Università degli Studi di Torino
Department of Chemistry
Doctoral School of Sciences and Innovative Technologies
PhD Program in Innovation for the Circular Economy XXXIII Cycle

Application of the Life Cycle Assessment methodology for a sustainable management of resources in the transition to the Circular Economy

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Abbreviations

AC activated carbon
AOPs Advanced Oxidation Processes
AP Acidification Potential
CCS Carbon capture and storage
CE Circular Economy
CED Cumulative Energy Demand
CPC Compound Parabolic Collector
DoE Design of Experiment
EEA European Environment Agency
EoL End of life
EP Eutrophication Potential
EU European Union
FCD Faced centered design
FU Functional Unit
GAC granular activated carbon
GDP Gross Domestic product
GHG Greenhouse Gas
GLO Global
GWP Global Warming Potential
HREEs Heavy rare earth elements
ILCD International Reference Life Cycle Data System
ISO International Organization for Standardization
LCA Life Cycle Assessment
LCI Life Cycle Inventory
LCIA Life Cycle Impact Assessment
JRC Joint Research Centre
MH metal hydride
ODP Ozone Depletion Potential
OECD Organisation for Economic Co-operation and Development
PSA Pressure Swing Adsorption
REE Rare earth element
REO Rare earth oxide
SBO Soluble bio-organic substances

SDGs Sustainable Development Goals
TOC Total Organic Carbon
UNEP United Nations Environment Programme
UV Ultraviolet
UV-A Ultraviolet radiation in the range 315-400 nm
UV-B Ultraviolet radiation in the range 280-315 nm
UV-Vis Ultraviolet/visible light
WCED World Commission on Environment and Development
WWTP Wastewater Treatment Plant

Chapter 1: Objective and structure of the study

1.1 Problem setting

There is only one planet Earth, yet by 2050, the mankind, to sustain current lifestyles, will be consuming as if there were three (Sustainable Development Goals, goal 12). This sentence was taken from the United Nation website dedicated to the Sustainable Development Goals (SDGs), and provides an idea of how unsustainable our production/economic system is. In recent years, international organizations have made increasingly frequent reference to the problem of non-viable consumption of resources, with more negative prospects looking to the future. Just think that the global consumption of materials such as biomass, fossil fuels, metals and minerals is expected to double in the next forty years (*OECD, 2018)*. The downside is the increase in the amount of waste, indeed annual waste production is expected to increase by 70% by 2050 (*World Bank, 2018)*.

The challenges and risks faced in sectors such as rural development, environmental conservation, energy, climate change, human wellbeing etc., have allowed concepts like sustainability and sustainable development to evolve and be accepted at national and global level (Axelsson et al., 2011). One of the more comprehensive definition of sustainable development was given by the Brundtland Commission report in 1987. In this document sustainable development was defined as the development that should allow "to meet the needs and aspirations of the present without compromising the ability to meet those of the future" (WCED, 1987). Hence sustainable development also helps to find a balance between preserving the ecosystem and meeting human needs. In order to achieve a holistic sustainable development, it is of fundamental importance to recognize and subsequently harmonize together, what are the three pillars constituting this kind of development: environmental, social and economic sustainability.

The first is concerned with confining human activity within the carrying capacity of the ecosystem (such as materials, energy, land, and water, etc.) and places emphasis on the quality of human life (air quality, human health). The social sustainability focuses on the social well-being of the population, balancing the need of an individual with the need for the group (equity), public awareness and cohesion, and participation and utilization of local labours and firms. Moreover, improving operational profit and maximizing market value falls within the objectives of the economic sustainability. This also deals with replacing natural for manmade resources, reuse, and recycling (Olawumi and Chan, 2018).

Starting from the last decades, but with increasing intensity and determination in the recent years the European Union has been able to recognize the need to take note of the impact of anthropic activity on the environment and the pressing limitation of resources that the current economic model is causing. Since the mid-70s of the last century, European Union (EU) environmental policy has been guided by action programs aimed at defining the priority objectives to be achieved in a given period of time. These programs are a common strategy aimed at guiding the future actions of the EU institutions and the Member States, which jointly assume responsibility for its implementation and the achievement of its priority objectives. The vision behind the 7th Environmental Action Programme, adopted in 2014, is enclosed by the following statement:

"In 2050, we live well, within the planet's ecological limits. Our prosperity and healthy environment stem from an innovative, circular economy where nothing is wasted and where natural resources are managed sustainably, and biodiversity is protected, valued and restored in ways that enhance our society's resilience. Our low-carbon growth has long been decoupled from resource use, setting the pace for a safe and sustainable global society." (7th *Environment Action Programme to 2020)*

It is clear the decision to improve and pursue a different model of economy, that entails rethinking current production models and may at the same time have strong repercussions on the environment and society. This model is called Circular Economy.

The path to a sustainable development in Europe was defined, more precisely, and consolidated with the release of the "European Green Deal", at the end of 2019 (A European Green Deal, 2019). This is a strategy to guide European nations towards a climate-neutral, resource-efficient and competitive economy. The central role of circular economy is emphasized by the fact that one of the main pillars of this strategy is constituted by the "Circular Economy Action Plan" (EU Circular Economy Action Plan, 2020).

The path to sustainable development is dotted with difficulties and barriers. It is also necessary to take note of a real need in obtaining objective assessments of the quality of the actions taken. The adoption of integrated assessment methodologies allows improving the comprehensiveness of the sustainability assessment. In this context, Life Cycle Assessment (LCA) is considered crucial to provide support in better integrating environmental sustainability (Serenella et al., 2016*)*. This methodology is highly appreciated for its systemic approach which enable us to get information to the environmental impacts of the process/product studied.

1.2 Objective of the study

The aim of this thesis is to study the resources management through the application of a quantitative life cycle approach in the perspective of a transition towards a circular economy and environmental sustainability model.
The LCA methodology will be applied to some case studies concerning different areas: water, materials, energy, services.

The considered case studies, in addition to touching different topics, concern technologies at different readiness levels: laboratory-level research, prototype construction, pilot plants, processes and activities already underway. The general aim is to probe different cases, all united by the aim of reducing the "human impact" on the planet. The analyses carried out in this work made it possible to obtain information on the environmental impacts of the systems studied. Through the results obtained it is possible to identify the main environmental hotspots and, in a second time, this information can be used as a starting point to really improve the systems studied. In fact, usually, the decisions underlying both research projects and the development of new technologies and new types of business aiming at improving sustainability are based on subjective assumptions or ideas; the influence exercised by similar studies or realities, without, however, an objective evaluation, is often very relevant. Often this information is used and adapted to its context without a thorough analysis of the actual associated effects. For all these reasons it is essential to be able to analyse the environmental burden -

of what has been suggested, studied and on which one has economically invested - in a simple and objective way.

1.3 Structure of the study

This work is structured in 7 chapters. Chapters 2 and 3 constitute the theoretical framework of the thesis, while in chapters from 4 to 6 different case studies are developed, divided by topic. The description of the case studies is always reported with the same structure: it begins with a general introduction to the topic, an explanation of the process / system considered and the underlying technologies, these parts are followed by the LCA analysis and the work ends with the conclusions related with the specific case study. Finally, chapter 7 corresponds to the general discussion and conclusions.

Chapter 2 introduces the concept of Circular Economy, retracing its evolution in history and outlining the main aspects of this economic paradigm.

Chapter 3 aims to introduce the tool used in the thesis to assess the environmental profile of the process under study: the LCA methodology.

Chapter 4 deals with water resources, a specific step in the treatment of waste water has been taken into consideration; this step, through Advanced Oxidation Processes (AOPs), allows the degradation of pollutants, present in the water and not removed by conventional treatments. Three different case studies relating to this topic were evaluated. Given the common topic of the three case studies, the chapter, in its initial part, reports a quick presentation of the technologies subsequently analysed. In detail the three case studies assessed: (I) the environmental performance of specific heterogeneous zinc oxide photocatalysts; (II) the impacts associated with the life cycle of a pilot plant for water remediation, that uses sunlight to operate; (III) the performance of photo-Fenton catalysts, synthesized using waste materials.

Chapter 5 concerns topics related with the general energy issue. The first part of this chapter takes into consideration the environmental impacts of the production process of porous carbon materials, which can have different applications such as carbon capture and storage (CCS) technologies or more generally in gas purification. The second case study assess the environmental impacts of an hydrogen compression system - in detail a metal hydride compressor is analysed. Hydrogen is considered an energy carrier to achieve a sustainable alternative to the use of fossil fuels, but the technologies necessary for its development require careful evaluation. The compression phase, necessary for hydrogen storage, often causes high energy consumption, which leads to an increase in environmental impacts and a decrease in the overall energy balance.

Chapter 6 groups case studies related to circular economy business models. In the first work, the LCA analysis was applied to compare the impacts generated by the use of disposable vs reusable cups from an environmental point of view, cups that find their use in restaurants, pubs and catering services. The last case study examined the environmental profile of a business model based on the garment rental service. The analysis has taken into consideration a specific category of garments (formal dresses), comparing the rental business model with an online purchase model.

Chapter 7 reports a summary of the conclusions of each of the previous case studies. Here the general conclusions on the relationship among LCA, circular economy and environmental sustainability are also outlined.

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Chapter 2: Circular Economy

This chapter aims to outline the concept of circular economy, starting from its origins and to understand the potential of this paradigm. In the following section, an attempt was made to describe the background of the circular economy, why and where the concept originated from, what the concept and transition mean and the possible advantages of moving to more circular models. This theoretical framework takes a rather general approach to the concept and its applications, as it is not the aim of this thesis to go into detail on these aspects of circular economy.

2.1 The current economic model and its drawbacks

Before going on to define the circular economy paradigm, it is necessary to clarify which is the current economic model that has allowed the development of society up to the present day.

Since industrialization, the economic paradigm of the global industrial setting has been based on the same processes defined as an open ended linear economy, which consist in extracting resources and disposing of them after use (Andersen, 2007; World Economic Forum, 2016). One of the reasons that has favoured the consolidation of this economic model is to be found in the abundance of material and energy resources that industrialized nations have experienced so far. This abundance is because the consumers of resources have been concentrated in the more developed regions, instead the material inputs have always been purchased from the global arena. This context meant that the cost of resources was considerably lower than the cost of human labour. As a result, the producers have been motivated to adopt business models that relied on extensive use of materials and economized on human work (Sariatli, 2017; Ellen MacArthur Foundation, 2013). The increase in GDP, from 23 trillion euros in 1990 to 78 trillion euros in 2015, is a sign of how the linear economy allows to thrive in terms of industrial and economic growth (Stuchtey et al., 2016). The natural consequence of low cost material involves neglecting all possible processes related to recycling, reuse as well as underestimating the problem of waste. The essence of the linear economy is generally summarized as take - make – dispose (Sariatli, 2017). However, this development model leads to an increase in negative externalities related to consumption styles and production patterns (World Wildlife Fund 2016). For some decades it has therefore been clear that the traditional linear extract-produce-use-dump material and energy flow model is unsustainable (Frosch and Gallopoulos, 1989).

2.2 Circular Economy: origins and definition

The circular economy model emerged as a solution to the abovementioned stressing issues, generated by the linear model. This new wave of conducting business starting a path towards sustainability is seen as disrupting the current linear model, according to Stuchtey et al. (2016).

It seems that Pearce & Turner (1990) first used the term circular economy formally. In the work *"Economics of Natural Resources and the Environment"* they took a critical look at the traditional linear economic model and developed a new economic paradigm, named the circular economy. The bases of their considerations were modelled on the principle that "everything is an input to everything else" and on the application of the principles of the first two laws of thermodynamics[1]. Their work and line of thought were inspired by the work of Kenneth Boulding *"Environmental Quality in a Growing Economy"* (1966). In this work he discussed the biophysical limits of the present economic system built on overconsumption and a growing ecological deficit.

Our present interpretation of the circular economy has been influenced and shaped by a growing body of literature from various disciplines, literature developed in the last few decades (Lieder and Rashid, 2016). Below are quickly introduced some research disciplines that have contributed to the development of the circular economy concept.

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[1] The first law of thermodynamics stipulates that neither energy nor matter can be created or destroyed and therefore any natural resources used will return to the environment in the form of solid waste or emissions. According to the second law of thermodynamics, there are physical boundaries that prevent the set-up of a system in which all waste is recycled and transformed back into natural resources with 100% efficiency (Pearce & Turner, 1990; Čiegis & Čiegis, 2008).

Industrial ecology is the study of material and energy flows through industrial systems. This research discipline is supported by a systems approach and involves a holistic perspective when dealing with human economic activity and sustainability (Garner and Keoleian, 1995). The principles of industrial ecology find application in the industrial symbiosis, that through the exchange of resources and by-products aims to develop synergistic and profitable collaborations between companies (Chertow, 2000).

A different approach aimed at transforming the industrial material flows is given by the *Cradle to Cradle* design. Unlike other concepts focusing on implementing environmental sustainability, this approach does not aim to directly reduce or eliminate the environmental impacts of human activity; cradle-to-cradle design endeavour to maintain and even enhance the value, quality and productivity of resources in order to have a net positive environmental effect (Braungart et al., 2006; Ankrah et al., 2015).

In the mid-1990s a research field called *product-service systems* (PSS) is emerged; the basic idea is that a shift towards business models that focus on offer a service rather than the product sold can improve competitiveness and deliver environmental benefits (Tukker, 2015). According to Tukker & Tischner (2006), PSS "*consist of a mix of tangible products and intangible services designed and combined so that they jointly are capable of fulfilling final customer needs*".

The *Blue Economy* is another relevant concept that addresses the business case for sustainability and resource efficiency. In this approach, innovation is considered to be a fundamental lever in guiding businesses towards a transformation of practices influenced by the design and functions of natural ecosystems. One example, taken from the official manifesto, states "*using the resources available in cascading systems, (…) the waste of one product becomes the input to create a new cash flow*" (Pauli, 2010).

As previously said, the circular economy model was influenced by the concepts described above. Several authors have provided resource-oriented definitions and/or interpretations. The main aspects, which make up the CE concepts, seek to emphasize the need to create closed loops of material flows, reduce both the consumption of virgin resources and harmful environmental impacts (Rizos et al., 2017).

Zhijun and Nailing (2007) present one definition of circular economy in Sustainable Science, built on three principles: *(I) reducing resource use* - minimizing the use of raw materials and energy as well as decreasing pollution, *(II) reusing* - using the product for other applications after its original consumption and in that way, avoid waste, and *(III) recycling* - using the product many times.

One of the most-frequently cited definitions that incorporate elements from various different disciplines has been provided by the Ellen MacArthur Foundation (2013) which describes the circular economy as "*an industrial system that is restorative or regenerative by intention and design. It replaces the 'end-of-life' concept with restoration, shifts towards the use of renewable energy, eliminates the use of toxic chemicals, which impair reuse, and aims for the elimination of waste through the superior design of materials, products, systems, and, within this, business models*".

Another definition is given by Korhonen et al. (2018); this definition is built by critically considering the concept of CE from the perspective of sustainable development and its three dimensions, economic, environmental and social. "*Circular economy is an economy constructed from societal production-consumption systems that maximizes the service produced from the linear nature-society-nature material and energy throughput flow. This is done by using cyclical materials flows, renewable energy sources and cascading-type energy flows. Successful circular economy contributes to all the three dimensions of sustainable development. Circular economy limits the throughput flow to a level that nature tolerates and utilises ecosystem cycles in economic cycles by respecting their natural reproduction rates.*"

A work published by Kirchherr et al. (2017) makes a critical and thorough analysis of the definitions of circular economy present in literature. At the end of the work they give a comprehensive definition of CE with the hope that it will be a conceptual basis for future works: "*We defined CE within our iteratively developed coding framework as an economic system that replaces the 'end-of-life' concept with reducing, alternatively reusing, recycling and recovering materials in production / distribution and consumption processes. It operates at the micro level (products, companies, consumers), meso level (eco-industrial parks) and macro level (city, region,* *nation and beyond), with the aim to accomplish sustainable development, thus simultaneously creating environmental quality, economic prosperity and social equity, to the benefit of current and future generations. It is enabled by novel business models and responsible consumers".*

2.3 Some key concepts on Sustainability and Circular Economy

The term "sustainability" remains an open concept currently, with myriad interpretations and context-specific understanding. One recurrent description of "sustainability" in literature employs three interconnected "pillars", "dimensions", "components", etc. encompassing Economic, Social, and Environmental factors or "goals" (Purvis et al., 2019). To cope with environmental impacts, politicians and businesses have set themselves the goal of achieving a balance between these pillars. The three pillars of sustainability making up the so-called sustainability triangle or The Triple Bottom Line, also called People, Planet, Profit (Circular Ecology, 2016*)*. Often the concept of sustainability, described by these pillars, is presented in the form of three intersecting circles of society, environment, and economy, with sustainability being placed at the intersection, as shown in Figure 1.

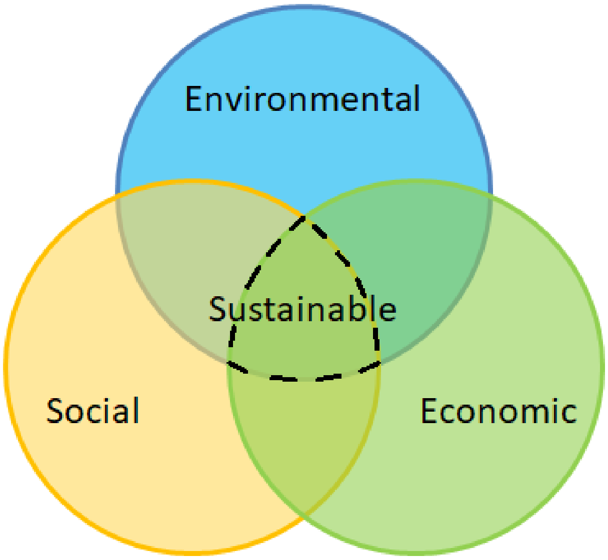

Figure 1. The figure illustrates the three pillars of sustainability, The Triple Bottom Line.

The Environmental Sustainability (Planet), denotes the consumption of natural resources at a sustainable rate, The Economic Sustainability (Profit), relates to efficient and responsible resource use for a sustainable and profitable operation and The Social Sustainability (People), considers maintaining social well-being. To achieve true sustainability it is of primary importance that politicians, businesses and any decision makers balance economic, social and environmental sustainability factors in equal harmony (Circular Ecology, 2016).

As already mentioned, the circular economy paradigm arises as an alternative to the traditional linear model. Figure 2 provides a graphical representation of how the circular model closes the cycle with respect to the linear model. It is possible to observe the various steps involved in circular economy aiming at eliminate waste and reduce the use of resources.

Figure 2. The figure illustrates the linear open model (on the left) and the circular closed loop model (on the right). (European parliament, 2015)

According to Pollard et al. (2016) oftentimes the linear model efforts toward sustainability focused to prevent harm or solely to minimize environmental or social liabilities, when instead the closed system of circular economy urges to creatively rethink it.

Rizos et al. (2017) identify eight processes that can fit under the umbrella of circular economy and allow to reach a better understanding of this model. They also grouped these processes in three different categories, namely I) using fewer primary resources, II) maintaining the highest value of materials and products and

III) changing utilisation patterns. Since many of the component elements of the processes are often interconnected, it should be emphasized that these three categories are not reciprocally exclusive. Table 1 reports the three categories with the corresponding processes.

CATEGORIES	PROCESSES
Use less primary resources	**Recycling**
	Efficient use of resources
	Utilisation of renewable energy sources
Maintain the highest value of materials and products	**Remanufacturing, refurbishment and re-use of products and components**
	Product life extension
Change utilisation patterns	**Product as service**
	Sharing models
	Shift in consumption patterns

Table 1- Main circular economy processes (Rizos et al. 2017)

Below is reported a brief description of the identified processes.

Recycling. According to United Nations et al. (2003) recycling has been defined as "the re-introduction of residual materials into production processes so that they may be re-formulated into new products''. The definition allows to go beyond the classic concept of recycling as mere recovery of materials, the key factor is the possibility to redirecting the recovered materials towards their next lifecycle. To effectively re-introducing materials in the production process it is important to achieve a high quality of recycling. The environmental benefits of recycling are to be found in reducing the extraction of primary resources (EEA, 2016).

Efficient use of resources. The efficiency of resources use is another process that can lead to the use of less raw materials. This process is linked to the concept of cleaner production, which aims to achieve greater process efficiency by optimizing the materials and energy demands (UNEP & Sida, 2006). The concept of cleaner production can involve both the careful use of resources and the replacement of resources that are hazardous or have a short life span (Nilsson et al., 2007). Another concept link to the efficient use of resources is the eco-design. Eco-design can incorporate not only elements related to recycling, remanufacturing and product life extension, but also other aspects such as dematerialisation and material selection (Almeida et al., 2010).

Utilisation of renewable energy sources. The increasing use of renewable energy sources is a core requirement for the transition to circular economy. The energy generation by mean the combustion of fossil fuels is by definition not restorative.

Remanufacturing, refurbishment and reuse of products and components. The terms of regeneration, renewal and reuse refer to strategies / activities put in place to give a next life to the products recovered after their use. In the category of maintaining the value of materials, both the terms of refurbishment and remanufacturing are used. Both indicate a way in which the main parts of the products are restored. Remanufacturing entails the idea of more in-depth process aiming to restore the product into an as-new condition. While refurbishment is understood as referring to less in-depth restoration of a product or a component's value (Van Weelden et al., 2016). The term reuse of a product is intended to indicate the direct re-usage or re-sale of a whole product or also a part of it (JRC, 2011). All these processes can allow companies to earn a second or a third (or more) income from the sale of the product and by adopting this approach it is possible to modify and diversify the revenue streams.

Product life extension. The concept of product life extension is strongly correlated to the previously mentioned economic processes. If we consider the remanufacturing concept the approach of life extension is implemented through increasing the emphasis on the design phase of the product (Bocken et al., 2016a). This translates for example into standardisation of components in terms of size or material. In addition to the approach based on the design of products for remanufacturing or reuse, another possibility, to achieve the goal of extending life, derives from the quality of the materials (durability) and attention to customer service (Bocken et al., 2016b). There are also some concerns regarding the net benefits of the product life extension. In particular, it has been suggested that in some cases this process might postpone the market penetration of new technologically advanced products, which, for example, show improvements in terms of energy or fuel consumption (Demailly & Novel, 2014).

Product as service. Product as a service challenge the traditional business approach of selling tangible products, the concept is to offer the product as a service. It means that the company retains the ownership of the product in question and offers the customer access to the product. By applying this business model, the company manages to keep the resources at its disposal. This practice motivates the company to repair and maintain the product in use for a longer period of time, allowing to obtain an environmental benefit (Accenture, 2014). Some strategies to implement the product as a service are the practicing of leasing, renting, pay-per-use or performance-based business models

Sharing models. Sharing models facilitate the sharing of under-utilised products and can therefore reduce demand for new products and their embedded raw materials. These models are inextricably linked to the circular economy concept and can also contribute to the creation of genuine social capital (JRC, 2016). With the current economic model, people feel the need to own a product, such as a car therefore in order for business models, such as products as a service and sharing economy, to thrive and spread, a change in consumer mentality is needed (Bocken & Short, 2016b).

Shift in consumption patterns. The change in consumption patterns is something that people are already experiencing, this change has occurred thanks to the technological progress achieved in the last decades. Many consumers choose products or services that deliver utility virtually instead of materially (examples digital books, smart phones, music and online stores). Although these shifts can in turn lead to resource savings and productivity gains, it is necessary to keep in mind the possible rebound effects and high energy consumption of the data center; these two aspects can generate concern and limit the benefits offered by these products and services (Whitehead et al., 2014).

Although it is generally agreed that these models and processes have the potential to radically transform our consumption patterns to the benefit of the environment, given the possible generation of negative and disadvantageous effects, a more in-depth analysis of the environmental benefits and impacts associated with the implementation of these processes becomes of primary importance. This kind of analysis allows us to take note of the progress made, towards greater sustainability, by following the principles of the circular economy.

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Chapter 3: Life Cycle Assessment

This chapter, directly relating to the need described above for methodologies able to assess environmental impacts, is devoted to introducing the theoretical framework of Life Cycle Assessment analysis.

For the purpose of this work the choice to use LCA is not accidental, but based on the considerable number of publications and case studies that have chosen this methodology as one of the main tools for assessing environmental impacts.

3.1 Introduction and definition

In general terms, LCA is a science-based methodology, that allows the analysis and assessment of the environmental impacts of product systems; this analysis takes into account the whole life cycle, from the extraction of raw materials and fuels to the production of the investigated objects and the disposal or recycling of the same (Klöpffer, 2014).

The LCA methodology is defined by the International Organization for Standardization (ISO) standards 14040 and 14044: the first describes the principles and framework (ISO, 2006a), while the second presents the requirements and guidelines (ISO, 2006b) on how to conduct Life Cycle Assessment.

The process of defining LCA by ISO started in 1997, with the first draft of the standard of the series 14.04X. According to ISO LCA is:

"A technique for assessing the environmental aspects and potential impacts associated with a product by:

- *compiling an inventory of relevant inputs and outputs of a product system,*
- *evaluating the potential environmental impacts associated with those inputs and outputs,*
- *interpreting the results of the inventory analysis and impact assessment phases in relation to the objectives of the study.*

LCA studies environmental aspects and potential impacts through the product's life cycle (from cradle to grave), from raw material acquisition to production, use, and final disposal".

This definition highlights the need of taking into account in the analysis the entire product chain and the potential consequences on the environment, based on the compilation of a mass and energy balance of the product system.

The supervision necessary to support the consistency and quality assurance of the LCA studies and the main guiding role of the orientation is carried out by the International Reference Life Cycle Data System (ILCD) handbook. The ILCD Handbook is a series of technical documents providing guidance for good practice in Life Cycle Assessment which is produced by European Commission (ILCD, 2010a).

The following data has been drafted from ILCD handbook and ISO standards for a short guide over modelling frameworks and method approaches to the LCA study.

3.2 Methodology

According to the ISO standards, the LCA methodology is carried out in four distinct phases (Figure 3): Goal and Scope definition, Life Cycle Inventory analysis (LCI), Life Cycle Impact Assessment (LCIA) and Interpretation. All four phases are interconnected and performed iteratively.

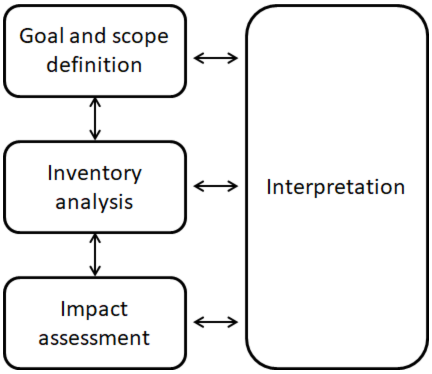

Figure 3. The four phases of LCA. (ISO, 2006a)

3.2.1 Goal and scope definition

In this stage the purpose, the scope and main hypotheses considered in the study are defined; since these elements are the key point of the entire work, this phase is very important and delicate.

It is necessary to define the goal of the study, as well as the reasons beyond its realization, the kind of decisions that will be made from the results obtained, and the intended audience (for a company or to inform the general public or an institution).

Afterwards, the scope of the study is defined. This implies, among other elements, defining the system, its boundaries, the quality of the data used, the main hypothesis, as well as the limitations of the study and LCIA methodology with the chosen impact categories. The definition of the functional unit is a key issue in this first part of the analysis. The functional unit expresses and quantifies the function (performance characteristic) of the products and provides a reference to which the inputs and outputs are related.

To carry out the environmental assessment, physical systems are described using models called *product systems*; these are simplified models of the key elements of the real system. The "system boundary" allows defining the set of criteria that specifies which unit processes are considered in the product system. Indeed, when defining the system boundary, different life cycle stages, unit processes and flows must be considered (e.g. raw materials acquisition, inputs and outputs in the main manufacturing sequence, transportation, use and maintenance of products, disposal of process wastes and products etc.). Sometimes, the initially defined system boundary will subsequently need to be resetting.

3.2.2 Inventory analysis

This is the phase of the LCA involving the compilation and quantification of inputs and outputs for a product throughout its entire life cycle. To make the collection of the data easier, the system under study is split up in several subsystems and unit processes (Figure 4) and the inputs and outputs are grouped in different categories.

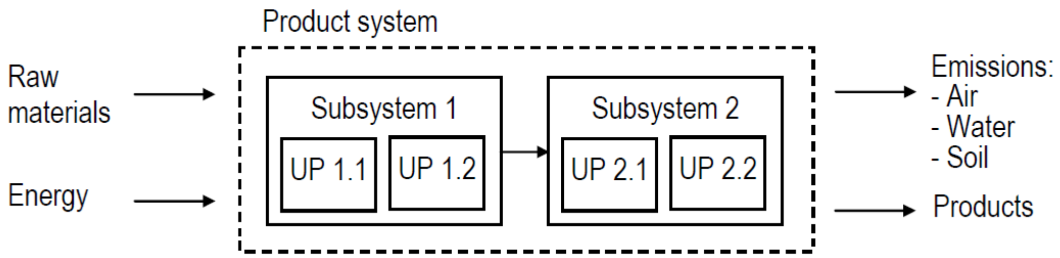

Figure 4. Framework of the model of a generic product system. UP: unit process.

As already mention the product system consists in the construction of a model of the reality that shall represent all the exchanges among the single unit processes of the analysed system. These exchanges with the environment are represented as elementary flows crossing the system boundary. The main challenge of this step is the data collection.

The input and output data (e.g. energy and raw materials consumed, emissions to air, water, soil, and solid waste produced) shall be referenced to the functional unit and they are calculated for the entire life cycle of the product or service.

3.2.3 Impact assessment

In this phase, the objective is to understand and evaluate the magnitude and significance of the potential environmental impacts of the product system analysed. The large number of resources and emissions that make up the inventory is translated into a handful of environmental impact categories (expressed at midpoints or endpoints,[2] see Figure 5). As a consequence, the quality and reliability of the data collected during the inventory analysis is a key issue for the overall assessment.

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[2] A midpoint is considered a point in the cause-effect chain (environmental mechanism) of a particular impact category, prior to the endpoint (where the environmental effect occurs). The characterization factors for midpoints reflect the relative importance of an emission or extraction in a Life Cycle Inventory (LCI) (e.g., global warming potentials defined in terms of radiative forcing and atmospheric half-life differences) (Bare et al., 2000).

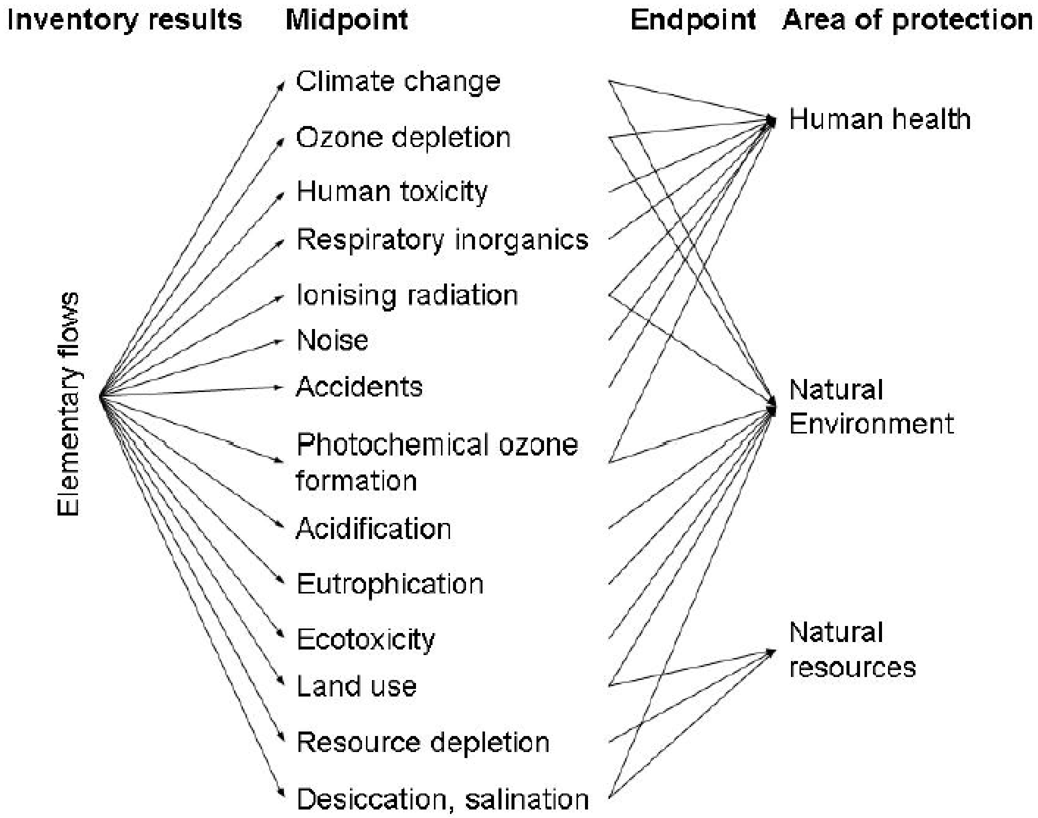

Figure 5. Framework of impact categories for characterization modelling at midpoint and endpoint (=Area of Protection) levels. (ILCD, 2010b).

According to ISO 2006a LCIA consists of four steps that are briefly described below (only the first two are mandatory, the others are optional, and their implementation depends on the goal and scope of the LCA study).

- The classification consists in grouping the environmental interventions (resources consumed and emissions to the environment), identified in the inventory analysis, in different impact categories or indicators; the criterion is based on the environmental effects they are expected to produce (e.g. the emissions of CO_2 and CH_4 are classified in the category Climate Change).
- The characterization phase consists in weighting the previous results by multiplying them by characterization factors. The characterization factors are used to express properly the different magnitude of each substance in determining the impacts on a specific impact category. For each of the latter an aggregated result is produced, in a given unit of measure. For

example, Climate Change is calculated in kg CO_2 eq., from the contribution of CO_2 and CH_4 emissions, among others. At the end of these first two phases a set of indicators is obtained which allow to define the so-called environmental profile of the system.

- The third step is normalisation, where the characterised impact scores are associated with a common reference, such as the impacts caused by one person during one year in a stated geographic context.
- The last step, called weighting, allows to obtain the impact expressed as a single score, through weighting factors. Must be specified that these factors are based on subjective value judgment and the weighted results are a simplification of the real problem. The advantage of this stage is that the different impact categories are converted to a numerical score of environmental impact with a common unit of measurement, thus making it easier to make decisions.

3.2.4 Interpretation

According to ISOs, the last phase of an LCA is interpretation. In this phase the findings of either the inventory analysis or the impact assessment, or both, are evaluated in relation to the defined goal and scope in order to reach conclusions and recommendations. Furthermore, the results are analysed in terms of accuracy and completeness of the data and the assumptions.

3.3 LCA software and databases

To simplify and support the execution of an LCA analysis, there are various dedicated software. These tools allow to cover every phase of the life cycle from the extraction of the raw material until the end of the product life cycle and at the end of the analysis to obtain the environmental impact associated with the product system.

To the purpose of this thesis, Life Cycle Assessment has been performed by means of the LCA software: SimaPro.
SimaPro is developed and distributed by Pré Consultants since 1990 and the software tools include:

- a user interface for the modelling of the product system;
- a life cycle unit process database;
- an impact assessment database, with data supporting several LCIA methods;
- a calculator for combining the LCI numbers from the databases according to the product modelling chosen.

There are several databases in order to facilitate the collection of all data to compile the inventory. The Ecoinvent database (versions 3.3 and 3.6) was used in this study; it is one of the largest and most used database worldwide and provides over 10000 LCI datasets in many areas, such as energy supply, agriculture, chemicals, construction materials, fuels and biofuels, wood, electronics, waste treatment. The Ecoinvent database relays in part on data from companies and partly on previous studies.

3.4 Key aspect of LCA

3.4.1 Decision-context

The goal definition is the first phase of any life cycle assessment, independently whether the LCA study is a complete LCA study to be published or is limited to the development of a single unit process data set. Provide a clear goal and scope is hence essential for a correct interpretation of the results. As previously reported, the goal definition shall explain the reasons for carrying out the LCA study, name the drivers and motivations, and especially identify the decision-context(s).
The decision-context plays an important role in the modelling of the whole system. At a methodological level it allows to define the most appropriate methods for modelling the inventory: defining the LCI modelling framework (i.e. “attributional” or “consequential”) and the related approaches (i.e. “allocation” or “substitution”) (ILCD, 2010).

According to ILCD (2010), three different decision-context situations of practical relevance in LCA can be differentiated, called situation A, B, and C.

Situation A): the purpose of the LCA analysis is to support decision at micro-level (e.g. for product-related questions). The extent of changes that the decision implies cause none or only small changes in the background system or other systems of the economy that would not directly or indirectly structurally change it (structural changes means e.g. the installation of new production plants or even technologies). Generally, this situation refers to a small-scale study with a short/medium term (up to 5 years).

Situation B): also in this case, LCA serves as support to a decision, but unlike the previous case, the extent of changes that the decision implies in the background and in other systems are extensive (i.e. structural changes). The decisions are on a meso or macro-level, such as for strategies (e.g. raw materials strategies, technology scenarios, policy options, etc.). This type of study takes into consideration a medium-long period of time (from 5 years to above).

Situation C): The LCA is not used to support a specific decision, but it is purely descriptive accounting / documentation of the analysed system. For this case, two further situations can be possible: the studies that want to include any existing interactions outside the system represent the Situation C1 (e.g. considering recycling benefits or avoided production for co-products); while, the studies that aim at analysing the system in isolation, without considering such interactions, are defined as Situation C2.

Table 2 shows a scheme of the decision-context situations:

		Kind of process-changes in background system / other systems	
		None or small-scale	**Large-scale**
Decision support?	**Yes**	**Situation A** **"Micro-level decision support"**	**Situation B** **"Meso/macro-level decision support"**
	No	**Situation C** **"Accounting"** **(with C1: including interactions with other systems, C2: excluding interactions with other systems)**	

Table 2. Decision-context situations according to the ILCD Handbook Guidance (Source: ILCD, 2010)

3.4.2 Attributional and consequential modelling

The decision-context allows to define the LCI framework by distinguishing between attributional and consequential modelling.

Attributional LCA has retrospective, accounting or cause-oriented features. This LCA modelling framework is conducted to learn about existing impacts, to identify areas for improvement or to make market claims (Schrijvers et al., 2016).

Instead a LCA model focused on prospective, effect-oriented, that studies the effects of changes is defined as consequential. This approach is applied to obtain information on the direct and indirect changes in the environmental impact due to a decision or a change in demand for a product (Schrijvers et al., 2016).

The difficulties in modelling through these two approaches lay on the choice of data (current or marginal data). Also the management of multifunctionality issue is strongly related with the choice of the appropriate LCI modelling framework (see paragraph 3.4.3).

3.4.3 Dealing with multifunctionality

According to ILCD (2010) a process is defined multifunctional if provides more than one function i.e. delivering several goods or services (often also named simplified co-products). For example, during the electrolysis of sodium chloride solution, sodium hydroxide, chlorine gas and hydrogen gas are co-produced. Another example of multifunctionality is the co-treatment of different wastes in a waste incinerator; in that case the process provides several co-services of treating distinct wastes. Usually, most of the LCA studies are focused in the specific life cycle of only one of the co-functions (e.g. only of the sodium hydroxide solution or the chlorine gas, of the above example). To perform this analysis, it is necessary to isolate the inventory of the specific function: only the appropriate inputs and outputs of the process are to be counted.

The multifunctionality can be solved by referring to different approaches. The choice of the most appropriate approach depends among others on the goal situation, available data and information, and the characteristics of the multifunctional process or product.

To solve multifunctionality problem ISO 14044:2006 presents a hierarchy of different approaches; all these are placed under the heading "*Allocation*".

Subdivision of multifunctional processes - refers to the collection of data individually for those of the mono-functional processes that are contained in the multifunctional process. In other words, this approach indicates to sub-divide the unit process into mono-functional processes.

System expansion (including substitution) - this approach can be implemented into two ways: system expansion in stricter sense or system expansion with substitution. In general terms this approach means to add another not provided function to make to system comparable i.e. system expansion in stricter sense (Figure 6); in this first methodology the co-functions of the process are included in the functional unit.

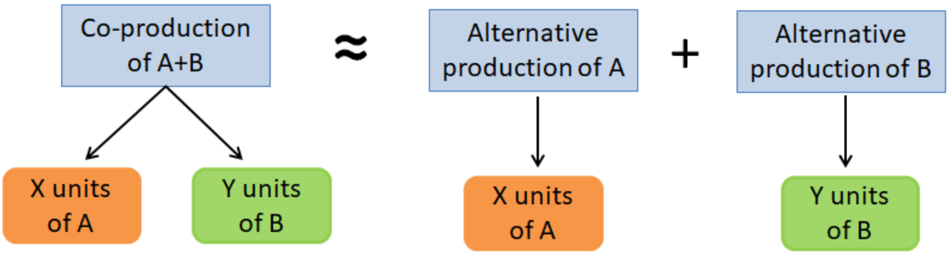

Figure 6. System expansion in stricter sense; the FU will refer to the production of A plus the production of B.

The second way suggest subtracting the not required function(s) with an alternative way of providing them i.e. system expansion with substitution (Figure 7); Substitution means to subtract the inventory of another system from the analysed system. The practice of this method is common when the co-product of a system can replace one or more other products: for example, heat from co-generation to substitute heat from oil.

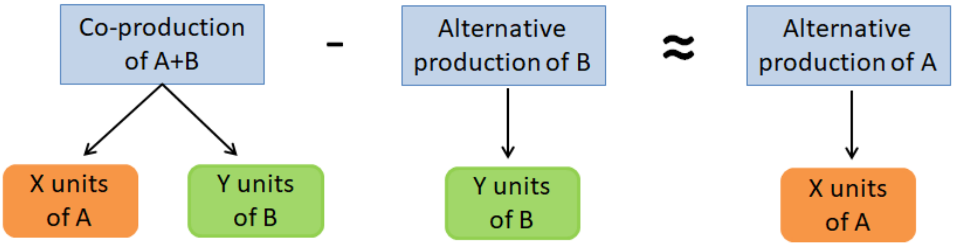

Figure 7. System expansion with substitution. The not required co-functions, production of B, is substituted (subtracted).

Allocation – also called **partitioning**, is the last step in the ISO hierarchy, this approach allows to solve multifunctionality by partitioning the inputs and outputs between the co-functions according to some allocation criterion (e.g. element content, energy content, mass, market price etc.). It should be noted that it is often difficult to clearly identify the most appropriate allocation key.

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Chapter 4: LCA case studies related to water treatments

The purpose of this chapter is to introduce the topic related to water resource, in particular the wastewater treatments; essential treatments to make water reusable both by people and for any activity (industrial, agricultural,...).

Since the theme of wastewater treatment has played an important role, both in terms of commitment and knowledge gained, it was decided to make a slightly more in-depth introduction related to the problem in question and the technologies involved. This introduction explains why this water resource is so important and what are the main problem related to it. So the focus will first shift to wastewater treatments, to present the Advanced Oxidation Processes (AOPs), a group of technologies increasingly used to decontaminate water. Of this group, only the technologies assessed in the following case studies are presented in detail, namely heterogeneous photocatalysis and photo-Fenton processes; of these technology the fundamental mechanisms, advantages and drawbacks are described, as well as the state of the art.

After this general introduction, the LCA analysis of three case studies relating to AOPs are presented and discussed.

4.1 Introduction

Water is one of the essential elements required for life to exist. This resource is vital for all global ecosystem. Water not only provides the basic needs for organisms on the planet, but it is also the key to economic development, as it is used in agricultural, industrial, domestic, recreational and environmental activities.

The water resource lends itself easily to the implementation of the circular economy principles. In order to avoid waste and ensure that the quality of this resource is maintained, for years research has moved in the direction of trying to "close the water cycle". In the literature, the terms water recycling and water reuse are often used synonymously and refer to the use of properly treated waste water for other purposes (Lazarova et al., 2012). However, the facts show that we face a global water crisis and more than ever before there is a need to progress rapidly towards a circular approach applied to the water resource.

Fresh water reserves are limited, similarly to other natural resources. Indeed, less than 1% of the planet's water is available for human consumption. Population growth, socio-economic development and changing consumption patterns have led to an increase in water demand of 1% per year since 1980 (UNESCO, 2019). The industrial and domestic sectors are considered the main players in the increase in global water demand, until 2050 an increase of 20-30% above the current level of water use is expected. It is estimated 4 billion people suffer from severe water scarcity during at least one month a year and 2 billion people worldwide live in a country under severe water stress. Stress levels will continue to increase as demand for water grows and the effects of climate change intensify (UNESCO, 2019). According to a projection of the European Environment Agency, a marked increase in meteorological droughts is estimated by the middle of the 21st century in most of Europe, especially in southern Europe (EEA, 2020).

The problem is not only linked to ever increasing volumes of water required by the population, but also to the quality of the same. In the third world about 80% of all infectious diseases are directly related to the quality and quantity of drinking water and it is estimated that over 1.2 billion people worldwide do not have access to drinking water supplies (UN, 2003). Even in the so-called developed countries, water quality represents a serious problem, in fact in Europe data show that 20% of surface water is seriously at risk of pollution (EU, 2000).

Having acknowledged the numerous and growing pressures on water resources, it is vitally important to apply legislative and technical instruments that effectively address these problems. Such actions should aim to maintain this resource so as not to penalize future generations; the importance of access to clean water and sanitation is embedded in Goal 6 of the United Nations' Sustainable Development Goals (SDGs, 2015).

"It is easy to take water for granted. Clean water comes out of a tap, we use the water and then 'dirty' water disappears down the drain. In this way, the water that leaves our homes, schools and workplaces is contaminated. For most European citizens, such waste water is collected, transported and then treated at an urban waste water treatment plant, to remove

components harmful to the environment and human health, before the water is returned to nature" (EEA, 2018).

Supplying clean water and collecting waste water has required huge investment across Europe in recent decades and further investment will still be needed. The reason behind these huge investments must be sought in the difficult challenges posed by the impacts of climate change, as well as the presence of antibiotics and other micro-pollutants in waste water; these challenges can only be faced by using appropriate technologies and treatment plants (EEA, 2019). Laws and regulations, such as the European Water Framework Directive (EU, 2000) address many types of pollutants not amenable to conventional biological treatments, due to their toxicity, chemical stability or difficulty in being completely mineralised. Most of these persistent pollutants are organic substances and the degradation must be demanded to other non-conventional technologies, such us the so-called Advanced Oxidation Processes (AOPs) (Michael et al., 2016; Stefan, 2018). AOPs are based on the in situ generation of strong oxidants (such as $OH^{\cdot}$, $SO_4^{\cdot -}$),capable of oxidizing the organic compounds. Many methods are used to generate such oxidant species (Parsons, 2004):

- Heterogeneous photocatalysis
- Ozonation processes
- Fenton and photo-Fenton processes
- Hydrogen peroxide/UV processes
- Photoelectrocatalysis processes
- Ultrasound processes
- UV/electron beam irradiation processes

It must be highlighted that the application of AOPs to wastewater treatment makes use of large amounts of reactants as hydrogen peroxide or ozone, as well as considerable amounts of energy, altogether leading to high operation costs. Therefore their application seems advisable only when it is not possible to use cheaper options and at the same time the implementation of these methods should be supported by careful environmental impact studies. According to Andreozzi et al. (1999) the AOPs are suggested as suitable processes to treat water with small amount of Chemichal Oxygen Demand (COD), namely below 5 g per litre (Figure 8), since higher COD contents would require the consumption of too large amounts of expensive reactants. When COD contents are substantially high, other techniques such as wet oxidation and incineration, are more suitable for wastewaters treatment.

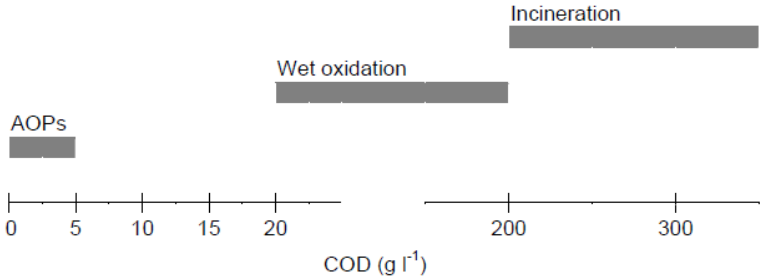


Figure 8. Suggested technologies for wastewater treatment according to COD contents. (Andreozzi et al., 1999)

In this chapter, only the heterogeneous photocatalysis and photo-Fenton methods are described in detail, as they are the processes behind the three case studies presented below.

4.1.1 The oxidant species

One of the main oxidizing species generated by the AOP is the hydroxyl radical (OH·). This species, characterized by a short-life, is an extremely powerful oxidant capable of attacking almost any organic molecule. Another useful attribute of hydroxyl radical is the low selectivity of attack. This is an important feature for an oxidant used in wastewater treatment, as it allows it to react with a large number of substances (Andreozzi et al. 1999).

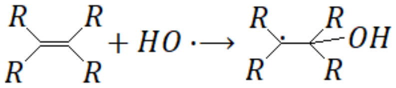
Hydrogen abstraction is the main mechanism by which OH· attack organic molecules (eq. 4.1). This reaction generates organic radicals R·. In the presence of oxygen these radicals may react with O_2 to give peroxyl radicals (ROO·), or oxyl radicals (RO·), as seen in Eq. 4.2, which can be ultimately degraded into CO_2, H_2O, and organic acids. It should be noted that a consistent number of competitive reactions occurred and can negatively affect the oxidation process (Wang & Xu, 2012).

Yet other mechanisms of oxidative degradation are electron transfer to $OH^{\cdot}$ radicals (eq. 4.3) and electrophilic addition to unsaturated bonds (eq. 4.4) (Legrini et al. 1993).

$$RH + HO\cdot \longrightarrow R\cdot + H_2O \tag{4.1}$$

$$R\cdot + O_2 \longrightarrow ROO\cdot \longrightarrow\longrightarrow RO\cdot \tag{4.2}$$

$$RX + HO\cdot \longrightarrow RX\cdot^{+} + HO^{-} \tag{4.3}$$



(4.4)

Another oxidant presented in this work is the persulfate ion ($S_2O_8^{2-}$), responsible for generating the sulfate radical anions ($SO_4^{\cdot -}$). The persulfate shows a high oxidation potential, similar to $OH^{\cdot}$, but at the same time it is less subject than this to the components of real water samples, presenting a higher selectivity towards some pollutants. For these reasons the interest in this oxidant has increased recently (Gonçalves et al., 2019).

4.1.2 Heterogeneous Photocatalysis

Heterogeneous photocatalysis can be defined as the acceleration of a chemical reaction by the irradiation of a catalyst; the use of the catalyst, in this case a semiconductor, is of primary importance because it allows to reduce the activation energy of the reaction. Since the reaction takes place in aqueous phase but the catalyst is in solid form this process is defined "heterogeneous". The catalyst accelerates the chemical process as it can be activated by the absorption of light of energy greater than its band gap; this energy absorption allows to generate electron-hole pairs (eq. 4.5). The photogenerated holes and electrons are responsible for oxidation and reduction processes, respectively. Since the reaction takes place in an aqueous solution there is oxidation of the water molecules, with the generation of $OH^{\cdot}$ radicals (eq. 4.6); it should be noted that only the molecules adsorbed on the semiconductor surface react. The reduction reaction generally takes place with the oxygen molecules since the processes are usually carried out in aerobic condition (eq. 4.7). The organic molecules presented in the water are subsequently oxidized by the OH· radicals, as described in the previous paragraph.

$$Semiconductor + h\nu \longrightarrow h^+ + e^- \tag{4.5}$$

$$h^+ + H_2O \longrightarrow OH\cdot + H^+ \tag{4.6}$$

$$e^- + O_2 \longrightarrow O_2^- \tag{4.7}$$

The reason why the OH· radical is believed to be most responsible for the oxidation reactions derives from the observation that intermediates detected during the photocatalytic degradation of halogenated aromatic compounds are typically hydroxylated structures, similarly as the reaction products of the reactions between aromatics and OH· radicals (Pérez, 2001).

As already mention heterogeneous photocatalysis has a great potential to be a cost-effective water purification technology (Lee et al., 2015) for the removal of low concentration recalcitrant organic pollutants from wastewater. Most of the studied semiconductors acting as photocatalysts are metal oxide (TiO_2, ZnO, SnO_2, WO_3). Among these oxides, titanium dioxide and zinc oxide are the most promising candidates (Lee et al., 2015), particularly when the latter system is doped with rare earth elements (REEs) such as cerium (Ce), lanthanum (La), praseodymium (Pr), erbium (Er) and ytterbium (Yb) (Calza et al., 2017; Sordello et al., 2019).

The photocatalytic reaction may depend on several operating parameters such as dissolved oxygen, pH, catalyst concentration, initial substrate concentration, radiation intensity, and temperature (Blanco and Malato 2003):

- Since the aim of the photocatalytic process is to mineralize an organic pollutant to carbon dioxide, water and mineral acid, the presence of **oxygen** is essential (see eq. 4.2) and its concentration affects the degradation rate. Consequently, a suitable liquid-gas contact must be assured.
- The **pH** of the aqueous solution affects the metal oxide, including the charge of the particle and the size of the aggregates. The point of zero charge (PZC) is defined as the pH at which the surface of an oxide is

uncharged; for pH values far enough from the PZC the particle size decreases, while aggregation increases near the PZC. Also the particle size has an important influence on the photocatalytic process.

- The **catalyst concentration** is directly proportional to the initial reaction rate. Nevertheless, when a certain concentration is reached, the reaction rate becomes independent of the catalyst mass. Above this point, turbidity avoids proper penetration of light in the reactor and activation of all catalyst particles.
- With low **pollutant concentration** the degradation rate is slow, as there is a lower frequency of contact between the catalyst surface and target molecules. Generally during the oxidation process, the surface of metal oxide particles is progressively less covered with the pollutant, as the latter is decomposed. The degradation rate is thus expected to decrease with increasing illumination time.
- The photodegradation rate depends on **radiation intensity**, initially in a linear way. According to Herrmann (1995) as intensity increases, reaction rate decrease and if it keeps increasing, a point is reached where the rate no longer increases.
- **Thermal energy** does not increase catalyst activation. However, the photocatalytic activity decreases at low (-40° - 0° C) and high temperatures (> 70°C) (Blanco and Malato 2003).

4.1.3 Fenton and photo Fenton processes

Fenton and photo-Fenton processes, that employ hydrogen peroxide (H_2O_2) and iron species, have been extensively studied and increasingly used in the treatment of contaminated water and soil. In particular the photo-Fenton process is believed to be one of the most environmentally friendly and cost effective treatment among AOPs for remediation of highly contaminated waters (Foteinis et al., 2018). The difference between the two processes is the presence or absence of irradiation, Fenton process takes place in dark conditions, while photo-Fenton process is assisted by light.

In the **Fenton** process the reaction between dissolved iron (II) and hydrogen peroxide in acidic aqueous solution leads to oxidation of iron (II) to iron (III) and is thought to form OH· radicals, as shown in equation 4.8. In this case the reaction is spontaneous and takes place without the influence of light.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^{\cdot} + HO^{-} \tag{4.8}$$

At a proper pH (2.7 – 2.8) the reduction of iron (III) to iron (II) takes place, regenerating iron (II) (eq. 4.9; eq. 4.10). As these reactions occurred at an appreciable rate, a catalytic cycle is generated (Andreozzi et al., 1999).

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe - OOH^{2+} + H^{+} \tag{4.9}$$

$$Fe - OOH^{2+} \leftrightarrow HO_2^{\cdot} + Fe^{2+} \tag{4.10}$$

Similar to what just seen, the homogeneous **photo-Fenton process** is based on the decomposition of H_2O_2 to produce OH· radicals by iron species. However in this case the reaction is accelerated by irradiation, specifically by light with wavelengths in the UV-Vis region. In these conditions, the photolysis of iron (III) complexes allows regeneration of iron (II), which can further react with more hydrogen peroxide. The process can be described by the following reactions (Foteinis et al., 2018):

$$Fe^{3+} + hv + H_2O \longrightarrow Fe^{2+} + OH^{\cdot} + H^{+} \tag{4.11}$$

$$Fe^{3+} + hv \longrightarrow Fe^{2+} + OH^{\cdot} \tag{4.12}$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \tag{4.13}$$

Given the range of wavelengths that allow this process (UV-Vis light), this can be driven by solar energy, leading to a reduction in cost. Photo-Fenton processes can take place with an iron (II) concentration orders of magnitude lower than dark Fenton and this represent an advantage. On the other hand, hydrogen peroxide is continuously consumed, just as it is in dark Fenton and to avoid iron precipitation, also in this case, the process requires rigorous pH control (acid pH must be maintained) (Foteinis et al., 2018).

So far only homogeneous Fenton and photo-Fenton processes have been described, therefore the catalyst is solubilized in water. At the end of the wastewater treatment a considerable amount of sludge is generated; these useless sludge must be dismissed increasing the costs of managing the process. A way to avoid this disadvantage is using iron-based catalyst easily to be recovered. In heterogeneous Fenton and photo-Fenton reactions the H_2O_2 is activated by iron supported in a solid matrix at acidic or even circumneutral pH. In this way the reactions proceed as seen previously, but at the end the catalysts can be easily removed from the solution and reuse (Gonçalves et al., 2019).

Similarly the case of photocatalysis the reaction rate and stoichiometry of Fenton and photo-Fenton processes can be affected by water constituents and several variables, such as pH, Fe : H_2O_2 ratio, temperature, and inorganic anion concentration:

- **pH** directly influence the performance of this reactive system. In the Fenton process the reactions that regenerate iron (II) are optimal at pH 2.8. The photo-Fenton process is strongly related to this variables because at high pH values, the rate decreases, due to the precipitation of $Fe(OH)_3$, while for pH values lower than the optimal ones, complexes with a low light absorption coefficient are generated and this causes a decrease in the degradation rate.
- It seems that there is no agreement on an optimal value for the **Fe:H_2O_2 ratio**, since different authors have reported different ratios (Pérez 2001). As a general indication large excesses of either iron or hydrogen peroxide could be detrimental, as they are also scavengers of $OH^\cdot$ radicals.
- Unlike photocatalysis processes, in photo-Fenton processes the regeneration of iron (II) can be assisted by **thermal energy**. Therefore, increasing the solution temperature leads to an increase in the observed reaction rates (Lee and Yoon, 2004).
- The presence of **anions** in solution can cause a decrease in the degradation rate; this decrease is due to either the scavenging $OH^\cdot$ role or to the formation of unreactive species with iron. Common species are: SO_4^{2-}, Cl^-, NO_3^-, ClO_4^- and $H_2PO_4^-$.

In the following subchapters three case studies, relating to the LCA analysis applied to AOPs, are presented and discussed. The first case study examined an example of heterogeneous photocatalysis, at the laboratory level. The second and third case studies investigated the environmental burdens of the photo-Fenton processes both at the pilot plant and at the laboratory level.

4.2 Case study 1: LCA analysis of heterogeneous photocatalytic processes.

In this first work, the degradation rate of phenol in water by using different photocatalysts based on zinc oxide doped with rare earth elements has been evaluated. Aiming at identifying the best operating conditions that couple the highest degradation efficiency with the lowest environmental burdens. To achieve this goal the results of an experimental design face centred model (DoE) were combined to Life Cycle Assessment. Using as a starting point the data obtained in preliminary studies (Calza et al., 2017; Sordello et al., 2019), we wanted to investigate in detail the efficiency of zinc oxide based catalysts doped with rare earth elements (REEs): cerium (Ce), lanthanum (La), praseodymium (Pr), erbium (Er) and ytterbium (Yb). The term efficiency includes both the concept of effectiveness, to degrade organic molecules in aqueous solution, and the concept of minimization of the environmental impacts associated with the process.

The activity directly carried out that allowed the realization of this case study concerned both the LCA analysis part and also all the previous experimental part in the laboratory.

4.2.1 Materials and methods

As mentioned pure and Ce-doped ZnO catalysts were utilised to investigate the degradation of phenol and several refractory compounds in ultrapure water at natural pH and under UV-Vis light conditions (Calza et al., 2017). The hydrothermal route was followed to prepare the catalytic systems from different precursors. This production route complies with the Green Chemistry principles and enables to obtain controlled nanostructures. The synthetized bare ZnO catalysts and those doped with REEs were characterized by means of scanning electron microscopy, transmission electron microscopy, X-rays diffraction, UV visible diffuse reflectance spectroscopy, electron paramagnetic resonance, chronopotentiometry, and cyclic voltammetry (Calza et al. 2017; Cerrato et al., 2018; Sordello et al., 2019). The synthesized materials resulted particularly promising so that in a subsequent study the investigation was extended to other dopants, namely Er and Yb (Sordello et al., 2019). These studies constituted the basis on which the DoE model was built and applied to a systematic investigation of the photocatalytic degradation of phenol in water solution in presence of ZnO photocatalysts doped with Ce, Er, and Yb.

Experimental design - As reported in the section 4.1.2, the photocatalytic reaction may depend on several operating parameters. However, the type and concentration of dopant in the photocatalyst (X_1) and the concentration of the catalytic system in solution (X_2) were set as the only factors of interest in DoE. The choice to focus only on these two parameters was based on the results obtained in previous studies (Calza et al., 2017; Sordello et al., 2019) and the experience of the practitioners. A faced centered design (FCD) model was utilised to determine linear and quadratic effect of X_1 and X_2 as well as interactions between X_1 and X_2. In FCD, a full factorial, a star design, and N replicates of the center pointes are modelled. Three levels (–1, 0, +1) were set for each variable (Table 3) based on concentration ranges derived from previous experiments. The three REEs (i.e., Ce, Er, and Yb) used as dopants of ZnO are treated as qualitative variables in FCD. Thus, the total number of experiments (N) for each doping element is computed as follows:

$$N = 2^f + 2f + N_0 \tag{4.14}$$

Where f is the number of variables and N_0 is the number of replicates in the centre points. Setting f = 2 and N= 2 respectively, the total number of experiments is 20 or 10 for each precursor (i.e., chloride and nitrate). However, the subset of experiments for X_1 at level –1, which correspond to bare ZnO photocatalyst, is common to both precursors. Thus, for each REEs investigated, the resulting total number of independent experiments reduced to 17 with two replicates of experiments in the centre. The mathematical model resulting from the FCD is in the form:

$$Y = B_0 + B_1X_1 + B_2X_2 + B_{11}X_{12} + B_2X_2 + B_{12}X_1X_2 \tag{4.15}$$

Where Y is the calculated response (the reaction rate constant k), X_1 is the dopant concentration in the photocatalyst, X_2 is the concentration of the catalytic system employed in the degradation process, B_0 is the constant, B_1 is the coefficient of the linear effect of X_1, B_2 is the coefficient of the linear effect of X_2, B_{11} is the coefficient of the quadratic effect of X_1, B_{22} is the coefficient of the quadratic effect of X_2, B_{12} is the coefficient of the interaction effect between X_1 and X_2.

Variable			Level		
#	**Description**	**Unit**	**–1**	**0**	**+1**
X_1	Rare earth element concentration	% w/w	0	0.5	1
X_2	Photocatalyst concentration	mgL^{-1}	100	800	1500

Table 3. Variables, investigated levels and their actual values utilized in the design of experiments. The experiments were randomized to avoid external influence on the results and elaborated with the Chemometric Agile Tool (CAT) software (Gruppo di Chemiometria, 2019).

The full experimental matrix for the FCD model created is reported in Table 4.

ZnO doped with cerium					
Chloride precursor			**Nitride precursor**		
n. exp	**[Ce]/%**	**[cat]/mgL^{-1}**	**n. exp**	**[Ce]/%**	**[cat]/mgL^{-1}**
1	0.5	800	1	0.5	800
2	1.0	1500	2	1.0	1500
3	1.0	800	3	1.0	800
4	0.5	100	4	0.5	100
5	0.0	800	5	0.0	800
6	0.0	100	6	0.0	100
7	1.0	100	7	1.0	100
8	0.0	1500	8	0.0	1500
9	0.5	1500	9	0.5	1500
10	0.5	800	10	0.5	800
ZnO doped with erbium					
Chloride precursor			**Nitride precursor**		
n. exp	**[Er]/%**	**[cat]/mgL^{-1}**	**n. exp**	**[Er]/%**	**[cat]/mgL^{-1}**
1	0.5	800	1	0.5	800
2	1.0	2000	2	1.0	2000
3	1.0	800	3	1.0	800
4	0.5	100	4	0.5	100
5	0.0	800	5	0.0	800
6	0.0	100	6	0.0	100
7	1.0	100	7	1.0	100
8	0.0	2000	8	0.0	2000
9	0.5	2000	9	0.5	2000
10	0.5	800	10	0.5	800

ZnO doped with ytterbium					
Chloride precursor			Nitride precursor		
n. exp	[Yb]/%	[cat]/mgL^{-1}	n. exp	[Yb]/%	[cat]/mgL^{-1}
1	0.5	800	1	0.5	800
2	1.0	2000	2	1.0	2000
3	1.0	800	3	1.0	800
4	0.5	100	4	0.5	100
5	0.0	800	5	0.0	800
6	0.0	100	6	0.0	100
7	1.0	100	7	1.0	100
8	0.0	2000	8	0.0	2000
9	0.5	2000	9	0.5	2000
10	0.5	800	10	0.5	800

Table 4. Full experimental matrix for the FCD model.

Experimental section - A bare ZnO sample was synthesized starting from a water solution of $Zn(NO_3)_2{\cdot}6H_2O$ (1 M). Then, NaOH (4 M) was added dropwise until the pH was 10-11. The solution was transferred into a 100 mL PTFE lined stainless steel autoclave (occupying 70% of the effective volume) and then treated at 175°C overnight. The product was centrifuged, washed with deionized water, and dried at 70°C.

The ZnO samples doped with REEs (0.01 M) were prepared by adding stoichiometric amounts of Ce, Er, and Yb to the starting solution. The precursor salts employed were respectively $CeCl_3{\cdot}7H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ for Ce, $ErCl_3{\cdot}6H_2O$ and $Er(NO_3)_3{\cdot}5H_2O$ for Er, $YbCl_3{\cdot}6H_2O$ and $Yb(NO_3)_3{\cdot}5H_2O$ for Yb. The synthesis route then followed the same procedure described above for the bare ZnO sample (Calza et al., 2017).

The samples were labelled as XZp-S where X = dopant element (i.e., REE); Z = Zinc oxide; p = percentage of dopant in the photocatalysts (i.e, 0%, 0.5%, 1%); S = type of salt used for as dopant precursor (i.e., Cl or NO_3).

Figure 9. Pictures of the oxide powder obtained as a result of the synthesis process (in this case: CeZn1-NO_3)

The photocatalytic degradation of synthesized photocatalysts was assessed using 60 mgL^{-1} of phenol as a probe molecule. Phenol was chosen as the representative for the class of phenolic compounds. These pollutants can commonly be found in industrial wastewater. Phenol is soluble in water and relatively stable in the environment, therefore needs specific treatments to degrade it (Chiou and Juang, 2007). Samples were load into cylindrical Pyrex cells (4.0 cm diameter and 2.5 cm height, cut-off at 295 nm) filled with 5 mL of an aqueous suspension containing phenol and the photocatalyst powder at selected concentrations. Samples were subjected to different irradiation times (ranging from 5 min to 3 h), using a set of six Actinic BL TL-D 15W (Phillips, Eindhoven, Nederland). The spectral region extended from 340 to 410 nm, with a maximum centred at 370 nm and a narrow band centred at 435 nm. The UV integrated irradiance on the cells in the 290–400 nm range wavelengths was 35 ± 1 Wm^{-2} (lamps emission spectra and incident irradiance were recorded with a calibrated spectrum radiometer (Ocean Optics SD2000 CCD spectrophotometer, equipped with an optic fiber and a cosine corrector CC-3-UV-T)). During irradiation the suspensions were magnetically stirred.

After irradiation, the suspensions were filtered by means of a 0.45 μm hydrophilic PTFE membrane (Millipore Millex-LCR). All samples were analysed using a Merck-Hitachi liquid chromatographer equipped with a Rheodyne injector L-6200 and L-6200A pumps for high-pressure gradients, a L-4200 UV-Vis detector (the detection wavelength was set at 220 nm) and a column LiChrocart RP-C18 (Merck, 12,5 cm x 0,4 cm). Elution was carried out at 1 mL min^{-1} with 4.2 mM aqueous H_3PO_4:CH_3CN 70:30 in isocratic mode. The injection volume was 50 μL.

With the exception of Carlo Erba's fosforic acid (pure at 85%), all the reactants were purchased from Sigma-Aldrich with purity higher than 99.9% and were used without any further purification. HPLC grade water was obtained from MilliQ System Academic (Waters, Millipore).

Assessment of environmental impacts – This section lists the parts that make up the LCA analysis: goal and scope definition, life cycle inventory, life cycle impact assessment and results interpretation.

The goal and scope definition sets the object of the study, the system boundaries and the functional unit. As mentioned above, the aim of this study is to evaluate and compare the efficiency of different photocatalysts that can be used for the degradation of organic pollutants in water streams. The term efficiency refers here to the degradation rate of phenol and the environmental performance attributable to the photocatalytic systems. The reaction constant (k) to complete degradation of 60 mgL^{-1} of phenol in MilliQ water was set as the functional unit and measured in min^{-1}. All the steps for the preparation of the photocatalysts and the degradation process were included in the system boundaries. Infrastructure and equipment used during the experimental analysis were excluded from calculation as well as the transport of direct input materials because their impact is expected to be marginal.

An inventory of inputs and outputs was compiled to create a representative model of the system under scrutiny (see Figure 10). LCI of material and energy flows for the synthesis of the precursors and for carrying the photodegradation out was modelled from direct measurements in the laboratory. Instead, literature dataset were used to model the production of rare earth oxide (REO) and the synthesis of the precursors. More in detail, REEs extraction is mainly carried out in China (Hellman and Duncan, 2014) via either open-pit mining of bastnäsite and monazite minerals or leaching of ion-adsorption clays. The Ecoinvent process "Rare earth concentrate, 70% REO, from bastnäsite, at beneficiation" provided the initial dataset to typical bastnäsite mining and refining in China (Althaus et al., 2007). Nuss and Eckelman (2014) updated the Ecoinvent data by re-allocating energy and materials inputs and emissions based on Bayan Obo bastnäsite composition provided in Chinese Rare-Earth Year book 2010 and 2006–2010 REO prices. It is worth noting that the bastnäsite mineral usually contains about 50% of Ce and only traces of the other two elements used as dopant in this study (i.e., Er and Yb). These two elements are part of the so-called group of heavy rare earth elements (HREEs), which are mainly extracted from ion absorption deposits (Peiró and Méndez, 2013). This production route was not investigated by Nuss and Eckelmann (2014). More integrative research in this sense is needed.

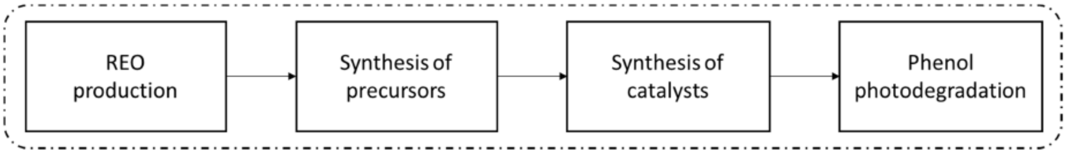


Figure 10. System layout with the main processing stages considered in the LCA model. REO – rare earth oxide.

The Ecoinvent process "Electricity, low voltage {IT}" was used to model the environmental impacts from the national electricity production mix, supplied to the synthesis of precursors and the photodegradation process. The inventory for the preparation of zinc nitrate hexahydrate was compiled from a patent (August, 1965). For Ce precursors, the modelling was based on information reported in Blanchard (1936) for chloride salts and in Pitts (1979) for nitrates.

The inventory for the preparation of erbium chloride was modelled according to the work of Gupta and Krishnamurthy (2005), while data for ytterbium chloride were obtained from Sebastian and Seifert (1998). For Er and Yb nitrates, the input of nitric acid was gathered from "Handbook of Chemistry and Physics" (2018) (Rumble, 2018). Instead, inputs of water, energy and the synthesis yields were set as those reported for the synthesis of zinc nitrate because of a lack of primary data. All the data employed in the model refer to the laboratory scale (see Table 5).

Precursor	Amount (kg)	Water (l)	Energy (kWh)
$Zn(NO_3)_2·6H_2O$	1	6.6	5
$CeCl_3·7H_2O$	1	1.1	0.5
$Ce(NO_3)_3·6H_2O$	1	1.1	0.7
$ErCl_3·6H_2O$	1	0.7	2
$Er(NO_3)_3·5H_2O$	1	0.85	0.8
$YbCl_3·6H_2O$	1	0.7	2
$Yb(NO_3)_3·5H_2O$	1	6.6	5

Table 5. Estimate of inputs of water and energy used to model the precursors' synthesis.

The LCIA was conducted with SimaPro 8 selecting Cumulative Energy Demand (CED) and the IPCC 2013 GWP 100a method as the impact assessment indicators. More specifically, CED accounts for gross energy requirements and includes "the direct uses as well as the indirect […] consumption of energy due to the use of […] raw materials”. CED indicator is split up into non-renewables and renewable energy carriers, the intrinsic value of which is determined by the amount of energy withdrawn from nature and it is expressed in MJ (Frischknecht et al., 2007). Instead, IPCC 2013 GWP 100a is a metric for estimating the relative global warming potential (GWP) due to atmospheric emission of 1 kg of a particular greenhouse gas (GHG) compared to the emission of 1 kg of carbon dioxide (Houghton et al., 2001) over a time horizon of 100 years.

4.2.2. Results and Discussion

The results of the photocatalytic degradation of phenol, DoE and LCA are here presented and discussed. Implications for theory and for possible industrial applications are also commented at the end of this section.

Table 6 shows the DoE results for the photocatalytic degradation reaction obtained from ZnO–based materials doped with Ce, Er, and Yb and synthesized using either chloride or nitrate precursors. Overall, the presence of the REE–based dopant results in faster degradation rates than those achievable by bare ZnO photocatalyst. These findings are aligned with preliminary results (Calza et al., 2017; Sordello et al., 2019), but the FCD outcomes enabled here to investigate the entire domain of responses. A heat map introduces a colour gradient that marks the results from red (slower reaction) to green (faster reaction).

k, min^{-1}	Photocatalyst concentration, mgL^{-1}				
Photocatalyst	**100**	**800**	**1500**	**1700**	**2000**
ZnO	0.014	0.055	0.078		0.059
CeZn0.5-Cl	0.02	0.077	0.085		
CeZn1-Cl	0.021	0.088	0.139	0.152	0.128
CeZn0.5-NO_3	0.012	0.074	0.109		
CeZn1-NO_3	0.014	0.074	0.114	0.167	
ErZn0.5-Cl	0.011	0.061			0.091
ErZn1-Cl	0.013	0.062		0.127	0.1
ErZn0.5-NO_3	0.012	0.048			0.081
ErZn1-NO_3	0.014	0.062		0.124	0.111
YbZn0.5-Cl	0.013	0.061			0.086
YbZn1-Cl	0.012	0.06		0.107	0.084
YbZn0.5-NO_3	0.011	0.062			0.109
YbZn1-NO_3	0.012	0.066		0.114	0.109

Table 6. Rate constants (k, min^{-1}) of phenol degradation obtained in the presence of different photocatalysts as a function of photocatalyst concentration. The samples are labelled as XZp-S where X = dopant element (i.e., REE); Z = Zinc oxide; p = percentage of dopant in the photocatalysts (i.e, 0%, 0.5%, 1%); S = type of salt used for as dopant precursor (i.e., Cl or NO_3).

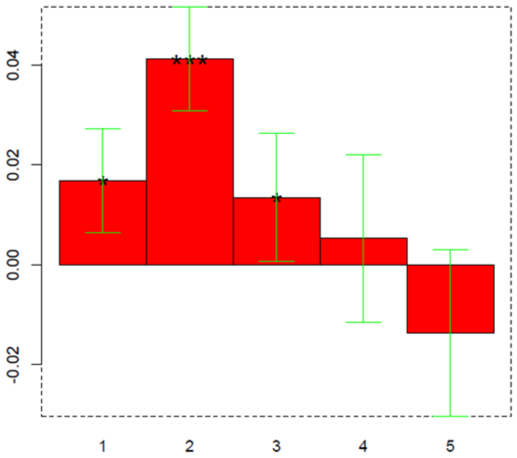
While for Ce– and Er–doped photocatalysts the choice of precursor seems not to influence the degradation rate of phenol remarkably, for Yb–doped photocatalyst a net preference is given to the nitrate salt precursor. In terms of the calculated response, the three REEs used as dopants in ZnO photocatalyst rank as follows: Ce > Yb > Er. For Ce–doped ZnO catalytic systems from nitrate precursor the relationship between the degradation rate and the investigated variables at coded scores is described by the model in eq. 4.16. Similar results were obtained for Er– and Yb–doped photocatalysts.

$$Y = 0.0696 + 0.0168X_1 + 0.0412X_2 + 0.0135X_1^2 + 0.00536X_2^2 - 0.0136X_1X_2 \qquad (4.16)$$

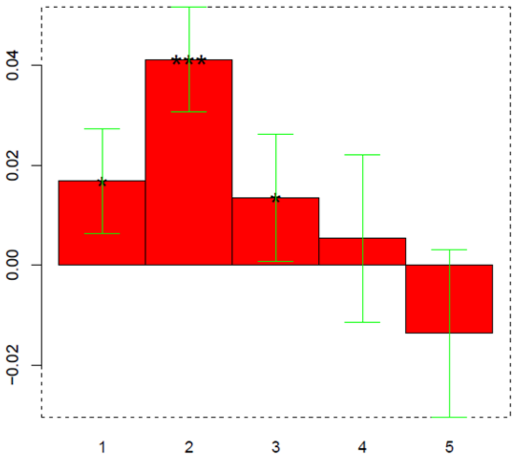
The adjusted r^2 and the standard deviation of the residuals resulted in 0.94 and 0.0092 respectively.

Figure 11 shows the significance of coefficients (i.e., *: $p < 0.05$; **: $p < 0.01$; ***: $p < 0.001$) for REEs-doped ZnO from chloride and nitrate precursors. Both X_1 and X_2 have an effect on the photochemical degradation, but the model seems to attribute the greatest significance (marked with ***) to the concentration of the photocatalyst (i.e., X_2). The concentration of the doping REE (X_1) in ZnO has a smaller linear effect but, notably, a more significant quadratic effect (at 95% confidence) than X_2. This evidence is detectable from the curve response surfaces of the FCD model but it cannot be deduced from the sole kinetic curves (see Figure 12), confirming the usefulness of DoE in maximizing understanding of chemical reactions.

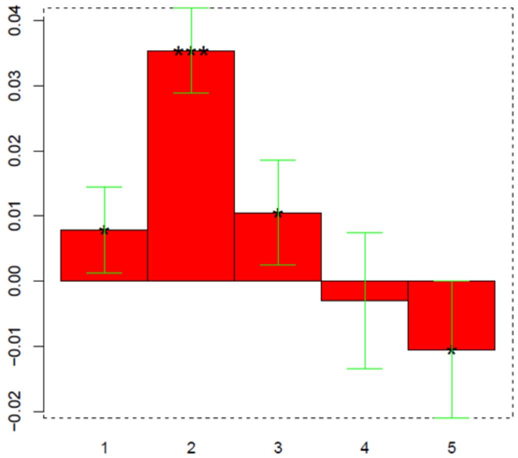
Figure 11. Significance of coefficients for REEs-doped ZnO from chloride and nitrate precursors. Each figure shows the estimation of the coefficients of the dopant (i.e., rare earth element) concentration in the photocatalyst (X_1) and of the concentration of the photocatalytic system employed in the degradation process (X_2). B_1 is the coefficient of the linear effect of X_1, B_2 is the coefficient of the linear effect of X_2, B_{11} is the coefficient of the quadratic effect of X_1, B_{22} is the coefficient of the quadratic effect of X_2, B_{12} is the coefficient of the interaction effect between X_1 and X_2. Significance of coefficients – *: $p < 0.05$; **: $p < 0.01$; ***: $p < 0.001$).



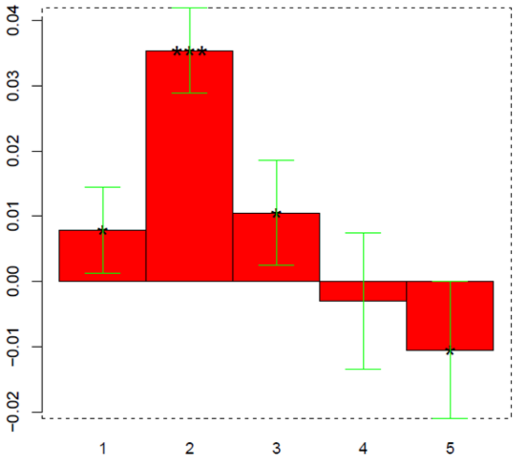
Cerium (chloride)



Cerium (nitrate)



Erbium (chloride)



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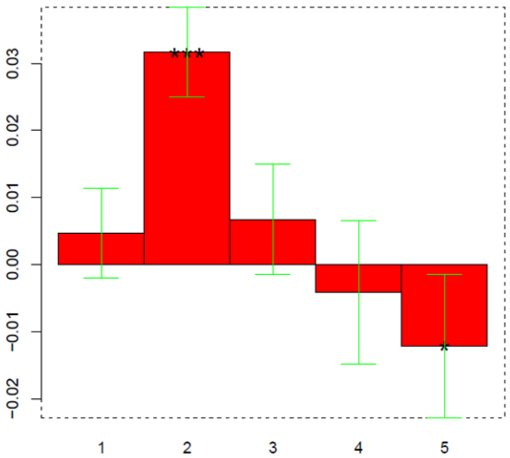
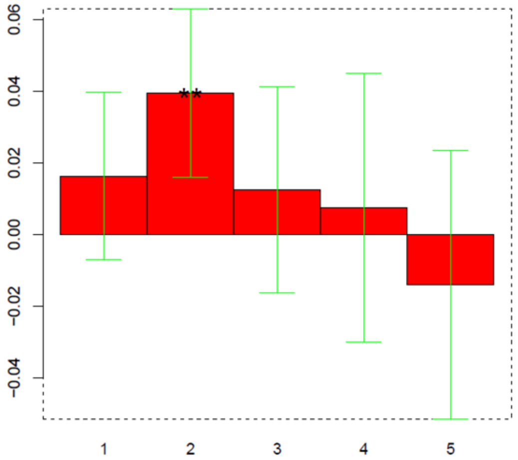
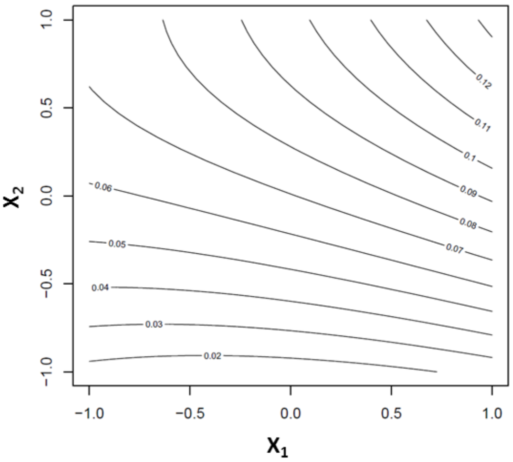


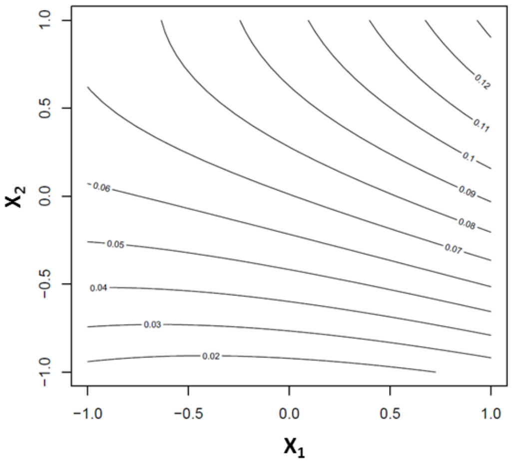
Ytterbium (chloride)



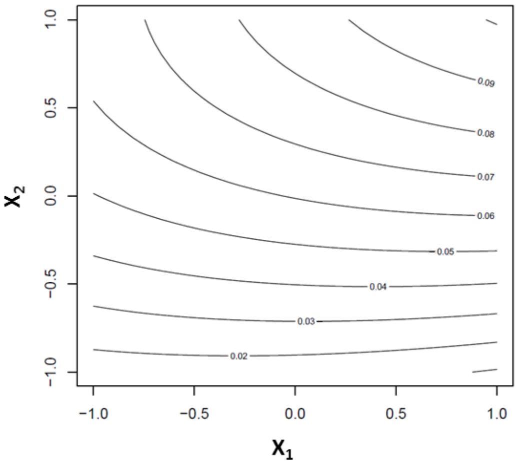
Ytterbium (nitrate)



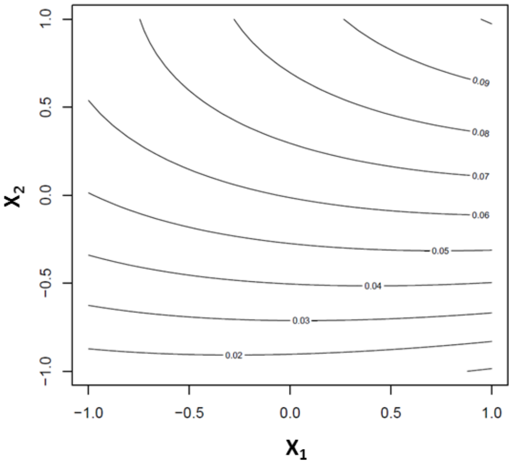
Cerium (chloride)



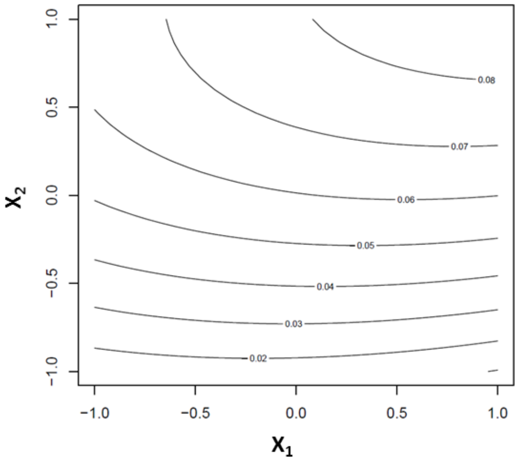
Cerium (nitrate)



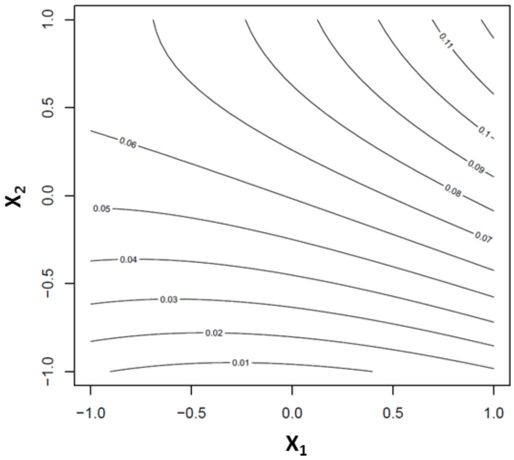
Erbium (chloride)



Erbium (nitrate)



Ytterbium (chloride)



Ytterbium (nitrate)

Figure 12. Response surface for the effect of interactions between X_1 and X_2 on the rate to complete photochemical degradation of phenol. X_1 is the rare earth element concentration, X_2 is the photocatalyst concentration in analyzed solutions containing phenol. Axes are dimensionless.

As early mentioned, the higher k values were observed at the maximum value of X_2 and X_1 (Table 6), with the degradation rate increasing along the diagonal of Figure 12 X_1, implying that the effect of the photocatalyst increases at relatively high dopant concentrations. Because the best calculated responses were observed at the maximum values of X_2 and X_1, we decided to extend the investigated domain by carrying out, respectively, one experiment at bare ZnO concentration of 2000 mgL^{-1}, and two experiments with CeZn1-Cl at 1700 mgL^{-1} and 2000 mgL^{-1}.

The degradation curves obtained for phenol as a function of the irradiation time in ultrapure water are plotted in the following figures.

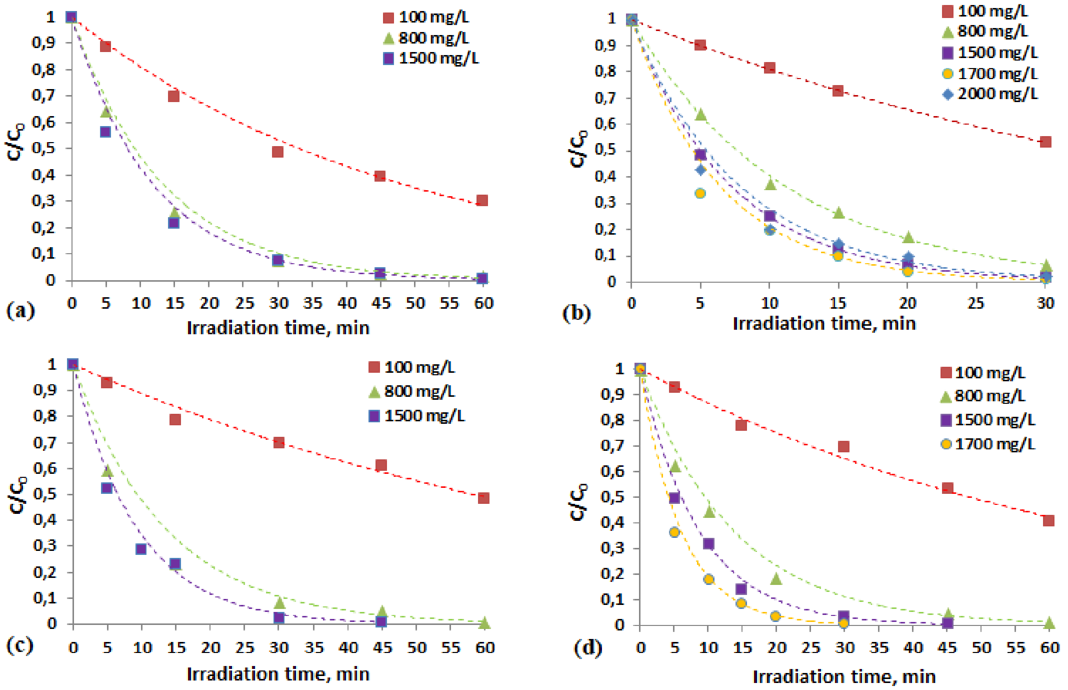


Figure 13. Phenol degradation using the different photocatalysts based on ZnO doped with Cerium: a) CeZn0.5-Cl; b) CeZn1-Cl; c) CeZn0.5-NO_3; d) CeZn1-NO_3.

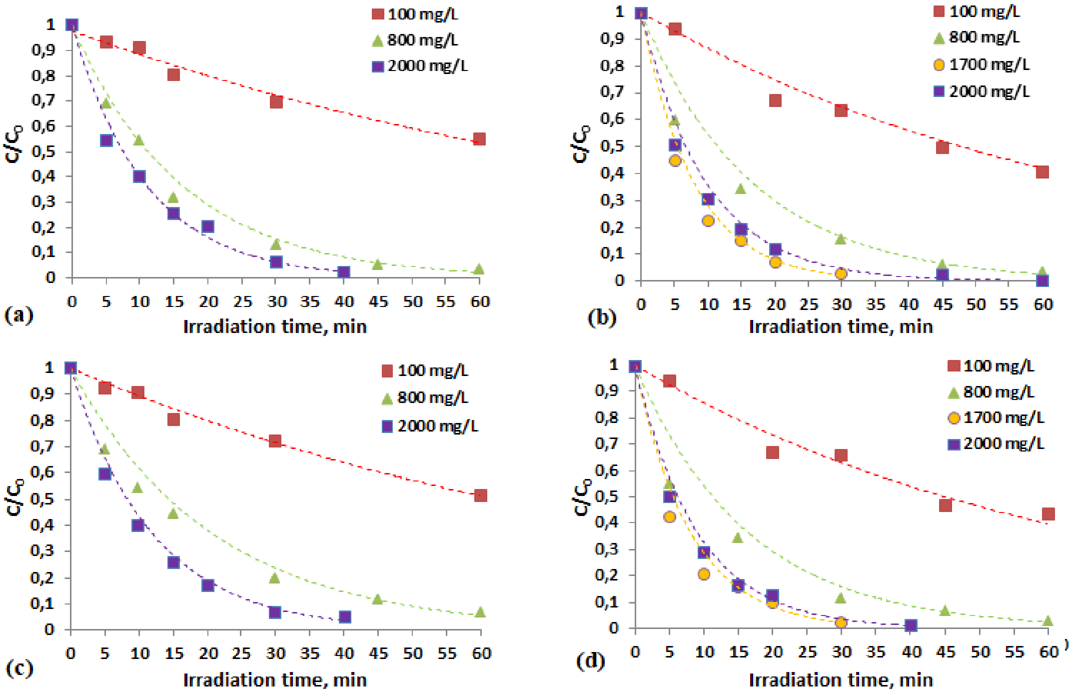


Figure 14. Phenol degradation using the different photocatalysts based on ZnO doped with Erbium: a) ErZn0.5-Cl; b) ErZn1-Cl; c) ErZn0.5-NO_3; d) ErZn1-NO_3.

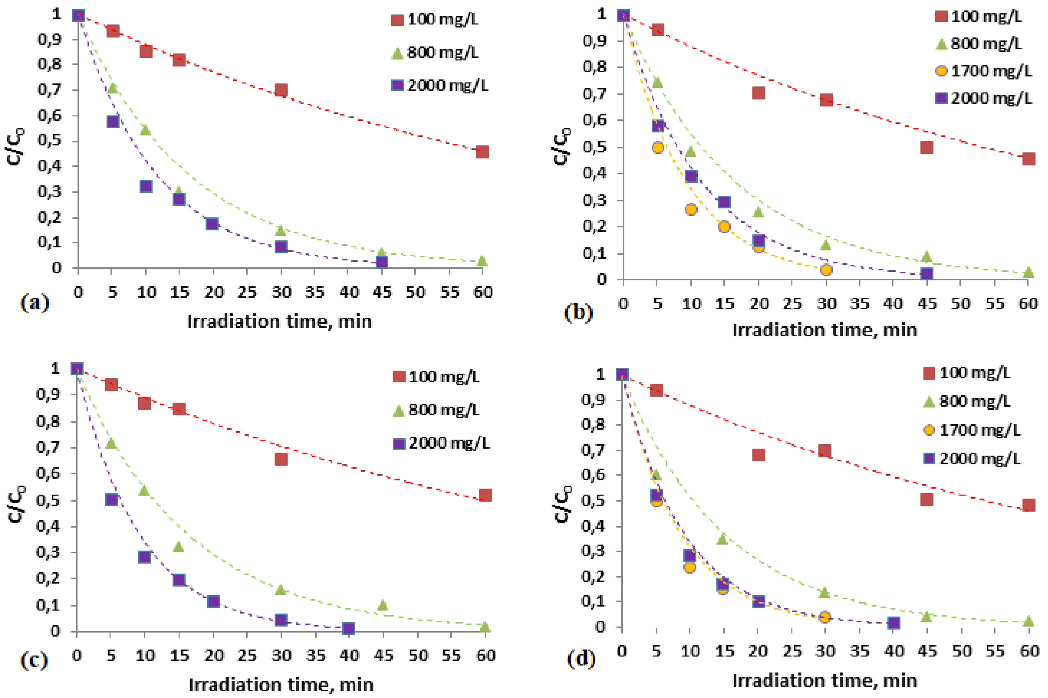


Figure 15. Phenol degradation using the different photocatalysts based on ZnO doped with Ytterbium: a) YbZn0.5-Cl; b) YbZn1-Cl; c) YbZn0.5-NO_3; d) YbZn1-NO_3.

For an easier comparison Figure 16 report the degradation curves in presence of bare and Ce-doped ZnO. Panel (a) displays the degradation rates resulting from bare ZnO at different concentrations, while panel (b) shows the degradation rates obtained using ZnO doped with 1% of Ce synthetized from chloride salt. These supplemental tests showed an increase in the photochemical degradation rate at photocatalyst concentrations between 1500 mgL^{-1} to 2000 mgL^{-1}, with a relative “optimum” result achieved at 1700 mgL^{-1}. At higher concentrations, the degradation rate decreases. Possible reasons for such a slowdown of phenol photodegradation rate are a detrimental effect of the photocatalyst due to back reactions (Minero and Vione, 2006) as well as adsorption of phenol on the catalytic material and/or saturation phenomena. Similar results occurred also with Er– and Yb–doped photocatalysts.

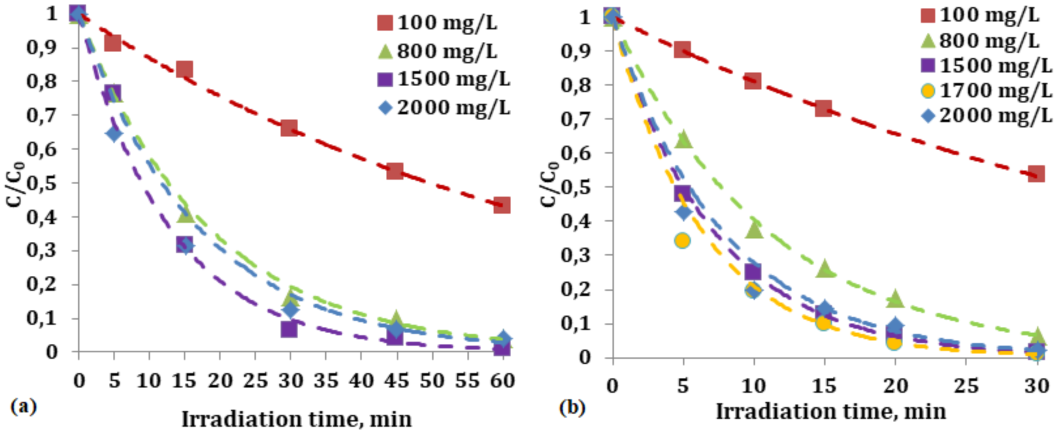


Figure 16. Reaction rate constant of phenol photodegradation at investigated concentrations of: bare ZnO (on the left); and ZnO doped with 1% of cerium, synthesized from chloride salts CeZn1-Cl (on the right). C/C$_0$ indicates the ratio between the phenol concentration measured at a specific degradation time (C) and the initial concentration (C$_0$).

Figure 17 and Figure 18 show LCIA results for the production of 1.7 g of CeZn1-Cl; respectively using the CED and IPCC 2013 GWP 100a method. The results are similar for both methods, greatest energy requirement and most CO_2 production are associated with the electricity consumed during the sample treatment at 175°C overnight (i.e. about 98% of the total impact), followed by the energy required for the synthesis of ZnO from zinc nitrate and sodium hydroxide. Figure 18 shows how the synthesis process, of the entire catalyst, results in the release of 1.8 kg CO_2 eq to produce 1.7 g of CeZn1-Cl.

Conversely, the synthesis of the dopant is marginal. Similar process contribution results were also achieved for Er- and Yb-doped photocatalytic systems with a relatively small deviation due to the production route of dopant precursors.

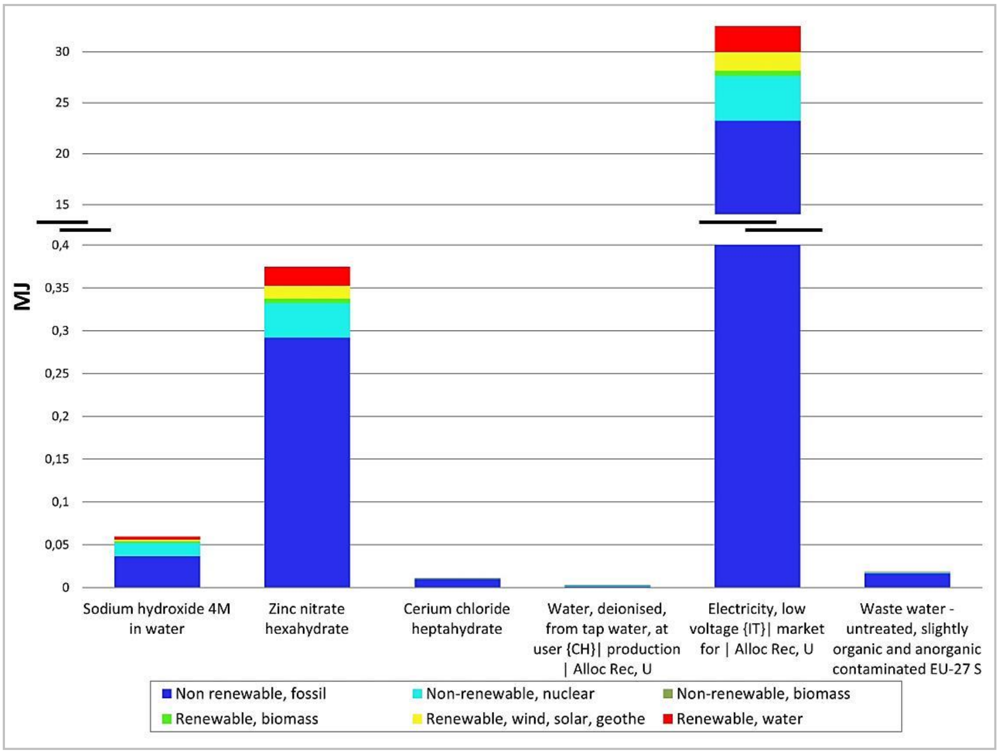


Figure 17. Cumulative Energy Demand (CED) and process contribution associated with the synthesis of 1.7 g of Ce-doped ZnO photocatalyst (i.e., CeZn1-Cl).

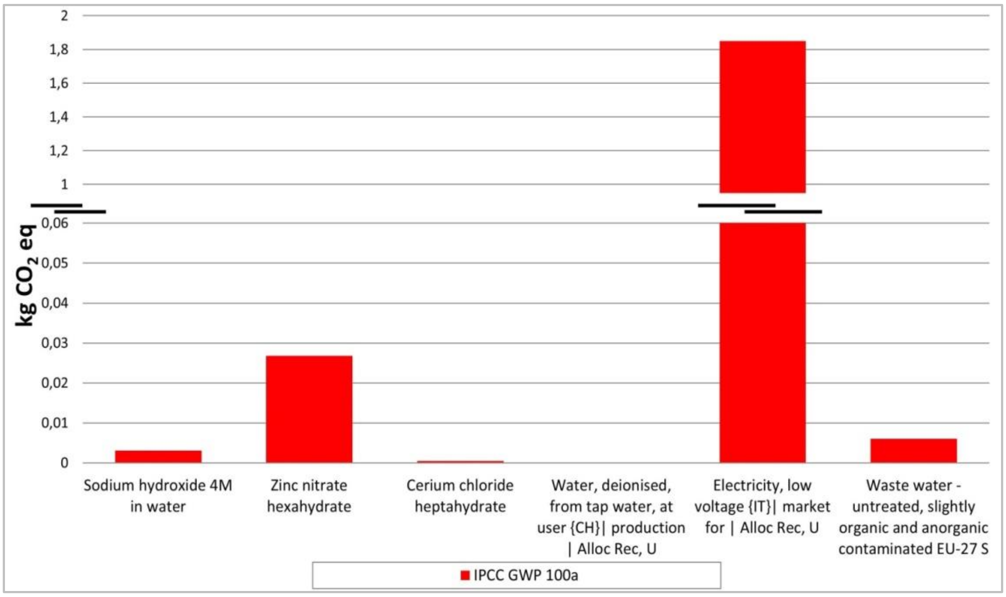


Figure 18. Global Warming Potential IPCC 2013 GWP 100y of the synthesized catalyst: CeZn1-Cl. Output of the synthesis is 1.7 g of photocatalysts.

The effect of the photocatalyst concentration on the energy requirement and greenhouse gas emission is explored in Figure 19 and Figure 20. CED results are computed as a function of CeZn1-Cl concentrations in the range 100-2000 mgL^{-1}. The complete degradation of 60 mgL^{-1} of phenol in 5 ml of solution was selected as the functional unit for comparison. At catalyst concentration of 100 mgL^{-1}, the complete photodegradation of phenol requires relatively longer irradiation time and it results in the largest amount of energy inputs. The system demands for the lowest energy inputs when the photocatalyst concentration is set at 800 mgL^{-1}. At higher concentrations, CED progressively increases but it remains lower than the energy inputs required at 100 mgL^{-1}. Absolute CED associated with electricity consumption is almost constant from 1500 to 2000 mgL^{-1}, suggesting that the lowest energy requirement ensues at photocatalyst concentration ≥ 1500 mgL^{-1}. On the other hand, the synthesis of the photocatalyst at intermediate to high concentrations (i.e., 800-2000 mgL^{-1}) requires higher CED and results in up to about 75% of the total energy required. Exactly the same observations can be made for the results obtained with the IPCC 2013 GWP 100a (Figure 20).

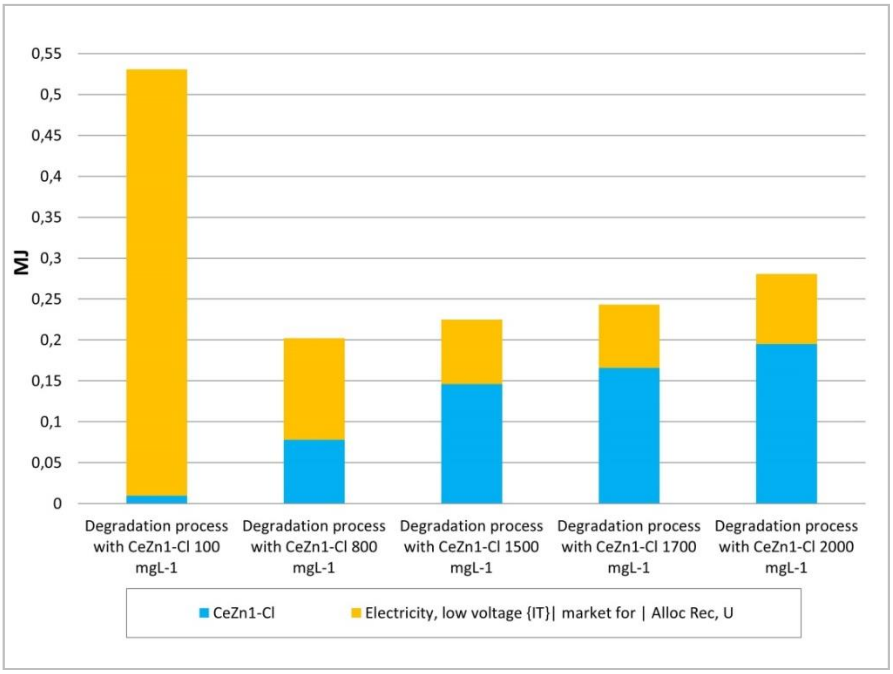


Figure 19. Cumulative Energy Demand (MJ) for the degradation process as a function of the photocatalyst concentration.

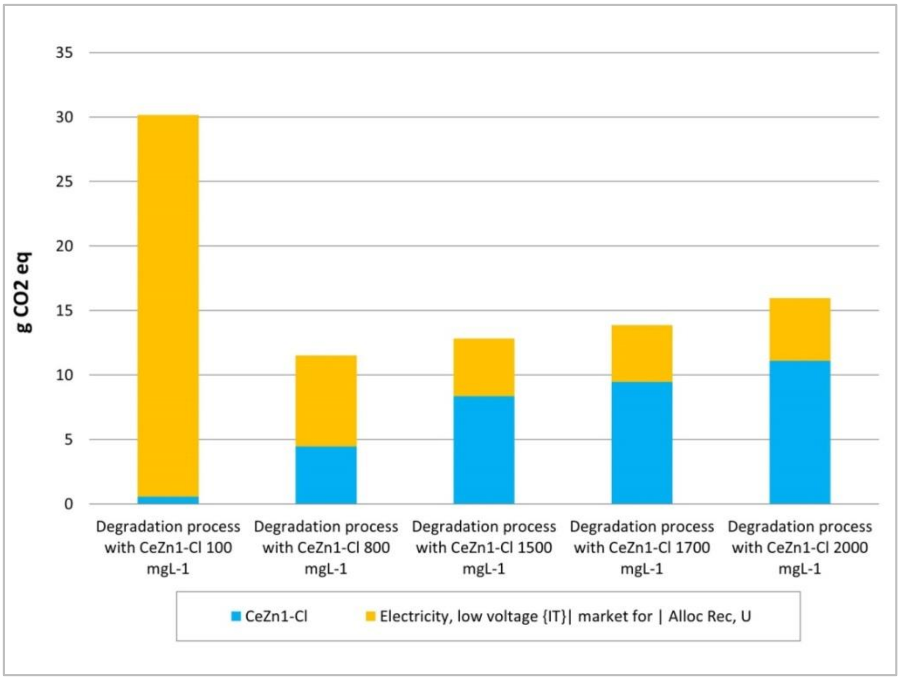


Figure 20. Comparison of the LCIA results for the degradation process using the Global Warming Potential IPCC 2013 GWP 100y (g CO_2 eq) method.

Table 7 summarises FCD results (on the top) and LCA findings (on the bottom) providing the basis for comparing the kinetics outcomes and environmental implications of phenol photodegradation. In both panels a heat map introduces a colour gradient that marks the results from red (the worst score) to green (the best score). Even if a combination of the fastest degradation rate with the lowest energy inputs is not achieved, the most promising outcome matches with Ce-doped (1%) ZnO and set the basis for the "best" working conditions.

In particular, the highest degradation rate was achieved with CeZn1-NO_3 at a concentration of 1700 mgL^{-1}, i.e. when employing the highest quantity of photocatalyst and dopant. The (relative) optimal working conditions could be achieved by reducing the photocatalyst concentration from 1700 mgL^{-1} to 1500 mgL^{-1}. This reduction would result in only 9% decrease of the degradation rate. In contrast, the lowest energy requirement seems to occur for CeZn1-Cl at 800 mgL^{-1}. Setting the concentration of CeZn1-Cl at 1500 mgL^{-1} and 1700 mgL^{-1} determines respectively an increase of 11% and 18% in CED results. From this, the optimal conditions for the degradation of phenol in water are reasonably obtained when CeZn1-Cl is in the range 800-1500 mgL^{-1}.

	k, min^{-1}				
photocatalyst	**100 mgL^{-1}**	**800 mgL^{-1}**	**1500 mgL^{-1}**	**1700 mgL^{-1}**	**2000 mgL^{-1}**
ZnO	0.014	0.055	0.078		0.059
CeZn0.5- Cl	0.02	0.077	0.085		
CeZn1-Cl	0.021	0.088	0.139	0.152	0.128
CeZn0.5-NO_3	0.012	0.074	0.109		
CeZn1-NO_3	0.014	0.074	0.114	0.167	
ErZn0.5-Cl	0.011	0.061			0.091
ErZn1-Cl	0.013	0.062		0.127	0.1
ErZn0.5-NO_3	0.012	0.048			0.081
ErZn1-NO_3	0.014	0.062		0.124	0.111
YbZn0.5-Cl	0.013	0.061			0.086
YbZn1-Cl	0.012	0.06		0.107	0.084
YbZn0.5-NO_3	0.011	0.062			0.109
YbZn1-NO_3	0.012	0.066		0.114	0.109

	CED (MJ)				
photocatalyst	**100 mgL^{-1}**	**800 mgL^{-1}**	**1500 mgL^{-1}**	**1700 mgL^{-1}**	**2000 mgL^{-1}**
ZnO	792	280	292		388
CeZn0.5- Cl	557	222	278		
CeZn1- Cl	531	202	225	238	280
CeZn0.5-NO_3	922	227	249		
CeZn1-NO_3	792	226	242	231	
ErZn0.5-Cl	1010	259			318
ErZn1-Cl	852	254		251	303
EZ0.5-H NO_3	922	307			333
ErZn1-NO_3	792	254		253	292
YbZn0.5-Cl	852	259			326
YbZn1-Cl	922	260		267	324
YbZn0.5-NO_3	1010	256			299
YbZn1-NO_3	922	243		261	294

Table 7. Kinetic results from Faced Centered Design experiments (top) and associated life cycle impact assessment results for Cumulative Energy Demand (CED, bottom). The heat map introduces a color gradient that differentiates the results from red (the worst score) to green (the best score). The samples are labelled as YZp-S where Y = dopant element (i.e., REE); Z = Zinc oxide; p = percentage of dopant in the photocatalysts (i.e, 0%, 0.5%, 1%); S = type of salt used for as dopant precursor (i.e., Cl or NO_3).

The relative global warming contribution results are summarized in Table 8. Setting the best operational conditions identified above, the photodegradation of phenol would determine the release of 11.5-13.2 g CO_2 eq.

	k, min^{-1}				
photocatalyst	100 mgL^{-1}	800 mgL^{-1}	1500 mgL^{-1}	1700 mgL^{-1}	2000 mgL^{-1}
ZnO	0.014	0.055	0.078		0.059
CeZn0.5- Cl	0.02	0.077	0.085		
CeZn1-Cl	0.021	0.088	0.139	0.152	0.128
CeZn0.5-NO_3	0.012	0.074	0.109		
CeZn1-NO_3	0.014	0.074	0.114	0.167	
ErZn0.5-Cl	0.011	0.061			0.091
ErZn1-Cl	0.013	0.062		0.127	0.1
ErZn0.5-NO_3	0.012	0.048			0.081
ErZn1-NO_3	0.014	0.062		0.124	0.111
YbZn0.5-Cl	0.013	0.061			0.086
YbZn1-Cl	0.012	0.06		0.107	0.084
YbZn0.5-NO_3	0.011	0.062			0.109
YbZn1-NO_3	0.012	0.066		0.114	0.109

	GWP (g CO_2 eq)				
Photocatalyst	100 mgL^{-1}	800 mgL^{-1}	1500 mgL^{-1}	1700 mgL^{-1}	2000 mgL^{-1}
ZnO	45.0	15.9	16.7		22.1
CeZn0.5- Cl	31.7	12.6	15.8		
CeZn1-Cl	30.2	11.5	12.8	13.9	16.0
CeZn0.5-NO_3	52.4	12.9	14.2		
CeZn1-NO_3	45.0	12.9	13.8	13.2	
ErZn0.5-Cl	57.1	14.7			18.2
ErZn1-Cl	48.4	14.5		14.3	17.3
ErZn0.5-NO_3	52.4	17.5			19.0
ErZn1-NO_3	45.0	14.5		14.4	16.7
YbZn0.5-Cl	48.4	14.7			18.6
YbZn1-Cl	52.4	14.8		15.2	18.5
YbZn0.5-NO_3	57.1	14.6			17.0
YbZn1-NO_3	52.4	13.8		14.9	16.8

Table 8. Kinetic results from Faced Centered Design experiments (table at the top) associated with life cycle impact assessment results for Global Warming Potential (GWP). The heat map introduces a color gradient that differentiates the results from red (the worst score) to green (the best score).

4.2.3. Conclusion

Guaranteeing water quality and water access for all is one of the main objectives of a sustainable development. The possibility of treating waste water, in order to remove polluting substances, allows diversification and increase of water sources without affecting the sources naturally present in the environment.

Among others, heterogeneous catalysis, with REEs-doped ZnO photocatalytic systems being an example of particular interest, have the potential for achieving an efficient removal of pollutants at relatively low cost. A full implementation of REEs-doped ZnO, however, comes also through a systematic evaluation of operating conditions to set the basis for achieving the greatest degradation efficiency at the preferable environmental performance.

The results of this study pointed out that even if the highest degradation efficiency is obtained with 1700 mgL^{-1} of ZnO doped with 1% of Ce from nitrate precursor, setting the photocatalyst concentration at 800 mgL^{-1} may be preferable to reduce the environmental impacts, and likely the economic costs, associated with the input of electrical energy and the synthesis procedure. To this aim, however, the chance of exploiting the solar light to promote photocalysis and the possibility to hold the catalyst on supports that may facilitate its recovery for regeneration are of great interest for a full implementation of ZnO-based advanced oxidation processes at lower economic and environmental cost.

Data used to model the system were obtained at the laboratory scale and can only offer a partial view of the real behaviour of these materials. This is a main limitation to the feasible scaling up of laboratory processes to real systems. Therefore, perspectives for future works include the assessment of photodegradation in real wastewater matrixes. To this aim, a combination of DoE and LCA is highly recommended to assess the environmental performance of the entire domain of the system under scrutiny.

4.3 Case study 2: Environmental Assessment of Solar Photo-Fenton Processes at Mild Condition with Soluble Bio-Organic Substances

As pointed out in the paragraph 4.1.3. photo Fenton reactions provide a viable and effective water remediation option due to the oxidation of a wide range of organic substances. However, the environmental implications of these treatments, over their life cycle, remain uncertain. In this work, several photo Fenton processes, at a semi-industrial scale, were examined through the LCA methodology. The general purpose of this study is to evaluate, from an environmental point of view solar photo Fenton processes carried out in mild conditions in the presence of waste derived soluble bio-organic substances (SBO, similar to humic substances under the structural and physical-chemical point of view). More specifically, the objective is to identify the hotspots related to these specific treatments and evaluate the environmental burden of the SBO as iron complexing agents, used to run the process at milder pH conditions, compared to the optimum ones (i.e. pH about 3). Generally, conducting photo Fenton processes using solar radiation and at near neutral pH, leads to a decrease in the efficiency. It therefore becomes of fundamental importance to carry out an assessment of the real environmental impacts associated with these processes.

4.3.1 Materials and methods

For a reliable and realistic assessment of the actual environmental impacts of solar photo Fenton process it was decided to use a real pilot plant, built to test technology for waste water treatment. The fulfilment of this case study was made possible thanks to the research group on "Advanced Oxidation Processes" of the University of Valencia, Alcoy (Spain).

Goal and scope definition

The aim of the study is to assess the environmental impacts of solar photo Fenton processes for the treatment of contaminated water. The photo Fenton processes, assisted by solar light, allow to remove the organic pollutants present in water through a degradation reaction.

A solution of caffeine at a specific concentration was used to have a representative and reproducible sample of water contaminated by a contaminant of emerging concern. In fact, for an easier evaluation of the process degradation effectiveness, it was decided to simplify the matrix by using tap water instead of a real waste water. To evaluate the effect of performing at different pH the degradation process it has been decided to work both at pH 2.8 and pH 5.

The operating conditions of the processes considered can thus be summarized:

- solar photo-Fenton at pH 2.8, caffeine concentration 1 mg/L
- solar photo-Fenton at pH 2.8, caffeine concentration 50 mg/L
- solar photo-Fenton at pH 5, caffeine concentration 1 mg/L
- solar photo-Fenton at pH 5, with humic substances (SBO) and caffeine concentration 1 mg/L (*)
- solar photo-Fenton at pH 5, with humic substances (SBO), caffeine concentration 50 mg/L and increase of the reactants concentration (**)

(*) It is necessary to specify in the case of the degradation experiment conducted at pH 5 with SBO and caffeine at a concentration of 1 mg/L, only a slight decrease in the concentration of pollutants was observed. This is because humic substances, in cases where the pollutant concentration is small, are counterproductive, as they suppress the degradation reaction. Since in these conditions the tested system did not work, it was decided not to include the case in question in the LCA analysis.

(**) To make the degradation of caffeine appreciable in the tested conditions (pH 5, + SBO, caffeine concentration 50 mg/L), it was necessary to increase the concentration of iron and hydrogen peroxide in solution.

For the assessment of the solar photo Fenton process it was chosen as functional unit the treatment of 1 m^3 of water contaminated with caffeine per day.

The study was modelled with a cradle-to-grave approach, encompassing the construction, the use phase and the decommissioning of the treatment plant.

Inventory analysis

Data from the Ecoinvent 3.3 database were used to model the system.

The processes tested at semi industrial level were carried out in a solar photoreactor Solardetox Acadus-2015 (Ecosystem SA) (Figure 21), designed for decontamination of wastewaters, based on compound parabolic collector technology, CPC (Malato et al., 2003).

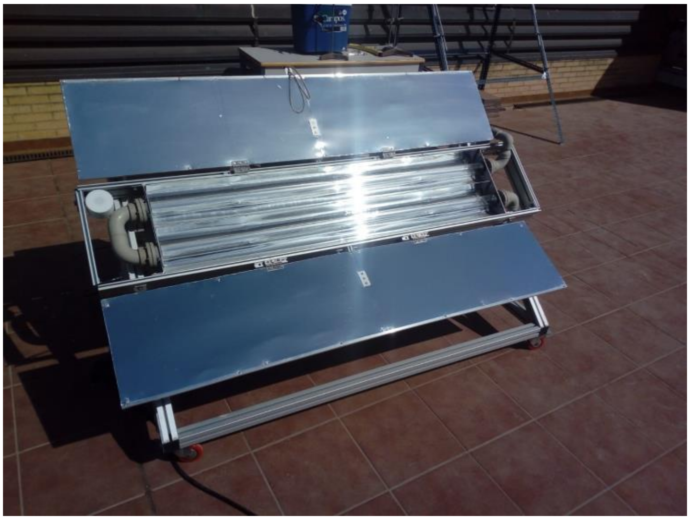


Figure 21. Picture of the pilot plant.

The plant consists of two borosilicate tubes (diameter 50 mm, thickness 2.5 mm), through which the solution to be treated flows. Two aluminium parabolic mirrors concentrate the sunlight in the axis of each tube. The total surface of the photoreactor is 0.45 m^2, with an irradiated volume of 4.5 L. The surface is tilted 40° with the horizon and left in a sunny place with a southern orientation. By means of a pump the water is circulated inside the reactor. The reactor is equipped with a radiometer (Acadus 85-PLS), which measured the received UV-A radiation; the radiometer contribution however, it has been neglected in LCA modelling. The inventory data relative to the pilot plant are reported in Table 9.

Materials / Process / Parts	Amount	Units
Stainless steel	55	kg
Aluminium	9	kg
Borosilicate glass	5.57	kg
Anodizing process	2	m^2
Polypropylene (PP)	7	kg
Pumps	2	items
Transport	36	tkm

Table 9. Inventory data for the pilot plant.

It was assumed that the system was manufactured in Barcelona and that the transport to its final destination (Alcoy) was done by truck. The lifespan of the entire plant is estimated to be 20 years; the borosilicate glass tubes and the pump, on the other hand, must be replaced after 10 years of work (inputs already considered in the inventory reported in Table 9). To model the decommissioning phase of the plant, it was assumed that the main materials (steel, aluminium, glass and polypropylene) are recycled.

To make the water treatment process more realistic, it was chosen to model the system in order to treat 1 m^3 of water per day. The sizing of the pilot plant was made taking into account the m^2 of surface needed for the treatment of the desired volume of water in one day. In fact, this value can be obtained knowing the daily solar radiation in the Alcoy region and the accumulated radiation needed to treat the water:

- the average radiation received in a day, in the Alcoy region, is 18 W/m^2, equivalent to 1555.2 KJ/m^2;
- the accumulated radiation (AR) necessary for water treatment is measured by means of the radiometer, during the caffeine degradation tests; this value corresponds to the amount of solar energy necessary for the complete degradation of the contaminant.

By applying a simple proportion (4.17):

$$1555.2\ (kJ) : 1\ (m^2) = AR\ (kJ) : X\ (m^2) \tag{4.17}$$

it is possible to calculate the m^2 of reactor surface that would be necessary to treat 1 m^3 of water per day in the different conditions tested. The number of equivalent pilot plants to obtain the desired surface is easily determined, knowing the real m^2 of the reactor area. Table 10 shows the accumulated radiation, the required surface and the corresponding number of equivalent pilot plants, necessary for the caffeine degradation.

	1 mg/l caffeine		**50 mg/l caffeine**	
	pH 2.8	**pH 5**	**pH 2.8**	**pH 5**
Accumulated radiation (kJ)	90	11271	5713	16635
Required surface (m^2)	0.058	7.25	3.67	10.7
N° of pilot plants equivalent	1*	16.11	8.16	23.77

Table 10. Accumulated radiation, the required surface and the corresponding number of equivalent pilot plants, necessary for the caffeine degradation. (*) Even if a smaller plant would be sufficient, it was decided to keep the value of 1 pilot plant in the modelling.

The degradation efficiency is much greater for processes performed at pH 2.8, both for low and high concentrations of caffeine; these processes require a smaller surface area for capturing sunlight and therefore a small-sized plant is sufficient.

It should be noted that the process at pH 2.8 with a caffeine concentration of 1 mg/L has proved to be very effective; a smaller plant, than the modeled one, would therefore be sufficient; however, it was decided to keep the minimum value of 1 plant in the modeling.

Since the functional unit refers to the process completed in 1 working day, the contributions of the equivalent pilot plants have been normalized assuming that during its life (20 years) it can be used for 4400 working days (see Table 11).

The modelling of the use phase was carried out on the basis of the input-output data determined with the tested photo Fenton processes. In addition to these values, it is also necessary to consider the energy demand of the pump (0.44 kWh/day, per pilot plant), which allows the circulation of water inside the system.

The photo Fenton processes were carried out as follows: the pH was adjusted to the desired value with sulphuric acid; as input of Fe^{3+} was used $FeCl_3·6H_2O$; at the end of the process sodium hydroxide is added to restore the initial pH. The water to treat was contaminated by caffeine as proxy of organic pollutant. According to what reported in the goal and scope definition four different condition were tested: pH 2.8 with 1 mg/L of caffeine; pH 5 with 1 mg/L of caffeine; pH 2.8 with 50 mg/L of caffeine; pH 5 with 50 mg/L of caffeine, using a greater quantity of reagents and humic substances as complexing agent (30 g/L). The inventory values for each of the four processes, with the number of equivalent pilot plants considered and the energy demand are shown in the Table 11.

	1 mg/L caffeine		**50 mg/L caffeine**	
	pH 2.8	**pH 5**	**pH 2.8**	**pH 5**
Sulfuric acid (g)	284.88	174.66	270.47	220.45
Hydrogen peroxide (g)	100.90	100.90	100.90	303.03
$FeCl_3·6H_2O$ (g)	20.00	20.00	20.00	50.00
Sodium hydroxide (g)	56.80	/	57.60	18.00
Humic substances (g)	/	/	/	30
Transport of chemicals (tkm)	0.05	0.05	0.05	0.05
N° of pilot plants equivalent normalized	$2.3x10^{-05}$	0.0037	0.0019	0.0054
Electricity (kWh)	0.44	7.08	3.59	10.45

Table 11. Inventory data for the use phase: the treatment of 1 m^3 of contaminated water, with the 4 solar photo Fenton processes considered. Data are grouped for caffeine concentration and working pH.

As Table 11 shows, the inputs for the process with 50 mg/L of caffeine, at pH 5, are higher than the others; this is because the degradation process in this condition is less effective and a greater amount of chemicals is required to make it happen.
At the end of the degradation processes some chemical species, generated by the incoming substances, remain in the water (iron in the form of oxide, hydroxide or complexes and sodium sulphate). These emissions are not reported in the inventory for two reasons: (I) no qualitative and quantitative analysis was carried out for the determination of these species; (II) since the main LCIA methods do not have characterization factors for these species, even considering them in the modelling would have no repercussions on any impact category.

According to some recent studies (Gallego-Schmid et al., 2019) the acidic solar photo-Fenton process are more environmental friendly compared to the process performed at higher pH. In fact for neutral solar photo-Fenton, the main hotspot is the complexing agent. Therefore, the evaluation of the use of different agents could help reduce the impacts for this type of reaction. For this reason in this work also the environmental impact associated with the humic substances production phase, used as complexing agents, has been analysed. The interesting aspect is that these substances can be obtained from secondary raw materials such as urban bio waste (Bianco Prevot et al., 2017; García-Ballesteros et al., 2018).
The humic substances used as complexing agent in this study were obtained from olive oil mill waste, through an isolation process performed under basic conditions (for more details see García-Ballesteros et al., 2018). The inventory data used to model the isolation process of 1 kg of SBO are reported in Table 12.

Input	Amount	Unit of measure
Transport	0.15	tkm
Potassium hydroxide (digestion step)	56.11	g
Potassium hydroxide (washing step)	561	g
Distilled water	100	kg
Electricity (heating and stirring)	1.43	kWh
Electricity (filtration)	0.036	kWh
Electricity (drying)	0.8	kWh

Table 12. Inventory data for the isolation process of 1 kg of humic substances from olive oil mill wastes.

It has been decided to model the system with a cut-off approach (Shen et al., 2010); the transport of the pomace from oil, from the production plant to the Alcoy laboratory, it is considered as the “cradle” of our process. Any input and output related to the previous processes of cultivation of olives and oil production have been neglected. The pomace from oil is considered a waste and therefore, using this approach, it does not bear any environmental burdens from the previous life. Since the modelling of the study was carried out by locating the system in Spain, the energy mix used is that of this country.

4.3.1 Results and discussion

The software SimaPro 8.2 has been used to model the system and the environmental impacts have been estimated according to the ReCiPe 2008 method. The impacts are reported at midpoint level and 8 categories have been considered: climate change (CC), depletion potential of fossil fuels (RDPf) and metals (RDPm), ozone depletion potential (ODP), freshwater and marine eutrophication (FE and ME), terrestrial acidification (TA) and human toxicity (HT). It should be noted that according to the Technical Report by JRC (Fazio et al., 2018) CC and ODP are recommended and considered satisfactory impact categories; TA, FE, ME, RDPf and RDPm are recommended although they need some improvement; HT falls into the impact categories group of recommended, but to be applied with caution.

The impacts associated with the isolation of 1 kg of humic substances, from oil mill waste, are reported in Table 13. A heat map introduces, for the values of each impact category, a colour gradient that marks the results from red (major impacts) to green (more limited impacts).

	Total	**KOH (digestion)**	**KOH (wash)**	**Water**	**Electricity (heat & stir)**	**Electricity (filtration)**	**Electricity (drying)**	**Transport**
CC kg CO_2 eq	$1,98*10^{+00}$	$9,11*10^{-02}$	$9,11*10^{-01}$	$7,62*10^{-04}$	$5,12*10^{-01}$	$1,66*10^{-02}$	$3,68*10^{-01}$	$7,79*10^{-02}$
ODP kg CFC-11 eq	$2,31*10^{-07}$	$9,54*10^{-09}$	$9,54*10^{-08}$	$5,47*10^{-11}$	$6,33*10^{-08}$	$2,11*10^{-09}$	$4,68*10^{-08}$	$1,34*10^{-08}$
TA kg SO_2 eq	$8,15*10^{-03}$	$3,73*10^{-04}$	$3,73*10^{-03}$	$2,88*10^{-06}$	$1,47*10^{-03}$	$1,03*10^{-04}$	$2,29*10^{-03}$	$1,83*10^{-04}$
FE kg P eq	$8,26*10^{-04}$	$5,83*10^{-05}$	$5,83*10^{-04}$	$2,65*10^{-07}$	$5,63*10^{-05}$	$5,15*10^{-06}$	$1,14*10^{-04}$	$8,56*10^{-06}$
ME kg N eq	$3,46*10^{-04}$	$2,02*10^{-05}$	$2,02*10^{-04}$	$2,16*10^{-07}$	$3,87*10^{-05}$	$3,38*10^{-06}$	$7,51*10^{-05}$	$6,26*10^{-06}$
HT kg 1,4-DB eq	$7,29*10^{-01}$	$4,99*10^{-02}$	$4,99*10^{-01}$	$3,80*10^{-04}$	$4,90*10^{-02}$	$4,80*10^{-03}$	$1,07*10^{-01}$	$1,93*10^{-02}$
RDPm kg Fe eq	$8,97*10^{-02}$	$6,35*10^{-03}$	$6,35*10^{-02}$	$3,47*10^{-04}$	$3,39*10^{-03}$	$5,15*10^{-04}$	$1,14*10^{-02}$	$4,22*10^{-03}$
RDPf kg oil eq	$5,84*10^{-01}$	$2,59*10^{-02}$	$2,59*10^{-01}$	$1,81*10^{-04}$	$1,66*10^{-01}$	$4,54*10^{-03}$	$1,01*10^{-01}$	$2,72*10^{-02}$

Table 13. Impact at midpoint level for the production process of 1 kg of humic substances, from oil mill wastes.

For all the considered categories it can be observed how the main impacts are associated to the amount of potassium hydroxide (KOH), used during the washing phase. From the analysis emerged as the climate change of 1 kg of SBO obtained from oil mill waste is 1.98 kg CO_2 eq. Gallego-Schmid et al. (2019) in their work analysed the environmental performances of different photo Fenton processes, including processes carried out at neutral pH using Ethylenediamine N,N′ disuccinic acid (EDDS) as a complexing agent. They estimate an impact of 5.06 kg CO_2 eq per kg of substances and from the analysis of the photo Fenton process at near neutral pH it appears that the complexing agent is the cause of about 60% of the total impact. Undoubtedly EDDS is much more efficient as a complexing agent than SBO, however the more limited impact of the latter is an interesting aspect.

Table 14 shows the environmental impacts generated by production of the pilot plant (the materials subject to replacement over time were also considered).

	Total	**Steel**	**Aluminum**	**Borosilicate glass**	**PP**	**Anodizing process**	**Pumps**	**Transport**
CC kg CO$_2$ eq	428.623	263.417	93.085	14.922	14.369	7.336	16.806	18.688
ODP kg CFC-11 eq	$2.49*10^{-05}$	$1.28*10^{-05}$	$6.09*10^{-06}$	$9.91*10^{-07}$	$1.01*10^{-07}$	$8.36*10^{-07}$	$8.96*10^{-07}$	$3.22*10^{-06}$
TA kg SO$_2$ eq	2.423	1.402	0.589	0.099	0.043	0.034	0.212	0.044
FE kg P eq	0.201	0.101	0.047	0.005	0.001	0.005	0.040	0.002
ME kg N eq	0.093	0.052	0.021	0.004	0.001	0.002	0.011	0.002
HT kg 1,4-DB eq	295.606	146.481	48.437	4.498	0.295	3.970	87.300	4.624
RDPm kg Fe eq	797.339	751.318	2.142	0.627	0.040	0.440	41.760	1.013
RDPf kg oil eq	111.714	63.546	20.276	4.085	11.197	1.929	4.153	6.528

Table 14. Impact at midpoint level for the pilot plant analyzed.

The main impacts, for all the categories, are associated with the metals used for the structure of the plant and especially the amount of steel.

Figure 22 shows the comparison of the LCIA results of the treatment of 1 m^3 of water per day; the results related to the SPF treatments of a solution of water contaminated with 1 mg/L of caffeine are shown in the figure a); instead the results to treat a solution contaminated with 50 mg/L of caffeine are reported in figure b). The impacts calculated in this way take into account the contribution due both to the chemical process and to the pilot plant itself (plant sized according to what is reported in Table 10). The results are reported in percentage, assigning the value of 100% to the greatest impact for each impact category.

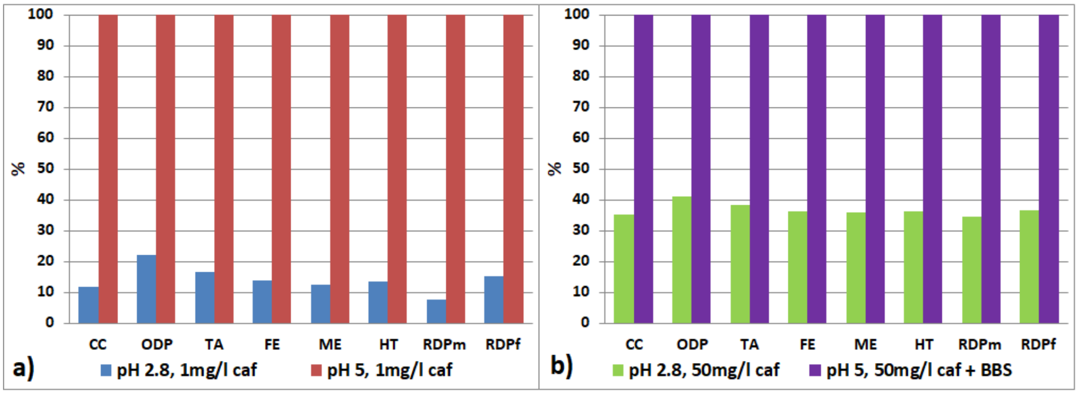


Figure 22. Comparison of the photo Fenton option for the degradation process of 1 m^3 of water, per day: a) caffeine concentration of 1 mg/L; b) caffeine concentration of 50 mg/L. The values are reported grouped for impact category and as a percentage, assigning 100% to the greatest impact for each category analyzed.

It can be observed how, both at 1 mg/L and 50 mg/L of caffeine, the processes at pH 5, have greater impacts for each category when compared to processes at acidic pH.

As already reported, the process at pH 5, for the degradation of a 1 mg/L caffeine solution, was carried out without the use of SBO as a complexing agent; in fact in a previous experiment it was observed how at this concentration of pollutant the SBO suppress the degradation process.

The comparison highlights a clear better environmental profile for the processes conducted at acidic pH; although in these conditions it is necessary a side phase to restore the pH through the addition of sodium hydroxide, this step does not have a considerable influence on the overall environmental impact.
However, it can be observed that the difference in impacts between acidic and near neutral pH is less marked when SBO is used to treat an higher concentrations of pollutants; in this case the contribution of SBO to improve the degradation efficiency is evident, compared to the case at 1 mg/L where the pH 5 process was clearly inefficient (see also Table 10).

For a better understanding of the individual contribution of the impacts for each process the single processes must be analysed separately. For this reason the individual LCIA results of the treatment of 1 m^3 of water carried out in the various conditions tested are shown below.

pH 2.8 - 1 mg/L of caffeine

	Total	Plant	H_2SO_4	NaOH	$FeCl_3$	H_2O_2	Transport	Electricity	Plant EoL
CC **kg CO_2 eq**	$4.58*10^{-01}$	$1.07*10^{-01}$	$2.98*10^{-02}$	$4.62*10^{-02}$	$1.20*10^{-02}$	$1.08*10^{-01}$	$2.60*10^{-02}$	$2.03*10^{-01}$	$-7.35*10^{-02}$
ODP **kg CFC-11 eq**	$1.12*10^{-07}$	$6.22*10^{-09}$	$1.97*10^{-08}$	$4.25*10^{-08}$	$4.05*10^{-09}$	$1.18*10^{-08}$	$4.47*10^{-09}$	$2.57*10^{-08}$	$-2.34*10^{-09}$
TA **kg SO_2 eq**	$4.25*10^{-03}$	$6.06*10^{-04}$	$2.01*10^{-03}$	$2.17*10^{-04}$	$6.49*10^{-05}$	$3.80*10^{-04}$	$6.11*10^{-05}$	$1.26*10^{-03}$	$-3.54*10^{-04}$
FE **kg P eq**	$2.08*10^{-04}$	$5.02*10^{-05}$	$2.19*10^{-05}$	$3.85*10^{-05}$	$8.71*10^{-06}$	$4.47*10^{-05}$	$2.85*10^{-06}$	$6.29*10^{-05}$	$-2.22*10^{-05}$
ME **kg N eq**	$1.10*10^{-04}$	$2.33*10^{-05}$	$1.42*10^{-05}$	$1.40*10^{-05}$	$3.21*10^{-06}$	$2.36*10^{-05}$	$2.09*10^{-06}$	$4.13*10^{-05}$	$-1.21*10^{-05}$
HT **kg 1,4-DB eq**	$2.45*10^{-01}$	$7.39*10^{-02}$	$3.63*10^{-02}$	$3.29*10^{-02}$	$1.07*10^{-02}$	$4.69*10^{-02}$	$6.42*10^{-03}$	$5.87*10^{-02}$	$-2.10*10^{-02}$
RDPm **kg Fe eq**	$2.15*10^{-01}$	$1.99*10^{-01}$	$1.01*10^{-02}$	$4.04*10^{-03}$	$2.17*10^{-03}$	$8.28*10^{-03}$	$1.41*10^{-03}$	$6.29*10^{-03}$	$-1.70*10^{-02}$
RDPf **kg oil eq**	$1.71*10^{-01}$	$2.79*10^{-02}$	$4.33*10^{-02}$	$1.17*10^{-02}$	$2.99*10^{-03}$	$3.81*10^{-02}$	$9.07*10^{-03}$	$5.55*10^{-02}$	$-1.70*10^{-02}$

Table 15. LCIA results for the degradation process of 1 m^3 of water contaminated with 1 mg/L of caffeine, at pH 2.8.

pH 5 - 1 mg/L of caffeine

	Total	Plant	H_2SO_4	$FeCl_3$	H_2O_2	Transport	Electricity	Plant EoL
CC **kg CO_2 eq**	$3.92*10^{+00}$	$1.57*10^{+00}$	$1.83*10^{-02}$	$1.20*10^{-02}$	$1.08*10^{-01}$	2.60*10-02	$3.26*10^{+00}$	$-1.08*10^{+00}$
ODP **kg CFC-11 eq**	$5.03*10^{-07}$	$9.11*10^{-08}$	$1.21*10^{-08}$	$4.05*10^{-09}$	$1.18*10^{-08}$	4.47*10-09	$4.14*10^{-07}$	$-3.42*10^{-08}$
TA **kg SO_2 eq**	$2.57*10^{-02}$	$8.87*10^{-03}$	$1.23*10^{-03}$	$6.49*10^{-05}$	$3.80*10^{-04}$	6.11*10-05	$2.03*10^{-02}$	$-5.19*10^{-03}$
FE **kg P eq**	$1.49*10^{-03}$	$7.35*10^{-04}$	$1.34*10^{-05}$	$8.71*10^{-06}$	$4.47*10^{-05}$	2.85*10-06	$1.01*10^{-03}$	$-3.25*10^{-04}$
ME **kg N eq**	$8.66*10^{-04}$	$3.41*10^{-04}$	$8.70*10^{-06}$	$3.21*10^{-06}$	$2.36*10^{-05}$	2.09*10-06	$6.65*10^{-04}$	$-1.77*10^{-04}$
HT **kg 1,4-DB eq**	$1.80*10^{+00}$	$1.08*10^{+00}$	$2.22*10^{-02}$	$1.07*10^{-02}$	$4.69*10^{-02}$	6.42*10-03	$9.44*10^{-01}$	$-3.08*10^{-01}$
RDPm **kg Fe eq**	$2.79*10^{+00}$	$2.92*10^{+00}$	$6.18*10^{-03}$	$2.17*10^{-03}$	$8.28*10^{-03}$	1.41*10-03	$1.01*10^{-01}$	$-2.49*10^{-01}$
RDPf **kg oil eq**	$1.13*10^{+00}$	$4.09*10^{-01}$	$2.65*10^{-02}$	$2.99*10^{-03}$	$3.81*10^{-02}$	9.07*10-03	$8.93*10^{-01}$	$-2.49*10^{-01}$

Table 16. LCIA results for the degradation process of 1 m^3 of water contaminated with 1 mg/L of caffeine, at pH 5.

pH 2.8 - 50 mg/L of caffeine

	Total	Plant	H_2SO_4	NaOH	$FeCl_3$	H_2O_2	Trans-port	Electri-city	Plant EoL
CC kg CO_2 eq	$2.12*10^{+00}$	$7.97*10^{-01}$	$2.83*10^{-02}$	$4.69*10^{-02}$	$1.20*10^{-02}$	$1.08*10^{-01}$	$2.60*10^{-02}$	$1.65*10^{+00}$	$-5.47*10^{-01}$
ODP kg CFC-11 eq	$3.21*10^{-07}$	$4.63*10^{-08}$	$1.87*10^{-08}$	$4.31*10^{-08}$	$4.05*10^{-09}$	$1.18*10^{-08}$	$4.47*10^{-09}$	$2.10*10^{-07}$	$-1.74*10^{-08}$
TA kg SO_2 eq	$1.48*10^{-02}$	$4.51*10^{-03}$	$1.91*10^{-03}$	$2.20*10^{-04}$	$6.49*10^{-05}$	$3.80*10^{-04}$	$6.11*10^{-05}$	$1.03*10^{-02}$	$-2.64*10^{-03}$
FE kg P eq	$8.38*10^{-04}$	$3.74*10^{-04}$	$2.08*10^{-05}$	$3.90*10^{-05}$	8.71*10-06	$4.47*10^{-05}$	$2.85*10^{-06}$	$5.14*10^{-04}$	$-1.65*10^{-04}$
ME kg N eq	$4.77*10^{-04}$	$1.73*10^{-04}$	$1.35*10^{-05}$	$1.42*10^{-05}$	$3.21*10^{-06}$	$2.36*10^{-05}$	$2.09*10^{-06}$	$3.37*10^{-04}$	$-8.98*10^{-05}$
HT kg 1,4-DB eq	$1.00*10^{+00}$	$5.50*10^{-01}$	$3.44*10^{-02}$	$3.34*10^{-02}$	$1.07*10^{-02}$	$4.69*10^{-02}$	$6.42*10^{-03}$	$4.79*10^{-01}$	$-1.56*10^{-01}$
RDPm kg Fe eq	1.43*10+00	$1.48*10^{+00}$	$9.57*10^{-03}$	$4.10*10^{-03}$	$2.17*10^{-03}$	$8.28*10^{-03}$	$1.41*10^{-03}$	$5.13*10^{-02}$	$-1.27*10^{-01}$
RDPf kg oil eq	6.37*10-01	$2.08*10^{-01}$	$4.11*10^{-02}$	$1.19*10^{-02}$	$2.99*10^{-03}$	$3.81*10^{-02}$	$9.07*10^{-03}$	$4.53*10^{-01}$	$-1.27*10^{-01}$

Table 17. LCIA results for the degradation process of 1 m^3 of water contaminated with 50 mg/L of caffeine, at pH 2.8.

pH 5 - 50 mg/L of caffeine + SBO (increase reactants concentration)

	Total	Plant	H_2SO_4	NaOH	$FeCl_3$	H_2O_2	SBO	Trans-port	Electri-city	Plant EoL
CC kg CO_2 eq	$6.02*10^{+00}$	$2.31*10^{+00}$	$2.31*10^{-02}$	$1.46*10^{-02}$	$3.00*10^{-02}$	$3.24*10^{-01}$	$5.93*10^{-02}$	$2.60*10^{-02}$	$4.81*10^{+00}$	$-1.59*10^{+00}$
ODP kg CFC-11 eq	$7.81*10^{-07}$	$1.34*10^{-07}$	$1.52*10^{-08}$	$1.35*10^{-08}$	$1.01*10^{-08}$	$3.53*10^{-08}$	$6.92*10^{-09}$	$4.47*10^{-09}$	$6.11*10^{-07}$	$-5.05*10^{-08}$
TA kg SO_2 eq	$3.86*10^{-02}$	$1.31*10^{-02}$	$1.56*10^{-03}$	$6.88*10^{-05}$	$1.62*10^{-04}$	$1.14*10^{-03}$	$2.45*10^{-04}$	$6.11*10^{-05}$	$2.99*10^{-02}$	$-7.65*10^{-03}$
FE kg P eq	$2.31*10^{-03}$	$1.08*10^{-03}$	$1.69*10^{-05}$	$1.22*10^{-05}$	$2.18*10^{-05}$	$1.34*10^{-04}$	$2.48*10^{-05}$	$2.85*10^{-06}$	$1.50*10^{-03}$	$-4.79*10^{-04}$
ME kg N eq	$1.33*10^{-03}$	$5.03*10^{-04}$	$1.10*10^{-05}$	$4.43*10^{-06}$	$8.03*10^{-06}$	$7.10*10^{-05}$	$1.04*10^{-05}$	$2.09*10^{-06}$	$9.81*10^{-04}$	$-2.61*10^{-04}$
HT kg 1,4-DB eq	$2.77*10^{+00}$	$1.60*10^{+00}$	$2.81*10^{-02}$	$1.04*10^{-02}$	$2.67*10^{-02}$	$1.41*10^{-01}$	$2.19*10^{-02}$	$6.42*10^{-03}$	$1.39*10^{+00}$	$-4.54*10^{-01}$
RDPm kg Fe eq	$4.13*10^{+00}$	$4.31*10^{+00}$	$7.80*10^{-03}$	$1.28*10^{-03}$	$5.44*10^{-03}$	$2.49*10^{-02}$	$2.69*10^{-03}$	$1.41*10^{-03}$	$1.49*10^{-01}$	$-3.67*10^{-01}$
RDPf kg oil eq	$1.74*10^{+00}$	$6.03*10^{-01}$	$3.35*10^{-02}$	$3.71*10^{-03}$	$7.47*10^{-03}$	$1.14*10^{-01}$	$1.75*10^{-02}$	$9.07*10^{-03}$	$1.32*10^{+00}$	$-3.68*10^{-01}$

Table 18. LCIA results for the degradation process of 1 m^3 of water contaminated with 50 mg/L of caffeine, at pH 5, using SBO as complexing agent.

From the analysis of all the previous tables emerges how the electricity, used to circulate the water inside the system, is often the cause of the main impacts. The second major cause of impacts is the plant itself. This contribution is more marked especially for processes at pH 5, which, given the lower efficiency of degradation, require a larger surface to capture the sunlight and therefore a larger plant.

As regards the degradation process itself (chemicals), it can be observed how its contribution is appreciable only in the case at pH 2.8 and 1 mg/L of caffeine (Table 15). In fact, in this situation the dimensions of the plant are limited and the impacts due to the use of chemical substances are more influential on the final impacts. Working under these conditions it is noted that the use of sodium hydroxide and sulfuric acid cause the greatest impacts for the ODP and TA categories respectively. Obviously if analysed in detail the processes carried out at pH 5, these show reduced impacts due to the inputs of sulfuric acid and sodium hydroxide, given their minor or no use.

The hydrogen peroxide, the concentration of which has been kept constant in all processes except for the one at pH 5 with 50 mg/L of caffeine, is responsible for impacts that have roughly the same relative weight for each category considered. Unlike what Gallego-Schmid et al. (2019) observed the contribution of complexing agents (SBO) to the overall impacts is minimum; in this case the main problem, which worsens the environmental impacts, is the low degradation efficiency of the process performed in such conditions.

4.3.1 Conclusions

This study has assessed the environmental impacts of the treatment of water, for the degradation of persistent pollutants, via the solar photo Fenton process. The impacts were measured modelling the system on the base of a real pilot plant and using primary data obtained by tested processes.

Four photo Fenton processes were tested by modifying the working pH (2.8 and 5) and the concentration of pollutant to be degraded (1 mg/L and 50 mg/L of caffeine). For the process at pH 5 and 50 mg/L of caffeine, as complexing agent, humic substance, obtained from olive oil mill waste, was added. The interest in evaluating the environmental performance of photo Fenton processes at different pH arises from the fact that research is moving towards a decrease in the use of chemicals to carry out such treatments; working at near neutral pH would allow to limit the use of acids and subsequently of bases to modify the pH, with consequent economic savings. At the same time advanced oxidation processes often need a fair amount of energy; therefore, moving to a cheap energy source like solar light seems to be unavoidable. The research direction that aims to reduce the use of chemicals, for these processes, does not seem to be the best solution if the efficiency of the treatment decreases. In fact, working at pH near neutral results in a decrease in the environmental impacts associated to the use of chemicals, but at the same time there is also a decrease in the effectiveness of the processes.

It is important to underline that if we set a temporary limit for the amount of water to be treated (e.g. 1 m^3 in one day), with processes less effective, we must increase the size of the plant; consequentially the environmental burden associated with this choice will also increase.
It is not obvious that decreasing the amount of reagents (i.e. not acidifying the water at low pH and subsequently not neutralizing it after the treatment) is always advantageous if a "threshold" of efficiency is not attained.
An encouraging aspect rise from our analysis is that the possibility of obtaining complexing agents from organic waste (such as SBO) allows to obtain such substances with limited environmental impacts. This possibility could be very interesting as a future perspective. In fact, if scientific research is able to identify a SBO capable to form photoactive iron complexes and therefore to improve the efficiency of processes at near neutral pH, then a real and sustainable application of these technologies can be considered.

4.4 Case study 3: the environmental assessment of humic acid coated magnetic materials used as catalyst in photo-Fenton processes

As seen in the introduction of this chapter in the classic (photo)-Fenton process, OH· radicals are generated by the H_2O_2 decomposition mediated by iron species (Fe(II)/Fe(III)) in solution (Fiorenza et al., 2020). However, this process is limited by the need to adjust the pH to the optimal conditions (pH≈3) and by the subsequent neutralization before water discharge, creating a serious operational and economic constraint for its large-scale application (Malato et al., 2009). Additionally, the classic Fenton is well-known for the iron consumption that requires constant Fe(II) addition and consequently sludge formation, impacting the cost-effectiveness of the process for its removal (Lastre-Acosta et al., 2019).

The use of magnetite (Fe_3O_4), a mixture of Fe(II) and Fe(III), as heterogeneous (photo)-Fenton catalyst represents a promising approach to overcome some limitations of the classic process. Magnetite can act as an iron source that can be easily recovered from the reaction medium employing a costless and environmental friendly magnetic field and reused in successive cycles (Feijoo et al., 2020; Gonçalves et al., 2019). However, the natural oxidation of Fe(II) forms an outer layer of Fe(III) that passivates the magnetite slowing the generation of reactive species. The addition of an external organic layer of humic acid, when in proper amounts, has been described as enhancing the efficiency for drugs removal and stabilizing the magnetite core from iron oxidation, keeping the catalyst active without losing efficiency in consecutive cycles (García-Ballesteros et al., 2018). Moreover, even if the light-driven photo-Fenton process can be activated by the natural sun-light, due to its seasonality, the irradiation energy, required for a continuous process, strongly affects their environmental burden (Chatzisymeon et al., 2013; Giménez et al., 2015).

In this work, we focus on the actual environmental impacts generated by the heterogeneous photo-Fenton processes. The methodology of LCA was applied to identify the hotspots of using the magnetite particles covered with humic acid (Fe_3O_4/HA (Gonçalves et al., 2019)) as heterogeneous photo-Fenton catalyst for water remediation. The introduction of humic acid has been shown to improve the efficacy and stability of the catalyst. An interesting aspect of the application of humic acids is the potential replace by humic-like substances derived from food or urban waste valorizing materials that would be considered waste (Montoneri et al., 2013; Nisticò et al., 2017). The overall process sustainability was considered and a comparative LCA study was performed applying Fe_3O_4/HA materials for the activation of hydrogen peroxide and persulfate. The burdens related to catalyst preparation, chemicals, pH adjustment and electricity consumption were evaluated, at laboratory scale. Bisphenol A (BPA) was studied as target contaminant of emerging concern, and its removal was evaluated in the different experimental conditions. Considering the potential photo-Fenton activation by natural solar light in the wastewater treatment plant, it was explored more in detail the effect of the other experimental parameters, better evidenced when neglecting the contribution of the irradiation energy demand.

4.4.1. Materials and Methods

The assessment of environmental impacts was carried out with data obtained at the laboratory level, for more information beyond the LCA analysis, refer to the work of Gonçalves et al. (2020).

The environmental impacts are estimated through LCA analysis, performed according to the ISO 14040/44 guidelines (ISO, 2006a; ISO, 2006b).

Goal and scope definition

The goal of the present study is to assess the environmental impacts of the use of photo-Fenton processes to treat polluted water. In detail, the environmental burdens of magnetite particles coated with humic acid for their application as heterogeneous photo-Fenton processes were investigated using bisphenol A as pollutant model molecule. For this, the environmental impact of different experimental conditions were considered: effect of humic acid coating; catalyst loading; type and oxidant loading at different pH.

To perform the degradation process a solution of oxidant and the heterogeneous catalyst were added to the polluted water (water contaminated with Bisphenol A with initial concentration of 20 μM); as light source an UVA/UVB lamp was applied. The removal of 90% BPA from 1 L of Milli-Q water, was chosen as functional unit. The obtained information can give insights for future industrial application for water remediation in water or wastewater treatment plants.

Figure 23 reports the system boundaries considered for the study. The unit processes included are: i) the production of each chemical reagents (H_2SO_4, H_2O_2, etc.), starting from the extraction of the resources, production of the chemicals and transport; ii) the synthesis of the catalyst, where the entire synthesis process was modelled using both data directly measured and data obtained from literature; iii) the production of electricity consumed by the different configuration of the degradation processes, including extraction of resources, transport and energy conversion; iv) as the last unit process the production of sodium hydroxide, to restore the natural pH, was considered.

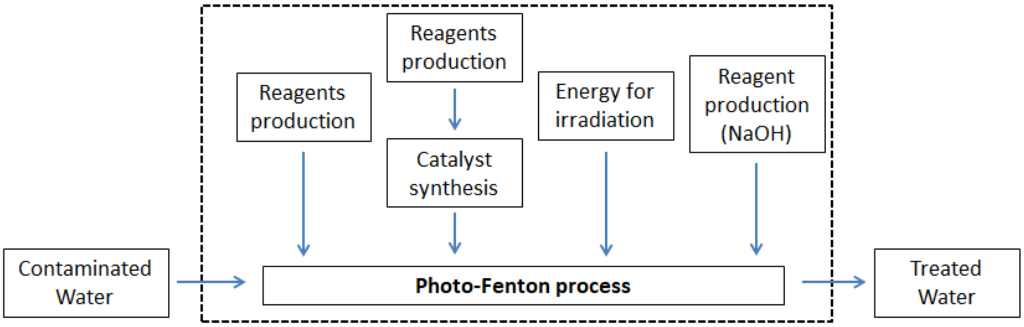


Figure 23. System boundary for the heterogeneous photo-Fenton processes. (Only the unit processes contained in the dashed box were considered during the LCA analysis)

The amount of energy to reduce the initial concentration of the target pollutant by 90% was determined by the kinetic constant (k). The necessary time to degrade 90% of the pollutant and consequently the energy necessary to irradiate the system for the same time was determined from k value.

Infrastructure and equipment used during the experimental analysis were excluded from the calculation.

The main assumptions were made to model the catalyst synthesis. As reported by Gonçalves et al. (2019) the catalyst was synthesized with commercial humic acids, but given the lack of information on the humic acid production process, it was decided to reconstruct the procedure described by Montoneri et al. (2009). The decision allows to effectively model the recovery of humic substances from compost obtained from organic wastes, so to have information on the associated impacts; at the same time, given the absence of a unique structure of humic acids, their behaviour should not be influenced by their origin.

To estimate the energy consumption associated with the heating step in both, humic substances extraction and catalyst synthesis the instructions given by

Piccinno et al. (2016) were followed. The energy consumption has been estimated assuming ad hoc reactors and using the equations that allow to quantify the heat needed to reach a certain temperature and to compensate for the losses due to the reaction (Piccinno et al., 2016). The reason behind this choice is related to the high energy input values directly measured at laboratory level. In fact, the tools used to follow the extraction and synthesis procedures are not meant only for these purposes and therefore a large amount of energy is wasted.

Inventory analysis

The second step of LCA consists in the creation of a model of the real system under analysis by collecting all the raw materials, resources, energy, outputs and emission related to the considered functional unit.

The extraction of 1 kg of humic substances from compost was modelled using the data reported in Table 19. Similarly to what was done for the previous case study, the system was model with a cut-off approach (Shen et al., 2010); we considered the "cradle", of the humic substances, the transport of the compost from the production plant to the Turin laboratory. Any input and output related to the previous life of the materials that have given origin to the compost and the processes themselves to obtain the compost, have been neglected. Basically, based on the cut-off principle, we consider compost as waste and waste does not bear any environmental burden from the previous life.

Input	Amount	Unit of measure	Type of measure
Transport	0.075	tkm	directly measured
NaOH	39.997	g	estimated value(*)
$Na_4P_2O_7$	265.9	g	directly measured
Energy for heating and stirring	5140	kJ	estimated value(*)
Energy for centrifugation	0.166	kWh	directly measured
Distilled water	60	L	directly measured
H_2SO_4	1390	g	directly measured
Energy for centrifugation	0.166	kWh	directly measured
Distilled water	30	L	directly measured
Energy to dry	2880	kJ	estimated value(*)

Table 19. Inventory for the extraction process of 1 kg of humic substances from compost, according to (Montoneri et al, 2009, Piccinno et al., 2016). (*) Value estimated according to the equation reported in (Piccinno et al., 2016).

The data used to model the synthesis of the magnetite particles are reported in Table 20. The only difference in the synthesis procedure between Fe_3O_4/HA and Fe_3O_4 particles is the presence of humic acid for the coated particles.

Input	Amount	Unit of measure	Type of measure
$FeCl_3$	2581.366	g	directly measured
$FeSO_4$	1678.950	g	directly measured
Distilled water	106.336	L	directly measured
Energy for heating and stirring	10312.590	kJ	estimated value(*)
Humic acid(**)	100.317	g	directly measured
NH_3	882.789	g	directly measured
Energy to dry	57782.590	kJ	estimated value(*)
Energy for centrifugation	6.420	kWh	directly measured
Energy to dry	80253.60	kJ	estimated value(*)
N_2	21467.840	g	directly measured

Table 20. Inventory for the synthesis of 1 kg of magnetite particles (Fe_3O_4/HA), according to (García-Ballesteros et al., 2018, Piccinno et al., 2016). (*) Value estimated according to the equation reported in (Piccinno et al., 2016). (**) For the synthesis of bare Fe_3O_4 the input of humic acid is not considered.

Table 21 reports the data on chemicals and energy consumption per functional unit. The tested variables were: pH, type of oxidant and type of catalyst. The amount of catalyst used is the same both for the processes with Fe_3O_4/HA and with Fe_3O_4. The quantity of sodium hydroxide refers to the quantity theoretically added to the treatment to restore the natural pH. The energy consumption refers to the energy spent to irradiate the system and is directly proportional to the kinetic constant. The kinetic constant values were determined by degradation experiments (Gonçalves et al, 2019), the lower is the k value the faster is the degradation and therefore the process is more effective, as presented in the Table 22.

pH 3	**Oxidant type :**	$S_2O_8^{2-}$		H_2O_2	
	Oxidant (g)	0.238		0.034	
	Catalyst (g)	0.1		0.1	
	Sulfuric acid (g)	0.0490		0.0490	
	Sodium hydroxide (g)	0.04		0.04	
	Catalyst type :	**Fe_3O_4/HA**	**Fe_3O_4**	**Fe_3O_4/HA**	**Fe_3O_4**
	Energy consumption (kWh)	1.425	2.151	1.448	3.154

pH 4	**Oxidant type :**	$S_2O_8^{2-}$		H_2O_2	
	Oxidant (g)	0.238		0.034	
	Catalyst (g)	0.1		0.1	
	Sulfuric acid (g)	0.0049		0.0049	
	Sodium hydroxide (g)	0.004		0.004	
	Catalyst type :	**Fe_3O_4/HA**	**Fe_3O_4**	**Fe_3O_4/HA**	**Fe_3O_4**
	Energy consumption (kWh)	2.601	3.049	8.373	11.808

pH 6	**Oxidant type :**	$S_2O_8^{2-}$		H_2O_2	
	Oxidant (g)	0.238		0.034	
	Catalyst (g)	0.1		0.1	
	Sulfuric acid (g)	$4.9x10^{-05}$		$4.9 x10^{-05}$	
	Sodium hydroxide (g)	$4 x10^{-05}$		$4 x10^{-05}$	
	Catalyst type :	**Fe_3O_4/HA**	**Fe_3O_4**	**Fe_3O_4/HA**	**Fe_3O_4**
	Energy consumption (kWh)	2.990	5.233	30.297	41.865

pH 6.5	**Oxidant type :**	$S_2O_8^{2-}$	
	Oxidant (g)	0.238	
	Catalyst (g)	0.1	
	Sulfuric acid (g)	$1.96 x10^{-05}$	
	Sodium hydroxide (g)	$1.6 x10^{-05}$	
	Catalyst type :	**Fe_3O_4/HA**	**Fe_3O_4**
	Energy consumption (kWh)	6.059	7.427

Table 21. Inventory of the input related to the treatment of 1 L of Milli-Q water contaminated with BPA (20 µM). The tested variables were: pH (3, 4, 6, 6.5); oxidant type ($S_2O_8^{2-}$ and H_2O_2); catalyst type (Fe_3O_4/HA and bare Fe_3O_4)

k (min^{-1})	$S_2O_8^{2-}$		H_2O_2	
	Fe_3O_4/HA	Fe_3O_4	Fe_3O_4/HA	Fe_3O_4
pH 3	0.0323	0.0214	0.0318	0.0146
pH 4	0.0177	0.0151	0.0055	0.0039
pH 6	0.0154	0.0088	0.00152	0.0011
pH 6.5	0.0076	0.0062		

Table 22. Kinetic constant (k) for the degradation processes changing different parameters: pH, catalyst type (Fe_3O_4/HA and Fe_3O_4) and type of oxidant (persulfate and hydrogen peroxide).

Another set of experiments was conducted by varying the concentration of hydrogen peroxide; considering the low efficiency above pH 4, these tests were carried out at pH 3 and 4. The variables kept constant were the type and concentration of catalyst. Input values are reported in Table 23.

Table 24 shows the kinetic constant collected for this set of experiments.

	[Oxidant] =	**0 mM**	**0.5 mM**	**1 mM**	**2 mM**	**3 mM**	**5 mM**	**10 mM**	**20 mM**
pH 3	H_2O_2 (g)	0	0.017	0.034	0.068	0.102	0.170	0.340	0.680
	Catalyst (g)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Sulfuric acid (g)	0.0490	0.0490	0.0490	0.0490	0.0490	0.0490	0.0490	0.0490
	Sodium hydroxide (g)	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
	Energy consumption (kWh)	92.103	2.193	1.448	1.842	1.919	1.706	1.396	2.162
pH 4	H_2O_2 (g)	0	0.017	0.034	0.068	0.102	0.170	0.340	0.680
	Catalyst (g)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Sulfuric acid (g)	0.0049	0.0049	0.0049	0.0049	0.0049	0.0049	0.0049	0.0049
	Sodium hydroxide (g)	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
	Energy consumption (kWh)	153.506	15.351	8.373	3.289	3.070	4.187	2.002	2.122

Table 23. Inventory of the input for the treatment of 1 L of Milli-Q water contaminated with BPA (20 µM) in the presence different H_2O_2 concentrations catalyzed by Fe_3O_4/HA (100 mg/L) at pH 3 and 4.

k (min^{-1})	H_2O_2 concentration							
	0 mM	0.5 mM	1 mM	2 mM	3 mM	5 mM	10 mM	20 mM
pH 3	0.0005	0.021	0.0318	0.025	0.024	0.027	0.033	0.0213
pH 4	0.0003	0.003	0.0055	0.014	0.015	0.011	0.023	0.0217

Table 24. Kinetic constant (k) for the degradation processes at different H_2O_2 concentrations at pH 3 and 4 in the presence of Fe_3O_4/HA as catalyst. The higher the value expressed by the kinetic constant, the higher the rate of degradation, which results in a better efficiency of the system.

The effect of catalyst loading was evaluated as well for the activation of hydrogen peroxide as shown in Table 25. The kinetic constant values are reported in Table 26.

	Catalyst concentration	**100 mg/L**	**200 mg/L**	**500 mg/L**
pH 3	H_2O_2 (g)	0.034	0.034	0.034
	Catalyst (g)	0.1	0.2	0.5
	Sulfuric acid (g)	0.0490	0.0490	0.0490
	Sodium hydroxide (g)	0.04	0.04	0.04
	Energy consumption (kWh)	1,448	0,980	0,598
pH 4	H_2O_2 (g)	0.034	0.034	0.034
	Catalyst (g)	0.1	0.2	0.5
	Sulfuric acid (g)	0.0049	0.0049	0.0049
	Sodium hydroxide (g)	0.004	0.004	0.004
	Energy consumption (kWh)	8,373	2,193	4,605
pH 6	H_2O_2 (g)	0.034	0.034	0.034
	Catalyst (g)	0.1	0.2	0.5
	Sulfuric acid (g)	$4.9x10^{-05}$	$4.9 x10^{-05}$	$4.9 x10^{-05}$
	Sodium hydroxide (g)	$4 x10^{-05}$	$4 x10^{-05}$	$4 x10^{-05}$
	Energy consumption (kWh)	30,297	15,351	11,513

Table 25. Inventory of the input related for the treatment of 1 L of Milli-Q water contaminated with BPA (20 μM) in the presence of different Fe_3O_4/HA loading (from 100 to 500 mg/L at pH 3, 4 and 6 in the presence of 1mM of H_2O_2.

k (min^{-1})	Catalyst concentration (mg/L)		
	100	200	500
pH 3	0.0318	0.047	0.077
pH 4	0.0055	0.021	0.01
pH 6	0.00152	0.003	0.004

Table 26. Kinetic constant for the degradation processes at different Fe_3O_4/HA concentrations in the presence of H_2O_2 (1 mM) at different pH.

In general, the data present in the Ecoinvent 3.3 database was used as input to model the system; for the production of chemicals, reference was made to the European context (when present), instead the Italian energy mix was used to model the energy consumption.

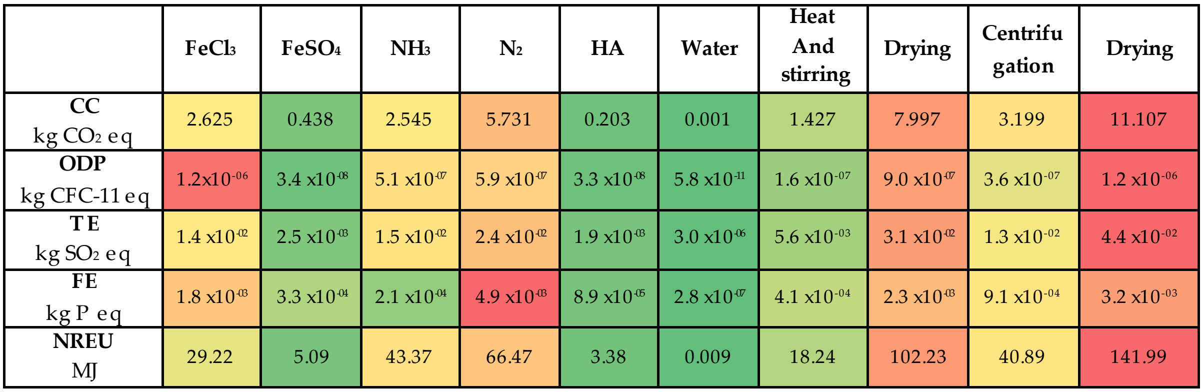
Life cycle impact assessment

The inputs and outputs collected that make up the inventory, are transformed into a handful of environmental impact categories. SimaPro 8.2 has been used for LCA modelling and environmental impacts have been estimated according to two different methods: the ReCiPe 2008 method (Goedkoop et al, 2009) and the Cumulative Energy Demand method (Frischknecht et al, 2007). The ReCiPe 2008 method includes both midpoint (problem oriented) and endpoint (damage oriented) impact categories; as seen in Chapter 3: midpoints are considered to be a point, between the emission and the endpoint, in the cause-effect chain of a particular impact category (Bare et al., 2012). In general, indicators that are chosen close to the inventory result (midpoint) have a lower uncertainty, as only a small part of the environmental mechanism needs to be modelled, while indicators near endpoint level can have significant uncertainties. Given the high number of impact categories analyzed by the ReCiPe method at midpoint level, it has been preferred to use a limited group of impact categories. The most widely used impact categories chosen for this study were: climate change (CC, kg CO_2 eq), ozone depletion potential (ODP, kg CFC-11 eq), terrestrial acidification (TA, kg SO_2 eq), freshwater eutrophication (FE, kg P eq). For the assessment of energy consumption, only the impact category relating to non-renewable (fossil) resources was considered (NREU, MJ); inputs based on renewable energy are not taken into account, as these are regarded as sustainable.

4.4.2. Results and discussion

Life Cycle Impact Assessment of the catalyst synthesis

Table 27 shows the environmental impacts calculated for the 1 kg scale synthesis of magnetite particles covered with humic acid following the previously described procedure (Gonçalves et al., 2020). All used chemicals and necessary energy in the process were evaluated considering the impact categories: climate change (CC), ozone depletion potential (ODP), terrestrial acidification (TA), freshwater eutrophication (FE) and non-renewable (fossil) energy use (NREU). A heat map introduces, for the values of each impact category, a colour gradient that marks the results from red (the worst score, major impacts) to green (the best score, more limited impacts).



	$FeCl_3$	$FeSO_4$	NH_3	N_2	HA	Water	Heat And stirring	Drying	Centrifu gation	Drying
CC kg CO_2 eq	2.625	0.438	2.545	5.731	0.203	0.001	1.427	7.997	3.199	11.107
ODP kg CFC-11 eq	1.2x10^{-06}	3.4 x10^{-08}	5.1 x10^{-07}	5.9 x10^{-07}	3.3 x10^{-08}	5.8 x10^{-11}	1.6 x10^{-07}	9.0 x10^{-07}	3.6 x10^{-07}	1.2 x10^{-06}
TE kg SO_2 eq	1.4 x10^{-02}	2.5 x10^{-03}	1.5 x10^{-02}	2.4 x10^{-02}	1.9 x10^{-03}	3.0 x10^{-06}	5.6 x10^{-03}	3.1 x10^{-02}	1.3 x10^{-02}	4.4 x10^{-02}
FE kg P eq	1.8 x10^{-03}	3.3 x10^{-04}	2.1 x10^{-04}	4.9 x10^{-03}	8.9 x10^{-05}	2.8 x10^{-07}	4.1 x10^{-04}	2.3 x10^{-03}	9.1 x10^{-04}	3.2 x10^{-03}
NREU MJ	29.22	5.09	43.37	66.47	3.38	0.009	18.24	102.23	40.89	141.99

Table 27. Impact at midpoint level for the synthesis process of 1 kg of catalyst (Fe_3O_4/HA).

The data show that for all impact categories (CC, ODP, TE and NREU) the main contribution derives from energy consumption; in particular, the drying phase at the end of the synthesis procedure is responsible for the greatest impacts. The impact on ozone depletion potential derives not only from the energy contribution, but is also due to the use of $FeCl_3$, attributable in turn to the use of chlorine gas. Instead, the highest impact for the FE is generated by the use of nitrogen, which in turn requires energy for its production. For each impact category examined, the contribution of humic substances (humic acid - HA) is very low.

As the synthesis process of bare magnetite particles (Fe_3O_4) is identical, results comparable to those reported above are obtained, obviously excluding the addition of humic acids.

LCIA of the degradation process

A comparative LCIA of Fe$_3$O$_4$/HA (100 mg/L) as heterogeneous photo-Fenton catalyst for the persulfate and hydrogen peroxide (1 mM) activation was performed, and the results are shown in Table 28 and Table 29, respectively. The impact of catalyst, reagents, all chemicals for pH adjustment (pH 3) and subsequent neutralization as well as irradiation energy (UVA/UVB lamp), for 90% bisphenol-A (20 μM) removal from water, in 1 L scale were considered. A heat map introduces, for the values of each impact category, a colour gradient that marks the results from red (major impacts) to green (more limited impacts).

	Total	Sodium persulfate	Sulfuric acid	Fe$_3$O$_4$/HA	Sodium hydroxide	Electricity
CC kg CO$_2$ eq	0.714	0.000341	7.91 x10^{-06}	0.003527	4.97 x10^{-05}	0.710341
ODP kg CFC-11 eq	8.02x10^{-08}	9.19 x10^{-11}	3.17 x10^{-12}	5.03 x10^{-10}	2.98 x10^{-11}	7.96 x10^{-08}
TE kg SO$_2$ eq	0.003	2.76 x10^{-06}	3.18 x10^{-07}	1.52 x10^{-05}	2.44 x10^{-07}	0.002808
FE kg P eq	0.0002	1.94 x10^{-07}	9.73 x10^{-09}	1.42 x10^{-06}	2.99 x10^{-08}	0.000203
NREU MJ	9.132	5.33 x10^{-03}	3.16 x10^{-04}	4.51 x10^{-02}	5.53 x10^{-04}	9.081036

Table 28. Impact at midpoint level for the degradation process of 90% of 20 μM BPA in 1 L of water in the presence of Fe$_3$O$_4$/HA (100 mg/L) and persulfate (1 mM) at pH 3.

	Total	Hydrogen peroxide	Sulfuric acid	Fe$_3$O$_4$/HA	Sodium hydroxide	Electricity
CC kg CO$_2$ eq	0.725	4.19x10^{-05}	7.91 x10^{-06}	0.003527	4.97 x10^{-05}	0.721501
ODP kg CFC-11 eq	8.14x10-08	3.80 x10^{-12}	3.17 x10^{-12}	5.03 x10^{-10}	2.98 x10^{-11}	8.09 x10^{-08}
TE kg SO$_2$ eq	0.003	1.69 x10^{-07}	3.18 x10^{-07}	1.52 x10^{-05}	2.44 x10^{-07}	0.002852
FE kg P eq	0.0002	1.54 x10^{-08}	9.73 x10^{-09}	1.42 x10^{-06}	2.99 x10^{-08}	0.000206
NREU MJ	9.270	6.55 x10^{-04}	3.16 x10^{-04}	4.51 x10^{-02}	5.53 x10^{-04}	9.223713

Table 29. Impact at midpoint level for the degradation process of 90% of 20 μM BPA in 1 L of water in the presence of Fe$_3$O$_4$/HA (100 mg/L) and hydrogen peroxide (1 mM) at pH 3.

For both systems, persulfate and hydrogen peroxide, the contribution of electricity on the final impacts is evident. This energy consumption derives from the electricity spent to irradiate the system (UVA/UVB lamp) and is directly proportional to the time required by the processes to degrade 90% of BPA (the greater the time required, the greater energy demand). For each impact categories more than 99% of the total impacts is due to electricity. Taking into account the energy consumption (electricity input), it is therefore clear how the overall environmental impacts are directly proportional to the kinetic constants (k) deriving from degradations (see Table 22); the higher the value expressed by the kinetic constant, the higher the rate of degradation, which results in a better efficiency of the system. It can be observed how the working conditions of the degradation processes analysed in Table 28 and Table 29 have k values among the highest and therefore can be considered examples of efficient processes. Despite what has just been observed the high consumption of electricity, highlighted by the LCA analysis, derives from the fact that at laboratory scale, in order to activate the degradation reaction, it is necessary to use lamps that emit specific wavelengths (in this case UVA-UVB range). In summary, the energy demand to irradiate the system is therefore directly proportional to (i) the concentration of pollutant, (ii) the volume of water to be treated and obviously (iii) the effectiveness of the catalytic system.

Focusing attention only on the impacts generated by the oxidants, it was observed that the input of persulfate has slightly greater impacts than hydrogen peroxide; in fact, for four impact categories (CC, ODP, TE and FE) the impact related to H_2O_2 is lower (or similar) than the impact related to sulfuric acid, while in the case of persulfate the impacts are always greater than those relative to sulfuric acid.

The impact of the humic acid coating was evaluated by comparing the coated magnetite with the pristine material (Fe_3O_4) for the activation of persulfate and hydrogen peroxide at different pH (3, 4, 6 and 6.5) as presented in Table A1 and Table A2 (see the appendix at the end of the chapter). A general trend similar to that reported for cases at pH 3 can be observed; the greatest impacts derive from the energy consumption, consumption that increases raising the pH (as degradation times slow down and greater exposure to the light source is required to degrade BPA). At circumneutral pH, a decrease in impacts due to less use of sulfuric acid and sodium hydroxide is noted, shown in more detail later (Figure 25). However, these minor impacts do not affect the final result.

As the trends of all the impact categories analyzed are similar, in the subsequent analyses only the results relating to the climate change category will be shown.

Climate Change

The humic acid coating impact on CC was evaluated by comparing the degradation process performed in the presence of coated magnetite with the bare magnetite at different pH conditions, as shown in Figure 24. Moreover, the impact of using persulfate or hydrogen peroxide activation for BPA degradation was also evaluated in the presence of both materials. For all tested pH, it was observed a higher CC impact for the bare magnetite comparing with the humic acid coated material for both, persulfate and hydrogen peroxide at all tested pH conditions. This feature can be justified by the slower degradation occurring in the presence of the bare material. It was also observed a CO_2 emission increase raising the pH, due to slower degradation rate in these conditions and longer irradiation time needed (more energy consumed) to achieve the pollutant removal. In fact, when working in the presence of hydrogen peroxide at pH 6, an enormous impact for both materials was observed, while this effect was significantly lower in the presence of persulfate, even at pH 6.5.

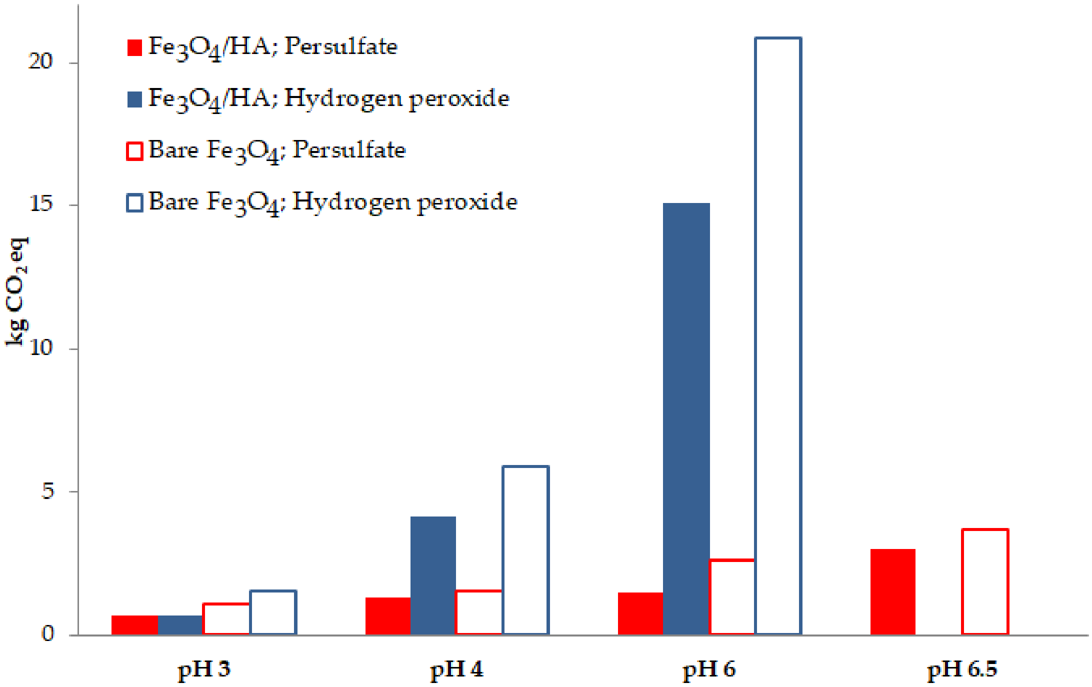


Figure 24. Comparison of the Climate Change (kg CO_2 eq) results of the degradation processes conducted by varying different parameters: pH, oxidant: persulfate and hydrogen peroxide and catalyst type Fe_3O_4/HA and bare Fe_3O_4.

When neglecting the electricity impact, it was observed that working at a circumneutral pH allows to obtain a slightly lower impact as presented in Figure 25. As expected, the degradation process shows a lower impact raising the pH, due to the progressive lower chemicals used for the pH adjustment and neutralization necessary to carry out the degradation. Additionally, neglecting the electricity impact, significantly lower CO_2 emissions were found when using hydrogen peroxide instead of persulfate.

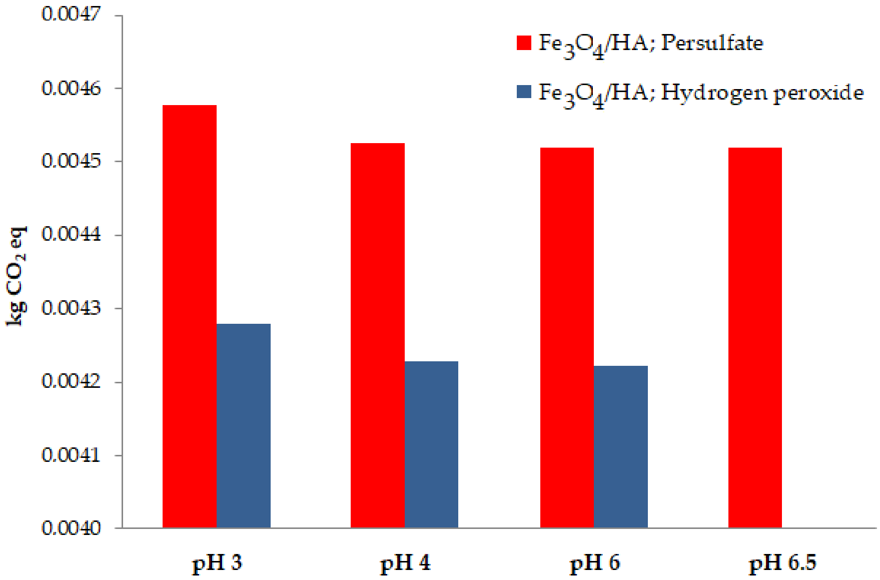


Figure 25. Comparison of the Climate Change (kg CO_2 eq) results of the degradation processes neglecting the electricity input. The bars report the results obtained by varying two parameters: pH and oxidant: persulfate and hydrogen peroxide (1.0 mM) in the presence of Fe_3O_4/HA (100 mg/L).

Considering the lower CO_2 emissions of the degradation system when using hydrogen peroxide instead of persulfate, the effect of raising the H_2O_2 concentration up to 20 mM, at pH 3 and 4 was investigated; the obtained results are presented in Table 30. This choice aimed to investigate if higher concentrations of H_2O_2 promote greater efficiency with more limited impacts (higher rate of degradation and lower energy consumption). The results of the LCA analysis reported in Table 30 were obtained taking into account the energy demand to irradiate the system. From the heat map, identifying the best (green colour) and worst (red colour), it was possible to observe a lower CO_2 emission for the degradation when performed at pH 3 than 4. Additionally, the lower impact was observed for those H_2O_2 concentrations that allowed faster degradation kinetics, i.e. 1 mM and 10 mM, as presented in Table 24.

kg CO_2 eq	**H_2O_2 concentration**							
	0 mM	**0.5 mM**	**1 mM**	**2 mM**	**3 mM**	**5 mM**	**10 mM**	**20 mM**
pH 3	45.894	1.097	0.726	0.922	0.96	0.854	0.7	1.082
pH 4	76.487	7.652	4.176	1.643	1.534	2.09	1.002	1.062

Table 30. Comparison of the CC (kg CO_2 eq) degradation processes results at different H_2O_2 concentration in the presence of Fe_3O_4/HA (100 mg/L) as catalyst, at pH 3 and 4.

The effect of raising significantly the H_2O_2 concentration was more extensively evaluated by comparing the CC analysis of the degradation system at 1 and 10 mM concentration (Table 31). The CO_2 emission related to hydrogen peroxide is directly proportional to the amount of oxidant put in solution. Therefore, the emission in the order of 10^{-5} kg, in the case of a concentration of H_2O_2 of 1 mM, was raised to 10^{-4} kg for a concentration of 10 mM. As shown in Table 31, a factor of ten increasing does not affect the total impacts significantly, since about 99% of the CO_2 emission are due to energy consumption. Observing the data reported in Table 30 there is no clear decrease in impacts passing from a concentration of 1 to 10 mM of H_2O_2. This aspect, therefore, does not justify the higher economic costs of working at higher concentrations in industrial applications.

CC kg CO_2 eq	**Total**	**Hydrogen peroxide**	**Sulfuric acid**	**Fe_3O_4/HA**	**Sodium hydroxide**	**Electricity**
$[H_2O_2]$ = 1 mM	0.726	$4.19x10^{-05}$	$7.91\ x10^{-06}$	0.00353	$4.97\ x10^{-05}$	0.722
$[H_2O_2]$ = 10 mM	0.699	$4.19\ x10^{-04}$	$7.91\ x10^{-06}$	0.00353	$4.97\ x10^{-05}$	0.695

Table 31. Comparison of the Climate Change (kg CO_2 eq) results of the degradation process of 90% of 20 μM BPA in 1 L of water in the presence of 1mM and 10 mM of H_2O_2 activated by Fe_3O_4/HA (100 mg/L) at pH 3.

The effect of the catalyst loading concentration was also evaluated. Table 32 shows the CC results of the degradation processes performed with 1 mM of H_2O_2, at three different pH, changing the catalyst concentration (100, 200 and 500 mg/L). The results of the LCA analysis reported in Table 32 were obtained taking into account the energy demand to irradiate the system. Lower CO_2 emission was assessed for the BPA degradation when 500 mg/L of catalyst was applied adjusting the pH medium to 3. Due to the slow degradation rate observed at pH 6 (see Table 26) higher greenhouse gases emissions were estimated. However, increasing the catalyst loading leads to a decrease of CC impact.

CC Kg CO_2 eq	**Catalyst concentration (mg/L)**		
	100	**200**	**500**
pH 3	0.72578	0.49665	0.31898
pH 4	4.17599	1.10102	2.31543
pH 6	15.0995	7.65667	5.75714

Table 32. Kinetic constant for the degradation and comparison of the CC (kg CO_2 eq) results of degradation processes at different Fe_3O_4/HA concentrations in the presence of H_2O_2 (1 mM) at different pH.

Table 33 shows the results of the LCA analysis for the processes conducted at pH 3, with a catalyst loading of 100 and 500 mg/L aiming to investigate the role of the catalyst concentration on the final impact. From the BPA degradation process at different catalyst loading it was possible to observe a significant impact of the electricity consumption, representing ≈ 94% of the global impact. By neglecting the energy contribution, it is possible to observe how using the catalyst at high concentrations involves a substantial CO_2 emission. Also, in this case this emission is directly proportional to the concentration of the catalyst. However, the contribution to the final impacts due solely to the catalyst is limited to 6%.

CC kg CO_2 eq	**Total**	**Hydrogen peroxide**	**Sulfuric acid**	**Fe_3O_4/HA**	**Sodium hydroxide**	**Electricity**
100 mg/L	0.726	$4.19\text{x}10^{-05}$	$7.91\ \text{x}10^{-06}$	0.00353	$4.97\ \text{x}10^{-05}$	0.722
500 mg/L	0.316	$4.19\ \text{x}10^{-05}$	$7.91\ \text{x}10^{-06}$	0.01764	$4.97\ \text{x}10^{-05}$	0.298

Table 33. Comparison of the Climate Change (kg CO_2 eq) results of the degradation process of 90% of 20 μM BPA in 1 L of water, between the processes conducted using a catalyst concentration of 100 and 500 mg/L. The pH and oxidant concentration were pH 3 and hydrogen peroxide (1 mM).

These data highlight how, by using high concentrations of catalyst, an effective improvement of the system can be achieved by impacting the degradation kinetics and the environmental footprint. At the same time energy consumption, directly related to the efficiency of the system, plays a predominant role. This CO_2 emission thus marked, covers the effect of all the other variables that contribute to the process.

Furthermore, the potential environmental impacts resulted from the higher catalyst loading can be mitigated by its reusability in consecutive water treatment cycles. Indeed, previous reusability experiments, after magnetically recovering the Fe_3O_4/HA catalyst, shown no significant activity decrease until the third consecutive catalytic cycle (Gonçalves et al., 2019). These experiments performed at laboratorial scale do not allow to estimate the environmental impact related to the catalyst recovery, however, on a larger scale (pilot plant or industrial level), this process should be automated and therefore lead to additional (presumably limited) energy consumption.

4.4.3. Conclusions

Established that the advanced oxidation processes and specifically heterogeneous photo-Fenton processes, are a viable and effective approach for waste water treatment, it becomes fundamental to assess also their environmental sustainability. This assessment should allow to avoid the risks of rebound effects that offset the environmental gains, deriving from water treatment. In this work, the methodology of Life Cycle Assessment was applied to identify the hotspots of use the Fe_3O_4/HA as heterogeneous photo-Fenton catalyst for water remediation. The addition of humic substances proved to improve the operational effectiveness of the catalyst without significant environmental impacts, despite the use of energy and chemicals during the extraction of HA.

The environmental impacts of all the conditions that affect the photo-Fenton process were also considered, highlighting the significant impact due to energy consumption mainly due to irradiation. In fact, energy consumption is significant above all for processes with lower efficiency and which therefore require a longer irradiation time to degrade the target molecule. The contribution of pH adjustment and subsequent neutralization was highlighted by neglecting the energy consumption. It has been observed that actually working at almost neutral pH allows to limit environmental impacts; this however involves a reduction in the efficiency of the processes.

Even if persulfate proved to promote a faster BPA removal at higher pH relatively to hydrogen peroxide, the last proved to be more environmentally friendly due to the lower impacts associated with its production.

The higher efficiency observed increasing the catalyst concentration evidenced a decrease in environmental impacts, what is very encouraging considering the easier recover and reusability of the catalyst (Gonçalves et al., 2019).

It should be pointed that, although the modelling of the degradation processes reported here are based on a laboratory scale, can give insights for larger scale applications. In fact, at the laboratory level the impact of the energy to irradiate the system is high and is proportional to the time required to treat a certain amount of water. If the constraint of a certain volume of water to be treated daily remains, a hypothetical system, which does not require electricity to operate (e.g. solar plant like compound parabolic collector – CPC (Malato et al., 2003), must be large enough to allow daily treatment of this volume (see the previous case study (section 4.3)). Therefore, the impacts associated with electricity consumption would be converted into impacts resulting from the amount of steel and square meters of soil needed to build a plant of adequate size.

In conclusion, working at milder conditions (circumneutral pH) would effectively limit environmental impacts, but the benefits deriving from these conditions can only be perceived if the process has a high degradative efficiency. In fact, if the process is fast from the kinetic point of view it allows to limit the energy consumption or the size of the system to treat the desired volume of water. For a more comprehensive analysis, the work developed here can be integrated taking into account the environmental impacts (mainly related to toxicity) of the pollutants present in the water and also the contributions due to the by-products of the degradation reaction. In this way it will be possible to obtain a more precise idea of how much it is worth pushing the degradation process, in order to not generate rebound effects.

References to chapter 4

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Appendix to chapter 4

Table A1. Impact at midpoint level for the degradation process of 90% of 20 μM BPA in 1 L of water. The used catalyst was Fe_3O_4/HA (100 mg/L). The processes were carried out changing pH and type of oxidant: persulfate and hydrogen peroxide (both at a concentration of 1 mM).

		Total	**Sodium persulfate**	**Sulfuric acid**	**Fe_3O_4/HA**	**Sodium hydroxide**	**Electricity**
pH 3	**CC** kg CO_2 eq	0.714267	0.000341	$7.91*10^{-06}$	0.003527	$4.97*10^{-05}$	0.710341
	ODP kg CFC-11 eq	$8.02*10^{-08}$	$9.19*10^{-11}$	$3.17*10^{-12}$	$5.03*10^{-10}$	$2.98*10^{-11}$	$7.96*10^{-08}$
	TE kg SO_2 eq	0.002827	$2.76*10^{-06}$	$3.18*10^{-07}$	$1.52*10^{-05}$	$2.44*10^{-07}$	0.002808
	FE kg P eq	0.000204	$1.94*10^{-07}$	$9.73*10^{-09}$	$1.42*10^{-06}$	$2.99*10^{-08}$	0.000203
	NREU MJ	9.132332	$5.33*10^{-03}$	$3.16*10^{-04}$	$4.51*10^{-02}$	$5.53*10^{-04}$	9.081036
pH 4	**CC** kg CO_2 eq	1.300195	0.000341	7.91*10-07	0.003527	$4.97*10^{-06}$	1.296321
	ODP kg CFC-11 eq	$1.46*10^{-07}$	$9.19*10^{-11}$	$3.17*10^{-13}$	$5.03*10^{-10}$	$2.98*10^{-12}$	$1.45*10^{-07}$
	TE kg SO_2 eq	0.005143	$2.76*10^{-06}$	$3.18*10^{-08}$	$1.52*10^{-05}$	$2.44*10^{-08}$	0.005125
	FE kg P eq	0.000372	$1.94*10^{-07}$	$9.73*10^{-10}$	$1.42*10^{-06}$	$2.99*10^{-09}$	0.00037
	NREU MJ	16.62275	$5.33*10^{-03}$	$3.16*10^{-05}$	$4.51*10^{-02}$	$5.53*10^{-05}$	16.57224
pH 6	**CC** kg CO_2 eq	1.493756	0.000341	$7.91*10^{-09}$	0.003527	$4.97*10^{-08}$	1.489887
	ODP kg CFC-11 eq	$1.68*10^{-07}$	$9.19*10^{-11}$	$3.18*10^{-15}$	$5.03*10^{-10}$	$2.98*10^{-14}$	$1.67*10^{-07}$
	TE kg SO_2 eq	0.005908	$2.76*10^{-06}$	$3.18*10^{-10}$	$1.52*10^{-05}$	$2.44*10^{-10}$	0.00589
	FE kg P eq	0.000427	$1.94*10^{-07}$	$9.74*10^{-12}$	$1.42*10^{-06}$	$2.99*10^{-11}$	0.000425
	NREU MJ	19.09723	$5.33*10^{-03}$	$3.16*10^{-07}$	$4.51*10^{-02}$	$5.53*10^{-07}$	19.0468
pH 6.5	**CC** kg CO_2 eq	3.022904	0.000341	$3.16*10^{-09}$	0.003527	$1.99*10^{-08}$	3.019036
	ODP kg CFC-11 eq	$3.39*10^{-07}$	$9.19*10^{-11}$	$1.27*10^{-15}$	$5.03*10^{-10}$	$1.19*10^{-14}$	$3.38*10^{-07}$
	TE kg SO_2 eq	0.011953	$2.76*10^{-06}$	$1.27*10^{-10}$	$1.52*10^{-05}$	$9.76*10^{-11}$	0.011935
	FE kg P eq	0.000864	$1.94*10^{-07}$	$3.90*10^{-12}$	$1.42*10^{-06}$	$1.20*10^{-11}$	0.000862
	NREU MJ	38.64595	0.005334	$1.26*10^{-07}$	0.045093	$2.21*10^{-07}$	38.59552
		Total	**Hydrogen peroxide**	**Sulfuric acid**	**Fe_3O_4/HA**	**Sodium hydroxide**	**Electricity**
pH 3	**CC** kg CO_2 eq	0.725128	$4.19*10^{-05}$	$7.91*10^{-06}$	0.003527	$4.97*10^{-05}$	0.721501
	ODP kg CFC-11 eq	$8.14*10^{-08}$	$3.80*10^{-12}$	$3.17*10^{-12}$	$5.03*10^{-10}$	$2.98*10^{-11}$	$8.09*10^{-08}$
	TE kg SO_2 eq	0.002868	$1.69*10^{-07}$	$3.18*10^{-07}$	$1.52*10^{-05}$	$2.44*10^{-07}$	0.002852
	FE kg P eq	0.000207	$1.54*10^{-08}$	$9.73*10^{-09}$	$1.42*10^{-06}$	$2.99*10^{-08}$	0.000206
	NREU MJ	9.27033	$6.55*10^{-04}$	$3.16*10^{-04}$	$4.51*10^{-02}$	$5.53*10^{-04}$	9.223713
pH 4	**CC** kg CO_2 eq	4.175339	$4.19*10^{-05}$	$7.91*10^{-07}$	0.003527	$4.97*10^{-06}$	4.171764
	ODP kg CFC-11 eq	$4.68*10^{-07}$	$3.80*10^{-12}$	$3.17*10^{-13}$	$5.03*10^{-10}$	$2.98*10^{-12}$	$4.68*10^{-07}$
	TE kg SO_2 eq	0.016508	$1.69*10^{-07}$	$3.18*10^{-08}$	$1.52*10^{-05}$	$2.44*10^{-08}$	0.016492
	FE kg P eq	0.001193	$1.54*10^{-08}$	$9.73*10^{-10}$	$1.42*10^{-06}$	$2.99*10^{-09}$	0.001191
	NREU MJ	53.37789	$6.55*10^{-04}$	$3.16*10^{-05}$	$4.51*10^{-02}$	$5.53*10^{-05}$	53.33206

pH 6	**CC** kg CO_2 eq	15.0988	$4.19*10^{-05}$	$7.91*10^{-09}$	0.003527	$4.97*10^{-08}$	15.09523
	ODP kg CFC-11 eq	$1.69*10^{-06}$	$3.80*10^{-12}$	$3.18*10^{-15}$	$5.03*10^{-10}$	$2.98*10^{-14}$	$1.69*10^{-06}$
	TE kg SO_2 eq	0.059692	$1.69*10^{-07}$	$3.18*10^{-10}$	$1.52*10^{-05}$	$2.44*10^{-10}$	0.059677
	FE kg P eq	0.004311	$1.54*10^{-08}$	$9.74*10^{-12}$	$1.42*10^{-06}$	$2.99*10^{-11}$	0.00431
	NREU MJ	193.024	$6.55*10^{-04}$	$3.16*10^{-07}$	$4.51*10^{-02}$	$5.53*10^{-07}$	192.9782

Table A2. Impact at midpoint level for the degradation process of 90% of 20 μM BPA in 1 L of water. The used catalyst was bare Fe_3O_4 (100 mg/L). The processes were carried out changing pH and type of oxidant: persulfate and hydrogen peroxide (both at a concentration of 1 mM).

		Total	**Sodium persulfate**	**Sulfuric acid**	**Fe_3O_4**	**Sodium hydroxide**	**Electricity**
pH 3	**CC** kg CO_2 eq	1.076274	0.000341	$7.91*10^{-06}$	0.003713	$4.97*10^{-05}$	1.072163
	ODP kg CFC-11 eq	$1.21*10^{-07}$	$9.19*10^{-11}$	$3.17*10^{-12}$	$5.35*10^{-10}$	$2.98*10^{-11}$	$1.20*10^{-07}$
	TE kg SO_2 eq	0.004258	$2.76*10^{-06}$	$3.18*10^{-07}$	$1.59*10^{-05}$	$2.44*10^{-07}$	0.004239
	FE kg P eq	0.000308	$1.94*10^{-07}$	$9.73*10^{-09}$	$1.51*10^{-06}$	$2.99*10^{-08}$	0.000306
	NREU MJ	13.76017	$5.33*10^{-03}$	$3.16*10^{-04}$	$4.74*10^{-02}$	$5.53*10^{-04}$	13.70659
pH 4	**CC** kg CO_2 eq	1.523542	0.000341	$7.91*10^{-07}$	0.003713	$4.97*10^{-06}$	1.519483
	ODP kg CFC-11 eq	$1.71*10^{-07}$	$9.19*10^{-11}$	$3.17*10^{-13}$	$5.35*10^{-10}$	$2.98*10^{-12}$	$1.70*10^{-07}$
	TE kg SO_2 eq	0.006026	$2.76*10^{-06}$	$3.18*10^{-08}$	$1.59*10^{-05}$	$2.44*10^{-08}$	0.006007
	FE kg P eq	0.000436	$1.94*10^{-07}$	$9.73*10^{-10}$	$1.51*10^{-06}$	$2.99*10^{-09}$	0.000434
	NREU MJ	19.47795	$5.33*10^{-03}$	$3.16*10^{-05}$	$4.74*10^{-02}$	$5.53*10^{-05}$	19.42515
pH 6	**CC** kg CO_2 eq	2.611394	0.000341	$7.91*10^{-09}$	0.003713	$4.97*10^{-08}$	2.60734
	ODP kg CFC-11 eq	$2.93*10^{-07}$	$9.19*10^{-11}$	$3.18*10^{-15}$	$5.35*10^{-10}$	$2.98*10^{-14}$	$2.92*10^{-07}$
	TE kg SO_2 eq	0.010326	$2.76*10^{-06}$	$3.18*10^{-10}$	$1.59*10^{-05}$	$2.44*10^{-10}$	0.010308
	FE kg P eq	0.000746	$1.94*10^{-07}$	$9.74*10^{-12}$	$1.51*10^{-06}$	$2.99*10^{-11}$	0.000744
	NREU MJ	33.38509	$5.33*10^{-03}$	$3.16*10^{-07}$	$4.74*10^{-02}$	$5.53*10^{-07}$	33.33238
pH 6.5	**CC** kg CO_2 eq	3.704782	0.000341	3.16*10-09	0.003713	$1.99*10^{-08}$	3.700728
	ODP kg CFC-11 eq	$4.15*10^{-07}$	$9.19*10^{-11}$	$1.27*10^{-15}$	5.35*10-10	$1.19*10^{-14}$	$4.15*10^{-07}$
	TE kg SO_2 eq	0.014649	$2.76*10^{-06}$	$1.27*10^{-10}$	1.59*10-05	$9.76*10^{-11}$	0.01463
	FE kg P eq	0.001058	$1.94*10^{-07}$	$3.90*10^{-12}$	1.51*10-06	$1.20*10^{-11}$	0.001057
	NREU MJ	47.36302	0.005334	$1.26*10^{-07}$	0.047377	$2.21*10^{-07}$	47.31031
		Total	**Hydrogen peroxide**	**Sulfuric acid**	**Fe_3O_4**	**Sodium hydroxide**	**Electricity**
pH 3	**CC** kg CO_2 eq	1.575361	$4.19*10^{-05}$	$7.91*10^{-06}$	0.003713	$4.97*10^{-05}$	1.571549
	ODP kg CFC-11 eq	$1.77*10^{-07}$	$3.80*10^{-12}$	$3.17*10^{-12}$	$5.35*10^{-10}$	$2.98*10^{-11}$	$1.76*10^{-07}$
	TE kg SO_2 eq	0.00623	$1.69*10^{-07}$	$3.18*10^{-07}$	$1.59*10^{-05}$	$2.44*10^{-07}$	0.006213
	FE kg P eq	0.00045	$1.54*10^{-08}$	$9.73*10^{-09}$	$1.51*10^{-06}$	$2.99*10^{-08}$	0.000449
	NREU MJ	20.13967	$6.55*10^{-04}$	$3.16*10^{-04}$	$4.74*10^{-02}$	$5.53*10^{-04}$	20.09077

		Total	**Hydrogen peroxide**	**Sulfuric acid**	**Fe_3O_4**	**Sodium hydroxide**	**Electricity**
pH 4	**CC** kg CO_2 eq	5.887029	$4.19*10^{-05}$	$7.91*10^{-07}$	0.003713	$4.97*10^{-06}$	5.883268
	ODP kg CFC-11 eq	$6.60*10^{-07}$	$3.80*10^{-12}$	$3.17*10^{-13}$	$5.35*10^{-10}$	$2.98*10^{-12}$	$6.59*10^{-07}$
	TE kg SO_2 eq	0.023275	$1.69*10^{-07}$	$3.18*10^{-08}$	$1.59*10^{-05}$	$2.44*10^{-08}$	0.023259
	FE kg P eq	0.001681	$1.54*10^{-08}$	$9.73*10^{-10}$	$1.51*10^{-06}$	$2.99*10^{-09}$	0.00168
	NREU MJ	75.26014	$6.55*10^{-04}$	$3.16*10^{-05}$	$4.74*10^{-02}$	$5.53*10^{-05}$	75.21202
pH 6	**CC** kg CO_2 eq	20.86262	$4.19*10^{-05}$	$7.91*10^{-09}$	0.003713	$4.97*10^{-08}$	20.85887
	ODP kg CFC-11 eq	$2.34*10^{-06}$	$3.80*10^{-12}$	$3.18*10^{-15}$	$5.35*10^{-10}$	$2.98*10^{-14}$	$2.34*10^{-06}$
	TE kg SO_2 eq	0.082478	$1.69*10^{-07}$	$3.18*10^{-10}$	$1.59*10^{-05}$	$2.44*10^{-10}$	0.082462
	FE kg P eq	0.005957	$1.54*10^{-08}$	$9.74*10^{-12}$	$1.51*10^{-06}$	$2.99*10^{-11}$	0.005955
	NREU MJ	266.709	$6.55*10^{-04}$	$3.16*10^{-07}$	$4.74*10^{-02}$	$5.53*10^{-07}$	266.6609

Chapter 5: Applying the LCA methodology to materials and processes related to energy

This chapter presents two case studies concerning technologies strictly correlated with the broad topic of energy. Herein two different cases have been investigated from the environmental point of view. The first part presents the LCA analysis relating to the production of materials that can be used in carbon capture and storage (CCS) technologies or more generally in gas purification. The second study focuses on the environmental impacts of the hydrogen compression process by metal hydride.

Taking in consideration two of the definitions that characterize circular economy: *"an industrial system that is restorative or regenerative by intention and design. It replaces the 'end-of-life' concept with restoration, shifts towards the use of renewable energy…"*(Ellen MacArthur Foundation, 2013) and "*Circular economy is an economy constructed … This is done by using cyclical materials flows, renewable energy sources and cascading-type energy flows…"* (Korhonen et al., 2018) it is clear that the principles associated with this concept are also requiring to pay attention to the type of energy sources used. According to Griggs et al. (2013), the path to sustainable development passes through improved universal and affordable access to clean energy.

The use of clean energy helps to minimize local pollution, health impacts and mitigates global warming. The circular economy paradigm, with the main goal to accomplish sustainable development, embraces this thought, encouraging the use of clean and renewable energy sources.

The European Union itself recognized the problems of climate change and energy supply as one of key challenges for the future (Tomić et al., 2018). To tackle with these issues, the European Commission set a series of strategies and targets for reducing its greenhouse gas emissions progressively up to 2050 and to achieve the transformation towards a low-carbon economy (European Commission, climate strategies and targets).

The LCA analysis proves, once again, a powerful methodology to encourage the use of clean energy sources for sustainable development and environmental protection. In fact, the best energy strategies can be identified only through the analysis of the environmental profile of the processes, technologies, sources and emissions that lead to energy production.

The issue of energy production and consumption is huge and complex, so a comprehensive and comparative analysis of the different technologies involved is beyond the scope of this work; it has nevertheless proved interesting to examine, within limited borders, specific technologies associated with this sector.

For a better understanding of both the case studies, a brief introduction presents, at the beginning of each work, the context and the technologies.

5.1 Case study 4: LCA analysis of porous carbon materials obtained from cyclodextrin

5.1.1 Introduction

The 20th century has seen the rapid increase of population and an explosive growth in energy consumption. The U.S. Energy Information Administration (EIA) predicts that world energy demand will grow by nearly 50 percent between 2018 and 2050 (EIA, 2019). To fulfil these needs, approximately 90% of global energy is supplied through the use of fossil fuels. Carbon dioxide and greenhouse gases (GHGs) emissions have shown an increasing trend, directly correlated with the increase in energy consumption. These emissions have proven to be highly disadvantageous as a cause of global warming and many other environmental issues strictly related, such as extreme weather, unequal distribution of food, migration, etc.

Worldwide, these problems have been recognized by many actors and different strategies have been recently put in place to encourage clean or carbon neutral energy production. It is necessary to specify that although carbon dioxide is removed from the atmosphere through the biogeochemical carbon cycle a large amount of current and future CO_2 is beyond the capacity of the earth, especially considering a limited time interval (Ciais et al., 2013). To reduce CO_2 emissions in the atmosphere several possibilities exist, such as replacement of coal by natural gas, improving power plant efficiency, introducing higher thermal efficiency combined cycles of steam and gas for power generation, shifting to renewable resources and carbon capture and storage (Younas et al., 2016). The last solution, with the aim to find some efficient method for capturing and storing the CO_2, provides a mid-term solution to mitigate environment impacts (Yang et al., 2008). The existing industrial carbon dioxide capture systems are based on chemical absorption by means of liquids; technologies based on aqueous amine solutions are commercialized over 60 years (Kim and Svendsen, 2007). In literature it is possible to find processes based on a variety of different adsorbents such as carbonaceous materials, dry alkali metal-based sorbents, zeolites, metal–organic frameworks and microporous organic polymers (Younas et al., 2016).

A promising method for CO_2 recovering is the Pressure Swing Adsorption (PSA), based on the standard process used for gas separation. This technology involves the adsorption of gas by specific adsorbents: zeolite, carbon molecular sieve, silica gel and activated carbon. The mechanism of operation of this cyclical process uses the adsorbent's differences in gas adsorption rates to capture preferred gases (e.g., CO_2, O_2 and N_2) at a high pressure and then releases the adsorbates at a low pressure to regenerate the adsorbent (Yang and Ge, 2016). The PSA process is simple to use and is being investigated for the possibilities of using it in CCS technologies.

The need for specific materials that are selective for CO_2, at high temperatures and at different pressures, becomes evident. In fact these adsorbents are designed to have a specific pore size, which must be sized according to the size of the target molecules, therefore an appropriate synthesis procedure must be implemented. A class of materials suitable for this kind of application is represented by porous carbon. Of particular interest are carbon materials derived from nanosponge.

This case study focuses attention on the synthesis process of these materials, studied in the laboratories of the chemistry department of the University of Turin. In detail the studied materials are microporous carbon prepared by pyrolysis of hyper cross-linked cyclodextrins. The latter, obtained by the simple reaction between a cross-linker and a polysaccharide, are also known with the term nanosponge (Zanetti et al., 2016). The synthesis procedure allows to obtain spherical hollow particles. These particles show good adsorption of CO_2 at low temperature (204 mg/g at 30°C), but are still able to absorb carbon dioxide even at high temperature (133 mg/g at 120°C) and this is an interesting feature that can find different applications (Anceschi, 2018).

The analysis of the life cycle assessment made it possible to highlight the hotspots of the synthesis procedure and to suggest some alternatives to improve the environmental burdens.

5.1.2. Materials and methods

As introduced in Chapter 3 the first step of an LCA analysis requires defining the goal and scope of the study. The aim of this work is to analyse, from an environmental point of view, the synthesis process to obtain porous carbon materials, using β-cyclodextrins as the starting material. In more detail, we wanted to provide a more realistic and scalable estimate of the impacts associated with the production of this specific type of material. Therefore, the analysis, using as a basis the primary data obtained at the laboratory level, was extended by modelling an industrial-scale production. The interest is to model the production process in all its phases in order to identify the stages and material inputs that mostly contribute to the generation of environmental impacts. Being able to accurately identify hotspots in a stage of development still at the research level allows us to easily make and test changes to the process. For this reason the results of this study may be of particular interest to those involved in research on these materials.

The functional unit, which coincides with the service provided by the system, has been defined as the production of 1 ton of porous carbons obtained from cyclodextrins.

Figure 26 show the production system scheme of the porous carbon materials. The boundary of the system analysed with the LCA methodology encloses the synthesis of β-nanosponge and the production of porous carbons from the latter, as indicated by the red dotted box. The production of β-cyclodextrins is not considered in the analysis as these are directly provided by a company and the production process is not known.

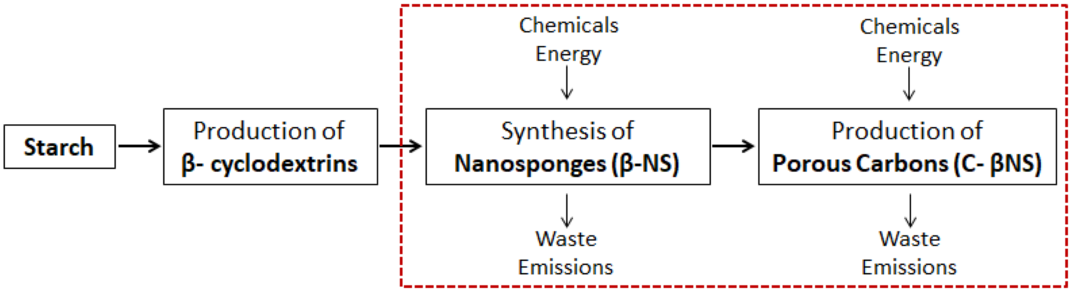

Figure 26. Porous carbon production scheme starting from β-cyclodextrins; the red dashed box highlights the system boundary examined in the LCA analysis

The boundaries of this study are from the "cradle to gate", they include processes and transport from the acquisition of the raw material to the production of the finished product. The phases of use and final disposal of the porous carbons have not been taken into account.

The study was carried out using the software SimaPro 8 and the Ecoinvent 3.3 database. The system was analysed by using an attributional approach (Brander et al., 2009). The environmental impacts have been estimated using the ReCiPe 2008 method (Goedkoop et al. 2009). The following midpoint impact categories were taken into account: climate change (CC, kg CO_2 eq), ozone depletion (OD, kg CFC-11 eq), terrestrial acidification (TA, kg SO_2 eq), freshwater eutrophication (FE, kg P eq), photochemical oxidant formation (POF, kg NMVOC) and human toxicity (HT, kg 1,4-DB eq). The assessment of energy consumption has been estimated according to the Cumulative Energy Demand method (CED, MJ) (Frischknecht et al., 2007). It should be noted that, among the many possibilities of impact categories as reported in the Technical Report by JRC (Fazio et al., 2018), CC and OD are recommended and considered satisfactory impact categories; TA, FE and POF are recommended although they need some improvement. It was also considered appropriate to measure the impacts relating to the HT and CED categories (despite the lower reliability of the results).

Inventory analysis

The inventory analysis allows to create a model of the real system under analysis by collecting all the raw materials, resources, energy, outputs and emission related to the considered functional unit. The starting point for modelling the system is given by the production process implemented at the laboratory level and reported in detail in Zanetti et al., 2016. According to the scheme reported in Figure 26 the first phase of the process (considered in this study) is the synthesis of the nanosponges (β-NS) from β-cyclodextrins. In the basic scenario the synthesis is carry out using as a cross-linking agent the pyromellitic dianhydride, as a catalyst the triethylamine and dimethilsulfoxide as solvent. After the completion of the reaction, the obtained block polymer was coarsely ground in a mill and the unreacted reactants were completely removed by washing with water and acetone; for further purification, an extraction was performed by means of Soxhlet with acetone. The second step of the process consists in the preparation of the carbons. These are obtained by placing the previously synthesized nanosponges in a furnace. The sample were heated to 800°C under nitrogen flux. The furnace was then cooled and the carbon was maintained under nitrogen flux until the room temperature was reached.

In addition to the base case, two different scenarios have been created to model the system by changing some variables. In scenario 1 a phase of solvent (acetone) recovery was included in the model, so as to limit the use of virgin substances and limit the waste. In fact, through the distillation process, many solvents can be easily recovered. Instead in scenario 2 it was hypothesized to carry out the synthesis of the nanosponges in an aqueous solvent rather than in dimethylsulfoxide; in this case the purification step with Soxhlet is avoided and the acetone distillation phase was maintained.

Below are some clarifications regarding the construction of the inventory.
To model the pyromellitic dianhydride input, substance not present in the Ecoinvent database, it was decided to use the data relative to the phtalic anhydride. This choice was made because the synthesis processes of the two substances are identical and the only difference is due to the precursor used (Röhrscheid 2000); in fact the precursor for the synthesis of pyromellitic dianhydride it is not the xylene (as for the phtalic anhydride), but the 1,2,4,5-tetramethylbenzene. Hence the process for the synthesis of phtalic anhydride was modified by replacing the xylene input with that of a general "alkylbenzene linear".

The catalyst for the synthesis of the nanosponges is the triethylamine, given its absence in the Ecoinvent database to model the system, this input has been replaced with an equivalent of trimethylamine.

The quantity of solvents (acetone and water) used in the process was estimated starting from the data measured on a laboratory scale; these values were multiplied to obtain a final quantity of material equal to 1 ton. To make the result more reliable, a reduction of the solvents used of 20% was assumed, as suggested by Piccino et al. (2016).

The indications reported in the work of Piccino et al. (2016) have also been used to model the energy inputs for the grinding phase. The modelling was carried out assuming a process that allows to obtain a quantity of 1 ton of porous carbons. For the grinding phase it was assumed an energy demand of 16 kWh/ton of grinded material; this value represents the highest extreme of the average of the values provided, this choice allows to obtain a conservative approximation.

In a synthesis process like the one in exam the energy contribution is of primary importance. To model the system using reliable values for an industrial application and not only for a laboratory scale, it was decided to use what is indicated in the work of Piccino et al. (2016). The energy demand for heating the system (both for the Soxhlet extraction phase and for the carbonization reaction) was obtained using the equation 5.1, assuming a common reactor.

$$Q_{react} = \frac{Q_{heat} + Q_{loss}}{\eta_{heat}} = \frac{C_p * m_{mix} * (T_r - T_0) + A * \frac{k_a}{S} * (T_r - T_{out}) * t}{\eta_{heat}} \tag{5.1}$$

Where C_p is the specific heat capacity of the material to be heated, T_r is the final temperature, T_0 is the starting temperature, m_{mix} is the mass of the reaction mixture, A is the surface area of the reactor, k_a is the thermal conductivity of the insulation material, S is the thickness of the insulation, (T_r-T_0) is the temperature difference between the inside and outside of the reactor, t is the time of the reaction and η_{heat} is the efficiency of the heating device.

Similar approach has been followed to model the distillation step of the solvents, energy consumption was estimated according to the equation 5.2 and 5.3.

$$Q_{dist} = \frac{Q_{heat} + Q_{vap} * (R+1)}{\eta_{heat} - 0.1} = \frac{C_p * m_{mix} * (T_{boil} - T_0) + \Delta H_{vap} * m_{dist} * (1.2 * R_{min} + 1)}{\eta_{heat} - 0.1} \tag{5.2}$$

$$R_{min} = \frac{1}{\alpha - 1} \left(\frac{X_{LD}}{X_{LF}} - \frac{\alpha * (1 - X_{LD})}{1 - X_{LF}} \right) \tag{5.3}$$

m_{dist} is the mass of the liquid that need to be vaporized, R_{min} is the minimum reflux ratio, that indicates the lowest ratio for which the distillation can take place, α is the relative volatility of the solvents (> 1); X_{LD} is the target purity of distillate (molar fraction); X_{LF} is the molar fraction of target compound in feed. Q_{loss} is excluded from equation 5.2, however, to reflect this decrease, a 10% efficiency loss is considered.

To model the recovery of the solvent, a recovery equal to 90% of the total was hypothesized, so only 10% is included as input of virgin acetone.

Table 34 shows the inputs - outputs data used to model the whole process for the production of 1 ton of porous carbons. The data are grouped according to the scenario considered.

		Base case	Scenario 1	Scenario 2
Inputs	Pyromellitic dianhydride (kg)	2546	2546	2546
	Triethylamine (kg)	286	286	286
	Dimethyl sulfoxide (kg)	16048	16048	/
	Energy (grinding) (MJ)	206	206	206
	Water (kg)	72946	72946	88994
	Acetone (kg)	28813	2881	2017
	Heat (Soxhlet extraction) (MJ)	1720	1720	/
	Energy (distillation) (MJ)	/	24522	22123
Outputs	Spent solvent mixture (kg)	44862	19215	7117
	Wastewater (m^3)	72.95	72.95	84.95
	Nanosponges (kg)	*3571*	*3571*	*3571*
Inputs	*Nanosponges (kg)*	*3571*	*3571*	*3571*
	Energy (heating) (MJ)	4781	4781	4781
	Nitrogen (kg)	178657	178657	178657
Outputs	***C- βNS (kg)***	*1000*	*1000*	*1000*

Table 34. Estimate of inputs and outputs of the entire process, for the production of 1000kg of porous carbons (C- βNS); the table show the data for the base case and Scenario 1 and 2.

5.1.3. Results and discussion

The environmental impact of the synthesis process of porous carbon materials are assessed in the LCIA phase. The objective of this step is to evaluate the magnitude of the environmental impacts throughout the life cycle of the product under scrutiny. In essence, in this phase, the inventory data are associated with specific environmental impact indicators.

Table 35 shows the environmental impacts, by category, of the synthesis process of 1 ton of porous carbon (C- βNS); the impacts reported refers to the base case scenario.

Impact category	CC kg CO_2 eq	OD kg CFC-11 eq	TA kg SO_2 eq	FE kg P eq	HT kg 1,4-DB eq	POF kg NMVOC	CED MJ
Total	**1.30x10^{+05}**	**5.13x10^{-03}**	**5.02x10^{+02}**	**2.44x10^{+01}**	**1.73x10^{+04}**	**4.31x10^{+02}**	**3.11x10^{+06}**

Table 35. LCIA results for the synthesis of 1 ton of porous carbons (C- βNS) in the base case scenario.

For a better understanding of the impacts, Table 36 shows the results divided by each input. A heat map introduces a colour gradient, for each impact category, that marks the results from red (the worst score) to green (the best score).

Impact category	PD	TEA	DMSO	Acetone	Water	N_2	Heat	Electricity	SSM	WW
CC **kg CO_2 eq**	1.1x10^{+04}	7.1x10^{+02}	2.2x10^{+04}	6.6x10^{+04}	7.4x10^{+01}	4.8x10^{+01}	1.7x10^{+02}	6.6x10^{+02}	3.0x10^{+04}	9.5x10^{-01}
OD **kg CFC-11 eq**	5.7x10^{-04}	1.3x10^{-04}	3.4x10^{-03}	2.7x10^{-04}	2.5x10^{-05}	5.0x10^{-06}	2.1x10^{-05}	6.6x10^{-05}	6.5x10^{-04}	1.0x10^{-07}
TA **kg SO_2 eq**	5.6x10^{+01}	4.8x10^{+00}	1.3x10^{+02}	2.8x10^{+02}	3.1x10^{-01}	2.0x10^{-01}	4.9x10^{-01}	2.7x10^{+00}	2.3x10^{+01}	9.8x10^{-03}
FE **kg P eq**	3.8x10^{+00}	1.6x10^{-01}	7.8x10^{+00}	4.7x10^{+00}	2.2x10^{+00}	4.1x10^{-02}	1.9x10^{-02}	5.7x10^{-01}	5.0x10^{+00}	2.9x10^{-03}
HT **kg 1,4-DB eq**	3.8x10^{+03}	2.5x10^{+02}	1.0x10^{+04}	1.3x10^{+03}	3.3x10^{+01}	2.6x10^{+01}	1.6x10^{+01}	3.6x10^{+02}	1.4x10^{+03}	6.5x10^{-01}
POF **kg NMVOC**	5.9x10^{+01}	2.3x10^{+00}	7.2x10^{+01}	2.7x10^{+02}	1.9x10^{-01}	9.9x10^{-02}	3.0x10^{-01}	1.3x10^{+00}	2.3x10^{+01}	5.4x10^{-03}
CED **MJ**	3.5x10^{+05}	2.3x10^{+04}	7.1x10^{+05}	2.0x10^{+06}	1.0x10^{+03}	1.1x10^{+03}	2.7x10^{+03}	1.5x10^{+04}	4.9x10^{+04}	1.6x10^{+01}

Table 36. Environmental impact for the synthesis of 1 ton of porous carbons (C- βNS) in the base case scenario, subdivided by the inventory contributions. [PD= Pyromellitic dianhydride; TEA= Triethylamine; DMSO= Dimethyl sulfoxide; SSM= Spent solvent mixture; WW= wastewater]

In the base case process it is used a large amount of virgin acetone during the purification step; this lead to greater impacts for four impact categories: CC, TA, POF and CED. Such impacts are generated during the solvent production, specifically by the emission in air and water of the production process. The second input that caused the greatest impacts is dimethylsulfoxide (DMSO), in particular for the categories: OD, FE and HT. An interesting result is given by the impacts associated with the consumption of electricity for the carbonization phase. In fact, despite this being an energy-intensive step, the impacts associated with it are two orders of magnitude lower than the main impact values for each category.

To limit the impact associated with the use of acetone, in scenario 1 it was performed the synthesis procedure recovering the used acetone. The recovery step was carried out by distilling the acetone after its use. Table 37 and Table 38 show the LCIA results for the synthesis of 1 ton of porous carbon in the scenario 1. As seen before Table 37 reports the sum of impacts by category, while Table 38 shows the contribution of each input to the environmental impacts.

Impact category	CC kg CO_2 eq	OD kg CFC-11 eq	TA kg SO_2 eq	FE kg P eq	HT kg 1,4-DB eq	POF kg NMVOC	CED MJ
Total	5.62x10^{+04}	4.81x10^{-03}	2.41x10^{+02}	1.75x10^{+01}	1.56x10^{+04}	1.76x10^{+02}	1.36x10^{+06}

Table 37. LCIA results for the synthesis of 1 ton of porous carbons (C- βNS) in the scenario 1.

Impact category	PD	TEA	DMSO	Acetone	Water	N_2	Heat	Electricity	SSM	WW
CC kg CO_2 eq	1.1x10^{+04}	7.1x10^{+02}	2.2x10^{+04}	6.6x10^{+03}	7.4x10^{+01}	4.8x10^{+01}	2.6x10^{+03}	6.6x10^{+02}	1.3x10^{+04}	9.5x10^{-01}
OD kg CFC-11 eq	5.7x10^{-04}	1.3x10^{-04}	3.4x10^{-03}	2.7x10^{-05}	2.5x10^{-05}	5.0x10^{-06}	3.2x10^{-04}	6.6x10^{-05}	2.8x10^{-04}	1.0x10^{-07}
TA kg SO_2 eq	5.6x10^{+01}	4.8x10^{+00}	1.3x10^{+02}	2.8x10^{+01}	3.1x10^{-01}	2.0x10^{-01}	7.5x10^{+00}	2.7x10^{+00}	9.7x10^{+00}	9.8x10^{-03}
FE kg P eq	3.8x10^{+00}	1.6x10^{-01}	7.8x10^{+00}	4.7x10^{-01}	2.2x10^{+00}	4.1x10^{-02}	2.9x10^{-01}	5.7x10^{-01}	2.2x10^{+00}	2.9x10^{-03}
HT kg 1,4-DB eq	3.8x10^{+03}	2.5x10^{+02}	1.0x10^{+04}	1.3x10^{+02}	3.3x10^{+01}	2.6x10^{+01}	2.5x10^{+02}	3.6x10^{+02}	6.0x10^{+02}	6.5x10^{-01}
POF kg NMVOC	5.9x10^{+01}	2.3x10^{+00}	7.2x10^{+01}	2.7x10^{+01}	1.9x10^{-01}	9.9x10^{-02}	4.5x10^{+00}	1.3x10^{+00}	1.0x10^{+01}	5.4x10^{-03}
CED MJ	3.5x10^{+05}	2.3x10^{+04}	7.1x10^{+05}	2.0x10^{+05}	1.0x10^{+03}	1.1x10^{+03}	4.0x10^{+04}	1.5x10^{+04}	2.1x10^{+04}	1.6x10^{+01}

Table 38. LCIA results for the synthesis of 1 ton of 1 ton of porous carbons (C- βNS) in the scenario 1. [PD= Pyromellitic dianhydride; TEA= Triethylamine; DMSO= Dimethyl sulfoxide; SSM= Spent solvent mixture; WW= wastewater]

It can be observed that the main impacts are associated with DMSO, since the amount of virgin acetone is drastically reduced. At the same time, heat must be used to distil the solvent; this causes an increase in the impacts attributable to this input, but these impacts are still contained.

As a last assessment, synthesis in water was attempted instead of using DMSO (scenario 2). The results, reported in Table 39 and Table 40, show a better environmental profile and the synthesized materials have the same characteristics as those obtained with previous synthesis procedures.

Impact category	CC kg CO_2 eq	OD kg CFC-11 eq	TEA kg SO_2 eq	FE kg P eq	HT kg 1,4-DB eq	POF kg NMVOC	CED MJ
Total	2.39x10^{+04}	1.19x10^{-03}	9.37x10^{+01}	8.66x10^{+00}	4.98x10^{+03}	8.93x10^{+01}	5.71x10^{+05}

Table 39. LCIA results for the synthesis of 1 ton of porous carbons (C- βNS) in the scenario 2.

Impact category	PD	TA	Acetone	Water	N_2	Heat	Electricity	SSM	WW
CC kg CO_2 eq	1.1x10^{+04}	7.1x10^{+02}	4.6x10^{+03}	9.0x10^{+01}	4.8x10^{+01}	2.2x10^{+03}	6.6x10^{+02}	4.8x10^{+03}	1.1x10^{+00}
OD kg CFC-11 eq	5.7x10^{-04}	1.3x10^{-04}	1.9x10^{-05}	3.1x10^{-05}	5.0x10^{-06}	2.7x10^{-04}	6.6x10^{-05}	1.0x10^{-04}	1.2x10^{-07}
TA kg SO_2 eq	5.6x10^{+0}1	4.8x10^{+00}	2.0x10^{+01}	3.8x10^{-01}	2.0x10^{-01}	6.3x10^{+00}	2.7x10^{+00}	3.6x10^{+00}	1.1x10^{-02}
FE kg P eq	3.8x10^{+00}	1.6x10^{-01}	3.3x10^{-01}	2.7x10^{+00}	4.1x10^{-02}	2.4x10^{-01}	5.7x10^{-01}	8.0x10^{-01}	3.4x10^{-03}
HT kg 1,4-DB eq	3.8x10^{+03}	2.5x10^{+02}	9.1x10^{+01}	4.1x10^{+01}	2.6x10^{+01}	2.1x10^{+02}	3.6x10^{+02}	2.2x10^{+02}	7.6x10^{-01}
POF kg NMVOC	5.9x10^{+01}	2.3x10^{+00}	1.9x10^{+01}	2.4x10^{-01}	9.9x10^{-02}	3.8x10^{+00}	1.3x10^{+00}	3.7x10^{+00}	6.3x10^{-03}
CED MJ	3.5x10^{+05}	2.3x10^{+04}	1.4x10^{+05}	1.3x10^{+03}	1.1x10^{+03}	3.4x10^{+04}	1.5x10^{+04}	7.7x10^{+03}	1.8x10^{+01}

Table 40. LCIA results for the synthesis of 1 ton of 1 ton of porous carbons (C- βNS) in the scenario 2. [PD= Pyromellitic dianhydride; TEA= Triethylamine; DMSO= Dimethyl sulfoxide; SSM= Spent solvent mixture; WW= wastewater]

The main impacts are due to the pyromellitic dianhydride, but this substance cannot be easily replaced, since, used as a crosslinker, it allows to obtain the best performance of the synthetized materials (Anceschi, 2018).

The direct comparison among the environmental results obtained for the three scenario is shown in Figure 27. To normalize the results, among the various impact categories, these have been reported as a percentage, assigning 100% to the greatest impact for each category analysed.

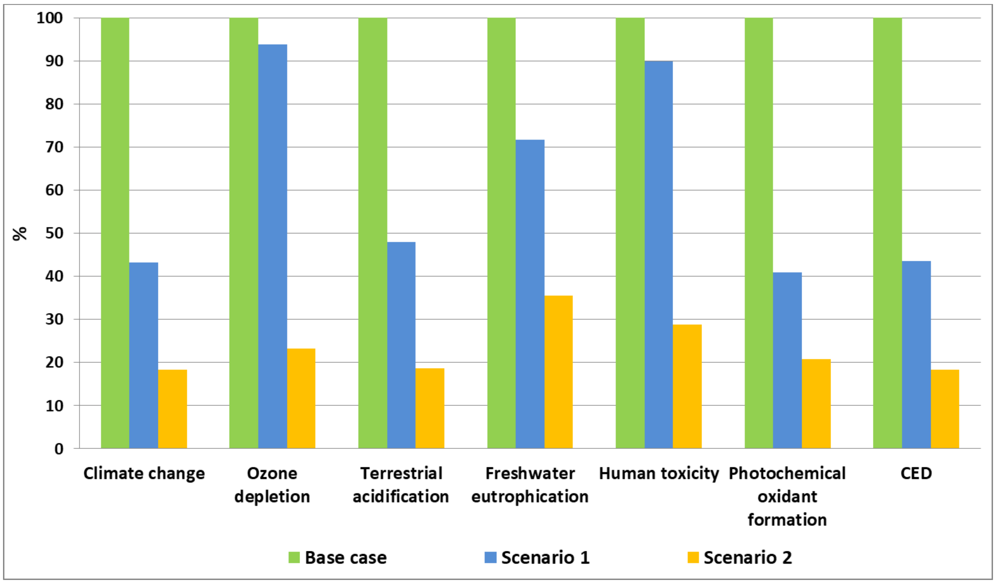

Figure 27. Comparison of environmental impacts, by impact category, among the three different modeled scenarios. The values are reported as a percentage, assigning 100% to the greatest impact for each category analyzed.

It can be observed how the precautions adopted during the modelling of the various scenarios lead to a decrease of the environmental impacts (base case > scenario 1 > scenario 2). The best environmental burden of the synthesis procedure is obtained with the scenario 2, therefore carrying out the synthesis in water and maintaining the solvent recovery phase by acetone distillation.

Comparison of results with literature

The direct comparison with other studies on porous carbon materials is difficult either because of the differences in the goal and scope, impact assessment methods, scale of the plant or geographical location. However, an attempt is made to compare the results shown above with the studies found in literature. These results are shown in Figure 28.

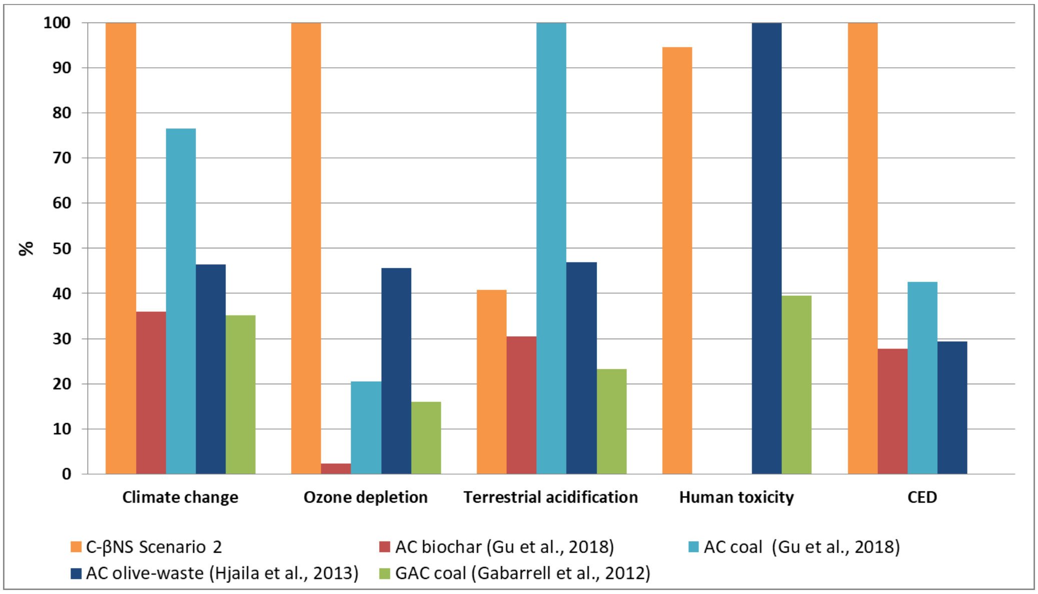

Figure 28. Comparison with the results, found in the literature, of some impact categories for porous carbon materials. The values are reported as a percentage, assigning 100% to the greatest impact for each category analyzed.

Figure 28 reports the LCIA results of production of 1 ton of activated porous carbon materials (AC) from different studies. The results are grouped per impact categories (not all studies took into consideration all the categories here analysed) and compared with the impacts measured for the production of 1 ton of C- βNS (in the scenario 2). Gu et al. (2018) analysed the impacts of the production of 1 ton of activated carbon from woody biomass; the analysis was extended by comparing the environmental profile of biochar-based carbon activation (AC biochar) with commercial coal-based carbon activation (AC coal). To adapt the analysed plant to the production of 1 ton of material, they also modelled the system assuming a scale up of the system. Hjaila et al. (2013) quantified the environmental impacts associated with the activated carbon (AC) production process from olive-waste in Tunisia; these results are based on lab-scale data. Gabarrell et al. (2012) assess the industrial scale production of granular activated carbon (GAC) from hard coal. It can be observed that for three impact category (climate change, ozone depletion and CED) the main impacts are associated with the C- βNS. For human toxicity category seems that the production of AC from olive-waste has the greatest impact, even if slightly higher than C- βNS. While the AC produced from coal are responsible for the main impact on the terrestrial acidification (impact due to the greater quantity of gases released into the air during the process).

Although as previously reported, the data used for the comparison of the different impacts are to be considered with the necessary precautions, it is clear how the production of porous carbon materials through the carbonization of β-nanosponges, from cyclodextrins, has been shown to have a greater impact on the environment. However, it should be noted that the final use of these materials may differ from the average of the AC. This is because the structure and the chemical-physical properties of C- βNS can be varied through the synthesis process, allowing to obtain a performing material, especially for specific uses (e.g. CO_2 capture at high temperatures). At the moment there are no literature studies that have assessed the environmental impacts of materials directly comparable with this.

5.1.4 Conclusions

The use of substances and materials capable of capturing and storing carbon dioxide has proven to be fundamental in the decarbonisation process. Of great importance is the possibility to capture the CO_2 at high temperatures or pressure. An example of materials able to operate in these conditions is represented by porous carbons synthesized starting from very precise chemical structures. This study assessed the environmental burdens generated by the production pathway of a porous carbon materials produced with this goal. The synthesis process starts by using β-cyclodextrins, derived from corn starch, and through a chemical reaction and a carbonization phase, it allows to obtain porous carbons materials with a precise structure and specific chemical-physical properties.

The LCA analysis, performed on a scaled up plant, allows to identify the hotspots of the production process. Hotspots represented by the use of large quantities of virgin solvent (acetone) and DMSO for the synthesis phase. To limit the impacts of these inputs, two different scenarios (scenario 1 and 2) were modelled by recovering acetone by distillation and replacing the DMSO with water in the synthesis process. These two changes make it possible to considerably reduce the environmental impacts. The scenario 2 (with the distillation step and using water instead of DMSO) shows the lower impacts for each category: climate change, ozone depletion, terrestrial acidification, freshwater eutrophication, photochemical oxidant formation, human toxicity and cumulative energy demand. In this scenario the main impact is due to the pyromellitic dianhydride that cannot be easily replaced, because it is an essential reagent to obtain the desired properties of the final product.

By the comparison of the synthesis process of this materials with others found in literature it results how the C- βNS show less positive environmental profile; nevertheless it should be noted that this porous carbon materials have specific properties that allow a good CO_2 adsorption also at high temperatures, where the common activated carbons are not able to work optimally.

Given the absence of specific studies evaluating only the environmental impacts of materials similar to this as a perspective for the future, the environmental analysis of a gas capture plant that uses these materials should be envisaged, and compared with other technologies present on the market.

5.2. Case study 5: Environmental analysis of the hydrogen compression process through the metal hydride technology

5.2.1 Introduction

According to the International Energy Agency, it will be a particular challenge to reduce energy demand in energy and heat supply, as well as in the transport and industry sectors; in fact, these are the sectors that today have the highest energy demand (International Energy Agency, 2015). To address these problems, one solution is to positively promote power generation from renewables to substitute fossil energy consumption, while increasing the efficiency of energy conversion. The European Community - on its path towards a reduction of greenhouse gas emissions and an increase in renewable energy - has the new goal of reaching at least 32% of energy production from renewable sources by 2030 (European Commission, 2014). In this scenario of change, hydrogen is thought of as an important energy carrier, that can be used for the storage of renewable energies (Lin, 2011) and have great potential in stationary, portable and transport applications (Mansilla et al., 2018). Europe has recognized as significant and stimulating elements in the incentive of a hydrogen economy: (I) the mitigation of climate change effect, (II) the enhancement of energy security and (III) the promotion of renewable energy utilization. However, the implementation of an hydrogen economy presents various challenges from the point of view of technology, infrastructures, constructions, and regulations; these are some of the topics of concern: (I) cost reduction, (II) safety and convenience in use, (III) infrastructure extension, (IV) technology development (Dou et al., 2017).

In the transportation sector, there is a great interest for the benefits derived from the application of Proton Exchange Membrane fuel cells (PEM FC). It has been found that such environmental benefits, in terms of GHG reduction, can be substantial with the use of hydrogen produced from renewable energy sources (Cox and Mutel, 2018; Karaaslan et al., 2018; Koroneos et al., 2004; Walker et al., 2015). An interesting and promising application market, for fuel cell technology, is that of vehicles for handling units / forklifts. Some works - which have conducted market analyses on this topic - confirm that under certain conditions (energy efficiency, fleet size, etc.), the fuel cell forklifts show advantages both in economic terms and in the possible reduction of energy consumption and GHG emissions (Elgowainy et al., 2009; Larriba et al., 2013).

From the technological viewpoint, the use of hydrogen as an efficient fuel is slowed down by some issues: one of the main ones is undoubtedly that hydrogen production needs energy to be produced, being only an energy carrier and not an energy source. This very delicate aspect must be the subject of careful specific studies (Armaroli and Balzani, 2011). In fact, in order to enable and spread this technology, it is also necessary to study and improve other aspects, such as storage, transportation and distribution. A not negligible point that deserves to be carefully examined is that linked to gas compression. In fact, hydrogen has the lowest volumetric energy density among the commonly used fuels (Sherif et al., 2014). To overcome this aspect and increase the volumetric energy density, one of the most used methods is gas compression. The compression of hydrogen at high pressures is required for specific applications; as an example, for the transport sector, hydrogen needs to be pressurized above 700 bar to enable refuelling of high pressure storage tanks (Rothuizen and Rokni, 2014). The need to increase gas pressure makes it possible to optimize storage and make the hydrogen transportation or use more efficient (Sdanghi et al., 2019). It should be noted that in counting the benefits deriving from the use of hydrogen as an energy vector, the entire energy chain must be considered: the primary energy used for its production, compression, storage and transport / use (Grouset and Ridart, 2018). According to Grouset and Ridart (2018), the compression phase has to be considered with care, because it is an operation that requires high energy demand. In fact, if the compression is not managed carefully, it can cause a loss around 20% of the hydrogen energy potential. In literature, apart some techno-economic analyses of hydrogen refuelling stations (Grouset and Ridart, 2018; Nistor et al., 2016; Kriha et al., 2017), which have also taken into consideration the compression phase, there is a lack of specific studies focused on the environmental burden of these technologies. Currently, there are several different technologies for hydrogen compression, each with specific advantages and drawbacks. For example, mechanical compressors are the most widespread type of compressors used nowadays and they use mechanical energy to compress gases (Sdanghi et al., 2019). The so-called reciprocating compressors, which represent a mature technology, adaptable to a wide range of flow rates, belong to this family; they consist of several moving parts, but this feature increase both the cost of manufacturing and also the difficulty in carrying out effective maintenance (Arjomand Kermani and Rokni, 2015). At the same time, the presence of moving parts, like the piston, leads to an increase in the heat produced and makes it more difficult to manage thermal transfers (Tuhovcak et al., 2016).

An interesting alternative, that does not require usage of moving parts, is represented by the use of metal hydride to compress hydrogen; in fact, this typology of compressors is known as thermally-driven compressors (Sdanghi et al., 2019). The compression with metal hydride is based on the reversible reaction between hydrogen and a solid phase (elemental metal, alloy or intermetallic compound). Hydrogen absorption is an exothermic process, implying the release of heat, while desorption is endothermic, so that hydrogen is released only upon supply of heat. As shown in Figure 29 the metal can absorb H_2 at low temperatures and pressures (T_0 and P_0), forming the metal hydride (MH). Then, by heating MH to a temperature greater than the previous one ($T_1>T_0$), H_2 is released at a pressure higher than the absorption one ($P_1>P_0$).

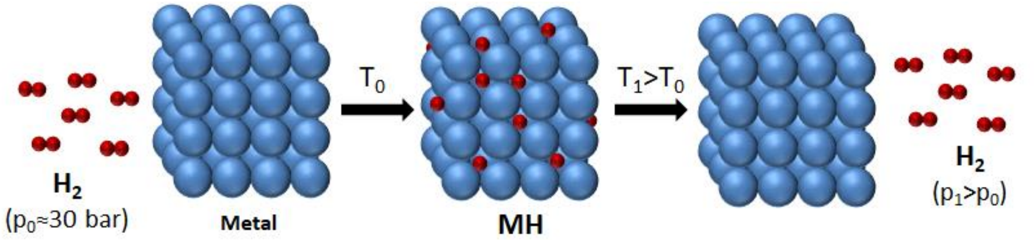

Figure 29. Illustrative scheme of compression with metal hydrides.

According to (Lototskyy et al., 2014) this technology has several advantages, such as not having moving parts, so it does not require frequent maintenance, it is compact and safe and for the operation phase offers the possibility of using industrial waste heat.

The use of metal hydride compressors in forklifts refuelling stations is particularly interesting, first of all because the maximum pressure reachable for the storage of hydrogen is about 200 bar, a value that can be obtained with commercial metal hydride compressors (Bellosta von Colbe et al., 2019). Secondly, it is easily conceivable that in the place where the refuelling station is located (a factory), excess heat can be easily recovered to allow the operation of these compressors. In fact, one of the main advantages of this technology is that for its operation a metal hydride compressor only needs a source of heat (a hot fluid, such as steam, between 130 -150 °C) and water for cooling (temperature below 25 °C) (Lototskyy et al., 2016).

In this work the environmental burden of a metal hydride compressor has been assessed by means of the Life Cycle Assessment methodology. The goal of the study was to objectively quantify the actual advantages and disadvantages of a MH compressor, with respect to more established technologies. The expected result is the identification of the main environmental hotspots, in order to obtain indications to make this type of technology more sustainable and competitive. This study has been inserted in a wider context, by comparing three different system that allow the hydrogen compression, in order to have a better understanding which technology is most suitable for a specific use. More in details, the analysis considers the technology of a metal hydride compressor, a generic H_2 compressor and an air booster. The main novelty brought by this study, is to conduct an environmental analysis of hydrogen compressors; in fact, currently in literature there is no evaluation of the environmental impacts generated either by MH compressors or by other technologies for hydrogen compression.

5.2.2. Materials and methods

This work uses the LCA methodology to investigate the environmental impacts associated with the hydrogen compression phase in a refuelling station for fuel cell forklifts. The attention was focused only on the compression phase and three different systems were analysed and compared: a metal hydride compressor, a generic H_2 compressor and a system that uses an air booster to increase the hydrogen pressure.

The entire work was conducted with software SimaPro 9 and using the Ecoinvent v.3.6 database.

Goal and scope definition

The goals of the work were the following:

- Quantify the environmental impacts related to the production of the MH compressor and identify the main hotspots related to it.

- Quantify the environmental impacts associated with the MH compressor use phase, comparing different scenarios: heat recovery and cooling from another system, use of electricity generated by a photovoltaic system, direct use of natural gas to heat the system and use of energy from the electrical national grid.
- Compare the system under analysis with systems providing the same services, i.e. generic H_2 compressor and air booster. This comparison was extended to the use phase of the system.
- Extend the analysis by also examining the costs associated with the hydrogen compression with the various systems studied.

The functional unit identified for this study is the compression of 1.79 kg of H_2, at 200 bar, per day and the dimensions of the integrated system have been modelled to achieve this goal.

The choice of the amount of hydrogen to be compressed was based on some works that have identified this value as a reference point for the correct daily operation of a forklift (Lototskyy et al., 2016; Renquist et al., 2012).

For the sake of clarity, it should be noted that the compressed gas is not immediately directed to the forklift tank, but it is stored in buffer tanks. In this way, it is not necessary to use compressors with high hourly flow rates of compressed gas. This configuration is preferred because, in economic terms, it is cheaper to have a small compressor that works almost all day than a large compressor working for short times (Grouset and Ridart, 2018).

The considered impact categories, corresponding units and the related methods, used to calculate the impacts, are shown in Table 41.

Impact category	Unit	LCIA method used
Climate change	kg CO_2 eq	Baseline model of 100 years of the IPCC (based on IPCC 2013)
Particulate matter	Disease incidences	PM method recommended by UNEP (UNEP 2016)
Photochemical ozone formation	kg NMVOC eq	LOTOS-EUROS (Van Zelm et al, 2008)
Acidification	mol H^+ eq	Accumulated Exceedance (Seppälä et al. 2006, Posch et al, 2008)
Resource use, energy carriers	MJ	ADP for energy carriers, based on van Oers et al. 2002 as implemented in CML, v. 4.8 (2016).
Resource use, minerals and metals	kg Sb eq	ADP for mineral and metal resources, based on van Oers et al. 2002 as implemented in CML, v. 4.8 (2016).

Table 41. List of impact categories and the corresponding units and methods used to calculate the impacts.

Life cycle inventory

The data that constitute the inventory of this study derive both from direct measurements on the system (primary data) and from the literature.

Below are the details of the inventory of the various components taken in consideration: a MH compressor, an air booster and a generic H_2 compressor.

The data to model the metal hydride compressor were estimated by considering, as starting information, a real MH compressor (Figure 30), studied and developed in the University of Turin with the contribution of Tecnodelta Impianti Srl.

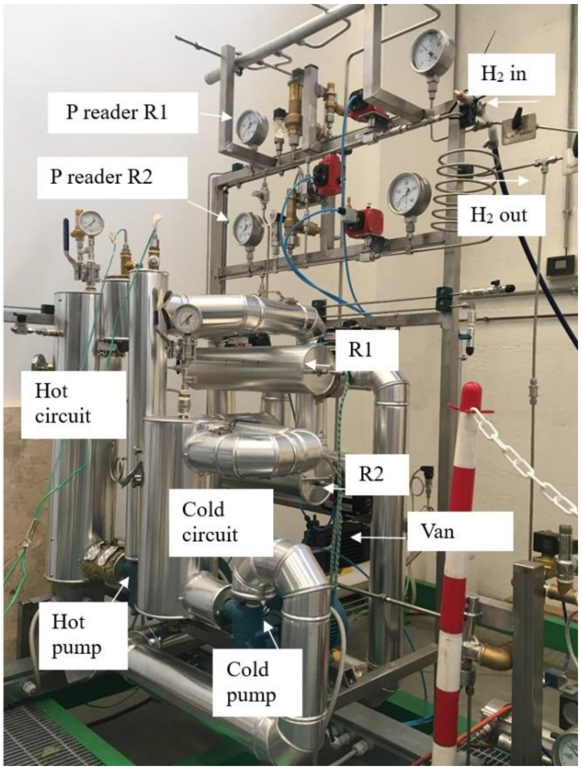

Figure 30. MH compressor developed by the University of Turin with the contribution of Tecnodelta Impianti Srl.

The scale up of the components made it possible to move from a compressor of limited dimensions, that allows the increase of pressure up to 200 bar of a few grams of hydrogen per hour, up to the hypothetical system that allows to compress the quantity of gas reported in the functional unit. It should be noted that, for the purposes of LCA modelling, the increase in the dimensions and amount of materials has been done in a linear way, without taking into account possible improvements introduced by the engineering optimization of the system. In fact, since the prototype used as a starting base had to perform a demonstrative function only, it has not been optimized for large-scale production.

The structural part of the metal hydride compressor used as reference is made up of 2 reactors (R1 and R2 in Figure 30) placed in series and connected by a valve system. Each of these reactors consists of a stainless steel tube, surrounded by an external jacket that allows the maintenance and/or variation of the temperature. Between the internal pipe and the external jacket, depending on the moment (absorption or desorption), it flows a fluid for the heating and cooling phases. The outer jacket is thermally insulated from the environment by a layer of glass fiber. Two different metal alloys in the form of powder are placed inside the reactors; when these alloys come into contact with hydrogen, they form the metal hydrides and the consequent operation of the compressor.

The system is assembled so that the gas, coming from the hydrogen source, reaches the first reactor and after the absorption/desorption stages it flows into the second reactor and eventually reaches the tanks where it is stored. To clarify the operation of the MH compressor, a description of a single compression cycle is given: the H_2 gas at low pressure (20 - 30 bar) flows in the first reactor, that is kept at room temperature, and is absorbed by the first alloy. Then the reactor is heated (130 – 150 °C) and the hydrogen is released at a pressure greater than 30 bar and flows into the second reactor. In this phase, the second reactor is kept at room temperature and the alloy adsorbs the incoming H_2. As a last step, the second reactor is heated and then the H_2 is released at 200 bar. The specific system shows in Figure 30 allows the compression of 0.052 kg of hydrogen at 200 bar; to compress this amount of gas, 7 adsorption / desorption cycles are required for each reactor. Since the duration of 1 cycle is approximately 1 hour, a total of 7 hours are required to compress the desired amount of hydrogen. All the inputs related to the production and operation of this compressor have been scaled in order to compress 1.79 kg of hydrogen, at 200 bar, during 7 working hours (equals to 7 cycles of adsorption/desorption); the ratio of compressed gas masses was used as conversion factor.

Below are the inventory data of the MH compressor. The materials used for the reversible adsorption of hydrogen are two commercial alloys (purchased by companies: LabTech and GfE) in the form of powders. The first reactor contains 30.29 kg of the first alloy: $La_{0.9}Ce_{0.1}Ni_5$. The powder placed in the second tube is an alloy named Hydralloy C5 with composition $Ti_{0.95}Zr_{0.05}Mn_{1.55}V_{0.45}Fe_{0.09}$ (24.30 kg); the amount of single elements in each alloy is reported in Table 42.

Alloy	Element	Amount (kg)	Input (inventory)	Amount (kg)
$La_{0.9}Ce_{0.1}Ni_5$ 30.29 kg	La	8.16	$LaNi_5$ (electrode material)	30.29
	Ce	1.07		
	Ni	21.07		
$Ti_{0.95}Zr_{0.05}Mn_{1.55}V_{0.45}Fe_{0.09}$ 24.30 kg	Ti	6.82	Titanium (primary)	6.82
	Zr	0.72	Zirconium*	0.72
	Mn	12.63	Manganese	12.63
	V	3.41	Titanium (primary)	3.41
	Fe	0.72	Cast iron	0.72

Table 42. Elemental composition and inventory inputs of the two commercial alloy.
*The process to obtain it was reconstructed with data from literature (Nuss and Eckelman, 2014).

Given the lack of specific data within the Ecoinvent database, it has been decided to use, for the $La_{0.9}Ce_{0.1}Ni_5$ alloy, the process used to produce $LaNi_5$ (electrode material), neglecting the contribution given by the small amount of cerium. The Ecoinvent database does not contain any data for the elemental zirconium, so the process for its production was reconstructed starting from the respective oxide, according to Nuss & Eckelman (2014). Also for the vanadium there are no data in literature and commercial dataset with sufficient quality to model its contribution. It was therefore chosen to use the titanium process as a replacement. The quantity of titanium, reported during the modelling, is equal to the stoichiometric value obtained for the vanadium multiplied by a numerical factor of 1.1; this choice was based on the work of (Nuss and Eckelman, 2014).

The inventory of the MH compressor is reported in Table 43.

Input	Amount
Stainless steel (kg)	946.63
Metal working (kg)	946.63
$La_{0.9}Ce_{0.1}Ni_5$ (kg)	30.29
Hydralloy C5 (kg)	24.30
Glass fibre (kg)	34.42
Pump 40W (unit)	34

Table 43. Inventories for the compressor system with metal hydride.

The amount of stainless steel reported in Table 43 refers to the reactors, pipes, connections and valves that make up the entire system. The pumps allow the circulation of the fluids responsible for heating and cooling the system.

At the moment, there are no precise studies or information regarding the life span and performance over time of the technology used in the MH compressor; on the basis of the little information collected so far, it is possible to assume, with a good approximation, the possibility of cycling the alloys for a number of 10000 times. Assuming a number of 7 daily cycles means that the alloys will have to be replaced on average every 5.5 years (taking 253 working days per year). Since the steel structure - which constitutes the reactors and the gas lines - is subjected to repeated work cycles, also in this case it is assumed that it must be replaced every 10 years (2530 working days). Also the amount of glass fiber and the pump have been considered to be replaced after 10 years of use.

The amount of energy used during the compression of 1.79 kg of H_2, at 200 bar - to operate the compressor in the absence of a waste heat source - was determined; this energy is consumed to cyclically heat and cool a fluid (in the range 30 – 150 °C). The consumption related to the functional unit is equal to 100 kWh. The system was modeled using both electricity coming exclusively from solar energy (Electricity, low voltage {IT} | electricity production, photovoltaic, 3kWp slanted-roof installation, multi-Si, panel, mounted), energy got from the grid (Electricity, low voltage {IT} | market for) and heat produced by natural gas (Heat, central or small-scale, natural gas {Europe without Switzerland}| market for heat, central or small-scale, natural gas | Alloc Rec, U).

The hydrogen compression at high pressure can be realized also by means of a booster; this device uses a low pressure air flow to increase the pressure of the desired gas. In this case, the commercial booster used is a high pressure booster, suitable for the oil free compression of gases and air. The use of an air booster to raise the pressure of a gas is particularly suitable in cases where high hourly flow rates are not required and only for not continuous uses of the booster (there is no cooling system). These two conditions are fully fitting for the application reported in this study.

The main constituting materials and relative amounts are reported in Table 44; some materials, due to their very low relative weight, have been neglected.

Material	Amount (kg)
Stainless steel	19.5
Metal working (kg)	19.5
Acrylonitrile-butadiene-styrene copolymer	0.2
Polypropylene	0.15

Table 44. Inventory for the commercial booster.

To operate, the booster requires only a flow of air, in a range pressure of 4-8 bar, easily obtained from an air compressor. In the Ecoinvent database, there is a process that allows to directly obtain the environmental impacts related to the production of a specific amount of compressed air. In this case, 1.2 m^3 of air are required to compress 1.79 kg of H_2 up to 200 bar, using an air driving pressure of 6 bar. The electricity consumption associated with the production of 1.2 m^3 of compressed air is 0.238 kWh; this energy contribution was modeled using, in one case, electricity from the Italian grid and, in a second case, electricity produced from a photovoltaic system.

Given the lack of primary and/or secondary information to model the compression of hydrogen using a generic compressor, it was decided to use the data present in the Ecoinvent database relating to an air compressor (screw-type 4kW). This assumption tends with high probability to underestimate the impacts associated with the compressor itself; in fact - due to the properties of the substance to be compressed - a compressor for hydrogen undoubtedly requires more efficient materials and technologies than an equivalent for air. The contribution of the compressor has been scaled by assuming that it has a life span of 10 years (2530 working days); a life span of only 10 years was chosen to compensate for the difference in technology of the screw type compressor compared to a generic H_2 compressor. The energy consumption for the hydrogen compression was obtained from literature (Agostini et al., 2018) and is specific for hydrogen: 3.3 kWh/kg H_2, for a final pressure of 200 bar. Also in this case, the system was modeled using in one case electricity from the grid and electricity from a photovoltaic system only. The production of energy, in both cases, always refers to the Italian context.

5.2.3. Results and discussion

The following section shows the results of the LCIA analysis.

Figure 31 shows the results for all the impact categories analysed for the production of one unit of MH compressor. The results were reported as a percentage of the total impacts for each category; table A3 (in the appendix section at the end of the chapter) reports the numerical results.

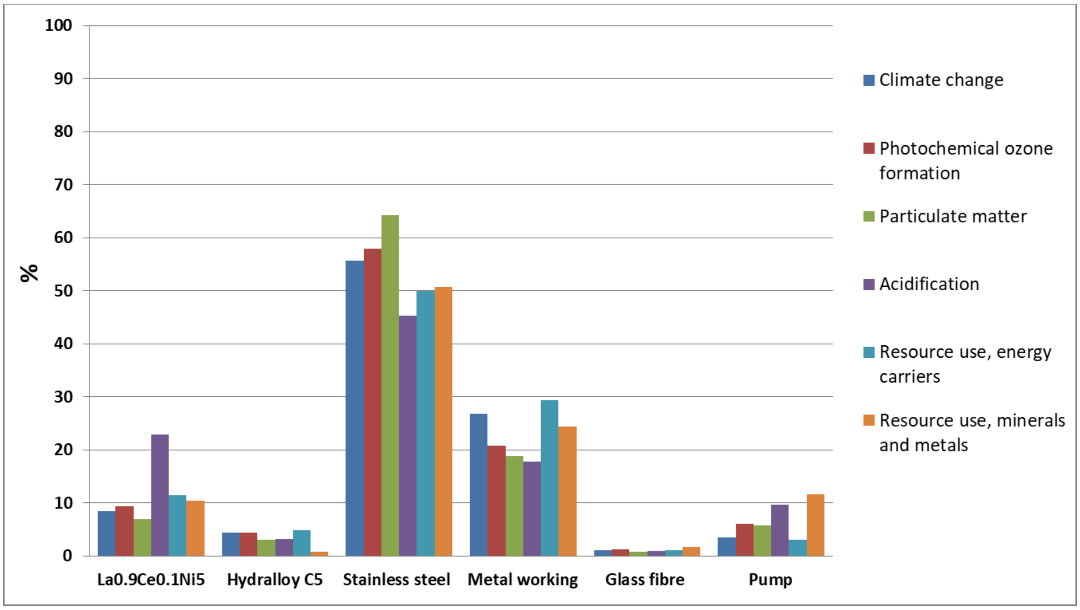

Figure 31. LCIA results – express as a percentage of the total - for the production of the MH compressor.

From the results shown in Figure 31, relating to the production of an MH compressor, as described in the inventory phase, it can be seen that the greatest impacts are attributable to the amount of stainless steel used and its working. In fact, for all the categories considered, the effects generated by the use and processing of steel are always more than 50% of the total impact (in detail: 83% for Climate change, 83% for Particulate matter, 79% for Photochemical ozone formation, 63% for Acidification, 79% for Resource use, energy carriers and 75% for Resource use, minerals and metals). The metal alloys, on which the operation of the compressor is based, have lower impacts, despite requiring elements in the oxidation state 0; in fact, elements in this oxidation state generally involve high economic and environmental costs for their production. In detail, the impacts of $La_{0.9}Ce_{0.1}Ni_5$ alloy, relating to the acidification category, are due to the nickel mining processes, while for all the other categories considered, they are equally caused by the extraction and processing of the two elements belonging to the rare earth groups (La and Ce); the extraction of rare earth elements and the manufacturing processes involve the use of considerable amount of hydrochloric acid, sodium hydroxide and energy, that are the main responsible for the impact among the analyzed categories. The impacts related to the second alloy, Hydralloy C5, are mainly due to the amount of titanium used, for all impact categories. The impacts associated with titanium are mainly caused by the high energy consumption that the processing - during the industrial extraction and purification phases – requires.

The glass fiber – used as thermal insulation– shows the lowest impacts for each category.

The environmental impacts generated by the compression of 1.79 kg of H_2, at 200 bar, were evaluated by comparing several systems:

- metal hydride compressor that uses a recovery heat source (MH comp)
- metal hydride compressor that uses heat from natural gas (MH comp + heat NG)
- metal hydride compressor that uses electricity from the grid (MH comp + grid el)
- metal hydride compressor that uses electricity from a photovoltaic system (MH comp + PV el)
- air booster
- air booster that uses electricity from a photovoltaic system (air booster + PV el)
- H_2 compressor that uses energy from the grid (H_2 comp + grid el)
- H_2 compressor that uses electricity from a photovoltaic system (H_2 comp + PV el)

The following figures show the bar graphs – for each impact category - obtained by comparing the various compression systems; the numerical values of the calculated impacts are shown in Table A4.

Figure 32 shows the impacts related to the Climate change category. The impacts generated for gas compression in accordance with the functional unit were reported by dividing the total into two contributions: impact due to the system (physical compressor) and impact generated by energy consumption to compress the gas.

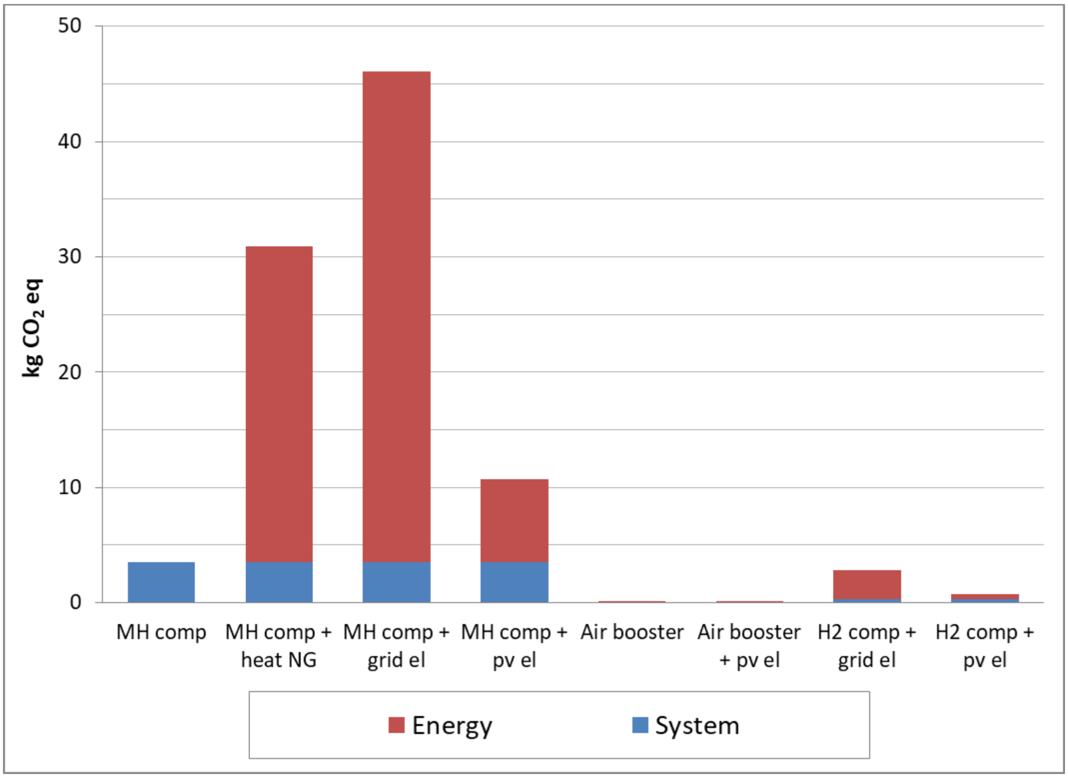

Figure 32. Comparison of results for the Climate change impact category associated with the compression of 1.79 kg of H_2 at 200 bar using different systems.

Figure 32 shows how for Climate change impact category the main burdens are associated with the MH compressor that need energy to operate; the greatest impacts are generated by using electricity from the national grid, followed by heat from natural gas and electricity from a photovoltaic system. The high energy consumption associated with the MH compressor - when a source of waste heat cannot be used - is the main cause of the high greenhouse gas emissions. As observed, the use of energy from the national grid involves the greatest impacts (≈ 46 kg CO_2 eq), while using heat obtained from the combustion of natural gas allows to reduce the impact (≈ 31 kg CO_2 eq). An even better result is obtained by using electricity produced by a photovoltaic system (≈ 11 kg CO_2 eq).

The use of the MH compressor, with heat recovery from an external source, allows to contain the environmental impacts related to the H_2 compression. The emission of CO_2 eq. is slightly higher than that generated by compression using a generic H_2 compressor that uses energy from the national grid (respectively, 3.52 and 2.80 kg CO_2 eq).

Based on greenhouse gas emissions the best way to compress H_2 is through the use of a booster that uses compressed air; the impacts are minimal if compression is done using electrical energy produced from a photovoltaic system (≈ 0.08 kg CO_2 eq).

The results related to the Particulate matter impact category – express as disease incidence - are reported in Figure 33.

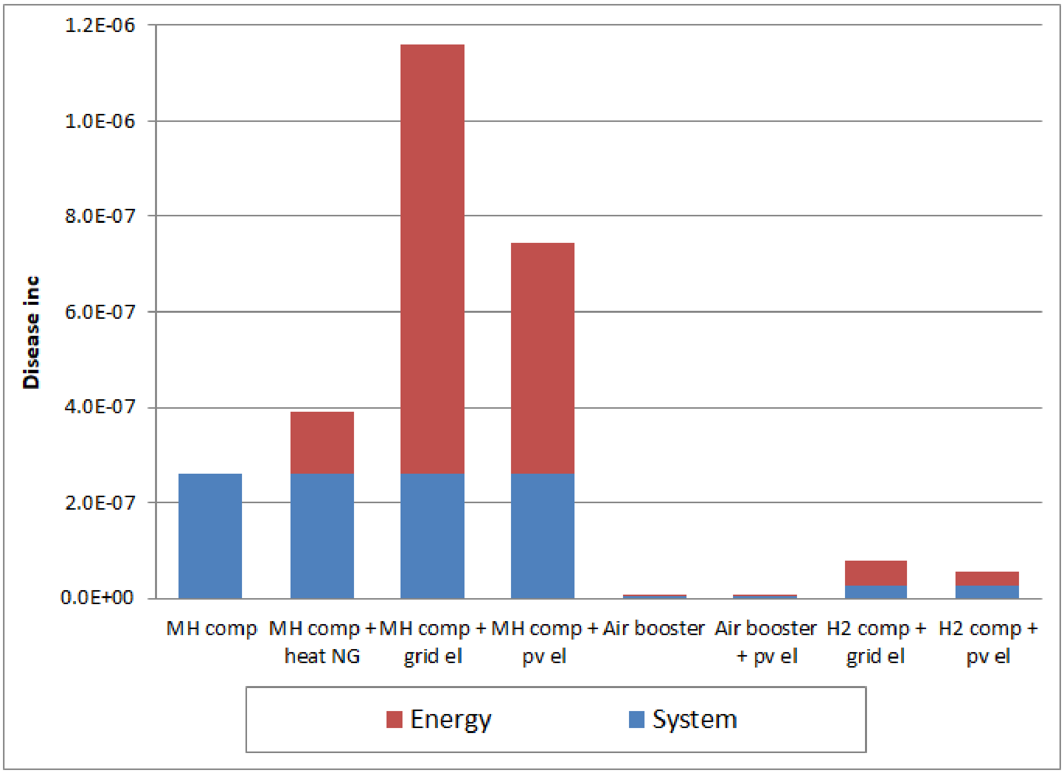

Figure 33. Comparison of results for the Particulate matter impact category associated with the compression of 1.79 kg of H_2 at 200 bar using different systems.

The reciprocal trend of some impacts is quite similar to Climate change results: the greatest impact is observed using the MH compressor - which uses electricity from the national mix - and the lowest is always obtained from compression with the booster and air compressor system. However, some differences are noted. In fact, the impact generated by the compression with the MH compressor alone (without the use of energy) reaches much higher values than the generic H_2 compressor (more than three times). About 75% of the impact generate by the MH compressor is due to the stainless steel (materials and processing) used to build the system and in detail a large part of the particulate emission derives from the energy spend during the extraction phases of minerals used for the production of steel – i.e. ferronickel and ferrochromium. As introduced in the previous section, the amount of steel used for the modeling of the compressor was not calculated on the basis of an optimization of the system; for this reason it is probable that the impacts associated with it would be considerably reduced if the amount of steel is also reduced.

The production of electricity through a photovoltaic system causes a greater emission of particulate matter compared to the equivalent heat – in energy terms - produced by the combustion of natural gas. This major impact is attributable to the production phase of silicon panels.

It can be observed that even in the system that uses a generic H_2 compressor shows greater sharing of the impacts, both by the physical system and by the energy used, compared to the impacts on Climate change; in fact, the impact on the climate change category is strongly caused by energy consumption, instead the use of metals - steel, aluminum and copper, present in the generic compressor - involves an emission of atmospheric particulate that has a greater relevance in this category.

Figure 34 shows the impacts related to the Photochemical ozone formation category.

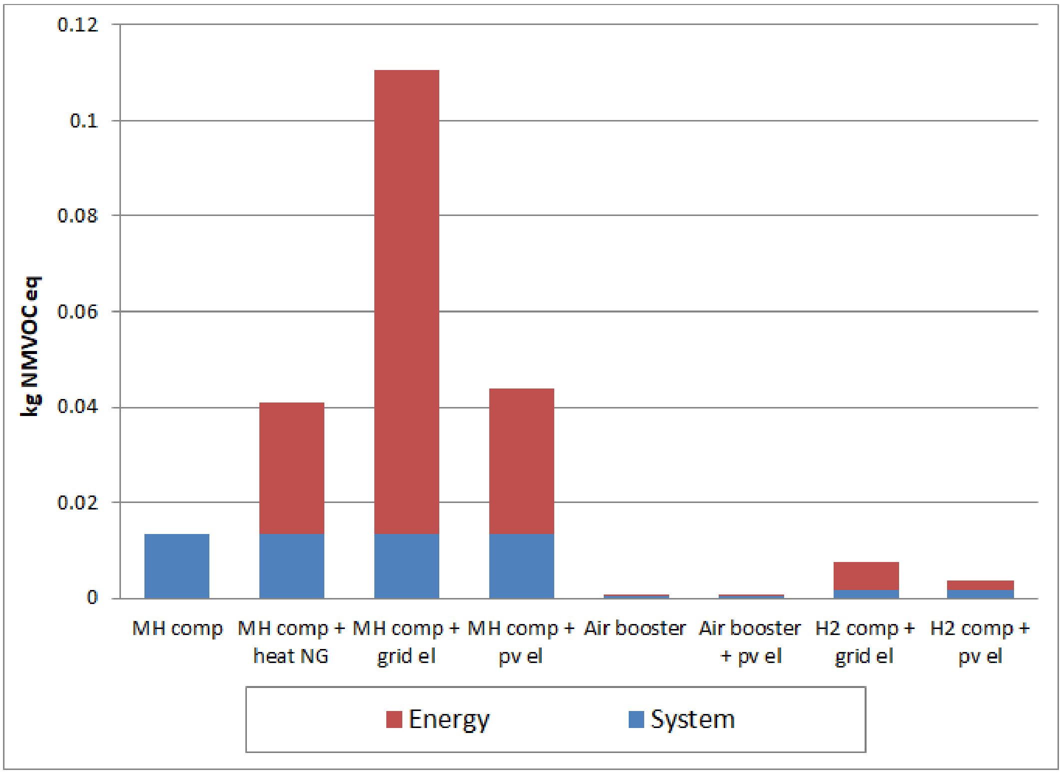

Figure 34. Comparison of results for the Photochemical ozone formation impact category associated with the compression of 1.79 kg of H_2 at 200 bar using different systems.

The release of NMVOC eq. into the atmosphere (Figure 34) is particularly marked during compression that uses electricity produced with the Italian national mix. This impact is largely due to the percentage of electricity that derives from the use of coal as an energy resource. It can be seen that there is only a slight difference in terms of NMVOC eq. emissions when using heat - produced from natural gas - or electricity - from solar energy.

Again, the system consisting of booster with air compressor proves to be the best from an environmental point of view.

Although the impacts associated with compression using the hydride system alone are limited, they are slightly higher than the use of a generic compressor.

The results related with the Acidification impact category are shown in Figure 35.

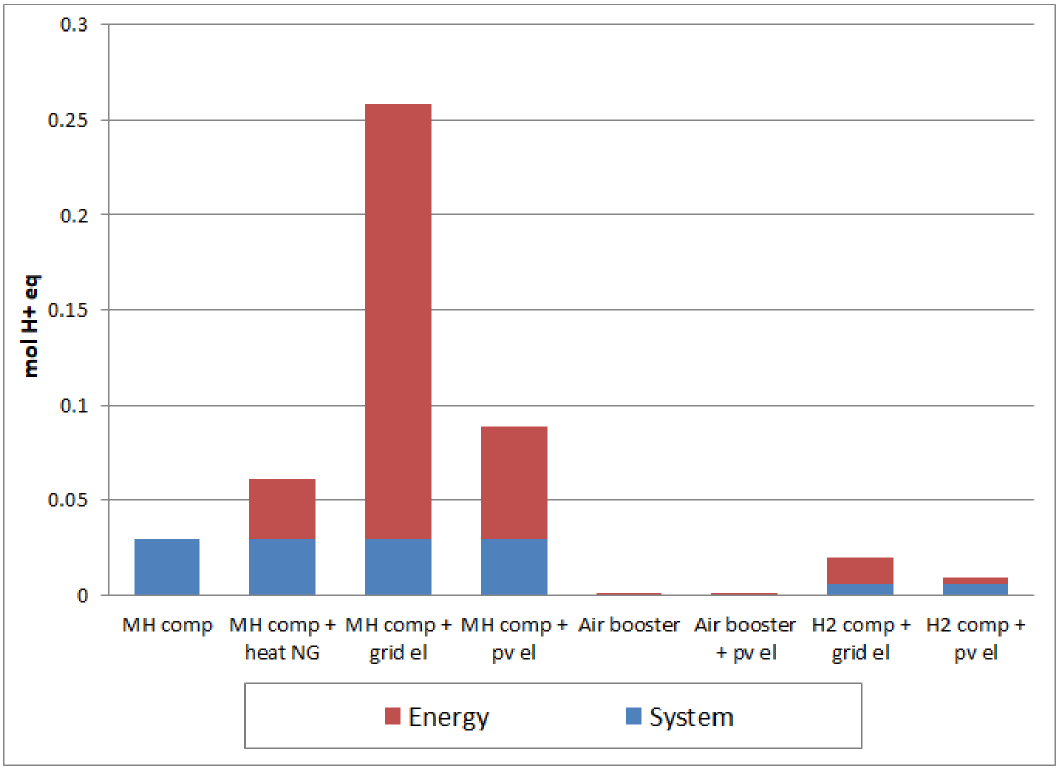

Figure 35. Comparison of results for the Acidification impact category associated with the compression of 1.79 kg of H_2 at 200 bar using different systems.

The comparison among the impacts related to the Acidification category proposes a similar trend to that previously observed: the compression of hydrogen with the metal hydride system, that uses electricity, causes once again the greatest impacts, instead the best solution is represented by the use of the booster + air compressor system. The high impact associated with the use of energy produced using the Italian energy mix derives from the combustion of coal. Although this contribution corresponds to only 14% of the total energy production (year 2016), it is the cause of 50% of the total impact. During the coal combustion nitrogen and sulfur oxides are released into the atmosphere which, when deposited, can cause an increase in the pH of soils and fresh water. It should be noted that coal is subjected to treatments for the removal /abatement of sulfur species, but these treatments do not allow complete removal of these chemical species.

The use of energy produced by a photovoltaic system shows higher impacts compared to the production of heat, deriving from the combustion of natural gas; the greatest impacts caused by the use of electricity produced by the sun find their

origin in the production phases of crystalline silicon and in the other components that make up a solar panel.
As shown in Figure 31 the impact generated by the MH compressor is split between the inputs of the stainless steel and the nickel, present in the first alloy. The numerical value of the MH compressor impact (0.029 molc H^+ eq) is slightly higher than that generated by compression with the generic H_2 compressor (0.019 molc H^+ eq), which uses energy from the grid.

Figure 36 shows the impacts related to the Resource use, minerals and metals category.

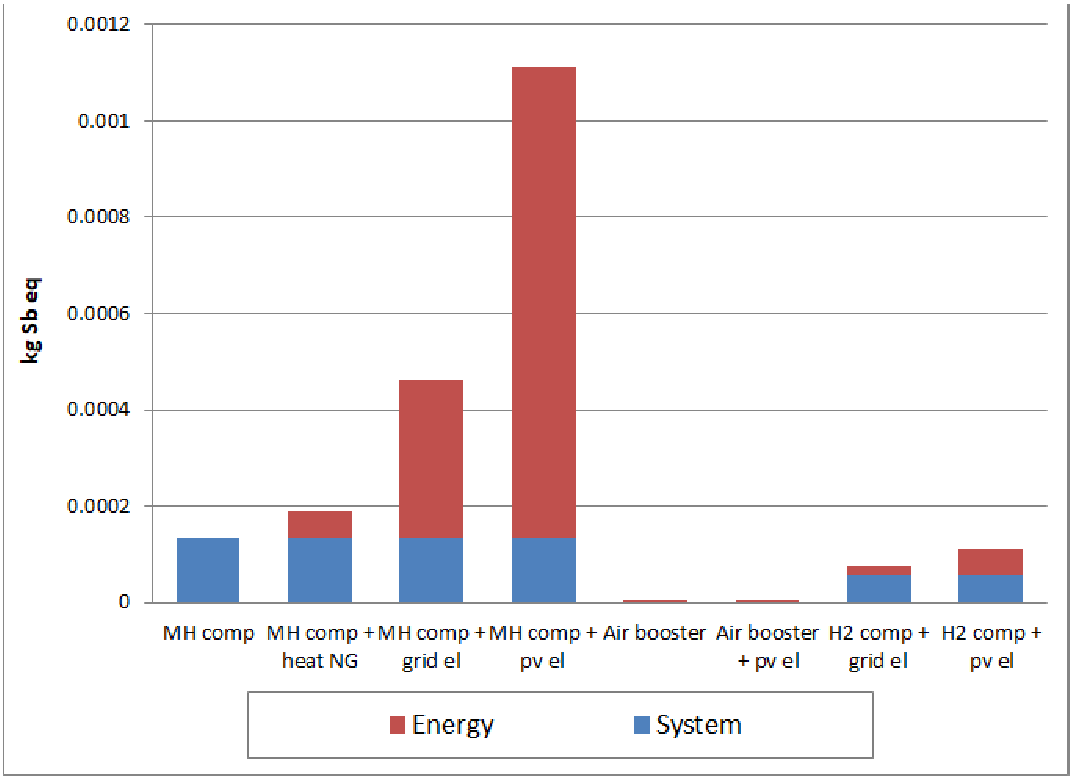

Figure 36. Comparison of results for the Resource use, minerals and metals impact category associated with the compression of 1.79 kg of H_2 at 200 bar using different systems.

Figure 36 shows the comparison of the impacts - with respect to the depletion of minerals - caused by the process of H_2 compression. A change in the relative impacts - with respect to the previous - categories is immediately evident: in this case the system that uses the MH compressor, powered by solar energy, causes the greatest impacts. The impacts associated with the use of photovoltaic panels are generated by the use of metals such as steel, copper and silver in the panels production chain.

It is interesting to underline that the use of alloys - made up of metallic and rare earths elements - does not generate such marked impact. Only 18% of the MH compressor impact - related to resource use - is caused by alloys, the remaining fraction is almost entirely due to stainless steel.

Compared to the previous categories there is a strong difference in the impacts between the MH compressor and the generic H_2 compressor; it should be noted that the latter was modeled by making an assumption - particularly weak in consideration to type and amount of materials used - therefore the impacts for this category are most likely underestimated.

The results of the last impact category: Resource use, energy carriers, are reported in Figure 37.

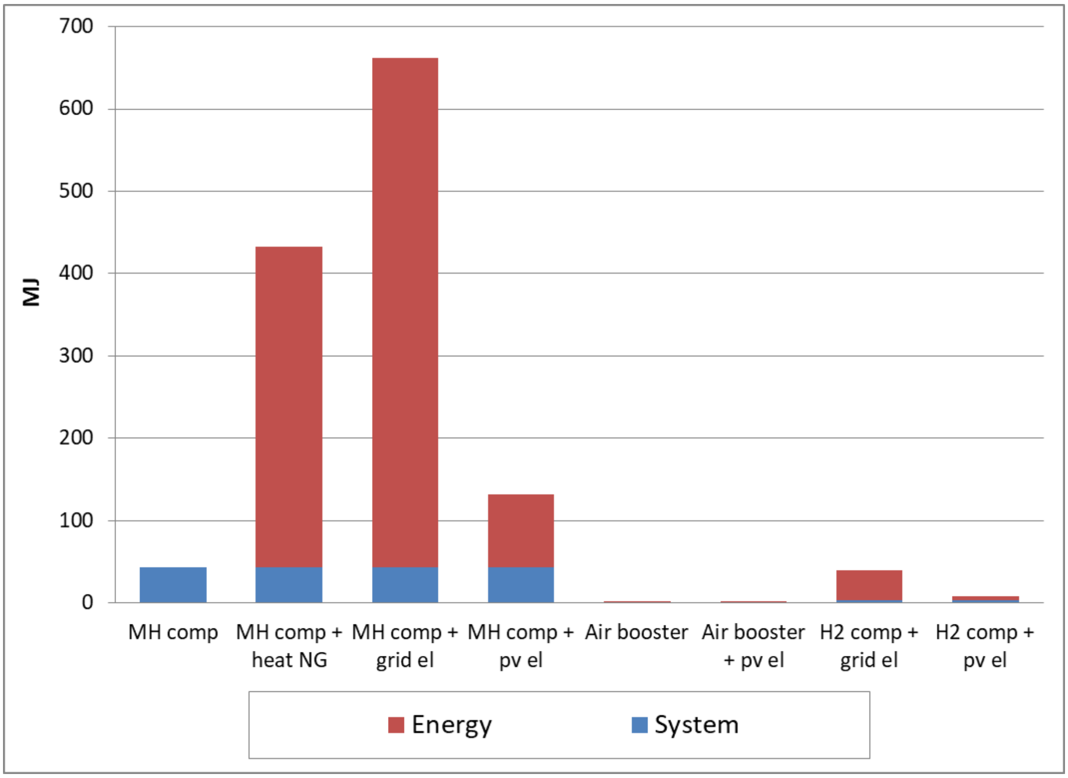

Figure 37. Comparison of results for the Resource use, energy carriers impact category associated with the compression of 1.79 kg of H_2 at 200 bar using different systems.

Figure 37 shows the MJ of fossil fuels consumed by the use of compared systems for the H_2 compression. The impacts show exactly the same trend as for the impacts related to Climate change. The best system is always represented by the air booster and the worst by the MH compressor powered with energy from the grid. This result is not surprising because the impacts are strongly generated by energy consumption; the use of electricity from a photovoltaic system makes it possible to greatly reduce the consumption of fossil resources. The impact generated by the MH compressor (without energy consumption) is very similar to the use of an H_2 compressor that operate with electricity from the national mix (respectively 43 MJ and 40 MJ).

Sensitivity analysis

As stated in the inventory section, the modeling for the MH compressor does not take into account an optimization for industrial purposes and comparing the input data with information found in literature (Lototskyy et al., 2016) the actual quantity of steel could be considerably lower than modeled; for this reason, in the scenario 1 the system was modeled assuming that the MH compressor needs half of steel compared to the base scenario. This assumption was made to investigate how the amount of steel influences the final results. In fact, as seen before, in Figure 31 , stainless steel is the main responsible for the environmental impacts. Figure 38 shows the details of the impacts with respect to the Climate change category of the baseline scenario and scenario 1; the impacts were calculated with reference to the compression of 1.79 kg of H_2, at 200 bar, as reported in the functional unit.

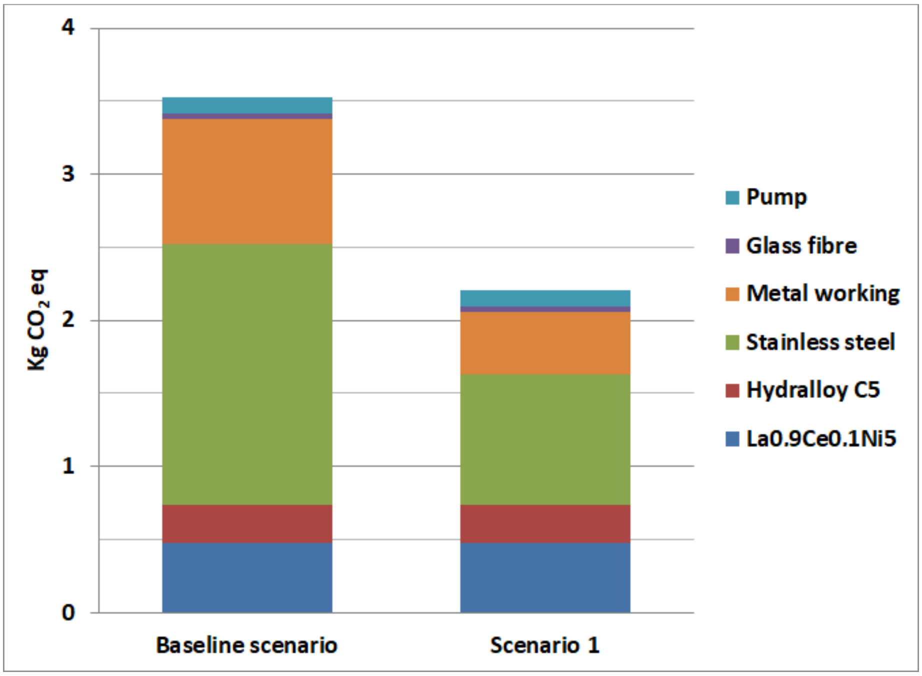

Figure 38. GHG emissions for the H_2 compression in the baseline scenario and when the amount of steel use to produce the MH compressor is halved (scenario 1).

Halve the amount of steel and its processing allows to reduce the environmental impacts by about one third compared to the baseline scenario. However, in general the contribution linked to stainless steel would always remain marked.

To understand the extent of the reduction of the impact for scenario 1 on the various categories investigated, a comparison was made with the other systems. Figure 39 shows this comparison - for the H_2 compression between:
- MH compressor that uses a recovery heat source (baseline scenario)
- MH compressor that uses a recovery heat source, with halved steel (scenario 1)
- air booster
- air booster that uses electricity from a photovoltaic system (air booster + PV el)
- H_2 compressor that uses energy from the grid (H_2 comp + grid el)
- H_2 compressor that uses electricity from a photovoltaic system (H_2 comp + PV el)
The impacts are reported normalized with respect to the maximum value for each impact category.

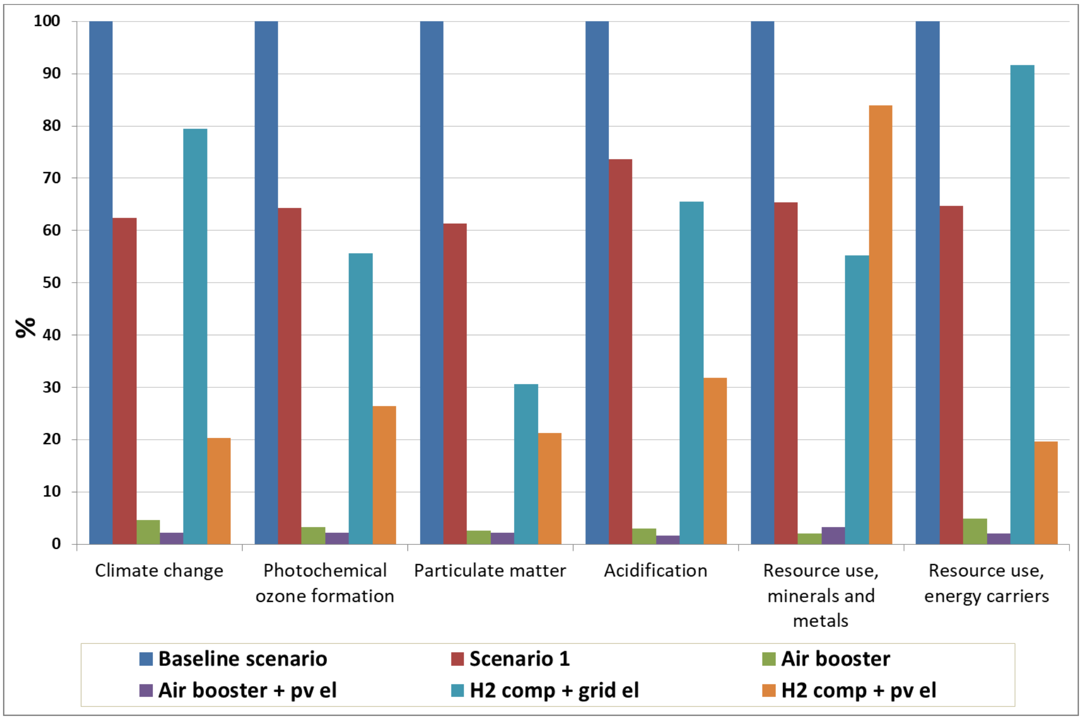

Figure 39. LCIA results - normalized with respect to the maximum value - associated with the compression of 1.79 kg of H_2 at 200 bar using different systems.

As already highlighted above, for all impact categories, the best way to compress hydrogen - under the conditions described by the functional unit - is through a system that uses a booster coupled with an air compressor. This result is valid whether electricity, to produce the compressed air, is taken from the grid (air booster) or generated from renewable sources (air booster + pv el).

However halving the amount of steel and the corresponding treatment process, improves the environmental profile of the MH compressor; for two categories – i.e. Climate change and Resource use, energy carriers - the impacts of scenario 1 are lower than those generated by a generic H_2 compressor. The use of solar energy, to power the generic H_2 compressor, causes significant impacts for the resource use, minerals and metals category; considerably higher than the use of the MH compressor in scenario 1.

For the categories - Photochemical ozone formation, Acidification and Resource use, minerals and metals - the difference between compressing with metal hydrides or with a generic compressor is minimal.

Despite being decreased, the impacts relating to the Particulate matter category for the scenario 1 are still markedly higher than the other systems analyzed.

Economic analysis

The comparison between the three H_2 compression systems has been extended to include a cost analysis.

The costs of the alloys that make up the MH compressor have been obtained by the companies that sell these materials; the cost of the other materials making up the MH compressor were obtained from an online market research. The cost of the air booster refers to a specific device directly purchased. The prices of the air compressor and the generic H_2 compressor correspond to average values obtained from various quotations via web search.

Figure 40 shows the cost distribution among the main components of the three considered systems. The detailed cost for the three system is reported in TableA5.

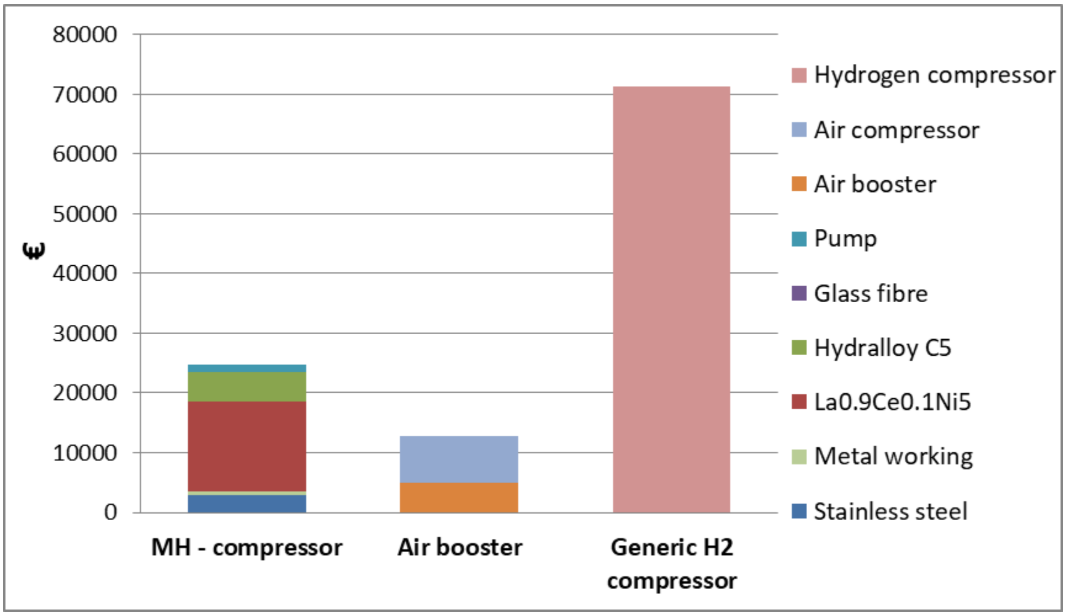

Figure 40. Total cost of the three system analyzed

The greatest investment is for the generic H_2 compressor, followed by the MH compressor and finally by the system: booster + air compressor. The MH compressor has a cost equal to around one third of the generic H_2 compressor and almost double the system booster + air compressor. The main costs for the MH compressor are attributable to the alloys, and in particular to the $La_{0.9}Ce_{0.1}Ni_5$ alloy.

Since it has been assumed that the three compression systems can be powered by energy from different sources, Table 45 shows the prices of electricity corresponding to the Italian mix, electricity produced with a photovoltaic system and natural gas.

Energy	Electricity Italian energy mix	0.23	€/kWh	Eurostat, 2019a
	Natural gas	0.09	€/kWh	Eurostat, 2019b
	Solar photovoltaic	0.05	€/kWh	(IRENA, 2020)

Table 45. Price of the energy used to model the systems.

Figure 41 shows the cost of the hydrogen compression - per functional unit - distributed among the main components of the three considered systems. The cost of energy was also considered among the contributions. It was assumed that the MH compressor operates using recovery heat, while the air compressor and the hydrogen compressor use electricity from the Italian national mix. Table A6 shows the corresponding numerical cost.

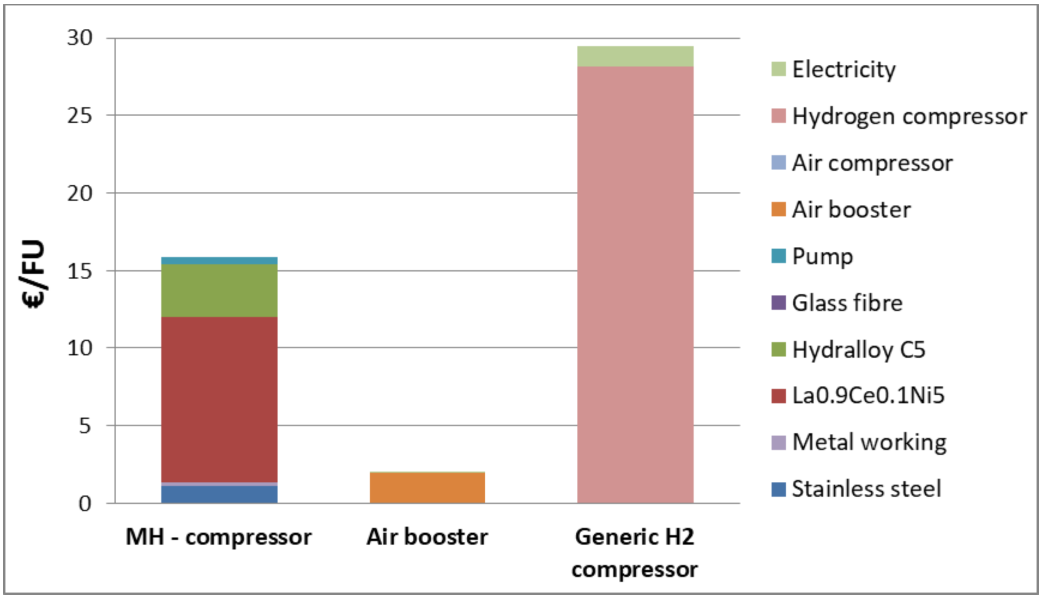

Figure 41. Cost for the compression of 1.79 kg of H_2, at 200 bar, with the three systems analyzed; no energy consumption was hypothesized in the case of the MH compressor, instead the use of energy from the national mix was assumed to power the system with booster and the compressor for H_2.

The inclusion of the cost of the electricity for the air booster and H_2 compressor does not change significantly the results. The higher cost for the hydrogen compression originates from the investment for the purchase of the H_2 compressor; as regards the metal hydride compressor, the alloy $La_{0.9}Ce_{0.1}Ni_5$ causes the highest costs. As regards the compression carried out with the air compressor booster system, almost all of the cost derives from the purchase of the booster. Also from an economic point of view, the best way to compress - under these conditions - hydrogen is the booster system coupled with an air compressor.

5.2.4. Conclusions

The results presented in this study report that the best solution to compress hydrogen - if few kg per day are required - is to use a system based on a booster coupled to an air compressor. This technology is simple and requires only a minimum amount of energy, thus allowing to stem the environmental impacts associated with the overall compression phase.

The metal hydride compressor - modeled on the basis of current data from the development / research phase - generates significant environmental impacts, especially when it is unable to use a source of waste heat. In fact, the energy (as heat) that needs to be supplied - to make the phases of hydrogen absorption and desorption take place - is quite high. The environmental impacts remain much higher than the alternatives, even by using renewable resources (electricity produced by a photovoltaic system) or by producing heat by direct combustion of natural gas. For certain categories analyzed - i.e. Climate change, Photochemical ozone formation, Acidification and Resource use, energy carriers - the impacts generated by compression with the metal hydride system, that take advantage of a waste heat source, are very similar to those produced during compression with a generic H_2 compressor. For other categories instead - i.e. Particulate matter and Resource use, minerals and metals - a marked difference also remains between these two systems.

The difference in impact between the MH compressor and the generic compressor is reduced and even reversed if the amount of steel - which constitutes the structure of the metal hydride compressor - is halved. Such scenario is very probable, since the data used to model the system were not obtained following an engineering optimization and therefore there is a substantial possibility of improvement from this point of view.

An interesting fact is the low impacts of the alloys that make up the metal hydride system. The $La_{0.9}Ce_{0.1}Ni_5$ alloy shows slightly higher impacts only in relation to the

Acidification and Resource use, energy carriers categories, but in any case almost completely negligible compared to those attributable to stainless steel.

It must be considered that, as a possible limitation of this study, the impacts associated with the generic H_2 compressor are very likely underestimated compared to reality, the cause must be sought in the way in which the system was modeled in this study.

At the same time, although the system based on metal hydrides, currently does not prove to be the most convenient, from an environmental point of view, it has a large room for improvement. In fact, as mentioned, the optimization of the compressor structure and the use of different alloys - which prove to be more efficient than those modeled here - could allow to considerably improve the effects on the environment and increase the competitive advantage of this compressor.

The results obtain in this study allow to fill a knowledge gap in the assessment of hydrogen compression technologies. They made it possible to identify - in relation to a case study and well defined conditions - which technology for hydrogen compression is better from an environmental point of view.

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Appendix to chapter 5

Table A 3. Numerical LCIA results for all the impact categories calculated for the production of the MH compressor.

Impact category	Total	$La_{0.9}Ce_{0.1}Ni_5$	Hydralloy C5	Stainless Steel	Metal working	Glass fibre	Pump
Climate change kg CO_2 eq	8124.94	688.55	364.61	4529.01	2175.57	85.90	281.31
Particulate matter Disease inc.	$6.14*10^{-04}$	$4.26*10^{-05}$	$1.92*10^{-05}$	$3.95*10^{-04}$	$1.16*10^{-04}$	$4.90*10^{-06}$	$3.60*10^{-05}$
Photochemical ozone formation kg NMVOC eq	30.82	2.92	1.36	17.87	6.40	0.40	1.88
Acidification molc H^+ eq	62.92	14.40	1.99	28.52	11.25	0.66	6.11
Resource use, minerals and metals kg Sb eq	0.31	0.033	0.003	0.158	0.076	0.006	0.036
Resource use, energy carriers MJ	97767.26	11240.31	4717.27	48918.59	28694.24	1128.58	3068.28

Table A 4. Comparison of the environmental impacts associated with the compression of 1.79 kg of H_2 at 200 bar using different systems.

Impact category	MH comp	MH comp + heat NG	MH comp + grid el	MH comp + pv el	Air booster	Air booster + pv el	H_2 comp + grid el	H_2 comp + pv el
Climate change kg CO_2 eq	$3.53*10^{+00}$	$3.09*10^{+01}$	$4.61*10^{+01}$	$1.07*10^{+01}$	$1.62*10^{-01}$	$7.72*10^{-02}$	$2.80*10^{+00}$	$7.15*10^{-01}$
Particulate matter disease inc.	$2.61*10^{-07}$	$3.90*10^{-07}$	$1.16*10^{-06}$	$7.45*10^{-07}$	$6.88*10^{-09}$	$5.89*10^{-09}$	$8.01*10^{-08}$	$5.57*10^{-08}$
Photochemical ozone formation kg NMVOC eq	$1.35*10^{-02}$	$4.08*10^{-02}$	$1.11*10^{-01}$	$4.38*10^{-02}$	$4.51*10^{-04}$	$2.92*10^{-04}$	$7.50*10^{-03}$	$3.56*10^{-03}$
Acidification molc H^+ eq	$2.98*10^{-02}$	$6.09*10^{-02}$	$2.58*10^{-01}$	$8.83*10^{-02}$	$9.12*10^{-04}$	$5.06*10^{-04}$	$1.95*10^{-02}$	$9.47*10^{-03}$
Resource use, minerals	$1.34*10^{-04}$	$1.87*10^{-04}$	$4.62*10^{-04}$	$1.11*10^{-03}$	$2.85*10^{-06}$	$4.40*10^{-06}$	$7.39*10^{-05}$	$1.12*10^{-04}$

and metals kg Sb eq								
Resource use, energy carriers MJ	$4.34*10^{+01}$	$4.32*10^{+02}$	$6.62*10^{+02}$	$1.32*10^{+02}$	$2.14*10^{+00}$	$8.82*10^{-01}$	$3.98*10^{+01}$	$8.56*10^{+00}$

Table A 5. Total cost of the three systems analysed: MH compressor, air booster + air compressor and generic H_2 compressor.

System	Detail	Price	Unit of measurement
MH - compressor	Stainless steel	2839.90	€/unit of compressor
	Metal working	615.31	€/unit of compressor
	$La_{0.9}Ce_{0.1}Ni_5$	15146.15	€/unit of compressor
	Hydralloy C5	4860.54	€/unit of compressor
	Glass fibre	103.27	€/unit of compressor
	Pump	1150	€/unit of compressor
Air booster	Air booster	4952	€/unit of compressor
	Air compressor	7876.67	€/unit of compressor
Generic H_2 compressor	Hydrogen compressor	71200	€/unit of compressor

Table A 6. Cost for the compression of 1.79 kg of H_2, at 200 bar, with the three systems analyzed; no energy consumption was hypothesized in the case of the MH compressor, instead the use of energy from the national mix was assumed to power the system with booster and the H_2 compressor.

System	Detail	Price	Unit of measurement
MH - compressor	Stainless steel	1.122	€/FU
	Metal working	0.243	€/FU
	$La_{0.9}Ce_{0.1}Ni_5$	10.602	€/FU
	Hydralloy C5	3.402	€/FU
	Glass fibre	0.041	€/FU
	Pump	0.462	€/FU
Air booster	Air booster	1.956	€/FU
	Air compressor	0.001	€/FU
	Electricity (Italian mix)	0.055	€/FU
Generic H_2 compressor	Hydrogen compressor	28.124	€/FU
	Electricity (Italian mix)	1.357	€/FU

Chapter 6: Assessment of circular economy business model from the environmental point of view

Circular economy paradigm is an inspirational approach for creating value for the economy, society and business while minimising resource use and environmental impacts. As reported in Chapter 2 this economic model is based on the assumption that the value of products, materials and resources in the economy is to be maintained for as long as possible. An efficient use of resources is the priority of the circular economy. According to Rizos et al. (2017) the possible approaches to achieve the CE goals can be made to converge in three categories, often interconnected: I) using less primary resources, II) maintaining the highest value of materials and products and III) changing utilisation patterns (see section 2.3). Although a clear view how about to implement the inspirational strategies set by the CE has not yet been outlined. In fact the transformations required to adapt to the new approach sets challenges for established companies and it is clear that radical innovations and disruptive business models are needed in order to tackle the current challenges and move towards the circular economy model. In this context of radical changes, which prove to be necessary, but also attractive for possible profits, a precise assessment of the environmental impacts generated by the new approaches is of primary importance. In fact, without an objective assessment, an approach deemed favourable for the environment can turn out to be negative when implemented. Therefore the possibility to combine LCA analysis with CE approaches it can prove to be a winning strategy in the search for greater environmental sustainability.

This chapter shows two case study that have tried to specifically address the issue outlined above. The development of business models, that can be considered part of the CE framework, have been evaluated from the environmental perspective.

The first case study addressed the relationship between single use and reuse of a product; in detail an LCA analysis has been conducted comparing four single-use

(PP, PLA, PET, and Cardboard+PE coat) and reusable (PP, PLA, PET and glass) cups for serving drinks.

The second case study has set the goal of carrying out an analysis of the environmental impacts related to the life cycle of formal dresses. In detail the analysis focused on the comparison between a business model based on rental of garments with an online purchase model. Since this is a simple case study, the field of investigation has been restricted to formal women's dresses only.

6.1. Case study 6: Assessment of the environmental impacts for a deposit return systems: comparing disposable and reusable cups

6.1.1. Introduction

Plastics are lightweight, durable and cheap materials. Since the ’60s, plastics, gradually substituting other materials such as wood, metal, and glass, have become the ubiquitous materials of the modern economy (Ellen MacArthur Foundation and World Economic Forum, 2016) due to their chemical properties and the low cost of raw materials. Plastics production is regularly growing and, nowadays, global production reached 359 Mt in 2018 and an industry turnover of 355 billion euros in 2017 in Europe (Plastics Europe, 2019). On the other hand, plastic waste causes impactful consequences in the environment (Jiang, 2018), in terms of degradation of natural systems (Ryberg et al., 2019; Jambeck et al., 2015), large quantity of greenhouse gas emissions, fossil feedstock depletion (Hopewell et al., 2009) and toxic additives circulation (Swan et al., 2015; Lien et al., 2015; Winton et al., 2020). The plastic issue have captured the attention of the public and private sectors around the world (European Commission, 2015; European Parliament, 2019; Ellen MacArthur Foundation, 2019). The industry is showing its inclination to gradually move away from today’s linear take-make-dispose model (Ellen MacArthur Foundation, 2016), by adopting innovative circular business models. So, waste is designed out from the linear model and resources are circulated back to the soil (compostable plastic) (Razza et al., 2009), to the producers (recycled plastic) (Accorsi et al., 2020), or to the consumers (reusable plastic) (Changwichan and Gheewala, 2020). The European Parliament, recently, approved the Directive 2019/904 on the “reduction of the impact of certain plastics products on the environment” to promote circular approaches (European Parliament, 2019). Several EU countries already adopted national legislations to increase the use of reusable plastic with deposit return systems (CM Consulting Inc and Reloop Platform, 2016).

Today the efforts towards the increase of recycling practices are remarkable, but still not sufficient. The plastic packaging recycling rate in European Union cannot be considered satisfactory at all, with an average percentage of 41% in EU 28+2 and a target for plastic packaging recycling of 50% by 2025 (Plastics Europe, 2018). At legislative level there is still a gap in terms of rules promoting good practices of recycling. Some of them have already been identified by previous research (Mariotti et al., 2019): taxes on the use of virgin plastics or differentiated value-added taxes for recycled plastics, the introduction of recycled content standards, targeted public procurement requirements, or recycled content labelling, just to name a few. An increasing number of countries are taking measures to reduce single-use plastic dispersion into the natural environment and, in 2019, the European Parliament issued a Directive (2019/904/EU) aimed at directly limit the production of determined single-use plastic products (European Parliament, 2019) (cups are one of these). Despite new recycling policies, promoting reuse remains the main effective solution to reduce the accumulation of plastic waste. In fact, to ensure reusability, the first step is to encourage the deposit return system (Cottafava et al., 2019). Although reusable products can successfully limit the use of virgin materials and can have a positive effect on the material extraction / production, the positive impact could not be always positive by considering various environmental indicators. An effective approach for an objective evaluation of these indicators is given by the use of the Life Cycle Assessment methodology.

LCA is one of the most adopted techniques to evaluate the environmental impacts of products and processes (Sonnemann et al., 2018). Several studies have evaluated the environmental effects arising from the reuse of plastic products, by comparing the same service offered by single-use materials (Garrido and Del Castillo, 2007; Almeida et al., 2018; Tua et al., 2019; Paspaldzhiev et al., 2018). However, what emerges from each LCA analysis is a snapshot of a precise situation, generally hard to be generalized (Ekvall et al., 2007; Finnveden, 2000), with specific boundary condition, End of Life (EoL) scenario or functional unit. Indeed, nowadays, an open debate within the Circular Economy (CE) framework is emerging on how to model multicycle circular processes including reuse, repair, refurbish or remanufacturing (Amasawa et al., 2020).

From the existing literature (Ardente and Mathieux, 2014; Boldoczki et al., 2020), it is straightforward that there is no single choice which is overall preferable in terms of single-use versus reusable products. To point out such considerations several researchers proposed various models to identify an environmental break-even point (BEP) - i.e. the minimum no. of reuses after which a reusable product is environmentally better than the single-use equivalent one – in case of reuse, repair, remanufacturing, refurbishing. For instance, Bobba et al. (2016) proposed a set of environmental and economic indicators to evaluate products durability, starting from the indicator proposed by Ardente and Mathieux (2014), which takes into account lifetime, energy consumptions, impacts of lifetime extension and of the replacement product. Boldoczki et al. (2020), instead, proposed a simple linear model to compare the reuse of devices with the purchase of new ones, by evaluating the environmental impact versus the usage duration (time). With respect to plastics products, similar analyses have been carried out by Almeida et al. (2018), who compared a commercial reusable coffee cup with single use cups, with the aim of identifying the environmental BEP. From the relevant literature, a standard methodology does not exist yet and, thus, the debate about robust formalisms to model multi-cycle closed-loop processes is still open.

To face up this issue related to environmental assessment through LCA, in this work a methodology for the interpretation of results is proposed, in order to facilitate comparisons between single-use and reusable products. To easily identify the BEP, the product efficiency (the efficiency of the production and EoL phases) and the use efficiency have been introduced. The suggested formalism allows to decouple, in the BEP assessment, the effect of the use from the production and the EoL. This methodology has been applied to a case study, comparing four single-use cups with four reusable cups, by analysing seven impact categories in three different use phase scenarios.

The following of the work is structured as follows. In materials and methods, the novel methodology is described by highlighting the differences with a traditional LCA analysis. In the results section, the comparison between reusable and single-use cups is discussed in terms of the environmental break-even point. In discussion, main results are compared with previous findings in literature and some limitations of the proposed methodology are pointed out. Finally, the main results are summarized in the conclusion part.

6.1.2. Materials and methods

The adopted methodology consists of two steps to further advance the well-consolidated LCA analyses and to support the results' interpretation for multi-cycle closed-loop processes where reuse, repair, refurbish or remanufacturing are introduced. The first step consists of a traditional LCA analysis. The aim of the second step, is to aggregate single results for the three main life phases (production, use, EoL) and to analyse the environmental BEP for each analysed impact category.

Case Study

Seven relevant impact categories - Climate Change (CC), Ozone Depletion (OD), Acidification (A), Photochemical Oxidant Creation (POC), Eutrophication (E), Non- Renewable Energy Use (NREU), and Water Scarcity Indicator (WSI) - have been considered. Among the many possibilities of impact categories, as reported in the Technical Report by the Joint Research Center (JRC) (Fazio et al.,2018), CC and OD are recommended and considered satisfactory; A, E, and POC are also recommended, although they are not yet considered fully mature and satisfactory. In fact, more precise and in-depth studies are still needed to evaluate the weight of all characterization factors. As the studied system here presents a direct consumption of chemicals, water and energy, both in the use phase and in the cups production, despite the lower reliability of the results, it was considered appropriate to measure the impacts also relating to the WSI and NREU categories. For a comprehensive comparison between the service offered by disposable cups and reusable cups, different scenarios related to the use phase have been analyzed. Figure 42 shows a detailed scheme of the system life cycle, highlighting the considered scenarios.

In particular, four scenarios for the use phase - 0) single-use without loop (baseline), 1) onsite washing, 2) offsite washing, and 3) onsite handwashing- have been considered. The baseline 0) case consists of using the cup once and then throwing it for disposal. The use phases have been modeled according to Martin et al. (2018) for 1) onsite washing with commercial washing machines, and 3) onsite handwashing. The onsite washing is modeled for the real situation, when the pubs/restaurants directly wash the cups. The 2) offsite washing refers to the use of industrial washing machines (primary data), which imply an increasing transport distance. It models real situations, such as temporary events, small pubs without washing machines, or catering for buffets during events.

The EoL phase have been modelled considering: 100% energy recovery for PP, PET, PLA and PE-coated cardboard cups and full recycling for glass cups. Landfill scenario has been discarded as possible scenario according to the Circular Economy European Directive (European Parliament, 2020).

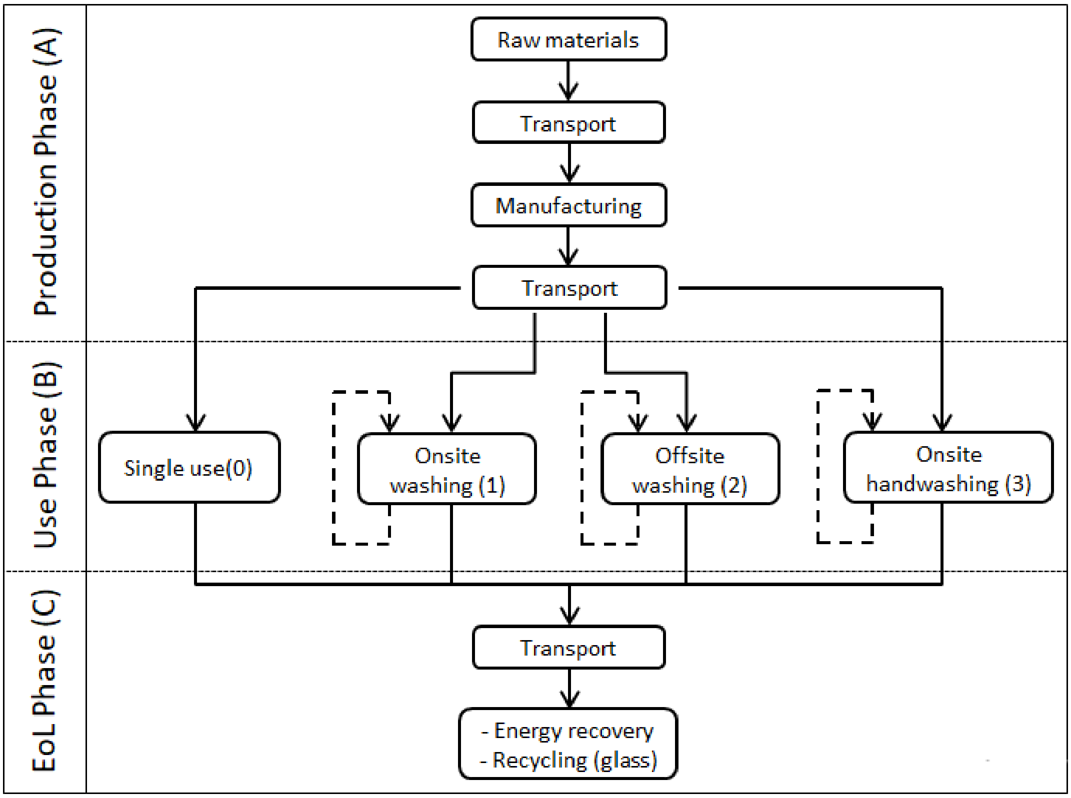


Figure 42. Overview of the analyzed scenarios.

Life Cycle Assessment

The entire work was conducted with software SimaPro 8 and using the Ecoinvent v.3.3 database.

Goal and scope definition

The aim of this work is to assess the environmental BEP of deposit back systems for cups, by identifying the minimum number of uses a reusable cup needs in order to be considered preferable than a single-use cup. To achieve this goal, the LCA analysis was applied to the case of disposable and reusable cups, in order to identify the main environmental impacts. These were later used to determine the break-even point between the two service delivery strategies.

The chosen functional unit was serving 0.4 liters of draught beverages in one go, which allows to collect the data relating to the service in a single supply. These data constitute the starting point for modelling and studying the function of serving beverages repeated n times over time (function performed by disposable and reusable cups). The system boundary has been defined considering the whole life cycle from the extraction of raw materials up to the EoL phase, as shown in Figure 42.

Life cycle inventory

The weights of the cups considered in the study are summarized in Table 46. Weight of all single-use and reusable cups has been calculated as an average of available commercial products in Europe.

	Reusable Weight [g]				**Single-use Weight [g]**			
	PP	PLA	PET	Glass	PP	PLA	PET	Cardboard
Min	35	150	60	330	6	6.5	8	7.5
Avg	40	175	70	360	7	7.5	9	8.5
Max	45	200	80	390	8	8.5	10	9.5

Table 46. Minimum, maximum, and average weight of the analyzed single-use and reusable cups

The sources from which all inventory values were derived or measured are indicated in Table 47.

Life cycle phase	Sub-phase process	PP	PLA	PET	Glass	PE-coated Cardboard
Production	Cradle to gate	1	2	1	4	3
	Transport of resin + cup production	3;4	3;4	9;4		
	Printing	3	3	3	11	3
	Packaging	3	3	3	3	3
	Transport from production site to city of use	10	10	10	10	10
Use	Onsite handwashing	6	6	6	6	-
	Onsite washing	6	6	6	6	-
	Offsite washing	7	7	7	7	-
	Transport to location of use	8	8	8	8	9
EoL	Transport to location of EoL	12	12	12	12	12
	EoL packaging	3	3	3	3	3
	Incineration	3	3	3	-	3
	Recycling	-	-	-	5	-

Table 47. List of all data sources for all materials and life cycle phases. The numbers within the table refer to: (1) impact values directly taken from Plastics Europe (Plastics Europe, 2020), (2) inputs/outputs values taken from Vink et al. (2007), (3) inputs/outputs values taken from Vercalsteren et al. (2007), (4) Ecoinvent database, (5) inputs/outputs values taken from Gaines and Mintz (1994), (6) inputs/outputs values taken from Martin, Bunsen, and Ciroth (2018), (7) inputs/outputs values taken from an analysis carried out on behalf of an Italian crockery washing company, (8) modeled by authors, (9) approximation based on Vercalsteren et al. (2007) taking into account the physical- chemical properties of the material, (10) modeled by authors, (11) same as cardboard, no direct information, (12) modeled by authors.

Input-output data for the production, use and the EoL phases, are specified in Table A7, A8, A9 and A10 in the Appendix section at the end of this chapter.

The production of the plastic cups was modeled using the thermoforming and injection molding processes for single use and reusable respectively. Given the lack of specific data related to the production of PET cups, the system was modeled in a similar way to PP cups, taking into account the different physical-chemical properties of the polymeric materials.

The input data for the packaging refer to reusable cups. As no specific data were obtained for the disposable cups, the system was left unchanged in the two cases.

To simplify the study and not to add variables that are not directly measurable, a distance of 100 km was assumed for the transport of raw materials to the production site of the cups. For the same reason, a distance of 1000 km between cup producer and place of use was considered. The latter is an average distance that allows covering the transport within single countries and between neighboring states in a territory such as Europe. Both transports have been modeled assuming a road service that uses freight lorries of 16-32 tons. Instead, the transport in the use phase (Table A8), used in the offsite washing scenario, takes place with light commercial vehicle.

The data used to model hand washing and dishwasher were obtained from Martin et al. (2018); the usage data of water, detergents and energy were reported. The data for modelling an industrial washing were directly measured in an Italian crockery washing company. In the case of industrial washing, the contribution of round-trip transport was also considered.

The EoL phase of incineration has been modelled for the cups in PP, PLA, PET and PE-coated cardboard; as process output, the production of an amount of energy, specific for each materials, was assumed. The EoL's scenario for glass cups was modelled according to a recycling process and the avoided production of a specific amount of raw materials was taken in account (89% of recycled material, Gaines and Mintz (1994)).

Life cycle impact assessment

In this study, the environmental impacts are expressed as midpoint results and the considered impact categories are CC, OD, A, POC, E, NREU, and WSI. The results of the first five impact categories were obtained using the EPD 2018 method (Environdec, 2019). In order to calculate the impacts, it refers directly to the CML-IA baseline method (for E, CC, OD) and CML-IA non-baseline method (for A). The EPD method was selected because of units of impact categories. In fact, for some raw materials (PP, PLA, PET, PE), the environmental impacts are usually obtained by the respective eco-profiles published in the literature, whereas eco-profiles calculated with the EPD method can be used directly. The results relative to the NREU impact category were obtained with the Cumulative Energy Demand (CED) method, which accounts for gross energy requirements (Frischknecht et al., 2007). For the WFI assessment, the Pfister et al. (2009) method has been adopted. This method allows to obtained geographically representative and accurate results.

Results interpretation

For the last phase, interpretation of the results, an assessment based on the environmental BEP has been conducted as described in next subsection. In particular, the proposed approach supports the interpretation of results phase of LCA analyses. The introduction of the environmental BEP, the product efficiency and the use phase efficiency, as it will be described in next subsection, allows to decouple the effects of a change in the production phase (it affect only "when" the BEP is achieved) or in the use phase (it affect "if" the BEP is reached) by facilitating the comparison among reusable and single-use products.

Break-even point assessment

To evaluate the BEP, according to Figure 42, let's define:

1. A = production, B = use, and C = EoL phase impact;
2. X = single-use, and Y = reusable product life cycle impact;
3. the subscripts 0, 1, 2, 3 refer to the different washing scenarios;
4. the subscripts also highlight the product material.

With this notation, for instance, $B_{PLA;Y1}$ is the impact of the use phase for the reusable PLA product for onsite washing. The subscript 0, for the use phase, represents the baseline, i.e. the use phase for the reusable product without loop. Thus, the environmental impact of the whole cycle is denoted in general, skipping, for now, the materials' subscripts and considering only the baseline scenario without closed loop (0), as X, for a single-use product, and Y_0, for a reusable product without loop. Thus, X and Y_0 are equal to:

$$X = A_X + B_X + C_X \tag{6.1}$$

$$Y_0 = A_Y + B_{Y0} + C_Y \tag{6.2}$$

The use phase impact for the baseline, i.e. the life cycle without loop, has been considered equal to zero ($B_X;B_{Y0}=0$). According to this notation three Key Performance Indices (KPIs) for a reusable product can be defined, as described in the following.

Product efficiency

The environmental product efficiency for reusable products KPI is defined as:

$$\eta_p = \frac{Y_0}{X} \tag{6.3}$$

η_P is, in other words, the no. of single-use products which impacts as much as the reusable product and it represents the efficiency of the production and EoL process of the reusable product with respect to a reference single-use product life cycle impact. Indeed, according to Okumura et al. (2001), a more durable product, such as a reusable one, implies a larger amount of materials and, thus $\eta_p > 1$. The larger is η_p, the less efficient is the reusable product related to the single-use one. If, $\eta_p < 1$, instead, it implies that the reusable product impacts less than the single-use product and it represents a very efficient production and EoL process.

Use phase efficiency

The environmental use phase efficiency for reusable product KPI is defined as:

$$\eta_{u,j} = \frac{B_{Y_j}}{X} \tag{6.4}$$

where B_{Yj} is the impact of the use phase for the reusable product for the use scenario j. $\eta_{u;j} > 1$ means that the use phase for the reusable product B_{Yj} impacts more than the whole life cycle of the single-use product X; thus, $\eta_{u;j} > 1$ represents an inefficient use phase. On the contrary, if $\eta_{u;j} < 1$, the use phase impact for the reusable product is lower than the single-use product life cycle and the smaller is $\eta_{u;j}$, the more efficient is the reusable product use phase with respect to the single-use product life cycle.

Environmental break-even point

The environmental break-even point KPI is calculated as:

$$n_j = \frac{Y_0}{X - B_{Y_j}} \tag{6.5}$$

where n_j is properly the environmental BEP for the reusable product, considering the reuse loop scenario j. n_j represents the minimum no. of reuses necessary to balance the impact of the reusable product with respect to the same no. of single-use product usages. The proof and rationale of Eq. 6.5 is explained in section A.1 of the Appendix. By substituting Eq. 6.3 and 6.4 into Eq. 6.5, the environmental BEP can be expressed in terms of the product efficiency η_p and the use efficiency $\eta_{u;j}$ according to:

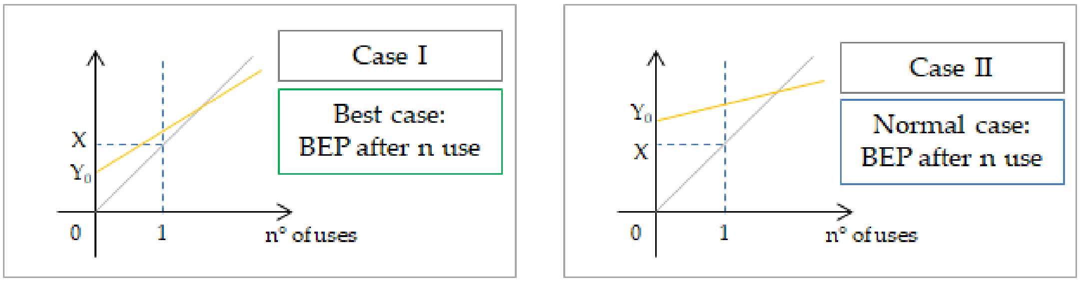
$$n_j = \frac{\eta_p}{1 - \eta_{u,j}} \tag{6.6}$$

From equation 6.5, two cases emerge. If $X > B_{Yj}$ implies that $n_j > 0$; thus, n_j represents the minimum no. of reuses in order to obtain an environmental benefit for the reusable product with respect to the single-use. Otherwise, if $X < B_{Yj}$ then n_j

< 0; thus, the reusable product does never reach an environmental BEP, since a negative number of usages is not possible.

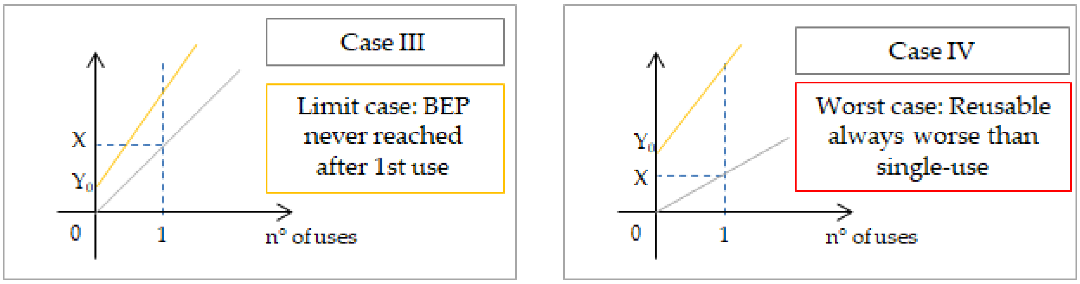
Mapping cases

From Eq. 6.3, Eq. 6.4 and Eq. 6.5 (or Eq. 6.6) four possible cases may be identified which explain the behaviour of the reusable with respect to the single-use product life cycle impacts. Figure 43 shows the four possible cases to compare reusable vs single-use products. The representation in Figure 43 describes the environmental impact as function of the number of uses n. The slope of the straight line for the single-use product is given by X, while for the reusable product is given by B_{Yj}. With this formalism, the single-use line passes from the origin while the reusable line crosses the y-axis at Y_0.



a) Efficient production and use phase.

b) Inefficient production phase and efficient use phase.



c) Efficient production phase and inefficient use phase.

d) Inefficient production and use phase.

Figure 43. Environmental break-even point representation of the four possible cases comparing reusable and single-use products. The y-axis represents the related midpoints. Gray lines refers to the single-use product, while yellow ones to the reusable product. Horizontal dashed lines show the impact X related to the whole life cycle of one single-use product, while the vertical ones refer to one use, i.e. n = 1.

Cases	**Environmental break-even point**	**Product efficiency**	**Use phase efficiency**
Case I	$n_j > 0$	$0 < \eta_p < 1$	$0 < \eta_u < 1$
Case II	$n_j > 0$	$\eta_p > 1$	$0 < \eta_u < 1$
Case III	$n_j < 0$	$0 < \eta_p < 1$	$\eta_u > 1$
Case IV	$n_j < 0$	$\eta_p > 1$	$\eta_u > 1$

Table 48. Four cases and relationships with the n, η_p, and η_u

According to Table 48, each case corresponds to a precise condition for n_j, η_p and η_u such as:

1. Case I: Best case. This solution happens when $n_j > 0$ (or $0 < \eta_u < 1$) AND $0 < \eta_p < 1$; it implies that the reusable product is better than the single-use product after n_j reuses when $\eta_p > 1- \eta_u$, while if $\eta_p < 1- \eta_u$, the reusable product is always better.
2. Case II: Normal case. This case occurs when $n_j > 0$ (or $0 < \eta_u < 1$) AND $\eta_p > 1$; it means that the reusable product is better than the single use only after n_j reuses.
3. Case III: Limit case. This one represents the transition case and it occurs when $n_j < 0$ (or $\eta_u > 1$) AND $0 < \eta_p < 1$; it corresponds to a particular condition when the reusable product is better only before the first use phase.
4. Case IV: Worst case. Finally, this last case refers to $n_j < 0$ (or $\eta_u > 1$) AND $\eta_p > 1$ and it means that the reusable product is always worse than the single-use product.

Negative environmental BEP $n_j < 0$ has no real physical meaning but it is a useful KPI to classify the results within the discussed formalism.

The four cases described in Table 48, if plotted, in logarithmic scale, in a scatter plot, correspond exactly to the four quadrants, i.e. best case ($\log(\eta_u) < 0$; $\log(\eta_p) < 0$), normal case ($\log(\eta_u) < 0$; $\log(\eta_p) > 0$), limit case ($\log(\eta_u) > 0$; $\log(\eta_p) < 0$) and worst case ($\log(\eta_u) > 0$; $\log(\eta_p) > 0$), as reported in Figure 44.

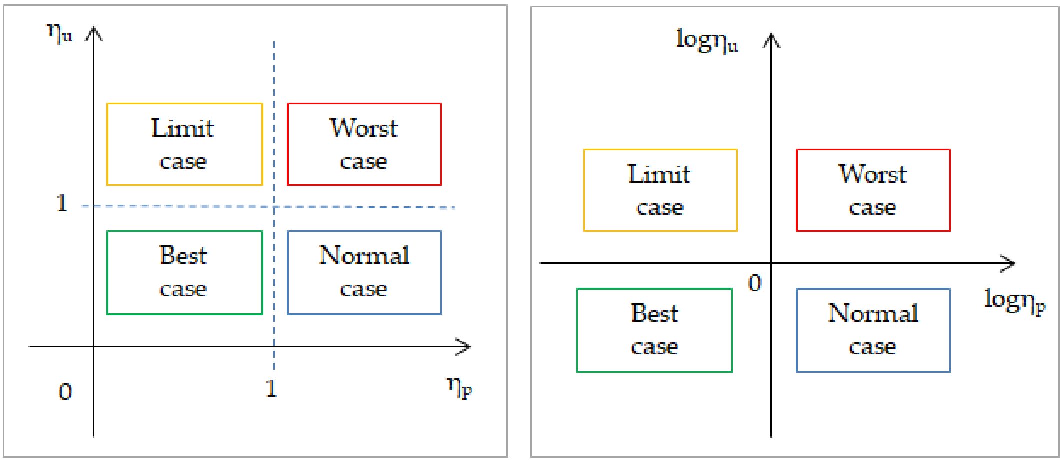


Figure 44. Scatter plot graph of use phase efficiency η_u vs production efficiency η_P (on the left) and the corresponding graph in logarithmic scale on the right.

Case study analysis

Materials

First, the four reusable cups (PP, PLA, PET, glass) have been compared with the four single-use cups (PP, PET, PLA, PE+cardboard) with respect to the seven impact categories (CC, OD, A, POC, E, NREU and WFI). The considered EoL for all plastics cups and for single-use Cardboard+PE cups refers to 100% energy recovery (Vercalsteren et al., 2007), while for reusable glass cups EoL reflects a recycling of 89% of the used materials (Gaines and Mintz, 1994). The use phase refers to the scenario 2 of Figure 42, i.e. offsite washing with 20km of transport roundtrip distance (10km+10km).

Transport distance

The analysis of the offsite industrial washing scenario has been enriched with a focus on transport distance. An upper distance limit, i.e. the maximum number of km $n_{km;max}$ during the use phase to have a positive environmental BEP, for an infinite number of reuses, has been calculated by decomposing B_{Y2} with respect to the washing impact $B_{Y2;washing}$ and the transport impact per cup per km $B_{Y2;km}$ according to:

$$n_{km,max} = \frac{X - B_{Y2,washing}}{B_{Y2,km}} \tag{6.7}$$

Eq. 6.7 (rationale in section A.2 of the Appendix) shows how $n_{km;max}$ does not depend on the production and EoL phase of the reusable cups (since it's a constraint for the slopes). Thus, for all reusable plastic cups (with the same weight) the $n_{km;max}$ is equal. Finally, the area of interest, in terms of the distance, was defined according to the following classification - 1) city (5km), 2) metropolitan area (30km), 3) district (80km), 4) region (200-300km), and 6) country (>400km).

Dispersion Rate

The dispersion rate *d* was also briefly analysed. *d* is defined as the average number of reuses before a reusable cup is dispersed and is substituted with a new one. Dispersed means that the use phase loop, whatever use strategy considered, immediately ends up, and the production of a new cup is considered. For the sake of simplicity, the EoL was considered the same as declared for the "not dispersed".

6.1.3. Results and discussion

All the LCIA results at midpoints for the production, use and EoL phases are reported in Table A11, A12 and A13 in the Appendix section.

Materials analysis

All results for the material analysis in terms of linear trends are reported in the following figures.

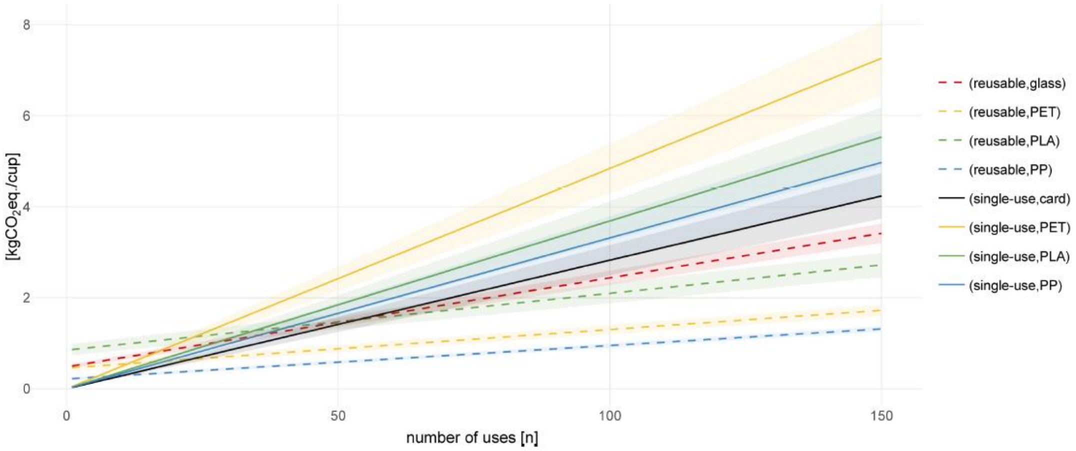


Figure 45. Climate Change (CC) for the offsite washing scenario with a transport distance of 20km during the use phase and energy recovery at EoL for plastic materials and recycling for glass. The shaded areas represent the uncertainty due to the minimum and maximum weights, while the line represent the average ones according to Table 46. Dashed lines refer to the reusable cups while the solid ones refer to the single-use cups.

Figure 45 shows the linear trend (lines) for the CC and the uncertainty due to the differences in the cup weights (shaded area), highlighting how the BEPs lie between 10 and 50 reuses in terms of CC depending on the material and the cupweight. The best single-use cup is the cardboard+PE coat, followed by the PP and PLA ones, while the worst one results to be the PET one. The cardboard+PE, PP, and PLA single-use cups CC impacts are very similar and the average impact (i.e. the solid lines) lie in the uncertainty shaded area. In particular, the PP single-use cup is comparable with both the cardboard+PE and PLA single-use, while the cardboard+PE can be considered better than the PLA one. With respect to the reusable cups, instead, after 50 uses, the best one is the PP cup and the worst the glass cup, even if its production and EoL impact is better than the PLA reusable cups and it is comparable with the PET cups, as shown in Figure 45. The PET (2nd best reusable cup) and the PLA (3rd one) cups lie in-between the PP and the glass cups. The slope differences among dashed lines mainly reflect the weight differences of the reusable cups (see Table 46), as a consequence of the carrying capacity during the transport of the use phase. Although the transport noteworthy affects the use phase, all reusable cups achieve the BEP for the CC impact category for less than 50 uses.

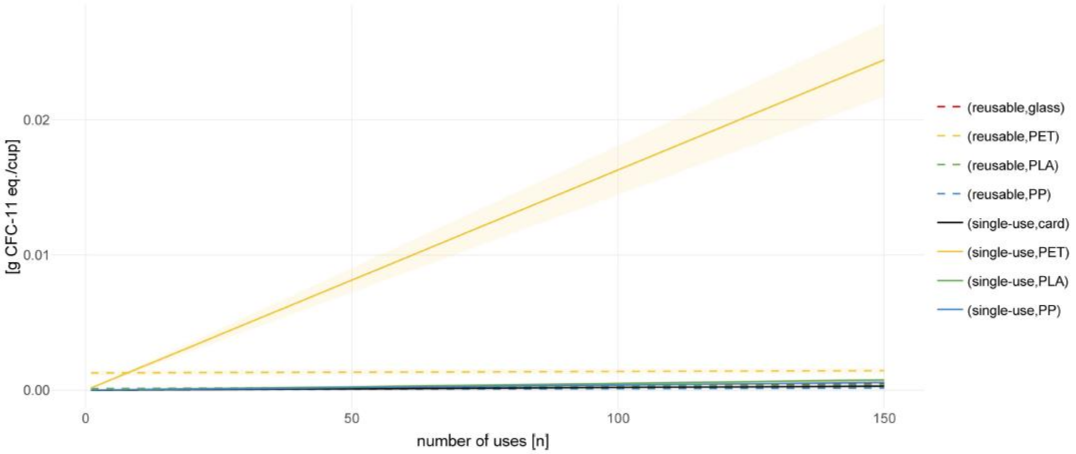


Figure 46. Ozone Depletion (OD) for the offsite washing scenario with a transport distance of 20km during the use phase and energy recovery at EoL for plastic materials and recycling for glass.

Figure 46 shows that only PET cups have a not negligible OD impact. The transport does not affect OD and such a big impact mainly derives from the production phase of the PET granulate (Plastics Europe, 2020). For this impact category, it turned out that the BEP for PET reusable cups is achieved for less than 10 uses.

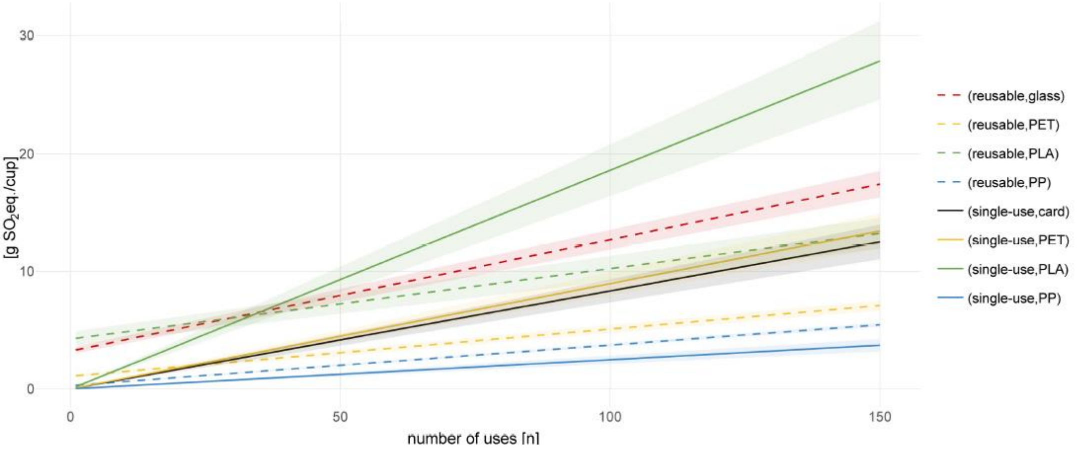


Figure 47. Acidification (A) for the offsite washing scenario with a transport distance of 20km during the use phase and energy recovery at EoL for plastic materials and recycling for glass.

The best solution with respect to the Acidification category (Figure 47) is the single-use PP cup for any number of uses, while the worst solution, for high number of uses, is the single-use PLA cup. An impacts for single-use PET and cardboard+PE cups are comparable, as evidenced by corresponding solid lines within the uncertainty shaded areas. Regarding the reusable cups, the best performance refers to the PP cups, followed by the PET cups, while the glass and PLA reusable cups are the worst ones. The bad performance of glass and PLA reusable cups is due both by a high impact during the production and EoL phase (see corresponding values at n=0) and by their high weight, which affects the use phase and thus the slope of the line. For this impact category, PP and PET reusable cups achieved the BEP for n < 20 with respect to all single-use cup types (avoiding the PP single-use cup), while PLA and glass reusable cups perform better than PLA single-use cup after 40 uses. Finally, PLA reusable cups, in comparison with the cardboard+PE and PET single-use cups, achieve the BEP after a large number of reuses (n > 150).

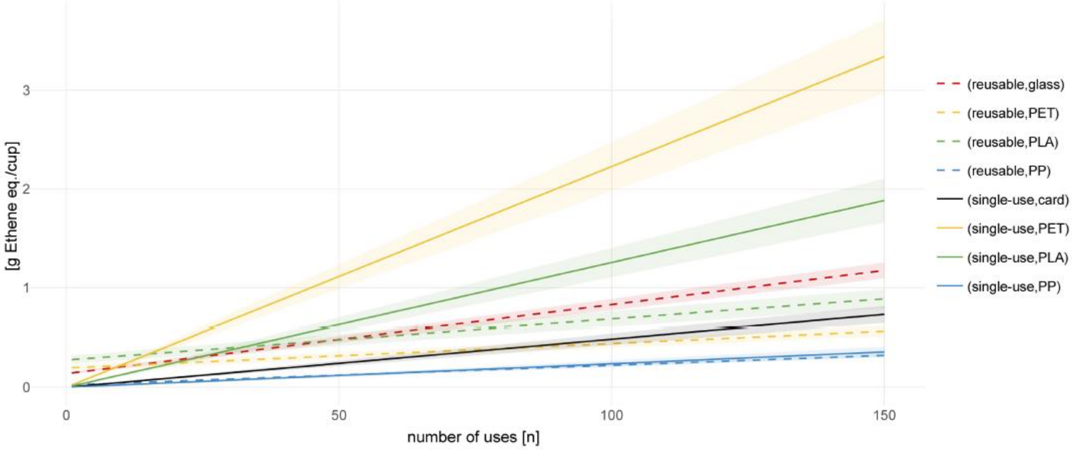


Figure 48. Photochemical ozone creation (POC) for the offsite washing scenario with a transport distance of 20km during the use phase and energy recovery at EoL for plastic materials and recycling for glass.

Figure 48 shows the LCIA results with respect to POC impact category; the best solutions for any n are the single-use and reusable PP cups. The PP reusable cups, in comparison with the PP single-use cups, achieve the BEP after about 50 uses. After 50 uses, the 2nd, 3rd and 4th best solutions for reusable cups are respectively the PET, PLA and glass cups, while for n < 50 the glass reusable cups perform better than the PLA reusable cups and for n < 10 they are even better than PET reusable cups. The PET reusable cup achieves the BEP for n < 100 with respect all single-use cup types (avoiding PP), while PLA and glass cups behave better than PLA and PET single-use cups (for n > 30). Finally, PLA reusable cups reach a BEP with respect to carboard+PE cup only after a very large number of reuses (n > 350).

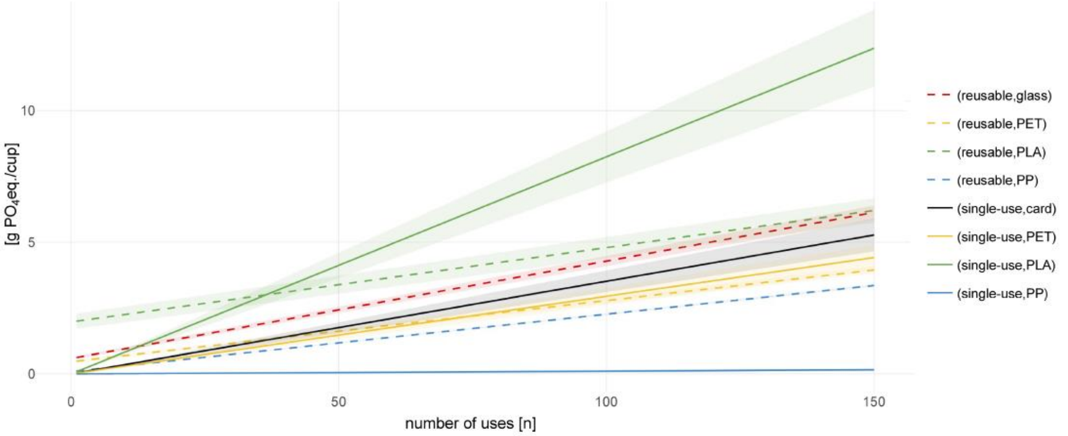


Figure 49. Eutrophication (E) for the offsite washing scenario with a transport distance of 20km during the use phase and energy recovery at EoL for plastic materials and recycling for glass.

In terms of eutrophication (E), Figure 49 points out that single-use PP are always better than reusable cups for any number of reuses. Reusable PP and PET cups, with respect all the others single-use cups, reach a BEP respectively, after less than five uses, and around 60 uses. PLA is very impactful in terms of eutrophication impact category and it is the worst one, even if due to the difference in weight glass reusable cups perform better only for less than 150 reuses.

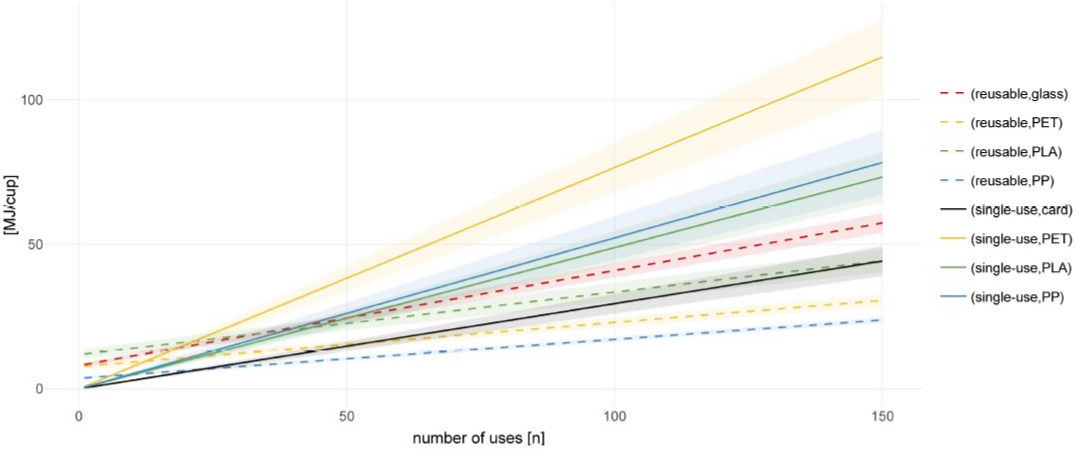


Figure 50. Non-Renewable Energy Use (NREU) for the offsite washing scenario with a transport distance of 20km during the use phase and energy recovery at EoL for plastic materials and recycling for glass.

The behaviour of the NREU impact category - reported in Figure 50 - is similar to that of the CC impact category. Reusable plastic cups reach the BEP for n < 50 versus all types of single-use cups, with the only exception that the cardboard+PE cups perform slightly better than in the CC case.

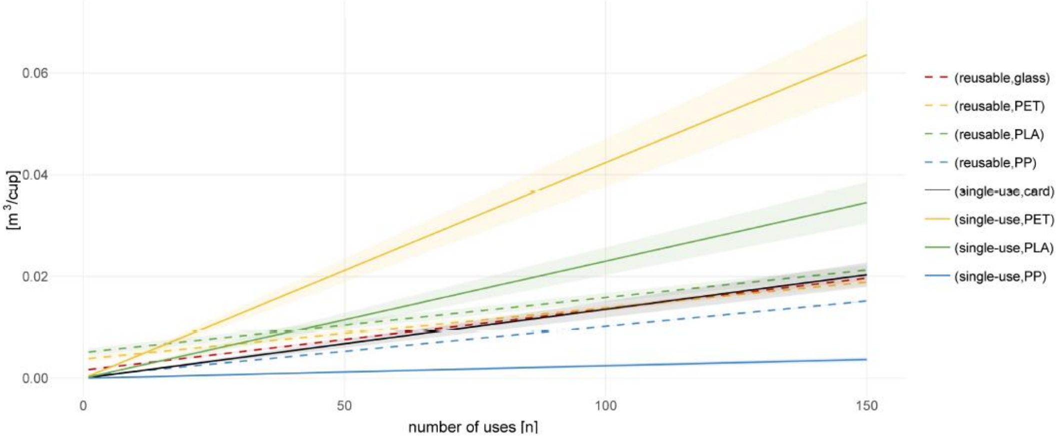


Figure 51. Water scarcity Indicator (WSI) for the offsite washing scenario with a transport distance of 20km during the use phase and energy recovery at EoL for plastic materials and recycling for glass.

Finally, according to Figure 51, the best solution for the WSI is the single-use PP cup which is always better than any other solution. With respect to reusable cups, the best cup material is again the PP, while the worst one is the PLA. All reusable cups achieve a BEP (avoiding the PP single-use cup) for n < 50 vs the PLA and PET single-use solution and for n < 150 vs the cardboard+PE cups.

In conclusion, single-use PP cups are the best solution with respect to OD (almost zero impact), A, POC (for n <100), E, and WSI, while reusable PP cups are the best ones among the other reusable solutions with respect all impact categories. PET and PLA reusable cups are, respectively, the 2nd and the 3rd best choice, among reusable cups except for the OD, E, and WSI impact categories. In fact, PET is the unique material with a not negligible OD impact (i.e. it is the worst material), and, PLA, due to the impact during the production phase, is the worst solution with respect to E and WSI impact categories. Regarding single-use cups, the cardboard+PE cups are the best considering the CC and NREU impact categories, while, for all the other impact categories, the PP single-use cup solution performs better. For all categories, PLA and PET single-use solutions, generally, impact more than PP and cardboard+PE. On the contrary, reusable plastic (PP, PET, PLA) cups reach a BEP for all the impact categories (except for the abovementioned cases against single-use PP cups) after a variable number of reuses, generally lower than 150. Finally, for all the impact categories, because of the high weight, the glass cups are strongly affected by the transport phase, and even if the production and EoL phases, in some cases, is better than reusable plastic cups, the impact for large n is always the worst. Thus, a more detailed analysis of transport distance is presented in the next paragraph.

Table 49 summarize the BEP for the current section.

Number of uses to achieve the break-even point (BEP)								
single use cups	reusable cups	CC	OD	A	POC	E	NREU	WSI
PP	PP	8	9	-29	61	-4	9	-5
	PLA	41	57	-121	-164	-73	39	-61
	PET	18	472	-70	-2631	-21	21	-49
	glass	35	80	-46	-30	-16	42	-17
PLA	PP	7	6	2	2	1	10	3
	PLA	35	35	34	33	36	43	41
	PET	16	324	7	19	8	23	29
	glass	28	31	35	24	13	50	15
PET	PP	5	0	5	1	12	6	1
	PLA	24	1	143	15	1571	22	16
	PET	11	8	22	10	74	13	12
	glass	17	0	-630	9	-78	18	5
Cardboard +PE	PP	10	25	6	8	7	23	9
	PLA	54	667	181	350	284	151	184
	PET	23	1472	25	82	39	54	109
	glass	55	-60	-285	-67	-320	-235	106

Table 49. Summary table of break-even point values related to the analysis of materials (use phase considered: offsite washing).

Use and product efficiency: scatter plot

The material analysis are also reported in the scatter plots (as discussed according to Table 48): Figure 52 shows all results in a unique graph and Figure 53 zooms in results in the range $-0.5 < \eta_u < 0.5$ and $0 < \eta_p < 1.5$. Different colours represents different materials for the reusable cups, while different gradients of the same colour point out the comparison of the same material for the reusable cups with the different materials for single use cups. The size of each point is proportional to the BEP n for $\log(\eta_u) < 0$, while for $\log(\eta_u) > 0$ represents a negative n. The graph straightforwardly shows, for any case, if, and when, the BEP is achieved simultaneously for all analysed midpoints.

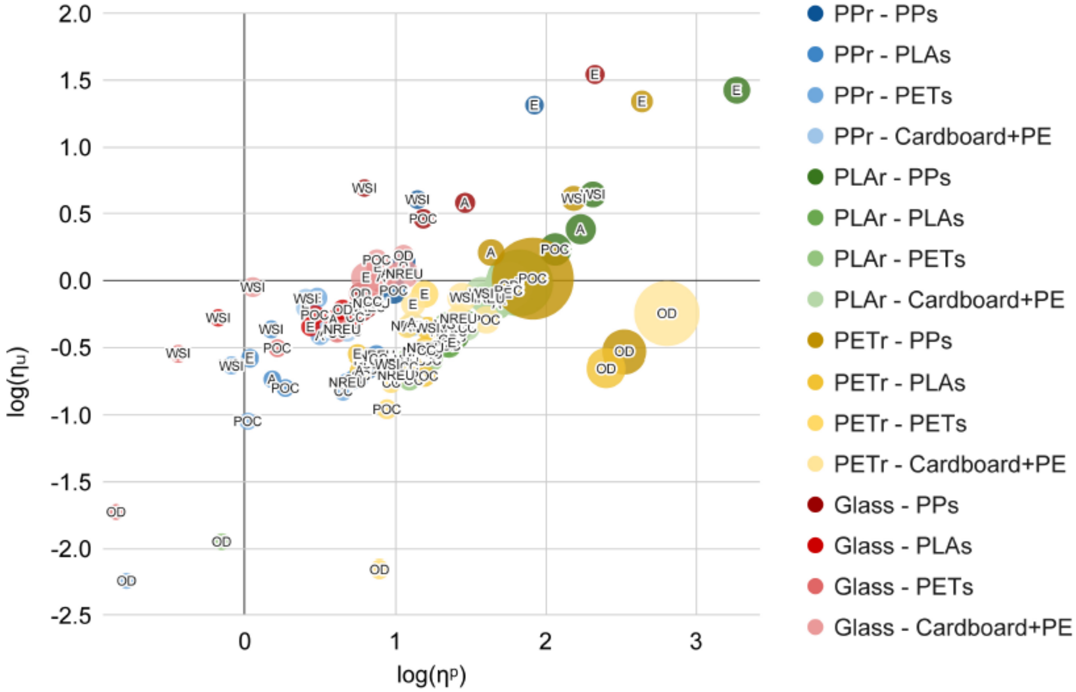


Figure 52. Scatter plot of the use efficiency η_u vs the product efficiency η_p related to the material analysis. LCIA results refer to offsite washing.

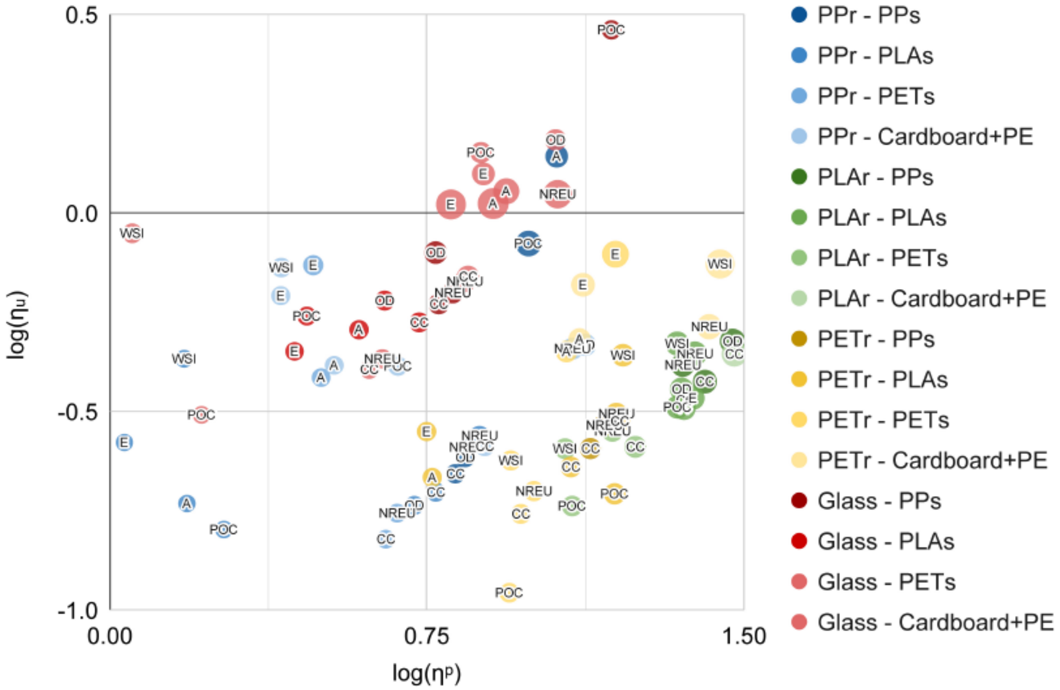


Figure 53. Zooms in results (range $-0.5 < \eta_u < 0.5$ and $0 < \eta_p < 1.5$) of the scatter plot reported in the previous figure.

The reusable glass cups (red series) are the worst performing solution since the majority of the LCIA results lies in the worst case quadrant ($\log(\eta_u)$, $\log(\eta_p) > 0$) and $\log(\eta_u)$ is generally closer to 0 than the other materials. In terms of product efficiency, the PLA is the worst performing plastic material for reusable cups (green series) for almost all impact categories since $\log(\eta_p)$ is generally larger with respect to PP (blue series) and PET (yellow series) reusable cups. Regarding PET reusable cups, the large size of POC and OD points shows that the BEP is achieved only after a large number of reuses. This result is simply explained by Eq. 6.6; indeed, as $\eta_u \rightarrow 1$ (i.e. $B_{x;j} \rightarrow X$), or $\log(\eta_u) \rightarrow 0$, $n \rightarrow \pm\infty$. PP reusable cups are slightly better than PLA and PET reusable cups for the production and EoL phases. With respect to the use efficiency η_u, all three types of reusable plastic cups achieve a BEP, since points lie in the third and fourth quadrant ($\log(\eta_u) < 0$) for all impact categories except for A, POC, E, and WSI with respect to the PP single use cups.

Use phases and transport distance analysis

Since PP reusable cups, from the previous section analysis, perform better than the other reusable cups for almost all impact categories, in this section results and graphs are presented referred mainly to PP reusable cups and the average weights. Figure 54 shows the results for the CC impact category related to the PP reusable cups and the four types of single-use cups with respect to the three use scenarios.

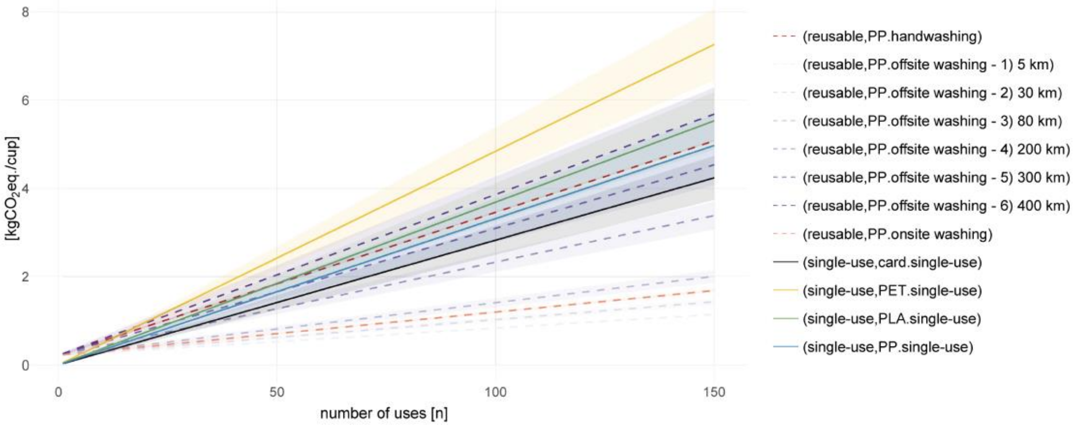


Figure 54. **CC of reusable PP cups for onsite handwashing/washing (dashed lines), and offsite washing (dotted lines) VS single-use (continuous lines).**

The graph highlights how, for the use phase, the best washing scenario is the offsite washing with a distance lower than 50km, then the onsite washing, subsequently the offsite washing with a distance lower than 350km, and, finally, the handwashing scenario. With a transport distance greater than 350km the offsite washing is always the worst scenario. In each scenario of the use phase: handwashing, dishwasher, and industrial dishwasher (for a distance of 10+10 km), the impacts are due, for a percentage higher than 75%, to the electricity consumed. The optimization of the system, achieved at an industrial level, allows to considerably reduce energy consumption and therefore limit impacts.

With respect to the single-use cups, the onsite handwashing scenario never achieves an environmental BEP, in terms of CC, vs the cardboard+PE and PP cups (although the line for onsite handwashing lies on the uncertainty shaded area of the PP cups) while the onsite washing scenario (or the offsite washing with equivalent CC impact) achieves the environmental BEP with a number of reuses lower than 20.

According to the area of interest classification, it emerges that local entities or institutions are necessary to manage the use phase. Indeed, for instance, CC impacts for the reusable plastic cups are lower than single-use cups if and only if distances are lower than 30-50km, thus, if a local entity in each City/Metropolitan Area is set up.

Maximum distance $n_{km;max}$ [km] for the use phase				
Impact category	PP	PLA	PET	cardboard
CC	357	406	556	293
OD	239	332	12217	100
A	-6	423	166	150
POC	33	364	681	113
E	-198	658	101	161
NREU	339	311	539	152
WFI	-528	986	2413	290

Table 50. Maximum distance [km] for the offsite washing scenarios in the use phase $n_{km;max}$, i.e for infinite number of reuse, for plastic reusable cups vs four different single-use cups. The use phase does not depend on the material of the reusable cup.

Table 50 points out how $n_{km;max}$ is negative, with respect to single-use PP cup, for Acidification, Eutrophication and WSI impact categories. The negative numbers represent the case when the environmental BEP is not achieved either for an infinite number of reuses. Although a negative number does not represent a real situation, it is still a useful indicator. Indeed, when a negative number is close to zero (e.g. the case of A for PP cups) it means that with a slight improvement in the washing process for that impact category the environmental BEP can be achieved. Excluding the negative numbers, the minimum value of maximum allowed km occurs for the POC impact category in the case of PP single-use cups (33km). All the other values are greater than 100km, which means that, for an infinite number of reuses, if the distance during the use phase is lower than 100km an environmental BEP is always reached (excluding the impact categories above mentioned). Finally, the same results can be obtained for the other reusable cups simply by multiplying the $n_{km;max}$ in Table 50 by a scaling factor due to the difference in weight between the cups. For instance, for glass cups the scaling factor, according to Table 46, is 0.11 (40/360 = 0.11) because of the glass cup weight (360gr) and the PP cup weight (40gr). Thus, the maximum number of allowed km for the glass reusable cups to achieve an environmental BEP, for all non-negative values in Table 50, is much lower, i.e. less than 15km.

Use phases and transport distance analysis

Finally, the best and the worst performing reusable cups, i.e. PP and glass cups, have been selected in order to analyse the different use phases. Results, in terms of use (η_u) and product efficiency (η_P) are plotted in Figure 55. Figure 56 presents the zoom for the range $-0.5 < \eta_u < 0.5$ and $0 < \eta_P < 1.5$. Colours represent the comparison between a different couple of materials (e.g. reusable PP cups vs PLA single-use cups) while the colour gradients highlight the different use phases for the same couple of materials.

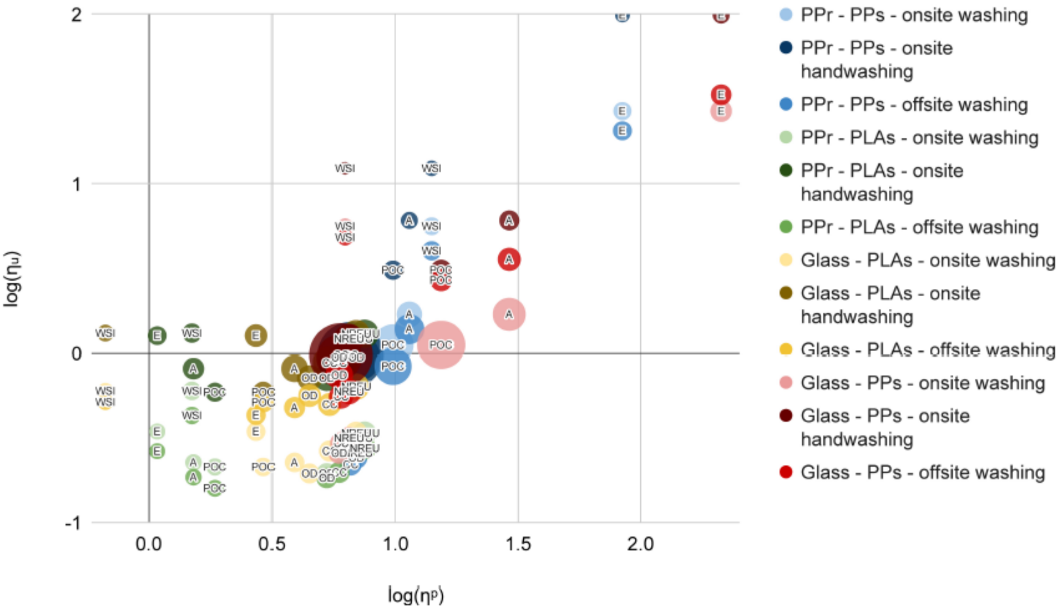


Figure 55. Scatter plot (logarithmic scale) of the use efficiency η_u vs the product efficiency η_p with different use phases.

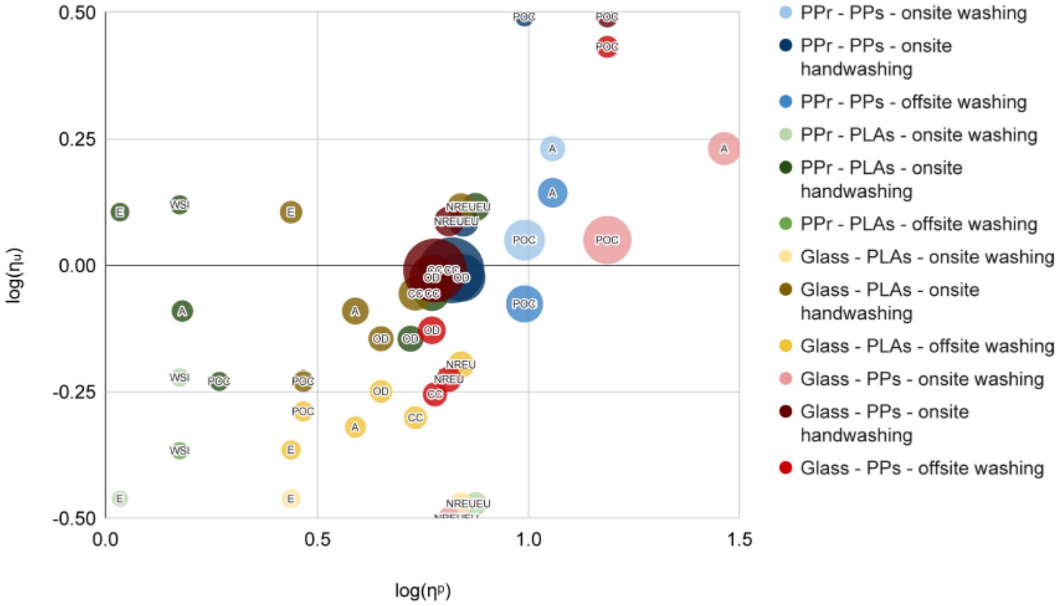


Figure 56. Zoom for $-0.5 < \eta_u < 0.5$ and $0 < \eta_p < 1.5$ of the scatter plot (logarithmic scale) of the use efficiency η_u vs the product efficiency η_p with different use phases.

Handwashing, as previously discussed, is the worst solution for all analyzed impact categories and the BEP in many cases is not reached. On the contrary, offsite washing for PP reusable cups is the best solution and the BEP is achieved with respect to PLA single-use cups for all impact categories. Comparing PP reusable and single-use cups, instead, the BEP is not achieved for A, E, and WSI. Reusable glass cups, again, are the worst-performing solution. The BEP is achieved, in terms of CC, OD, and NREU (vs PP single-use cups) and of CC, OD, A, POC, E, and NREU (vs PLA single-use cups).

Dispersion Rate

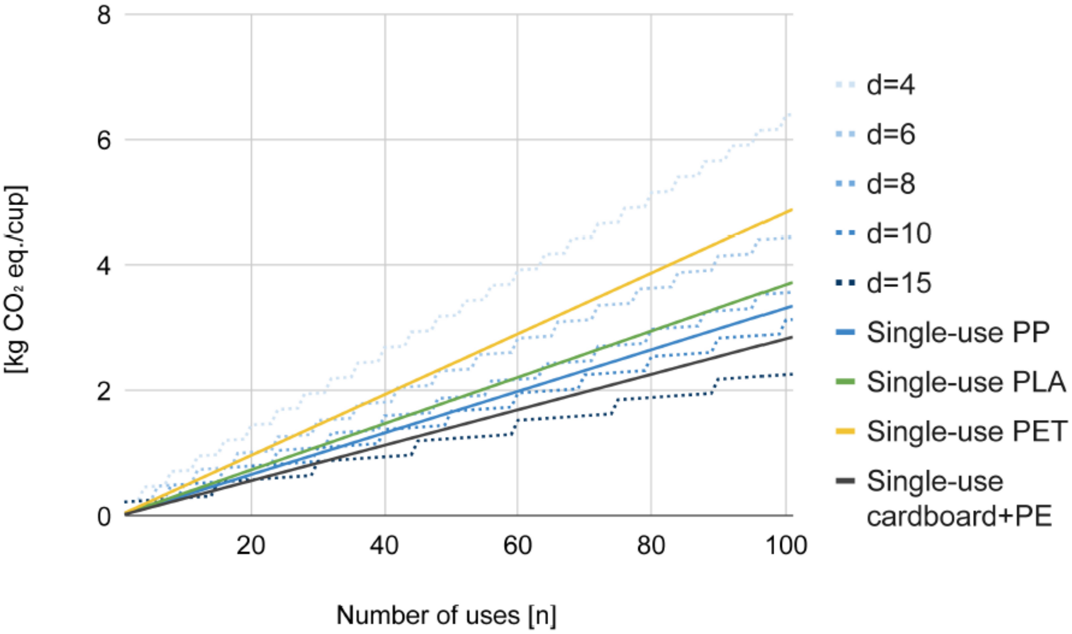


Figure 57. GWP of reusable PP cups for offsite washing (dotted lines) VS single-use (continuous lines) with different dispersion rate.

Figure 57 shows the CC for reusable PP cups (dotted lines) vs single-use cups (continuous lines) with an increasing dispersion rate d. d is the average number of reuses before a reusable cup is dispersed and is substituted with a new one. Thus, after d uses, the production and EoL impacts of a new reusable cup are taken into account; in Figure 57 this effect corresponds to a "jump" in the impact. Previous studies analyzed these scenarios comparing different dispersion rates for reusable cups (Vercalsteren et al., 2007) or for reusable plastic crates (Tua et al., 2019). Figure 57 shows how this is a "false" problem since the dispersion rate can be easily mapped into the environmental BEP n. Thus, for $d < n$ (see the case with $d = 4$) the environmental BEP is never reached, for $d \gg n$ (e.g. $d = 15$) once achieved the BEP the reusable cups are always better than the single-use cups, while for $d \sim n$

every time a reusable cup is dispersed into the environment the next usages of the reusable cup are environmentally worse up to the BEP is reached again (e.g. d = 8)

Comparison of results with literature

In the last decade, the comparison of environmental performance between reusable and disposable cups has been the subject of several studies. Studies often have shown the difficulty of completing an effective and objective comparison. For instance, van der Harst and Potting (2013) compared ten disposable cups, showing that, due to the different methodological choices and differences in legislative rules, it was not feasible a reliable comparison. Vercalsteren et al. (2010), instead, analyzed four types of cups - reusable polycarbonate and single-use polypropylene, PE-coated cardboard, and polylactide cups - in large and small events thanks to a comparative LCA study. To compare reusable versus single-use cups, they introduced the trip rate, i.e. the mean number of uses for a reusable cup. They concluded that none of the cases is always better neither at small nor large events. Garrido and Del Castillo (2007) compared single-use and reusable cups for large events in Spain concluding that the minimum number of uses to have a smaller impact is 10. A similar result was also determined in the present study by referring to the climate change category, in fact for a number of reuses between 10 and 50 times all types of reusable cups show less impacts than single use cups.

Although Garrido and Del Castillo (2007) reported that reusable cups with respect to ozone layer depletion, heavy metals, and carcinogenic compounds, are always worse than single-use due to the impact during the washing phase.

The comparison between reusable and single-use coffee cups - made of different materials - were performed in a work by Almeida et al. (2018). Polypropylene and glass reusable cups, produced by a specific company, were compared with generic PP and bamboo reusable cups and with paper and PLA single-use cups. From this study it emerges that PP and glass are the best materials for cups; in particular reusable cups - made of these materials - are better than disposable alternatives after around 10-20 uses. These results are partially in agreement with what we obtained from our analysis. The main difference is represented by the result of the glass cups in fact in the work of Almeida et al. the cups weight does not affect the impacts of the use phase because the study hypothesizes that the cups are used

and washed in a home context (therefore without the need of any kind of transport). In another work, Potting and van der Harst (2015) compared three disposable cups - polystyrene, biobased and compostable polylactic acid (PLA) and bio-paper - with polystyrene reusable cups (handwashed or dish-washed). Again, no overall preference was possible neither among the different disposable cups nor among the disposable ones and the reusable cups. More precisely, reusable cups with dishwashing (4 uses before washing) are worse than disposable polystyrene cups for four impact categories - terrestrial ecotoxicity, ozone layer depletion, human toxicity, marine aquatic ecotoxicity - out of the eleven considered categories, while, with handwashing, the results are worse for all categories.
In recent years, to facilitate comparison between single use and reusable products, the European Commission reported a thorough "life cycle inventories of single use plastic products and their alternatives" (Paspaldzhiev et al., 2018) for single-use plastics products (e.g. cigarette butts, drinks bottles, cutlery, straws, food containers, drinks cups,...), with suggestions about some non-plastic reusable alternatives. From the report, it emerged that washing impacts are strongly affected by the technology used and by ecodesign criteria but the report does not provide results in terms of the number of usages. The effect on the final impacts of the technology used to model the system in the use phase emerges from the comparison with the recent work by Changwichan and Gheewala (2020); as reported in this study, the impacts generated by handwashing are considerably lower than those obtained when using a dishwasher. Other aspects to keep in mind - when examining similar works - concern the geographical region and the technology used to model the production phase of the cups. In fact, Changwichan and Gheewala (2020) suggest how reusable steel cups show better environmental profile than PP, PET and PLA single use cups, for different impact categories. Thus results from previous works shows that they are all closely linked to the specific situation and the assumptions examined.

Limitations and advantages

Although results obtained from this study also depend on specific assumptions and boundary conditions due to the system itself, the proposed approach may facilitate the phase of interpretation of results in LCA analyses. In particular, the introduction of the environmental BEP n allows to easily analyze close-loop scenarios, by maintaining a simple functional unit (i.e. serving 0.4 liters of draught beverages in one go) instead of more complex ones (e.g. hundreds of uses). Moreover, by studying the environmental impacts in terms of the proposed KPIs, i.e. the environmental BEP n, the use phase efficiency η_u and the product phase efficiency η_p, it is possible to decouple the effects of a variation in the production phase, or in the use phase, of a reusable product. Indeed, a variation on the use phase may affect the achievement, or not, of an environmental BEP for a reusable product, while a variation on the production and EoL phases of the reusable product only affects when the BEP is achieved (i.e. the minimum number of reuses). Thus, depending on the values of η_u and η_p, possible strategies (Table 51) may be easily identified, to improve the efficiency of a reusable product and to achieve an environmental benefit with a reasonable number of reuses.

Cases	**Use efficiency**	**Product efficiency**	**Break-even point**	**Strategy**
Best Case	$0 < \eta_u < 1$	$0 < \eta_p < 1$	$n > 0$	1) Improve the use phase if n » 1
Normal Case	$0 < \eta_u < 1$	$\eta_p > 1$	$n > 0$	1) Improve the use phase if n » 1 2) Improve reusable product production or change material for reusable product
Limit Case	$\eta_u > 1$	$0 < \eta_p < 1$	$n > 0$	1) Improve the use phase to reach a break-even point
Worst Case	$\eta_u > 1$	$\eta_p > 1$	$n > 0$	1) Improve the use phase to reach a break-even point 2) Improve reusable product production or change material for reusable product

Table 51. Strategy to improve the reusable products impact in order to achieve an environmental benefit for reusable products.

On the contrary, a few limitations emerged. First, the environmental BEP assessment allows the simultaneous comparison of different impact categories, since the two KPIs for the use and product efficiency are dimensionless by definition, but the usual midpoint weighting process towards common endpoints still remains a challenge. Second, the results obtained for the use phase are strongly affected by electricity consumption. Indeed, more than 75% of the impact is due to energy consumption. Further investigations are needed to evaluate differences in assumptions for the electricity mix (e.g. 100% renewable energy) or for the soap and detergent composition, such as the detailed study conducted by Tua et al. (2019) on reusable plastic crates. Third, different possible EoL scenarios need an ad-hoc analysis with primary data from specific companies and plants to evaluate uncertainties and the results' accuracy.

6.1.4. Conclusions

The present study introduced a novel methodology for the interpretations of results from comparative LCA analyses in order to evaluate reusable versus single-use products. The methodology lies on three main KPIs: 1) the product phase efficiency (η_P), 2) the use phase efficiency (η_u), and 3) the environmental break-even point (BEP) (n). n represents the minimum number a reusable product has to be used in order to become environmentally better than an equivalent number of uses of a single-use product.

Four single-use cups (PP, PLA, PET, and Cardboard+PE coat) have been compared with four reusable cups (PP, PLA, PET, and glass) with respect to seven midpoint impact categories - Climate Change (CC), Ozone Depletion (OD), Acidification (A), Photochemical Oxidant Creation (POC), Eutrophication (E), Water Scarcity Indicator (WSI) and Non-Renewable Energy Use (NREU) - taking into account three use phase strategies for reusable cups (onsite handwashing, onsite washing and offsite washing).

Considering offsite washing use phase - i.e. transport distance of 20km and industrial washing machines - and energy recovery EoL phase, results highlight that reusable plastic (PP, PET, PLA) cups reach a break-even point for CC and NREU for $n < 150$, with respect to all analyzed single-use cups. On the contrary, in terms of A, E, and WSI, single use PP cups are the best option. Reusable glass cups are worse than any other solutions due to transport during the use phase. Generally, reusable cups impact categories are strongly affected by the distance during the use phase. A limit result has been quantified in terms of the maximum distance (km) allowed during the use phase in order to achieve an environmental break-even point after an infinite number of reuses. With respect to PP single-use cup, the environmental break-even point is never achieved for A, E, and WSI, while for PET, PLA, and cardboard single-use cup the environmental break-even point is attained for all impact categories. Excluding also POC impact category with respect to PP single-use cups, in all the other cases a break-even point is always achieved for a transport distance during the use phase lower than 100km.

Finally, onsite handwashing is the worst solution while onsite washing is an intermediate solution. For instance, in terms of CC, they are comparable with offsite washing with a distance of 350km and 50km, respectively.

By adopting this approach based on the environmental BEP, the product and use efficiency, a standard functional unit, i.e. one single-use, can be used, simplifying comparisons among LCA studies. Such an approach may be particularly suitable for monitoring the performance of an organization in the most recent framework of the Organizational LCA (OLCA) (Martínez-Blanco et al., 2015) but further studies are needed to homogenize results' interpretation according to UNEP (Blanco et al., 2015) guidelines and to the most recent ISO/TS 14072: 2014 (International Organization for Standardization, 2014).

6.2. Case study 7: Environmental implication of a business model based on the rental of formal dresses

6.2.1. Introduction

Apparel consumption has increased dramatically during the last few decades. The current business model, the fast fashion, characterized by mass production, variety, agility and affordability, has been adopted by large international fashion retailers (Bukhari et al., 2018). The amount of clothes bought in the EU per person has increased by 40% in just a few decades, driven by a fall in prices and the increased speed with which fashion is delivered to consumers (European Parliament, 2019). Based on the research published by the Think Tank of the European Parliament, clothing accounts for between 2% and 10% of the environmental impact of EU consumption but this impact is often felt in third countries, as most production takes place abroad (European Parliament, 2019).

The production of raw materials, spinning them into fibers, weaving fabrics and dyeing require enormous amounts of water and chemicals, including pesticides for growing raw materials such as cotton (Ghali et al., 2014). Also, on the consumer use side the environmental footprint due to the water, energy and chemicals used in washing, tumble drying and ironing is heavy (Muthu et al., 2015).

As a very low part of used clothes are collected for reuse or recycling and less than 1% of material used to produce clothing is recycled into new clothing, representing a loss of more than USD 100 billion worth of materials each year (EMF, 2017), the need to address these issues is clear.

However, many actions need to be considered contemporary and circular economy can be regarded as an umbrella concept connecting different goals such as improving resource productivity and value creation, reducing value loss and destruction (Blomsma et al.,2018)

Therefore, to support a systemic change in the fashion industry, a combination of new business models, innovative design, new technologies and materials is envisaged, and to be successfully implemented, circular economy transformation requires the design of innovative business models that can enable multiple value creation mechanisms (Pieroni et al.,2018).

A list of Business Models (BM) that change the usual way to run business in the Fashion sector (Linder and Williander, 2015) could include:

- Rental or Product-as-a-service (Paas): a one-off rental of a garment for a short time period
- Subscription-Rental: a monthly fee paid for access to a range of garments
- Clothing resale: the recovery and resale of a garment by the original retailer or after a rental framework (eg. consignment or peer-to-peer)
- Materials innovation (eg. fibres from regenerative sources / by-products)
- Designing products in a way that would make re-use and recycling easier
- Fibre-to fibre recycling technologies
- Clothing and textiles collection and sorting infrastructure
- Digital enabling tech (e.g. tracking and tracing)

Recognizing the value of utilization more than that of property, a performance driven economy, where the consumer pays for the use of the product, could be successful (Mont, 2002). This is the reason of the analysis of the rental model realized in this paper.

Some of the models mentioned above obviously cannot be considered novelties, such as the rental model. However, when this model leverages on new technologies, sharing platforms and the growing expertise on reverse logistics, could be considered as a disruptive innovation (Christensen et al., 2015) and could represent a key aspect of a product as a service system (PSS) strategy.

Rental-service platforms lend products for a specified term (multiple days to several months, depending on the product category) or on a monthly subscription basis. "The rental-service platform appeals to customers because it enables them to access items they otherwise could not afford." (Jin and Shin, 2020). In addition, those platforms offer many services connected to the choice of the garment, suggestions on the best outfits, multiple accessories coordinated, evaluations from previous customers.

Therefore, rental's main key driver is the ability to offer a dedicated and unprecedented service: the opportunity for the customer to wear garments that previously were too costly. This could be realized both using a traditional store as a base or, preferably, through a digital platform that provides an online solution for the customer (B2C). The hired garment is usually paid one-off for a specific period and then it is sent back (Feng et al.,2020).

The rental model or more in general the PSS is highlighted as an important enabler for improved resource productivity and value creation, as well as for reduced value destruction (Stahel, 2006).
PSS application in industry is often linked to multiple benefits such as reduction of environmental impact, increase in competitiveness and user value (Mont, 2002). Compared to traditional business models around product sales, these are considered to be less resource-intensive because they allow manufacturers to meet the same demand with less products (Tukker, 2015). Besides the environmental benefits, economic and competitive benefits of PSS model range from the opportunity to establish longer and stronger relationships with customers, i.e. increasing customer fidelity, to the chance to open up new business opportunities, empowering strategic positioning (Vezzoli et al., 2018).
The definition of PSS is still not completely univocal and in a recent study we even found 52 different definitions of PSS and associated concepts identified from 47 of the most prominent papers in the PSS field (Haase et al., 2017). In use-oriented PSS, the focus is on providing functionality or access, for example, through leasing, renting or sharing instead of selling products (Gaiardelli et al., 2014). Even if most of the traditional empirical cases in the servitization are connected to business-to-business and manufacturing context, more and more examples come from consumer markets as textiles (Armstrong et al., 2015). Anyway, there is still a lack of methods/tools for experimenting, testing, and implementing the business model concepts (Pieroni et al., 2019).

As previously reported, the environmental impacts related to the world of clothing and fashion are considerable. In literature there are several works that have examined the impacts generated by this sector through the Life Cycle Assessment methodology (Piontek and Müller, 2018). From many of these works it emerges that environmental impacts are strongly conditioned by consumer behavior (Zamani et al., 2017) and by the geographical place, where the production and use phase of the garments takes place (de Saxcé et al., 2014; Chapagain et al., 2006; Kim et al., 2015). As indicated, both the production and use phases play an important role in generating environmental impacts. A significant aspect in determining these impacts is related to the number of uses and washes to which the clothes are subjected during their life cycle, in fact these variables make the impacts associated more on the production phase (Steinberger et al., 1995) or on the use phase (Kim et al., 2015). Few works have still carried out an assessment of the environmental impacts associated with the development of business models based on rental and PSS (Piontek and Müller, 2018). Zamani et al. (2017) have shown how the development of clothing libraries allows to reduce environmental impacts. In fact, the development of collaborative consumption business model, such as the clothes libraries, allows to extend the service life of garments. This study also shows the importance of an efficient logistics service (transportation) in order to avoid rebound effects. To achieve environmental benefits Piontek et al. (2020) highlighted the importance of the number of uses associated with a clothing rental model. The possible benefits of increasing the number of uses per garments should be particularly significant in the case of formal garments.

The aim of this work is to try to verify the impact generated by the rental model, applied to formal garments. The work analyzes the service offered by a small Italian company. The business model is based on the rental of formal (elegant and / or ceremony) dresses for women. This type of clothes plays an important role in the fashion world and often the phase of use of these garments is very limited in time - for various reasons: subjective perception, fashion, etc. In the case examined in this study the rental of clothes takes place for a maximum period of 4 days and the main way to use this service is through the internet. The transport of clothes during the rental period is carried out by the company itself; the possibility of optimizing transport is a relevant aspect because, as indicated, transport can prove to be one of the main problems in making this business model sustainable. The company rents designer clothes at affordable prices, comparable to those of fast fashion. Keeping competitive prices, allows to enter a broader market segment and reach a greater number of hypothetical customers. Since this model based on rental is an alternative to the current model represented by the purchase of garments (fast fashion), the environmental analysis has also been extended to the latter, using it as a reference point for an assessment of the environmental impacts.

6.2.2. Materials and methods

The assessment of the environmental impacts, associated with the previously described business model, has been carried out using the life cycle assessment methodology. The LCA analysis has been conducted following the framework and principles described in the ISO standards 14040 and 14044 (ISO, 2006a; ISO, 2006b). SimaPro 8.2 software was used to model the entire system and for the background data it was used the Ecoinvent 3.3 database.

Goal and scope definition

The goal of this study was to assess the environmental impacts related to the garment rental service. More in detail the analysis takes into consideration a specific category of garments, formal dresses, and compares the rental business model (called rental scenario) with an online purchase model (called baseline scenario). The analysis, from cradle to grave, examined all the impacts related to the entire life of the product system: from the production of the garments, use/reuse phase, up to final disposal.

The chosen functional unit was one average use of a formal (elegant) dress. The term "one use" refers to the use occurring within a 24-hour time period, that could be a specific occasion as a party, a ceremony or similar. What is meant is that the type of clothes considered are not suitable for use that can usually occur in everyday life.

As mentioned, the LCA analysis considered the entire life cycle of the dress starting from the production of the garment, then its distribution to the store, the use phase which consists of clothes packaging, round-trip transport to the customer and washing, up to the final disposal. Figure 58 shows a scheme with the life cycle phases took into account in the rental scenario.

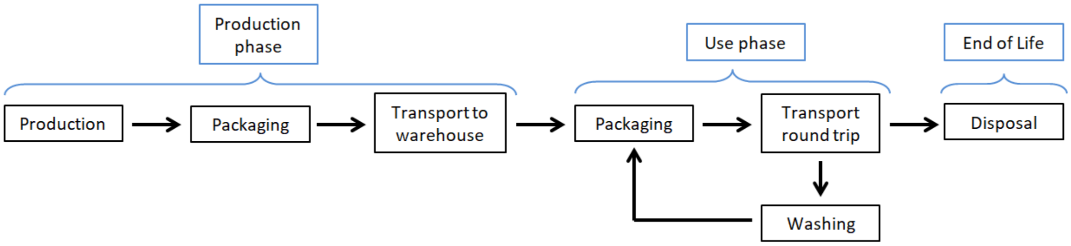


Figure 58. Scheme of the life cycle phases considered during LCA analysis in the rental scenario.

The entire life cycle is also considered during the environmental assessment of the baseline scenario. The analysed scenario is based on the more common model of online purchasing clothes: the dress is produced and subsequently sent to the buyer who uses it and then disposes of it; in this scenario a return path of the product sold before its use has been introduced. Figure 59 shows the phases considered during LCA.

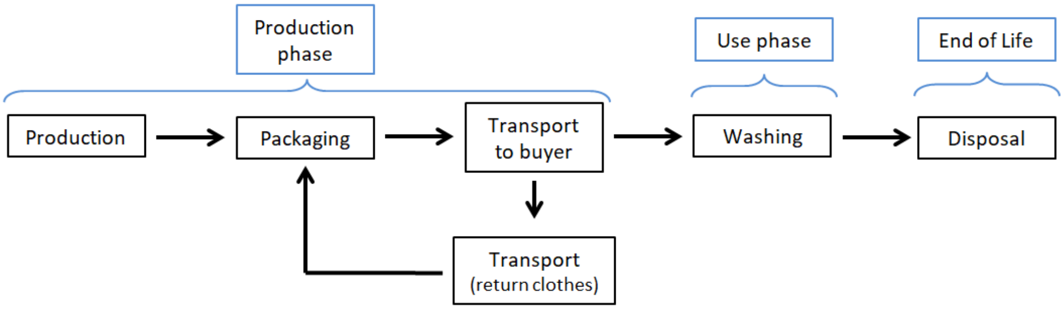


Figure 59. Scheme of the life cycle phases considered during LCA analysis in the baseline scenario.

Inventory analysis

Since in this work the aim was not related to the assessment of the environmental impacts associated with the production of garments, it has been decided to focus more on the use phase part of the clothes' life cycle. For this reason, in all the scenarios considered the production phase of a cloth was not modeled on the software by searching for primary or secondary inventory data, but the impacts relating to it were directly derived from the work of *Sandin et al. (2019)*. The impacts related to the production phase have been adapted to represent a 450 g weight dress made entirely of cotton. As reported in the previous figures, in this phase the packaging of the manufactured garment and the transport were also considered. As regards the transport, in the case of the rental scenario it was assumed as equivalent to the transport that takes place between the manufacturer and the warehouse of the rental company; on the other hand, in the case of the baseline scenario, the same value always represents the transport between producer and buyer.

All the data used to model the system are reported in Table 52;

Phases	Input - Output		Amount	Scenario
Production (1 dress)	Dress 100% cotton		/	rental - baseline
	Packaging		/	rental - baseline
	Transport		/	rental - baseline
Use phase (for a single use)	*Input:*	Cardboard (g)	450	rental
		Tissue paper (g)	40	rental
		Transport roundtrip (kgkm)	36	rental
		Transport (wash) (kgkm)	1.35	rental
		Residential washing	See Table 53	baseline
		Dry cleaning	See Table 53	rental
		Municipal waste collection- packaging (kgkm)	14.7	rental
		Incineration paperboard-packaging (g)	490	rental
	Output:	Electricity-packaging (kWh)	0.2695	rental
		Heat-packaging (MJ)	1.95	rental
End of Life (1 dress)	*Input:*	Municipal waste collection (kgkm)	13.5	rental - baseline
		Incineration paperboard (g)	450	rental - baseline
	Output:	Electricity (kWh)	0.2475	rental - baseline
		Heat (MJ)	1.79	rental - baseline

Table 52. Inventory of the analyzed system

The data to model the use phase for the rental scenario are primary data and have been obtained directly from an Italian company based in Milan; the service they offer and that has been modeled in this study involves women's clothes renting service. More in detail, the user can select the dress of interest online and this is delivered directly to his home for the desired period of time (maximum four days); after use, the dress is returned to the company warehouse to be washed and arranged for subsequent rentals. The garments are send to the users in a cardboard box (450 g) and wrapped in tissue paper (40 g); the phase of packaging disposal was also modeled, assuming that the paper was incinerated with energy and heat recovery (Sandin et al., 2019). The data provided by the company shows an average transport covered by the rental service of 40 km (although the service is extended nationwide, the main request is in the Milan area). In the rental scenario the washing of clothes is commissioned to an external company located near the warehouse; the system was developed considering a transport of 3 km round trip. All transport is assumed to be done by light commercial vehicles.

Concerning the washing step, two different alternatives were modelled: residential and dry cleaning. It has been assumed that in the baseline scenario people wash clothes directly at home, while in the rental scenario the washing phase is entrusted to an external company. To obtain more reliable results, for the baseline scenario, it was decided to directly model the residential washing phase using the input output data reported in the work of *Sandin et al. (2019)*. The data used to model the dry cleaning phase was obtained from the laundry. Table 53 shows the inventory of the two considered washing option (data are reported for a single dress), while Table 54 reports the data related to the production of 1 kg of detergent.

Residential Washing			
Phase	**Input**	**Amount**	Unit
Washing 40 °C	Tap water	2.79	kg
	Detergent (see Table 54)	0.00711	kg
	Electricity	0.101	kWh
	Wastewater treatment	0.00229	m^3
Drying	Electricity	0.057	kWh
Ironing	Electricity	0.081	kWh
Dry cleaning			
Phase	**Input**	**Amount**	Unit
Dry cleaning	Tetrachloroethylene	0.00168	kg
	Electricity	0.2	kWh
Ironing	Electricity	0.081	kWh

Table 53. Inventory for the washing phase; all data refers to a single dress.

Input	**Amount**	Unit
Citric acid	0.0228	kg
Glycerine	0.0285	kg
Polyethylene, low density, granulate	0.0466	kg
Soap	0.0241	kg
Sodium hydroxide	0.0231	kg
Water, deionised	0.7022	kg
Polyethylene, high density, granulate	0.0466	kg
Polypropylene granulate	0.0101	kg
Printed paper	0.00126	kg
Fatty alcohol sulfate	0.1	kg
Ethoxylated alcohol	0.0591	kg
Electricity	0.25	kWh
Output		
Detergent	1	kg

Table 54. Inventory for the production of 1 kg of detergent.

Some clarifications need to be made regarding the washing phase:

- the option that in the baseline scenario clothes are washed in a laundry was not investigated;
- the electrical energy used to model the system refers to the Italian energy mix;
- the energy consumption related to the drying phase has been supposed assuming that only 19% of the clothes need this step (*Sandin et al. 2019*);
- the energy input for ironing was determined as if it took 6 minutes to iron a dress; however, compared to what reported by *Sandin et al*, it was assumed that only 50% of the dresses needs this step.

The end of life stage of the garments was modelled according to Sandin et al. (2019); it is assumed that the clothes are collected by the municipal waste collection service and then incinerated. The heat and electricity recovered as a result of the process have been reported.

Based on the data collected over the years by the Italian company, on average, an item of clothing is used 7.5 times; this average value also takes into account the possibility that a garment will be irreparably damaged during its use (0.18%).

For the baseline scenario it was assumed that a dress is used for a number of times equal to 3 (personal communication based on company interviews), subsequently it is kept in the closet until disposal. The contribution of returned clothes was also included in the basic scenario since nowadays about 12.5% of the total clothing products sold are rejected by the buyer and returned to the seller (Appriss Retail's Report, 2019). To model this product return phase, 12.5% of the packaging and transportation value was added to the base production data.

Life cycle impact assessment

In the life cycle impact assessment phase, the large number of resources and emissions, that form the inputs and outputs of the inventory, are transformed into a handful of environmental impact categories. The considered impact assessment indicators are the IPCC 2013 GWP 100a method, Cumulative Energy Demand (CED) and Water Scarcity indicator (WSI). According to Piontek and Müller (2018) these are the environmental impact categories that appear most frequently in the works that dealing with the themes of LCA in textiles sector and PSS.

More specifically, IPCC 2013 GWP 100a is a metric for estimating the relative global warming potential (GWP) due to atmospheric emission of greenhouse gas (GHG) over a time horizon of 100 years (Houghton et al., 2001). The CED takes into account the gross energy requirement; the results are expressed in MJ and their calculation include both non-renewable and renewable energy carriers, whose intrinsic value is determined by the quantity of energy taken from nature (Frischknecht et al., 2007). For the WSI assessment the method used is based on the publication of Boulay et al. (2011).

Scenario analysis

To deepen the evaluation associated with the two comparative scenarios, the effect of the transport distance for the rental service and the number of uses of a garment during its life was analyzed in more detail. The effect of the two variables was analyzed only against the global warming potential, thus calculating the kg of equivalent CO_2 emitted in the different circumstances.

To assess the effect of the transport distance, between the warehouse and the final client, the model of the rental scenario has been modified by assuming that beyond 100 km of transport the service would be carried out mixing different means of transport: light commercial vehicles, for a distance always equal to 40 km and heavy vehicles (7.5 - 16 ton lorry), for the remaining distance. This assumption is intended to represent an optimization of the logistics service, an optimization that, for economic but also environmental reasons, is increasingly sought after by companies. By applying this form of transport and keeping all other variables of the model constant, the environmental impact was measured on the basis of the distance covered by the service. The baseline scenario was kept unchanged since, as noted above, the impact due to transport between the manufacturing industry and the end customer was assumed to be equal to the distance between the industry and the warehouse of the rental service, distances that have not been changed. Therefore, the impact generated in the baseline scenario is constant and independent of the distance.

Since the number of uses of a dress in the baseline scenario is based on an average value, it is interesting to assess the effect of changing this parameter on the overall environmental impact. Thus the life cycle impact of a dress was estimated in relation to the number of uses of the dress during its life cycle. The model, for the baseline scenario, was made for value of 3, 5, 7 and infinite uses; instead in the case of the rental, it was modeled only for an infinite value of uses and for the number of times the dresses are used (7.5), according to the company information.

6.2.3. Results and discussion

In this section the results obtained from the environmental assessment have been reported and discussed.

At first, the environmental impacts related to the previously identified functional unit (i.e. an average use of a formal dress) were analyzed. The following figures show the comparisons between the environmental impacts of the two different scenarios analyzed: the baseline scenario, that refers to the classical retail and the rental scenario.

Figure 60 shows the kg of CO_2 eq obtained for one average use of a dress in the two compared scenarios. As previously reported, it was assumed that in the baseline scenario during its life cycle a dress is worn for a maximum of 3 times, while in the rental scenario the number of uses of the clothes is extended to 7.5.

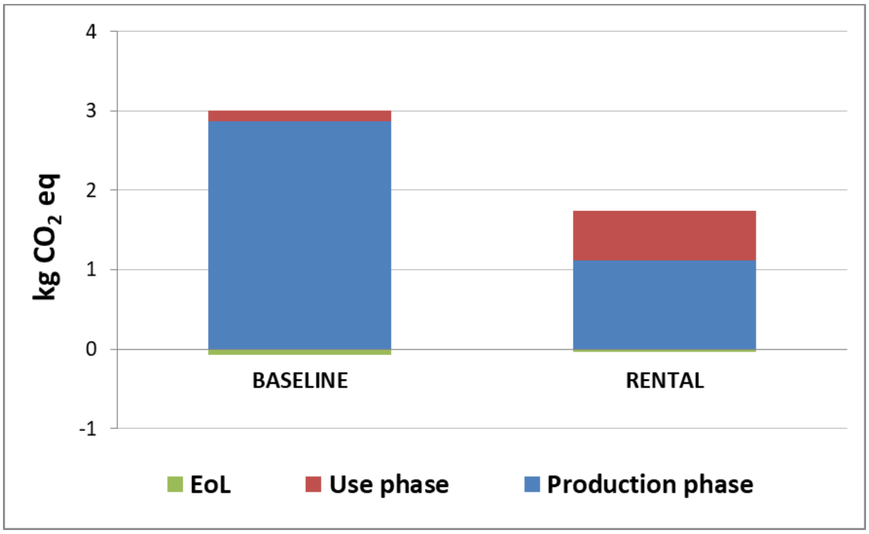


Figure 60. Comparison of the global warming potential results for an average use of a dress in the two scenarios. The results are grouped for life cycle phases.

It is possible to observe how the rental scenario shows better environmental profile than the classic retail (baseline case). In both cases the production phase (which includes production, packaging and distribution) is responsible for the major environmental impacts. This result is due to the limited number of uses to which this class of clothing is subject. Although the impacts due to the use phase are greater in the rental case, the lower overall impact, in the latter case, is due to the sharing of the impacts of the production phase over a greater number of uses.

Table 55 shows the numerical values of the impacts calculated for the two scenarios, split up by individual contributions.

Impact assessment indicator	**Life cycle phase**	**Individual contribution**	**BASELINE SCENARIO**	**RENTAL SCENARIO**
IPCC 2013 GWP 100a (kg CO_2 eq)	Production phase	Production	2.283	0.913
		Confectioning	0.453	0.161
		Distribution	0.136	0.048
	Use phase	Packaging	/	0.334
		Transport	/	0.070
		Transport (wash)	/	0.0026
		Washing	0.131	0.207
	EOL	Disposal	-0.074	-0.02947
Cumulative Energy Demand (MJ)	Production phase	Production	41.717	16.687
		Confectioning	7.347	2.612
		Distribution	2.178	0.774
	Use phase	Packaging	/	8.738
		Transport	/	1.112
		Transport (wash)	/	0.042
		Washing	2.36	3.04
	EOL	Disposal	-1.297	-0.519
Water Scarcity Indicator (m^3)	Production phase	Production	16.056	6.422
		Confectioning	0.042	0.015
		Distribution	0.015	0.005
	Use phase	Packaging	/	7.36x10^{-4}
		Transport	/	1.47x10^{-05}
		Transport (wash)	/	5.51x10^{-06}
		Washing	0.003	0.002
	EOL	Disposal	-4.00x10^{-04}	- 1.6x10$^{-0.4}$

Table 55. Life cycle impact assessment results for one average use of a dress in the two considered scenario (baseline and rental). The results, relative to the production and EOL phases, were normalized by the number of uses during the life cycle of the dress: 3 uses for the baseline scenario and 7.5 uses for the rental scenario.

Analyzing more in detail the results reported in Table 55 - related to the use phase of the rental scenario - emerges that around the 54% of the impact on global warming is caused by the packaging used during the service (cardboard and tissue paper); the 34% of the impact is due to the washing phase while only the

12% is related to the transport. For this impact category, the results relating to the washing phase show that dry cleaning causes about twice the CO_2 emissions compared to a residential wash with water; these emissions are mainly generated by the high energy consumption required by dry cleaning machines.
The impacts related to the end-of-life phase assume negative values in both scenarios; this is because it has been assumed that the clothes are sent to an incineration plant with consequent recovery of heat and electricity, that go to feed the national energy mix.

Figure 61 shows the results attained with the Cumulative Energy Demand method.

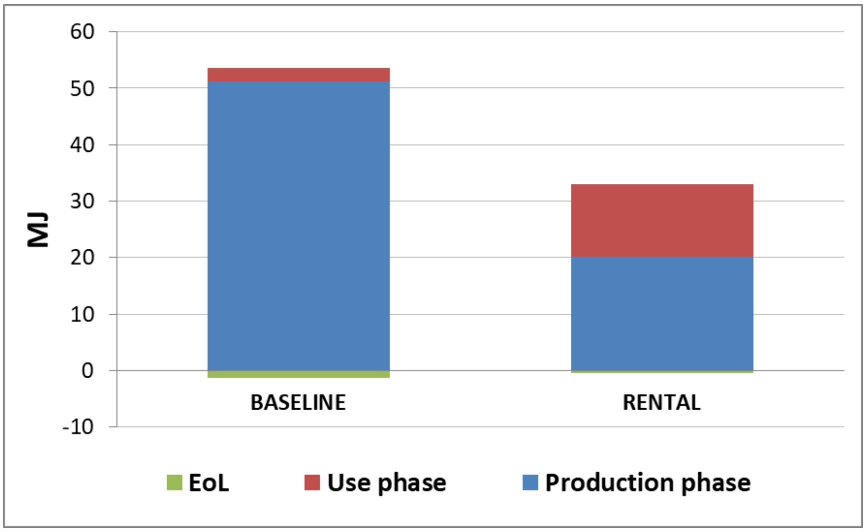


Figure 61. Comparison of the CED results for an average use of a dress in the two scenarios. The results are grouped for life cycle phases.

Also in this case the rental scenario shows minor impacts compared to the base case; the production phase is always responsible for the heaviest impacts.
Similarly to what was observed in the previous case, the impact of the use phase is made up of 67.5% by packaging, 23.5% by washing and only 9% by transport.
Also in this case there is a difference between the basic scenario and the rental as regards the impacts related to washing: residential washing requires 2.36 kWh per single wash instead dry cleaning 3.04 kWh.
Similarly, in this case the impacts related to EoL phase are negative.

The assessment of the water scarcity, sensitive category when it comes to cotton clothes and processes that require a washing phase, is reported in Figure 62.

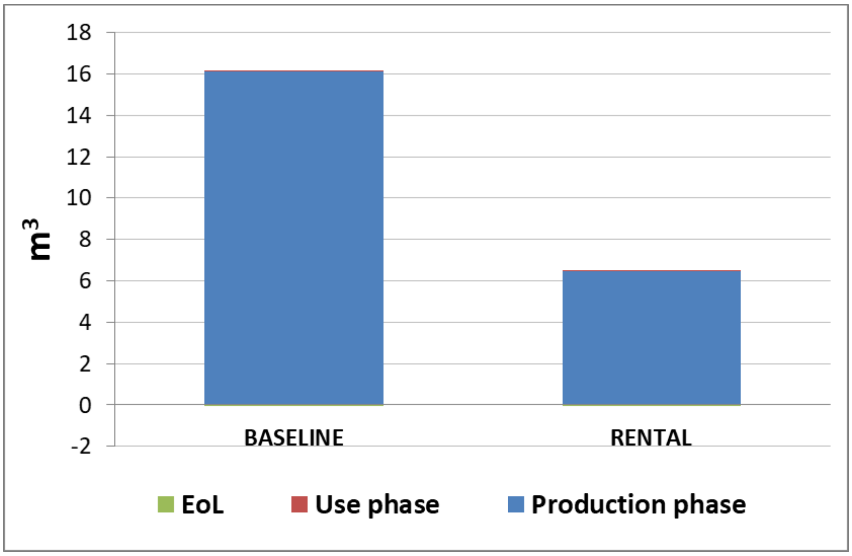


Figure 62. Comparison of the water scarcity indicator results for an average use of a dress in the two scenarios. The results are grouped for life cycle phases.

In this case it can be seen that almost all the environmental impact is attributable to the production phase; in fact, both during the cultivation phase and in the subsequent processing, cotton requires a considerable amount of water (Muthu, 2015). Analyzing the use phase (Table 55) it emerges that there is only a very slight difference in impacts between the two types of washing and that by adding all the contributions regarding the use phase of the rental scenario, the same impact is obtained as for the baseline (0.0027 m^3 and 0.0026 m^3)

Scenario analysis – transport distance

Figure 63 shows the trend of the environmental impact with respect to the distance that the rental service must cover. As a reference point, the kg CO_2 eq released by the baseline scenario are reported (red line); as this scenario is not affected by the effect of distance, the impact is represented by a horizontal line (constant value with increasing km).

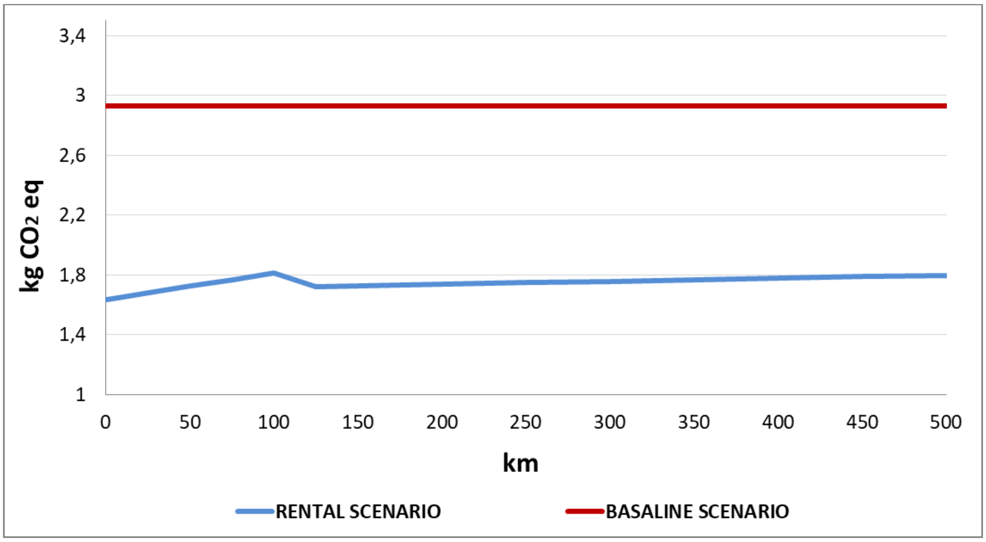


Figure 63. Effect of the transport distance on the overall impacts for the two scenarios.

The impact associated with the rental scenario is directly proportional with the increasing distance, but it can be noted how the slope of the curve is very flattened, especially after the distance equal to 100 km (where the transport was modeled with larger vehicles). Even if the clothes are transported with light commercial vehicles, a breakeven point between the impacts of the two scenarios would be achieved only for distances close to 1000 km. Obviously this result is valid only if the rental service, through the company who takes care of the transport, manages to keep the optimization of the loads constant. From these results it emerges that the impact due to the transport of the garment is really limited and has little effect on the final result. However, this result is strongly conditioned by the number of uses of the dress during its life cycle. In the baseline scenario the overall impact associated with the life cycle of a garment depends on the number of uses it undergoes; in fact if the number of uses increases (in this case it exceeds the value of 3) the impacts related to production and end life decrease. Thus, a situation can be reached in which the straight line of impacts caused by the baseline model approaches the line of the rental scenario or even positions itself below - in this case it will be the classic clothing purchase model that will generate the least environmental impacts.

Scenario analysis – number of uses of dresses during their life cycle

The effect of the number of reuses of a garment on the overall impact was modeled and the results, relative to the global warming potential, were reported in Figure 64. The X axis reports the possible number of uses, while the axis Y shows the corresponding environmental impact. The comparison has been made between the rental scenario (blue lines) and the baseline scenario (orange lines).

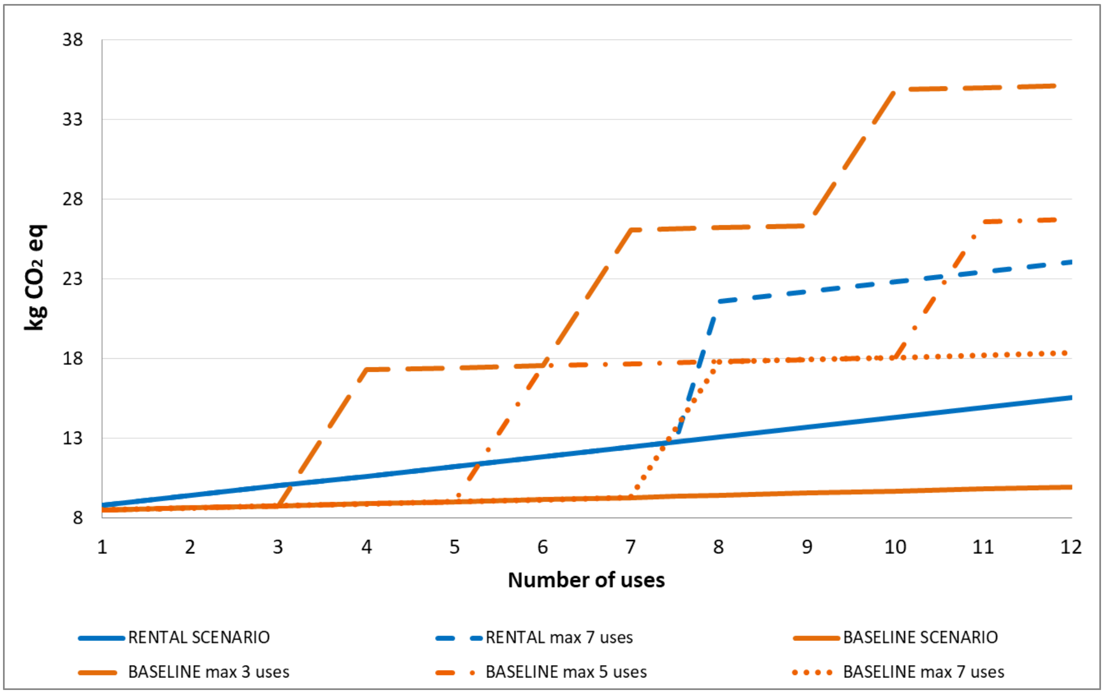


Figure 64. Effect of the number of uses of a dress during its life cycle on the environmental impact.

The two solid lines show the trend of the environmental impact (kg CO_2 eq), in the two scenarios, using a single dress for a number of uses > 12. It is immediately evident that the environmental impact associated with the rental service is greater than in the classic baseline case. From the first use it can be observed how the impact of the rental scenario is slightly higher than in the basic scenario; with the increase in the number of uses it can be observed that the line for the baseline scenario shows a lower slope than that generated by the rental model; this result are due to the greater impact linked to the use phase of the rental model, already observed previously (Table 55). However, when the modeling is made more realistic - assuming a precise and limited number of uses - a clear change in the trend of the impact is observed. In fact, the baseline scenario modelled assuming only a maximum of three uses of a dress during its lifespan, leads to a considerable increase in the environmental impact.

The difference between the two scenarios narrows as the number of uses of the single dress, in the baseline case, increases; when this value reaches 7 uses (dotted line), the environmental burdens associated with the baseline scenario were found to be better than those of the rental scenario. It should be noted that in the rental scenario the average use of each garment for a number of times equal to 7.5 is a reliable and real value. On the other hand, in the classic case of the purchase of a dress, the number of real uses can be very limited for various reasons (fashion, preferences, needs, social conditioning, etc.) and it is difficult to reach the same number of uses as the rental scenario.

Some clarifications must be made regarding the study and the results:

- the modeling of the two scenarios regarding the production phase is simple and is not based on primary data; the same impacts have been attributed to the two scenarios, but it should be noted that the company offering the rental service reserves the right to use clothes that have been manufactured trying to limit the environmental impacts and with a sustainable supply chain. This characteristic should favor the rental scenario from an environmental point of view;
- in the modeling of the return of clothes in the baseline scenario, a very sensitive aspect has been left out: in fact, often the returned clothes are directly disposed of without re-entering the market; this aspect for lack of objective justifications has not been modeled in the system;
- for a better evaluation of the differences between the two possible washing systems, an in-depth study is required; in fact, it would be appropriate to compare the two washing methods by expanding the number of impact categories considered, since some of these could be more affected by the use of tetrachloroethylene. There are other washing technologies that have been gaining ground in recent years (supercritical CO_2, professional wet cleaning…) and that could prove to be environmentally advantageous over tetrachloroethylene;
- in both scenarios the modeling of a possible second or more life of the clothes (resold, given away, given in charity ...) was omitted, as it would have complicated the system; it should be emphasized that some dresses, used in the rental scenario, once the period of use is over, return to the

manufacturer so that he can dispose and recover the fabrics present in them;
- the quality aspect of the dresses themselves has been deliberately omitted as it is linked to subjective perceptions.

6.2.4. Conclusions

The previous results show that the approach based on the clothing rental scenario is effectively able to extend the life of the product. This success makes it possible to limit environmental impacts since often the clothes purchased are used for a limited number of times. In fact, from the results of all three impact categories considered emerge how the rental scenario allow to limit the environmental impacts. While the impacts related to the use phase (packaging, transport ...) show a moderate growth, the possibility of extending the number of uses of the clothes, connected to the PSS model, allows to reduce the heavy impacts related to the production phase. This analysis showed that during the use phase, packaging plays a particularly influential role in generating environmental impacts. In fact, for the Global Warming and Cumulative Energy Demand categories, the packaging is responsible respectively for 54% and 67% of the impacts generated by the use phase of the clothes. Trying to limit the use of packaging or being able to reuse it could further improve the impact generated by clothing rental.

Conversely, transport does not cause such high impacts. This result derives from a modeling that assumes that transport is always optimized: in terms of load and type of vehicle used

The impacts caused by dry cleaning are approximately double those generated by a residential wash; impacts caused mainly by the high energy consumption of the dry-cleaning machinery. The possibility of changing the type of washing used with a more environmentally sustainable solutions could be of further benefit.

The idea put forward by the company to create an area dedicated to washing clothes inside the warehouse, without resorting to external companies, should be examined by further environmental and economic analyses. In fact, it should be noted that the environmental impacts - linked to the round-trip transport phase to the laundry - are very limited and that the purchase and use of an internal washing system could increase both environmental impacts and costs.

The economic issue is primary when it comes to business models and that is why as a future perspective it would be very useful to carry out an economic analysis relating to the life cycle of the rental model; since this business model can be considered appropriate only if, from an economic point of view, an effective profit is obtained from the rental of the clothes.

Finally, it is right to specify that the analysis addressed in this study refers to a specific and very restricted context. The results obtained are difficult to translate to different business models, for example where the rental takes place for everyday clothes. However, the overall result of the analysis could incentivize a niche market, such as that of fashion, to explore new business models with a view to greater environmental sustainability.

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Appendix to chapter 6

A.1 Environmental break-even point

The Environmental break-even point is calculated as:

$$n_j = \frac{A_Y + C_Y}{X - B_{Yj}} = \frac{Y_0}{X - B_{Yj}} \tag{1}$$

where n_j is properly the environmental BEP for the reusable product, considering the reuse loop scenario j. n_j represents the minimum no. of reuses necessary to balance the impact of the reusable product with respect to the same no. of single-use product usages.

Equation 1 can be simply proofed by declaring X_n, i.e. the impact of n_j single-use plastic products, as

$$X_n = n_j X = n_j(A_X + B_X + C_X) \tag{2}$$

and $Y_{n;j}$, the impact of a reusable product after n_j reuses for the use scenario j according to

$$Y_{n;j} = A_Y + n_j B_{Yj} + C_Y \tag{3}$$

Then, by balancing the impact of n uses for both the single-use (Eq. 2) and the reusable product (Eq. 3)

$$X_n = Y_{nj} \Rightarrow n_j X = A_Y + n_j B_{Yj} + C_Y \tag{4}$$

equation 1 is proofed.

A.2 Maximum distance

The upper distance limit, i.e. the maximum number of km $n_{km;max}$ for infinite uses during the use phase to have a positive environmental BEP, can be calculated by decomposing B_{Y2} with respect to the washing impact $B_{Y2;washing}$ and the transport impact per cup and per km $B_{Y2;km}$ according to:

$$B_{Y2} = B_{Y2;washing} + B_{Y2;transport} = B_{Y2;washing} + n_{km} B_{Y2;km} \tag{5}$$

where $B_{Y2;washing}$ and $B_{Y2;transport}$ are the washing impact per unit and the transport impact per unit for a distance of n_{km}, and $B_{Y2;km}$ is the transport impact per unit per km. Thus, by imposing the constraint on the slopes, i.e. parallel straight lines,

$$\eta_u = \frac{B_{Y2}}{X} = \frac{B_{Y2;washing} + n_{km;max} B_{Y2;km}}{X} = 1 \tag{6}$$

the maximum number of allowed km $n_{km;max}$ is:

$$n_{km;max} = \frac{X - B_{Y2;washing}}{B_{Y2;km}} \tag{7}$$

Table A7. Inventory data for the production phases of the cups grouped for material used. All the data refer to the weight of 1 kg of cups. (*) Inventory data from Vink et al. (2007).

Sub-phase process		For 1 kg of PP cup	For 1 kg of PLA cup	For 1 kg of PET cup	For 1 kg of Glass cup	For 1 kg of Cardboard +PE cup
Cradle to gate	PP resin (g)	1010	-	-	Packaging white glass = 1 kg	-
	PLA pellets	-	*			-
	PET bottle grade (g)	-	-	1010		-
	LDPE (g)	-	-	-		54.27
	Bleached board (g)	-	-	-		1031
Transport of resin	Transport, freight lorry 16-32 ton (tkm)	0.101	0.101	0.101		0.108
Cup production	PP/PET resin / PLA Pellets (g)	1010	1010	1010		-
	Electricity (kWh)	1.41	0.93	1.9		1.3
	Thermoforming (for single-use) / Injection moulding (for reusable)	1010	1010	1010		-
	Paper Waste (g)	-	-	-		84.5
Printing	Printing ink (g)	0.032	0.032	0.032	0.13	0.13
	VOC (mg)	-	-	-	0.019	0.019
Packaging	LDPE (g)	33.6	17.16	33.6	50.4	50.4
	Cardboard (g)	224	256.4	224	335.6	335.6
	Electricity (kWh)	0.018	0.018	0.018	0.018	0.018
Transport from production site to city of use	Transport, freight lorry 16-32 ton (tkm)	1	1	1	1	1

Table A8. Inventory data for the use phase of the reusable cups; all data refer to 1 single reusable cup. The transport value refers to the transport of 1 kg of cups.

Inventory data for the use phase	Offsite washing	Onsite washing	Onsite handwashing
Tap Water (kg)	0.23	0.14	0.5
Soap (g)	0.13	0.7	0.5
Electricity (kWh)	0.01	0.014	0.061
Wastewater (m^3)	0.00023	0.00014	0.0005
Transport for the offsite washing of 1kg of cups (tkm)	0.02	-	-
Carboxymethyl cellulose (g)	0.07	-	-
Fatty alcohol sulfate (g)	-	0.035	-
Polycarboxylates (g)	-	0.035	-
Sodium phosphate (g)	-	0.035	-
Sodium perborate (g)	-	0.105	-
Alkylbenzene sulfonate (g)	-	-	0.0675
Sodium hydroxide (g)	-	-	0.01985
Decarbonized water (g)	-	-	0.365

Table A9. Inventory data for the end of life phases of the cups grouped for material used. All data refer to the weight of 1 kg of cups.

Sub-phase process	Inventory data	For 1 kg of PP cup	For 1 kg of PLA cup	For 1 kg of PET cup	For 1 kg of Glass cup	For 1 kg of Cardboard +PE cup
Transport to location of EoL	Municipal waste collection (tkm)	0.015	0.015	0.015	0.015	0.015
EOL packaging	Municipal solid waste (g)	33.6	17.16	33.6	50.4	50.4
	Paper waste treatment (g)	224	256.4	224	335.6	335.6
Incineration	Oil (MJ)	0.169	0.169	0.169	-	0.169
	Gas (MJ)	0.289	0.289	0.289	-	0.289
	Electricity (kWh)	0.085	0.085	0.085	-	0.085
	Residue to landfill (kg)	0.0009	0.0009	0.0009	-	0.118
	Emissions to air	See Table A 6	See Table A 6	See Table A 6	-	See Table A 6
	Energy OUTPUT (kWh)	2.235	1.017	1.117	-	0.782
Recycling	Natural gas (m^3)	-	-	-	$3.3x10^{-06}$	-
	Diesel (kg)	-	-	-	0.0016	-
	Liquefied	-	-	-	$6.26x10^{-06}$	-

	petroleum gas (kg)					
	Electricity (kWh)	-	-	-	0.085	-
	Glass OUTPUT (kg)	-	-	-	0.89	-

Table A10. Emission to air, produced during the incineration process.

Emission to air	1 kg of PP	1 kg of PLA	1 kg of PET	1 kg of Cardboard+PE
CO_2 (kg)	3.08	1.81	2.27	1.45
NOx (kg)	4.24x10^{-04}	4.24x10^{-04}	4.24x10^{-04}	4.24x10^{-04}
SO_2 (kg)	2.70x10^{-05}	2.70x10^{-05}	2.70x10^{-05}	2.70x10^{-05}
PM (kg)	1.20x10^{-05}	1.20x10^{-05}	1.20x10^{-05}	1.20x10^{-05}
CO (kg)	5.00x10^{-06}	5.00x10^{-06}	5.00x10^{-06}	5.00x10^{-06}
As (kg)	3.29x10^{-09}	-	3.29x10^{-09}	3.29x10^{-09}
Cd (kg)	2.13x10^{-07}	-	2.13x10^{-07}	2.13x10^{-07}
Cr (kg)	1.30x10^{-06}	-	1.30x10^{-06}	2.63x10^{-07}
Pb (kg)	5.44x10^{-06}	-	5.44x10^{-06}	7.55x10^{-07}
Ni (kg)	5.03x10^{-07}	-	5.03x10^{-07}	1.69x10^{-07}
Hg (kg)	7.23x10^{-09}	-	7.23x10^{-09}	1.98x10^{-08}
Dioxins (kg)	1.80x10^{-13}	1.80x10^{-13}	1.80x10^{-13}	1.80x10^{-13}

Table A11. LCIA results for the production and EoL phase for reusable cups.

Impact category		A_y				C_{y1} (energy recovery)			C_{y2} (recycling)
Acronym	**Unit of measure**	**PP**	**PLA**	**PET**	**Glass**	**PP**	**PLA**	**PET**	**Glass**
CC	kg CO_2 eq./cup	0.137	0.608	0.331	0.480	0.081	0.240	0.124	-0.281
OD	g CFC-11 eq./cup	3.14x10^{-05}	1.23 x10^{-04}	1.28 x10^{-03}	6.32x10^{-05}	-4.8x10^{-06}	-8.7x10^{-06}	-3.9x10^{-06}	-4.1x10^{-05}
A	g SO_2 eq./cup	0.481	4.599	1.239	3.224	-0.197	-0.353	-0.161	-2.501
POC	g Ethene eq./cup	0.033	0.295	0.205	0.138	-0.010	-0.018	-0.008	-0.101
E	g PO_4 eq./cup	0.225	2.236	0.580	0.584	-0.136	-0.261	-0.116	-0.358
NREU	MJ/cup	4.521	13.432	8.450	8.043	-0.862	-1.602	-0.739	-4.665
WFI	m^3/cup	5.70x10^{-04}	5.60x10^{-03}	4.01x10^{-03}	1.59x10^{-03}	-2.30x10^{-04}	-5.40x10^{-04}	-2.40x10^{-04}	-1.44x10^{-03}

Table A12. LCIA results for the production and EoL phase for single-use cups.

Impact category		A$_X$				C$_{X1}$ (energy recovery)			
Acronym	**Unit of measure**	**PP**	**PLA**	**PET**	**Cardboard**	**PP**	**PLA**	**PET**	**Cardboard**
CC	kg CO$_2$ eq/cup	0.019	0.025	0.033	0.019	0.014	0.012	0.016	0.010
OD	g CFC-11 eq./cup	4.68x10^{-06}	5.49x10^{-06}	1.63x10^{-04}	2.31x10^{-06}	-8.4x10^{-07}	-4.2E^{-07}	-5x10^{-07}	-3.1x10^{-07}
A	g SO$_2$ eq./cup	0.059	0.203	0.110	0.096	-0.035	-0.017	-0.021	-0.013
POC	g Ethene eq./cup	0.004	0.013	0.023	0.006	-0.002	-0.001	-0.001	-0.001
E	g PO$_4$ eq./cup	0.025	0.095	0.044	0.045	-0.024	-0.013	-0.015	-0.010
NREU	MJ/cup	0.673	0.566	0.860	0.353	-0.151	-0.078	-0.095	-0.058
WFI	m^3/cup	6.40x10^{-05}	2.56x10^{-04}	4.55x10^{-04}	1.59x10^{-04}	-3.90x10^{-05}	-2.60x10^{-05}	-3.10x10^{-05}	-2.30x10^{-05}

Table A13. LCIA results per unit (B$_{Y;1}$, B$_{Y;3}$ and B$_{Y;2;washing}$) and per gram and per km (B$_{Y;2;km}$) adopted for the use phase for reusable cups.

Acronym	Unit of measure	B$_{Y;1}$ (Onsite washing)	B$_{Y;3}$ (Onsite handwashing)	B$_{Y;2;washing}$ (Offsite washing)	Unit of measure	B$_{Y;2;km}$ (Transport)
CC	kg CO$_2$ eq./cup	0.010	0.032	0.006	kg CO$_2$ eq./g/km	1.9x10^{-06}
OD	g CFC-11 eq./cup	1.0x10^{-06}	3.6x10^{-06}	7.0x10^{-07}	g CFC-11 eq./ g/km	3.3x10^{-10}
A	g SO$_2$ eq./cup	0.042	0.151	0.027	g SO$_2$ eq./g/km	9.4x10^{-06}
POC	g Ethene eq./cup	0.003	0.007	0.001	g Ethene eq./g/km	8.0x10^{-07}
E	g PO$_4$ eq./cup	0.029	0.105	0.020	g PO$_4$ eq./g/km	2.4x10^{-06}
NREU	MJ/cup	0.165	0.637	0.110	MJ/g/km	3.04x10^{-05}
WFI	m^3/cup	1.38x10^{-04}	3.03x10^{-04}	9.62x10^{-05}	m^3/g/km	3.4x10^{-09}

Chapter 7: Conclusions

The goal of this thesis was to carry out an objective assessment of the environmental impacts generated by the implementation of processes that aim to make anthropic activity more sustainable. The need to limit the environmental impacts linked to human activities and therefore set up a more sustainable development is an increasingly pivotal and structural topic of contemporary society; many actions, implemented by governments, organizations, individuals and community, have been and will be guided by this need. The intrinsic strategy in the concept of circular economy - which the European Union has taken as a paradigm to guide development in the coming years - should allow the creation of new social and territorial value, with the simultaneous prevention of negative environmental externalities.

The benefits introduced by a circular approach should, above all, allow greater efficiency of the resources management and a simultaneous reduction in waste; these goals can be achieved through the numerous processes attributable to the concept of circular economy (recycling, reuse, sharing model, etc.). Unfortunately, the only goodwill in having an ambitious and moral goal is not sufficient to obtain really positive results; hence the need to make an evaluation as objective as possible of the actions undertaken.

To achieve this goal in this study the methodology of Life Cycle Assessment was used, which also in this case, proved to be very effective for the objective set.

The topics examined touched upon disparate topics: water treatment, energy, materials and business models supported by the circular economy. These different topics - united by the common aim of making human impact on the planet more sustainable - have a more or less explicit connection with the concepts introduced by the circular economic approach.

The first topic studied in this work was related to the wastewater treatment. Water is one of the most important resources for human life, the maintenance of its quality and availability are among the most urgent global emergencies to be addressed in the next decade precisely because of anthropogenic activities. The LCA analysis was applied to evaluate specific wastewater treatments, which are necessary to restore the quality of this resource, and make wastewater reusable, thus closing the cycle of use by humans without waste. The environmental effects of some Advanced Oxidation Processes were examined. These processes aim at the degradation of pollutants present in the water, so that the treated water can be safely re-used. In fact, these pollutants can have negative effects on both human health and ecosystems. At the same time, the treatments for the removal of pollutants are not excluded from generating environmental impacts themselves, first of all the impacts due to the large energy consumption they often require. The LCA analysis has been applied with the goal of identifying the main hotspots linked to these treatments to precisely identify which phases or substances of the processes need improvement.

In a first study the degradation of a pollutant by means of different catalyst - based on zinc oxide, doped with rare earth elements - has been evaluated at laboratory level. Through the combination of experimental design and LCA it was possible to identify the best catalyst among the various tested (the zinc oxide catalyst doped with 1% of cerium). The results also allowed to determine the most favourable conditions of process (catalyst concentration around 800 mg/L) to obtain a degradation of the pollutant and at the same time to limit the environmental impacts generated by the process itself.

In a second study an LCA analysis was carried out at the pilot plant level. The objective of this analysis was to obtain a greater understanding of which variables are associated with the main environmental impacts during the scale up of an Advanced Oxidation Process. In this case, the photo Fenton reaction was used to degrade the pollutants. Therefore, the system needed iron-based catalysts and sunlight for their activation. The entire LCA analysis was conducted by examining a specific pilot plant for the process studied. Photo- Fenton processes are normally carried out at acidic pH (therefore with the need to modify the water pH), we wanted to analyse and compare the impacts in these conditions with the impacts of the same process carried out at near neutral pH and with the addition of complexing agents in solution. In detail, humic substance, obtained from oil mill wastes, was used as a complexing agent. Although a lower impact is observed in performing the processes at near neutral pH (since the addition of chemicals is avoided), this improvement is overwhelmed by the lower efficiency of the process itself. This loss of efficiency becomes particularly stringent in the case of fixing quantities of water to be treated daily: the process at acidic pH, given the greater effectiveness, is able to satisfy the demands, which does not occur in operating conditions at higher pH. In this case, to achieve the goal, the only solution is to expand the size of the plant with a marked increase in the impacts related to it. At the same time it is necessary to specify how the use of processes that use only solar energy (such as solar photo Fenton) seems to be a very promising way for wastewater treatment; just as the possibility of producing complexing substances directly from organic waste proved to be very interesting as a future research perspective.

The chapter, that deals with waste-water treatments, ends just with the analysis of photo-Fenton process, at laboratory level, with catalysts synthesized using waste materials. In this work, the LCA was applied to identify the hotspots of use the Fe_3O_4/HA as heterogeneous photo-Fenton catalyst. The addition of humic substances - that allow to work a near neutral pH - proved to improve the operational effectiveness of the catalyst without significant environmental impacts. The environmental burdens of all the conditions that affect the photo-Fenton process were also considered (type and concentration of oxidant, pH and concentration of the catalyst). In conclusion, working at milder conditions (circumneutral pH) would effectively limit environmental impacts, but the benefits deriving from these settings can only be perceived if the process has a high degradative efficiency. In fact, as in the previous study, the "environmental" efficiency of the process is inversely proportional to the impacts generated by the structure of the plant or, in this case, by the energy consumed to irradiate the system.

The topic to which the following two case studies refer can be traced back to energy. In fact, both the studies dealt with refer to materials and technologies used to make the production and consumption of energy more sustainable.

In a first study the environmental impacts of the production process of porous carbon materials have been taken into consideration. This kind of materials can be used as carbon capture and storage technologies – essential point in the decarbonisation process – or more generally in gas purification. In detail the studied materials are particles of microporous carbon prepared by pyrolysis of hyper cross-linked cyclodextrins. These particles show good adsorption of CO_2 even at high temperature, that is an interesting feature. The LCA analysis conducted during the study of these materials made it possible to identify the hotspots of the synthesis process: the use of DMSO and acetone as solvents. After having identified these hotspots, modifications were proposed to the synthesis process and to the organic wastes: replace DMSO with water and add a recovery step by distillation of the acetone. In conclusion these variations allowed to obtain the same material, but with a considerable reduction in environmental impacts and therefore LCA has proved to be a useful tool to support, already in the early stages, the development of a process. In fact, the parallel evaluation of the efficiency-effectiveness of the process and of the environmental impacts associated with it allows to achieve a valid optimization of the system.

The second case study of the chapter assessed the environmental burdens of a hydrogen compression system. Hydrogen is considered one of the solutions to achieve a sustainable alternative to the use of fossil fuels, but the technologies necessary for its development require careful evaluation. The compression phase often causes high energy consumption which leads to an increase in environmental impacts and a decrease in the overall energy balance. The use of metal hydride compressors seems to be a viable and secure alternative for the compression phase. According to the environmental analysis, this is true only under specific conditions (have a heat source that can be reused i.e. low-grade steam) and for a large-scale application it is necessary that the research relating to the type of alloys used in the process allows to achieve more satisfactory results than the current ones.

The last two case studies have analysed the environmental burdens of some business models that can be considered characteristic of the circular economy paradigm.

In the first work, the LCA analysis was applied to compare the environmental impacts generated by using of disposable vs reusable cups (cups that find their use in restaurants, pubs and catering services). The results from the LCA analysis have been used to assess the environmental break-even point of deposit-back systems for cups by identifying the minimum number of uses a reusable cup needs in order to be considered preferable than a single-use cup. Four single-use cups (PP, PLA, PET, and Cardboard+PE coat) have been compared with four reusable cups (PP, PLA, PET and glass) taking into account three use phase strategies for reusable cups. Considering offsite washing use phase - i.e. transport distance of 20km and industrial washing machines - and energy recovery EoL phase, results highlight that reusable plastic (PP, PET, PLA) cups reach a break-even point for CC and NREU for n < 150, with respect to all analyzed single-use cups. On the contrary, in terms of A, E, and WSI, single use PP cups are the best option. Reusable glass cups are worse than any other solutions due to transport during the use phase. Generally, reusable cups impact categories are strongly affected by the distance during the use phase. In general the results show the conditions (maximum km of transport and type of washing) under which it is possible to reach a break-even point and for which not, allowing to identify possible strategies to improve the efficiency of the reusable product in order to obtain an environmental benefit.

The last case study examined the environmental performance of a business model based on the garment rental service. The analysis has taken into consideration a specific category of garments: formal dresses and compares the rental business model with an online purchase model. The results show that it is possible to limit the environmental impacts associated with the fashion world and the solution must be sought in extending the life of the product in terms of the number of uses. In fact from the results of the impact categories considered emerge how the rental scenario allows to limit the environmental impacts, when compared with the classic clothing purchase model; in this scenario the clothes are used for a very limited number of times during their life cycle and the impacts related to the production remain very high, given the scarce use of these clothes.

The wide range of studies examined made it possible to establish how effectively the LCA methodology demonstrates an added value in determining environmental impacts with the aim of a more sustainable development. It allows to identify the most promising strategies to further reduce impacts in future development and it should be used more in order to have a greater awareness of the actions taken.

The application of this methodology from the earliest stages of laboratory research is interesting and useful; it allows to obtain a large number of information on the system studied and at this point there are still several opportunities for environmental improvement, as it is often quite simple to make changes to the system. However it should be noted that the information obtained at this level is affected by a low reliability in the description of the real future process: results and conclusions based exclusively on laboratory data do not necessarily match the results and conclusions obtained when a more complete and detailed LCA is performed at a higher level of development. For this reason, at the laboratory level LCA is only suggested as a screening tool and categorical conclusions are to be avoided.

A feature to keep in mind when examining the results of an LCA analysis is that these are case specific and in the absence of an analysis of different scenarios they have little predictive ability. These results cannot therefore be used freely to support hypotheses of other case studies, perhaps conducted in different geographical regions or with technologies that differ from the original ones. To support these statements, it is enough to give the example of energy consumption: the production of energy and the impacts associated with it change considerably from country to country, based on the use of fossil, nuclear or renewable resources; these differences, combined with the burdens of energy consumption (often one of the major causes responsible for the overall impact of a process), mean that the results are valid only if applied in the same geographical context.

As regards the actual ability of the LCA in evaluating circular processes, it should be noted that such an analysis is not easy to set up, because, in order to obtain reliable results, the analysed system must be expanded. This expansion obviously requires a considerable amount of input-output data (often difficult to obtain) and a large amount of assumptions - to simplify the analysed system - all aspects that undermine the real truthfulness of the results obtained. For these reason this methodology should be considered useful in assessing the environmental impacts of a process and the results obtained can be put beside a parallel assessment of the circularity of a system (e.g. Material Circularity Indicator), without however leaving the final judgment solely to the LCA analysis.

As a general perspective for the future, two aspects can be identified that would be worth considering more carefully. These aspects are intended to make the LCA methodology more reliable and easier to access, not only for experienced professionals.

The first is related with the growing need of data inside the available databases; given the ever growing interest in issues related to environmental sustainability, there has been an increase in LCA studies with a consequent increase in the topics analysed; such diffusion of the methodology would require the presence in the databases of processes, materials and substances currently not present or modelled with obsolete data. In fact, the lack of precise data to model the inventories can involve the risk of numerous assumptions, with partial loss of the reliability of the results.

It would also be interesting to explore the possibility of carrying out simplified LCA analyses, in order to have a preliminary confirmation of the environmental impacts. This information can be used during the development of technologies and products, but also during any decision-making process related to environmental aspects. Obviously, the creation of a simplified LCA can be solved and supported by the presence of a greater number and quality of data within the databases, which allow to describe and model many more processes and systems than the current ones.

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