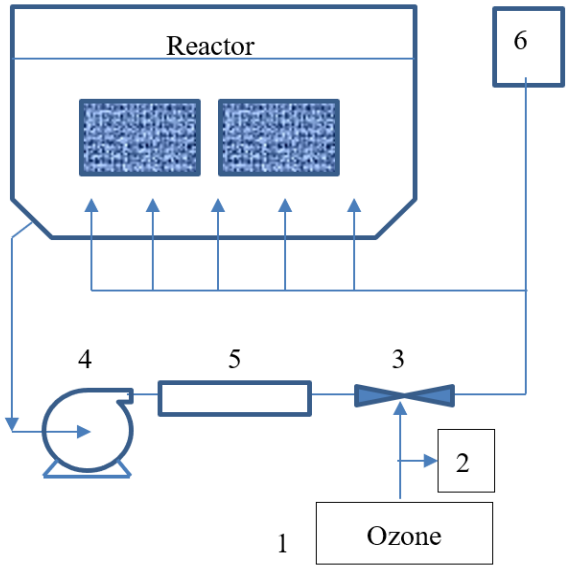


Figure 3. 6 Schematic diagram of the pilot scale ozonation (1: ozone generator; 2: ozone analyzer; 3: venturi injection system; 4: circulation pump; 5: filter; 6: dissolved ozone analyzer and pH meter)

Figure 3.6 shows the sketchup of the pilot scale ozonation. The decolorization process utilizing ozone was performed at ozone platform UniLaSalle,(France) as shown in the fig 3.6. The system consisted of two parts: (i) the ozone generator and (ii) the ozonation reactor. Ozone generation was done in the system from high purity gaseous oxygen (coming from the pure liquid oxygen) using the corona discharge method (Ozat CFS3-2G, Ozonia, France) with ozone concentration measurement in the inlet and in off-gas (ozone analyzer 964, BMT, Germany). Venturi system was used to inject the ozone

gas in the reactor system, combined with the circulation pump. This system enabled the transfer of the gaseous ozone in the ozone dissolved form for the color stripping process. The venturi system is more advantageous than the ozone diffused using a dome ceramic bubble column for the small reactor used in our study. The reactive dyed cotton textile was placed vertically in the ozonation reactor consisting of the reverse osmosis water.

3.2.1.5 Color stripping using organic reducing agent (glucose treatment).

Another method was established for the color stripping of the reactive dyed fabric with the use of an alkali and a natural reducing agent. The dyed fabric was treated for color stripping in a bath 10 g/l glucose and 10 g/l sodium hydroxide. The material to liquor ratio for the process was 1:30. The process was performed at different times and temperatures in terms of color stripping to get the optimized conditions. In all the experiments deionized water was used. After the color stripping process, the treated fabric was given hot wash followed by a cold wash then and eventually dried.

Figure 3. 7 Mathis LABOMAT dyeing machine (laboratory scale)

All the color stripping experiments were performed in a Mathis LABOMAT dyeing machine (figure 3.7). Here, all the chemicals, fabric were added at the room temperature and then the process was performed at the required temperature (3°c per minute) with the rota dyer program.

3.2.1.6 Experimental plan

The color stripping using the alkali and the glucose were performed with the following experimental conditions as shown in table 3.2:

Table 3. 2 Experimental conditions for the glucose assisted color stripping process

Sr No	Glucose concentration	Sodium hydroxide concentration	Temperature	Time
	(g/l)	(g/l)	(°C)	(mins)
1	10	10	60	60
2	10	10	80	60
3	10	10	100	60
4	10	10	60	30
5	10	10	80	30
6	10	10	100	30
7	10	10	60	15
8	10	10	80	15
9	10	10	100	15
10	10	10	60	5
11	10	10	80	5
12	10	10	100	5
13	20	20	100	30

The color stripping results have been discussed in the results chapter and also the mechanical properties of the optimized conditions.

3.2.2 Removal of the color from the pigment printed product

The decolorization of the pigment printed cotton textiles consisted of the process employed.

3.2.2.1 Ozonation process and In-situ color removal from the pigment printed cotton textiles

Since the pigment printed textiles, are difficult to remove as they are mechanically binded with the cotton fabrics, we have implemented the ozonation process to study the color removal efficiency from these printed cotton textiles. The ozonation process parameters utilized here are with higher ozone concentration and higher treatment time while keeping the same pH conditions as used in the reactive dyed cotton decolorization.

Also, a box Behnken response surface methodology was implemented to study the color stripping of the pigment printed textiles. For the in-situ color removal from the pigment printed cotton fabric using ozonation, three different ozone concentrations 40,100, and 160 g/m^3 NTP ozone; three different pH values (3, 5 and 7) and three treatment times (20, 70 and 120 min) were used. The color stripping was performed in the same pilot scale reactor. All the working parameters of the reactor were same like in the previous study on the reactive dyed goods. Here we have used the 30 litres of liquor volume for the treatment of the goods.

3.3 Optimization of the color stripping process using the Statistical analysis.

In our work, the statistical based experimental design system was implemented in order to optimize the cotton fabric decolorization using ozone. Here, the aim was to study the effects of various process parameters like pH, ozone concentration and the treatment time on the color stripping process. The effects of these process parameters variation was studied with respect to the color stripping and the mechanical properties

of the decolorized textiles. Also, our aim was to give optimum conditions, which gives good color stripping and low mechanical fabric loss. The response surface methodology, a statistical analysis tool gave the empirical formulae to enhance /optimize the parameters required.

Excel (Microsoft Office) was used in this study in order to analyze the data and calculate the predicted responses of the experimental design.

3.3.1 Box Behnken tool for the design for the design of the experiments

Experimental design methodology is a good strategy that makes simultaneous variation of all experimental variables feasible and gives information to optimize processes. Thanks to statistical analysis of the generated data, remarkable information is provided on the interactions among the experimental variables. From here, the number of tests and the required time would be reduced, leading to a considerable reduction in the overall required cost. Thus, Box–Behnken design was used. It is a cubic, independent quadratic and rotatable design with the treatment combinations at the midpoints of the edges of a multidimensional cube without embedded factorial or fractional factorial design and is used for fitting second-order response surfaces. (A. S. Powar et al., 2020).

Response surface methodology tools like the Box–Behnken design was implemented as the experimental design tool for optimizing the decolorization of the reactive dyed fabric using the ozone. The effect of pH on the decolorization was studied in the range of 3–7 by using the diluted solutions of phosphoric acid/sodium hydroxide. The ozone concentration was varied in the range of 5–85 g/m^3 with the varying power of the ozone generator and the influence of the treatment time from 10 to 50 min was also studied.

The total number of experiments (N) for the ozone based color stripping was defined using the following expression:

$N = 2K\ (K - 1) + C_0$ = 2*3*(3–1) + 4 = 16.

Wherein K represents the number of variables, C_0 represents the number of replications at the center point. K and C_0 were set to 3 and 4 respectively, for this study. Therefore, to perform a box Behnken experimental design, 16 experiments had to be done. Table 3.3 and 3.4 enlists the levels of each variable.

*Table 3. 3 Box–Behnken design experimental plan 3 factors * 3 levels.(Decolorization of the reactive dyed fabric)*

Experiment No.	pH	Ozone Concentration (g/m^3 TPN)	Time (Minutes)
F	X1	X2	X3
E1	5	5	10
E2	7	45	10
E3	5	85	10
E4	3	45	10
E5	3	5	30
E6	7	5	30
E7	7	85	30
E8	3	85	30
E9	5	5	50
E10	7	45	50
E11	5	85	50
E12	3	45	50
E13	5	45	30
E14	5	45	30
E15	5	45	30
E16	5	45	30

Table 3. 4 Experimental conditions. (Decolorization of the reactive dyed fabric)

Factor Level	Lower	Central	Upper
	−1	0	+1
pH	3	5	7
Concentration ozone g/m^3 TPN	5	45	85
time (minutes)	10	30	50

The responses can be modeled by a second-order polynomial equation:

$$Y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3 + a_{11}x_1^2 + a_{22}x_2^2 + a_{33}x_3^2$$

where Y denotes the color-stripping percentage varying as a function of x_1 (pH), x_2 (concentration of ozone), and x_3 (reaction time) variables. a_0 is the intercept, a_1, a_2, a_3 to a_{11}; a_{22} and a_{33} are the regression coefficients.

3.3.2 Statistical box Behnken design model for the experiments

Similar to the experimental design used for the color stripping of the reactive dyed fabric, another experimental design was created for the color stripping of the pigment printed goods. The color stripping of the pigment printed cotton fabric using ozone was optimized using the statistical RSM tool. The aim was to examine the influence of the combined process conditions such as pH, reaction time and the ozone concentration, and also to understand in a better way how the co-effects impact the end-product quality in terms of the color stripping and the tensile strength loss using the statistical analysis. Response surface methodology (RSM) is considered as a strong approach which can be used to test various parameters by utilizing a minimum number of experiments. Basically, it consists of a group of statistical and mathematical procedures which are conducted to construct an experimental design model which

can help in the analysis of the effects of parameters on the response variable to decide the optimized response. Optimization of the process variables was done using the Box-Behnken design (BBD), a RSM technique as it is very efficient and favorable. It can help in detecting the lack of fit of the model, also in determining the factors of the quadratic model and looks more attractive if the points are at the midpoints of edges of the process and at the center. Hence, in the current examination, the important purpose was optimization of the color stripping of the printed cotton in order to access the effects of the process parameters like the pH, ozone content and the treatment time in conserving the mechanical properties. An experimental series were performed with the values of these variables like pH, reaction time and the ozone content included in the suitable range (lower, middle and the upper levels). (Table 3.5).

Table 3. 5 Range and levels of parameter in Box-Behnken experimental design.(decolorization of the pigment printed fabric)

Parameter	Factors	Levels		
		-1	0	+1
pH	x_1	3	5	7
Ozone concentration (g/Nm^3)	x_2	40	100	160
Reaction time (minutes)	x_3	20	70	120

A statistical analysis of variance (ANOVA) established on the BBD, was carried out using Design Expert in order to determine the suitability, fitness and the significance of the model coefficient. It is vital to introduce ANOVA so as to examine the fit and the significance of the second-order polynomial equation. Several statistical parameters given by the Regression and Solver Function of Excels of Microsoft Office (ANOVA), multiple determination coefficients (R^2) test and the lack of fit test were utilized to determine the significance of the model. Also, an F test was applied for

determination of the significance of the effects. This F test was utilized for comparing the statistical models which have been fitted to a set of data so as to identify the model which gives the best fit to the population from which the data were obtained.

The Box Behnken matrix design for the experimental plan of our decolorization experiments in case of the pigment printed cotton is as per table 3.6.

Table 3. 6 Box-Behnken matrix used (decolorization of the pigment printed fabric)

Run	**Actual level of factors**		
	pH	$[O_3]$ g/Nm^3	Reaction time
E1	5	40	20
E2	7	100	20
E3	5	160	20
E4	3	100	20
E5	3	40	70
E6	7	40	70
E7	7	160	70
E8	3	160	70
E9	5	40	120
E10	7	100	120
E11	5	160	120
E12	3	100	120
E13	5	100	70
E14	5	100	70
E15	5	100	70
E16	5	100	70

3.4 Characterization methods for the color stripping:

The reactive dyed and the pigment printed cotton fabrics were analyzed before and after the color stripping using the spectrophotometer, scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), and a fabric tensile strength tester.

3.4.1 Spectrophotometer:

It is a color measurement device utilized for capturing and evaluating the color. Spectrophotometers are used by the brand owners and designers, as a part of the color control program, to specify and communicate the color, and used by the manufacturers throughout the manufacturing process to monitor the color accuracy. Spectrophotometers can measure wide range of things like plastics, metal, paper, liquids and fabrics and also help in ensuring that color remains consistent from the conception to delivery. (X-Rite, 2021). The spectral reflectance curve produced by a spectrophotometer is commonly referred to as the color's "fingerprint." The selection of the spectrophotometers relies on the desired functionality, portability and the application. They are available in a variety of sizes, including portable devices, bigger tabletop units, and in-line instruments. (X-Rite, 2021).

Konica Minolta cm3600d spectrophotometer (Konica Minolta Inc., Tokyo, Japan): The CM-3600d bench-top spectrophotometer is a very accurate instrument that can be controlled using Windows software on a computer. Using double-beam technology and a dual-channel sensor, it can measure at 10nm throughout the entire wavelength range of 360-740nm. The CM-3600d incorporates components that reduce the amount of time it takes to switch between SCI and SCE, as well as filter movements. It has three measuring diameters: 25.4mm, 8mm, and 4mm, allowing it to quickly measure a variety of sample sizes. This equipment is cutting-edge, with capabilities such as numerical gloss and UV control, as well as the ability to measure transparency color. The SpectraMagic NX software, which is simple to use and offers different perspectives of data results, is compatible with this instrument. (Konica Minolta Sensing, 2011).

3.4.1.1 Color stripping (%) measurements:

After the color removal process from the reactive or the pigment printed cotton textiles, the visual colour of each sample was evaluated using the Konica Minolta CM3600d spectrophotometer (Konica Minolta Inc., Tokyo, Japan). The data obtained through the measurement provided the K/S values, L*, a*, b* coordinates which represent the lightness (L*), redness-greenness coordinate value (a*), yellowness-blueness co-ordinate value (b*). The color depth on the textile substrate was determined using the the Kubelka-Munk theory. The reflectance values (R) were measured for different wavelengths varying from 350 nm to 750 nm, and the color intensity 'K/S value' was calculated from the reflectance values using the Kubelka–Munk equation as follows(Hunter Lab, 2008):

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$

EQN X.

Where R represents the diffused reflectance, K represents the absorption coefficient of the sample, and S represents the scattering coefficient. (EQN X).

On the standard dyed/ printed samples and the decolorized samples, the K/S values were determined from different places and on both sides of each fabric sample and the average K/S value was determined at 610 nm for the reactive dyed fabric and at 580 nm in case of the pigment printed fabric. The color stripping was calculated using the following formula (A. S. Powar et al., 2020):

$$Stripping\ percentage = \frac{\left[\frac{K}{S}\ value\ of\ dyed\ sample - \frac{K}{S}\ value\ of\ stripped\ sample\right]}{\frac{K}{S}\ value\ of\ dyed\ sample} X100$$

3.4.1.2 Color analysis using the CIELAB method:

The CIELAB methodology was applied additionally to analyze the color of the decolorized fabric samples. The CIELAB color space is also known as CIE L*a*b* or

sometimes simply referred as the "Lab" color space is a color space defined by the International Commission on Illumination (CIE) in 1976.(A. S. Powar et al., 2020). In the color space CIELAB, color is expressed as three values: L* represents the lightness from black (0) to white (100), a* represents values from green (−) to red (+), and b* represents values from blue (−) to yellow (+). The CIELAB method was designed so that the same amount of change in the numerical values corresponds roughly to the same amount of the visually perceived change.

3.4.2 SEM (Scanning electron microscope):

Many microscopic techniques like optical and electron microscopy have been employed for the characterization of textile materials (C.C. Giri, 2002). SEM is a technique which produces images of a sample surface by scanning the surface with a beam of electrons. The electrons interact with the various atoms that are present at the surface of the sample, thus producing different signals which reveal information surface morphology of the sample and the composition. (Alexandra M. F. R. Pinto Vania Sofia Oliveira Daniela Sofia Castro Falcao, 2018). For textiles, SEM can generate high resolution and depth of field of images, and gives useful tools for the examination of the structural as well as the surface characteristics of the textile materials. (C.C. Giri, 2002).

The surface morphology of the pigment printed and the decolorized samples was observed using the scanning electron microscope (SEM) Model JEOL JEM-1400 Plus, Japan. All the samples were coated with the carbon for 5 minutes on the JEOL JEE-4X vacuum evaporator before the measurements.

3.4.3 X-ray photoelectron spectroscopy (XPS):

X-ray photoelectron spectroscopy analysis can give the oxidation states of element, element species and also the bonding relationships for all types of the surface elements (except for H). (Zhu & Chen, 2019). It is extensively used surface analysis technique, with its application in various industries.

In the XPS instrument, an x-ray beam is used to excite the atoms on the solid sample surface , which spurs the photoelectrons release. From there, the kinetic energy and the number of electrons that escape from the top 0 to 10 nanometers of the sample are measured. To move a little deep, each atom in a material consists of core electrons. When the beam of x-ray hits the material surface, the the x-ray energy is absorbed by one of the core electrons. The energy essential to make the core electron to be emitted and then detected subsequently is unique towards each element. Because of this uniqueness, permits the utilization of the binding energy to identify the elements present on the surface of the analyzed material. (Jennifer Mathias, 2020).

Uniformity, thickness and the surface chemistry of the sample's surface, films and coatings can be estimated by XPS. The position of a peak on the x-axis signifies the elemental and chemical composition. Generally, this axis is presented as the "Binding Energy" in electron volts (eV). In XPS analysis, the intensity of surface material (i.e. how much of a particular element can be found at the surface) is recorded by the y-axis. Usually, the total number of photoelectron counts per second is displayed by this axis.

All the samples were analysed with a Kratos Axis ultra DLD instrument, equipped with an Al Kα monocromatized X-ray source. The analysed area for each sample was about 700 × 300 μm.

3.4.4 Mechanical properties:

After the ozone based color stripping process for both the dyed and printed goods, the mechanical properties were tested to evaluate the strength of the fabric for all the samples using the MTS Criterion Model 43 automated testing system. The tensile strength of each cotton sample (treated and untreated) were determined according to the International standard NF EN ISO 13934-1; 2013 by repetition of the test atleast five times for each sample. The cotton fabric samples were cut into the rectangular dimensions 30 x 5 cm length by width to determine the tensile strength properties, the test was performed only in one direction five times each and the average tensile

strength was calculated. Threads were removed equally till the sample width was obtained from each of the long edges of the fabric.

3.5 LCA study for environmental management:

3.5.1 LCA software tools:

In the modern environmental management, Life Cycle Assessment (LCA) tool is consolidated as a strong and complete technique. The results of LCA rely on the handling of the data, various databases, methods and models of impact assessment which have been developed and enforced in specific software tools to help in the LCA studies development. (Aparecido et al., 2019).

For the applications in different areas, LCA studies have been developed and currently the main LCA software tools are: Gabi, SimaPro, openLCA and Umberto. (Aparecido, Silva, & Piekarski, 2017). In our study, we chose to use the SimaPro software with the Ecoinvent database for LCA analysis due to the availability.

The SimaPro (Pré-Sustanability) software consists of many LCI databases, the ELCD database, the new industry-specific Agri-footprint database and including the renowned ecoinvent v3 database. (PRé Sustainability.B.V., 2021).

3.5.2 Ecoinvent LCI database :

Many life cycle assessment initiatives, ecodesign, and product environmental information use the ecoinvent Life Cycle Inventory (LCI) database. Since its inception in 2003, the ecoinvent database has helped businesses manufacture goods that are more ecologically friendly, legislators implement new policies, and consumers adopt more environmentally responsible behavior. (SimaPro, 2021).

Ecoinvent is largely regarded as the most comprehensive and consistent LCI database available. This database is a compliant data source for ISO 14040 and 14044 investigations and assessments. The Ecoinvent database consists of datasets for most of the industries and provides frequent updates upon the availability of the new data.

With the ecoinvent database, we have data access at the unit process (UPR) and system process (LCI) levels. (SimaPro, 2021).

Life cycle assessment, life cycle management, carbon footprint assessment, water footprint assessment, environmental performance monitoring, product design and eco-design (DfE) or Environmental Product Declarations (EPD) can all benefit from the ecoinvent LCI data.

With over 15,000 LCI datasets in the areas of energy supply, agriculture, transportation, biofuels and biomaterials, bulk and specialty chemicals, construction materials, packaging materials, textiles, basic and precious metals, metals processing, ICT and electronics, dairy, wood, and waste treatment, the LCI database is the most comprehensive in the world. SimaPro includes the ecoinvent v3 databases for allocation at the time of substitution (system and unit), allocation, cut-off by classification (system and unit), and consequential (system and unit). (SimaPro, 2021).

3.5.3 LCIA Methods:

As discussed in the literature review chapter previously about the phases of LCA, for the application of the third phase (Impact assessment – LCIA), it is essential to define the method that is utilized for the calculations of the normalization and the characterization operations. In the LCA context, the different methods which quantify the impacts are known as the Life Cycle Impact Assessment (LCIA) methods. (Leitão, 2016). In an online study conducted in 2018 to find out the most widely used LCIA indicator sets by the practitioners, demonstrated that majority of the participants use mainly the methods like ReCiPe, IPCC 2013, ILCD 2011, CML 2012, and the Cumulative energy demand. (iPoint-systems gmbh, 2021).

ReCiPe: It is a method for the life cycle impact assessment (LCIA). This method was developed first in 2008 with joint cooperation between the RIVM, Radboud University Nijmegen, Leiden University and PRé Sustainability. The ReCiPe method's main goal is transforming the long list of Life Cycle Inventory results to a limited number of environmental indicator scores. The relative severity of an environmental impact

category is expressed by these indicator scores. Environmental indicators are determined at two levels via ReCiPe: 18 midpoint indicators and 3 endpoint indicators.

Relative to the other approaches the ReCiPe framework has some advantages that include:

1. The broadest set of midpoint impact categories

2. Where possible, it uses impact mechanisms that have global scope

3. As compared to the other approaches like Eco-Indicator 99, LIME, Impact 2002+ and EPS Method, it doesn't include potential impacts from future extractions in the impact assessment while it assumes such impacts have been included in the inventory analysis.(ReCiPe, 2016).

ILCD: This method includes various documents and tools in order to assist the LCA practitioners develop of software-independent LCA models and databases. ILCD framework is an XML-based format along with 8 available dataset types for the elements in the database. The dataset types of the ILCD format are:

1. Process.
2. Flow.
3. Flow Property.
4. Unit Group.
5. LCIA method.
6. Source.
7. Contact.
8. Life cycle model.(Elsa Valencia, 2019) .

CML method (CML 2001): CML 2001 is a method of impact assessment that limits quantitative modeling to the early stages of the cause-effect chain in order to reduce uncertainty. It divides the LCI results into midpoint categories based on themes, which are either shared mechanisms (such as climate change) or groupings (e.g. ecotoxicity). CML 2001 is developed by the Institute of Environmental Sciences, Leiden University, Netherlands. (GaBi Solutions, 2021).

IPCC 2001 (climate change): One of the most often used methodologies in life cycle impact assessment (LCIA) is the characterization of distinct gaseous emissions based on their potential for global warming and the grouping of different emissions into the climate change impact category. Global warming potentials released by the IPCC (Intergovernmental Panel on Climate Change) are commonly used to characterize greenhouse gas emissions. (Hischier et al., 2010).

Cumulative energy demand: The cumulative energy demand (CED) is widely utilized as a screening indicator in case of environmental impacts. Additionally, CED-values can also be used to compare the findings of a detailed LCA analysis to those of other studies that merely report primary energy demand. Finally, CED-results can be utilized to perform plausibility checks because it is rather simple to determine whether or not big errors have occurred based on the CED. Cumulative energy analysis is a useful way to get started into thinking about the life cycle. However, it does not take the place of a thorough impact assessment using techniques like Eco-indicator 99 or ecological scarcity. (Hischier et al., 2010).

In our study, The method used for the assessment of the environmental impacts was from International Reference Life Cycle Data System ILCD 2011 Midpoint+ V1.07/EU27 2010, equal weighting.

3.5.4 LCA environmental impacts:

The method for converting the inventory data from a life cycle assessment (LCA) to a set of potential impacts is known as the Life cycle impact assessment (LCIA). This helps the decision makers and the practitioners to understand the damage due to

resource use and emissions in a better way. It is also important to study the environmental impact categories in LCA. (Laurin & Dhaliwal, 2017).

Climate Change: The release of greenhouse gases into the atmosphere, which is measured in the mass of carbon dioxide equivalents, causes a warming effect on the surface of the earth as an outcome of climate change impacts. (Pat Hermon, 2015).

In another terms, Climate change relates to all the inputs or outputs which result in greenhouse gas emissions. The combustion of fossil fuels like coil, oil and natural gas is generally the greatest contributor. The results include sudden regional climatic changes and the increased average global temperatures. On a global scale, climate change is an impact affecting the environment. The unit of measurement is Kilogram of Carbon Dioxide equivalent (kg CO2 eq.). While performing the calculations, the global warming potential of all greenhouse gas emissions are compared with the amount of the global warming potential of 1 kg of CO2.(European Commission, 2018)
.

Human Toxicity Cancer/Non-Cancer: When toxic compounds are released into the air, water, or land, they have a life cycle impact assessment (LCIA) that considers their fate, route of exposure, and toxicity impact. Pesticides, heavy metals, hormones, and organic compounds are examples of chemical substances that are frequently counted. The potential for toxic discharges or exposure to cause cancer in people is measured by human toxicity, cancer..(Pat Hermon, 2015).

In other words, it considers the potential impacts on the human health due to absorbing substances through the water, air and soil. Currently, the direct effects of the products on humans are not measured. People at local and regional scale are affected predominantly due to cancer in humans impact. The unit of measurement is Comparative Toxic Unit for humans (CTUh).This is established on a model called USEtox.(European Commission, 2018).

Ionizing radiation HH: Ionizing radiations are released when the radionuclides decay. Exposure of the humans to the ionizing radiation (radioactivity) can lead to the DNA

alterations, which in turn can cause different types of cancer and the birth effects. In other living organisms, similar effects must be expected, but at the moment damage to the ecosystems is not quantified. Thus, human health is the only area of protection covered. (Steinmann & Huijbregts, 2014).

The environmental footprint takes into consideration emissions under normal operating conditions only (i.e no accidents in the nuclear plants are considered). The unit of measurement is Kilogram of Uranium 235 equivalent (Kbq U235 eq). Here, the potential impact on human health of various ionising radiations is converted into equivalent of kilobequerels of Uranium 235. (European Commission, 2018).

Water resource depletion: The withdrawal of water from the rivers, lakes or groundwater can add up to the available water 'depletion'. This impact category takes into consideration the availability or scarcity of water in the regions where the activity is conducted, if this information is known. The unit of measurement is cubic metres (m^3) of water use that is related to the local scarcity of water. (European Commission, 2018).

Mineral, fossil, and renewable resource depletion: The earth consists of finite amount of non-renewable resources, like minerals, metals and fossil fuels such as oil, coal and gas. The primary concept behind this impact category is that extracting a high concentration of resources in the present will force the future generations to extract lower concentration or lower value resources. For instance, fossil fuels depletion may lead to the non-availability of fossil fuels for the upcoming generations. The unit of measurement is kilogram of Antimony equivalent (kg Sb eq). Here, the amount of materials contributing to the depletion of resource are converted to the equivalents of kilograms of Antimony.(European Commission, 2018).

Freshwater ecotoxicity: Here, the potential toxic impacts on an ecosystem, which may lead to the damage of individual species as well as the ecosystem functioning. Few substances have a tendency to accumulate in the living organisms. An impact like Eco-toxicity largely affects the environment at local and regional scale. The unit of

measurement is Comparative Toxic Unit for ecosystems (CTUe). This is also based on a model called USEtox. (European Commission, 2018).

Chapter 4 : Results and Discussion

The content of this chapter is based on the following publications:

1. Powar, A., Perwuelz, A., Behary, N., Hoang, L., Aussenac, T., Loghin, C., … 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*. https://doi.org/10.1177/1558925021992757
2. 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 (Switzerland)*, *12*(2). https://doi.org/10.3390/su12020471.

I have used these papers to write this chapter.

4.0 The research area: Processes for the color removal.

In this chapter, the processes implemented for the color stripping, their optimization and results along with the characterization are discussed broadly. Also, in addition to this, this chapter also consists of the study on the influence of the several process parameters such as the pH, ozone concentration and the treatment time on the color stripping efficiency at a pilot scale mechanism with respect to the ozonation process. The color stripped fabric quality was determined in terms of the color stripping %, mechanical properties, CIE Lab values.

4.1 Color stripping of the reactive dyed textiles using the conventional chemicals:

Here the discoloration of the Reactive Black 5 azo dyed cotton textile was studied by utilizing the conventional reductive treatment consisting of the NaOH and sodium hydrosulphite. This conventional treatment was studied in comparison with the ozone assisted process. The ozonation process consisted of the various parameters such as the pH, ozone concentration (g/m^3) and the treatment time.

4.1.2 Color stripping results:

As can be seen on figure 4.1, the blue color is completely removed from the dyed fabric sample after both conventional and ozone stripping treatments. However, after ozone treatment the sample is more yellow.

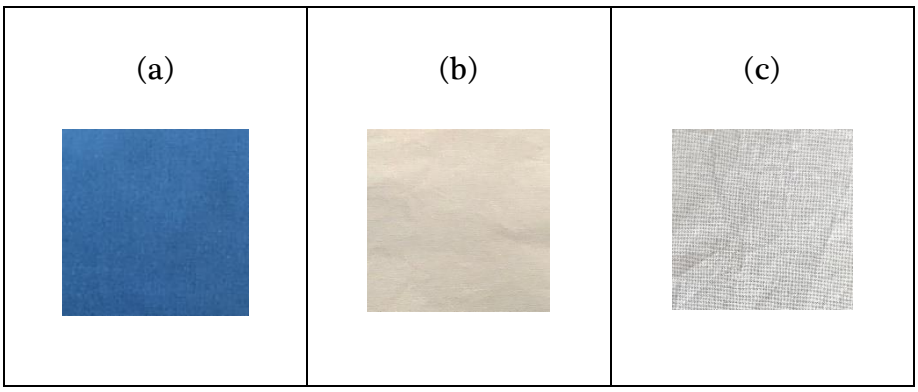


Figure 4. 1 Images of the standard dyed fabric and the ozonation treatment sample along with the conventional treatment sample. (a) Standard dyed fabric (b) ozone treated sample, (c) conventional treatment sample

From Table 4.1, it can be found out that, the lightness L* values are higher for stripped samples, which explains the fabric shade getting lighter and closer to the undyed fabric sample. The ozone treated sample is however lighter than the conventional ones (L* is higher) showing a better discoloration.

The a* values of the color stripped samples are near to the values of the undyed fabric. However, the b* values are higher, meaning that the stripped samples are more yellow than the undyed fabric. We can observe that this yellowness is more important in the ozone decolorized fabric as compared to the conventional method stripped samples.

Table 4. 1 Colorimetric values (L, a*, b*, dL*, da*, db*, dE*) for the standard and the decolorization sample experiments*

Description	L*(D65)	a*(D65)	b*(D65)	dL*(D65)	da*(D65)	db*(D65)	dE*ab(D65)	dE CMC (l:c)(D65)
Std dyed fabric	23.58	-3.9	-14.74	------	------	------	------	------
Undyed fabric	83.76	-0.08	0.47	------	------	------	------	------
Conventional color stripping	79.16	-1.06	-2.23	55.58	2.84	12.51	57.04	81.94
Ozone treatment	81.9	-1.69	10.6	49.32	2.89	28.32	56.95	64.18

The K/S colour strength has been measured with spectrocolorimeter from 360 to 740nm (figure 4.2). Taking into account the 2 Y-axis scale, a strong reduction of the color is obtain for the both methods: from more than 20 to 0.2 or less. Comparing the 3 undyed fabrics, at 610nm the ozone treated sample is closed to undyed fabric, that means that the blue color has been better removed compared with conventional treatment. However the K/S values are higher with ozone treated sample between 360 and 500 nm, corresponding to the yellow wavenlenghts. Those results are in good agreement with the CIE Lab ones. With ozone treatment the blue decoloration is very good but the yellowness needs to be taken care of by adapting proper post treatment sequence.

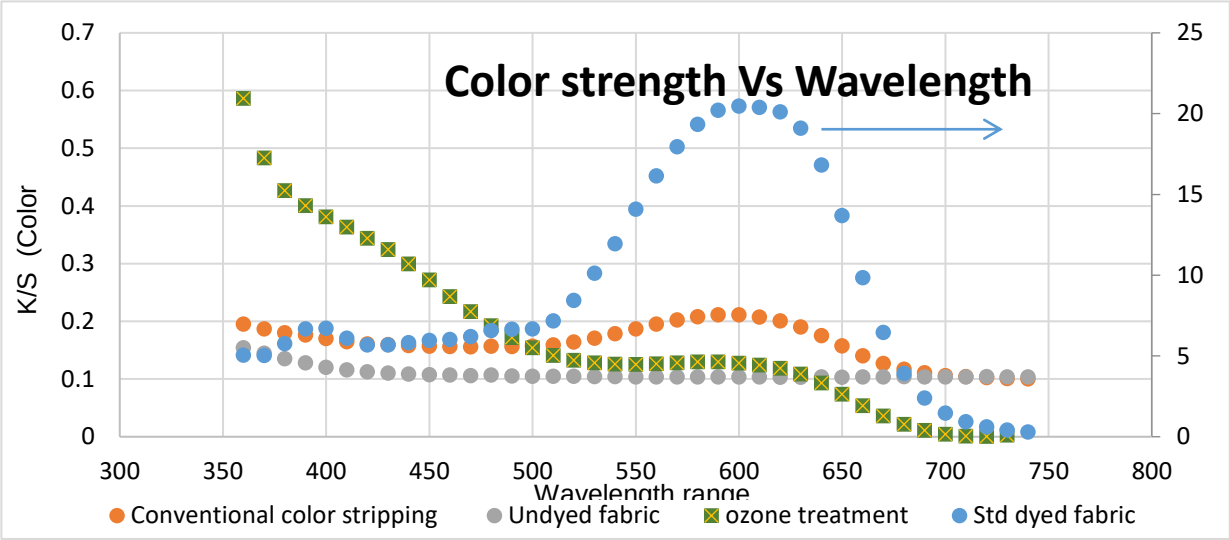


Figure 4. 2 K/S spectral curves of stripped fabric (ozone treated, conventional method) compared to that of the dyed cotton fabric.

The color stripping value corresponds to K/S reduction at wavelength range 610nm (table 4.2). If we consider the color stripping results, we get almost around 99 % color removal in the ozone assisted process than the conventional treatment which gives almost around 98 % color removal.

However, the ozone assisted process caused losses in the tensile strength almost around 10 % as compared to conventional treatment where the losses were found to be almost around 5 %.

Table 4. 2 Color stripping % and Tensile strength % values after the decolorization process treatments

Sr.No.	Treatment	Color stripping (%)	tensile strength loss (%)
1	Conventional reductive color stripping	98	5
2	Ozone assisted color stripping	99	10

The important parameter of the ozone assisted process is it has been performed at room temperature and also with less chemicals whereas the conventional alkaline reductive treatment comprises of the use of strong reducing agents and alkali assisted with high temperature conditions.

4.2 Color stripping of the reactive dyed textiles using the Ozone assisted process:

Here, the color stripping using ozonation is discussed firstly. As in the previous chapter we have discussed regarding the experiments designed using the box Behnken design. The experimental results obtained are discussed as per below:

4.2.1 Experimental Results for Different Decolorization Experiments

4.2.1.1 K/S Spectral Analysis of Samples Stripped Using Experiment E13

A dyed cotton sample stripped with the E13 experimental conditions (pH 5, 45 g/m3 of ozone, and treatment time of 50 min) was analyzed with a spectrophotometer. The fabric sample was scanned 20 times in 20 different areas of the same sample.

Figure 4.3 shows the different spectral curves before and after stripping. A strong decrease of the K/S at all wavelengths can be observed. The deviation between all the experiments is almost similar for K/S values measured at each wavelength, from λ = 350 to λ = 650 nm. The variation coefficient of the K/S values is highest at λ = 610 nm and is equal to 21%. That means that the dyed sampled has been stripped but there is still a small deviation due to heterogeneity of the ozone treatment on the sample.

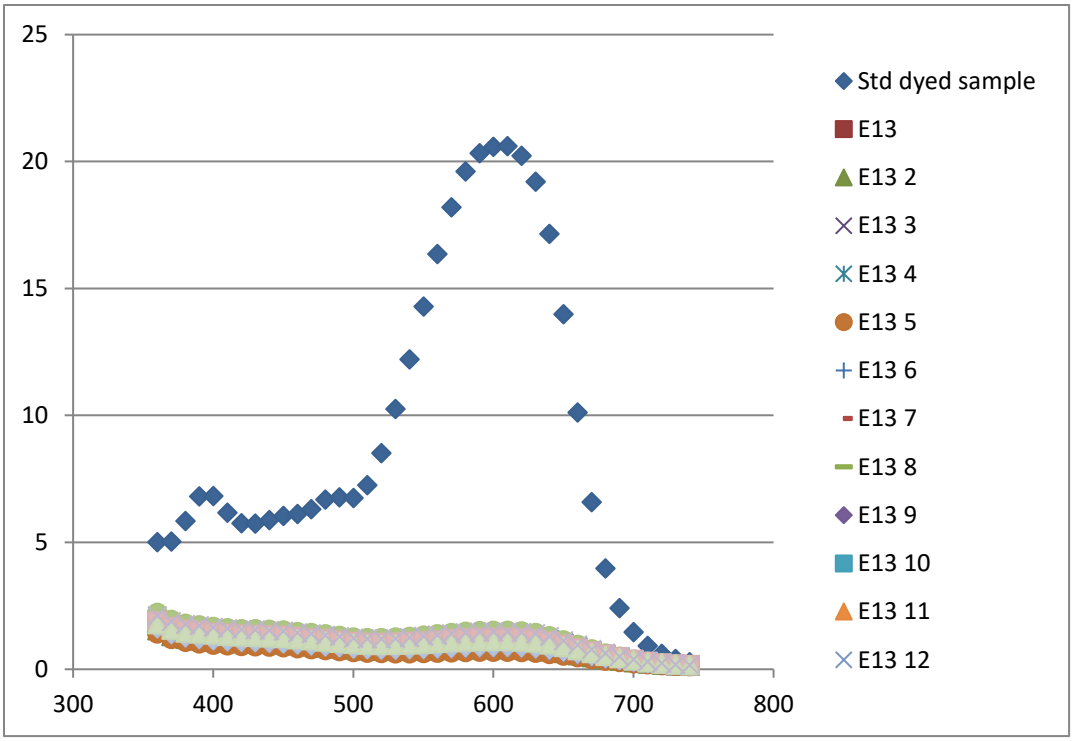


Figure 4. 3 K/S spectral curves of stripped fabric scanned 20 times in 20 different areas, compared to that of the dyed cotton fabric

4.1.1.2. Reproducibility of the Experiments

Four experiments, E13 to E16, were carried out using the same conditions as E13 (pH = 5, ozone flow = 45 g/m^3, time = 30 min) on four different samples of dyed fabric. From the graph (Figure 4.4), we can assess the repeatability of the central point of the experiments of the Box–Behnken design. All the experiments (E13, E14, E15, and E16) show the same values of *K*/*S* values variation. *K*/*S* values of stripped samples are close to that of the undyed sample. This means that these stripped samples can be used as potential alternatives for virgin (undyed) cotton, in the framework of textile processes and products.

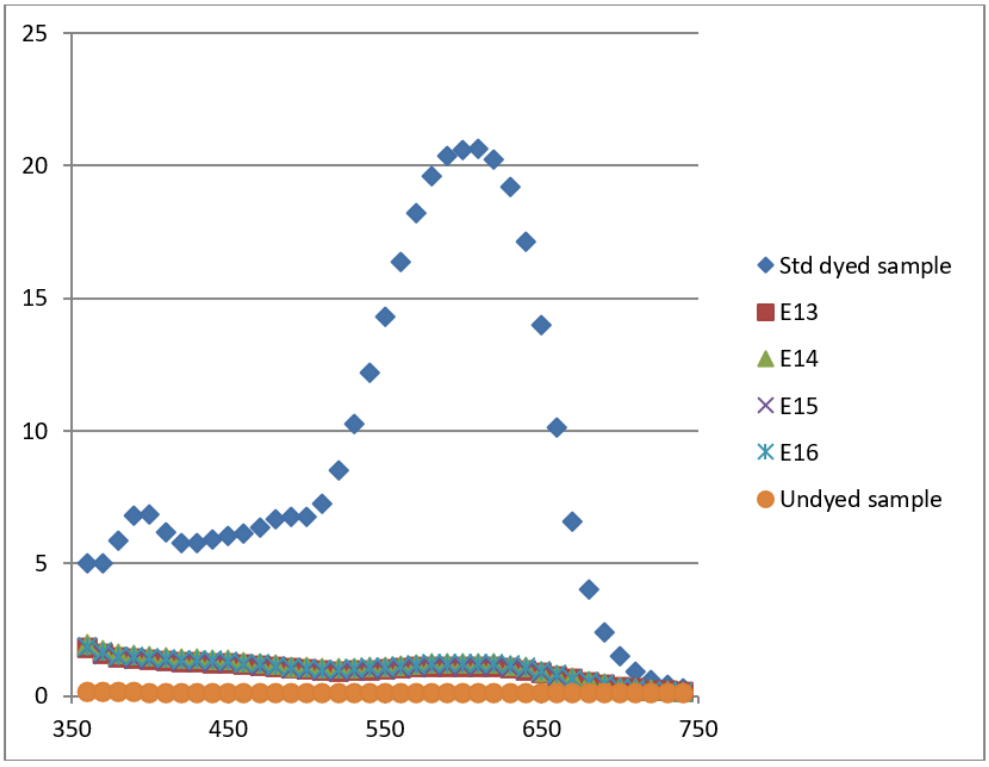


Figure 4. 4 Reproducibility of the central point of the experiments

4.1.1.3. Colorimetric Analysis of Fabrics Treated with 16 Experimental Conditions (E1 to E16)

K/*S* spectral curves of fabrics stripped using 16 different experimental conditions are shown in Figure 4.5. Considerable variation of *K*/*S* values, and hence of stripping treatment, is observed as a function of experimental conditions used.

For experiments E1, E2, and E6, the absorbance peak of each spectral curve at 610 nm is still high (*K*/*S* > 5), and the stripped samples are still blue (Figure 4.6). Small quantities of ozone combined with low treatment time or higher pH 7 are inefficient in yielding a good stripping.

The *K*/*S* values at 400 nm of the stripped samples are between 1 and 5, which are higher than that of the undyed fabric sample (*K*/*S* = 0.2) but much smaller than that of the dyed blue reference sample (*K*/*S* = 7).

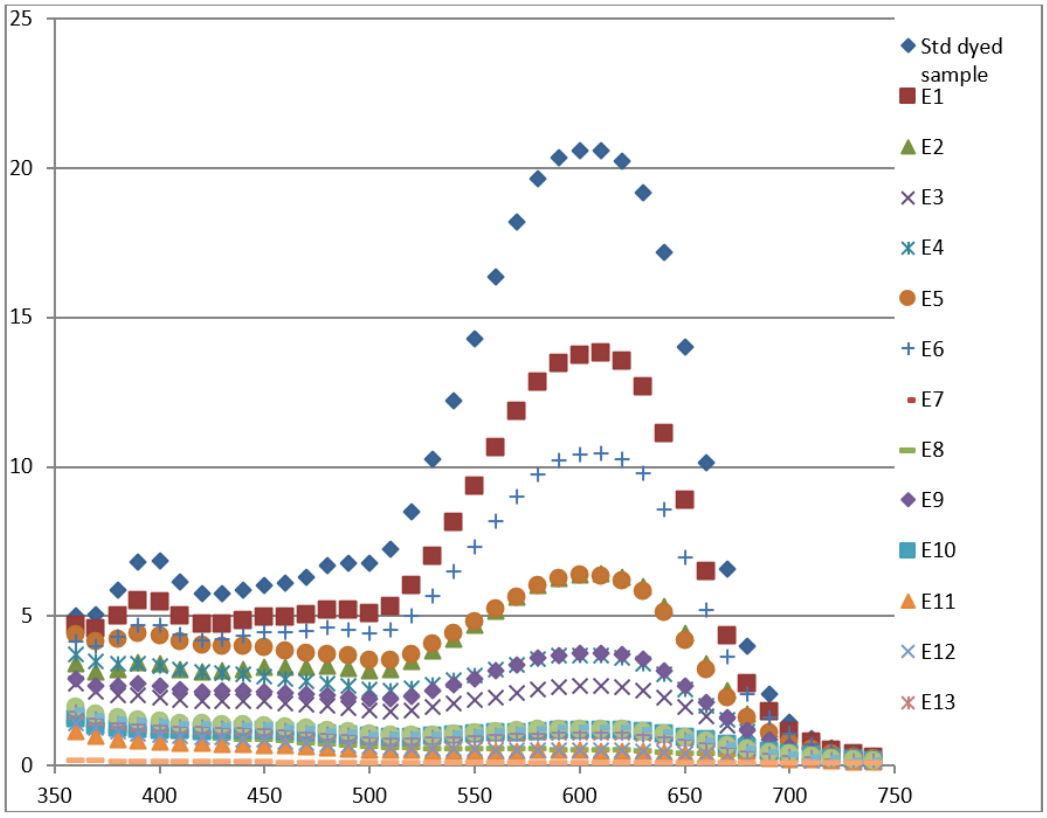


Figure 4. 5 K/S vs wavelength for all the decolorization experiments

(Std dyed fabric)

(E1)

(E2)

(E3)

(E4)

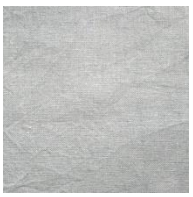
(E5)

(E6)

(E7)

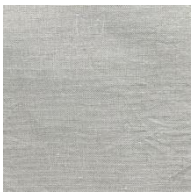
(E8)

(E9)



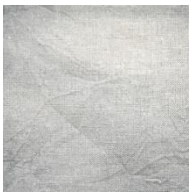
(E10)

(E11)



(**E12**)

(**E13**)



(**E14**)

(**E15**)

(**E16**)

Figure 4. 6 Images of the standard dyed fabric and the ozone-treated samples with different experimental parameters: standard dyed fabric, E1, E2, E3, E4, E5, E6, E7, E8, E9, E10, E11, E12, E13,E14, E15, E16

For the best stripping treatment, *K/S* is less than 1.5 for all wavelengths and the stripped fabric is almost white.

For certain stripping experiments, the *K/S* value at 360 nm (near the UV region) increases after stripping. This can be related to the absorbance by aromatic groups in the degraded dyestuff molecules, which stay in the fabric after the stripping experiment.

4.1.2. Color Analysis of the Decolorization Samples:

The fabric decolorizing was observed directly through photography of the stripped samples (Figure 4.6).

We can clearly observe that, among all stripping experiments, only E8 and E11 led to higher L* values (L*~68) compared to the unstripped dyed fabric (L* = 23), but these values are lower than that of an undyed white sample (L = 84) (Table 4.3). Also, the a* values are closer to that of the undyed fabric in these two experiments. However, for these experiments, there was increased yellowness in the fabric (b* = 9 and 5, for

E8 and E11, respectively) which can be related to the peak observed at 360 nm (Figure 6).

Table 4. 3 Colorimetric values (L, a*, b*, dL*, da*, db*, dE*) for the dyed, undyed, and decolorization experiments E1, E5, E8, E9, E11*

Description	L* (D65)	a* (D65)	b* (D65)	dL* (D65)	da* (D65)	db* (D65)	dE*ab (D65)	dE CMC (l:c) (D65)
Std dyed sample	23.41	−3.81	−14.7	------	------	------	------	------
Std undyed RFD fabric	83.76	−0.08	0.47	------	------	------	------	------
E1	28	−5.1	−12.01	4.59	−1.29	2.69	5.49	7.28
E5	36.07	−4.91	−4.27	12.66	−1.1	10.42	16.45	20.59
E8	66.61	−0.46	8.77	43.2	3.35	23.46	49.28	68.2
E9	43.3	−5.08	−3.84	19.89	−1.27	10.86	22.71	30.73
E11	67.98	−1.1	5.91	44.57	2.71	20.61	49.18	68.84

4.1.3. Tensile Strength Results

For each of the 16 experiments (E1 to E16), tensile strength of 10 different stripped samples was measured and the average value and standard deviation determined (Table 4.4). It can be seen that for all stripping conditions, there was a decrease in the fabric tensile strength, which is a usual phenomenon observed in chemical color-stripping processes. For experiments E8 and E11, tensile strength loss was almost 28% and 36%, respectively.

Table 4. 4 Tensile strength and CV % of the standard and the ozone-treated samples

Sr.No.	Tensile Strength (*N*)	CV % (Coefficient of Variation)
Std sample	386	5
E1	295	15
E2	298	16
E3	326	10
E4	330	11
E5	320	10
E6	325	4
E7	292	9
E8	278	13
E9	281	8
E10	284	15
E11	244	13
E12	292	6
E13	288	11
E14	273	9
E15	288	10
E16	329	4

4.1.4. Box–Behnken Results and Optimization

The values of color stripping (%) and tensile strength loss (%) for each experiment are given in Table 4.5.

Table 4. 5 Experimental design and observed response

Sr.No.	pH	Concentration Ozone (g/m^3 TPN)	Time (min)	Color Stripping %	Tensile Strength Loss %
Std sample	X1	X2	X3	N.A.	N.A.
E1	5	5	10	33.00	24
E2	7	45	10	68.98	23
E3	5	85	10	87.10	16
E4	3	45	10	82.12	15
E5	3	5	30	69.19	17
E6	7	5	30	49.19	16
E7	7	85	30	95.11	25
E8	3	85	30	97.45	28
E9	5	5	50	81.62	27
E10	7	45	50	94.30	27
E11	5	85	50	97.56	37
E12	3	45	50	97.48	25
E13	5	45	30	94.62	26
E14	5	45	30	94.10	29
E15	5	45	30	94.65	25
E16	5	45	30	93.93	15

4.1.4.1 Adequacy of the Model:

The effect of experimental variables on color stripping was investigated thoroughly by considering individual variables (the pH, ozone concentration, and reaction times) along with nonlinear and interaction effects (Table 4.6).

Table 4. 6 Regression Statistics

Coefficient of multiple determination	0.9955
Coefficient of determination R^2	0.9910
Coefficient of determination R^2	0.9730
Standard Error	3.1379
Observations	16

For each run, the color-stripping percentage was used as the experimental response. By using analysis of variance (ANOVA/Excel/Microsoft Office 2013), the significance of each term in the quadratic model was assessed (Table 4.7).

Table 4. 7 Analysis of variance (ANOVA) for the refined model

Source	**Degree of Liberty**	**Sum of Squares**	**Average Squares**	**F**	**Critical Value of F**
Regression	10	5419	541.9	55.0	0.00017586
Residues	5	49	9.9		
Total	15	5468			

The lack-of-fit test is designed to define whether the selected model is adequate to describe the observed data or a more complicated model is required. The test is performed by comparing the variability of the current model residuals to the variability between observations at replicate settings of the variables. Based on the ANOVA table, the *p*-value for lack-of-fit was found to be less than 0.05, thus the model appears to be adequate for the observed data at the 95.0% confidence level (Table 4.8).

Table 4. 8 Parameter estimation: lack-of-fit test

Term	Estimated Value	Standard Error	Statistical t	Probability (p)
Constant	94.325335	1.5689357	60.12059	0.0000001
X_1	−4.832944	1.1094051	−4.35634	0.0073154
X_2	18.028194	1.1094051	16.25033	0.0000161
X_3	12.469954	1.1094051	11.24022	0.0000973
X_1X_2	4.4139817	1.5689357	2.81336	0.0373999
X_1X_3	2.4886159	1.5689357	1.586181	0.1735572
X_2X_3	−9.5422213	1.5689357	−6.08197	0.0017372
X_1X_1	−2.8435008	1.5689357	−1.81238	
X_2X_2	−13.745048	1.5689357	−8.76075	0.0003212
X_3X_3	−5.7590606	1.5689357	−3.67068	0.0144331

4.1.4.2. ANOVA and multiple nonlinear regression results

The R-squared statistic demonstrated that the fitted model explains 99.55% of the variability in color-stripping percentage (Table 4.6).

In the current study, the adjusted R^2 obtained is 0.9910, which is within the acceptable limit of $R^2 \geq 0.80$, demonstrating a good fitting of the experimental data with second-order polynomial equation.

$$Y = 94.33 - 4.83x_1 + 18.03x_2 + 12.47x_3 + 4.41x_1x_2 + 2.49x_1x_3 - 9.54x_2x_3 - 2.84x_1^2 - 13.75x_2^2 - 5.76x_3^2$$

Coefficients with more than one factor term and those with second-order terms represent interaction terms and quadratic relationships, respectively. The sign of each coefficient shows how the related factor influences the response. If the coefficient is positive, the response increases (synergetic effect), and if it is negative, the response decreases (antagonist effect).

The relationship between the dependent and independent variables was further elucidated using response surface (3D) methodology.

4.1.5. Optimization of Color Stripping

The quadratic model obtained from the Box–Behnken design generates response surface images for mutual interactive effects as a function of two variables while another variable is kept constant (Figures 4.7 and 4.8). According to the coefficient factors, the concentration of ozone and reaction time have dominant positive effects in comparison with the effect of pH on the color stripping. It means that higher ozone concentration and longer reaction time lead to a better efficiency of color stripping. On the contrary, color stripping decreases with increasing pH.

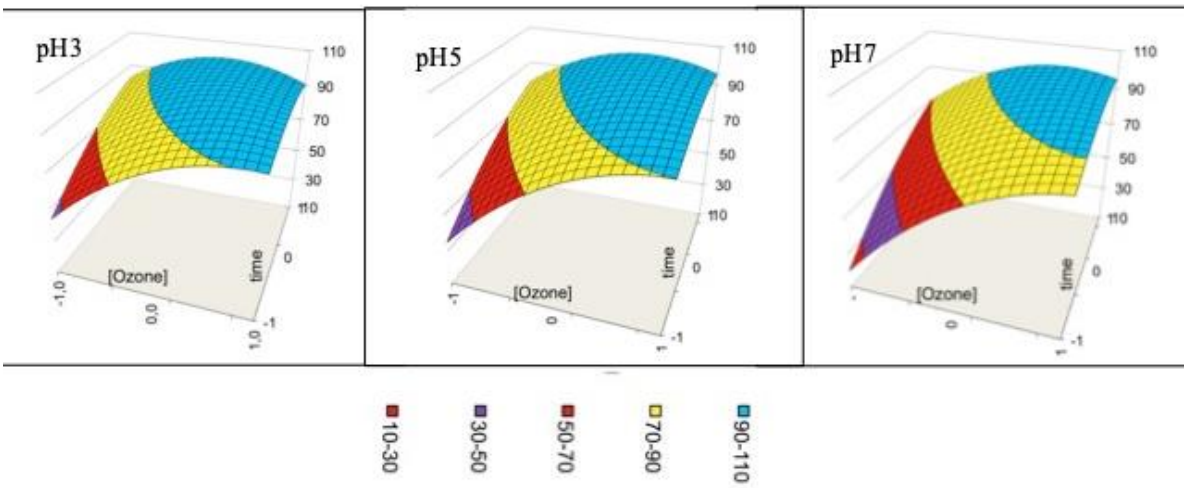


Figure 4. 7 Response surface, effect of ozone concentration and reaction time on color stripping of dyed fabrics at different pH (color of the graphs are related to color stripping %)

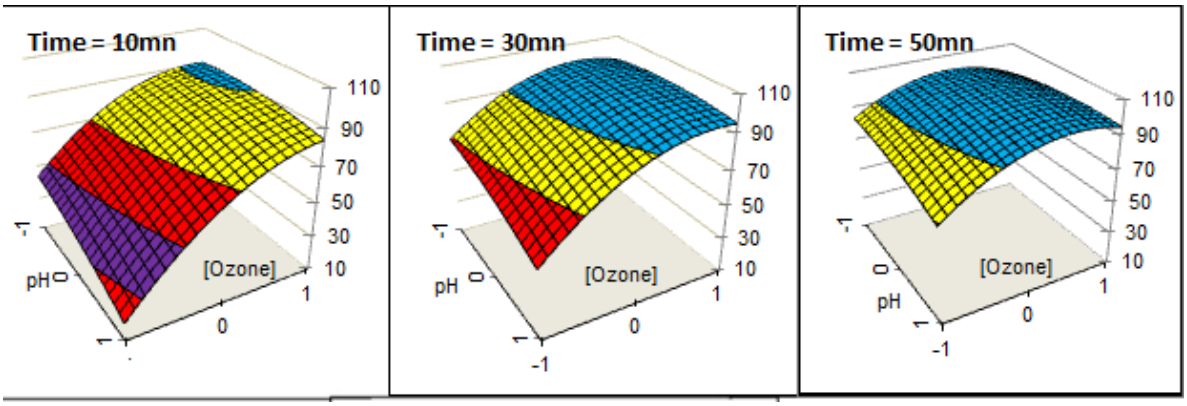


Figure 4. 8 Response surface, effect of pH and ozone concentration on the color stripping at different reaction times: 10 min; 30 min; and 50 min

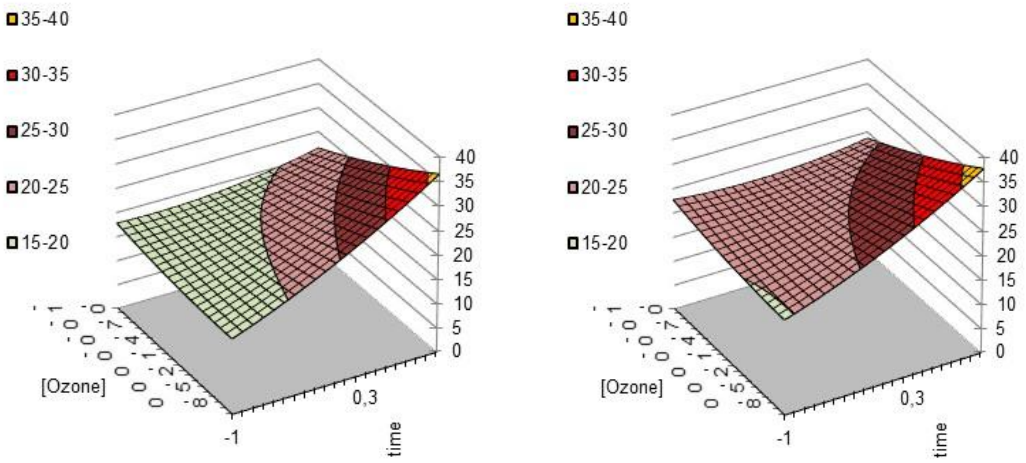
The optimum predicted point for the maximum decolorization was obtained at pH 5, using an ozone concentration of 85 g/m^3 and treatment time of 50 min.

4.1.6. Optimization of the Mechanical Properties

The same optimization methodology was used for the mechanical strength losses. Statistical results were less accurate than those obtained for color stripping. However, the R-squared value was 90.03% and the adjusted R^2 = 0.8105, showing the good fitting of the polynomial equation:

$$Y = 26{,}79 + 0{,}70x_1 + 2{,}67x_2 + 4{,}82x_3 - 0{,}55x_1x_2 - 1{,}59x_1x_3 + 4{,}33x_2x_3 - 4{,}60x_1^2 - 0{,}84x_2^2 - 0{,}07x_3^2$$

Figure 4. shows that the tensile strength loss increased with an increase in all variables (pH, ozone concentration, and time). The optimum condition was obtained when the tensile strength loss was at a minimum, that is, when pH = 3, with a concentration of ozone of 5 g/m^3 and treatment time of 10 min.



(**A**) (**B**)

Figure 4. 9 Effect of pH, [O3], and reaction time on the tensile strength loss %: (A) pH = 3; (B) pH = 7

4.1.7. Optimization of the Stripping Process

As discussed, a good stripping is generally associated with low mechanical properties. The optimal stripping process should fulfill maximum decolorization and minimum tensile strength loss. The optimum conditions have been calculated for atleast 80% color stripping and 20% maximum mechanical strength loss, and this can be achieved at pH 3, using an ozone concentration of 85 g/m^3 and a treatment time of 10 min. Experimentally, these conditions allowed having 90% color stripping and 13% mechanical strength loss.

4.1.8. Discussion

The optimized and highest stripping obtained in this study is, however, limited by the slight yellow coloration of the treated sample. According to Arooj (2014), aldehyde

In the ozonation process studied, ozone concentration and reaction time are favorable to the decolorization of the blue dyed cotton fabric. However, these conditions lead to the deterioration of the fabric sample, leading to loss in the tensile strength. The pH used plays a crucial role in the ozonation process, and as pH increases, decolorization becomes less effective and loss in mechanical strength increases. At low pH, color stripping is better and the fabric degradation is lower. It is known that cellulosic materials get degraded upon hydrolysis of glucoside bonds in acidic conditions, since the cellulosic chain length (DP) decreases (Arooj, 2014). Similar results were obtained for the mechanical properties by Arooj (2014), who studied the bleaching process of cotton fabric with ozone, and showed that degradation, measured by the DP decrease of the cellulose, was greater at low pH. However, this effect occurs mainly at pH 2. In our case, the lower degradation at acidic pH would be related to the more selective ozone molecular reaction. Two possible reaction mechanisms may occur: direct reaction consisting of the attack by the molecular ozone and the indirect reaction involving the free radical mechanism. Both of these exist simultaneously during the ozonation process (Sharma, Buddhdev, Patel, & Ruparelia, 2013). At low pH, ozone reacts directly in the molecular form and it is more soluble in water. However, at higher pH, the instability of ozone increases due to the reaction with hydroxyl ions OH-, thus generating free radicals. Recently, (Bilińska, Żyłła, Smółka, Gmurek, & Ledakowicz, 2017) have modeled the ozonation in aqueous solution of the Reactive Black 5 dye. At low pH, there is a direct attack of the chromophoric azo groups N = N by ozone (Bilińska et al., 2017). The kinetics modeling shows that when pH is higher than 4.0, the indirect oxidation mechanism with free radicals starts to occur, and the discoloration kinetics are highly increased. Our results are in agreement with this model.

groups and ozone residues are responsible for this coloration and could be removed by further post-treatments.

4.3 Color stripping of the reactive dyed textiles using the organic reducing agent:

We have also introduced a novel approach to study the color removal from the reactive dyed textiles with the help of an organic reducing agent. We have tried to optimize the process parameters of the color stripping process using the conditions like temperature and time variations while keeping the concentration of the chemicals constant. Here three temperature conditions were selected namely 60, 80 and 100 degree; four different time conditions were selected mainly 05, 15, 30 and 60 minutes. These variations were used to optimize the process conditions from the point of view of sustainable process.

4.3.1 Images of the color stripped fabric with the various experimental conditions:

Below we can see the standard fabric swatch and the decolorized samples after application of various process conditions. (Refer fig 4.10 and fig 4.11). With the visuals we can easily see the impact of the rise in temperature and treatment time on the decolorization of the samples.

Standard sample	Decolorized sample with 10 g/l glucose and 10 g/l sodium hydroxide at 100°c for 30mn
	

Figure 4. 10 Std dyed sample and decolorized sample with maximum concentration and time

Temperature / Time	60 ˚c	80 ˚c	100 ˚c
60 mn			
30 mn			
15 mn			
05 mn			

Figure 4. 11 Effect of temperature and treatment time on the decolorization of the Reactive dyed (CI reactive black 5) sample with 10 g/l glucose and 10 g/l sodium hydroxide

4.3.2 Color stripping results:

The color stripping results along with the CV% are mentioned in table 4.9.

Table 4. 9 Color stripping test results of the undyed standard, and color stripped fabrics.

Sr No	Glucose	NaOH	Temperature	Time	K/S values	Color stripping	CV
	(g/l)	(g/l)	(˚C)	(mn)		%	%
1	Standard sample				20.94	N.A.	N.A.
2	10	10	60	60	3.11	85.14	1.91
3	10	10	80	60	0.58	97.23	2.87
4	10	10	100	60	0.16	99.23	4.76
5	10	10	60	30	4.81	77.01	2.80
6	10	10	80	30	0.87	95.86	2.37
7	10	10	100	30	0.16	99.23	4.45
8	10	10	60	15	5.79	72.36	5.25
9	10	10	80	15	1.13	94.63	5.12
10	10	10	100	15	0.17	99.20	5.29
11	10	10	60	5	6.75	67.76	2.83
12	10	10	80	5	0.85	95.94	3.25
13	10	10	100	5	0.26	98.76	3.81
14	20	20	100	30	0.14	99.32	6.90

The color stripping test results of the undyed standard, and the color stripped fabrics were shown in Table X. The color strength values along with the color stripping and CV % values are given.

For the 60 minutes treatment time, we obtained the stripping percentages of the reactive dyed fabrics increased with the gradual increase in the temperature of the stripping treatment under the stripping chemicals combination of 10 g/l glucose and 10 g/l caustic soda when the fabrics were color stripped at 60, 80 and 100 deg respectively. Also, the Stripping percentages were found higher at 100˚C than 80˚C and 60 ˚C with the same set of the stripping chemicals. The same is evident in the color swatches of the standard sample in figure 4.10 and the color stripping experiments performed for 60 minutes shown in figure 4.11. In short, the color

stripping was more as the temperature of the stripping operation was more. Hence, our aim was to optimize the process with regards to the conditions of the stripping treatment time and also the temperature. So we tried to study the effect of reduced treatment time from 60 mins to 05 minutes with three different times 30, 15 and 05 minutes respectively. This reduction in the treatment time was also observed along with the three temperature ranges 60, 80 and 100 deg respectively.

For the 60 degrees temperature under combination of the stripping chemicals, the highest color stripping percentage was found 85 % with 60 minutes of the treatment time and the lowest stripping percentage was found at 05 minutes of the treatment i.e. 68 %. Both at 80˚C and 100˚C when the treatment time decreased from 60 mins to 05 minutes the color stripping percentages were also decreased. Similar trends were found in case of the 80 degrees and 100 degrees temperature stripping operation with respect to the change in the time but the difference was very small i.e there were no significant differences in the color stripping percentages with the change in the treatment time. The highest color stripping was obtained is 99.23 % using 10 g/l glucose and 10 g/l caustic soda and stripping at 100˚C for 60 minutes. However, we found the same color stripping for 30 minutes, there was no further increase in the color stripping.

Secondly, Since our aim was to use the optimized resources to get the good results from the point of view of sustainable process, so we used the 10 g/l glucose and 10 g/l caustic soda and stripping at 100˚C for 30 minutes and 05 minutes for the mechanical properties assessment. The color stripping values obtained with the 10 g/l glucose and 10 g/l caustic soda and stripping at 100˚C for 30 minutes and 05 minutes are 99.23 % and 98.76 % respectively.

Overall, the color stripping values obtained with the 80deg and 100 deg are much better as compared to the results obtained at 60deg. We have also performed an experiment with the maximum conditions to check the color stripping %, with of 20 g/l glucose and 20 g/l caustic soda at 100 deg for 30 minutes and found that 99.32 % color stripping was achieved. (refer figure 1). By increasing the concentration of the stripping chemicals no significant color stripping was achieved. Hence we could

further optimize the process by reducing the chemical concentration and optimizing the color stripping properties.

4.3.3. Colorimetric analysis:

Table 4. 10 Colorimetric analysis (L,a,b values study)

Sr. No.	Description	L*(D65)	a*(D65)	b*(D65)
1	Std blue dyed fabric reference	22.9	-3.58	-13.64
2	Std undyed RFD fabric	83.76	-0.08	0.47
3	60 deg for 60 minutes	42.8	2.66	-8.35
4	80 deg for 60 minutes	66.82	0.64	-3.68
5	100 deg for 60 minutes	79.95	-0.03	1.67

Here, In table 4.10 we have studied the Lab values of the dyed std fabric, undyed RFD fabric and some selected experiments. We can see that as the temperature increases the L values goes on increasing thus the fabric gets lighter. It is clearly seen that, among all the experiments selected here, the color removal treatment at 100 deg for 60 minutes gave higher L* values (L*~79.95) as compared with the unstripped std dyed fabric (L* = 22.9), and these values are slight lower than the undyed white sample (L = 83.76) which means the color stripping has been good. Also, the a* and b* values are closer to that of the undyed fabric in this experiment (the color removal treatment at 100 deg for 60 minutes). The same can be reflected through the color swatches of the samples seen earlier.

4.3.4 Mechanical properties:

Here, we have tried to study the mechanical properties of the std undyed and the decolorized fabrics in the form of the strength loss percentages. We have used selected optimized experiments for studying the mechanical properties.

Table 4. 11 Mechanical properties test results of the undyed std, and the selected color stripped fabrics

Sr. No.	Tensile Strength (N)	Strength loss %	CV %
Std sample	412	N.A.	2.4
100 deg 30 mn	384.29	6.7	8.8
100 deg 05 mn	403.29	2.1	4.3

In table 4.11, Strength loss percentages of the undyed std fabrics and the decolorized fabrics at 100 deg for 05 and 60 minutes is shown. We can see that the strength loss percentages were higher for 30 minutes as compared to 05 minutes treatment when the fabrics were treated in same parameter at 100°C. The strength loss % values when treated with 10 g/l glucose and 10 g/l caustic soda at 100°C for 05 minutes and 30 minutes are 6.7 % and 2.1 %.

4.4 Color stripping of the pigment printed textiles:

Here, the color stripping of the pigment printed goods using ozone assisted technique is studied. As in the previous chapter we have discussed regarding the experiments designed using the box Behnken design. The experimental results obtained using this response surface methodology are discussed as per below:

4.4.1 Evaluation of color stripping of the printed fabrics treated with different experiments(E1 to E16):

The figure 4.12 show the K/S spectral curves of the fabrics decolorized using the 16 different experimental conditions of ozone treatment. It can be observed that with the variation in the experimental conditions performed, we can see a substantial decrease in the K/S values and hence an enhancement of the decolorization.

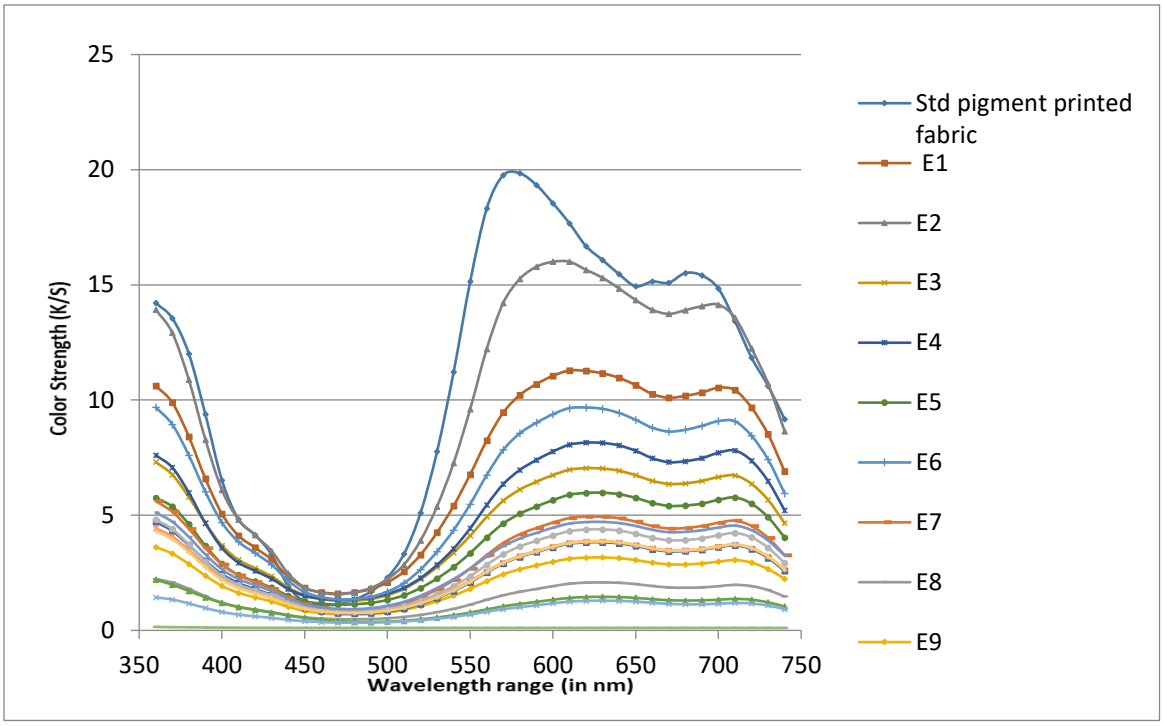


Figure 4. 12 K/S Vs Wavelength graph for all the color removal experiments carried with ozone under varying conditions

For the experiments (E1 to E7), it can be seen that the K/S values at maximum absorbance wavelength(580 nm) is still higher, with the K/S values still greater than 4 and the decolorized samples are still blue (Figure 5 E2, E4, E7). Smaller quantities of ozone concentration along with lower treatment time or higher pH value 7 are not sufficient to obtain a good color stripping.

The K/S values at 360 nm of the stripped samples are between 0.5 and 13.9, which are higher than that of the unprinted cotton sample (K/S = 0.15) but not that lower than the pigment printed reference sample (K/S = 14). This could be related to the presence of degraded pigment molecule. Similar trend was observed for K/S values at 680 nm. The results and experimental conditions show that the complete color removal from pigment printed goods is not easy and requires the use of process conditions involving acidic pH, huge ozone concentration and longer treatment times. The same can be observed through the photograph swatches of the ozone treated samples: it is difficult to obtain clear white fabric even after the extreme conditions of ozonation process. (figure 4.13).

4.4.2 Color analysis of the color stripping samples:

Sample photographs in figure 4.13 show, the color stripping results obtained for parameters selected in the designed experimental plan.

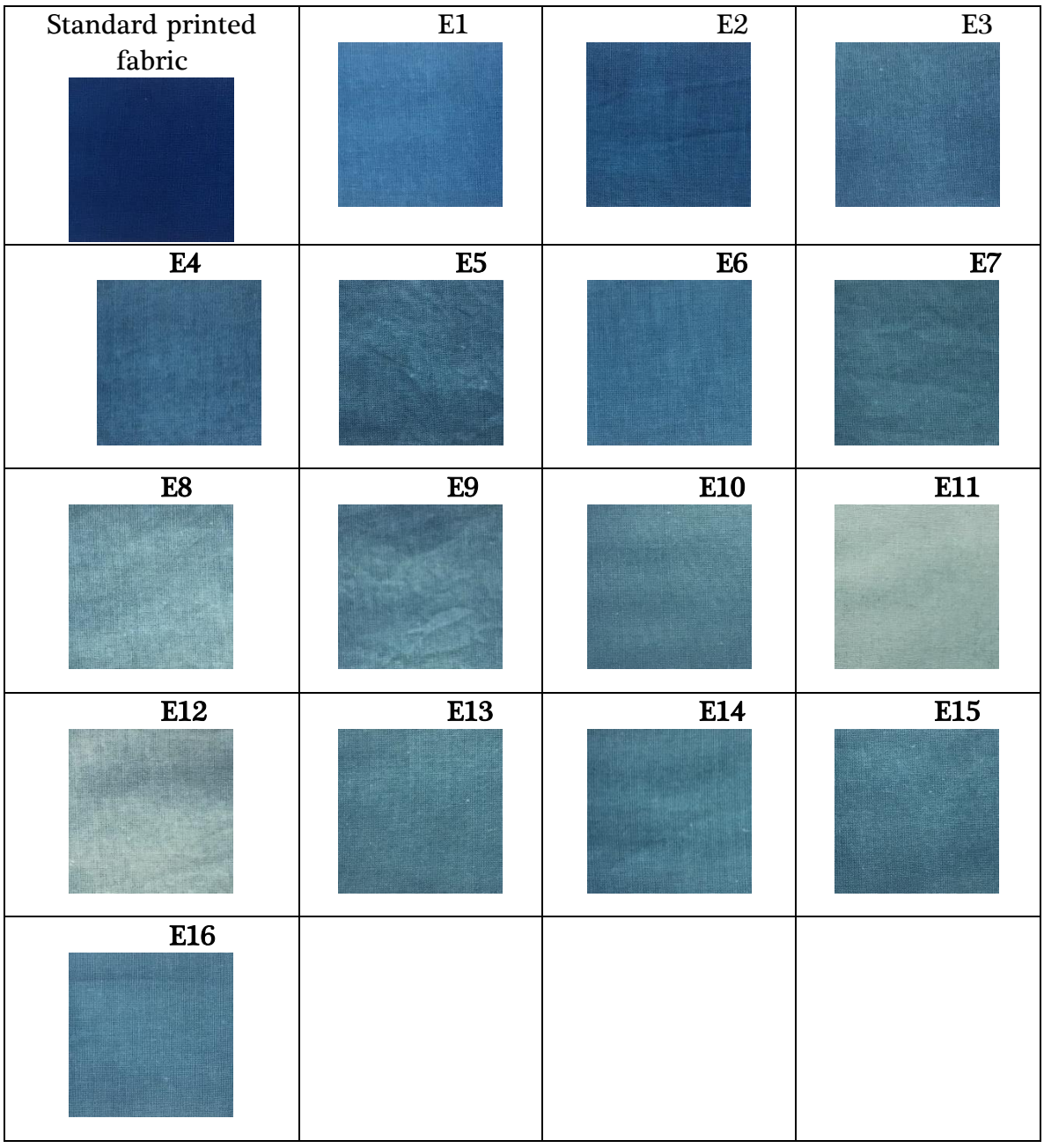


Figure 4. 13 Images of the small swatch of the standard printed fabric and the ozone assisted treatment samples with the various experimental parameters

The CIE Lab methodology was additionally used to carry out a colorimetric analysis of all fabric samples.(Table 4.12).

Referring to the results listed in (table 4.12), it can be clearly observed that the L* values are higher in case of experiment E12 as compared to experiments E2 and E4, and the standard fabric, which confirms that the shade of the fabric is getting lighter. However, the a* values are not closer to that of the unprinted fabric and the fabric turns out to be more on the greener side. Similar observation was found in case of b* values, which corresponds to the fabric getting less bluer as compared to the pigment printed fabric. When stripped samples subjected to selected experiments (E8,E11 and E12) are compared to the unprinted cotton fabric, it can be seen that there is still some part of degraded pigment present on the fabric.

Table 4. 12 Colorimetric values (L, a*, b*, dE*) for the printed, unprinted cotton and stripped printed cotton subjected to color stripping experiments E2,E4,E7,E8,E11,E12,E16*

Description	**L*(D65)**	**a*(D65)**	**b*(D65)**	**dE*ab(D65)**	**dE (l:c)(D65)**	**CMC**
Reference pigment printed fabric	31.54	-6	-36.21	------	------	
Unprinted cotton fabric	83.61	-0.14	0.19	63.81	64.97	
E2	32.42	-12.91	-25.88	12.47	8.36	
E4	40.08	-14.58	-19.78	20.64	16.4	
E7	46.97	-17.26	-15.75	28.31	25.05	
E8	59.03	-14.63	-12.49	37.73	37.93	
E11	63.51	-16.08	-6.69	45	44.73	
E12	65.37	-13.07	-9.59	44.02	45.43	
E16	46.68	-15.03	-16.28	26.86	23.8	

4.4.3 Box Behnken results and optimization:

In Table 4.13; the Box-Behnken matrix, the experimental results from all the tested combinations of factors and the corresponding responses for each run are polynomial equations obtained showing the empirical relationships between the responses and the independent variables in terms of coded factors for both Color Stripping (CS) and Tensile Strength Loss (TSL).

For the designed experimental model, the color stripping percentage was calculated and the tensile strength was measured along with the coefficient of variation determined for both the parameters (Table 4.13). We can see the effects of different process parameters on the decolorization of the pigment printed goods. However, there is deviation in the results obtained which may be attributed to the heterogeneity of the treatment. It can be observed that there is decrease in the tensile strength with an increase in color stripping.

Table 4. 13 Box-Behnken matrix and the experimental results

Run	Actual level of factors			Response				
	pH	$[O_3]$ g/Nm^3	Reaction time	Color stripping (%)	CV %	Tensile Strength (N)	CV %	Tensile strength loss (%)
E1	5	40	20	48.51	16	340	6	4
E2	7	100	20	23.1	14	342	7	3
E3	5	160	20	69.19	17	313	6	11
E4	3	100	20	64.91	21	329	6	7
E5	3	40	70	74.47	28	306	8	13
E6	7	40	70	56.89	14	310	4	12
E7	7	160	70	78.97	27	257	7	27
E8	3	160	70	91.56	40	244	7	31
E9	5	40	120	86.63	26	269	4	24
E10	7	100	120	83.93	26	224	7	36
E11	5	160	120	94.22	41	215	12	39
E12	3	100	120	94.92	45	231	3	34
E13	5	100	70	83.72	18	300	4	15
E14	5	100	70	81.64	24	260	6	26
E15	5	100	70	83.8	22	289	6	18
E16	5	100	70	79.9	22	287	10	18

Table 4. 14 ANOVA results of the quadratic model for Color stripping (%).

Source	Coefficient	Error type	Statistic t	p-value Prob>F
Constant	82.27	2.78	29.62	9.82E-08
x1(pH)	-10.37	1.96	-5.28	1.87E-03
x2 (ozone concentration)	8.43	1.96	4.29	5.13E-03
x3 (reaction time)	19.25	1.96	9.80	6.50E-05
x1x2	1.24	2.78	0.45	6.70E-01
x1x3	7.70	2.78	2.77	3.23E-02
x2x3	-3.27	2.78	-1.18	2.83E-01
x_1^2	-7.36	2.78	-2.65	3.81E-02
x_2^2	0.57	2.78	0.20	8.45E-01
x_3^2	-8.19	2.78	-2.95	2.56E-01

Table 4. 15 ANOVA results of the quadratic model for Tensile strength loss (%)

Source	Coefficient	Error type	Statistic t	p-value Prob>F
Constant	19.25	2.05	9.38	8.31E-05
x1(pH)	-0.88	1.45	-0.60	5.68E-01
x2 (ozone concentration)	6.88	1.45	4.74	3.19E-03
x3 (reaction time)	13.50	1.45	9.31	8.71E-05
x1x2	-0.75	2.05	-0.37	7.27E-01
x1x3	1.50	2.05	0.73	4.92E-01
x2x3	2.00	2.05	0.97	3.67E-01
$\mathbf{x_1^2}$	1.00	2.05	0.49	6.43E-01
$\mathbf{x_2^2}$	0.50	2.05	0.24	8.16E-01
$\mathbf{x_3^2}$	-0.25	2.05	-0.12	9.07E-01

The responses modeled by second-order polynomial equations have the following particular forms:

For the Color Stripping (CS):

$$Y(CS) = 82.27 - 10.37x_1 + 8.43x_2 + 19.25x_3 + 1.24x_1x_2 + 7.70x_1x_3 - 3.27x_2x_3 - 7.36x_1^2 + 0.57x_2^2 - 8.19x_3^2$$

For the Tensile Strength Loss (TSL):

$$Y(TSL) = 19.25 - 0.88x_1 + 6.88x_2 + 13.50x_3 - 0.75x_1x_2 + 1.50x_1x_3 + 2.00x_2x_3 + 1.00x_1^2 + 0.50x_2^2 - 0.25x_3^2$$

Where x1 is the pH of the aqueous solution, x2 is ozone concentration and x3 is reaction time. The highest value of color stripping was obtained at pH 3; ozone concentration of 100 g/Nm^3 and reaction time of 120 minutes.

ANOVA based on the Box-Behnken design was performed with Functional Objective to check the fitness and significance of the model coefficient. The ANOVA results for the responses of the optimized Color Stripping and Tensile Strength Loss are, respectively, summarized in table 4.14 and table 4.15 respectively.

When analyzing ANOVA results, a large value of F with a small value of p (i.e. $p<0.05$) show that the model is statistically significant. Among the ANOVA results reported in Table 4.14 and Table 4.15, the (Prof>F) value was found to be <0.05 for the Color Stripping and Tensile Strength Loss, with F value of 18.60 and 12.37, respectively, indicating a significant model fit. The F-test gave a low probability value, which also indicated the high significance of the model for both response. Moreover, the high coefficients of determination (R^2) of 0.965 and 0.949 for the Color Stripping and Tensile Strength Loss responses further indicated a good correlation between the measured and predicted responses.

In this study, the independent parameters of pH (x1), ozone concentration (x2) and reaction time (x3), interaction effect between the pH and reaction time (x1x3) and the second-order effect of pH (x12), reaction time (x32), were significant parameters for the response of Color Stripping with p-value < 0.05, as shown in the Table 5. Regarding the Tensile Strength Loss response, the ozone concentration (x2) and reaction time (x3), were highly significant parameters. However, the rest of the terms did not show any significant impact.

4.4.4 Response surface result analysis:

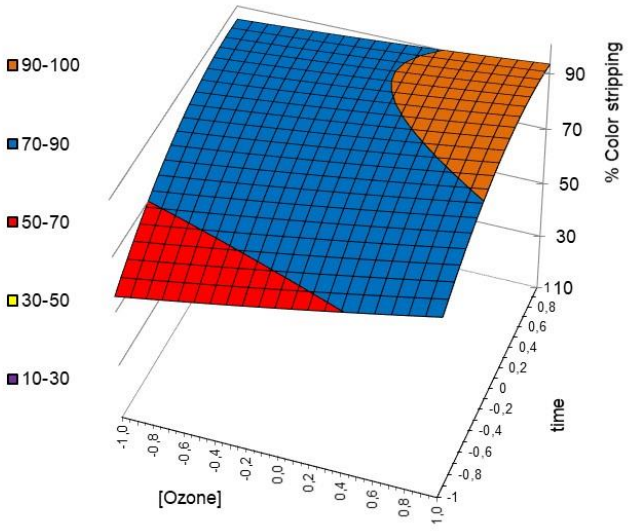


Figure 4.14 (A): pH 3

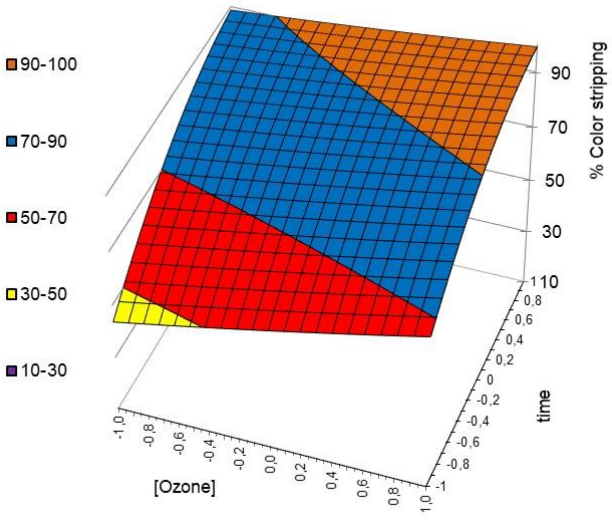


Figure 4.14 (B): pH 5

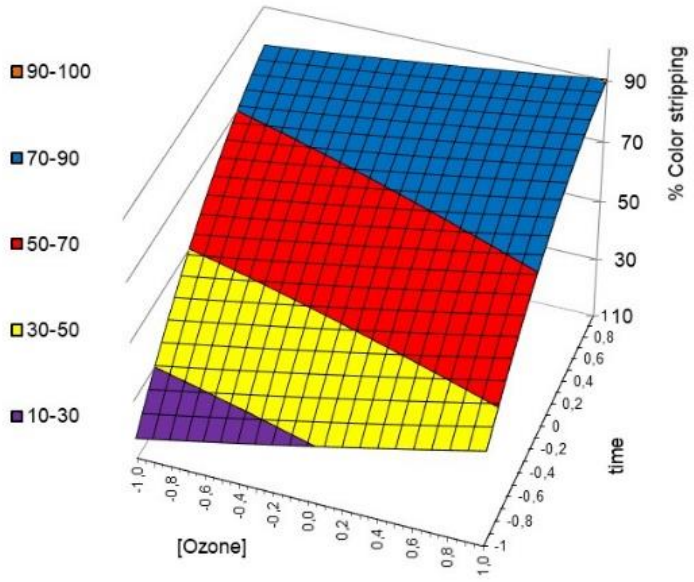


Figure 4.14 (C): pH 7

Figure 4. 14 (A,B,C): 3D response surface diagrams showing the effects of ozone concentration and treatment time on the color stripping of the pigment goods at different pH values.(color of the graphs are related to color stripping %).

From the response surface plots A, B and C in Figure 4.14, it can be seen that the pH of the ozonation process had a considerable impact on the decolorization of the pigment printed goods. As seen in the response surface plots, the acidic pH range showed good results in terms of the decolorization while the neutral pH showed adverse effects on the decolorization. Also the ozone concentration and the treatment time are important favorable conditions for the maximum decolorization. Severe process conditions like acidic pH, higher ozone concentration and higher reaction time were required for the efficient decolorization of the pigment printed goods.

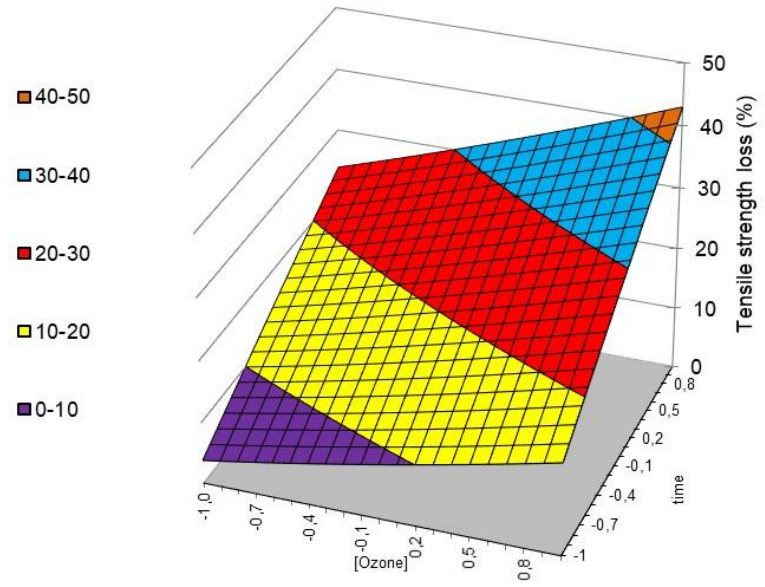


Figure 4.15 (A): pH 3

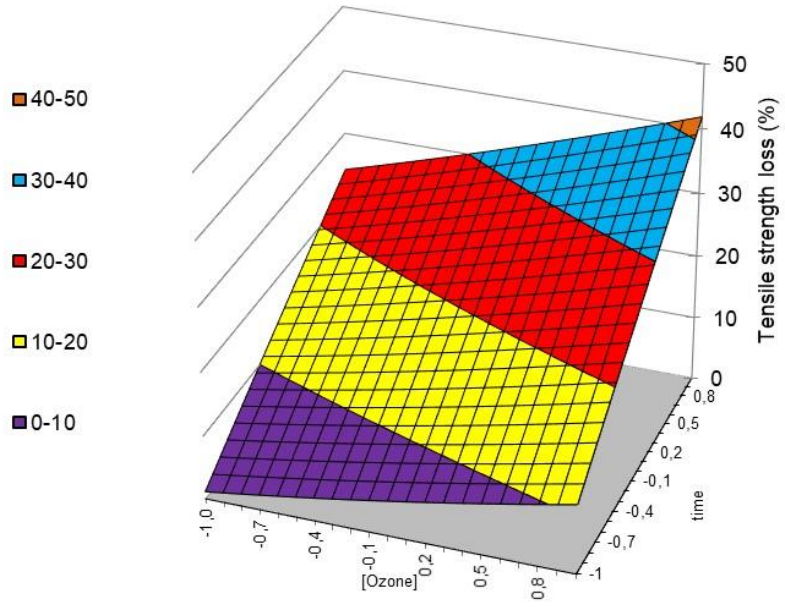


Figure 4.15 (B): pH 5

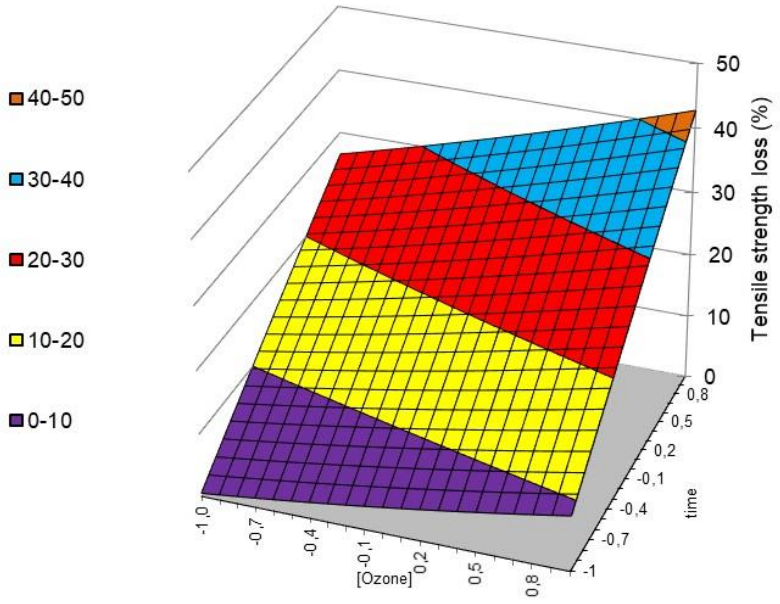


Figure 4.15 (C): pH 7

Figure 4. 15 (A,B,C): 3D response surface diagrams showing the effect of pH, [O_3], and reaction time on the tensile strength loss %: (A) pH = 3; (B) pH = 5; (C) pH = 7.

From the response surfaces A, B and C in Fig. 4.15, shows that the mechanical properties like tensile strength loss increased with an increase in all the process parameters (ozone concentration, and time).

Optimized process conditions and validation of model:

Based on the Color Stripping (CS) and for the Tensile Strength Loss (TSL) the responses modeled by second-order polynomial equations have been presented before. Thanks, of Solver function in Excel, the optimal value or operating's parameters were found targeting maximum Color Stripping and minimum of Tensile Strength Loss for a formula in one cell called the objective cell, subjected to certain constraints of limits, (for example: $x_1<1$; $x_1>-1$ it means that the pH is between 3 to 7, $x_2<1$; $x_2>-1$ it means that the ozone concentration is between 40 to 160 g/Nm^3 and $x_3<1$; $x_3>-1$ it

means that the reaction time is between 20 minutes to 120 minutes). The weight of CS and TSL were taken part in 50%/50%. This means that the Solver works with a group of cells called decision variables that were used in computing the formulas in the objective and constraint cells. Solver adjusts the values in the decision variable cells to satisfy the limits on constraint cells and produces the waiting results for the objective cell.

If the conditions; Color Stripping must be greater than 80%; and Tensile Strength Loss must be lower than 20% are set up, than the optimal conditions are pH 4, with ozone concentration 40 gO_3/Nm^3; and reaction time : 102 minutes.

4.4.5 Characterization of the stripped fabrics

In this study, the pigment printed samples subjected to the different ozonation process parameters were chosen as the representative fabrics to study the decolorization phenomenon. In addition to that, pigment printed fabric and blank cotton fabric were selected as reference to study the effect of ozone on the decolorization process (Table 4.16).

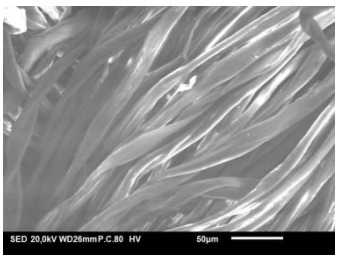
Table 4. 16 Selected samples for characterization

Experiment Number	pH	$[O_3]$ g/Nm^3	Reaction time	color stripping %
E11	5	160	120	94.2
E12	3	100	120	94.2
E13	5	100	70	83.7
E2	7	100	20	23.1

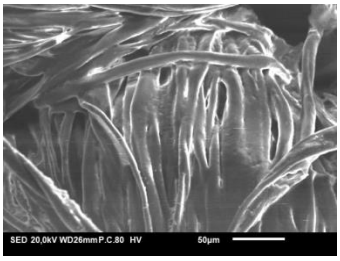
SEM Images:

Figure 4.16 shows SEM images of ozone treated samples compared with the untreated blank cotton and pigment printed cotton. SEM micrograph of unprinted cotton fabric shows the clear surface. When we look at the SEM image of the pigment printed

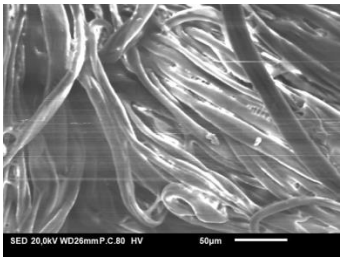
cotton fabric, it can be clearly observed that the fibers are coated with a polymeric binder film, which helps in the binding and fixation of the pigment particles onto the fabric samples. SEM micrographs of the decolorized samples with various ozonation process conditions, confirmed the presence of the binder deposition on the fiber surface of the printed samples. This shows that even after extreme ozonation it is difficult to remove the polymeric binder coating from the pigment printed fabric.



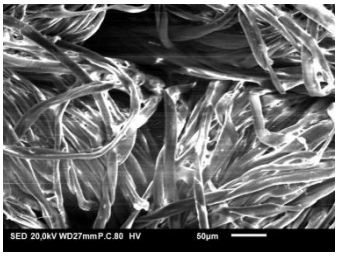
Blank fabric



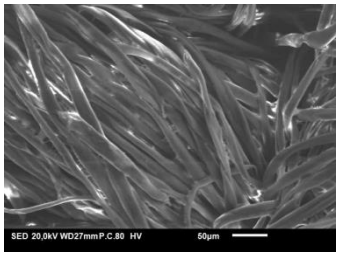
Pigment printed fabric



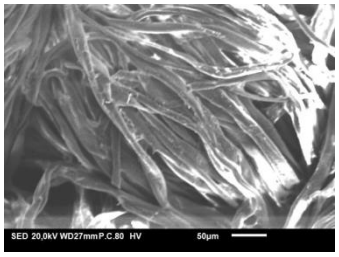
Sample treated E11



Sample treated E12



Sample treated E13



Sample treated E2

Figure 4. 16 SEM micrographs before and after ozone treatment. The scale bar of the images is 50 µm.

XPS analysis to study the surface chemistry:

On the survey XPS spectra, 4 peaks are observed corresponding to the electrons C1s of the C atoms (285/290 eV), O1s of O atoms (531/536 eV), to N1s of N atoms (398

eV), to Cu2p3/2 of Cu atoms (932/935 eV). The percentage of each species is calculated by the percent area of each peak (table 4.17).

Table 4. 17 XPS spectra for selected samples with Surface elemental composition

Sample	Surface atomic composition (at. %)			
	C	O	N	Cu
pigment printed cotton fabric	88.6	9.7	1.6	0.2
sample treated with E11	80.1	19.8	0	0.1
sample treated with E12	81.1	18.9	0	0
sample treated with E13	83.2	16.6	0	0.1
sample treated with E2	82.0	17.4	0.5	0.1

During the ozone treatment for the selected samples, the oxygen content increases due to the oxidation processes that occurs in presence of ozone. This treatment breaks the covalent bonds of the binder and the pigment, while introducing oxygen in the chain.

Copper and Nitrogen atoms are attributed to the pigments, thus there is a very small amount of those species and the XPS is not very accurate. However, it is obvious that the ozonation treatment decreases the amount of Copper and Nitrogen. This could be attributed either to the removal of the pigment due to chain scissions of the acrylic binder or to the oxidation of the pigment molecule by the ozonation treatment. Authors (Bigambo, Liu, Broadbent, Carr, & Rigout, 2018) have studied the effect of oxidative bleaching on the reactive dyed goods which is in line with results observed in our study.

Although the discoloration of the sample is very weak (23.1%) with the E2 treatment at pH 7 the degree of oxidation seems similar to that observed with the E13 treatment at pH 5 and longer time with better results of color stripping (83.7%). It can also be

observed that E11 and E12 experiments result in identical stripping, while the O_3 amount is much higher with E11. This could be attributed to the complete removal of the copper during E12 experiment. Again, the effect of the acidic pH for this experiment could be one explanation. As a conclusion, the XPS results confirm the interest of ozonation at lower pH, with a preferential oxidation of the pigment and a better discoloration of the samples.

4.4.6 Discussion:

Oxidation by ozone is considered to be a powerful technique for decolorization of the reactive dyes by the destruction of the chromophoric system. There may be occurrence of two possible reaction mechanisms: direct reaction involving molecular ozone attack and the indirect reaction consisting of the free radical mechanism. Both of these reaction mechanisms have been found to exist simultaneously during the ozonation reaction process. (Sharma et al., 2013).

Recent studies for color removal from pigment wastewater have demonstrated 90 % color removal using the ozone. The ozone dosage for color removal from pigment waste water was higher(4-5 times) than the dye waste water so as to obtain the same color removal efficiency using identical conditions. The high dosage of ozone required is probably explained by the presence of the low nucleophilic chromophores of the color imparting organics in the pigment waste water and the higher alkalinity (Lee et al., 2007). The color removal in pigment printed goods is in agreement with this study of color removal from the pigment waste water, we were able to achieve the decolorization of about 90 % and more, but the process conditions deployed were harsh (huge ozone concentration and treatment time; acidic pH range). This may be due to the cross-linking of the binder at the fabric surface.

Studies on the decolorization of the pigment wastewater with ozone have shown that 85 % decolorization rate was achieved. (Maija Saastamoinen, 2007). Ozonation was more successful at low pH (pigment dissolved in H_2SO_4, pH < 1), than at higher pH (pigment dissolved in ethanol, pH=6). The reason could be related to the unselective hydroxyl groups caused by higher pH or poor solubility.(Chu & Ma, 2000; Ciardelli,

Capannelli, & Bottino, 2001; Demirev & Nenov, 2005; B. W. Liu, Chou, Kao, & Huang, 2004; Maija Saastamoinen, 2007; Sevimli & Sarikaya, 2002). Also, the studies have shown that the decolorization rate increases with the increase in the ozone dose. This study assumes the possibility of the complete decolorization of the Pigment Blue 15 could be carried out with the higher amount of the ozone dosages. (Maija Saastamoinen, 2007; Tosik, 2005). However, the experimental conditions (for example the Pigment Blue 15 dissolved in concentrated H_2SO_4), were based on unrealistic scenarios and impossible for practical applications.(Maija Saastamoinen, 2007).

Considering the decolorization efficiency, lower pH values were often more efficient, the reason being selective direct ozone reactions targeting chromophoric bonds in the colored materials. (Adams & Gorg, 2002).

In a study related to the bleaching of cotton fabrics with ozone, highest DP loss was observed in case of ozone bleached fabrics as compared to the treatment with sodium hypochlorite and hydrogen peroxide. Also, it was found that in case of ozone bleaching, the DP of cotton was decreased largely based on the pH of the fabric. Hydrocellulose starts to form with an increase in the acidity of the fabrics and hence the DP decreases. Likewise, decrease in the DP values, the physical properties of fabrics like breaking strengths were also found to be decreased at the neutral and acidic pH values. (S. D. Perincek, Duran, Korlu, & Bahtiyari, 2007). While discussing the use of ozone in the textile industry, the author has stated that the strength loss is very high in the case of ozonated fabric, and research to minimize the damage due to the ozone are continued.(S. Perincek, K. Duran, A.E. Körlü, 2008). While studying the parameters affecting dry and wet ozone bleaching of denim fabric, it was found that ozone slightly damaged the denim fabrics by reducing the tensile strength. Morover, the ultimate tensile strengths decreased with an increase in the ozone concentration and the treatment time. The loss in the strength could be attributed to the damage induced by the ozone due to the hydrolysis of the glycosidic bonds (Ben Hmida & Ladhari, 2016). In our case, similar results were obtained with respect to the losses in mechanical properties of the printed goods.

There is a hypothesis in our study which may suggest that the main reaction of decolorization of the pigment printed goods occurred via oxidation of the binder with chain breaks (degradation) - so it allowed pigments to be removed - almost partially.

Chapter 5 : LCA Analysis of the Ozone Assisted Decolorization Process

5.0 Life cycle assessment tool (LCA) application to study the profile of processes.

For the color stripping process, the environmental impacts of the proposed ozonation method has to be quantified in order to justify the profile of the process (Jacquemin et al., 2012). In our study, we used gate-to-gate LCA methodology. The detailed color stripping and mechanical property characterization has already been discussed in our research paper (A. S. Powar et al., 2020). The environmental assessment in our work is based on defining a functional unit color stripping of 40 g of reactive dyed cotton fabric to achieve color removal, and the determination of different environmental impact categories for the ozone assisted color stripping method. The aim of the study was to highlight the main contributors to the environmental impact of the ozone stripping process and then to find the best conditions for reactive dyed decoloration. In addition, this work intends to identify and evaluate the potential impact of the ozonation process used and also encourages the sustainability profile of the process.

5.1 Comprehensive LCA of the color stripping using the ozonation.

LCA has been performed as a cradle to cradle analysis focusing the unit operation of the decolorization prior to the end of life option such as recycling of textiles. This LCA analysis based on "Gate-to-gate" only considers the color stripping or the decolorization process to study the ozone-assisted process and its environmental profile. The LCA was carried out according to the ISO 14040 (ISO14040, 2006a) and ISO 14044 (ISO14044, 2006b) standards. SIMAPRO LCA software was used.

5.2 Experimental work:

5.2.1 Woven Cotton Textile: A 100% Cellulosic (cotton) woven fabric (150 g/m^2) was implemented in this study. The cotton fabric was dyed with a 1% reactive dye (C.I. Reactive Black 5). This dyed cotton fabric was used for the decolorization treatment of the fabric.

5.2.2 System Considered: Color Stripping Using the Ozone-Assisted Treatment The ozone-assisted process was carried out using a pilot scale ozone reactor at the Unilasalle laboratory, France. The ozonation system is described in Figure X. (A. S. Powar et al., 2020).

The main conditions were, the oxygen O_2 flow rate is constant at F = 0.3 m^3/h, and the amount of ozone is measured in situ. The excess ozone is then destroyed in a 0.8 kW ozone destructor ODT-003. The water bath used was at a fixed volume of 60 L of tap water. The circulation pump of the reactor has a power of 0.75 kW, and we made the assumption that only 10% of the power is required. All the experiments are made at room temperature. The pH value was regulated by adding phosphoric acid (PanReac AppliChem) and sodium hydroxide (EMPLURA® Merck, Germany). The pH was measured in situ during the ozonation process.

The 40 g blue dyed cotton fabric was placed in the reactor and subjected to the ozone treatment. As a result, the treated fabric started to decolorize and the color stripping % was measured using a spectrocolorimeter (Figure 5.1).

Figure 5. 1 Cotton sample before and after ozonation treatment (A. S. Powar et al., 2020).

In this part of the LCA, we only considered experiments with stripping values more than 94% (Table 5.1).The best stripping was obtained with experiment E11 performed at pH 5. It had an ozone concentration in the oxygen gas flow of 85 g/m^3 NTP (normal pressure and temperature) and a treatment time of 50 min. We considered the E11 experiment as a reference. In the experiments E7 and E8, the treatment time decreased to 30 min only, while a lower ozone concentration was used in E10 and E12.

The E13–E16 experiments all had less ozone and less time, yet the stripping results were not good as compared to the reference.

Table 5. 1 Ozonation experimental conditions with color stripping %

Sr.No.	pH	Concentration Ozone	Time	Color Stripping
		(g/m^3 TPN)	(min)	%
E7	7	85	30	95.1
E8	3	85	30	97.45
E10	7	45	50	94.3
E11	5	85	50	97.6
E12	3	45	50	97.5
E13	5	45	30	94.6
E14	5	45	30	94.1
E15	5	45	30	94.65
E16	5	45	30	93.9

5.2.3. Material and Energy Requirement

The amount of resources required for the treatment of 40 g reactive dyed fabric was estimated from the treatment parameters and the characteristics of the devices of the process (Table 5.2).

a. Oxygen O_2 and ozone O_3 requirements:

The amount of O_2 required was calculated from the flowrate and the treatment time. For the reference process E11, the treatment time was 50 minutes. So the amount of

O_2 required was 0.25 m^3 corresponding to 0.357 kg of Oxygen as the oxygen 'O_2' density is 1.429 kg/m^3.

The concentration of O_3 in the oxygen flow was constant. Thus, the total amount of O_3 produced was calculated from the volume of oxygen 'O_2' gas used. With the oxygen concentration of 0.85g/m^3, the O_3 amount produced was equal to 21.25g

b. Energy requirements:

Energy-associated concerns:

- Ozone generation with plasma treatment: Specific energy required to produce one kg of ozone from liquid oxygen was 7–13 kWh/kg O_3 [(Suez, 2021)]. An average value of 10 Wh/g O_3 was selected for our study, and thus this energy in the reference experiment was 212.5 Wh.

- Ozone destructor ODT-003 operated at a power of 0.8 kW, which was associated with the maximum gas flow rate of 3.7 kg/h [(Suez, 2021)], or 2.59 m^3/h with oxygen gas. As we used only 0.3 m^3/h, then the power needed is 0.092 kW which when multiplied by the treatment time, yields the quantity of energy used. With experiment E11, which was carried for 50 min, the ozone destructor energy was 77 Wh.

- Water circulation pump of the reactor: Multiplying the 0.075 kW power by the treatment time provided the energy used, and for the E11 experiment, it was 62.5 Wh.

- For the reference treatment, E11, the total electricity requirement was 0.352 kWh.

c. Chemicals

The water bath was made with tap water. In case of the reference process at pH = 5, the amount of phosphoric acid and sodium hydroxide used were 6.75 and 3.65 g, respectively.

Table 5. 2 Ozone and energy requirements reference process E11

Sr. No.	Inputs from Technosphere	Quantity
1	Energy for ozone generation with plasma treatment (kWh)	0.213
2	Energy for the circulation pump (kWh)	0.0625
3	Energy for the ozone destructor ODT-003 (kWh)	0.077
4	Oxygen (Kg)	0.357

5.3 The functional unit (FU) defined and the considered system boundaries.

In our study, the functional unit (FU) was defined as treatment of 40 g of plain woven, reactive dyed cotton textile fabric to achieve color stripping of more than 94 %. Also several process scenarios related to the reactive dyed fabric decolorization were studied in case of the ozonation based color stripping processes.

The geographical scope was considered as France, since the ozone based color removal treatment was performed at Unilasalle premises, in Beauvais France. Hence, we considered hypothetically that the color stripping process was performed in the France. A typical life cycle based on the chemical removal process is depicted in figure 5.2. It consists of the unit operation ozonation used for the color stripping of the reactive dyed textiles. In the reported ozone based decolorization process, the decolorization step for the manufacturing of chemicals and electrical energy was included in the "gate-to-gate" system boundaries. In our study we omitted the dyed woven cotton fabric manufacturing as well as the chemical transportation. It was considered that the energy and the production site of the chemicals were in Europe. Elements such as the fabrication/maintenance of the ozone machine, wastewater treatment and the transport of chemicals were outside the system boundaries. For the LCA modeling study, we have considered the tap water in order to minimize the

impacts related to the use of reverse osmosis water or the deionized water. Hence, when we consider the actual results, there may be slight variations due to the tap water use. Additionally, for the ozone destruction, the catalytic process was used, and therefore the output considered the energy used for the leftover ozone destruction. As the drying of the samples did not differ from one treatment to another, so we have excluded it from our study.

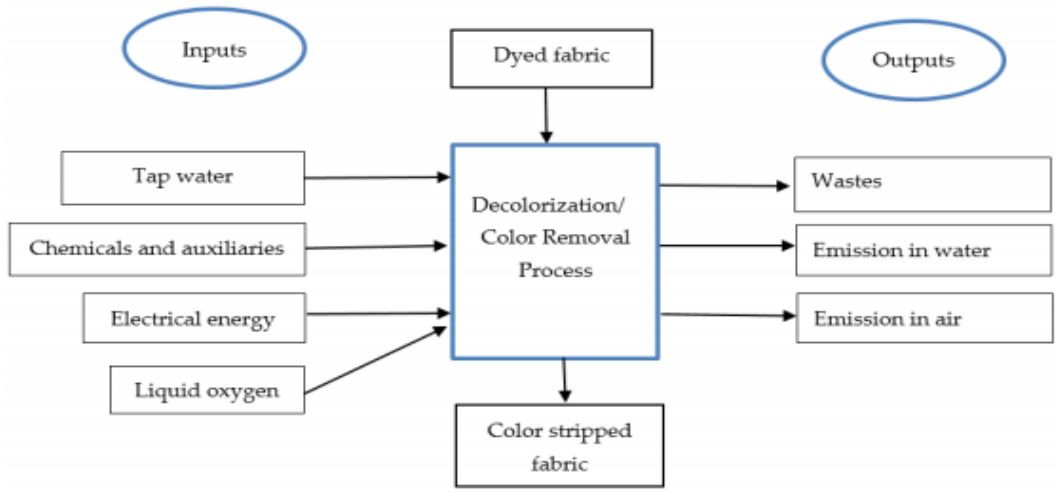


Figure 5. 2 System boundaries of the decolorization process for the reactive dyed cotton fabric

5.3.1 Life Cycle Inventory (LCI) and the comparative analysis.

The experimental data was used in case of the ozone-assisted process, with the consideration of the pilot scale machine. Laboratory experiments were the base for the determination of the scenarios. Data were obtained from these scenarios for quantifying the flow inputs (consumed resources) and the outputs (emissions or outcomes of the process). The data were obtained from various sources (Refer table 5.3). The specific data was obtained from the experiments performed in the laboratory and the ecoinvent database was used to collect the production data. These inventory data consisted of the liquid oxygen, the production of chemicals, and the tap water in Europe (RER datasets). Also the electricity production and distribution in France (FR datasets).

Inputs	Unit	Amount	Description	Source
Phosphoric acid	G	6.76	Phosphoric acid, industrial grade, without water, in 85% solution state {RER} | purification of wet process phosphoric acid to industrial grade, product in 85% solution state | Alloc Rec, S	Eco-invent database
Tap water	mL	60,000	Tap water {Europe without Switzerland} | tap water production | underground water without treatment | Alloc Rec, S	Eco-invent database
Sodium 1qhydroxide	G	3.55	Sodium hydroxide, without water, in 50% solution state {RER} | chlor-alkali electrolysis, diaphragm cell | Alloc Rec, S	Eco-invent database
Electricity	kWh	0.352	Electricity grid mix, AC, consumption mix, at consumer, Alloc Rec, S	Eco-invent database

Oxygen	G	0.357	Oxygen, liquid {RER} | air separation, cryogenic | Alloc Rec, S	Eco-invent database

Outputs	Unit	Amount	Description
Phosphoric acid	G	6.76	Wastewater content
Tap water	mL	60,000	Wastewater content
Sodium hydroxide	G	3.55	Wastewater content

Table 5. 3 The life cycle inventory for the decolorization of 40 g of reactive dyed cotton fabric using the ozonation technique (reference the E11 experiment)

5.3.2 LCIA (Life cycle impact assessment) interpretation

The results of the LCA significantly differ based on the assumptions, especially the system boundaries and the data sources used. Accordingly, this LCA of the unit process consists of the decolorization process of the reactive dyed cotton. The main aim of this study is to do study the chemical removal process prior to the recycling of textiles and also the environmental profile of this chemical removal process. Moreover, a comparative analysis was done between the reference ozonation process and the various process scenarios of the decolorization with the varied process conditions.

5.3.3 Environmental impact categories studied

The International Reference Life Cycle Data System ILCD 2011 Midpoint+ V1.07/EU27 2010, equal weighting method was utilized for the assessment of the environmental impacts. Out of the 16 impact categories of the ILCD method, in our study we have reported the following 6 namely: climate change; water resource

depletion; human toxicity (cancer effects); freshwater ecotoxicity; mineral, fossil, and renewable resource depletion; and the ionizing radiation of human health (HH).

All the impact categories were normalized with the 2010 normalization factors related to the EU-27 impacts, in order to compare the significance of each impact category. [17]. For this study, we have considered the environmental impacts of a european person annually in 2010.

5.4 LCA Results

5.4.1. LCIA Results and Interpretation for the Reference Scenario:

Table 5. 4 Impact categories and normalized values for the impacts in the ozonation

Impact Category	Unit	Value (Unit: See Column)	Normalized Value (Unit: PEeq.)
Climate change	kg CO2 eq	0.21388189	0.0000235
Mineral, fossil, and ren resource depletion	kg Sb eq	0.00001360	0.000135
Ionizing radiation HH	Kbq U235 eq	0.19096354	0.000169
Freshwater ecotoxicity	CTUe	2.01311521	0.000229
Human toxicity, cancer effects	CTUh	0.00000002	0.000549
Water resource depletion	m^3 water eq	0.16857161	0.002073

The main environmental impacts are described in Table 5.4. The total greenhouse gas (GHG) produced by the ozone treatment was 213 g of equivalent CO_2. The water

depletion was 168 L, while the resource depletion was 14 mg equivalent to Sb. The ionizing radiations were equivalent to 190 becquerel of the U235. The fresh water ecotoxicity was equivalent to 2 comparative toxic units (CTU), while the cancer human toxicity was calculated at 0.02 × 10−6 CTU. The normalization method was added to describe the extent to which the impact categories had a significant influence on the environment [18]. The normalized factor is the environmental impact caused annually by the activities of an average European, it is expressed as "person year equivalent", PEeq.

The LCA normalized results for every impact category in the ozone reference process (E11) are displayed graphically in Figure 5.3, with the same equivalent person year unit. The four major impacts are as follows: water resource depletion, human toxicity, cancer effects, freshwater ecotoxicity, and the ionizing radiation HH. The main environmental impact for the reference process E11 concerned the water resource depletion, as it had the greatest relative value after normalization amongst all of the impact indicators. From Figure 5.3, we observed that there was a minor impact on climate change, as well as the mineral, fossil, and renewable energy depletion.

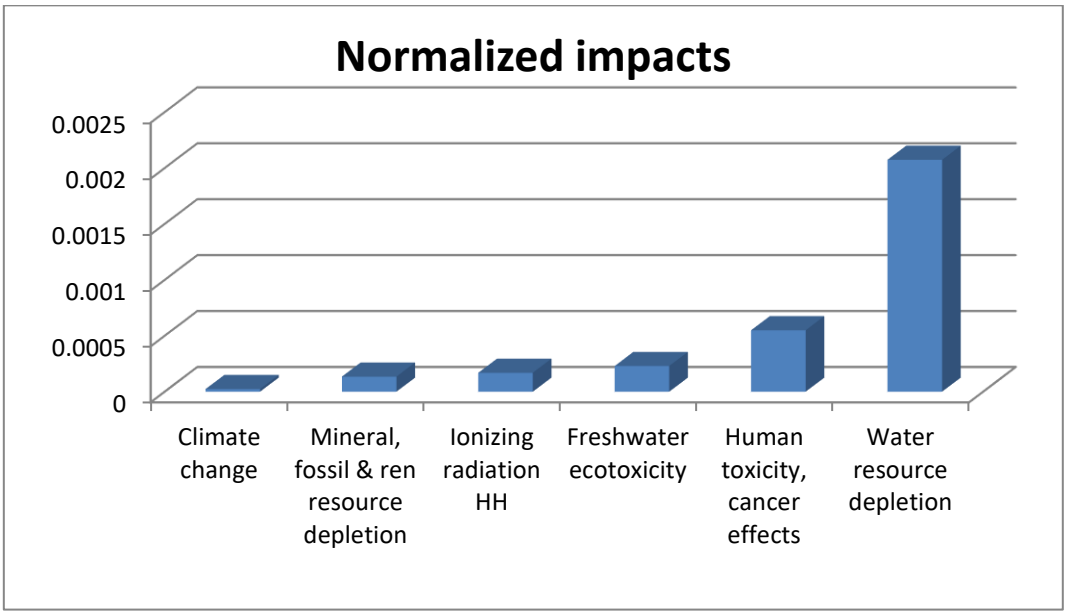


Figure 5. 3 The life cycle assessment (LCA) impact indicators normalized for the ozone-assisted decolorization process E11

5.4.2. Interpretation

Considering the reference E11 ozonation process, we studied the contribution of different materials and electricity for various environmental impacts (Figure 5.4). We observed that tap water and sodium hydroxide had a negligible share in the environmental impacts. Electricity contributed greatly to the environmental impacts, such as ionizing radiations, water resource depletion, and material depletion. Liquid oxygen contributed greatly to climate change and freshwater ecotoxicity, and, to a lesser extent, ionizing radiation. Phosphoric acid contributed to the human toxicity and freshwater ecotoxicity.

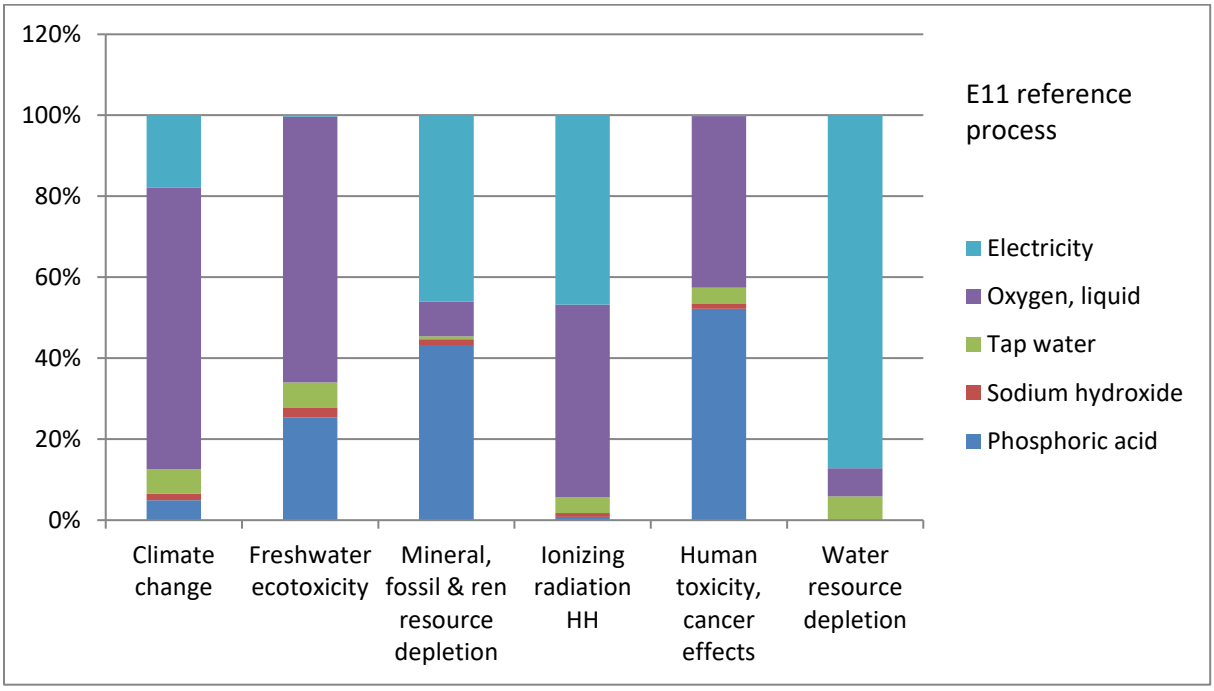


Figure 5. 4 The life cycle assessment (LCA) impact indicators normalized for the ozone-assisted decolorization process E11

Electricity and oxygen formation are the main contributors to environmental impacts. This is related to the ozone generation. Indeed, the main electricity consumption was the ozone generator.

5.4.3. Process Optimization Regarding Environmental Impacts

As we observed, the environmental impacts were caused by the reference process, and our aim herein was to find the best conditions in terms of the process optimization so that we could minimize such environmental impacts. The inventories for each experiment were calculated according to Section 2.3. (Table 5.5).

Table 5. 5 Inventories for the ozone experiment

Sr. No.	O_2 Required	Electricity	Phosphoric Acid	Sodium Hydroxide
	Kg	kWh	g	g
E7	0.214	0.211	3.72	1.96
E8	0.214	0.211	6.86	3.6
E10	0.357	0.252	3.72	1.96
E11	0.357	0.352	6.76	3.55
E12	0.357	0.252	6.86	3.6
E13	0.214	0.151	6.76	3.55
E14	0.214	0.151	6.76	3.55
E15	0.214	0.151	6.76	3.55
E16	0.214	0.151	6.76	3.55

When treatment time decreased (Tables 1 and 5), as was the case for experiments E7 and E8, we observed that there was a reduction in the required electricity and O_2 input with very good color stripping.

When the ozone concentration was reduced, such as in experiments E10 and E12 (Tables 1 and 5), we observed that there was reduction in the electricity compared with the reference process. Moreover, we observed very good color stripping.

To take into account both the O_3 concentration decrease and the time reduction, the midpoint experiments of the statistical model (e.g., experiments E13–E16) were selected (Table 5.5). We clearly observed that the required electricity and O_2 input were less than the reference process. Color stripping was a little bit worst but decolorization still seemed significant.

5.4.4. Introduction of the LCA Results

Based on the characterized results, we observed that the E13 ozonation process was preferable (Table 5.6). The largest differences in the impacts were observed between the reference process (E11) and the midpoint of the experiments (E13).

Table 5. 6 Characterization values of the impact categories for the E11 reference, and the E12, E8, and E13 processes.

Impact Category	Unit	E11	E8	E12	E13
Climate change	Kg CO_2 eq	0.21388189	0.13921773	0.20321215	0.13248698
Mineral, fossil and ren resource depletion	Kg Sb eq	0.00001360	0.00001072	0.00001191	0.00000956
Lionizing radiation HH	Kbq U235 eq	0.19096354	0.11885205	0.16565425	0.10358892

Freshwater ecotoxicity	CTUe	2.01311521	1.48916748	2.01922845	1.47962330
Human toxicity, cancer effects	CTUh	0.00000002	0.00000002	0.00000002	0.00000002
Water resource depletion	m^3 water eq	0.16857161	0.10504289	0.12684691	0.08000251

Figure 5.5 represents the LCA results for the E11 reference, as well as E12, E8, and E13 processes. Here, the reference ozone process (E11) was compared to the different optimized processes (E8, E12, and E13). Table 6 shows that the optimized processes E8 and E13 had much lower impact values than E12 process for environmental impacts such as climate change, ionizing radiation HH, and water depletion. The reference process E11 had the highest environmental impacts. In our LCA study based on normalized results, the atmospheric impacts, especially water resource depletion, exhibited the poorest performance among every environmental impact category. The reason could be attributed to the ozonation process setup by utilizing a large amount of water. When we observed the midpoint of the experiments, we saw that E13 had lower impacts than the reference, which used less liquid oxygen for the ozone generation and less electricity, thus reducing the overall environmental impacts. However, we obtained less color stripping, as already discussed. (Tables 1 and 6).

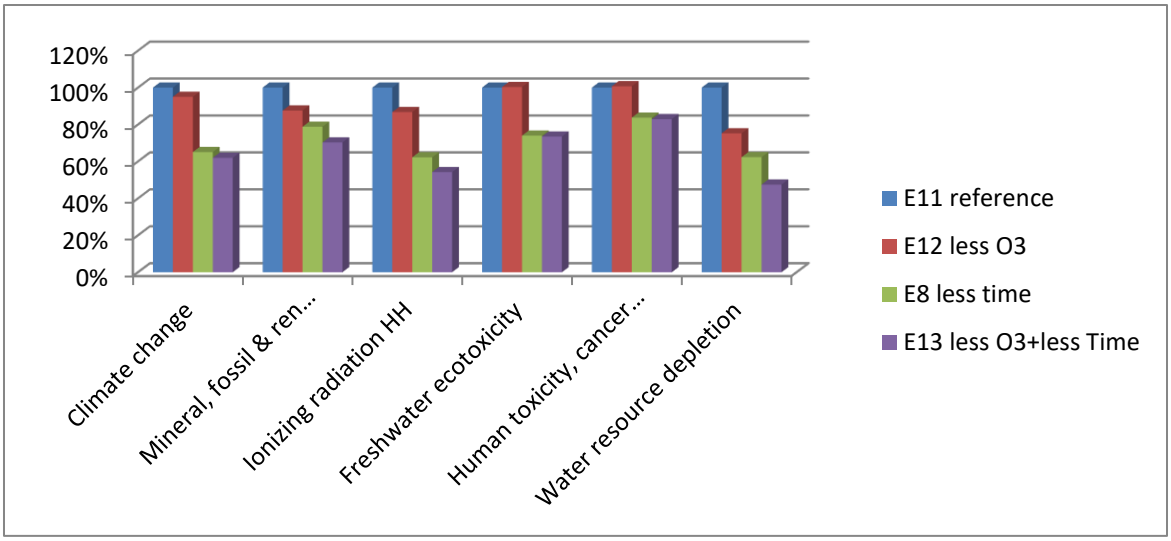


Figure 5. 5 Comparative LCA results (normalized values) for the E11 reference, as well as the E12, E8 and E13 processes

5.5. Discussion

So depending on the color specifications, the optimum value could be selected focusing either on the color stripping quality or on the environmental impact. If a color stripping of 94% is enough for example before dark dyeing, then the best conditions would have the lowest impact. The results obtained with the optimum conditions were good and comparable to the literature. Previous studies have shown that the reactive black 5 dyed cotton fabrics were color stripped with 96.1% and 94.4% of the stripping percent, via the electrochemical method [(Ma, Wang, Yin, Kan, & Wang, 2018)].

The environmental impact of the ozone-based decolorization process was primarily caused by water use and energy consumption. The reactor utilized operates at higher material to liquor ratios; as the reactor we have used is not dedicated to textiles. The reactor design needs to be improved in order to increase the amount of fabric that could be introduced for the treatment. Since the volume of the water in the reactor was large, this also resulted in the high consumption of chemicals and auxiliaries.

This study shows that electricity is very important. In fact the overall environmental impact depends on the electricity mix and in France the electricity mix has lot of

nuclear energy and that's the reason we have high ionizing radiation HH impacts. Impact categories are sensitive to the energy mix of the country. If we change the country with less electricity mix and high carbon content so we have high climate change and less ionizing radiation impact.

Moreover, the reactor utilized large amount of ozone and thus the liquid oxygen which is needed for the production of ozone. Thus, the ozone generator was also a contributor, as discussed previously. In previous studies available on wastewater treatments, the research findings showed that the ozonation process adds a 6% greater impact on climate change. This is attributed to the liquid oxygen and electricity production associated with the ozonation process [(Wencki, 2015)]. In another study on the application of the LCA to the Kraft pulp industrial wastewater treatment via different advanced oxidation processes, it clearly depicted that ozonation accounted for a higher environmental impact, owing to energy consumption produced by the oxygen and ozone [(Ortiz, 2003)]. These results coordinate with our study. The results in this study showed that combining the ozonation with UV-A light decreased the environmental impact by about 40% [(Ortiz, 2003)]. In a similar study on the analysis of the advanced oxidation process, results showed that high energy consumption was a great drawback in the ozonation process [(Arzate, P, Oberschelp, & Sánchez-pérez, 2019)].

Chapter 6 : Conclusions, Contributions and Future Work

6.0 Conclusions, Contributions and Future Work

Our strategy was to use an ozone based process for the color stripping of the reactive dyed textiles, and we succeeded in achieving color stripping of the Reactive Black 5 dyed textile.

Demonstrated the application of the ozone based process in a pilot scale reactor, and thus generating the possibility of the industrial scale up of the designed process.

Ozonation process can be effectively used for the decolorization of the pigment printed textiles (CI Pigment Blue 15). However, Complete removal of color is difficult to achieve with the ozonation process.

The color stripping of the reactive dyed textile(reactive black 5 dyed) could be also performed with natural reducing agents such as glucose and alkali assisted process.

This color removed substrate can be used for chemical recycling or extending the life of textiles by reprocessing it.

LCA results demonstrate the environmental profile of the ozonation process and strategies to reduce the environmental impacts.

6.1 Conclusions:

Following conclusions can be drawn from our study:

This Ph.D. thesis aims at developing ways to enhance the recycling of the textile products, especially cellulose textiles dyed with the reactive colorants.

The entire work can be split into two partitions:

1. Color removal from the cotton dyed and printed textiles to enhance the recycling process.

2. Comprehensive LCA to study the environmental profile of the designed process.

For the decolorization of the reactive dyed textiles as well as the pigment printed textiles, the results of this study show that the ozonation process can be effectively

used for the decolorization of the reactive dyed textiles (CI reactive black 5) and the pigment printed textiles (CI Pigment Blue 15). However, complete removal of the reactive dyed and the pigment printed product was not achieved with the ozonation as well as the conventional method. The removal of these colorants from old textiles could be a suitable way for the end of life options like recycling and other possible scenarios like reusability or improving the life of the garment of textile.

From the study of the mechanical properties of the cellulosic fabric after the decolorization using the ozone, the oxidative treatment causes damage to the strength of the cellulosic textile, which is due to the ozone treatment resulting in the oxycellulose formation and strong conditions of acid and alkali used. An LCA study was performed to confirm and evaluate the advantages of using the ozonation process for the decolorization of cellulosics.

In this study, an investigation was carried out on the color stripping cotton fabrics dyed with the CI Reactive black 5 using the ozone dissolved in water. This study evaluates the effect of working parameters such as ozone flow rate, time, and pH on the color stripping and the mechanical properties. Based on the experimental study, the following conclusions were drawn:

- Good decolorization results and less damage of the mechanical properties were obtained in the acidic pH.

- The reactive dyed sample when treated at pH 3, ozone concentration of 85 g/m^3 NTP ozone, and treatment time of 30 min gives the decolorization of almost 98%.

- Box Behnken design was used for the evaluation of the color stripping process and its optimization. This analysis defined the major role of the time in the degradation process and that of the ozone concentration for the color stripping process. Our experimental study was used to propose an optimal set of the experimental parameters.

- For the color stripping of a cotton fabric dyed with a CI reactive black 5 reactive dye, this ozone assisted process conducted at pilot scale has proven good selectivity. However, further studies need to be performed to avoid the slight yellowness obtained in the treated samples.

- Since the stripping is a process related to the dye destruction, there were losses in the mechanical properties due to the ozonation process. Hence the mechanical properties also need to be considered along with the better color stripping of the textiles.

The conventional treatment was carried out with 10 g/l sodium hydrosulphite and the 10 g/l sodium hydroxide at 100 deg for 30 minutes gave the color stripping of almost 98 %. The strength loss obtained was lower amongst all the process.

The glucose treatment yielded maximum color stripping of 99.23 % and 98.87 % at 100 deg for 30 min and 05 min respectively. The glucose treatment gave poor results at 60 deg and good results at 80 deg and 100 deg.

The mechanical properties of the decolorized fabrics with glucose treatment were found comparable with the conventional process practiced in the textile industry.

Results indicated that glucose can also be used along with the alkali effectively for the color stripping of the reactive dyed textiles and gave comparable color removal as compared with the most widely used reducing agent sodium hydrosulphite. Moreover, glucose can be considered as a ecofriendly green reducing agent in the color stripping of the reactive dyed textiles.

Trials were performed to study the decolorization of the pigment (C.I. Pigment Blue 15) printed cellulosic fabric based on the copper phthalocyanine chemistry using the pilot scale ozone process.

The best decolorization results were obtained at pH 5, ozone concentration of 100 gO_3/Nm^3 and the exposure time of 120min under the current experimental conditions.

Samples treated with the ozone process conditions such as treatment time of 120min and acidic pH yielded decolorization of 90 % and above.

Analytical tools such as SEM analysis indicate that it is difficult to remove the binder film and/or pigment decolorization completely. The XPS analysis suggests the decolorization of the pigment printed fabric with the oxidative ozone based process.

The proposed ozonation process has the potential for the scale up in the industry and it would be interesting to propose this study for a wide range of reactive dyed and pigment dyed/printed textiles for the color stripping operations.

It is necessary to study and determine the environmental profile of the designed process and the associated hotspots in case of the method used for the color stripping of the dyed cotton textiles. For this purpose, we used the “gate-to-gate” LCA tool.

In terms of the designed ozone assisted process, it was possible to conclude the following:

- In case of the environmental impacts, Electricity and the oxygen formation for the generation of ozone were the major contributors. The reason can be attributed to the ozone generation process using the liquid oxygen and included the electricity consumption due to the ozone generator.

- It was seen that as compared to the reference process, the environmental impacts could be reduced by decreasing the ozone input, decreasing the treatment time and by simultaneously decreasing the treatment time and the ozone input. But, this parameter change in the ozonation process had an impact on the color striping %.

- The energy consumption and wastewater (pollution) related impacts were higher. For the selected impact categories, “Water depletion” and “human toxicity cancer effects” were higher.

- The impacts can be further reduced by reducing the liquor use on the ozone based process. This “gate-togate” LCA study results provide the necessary

solutions that could reduce impacts, find possible solutions, and remodify the technique or process.

6.2 Future Work:

Suggestions for the future work are given as per below:

Since decolorization using ozone gives promising results with regards to the reactive dyed cotton textiles, its application can further be extended to various classes of dyestuffs like vat dyes, acid dyes, basic dyes, natural dyes etc. which are also used for the coloration of textiles. This study can also be applied for evaluation on other textile materials like viscose, bamboo, cellulosic blends, wool and silk textiles etc. Another category of textiles which can be implemented and evaluated easily is decolorization of denim and indigo dyed goods, since the denim good also amount for a good market share.

The color removal process using ozone has induced damage to the fabrics in terms of more mechanical strength loss compared to the conventional process. Hence, it is necessary to improve the strength of the decolorized textiles using ozone by improving the design of the pilot scale reactor and studying effects of various additives like organic acids, reducing agents etc.

The color removal from the reactive dyed fabrics can be further enhanced with ozone based AOPs like (O_3/H_2O_2) system, O_3/Ultraviolet (UV) irradiation etc. The decolorization using ozone based process and reduction with glucose could be studied further by applying to reactive dyes having various chromophores and reactive groups, as well as on the different types of pigments. Also, it would be interesting to check the possibility of applying enzyme based processes, use of ecotechnologies like ultrasound assisted process, microwave treatment and/or their subsequent combinations with the other oxidation-reduction treatments. These chemical removal techniques could be applied to removal of textile prints, finishes (both durable and non-durable types) as well as textile coatings.

The chemical removal processes were aimed at developing technologies for the removal of colorants from textiles in order to facilitate the recycling process. To further investigate this, it may be interesting to study the dissolution of the color removed fabric for chemical recycling as end of life. Furthermore, the color removal technologies can be applied to the real life garment and their impact on the different types of discarded cellulosic textiles should be evaluated. The findings of our research can also be implemented in the development and commercialization of the color stripping process in the coloration industry.

Another aspect of the end of life which can be derived is to increase the life of the garment. Here, the color stripped textiles could be assessed to check the feasibility of reprocessing i.e(redyeing and refinishing) and finally their reuse aspect. Also, while developing these chemical removal process or technologies, it is also necessary to study the environmental assessment of these technologies simultaneously using the LCA tool in order to maintain sustainability in the textile supply chain.

Results from the PhD work

Paper publications

1) **Ajinkya Sudhir Powar**, Anne Perwuelz, Nemeshwaree Behary, Levinh Hoang and Thierry Aussenac, "Application of Ozone Treatment for the Decolorization of the Reactive-Dyed Fabrics in a Pilot-Scale Process—Optimization through Response Surface Methodology", *Sustainability (MDPI)* 2020, 12(2); 471 (IF: 2.576).
2) **Ajinkya Sudhir Powar**, Anne Perwuelz, Nemeshwaree Behary, Levinh Hoang, Thierry Aussenac, Carmen Loghin, Stelian Sergiu Maier, Jinping Guan and Guoqiang Chen, "Environmental Profile Study of Ozone Decolorization of Reactive Dyed Cotton Textiles by Utilizing Life Cycle Assessment", *Sustainability (MDPI)* 2021, 13(3); 1225 (IF: 2.576).
3) **Ajinkya Sudhir Powar**, Anne Perwuelz, Nemeshwaree Behary, Levinh Hoang, Thierry Aussenac, Carmen Loghin, Stelian Sergiu Maier, Jinping Guan and Guoqiang Chen; "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 (Sage)*, 2021, 16; 1–13 (IF: 0.814).

Oral presentations

Ajinkya Sudhir Powar, Anne Perwuelz, Nemeshwaree Behary, Levinh Hoang and Thierry Aussenac, "Color stripping of the reactive dyed fabric by conventional and ozone assisted process - a comparative study", *24th IOA World Congress & Exhibition on Ozone & Advanced Oxidation,* October 20-25, 2019, Nice, France

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