

# POLITECNICO DI MILANO

School of Industrial and Information Engineering

Master of Science in Management Engineering – Energy and Environmental Management



## WATER MANAGEMENT FROM A CIRCULAR ECONOMY PERSPECTIVE: INDUSTRIAL SYMBIOSIS CASE STUDIES

Supervisor: Prof. Davide Chiaroni

Co-supervisor: Niccolò Musu

Author:

Axel Kimoslav Stari Marchant

897620

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*To people in Chile. Without justice, dignity, and equal opportunities, there will never be peace. Keep fighting for what is right.*

## Executive Summary

Even though Industrial Symbioses (IS) have been around several decades, there is still a limited amount of analyses with respect to the operation and practices of these systems, especially regarding their water networks. Of the over 20 studied cases, only 6 of them had the necessary information about the operating water network.

Circular water practices like water reuse and recycling in IS are deeply analysed in this work. Moreover, this research gathers qualitative and quantitative information about the water network of several IS cases. The objective is to assess the circularity of the IS systems, based on a qualitative and quantitative comparison between the different IS cases analysed.

This work presents a model to perform a qualitative analysis of water reuse and recycling practices in IS. Later, the model is applied to six case studies, analysing the circular water practices of different IS around the world. In addition, the work presents a quantitative description of the water network operation of several IS cases, by means of eco-efficiency indicators. Then the circularity of the water network of IS cases is described both qualitatively and quantitatively

The qualitative analysis is performed to six IS cases to compare the circularity of their water networks. As a result, the case of UPM showed to be entirely linear, with a model of water extraction, usage, and disposal. On the opposite, the case of HHG proposes a more efficient circular model, where all 9 waterflows are reused directly without any treatment in between.

Wastewater treatment plants absorb the misalignment in the circularity of water networks. These facilities provide an alignment between the produced and desired effluents of the primary and secondary users, respectively. This allows to make the circular connection in the water network of IS systems.

The quantitative description allowed to compare the efficiency in the circularity of additional IS cases. In some cases, the implementation of IS achieved a water saved from natural bodies in the range of thousands of megalitres per year. Additionally, in some cases it allowed to save energy in the order of tens of thousands of GJ per year.

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**Keywords:** Industrial symbiosis; circular economy; water reuse; water recycling; industrial wastewater treatment; industrial eco-efficiency

## Executive Summary in Italian

Anche se le simbiosi industriali (SI) sono in pratica da diversi decenni, sono disponibili ancora quantità limitate di analisi riguardanti le attività e le tecniche adottate in questi sistemi, in particolare per quanto riguarda le reti idriche dei sistemi stessi. Degli oltre 20 casi studiati, solo 6 hanno reso disponibili le informazioni necessarie sulla propria rete idrica.

In questo rapporto sono approfondite le pratiche di economia circolare riferite all'acqua come il riuso e il riciclo della risorsa nella SI sono approfondite. Inoltre, sono raccolte informazioni di tipo qualitativo e quantitativo sulla rete idrica di diversi casi di SI. L'obiettivo finale è valutare la circolarità delle diverse reti idriche, sulla base di un confronto qualitativo e quantitativo tra i diversi casi di SI analizzati.

Questo rapporto presenta un modello per attuare un'analisi qualitativa delle pratiche di riuso e riciclo dell'acqua nella SI. Successivamente, il modello viene applicato a sei casi studio, analizzando le pratiche di circolarità applicate ai flussi di acqua relative a diverse SI nel mondo. Inoltre, è presentata una descrizione quantitativa del funzionamento della rete idrica di numerosi casi di SI, mediante indicatori di ecoefficienza. La "circolarità" della rete idrica dei casi di SI è quindi descritta sia qualitativamente che quantitativamente.

L'analisi qualitativa viene eseguita su sei casi SI e viene eseguita al fine di confrontare la circolarità delle loro reti idriche. Il caso di UPM Kymi SI si è rivelato completamente lineare, applicando un modello di estrazione, utilizzo e smaltimento dell'acqua. Al contrario, il caso di HHG propone un modello circolare più efficiente, in cui i nove flussi di acqua vengono riusati direttamente da un attore secondario senza alcun trattamento intermedio.

Gli impianti di trattamento delle acque reflue assorbono disallineamento della circolarità delle reti idriche. Queste strutture forniscono un allineamento tra la qualità degli effluenti in output dagli utenti primari e quella richiesta dagli utenti secondari. Ciò consente di effettuare la pratica di economia circolare nella rete idrica dei sistemi di SI.

La descrizione quantitativa ha infine permesso di analizzare e confrontare l'efficienza nella circolarità di ulteriori casi di SI. In alcuni l'implementazione della SI rispetto a uno scenario non-SI ha consentito un risparmio idrico per quanto riguarda l'acqua estratta da falda nell'ordine di miliardi di litri all'anno. In altri invece l'implementazione di SI rispetto allo scenario non-SI ha permesso di risparmiare energia da circa decine di migliaia di GJ all'anno.

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**Keywords:** Simbiosi industriale; economia circolare; riuso dell'acqua; riciclo dell'acqua; trattamento delle acque reflue industriali; eco - efficienza industriale





# 1. Introduction

The concept of circular economy (CE) has gained notorious momentum, especially in the last decade. However, until now there is no clear consensus on the concept definition. In fact, Kirchherr, Reike and Hekkert (2017) developed an article analysing 114 different definitions of CE, all of them highlighting different ideas and emphasising in different concepts. Nevertheless, they were able to find common patterns in their study, which allows to form a better structured idea about how the concept can be defined.

As a general definition, CE refers to a systemic approach to the economic system regarding a broad range of applications at different levels. It refers to a change in the way the society approaches the production of goods. Moreover, it is a strategy aiming to reduce both the raw material consumption and waste generation, by closing economic and ecological loops of resource flows (Haas *et al.*, 2015). The main idea is to shift the current approach for production from a linear perspective to a closed – or circular – system.

According to Kirchherr, Reike and Hekkert (2017) CE is based on two building blocks, namely systems theory and Industrial Ecology. Systems theory is an interdisciplinary theory about the development of complex systems in nature, society, and science. It is a framework to analyse any group of interconnected elements working together to produce some result. Since CE is composed by several actors interconnected in the economic system at different levels, these actors are subjected to systems theory.

On the other hand, Industrial Ecology aims to minimize inefficiencies and waste generation in industrial systems, by imitating natural ecosystems. In fact, the concept of CE is reached from an analogy of the human society with the nature and all living things. In fact, in the natural world there is no landfill nor waste, but rather only materials flowing. Moreover, one species waste is another's' food, the energy is provided by the sun, and at the end of life the nutrients come back to the soil (Pakarinen *et al.*, 2010; Gong and Whelton, 2019).

The traditional – linear – approach to the production of goods focused on generating as much supply as possible. This was done in a linear fashion, from the extraction or acquisition of raw material, the production of goods, the consumption and final disposal. From a system perspective, this was done by introducing an unlimited amount of resources to the economic system of production, and then generating an unlimited amount of waste. This is commonly known as the take-make-dispose strategy.

On the contrary, CE limits the throughput flow to a level that nature tolerates, and mimics ecosystem cycles in economic cycles by respecting their natural reproduction rates (Korhonen, Honkasalo and Seppälä, 2018). Moreover, in order to shift to an ideal circular approach, the transition must be through a reduction of flows of materials, energy, and resources.

Subsequently, by using limited amount of resources there will be a limited amount of waste generation, to finally reach a perfectly closed system.

As a consequence, concepts like reuse, recycling, remanufacturing, eco-design, zero wastes, sustainable consumption, closed-loop supply chain, energy efficiency, industrial symbiosis, cleaner production, and similar, are all part of the broader family of CE principles. Accordingly, the concept of circular water management arises.

## 1.1. Circular Water Management

Circular water management are the characteristics, ideas, principles, and approaches of CE applied to water resources. It is in fact the relation between CE and sustainable water management. It focuses on the interface between the natural water system and managed systems, and how CE can be used to improve the interactions between them.

Just like materials, water resources are traditionally used in a linear fashion. In fact, the take-make-dispose strategy of materials is analogously applied to water resources as the take-use-discharge strategy. First, water is sourced or withdrawn from natural water bodies, namely streams, rivers, lakes, reservoirs, oceans, and groundwater aquifers as well as collected directly from rainwater. Then, water is used by different categories of users, namely industrial, municipal, or agricultural applications. Finally, water is returned to the basin after usage, either directly or after a treatment process (Antea Group, Arup and Ellen MacArthur Foundation, 2018).

On the contrary, according to Antea Group, Arup, and Ellen MacArthur Foundation (2018) the circular water management focuses on two cyclical systems, namely the nature managed and the human managed circles, which forms the “water butterfly”. Figure 1 shows the simplified version of the model, representing a single basin.

On one hand, nature managed system refers to the natural water cycle acting to re-optimize, reuse, and replenish water. The re-optimizing cycle refers to the specific supply of water that nature needs to maintain the ecosystem biodiversity. The reuse cycle refers to the natural treatment of water due to its movement from higher to lower elevations and interactions with flora and fauna. The replenish cycle refers to the ultimate return of water to the environment through evapotranspiration, infiltration, and surface waterflows.

On the other hand, human managed systems refer to the impact of human actions affecting the natural water cycle. This can be caused by the extraction of water from natural water bodies above its replenishment rate, accelerating water loss due to inefficient irrigation and distribution methods, polluting water and limiting its utility for other users, among others. All of them usually cause economic and environmental losses.

The final aim of circular water management is to align both nature and human managed systems. This is achieved by sustainable practices such as avoiding or reducing the use of water, reusing and recycling used water, and replenishing efficiently and effectively the water used, by returning it the basin (Antea Group, Arup and Ellen MacArthur Foundation, 2018).

Moreover, for the purposes of this work it is of paramount importance to understand the differences between these concepts, specially between reuse and recycling practices. In fact, water recycling is commonly used in literature as a synonym of both water reuse and water reclamation. However, for the purposes of this work they will be clearly distinguished.

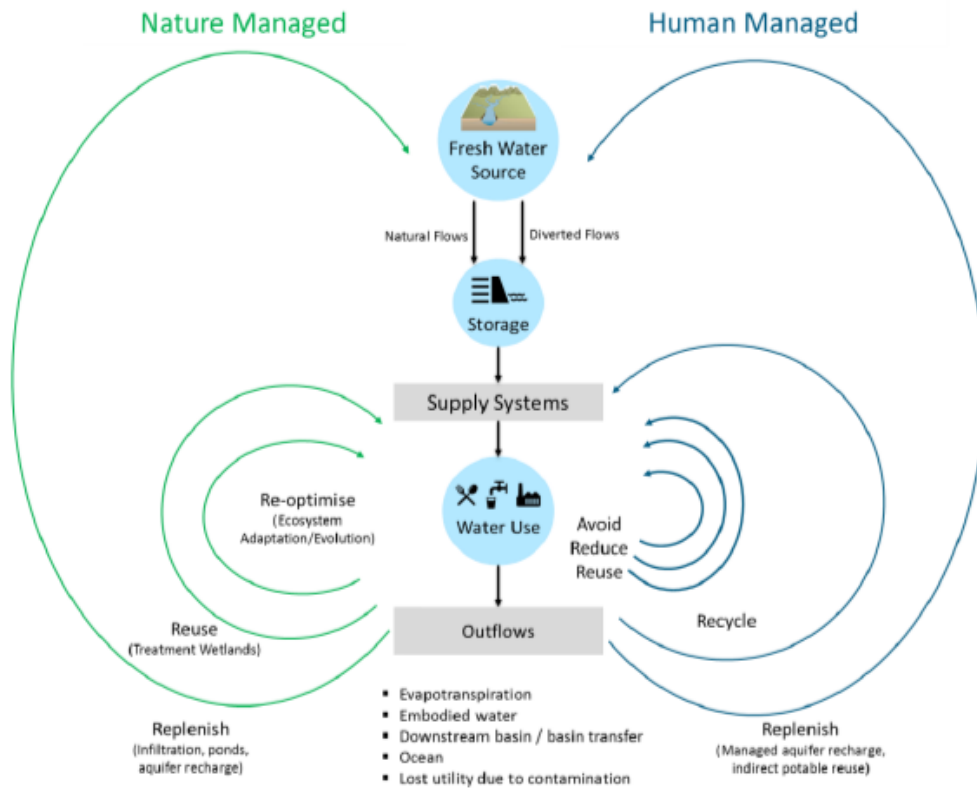


Figure 1. “Butterfly” of the circular water management model. Source: Antea et al. (2018)

On one hand, the United States Environmental Protection Agency, EPA (2018), states that the action of *recycling* means “to recover and reuse useful materials from garbage or waste”. Moreover, according to the European Parliament (2008) *recycling* means any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes. On the other hand, the European Commission (2012) defined the water *reuse* as an alternative supply option for industries and/or agriculture purposes, without mentioning water treatment processes.

This work will be based on the definitions proposed by the World Business Council for Sustainable Development (WBCSD) and Cramwinckel et al. (2017) explained below.

### 1.1.1. The 5Rs Approach

In order to clearly distinguish the concepts applied as sustainable water management practices, the International Water Association (IWA) developed the 5Rs approach to water management, namely reduce, reuse, recycle, restore, and recover. The definitions of the practices according to the World Business Council for Sustainable Development (WBCSD) and Cramwinckel et al. (2017) are shown on Figure 2.



Figure 2. IWA's 5Rs approach to sustainable water management. Source: Cramwinckel et al. (2017).

The main difference between water reusing and recycling is that the former does not imply a water treatment, while the latter does. These two sustainable practices are the ones that will be most used for the further development of this work.

To sum up, for the following pages the concept of *water recycling* will be used as the action of reusing *treated* wastewater for beneficial purposes (EPA, 2018). On the other hand, the concept of *water reusing* will be defined as the action of reusing non-treated water for beneficial

purposes. These beneficial purposes can be for example agricultural and landscape irrigation, industrial processes, among others.

Additionally, it is in fact true that the earth has recycled and reused water for millions of years through its natural cycle. However, water *recycling* and *reusing* refer to projects that use technology to speed up these natural processes, such as the ones that are mentioned and analysed in this research.

### 1.1.2. Benefits of Reusing and Recycling Water

The 5Rs approach to circular water management minimizes the pressure on water resources in terms of both quality and quantity, by using a systemic perspective on water, energy, and waste simultaneously (Cramwinckel *et al.*, 2017). In particular for reuse and recycling, there are numerous benefits that arise from these sustainable practices. These benefits contain social, economic, and environmental benefits.

An example of the social benefits arising from reusing and recycling water is the possibility to decrease the demand of potable and freshwater. In fact, inter-sector collaboration offers the possibility to use treated wastewater to supplement or replace the demand that does not require drinking quality water, such as industrial and agricultural applications. Furthermore, reusing and recycling wastewater can ensure a reliable water supply and independence from the seasonal weather and climatic conditions (Cramwinckel *et al.*, 2017).

On the same path, not all processes and uses require potable water. In fact, all of the following examples are potential applications for reusing and recycling water, all of them with the possibility to decrease the water demand of potable water and thus implying a social benefit for the communities involved. These include:

- Cooling system make-up water, process water, wash-down water and miscellaneous uses, such as site irrigation, fire protection, road cleaning, dust suppression, construction aggregates, beautification
- Agricultural irrigation (industrial crops, fodder and seed crops, orchards, forests, food crops)
- Indirect potable reuse (aquifer recharge, reservoir replenishment), direct potable reuse (extensive advanced treatment of municipal wastewater beyond conventional secondary and tertiary treatment directly into a water distribution system).

Additional applications for reuse and recycled water are further discussed in chapters 2 and 3.

From the economic point of view, the EPA (2018) states that water reusing and recycling offers resource and financial savings. They include, but are not limited to, risks reduction, investments reduction, and energy savings. On the same path, Cramwinckel *et al.* (2017) mentioned that “inter-sector collaboration for water reuse can respond both to water-risk exposure of a company and to water-risk sharing with other users in a watershed”.

Subsequently, water reuse and recycling become a key tool to develop appropriate strategic responses for water risks threats, either at industrial, agricultural, municipal, or even higher organizational level applications. Additionally, reusing and recycling wastewater can help reduce water stress and can often result in lower investment and energy costs.

As the water demand grows more effort is required to obtain water, and this requires an extra amount of energy. In fact, more demand of water implies more water extracted, treated, and transported which can require a lot of energy. As an example, if the water source is ground water, the level of ground water decreases as more water is removed, which rises the energy required to pump the water to the surface.

According to the EPA (2018), even though treating water for recycling requires an additional amount of energy, “the amount of energy required to treat and/or transport other sources of water is generally much greater”. Thus, designing a sustainable water recycling system aiming to treat water in a more efficient and effective way often reduces the amount of energy required. In addition, the energy requirement can further reduce by on-site reusing and recycling, decreasing the amount of energy required to transport water (Cramwinckel *et al.*, 2017; EPA, 2018). However, there is not always a reduction on energy consumption. A proper techno-economic evaluation of the treatment is required for each case, in order to evaluate if there is a reduction or not.

From the environmental point of view, the benefits of water reuse and recycling include, but are not limited to, decreasing the diversion of freshwater from sensitive ecosystems, creating, sustaining, enhancing, and/or remediating wetlands and riparian habitats, decreasing discharges of wastewater threatening ecosystems and preventing pollutant discharges to water bodies, and giving value to substances and pollutants of wastewater by reusing and recycling them by applying the CE principles to water management. Further explanations and examples of these benefits are explained in the following paragraphs.

Waterflows diversion for agricultural, industrial, and/or municipal purposes can produce the lack of available water resources for flora and fauna, directly affecting the ecosystem’s health. Thus, one benefit of water reuse and recycling is that organizations can supplement their demands by using this water, and subsequently setting free considerable amounts of the resource to the environment (EPA, 2018).

In the same path, there are streams that have been impaired or dried out by the diversion of waterflows. This imposes a huge environmental impact to the ecosystem, provided that

wetlands provide habitats for wildlife, and also brings water quality improvement, flood diminishment, and fisheries breeding grounds. Through reuse and recycling water, waterflow can be augmented to create, sustain, enhance, or remediate wetlands and riparian (stream) habitats (EPA, 2018). Subsequently, reusing and recycling water decreases the diversion of freshwater and then reduces the environmental impact suffered by the ecosystem, either remediating streams, protecting local flora and fauna, among other positive environmental effects.

In certain cases, the incentive for reuse and/or recycling water does not come from a need of water supply, but rather from a need to decrease or erase the wastewater discharge to natural water bodies (EPA, 2018). This is also related to the previous point, where the incentive is to protect the ecosystems, but in this point the incentive is to avoid the discharge of dangerous pollutants or other damaging elements through the disposal of wastewater.

In the same way, reusing and recycling water supports the pollution reduction of water bodies. Recycling and reusing water implies a lower amount of water discharges to ocean, rivers, and other water bodies. Some of these discharges usually contain pollutants that have a wide range of environmental impacts. Thus, diminishing the amount of water discharges to this water bodies can prevent the pollutant discharges to them. Subsequently, water reuse and recycling can decrease the discharges of wastewater that could endanger entire ecosystems.

In some cases, substances that pollute water bodies can be beneficially reused when recycling and treating water, thus increasing its value as a resource instead of a pollutant. As an example, recycled water may contain higher levels of nutrients than potable water, such as nitrogen. As stated by the EPA (2018) “the application of recycled water for agricultural and landscape irrigation can provide an additional source of nutrients and lessen the need to apply synthetic fertilizers”. This is the case of many industrial symbiosis systems.

Moreover, as mentioned previously one of the pillars of CE is systems theory. Thus, when circular water management is viewed from a systems approach, it can be noticed that water system is a sub-system of a “system of systems” including environmental systems, agricultural systems, industrial systems, and municipal systems, all of them interacting with each other. This, in fact, is where the concept of industrial symbiosis (IS) arises.

## 1.2. Industrial Symbiosis (IS)

Industrial symbiosis is a sub-field of industrial ecology. IS systems are defined as a group of local companies, communities, and other actors, which exchange energy, materials, water, and by-products (Yang and Feng, 2008; Pakarinen *et al.*, 2010; Roman and Chertow, 2011). Moreover, they are geographically close actors interchanging resources in order to obtain competitive advantages in a cooperative environment, seeking enhanced environmental, economic, and social performance.

In the CE context, IS are industrial systems that try to mimic the circularity of nature, with the main principle of actors using other actor's waste in order to eliminate the overall waste generation. In fact, the ideal IS would be when all material, water, and energy flows are cyclical, and all the energy input required by the system comes from the sun.

Moreover, IS are usually composed by actors from different categories. They can usually be clustered in industrial applications, municipal applications, and agricultural applications. Accordingly, IS can be defined as “systems of systems”, where environmental systems (natural managed systems), industrial systems, municipal systems, and agricultural systems interact with each other.

Therefore, circular water management applied to IS systems is a key tool to develop the CE in industrial systems. Moreover, the problem of water scarcity drives a huge interest on practices that reduce water stress, such as water reuse and recycling in the industrial context. Thus, the qualitative and quantitative analysis of water networks in IS systems rises as an important topic to develop.

The case of Kalundborg in Denmark is surely the most famous example of IS, although there are several other examples in recent literature. This case along with additional cases will be qualitatively analysed and quantitatively described in chapters 3 and 4, respectively.

### 1.3. Sustainability and Eco-efficiency

The concept of sustainable development was first introduced in the United Nations Conference on Environment and Development (UNCED) in 1992, also known as the Rio Conference. According to Pakarinen *et al.* (2010) this concept aims to “sustain the diversity of life and respect the limits of the earth's natural resources”. Moreover, the concept refers to the simultaneous economic, social, and environmental progress of the current generations, without compromising the ability of the future generations to achieve their own.

In industrial systems, and particularly on IS cases, there have been several attempts to make more tangible the abstract concept of sustainability. However, the sustainability of IS cases is difficult to assess. Most methods are data-intensive and may not capture measurements on sustainability, but rather evaluate only the environmental impact of the application of a project. Thus, they often exclude the social pillar of sustainability (Pakarinen *et al.*, 2010). In the same path, Sokka, Melanen and Nissinen (2008) claim that “evaluating the sustainability of IS as a whole requires a holistic framework which combines both quantitative and qualitative analysis”.

In this context arises the concept of eco-efficiency. Eco-efficiency is a concept that comprises only two of the social pillars of sustainability, namely the economic and environmental performance of a system. However, this concept lacks a single definition, usually explained by



the several applications levels it is applied on. In fact, it can be applied at a business, local, national, and global level. For the purposes of this report, the concept will be applied at individual industries and industrial system levels, i.e. to the actors of an IS and to the entire IS itself.

Eco-efficiency can be used to measure in a quantitative way the circularity of IS systems. In fact, there are several eco-efficiency indicators used to analyse and compare the operation of different industrial systems. Both from an economic and environmental perspective. Moreover, the final chapter of this research contains a quantitative description of the water network of IS cases through eco-efficiency indicators.

## 1.4. Final Aim of this Research

The final aim of this research is to analyse the world's best practices in industrial symbiosis cases, focused on the application of the circular economy concept to the water network of each system.

First, this work provides a classification of each single waterflow in the water network of six different IS cases, based on a comparison between both primary and secondary usages. On one hand, the users are considered. On the other hand, the quality of water is considered. Moreover, a qualitative model was developed in order to provide a structured classification for each case.

The Industrial Symbioses Waterflow Exchanges (ISWE) model is a qualitative model to analyse and compare the water reuse and recycling practices of different IS cases. The methodology of the model is explained in chapter 2, and the application of the model to real cases around the world is developed in chapter 3.

Finally, chapter 4 presents several indicators to quantify the benefits of applying the CE practices in the water network of IS cases. Several eco-efficiency indicators are presented in this chapter, taken mostly from literature and lifecycle assessment (LCA) studies. Additionally, an indicator created by the author is proposed and developed at the end of the chapter.

The final aim of the thesis is to give a precise overview of the circular water practices in industrial symbioses, and to underline its benefits in a quantitative way.

It is important to notice that the different exchange relationships between the different actors of an IS are conditions from a specific point in time, which is dynamically changing. Thus, the cases analysed in this research provides a snapshot of the state of an IS system in a particular time period. This applies for both the qualitative and quantitative assessments.

## 2. Methodology of the Industrial Symbioses Waterflow Exchanges (ISWE) Model

This chapter presents the methodology of the Industrial Symbioses Waterflow Exchanges (ISWE) model. This model is used to analyse and compare in a qualitative way the water network operating in different industrial symbiosis cases. In particular, it is used to analyse the actors involved and the level of reuse and recycling of each waterflow of the entire water network of a case.

### 2.1. Water Reuse and Recycling: Classification Categories

The water reuse and recycling activities and all of the elements involved in the process can be classified in many ways. For the purposes of the ISWE model, the classifications to be used are regarding the actors involved and the level of reuse/recycling of the exchange. It is important to mention that these classifications are only a few among the entire range of classifications there are for this matter.

The first classification refers to the actors involved in the water reuse or recycling, namely the supplier and the user. These actors will be clustered in three different *applications categories*, namely industrial, municipal, and agriculture applications. Table 1 shows some examples of activities using water grouped by their corresponding application categories.

*Table 1. Application types and their corresponding example activities*

<b>Application type</b>	<b>Example activities</b>
Industrial Applications	Cooling water for industrial purposes (e.g. power plants and oil refineries) Construction activities (e.g. concrete mixing) Chemicals manufacturing ...
Municipal Applications	Sewage and wastewater treatment (e.g. Municipal Wastewater Treatment Plants) District heating Potable water Public parks Governmental infrastructure (e.g. ports) Residential zones ...
Agriculture Applications	Farming irrigation Mariculture Mills (e.g. aquaculture and feed mills) ...

As stated previously, an IS is defined as closely clustered industries that share different types of resources. Even though this definition leaves agricultural and – especially – municipal actors outside its boundaries, usually these actors are important contributors to their water network.

Moreover, water resources often come from residential zones as the primary user, followed by reuse and recycling practices by industrial applications in the IS. Thus, even though the cases analysis is focused in industries, municipal and agricultural applications will be included in the boundaries of the study for often being important actors in the water network of the overall system.

In the category of industrial applications are located all the industrial organizations or entities that perform private activities for their own purposes, not related either to agricultural activities nor municipal (or local Governmental) services. According to this model, these waterflows exchanged can have five types of destinations, namely the same industry and same process, same industry but different process, another industry, a municipal application, or an agricultural application. The first two are not available for municipal nor agriculture applications since they are not classified as industries.

In the category of municipal applications there are all the local Governmental organizations or entities providing services typically performed by the municipalities and Governmental institutions. These include district heating for residential zones, municipal wastewater treatment, potable water distribution for residential zones, sewage water management, among others.

Organizations that perform these activities, but which are owned by private or non-governmental organizations, will not be included within this cluster. For example, a private wastewater treatment plant owned by an industrial application will be considered as an industrial application, since its intention is to treat water for industrial purposes. According to this model, these waterflows exchanged can have three types of destinations, namely an industrial application, another municipal application, or an agricultural application.

In the category of Agriculture Applications are included all the organizations or entities that perform agricultural activities, such as farms and growing zones. For simplicity, Agriculture Applications also include mariculture activities<sup>1</sup>, such as fish farming, general sea farming, or similar activities. According to this model, these waterflows exchanged can have three types of destinations, namely an industrial application, a municipal application, or another agricultural application

The base elements of study of the ISWE model are the water exchanges between the two actors involved. Thus, this model focuses on water exchanges either between the same or

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<sup>1</sup> Phillips, (2010) defines mariculture as “the farming of marine organisms for food and other products such as pharmaceuticals, food additives, jewellery (e.g., cultured pearls), nutraceuticals, and cosmetics, either in the natural marine environment, or in-land- or sea-based enclosures, such as cages, ponds, or raceways”.

different application categories. In fact, section 3.2 presents case studies of different IS systems, where several water exchanges take place between, for example, industrial applications and municipal applications, or municipal applications and agriculture applications. Moreover, an important part of this model is the application category of both the origin (or supplier) and destination (or user) of the water exchange.

It is of paramount importance to state that IS cases include several actors exchanging materials, energy, and water. The only actors analysed in this work are the ones involved in water exchanges. Moreover, actors that do not have any reported users of waterflows will not be included (e.g. wastewater treatment plants with no users of the treated water). In fact, only flows with defined users are accounted.

The second classification refers to the *level of reuse or recycling* that can be performed to water. A waterflow is reused or recycled when a primary user of the waterflow, or origin, sends water resources to the secondary user, or destination. As stated previously, the difference between both concepts is that the former do not imply any treatment, while the latter does.

Moreover, if the waterflow is treated – and thus recycled – it can be subclassified as upcycling, downcycling, or same level recycling. The concepts of downcycling and upcycling are already defined for other physical-solid products, different from water. Thus, section 2.2 transfers these concepts to water exchanges in order to structure the ISWE model.

## 2.2. Recycling: Upcycling, Same Level and Downcycling

In order to transfer the applicability of the concepts of upcycling and downcycling to water bodies, it will first be introduced their definition for “solid” elements. Adapting the definition provided by Pires *et al.* (2018) there can be three levels<sup>2</sup> of recycling: upcycling, *same level*<sup>3</sup>, and downcycling. These three levels will be mentioned in the following sections and will be the base of the development of this work. It is important to notice that this classification only affects the waterflows classified as *recycling*, and not the ones classified as *reusing*.

Firstly, upcycling and downcycling may occur inside the same product. As an example, in the case study performed by Niero *et al.* (2017) it was introduced a methodology for promoting eco-efficiency and eco-effectiveness for aluminium cans, which tried to upcycle the can continuously and where every time that the can was recycled it improved its features (Pires *et al.*, 2018). Just as in the mentioned example, for the purposes of this work the analysis to be used will be the one on the same product: the waterflow. Thus, the water belonging to a

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<sup>2</sup> Pires *et al.*, (2018) refer to “*types*” of recycling instead of “*levels*” of recycling. For the further development of this research the concept to be used will be the latter.

<sup>3</sup> Pires *et al.*, (2018) refer to “*recycling*” level of recycling instead of “*same level*” of recycling. For simplicity and to avoid confusions the concept to be used will be the latter.

specific waterflow can be recycled at the level of upcycling, same-level recycling, or downcycling.

Secondly, upcycling is defined by McDonough and Braungart (2002) as “the practice of taking something that is disposable and transforming it into something of greater use and value”. Moreover, according to Chandler and Werther (2014) upcycling refers to processes that increase the value of the recycled material over time, in which the material is reemployed for a more significant use or with a higher environmental value. Subsequently, it can be noticed that in both definitions upcycling suggests the concept of *increasing value*, since both are related to the conversion of one product into a more valuable – but different – product.

Same-level recycling occurs when the process used to recycle the waste maintains its value over time. As mentioned by Pires *et al.* (2018), same-level recycling cases occurs when “the waste materials are recycled again into the initial products”. Thus, the concept of closed-loop recycling is used as a synonym of the same-level recycling. An example of same-level recycling is the case of glass-to-glass because it can be recycled several times without losing its properties.

Downcycling, as the total opposite of upcycling, refers to a recycling process where the value of the recycled material decreases over time, being used in less valued processes, with lesser quality material and with changes in inherent properties, when compared to its original use (Ashby, Shercliff and Cebon, 2007; Chandler and Werther, 2014; Geyer *et al.*, 2016; Pires *et al.*, 2018). Moreover, downcycling can be simplified to the practice of taking something that is disposable and transforming it into something usable, although of lower value. For example, as stated by Pires *et al.* (2018) most of the time “the actual recycling of municipal waste streams [...] is considered more like a downcycling and not recycling”.

These concepts applied for “solid bodies” can be analogously defined to “water bodies”. In fact, these can be similarly defined for the water exchange between two organizations, and its classification depends solely on the *water value* that the two organizations perceive for that water exchange. Moreover, the value of water perceived will be the value of the water inflow of each organization involved.

*Upcycling* will be used in the following sections as the water exchange (or waterflow) between two organizations, where the supplier (or origin) requires a “less valuable water” than the user (or destination). Subsequently, when the water inflow of the user is “more valuable” than the water inflow of the supplier. Moreover, since recycling implies performing a water treatment, upcycling implies that the organization uses the water inflow, then performs a water treatment to the used water, and finally delivers a water outflow of higher value than the inflow.

In contrast, *downcycling* will refer to the water exchange between two organizations where the supplier requires a “more valuable water” for its purposes than the user. This is, when the water inflow of the user is “less valuable” than the water inflow of the supplier. Moreover, since recycling implies performing a water treatment, downcycling implies that the

organization uses the water inflow, then performs a water treatment to the used water, and finally delivers a water outflow of lower value than the inflow.

Lastly, *same level recycling* will refer to the water exchange where the supplier requires the “same value of water” (or quite similar) to the one required by the user. This is, when the water inflow of the user is “equally valuable” than the water inflow of the supplier. Moreover, since recycling implies performing a water treatment, same-level recycling implies that the organization uses the water inflow, then some water treatment is performed to the used water, to finally deliver a water outflow of equal – or quite similar – value compared to the inflow.

To classify each waterflow level of reuse/recycling, the notation will be “*R*” for reuse, “*D*” for downcycling level of recycling, “*S*” for same-level recycling, and “*U*” for upcycling level of recycling. Figure 3 shows an algorithm to analyse the reuse or recycling level classifications, according to each case.

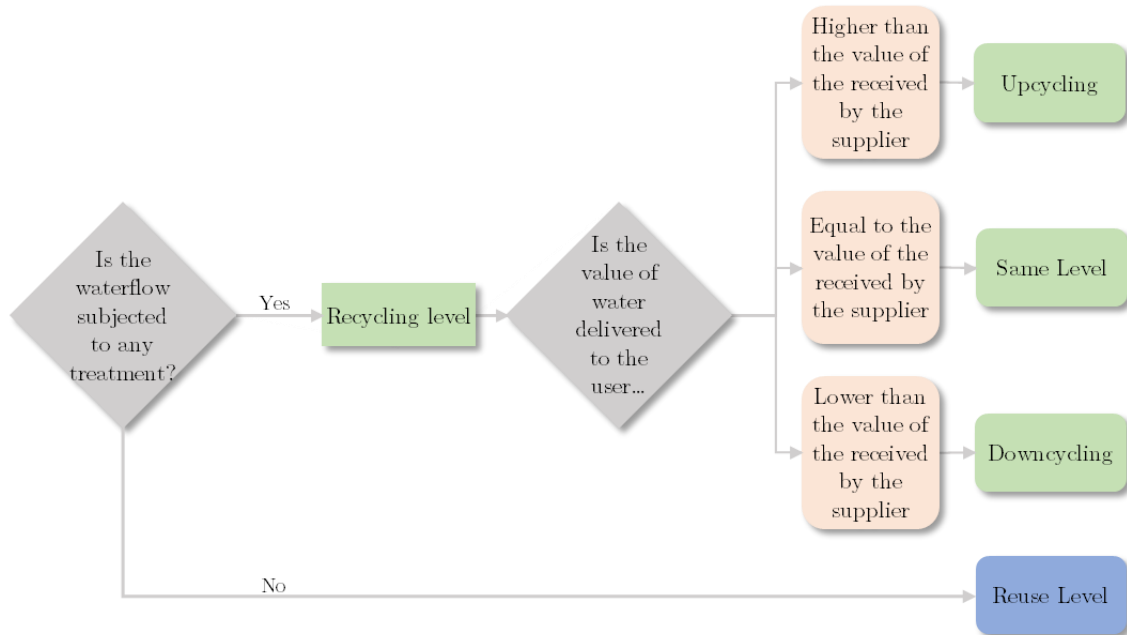


Figure 3. Algorithm to define the reuse or recycling level in the ISWE model

At this point it has been defined the *recycling level* as a function of *the value of water used by the actors* participating on its exchange. Thus, it is of paramount importance to define how this value is analysed on the ISWE model. For the following sections of this model, the “value of water” will be defined by the water quality. Moreover, higher water quality will represent a higher value of water, and vice versa.

It is important to state that water quality can be a subjective measurement of the “value of water” for different organizations. Depending on their purposes, each organization requires

different quality between several water quality indicators, not necessarily correlating with that water being better or worse<sup>4</sup>.

For the purposes of this model each waterflow will be analysed, and a perception on the “water quality” will be defined for each case. Thus, a general rule of water quality will prevail for all the cases. This is, all waterflows will be classified according to a water quality indicator, being the ones with the higher indicator the ones more valuable, and the ones with lower one the less valuable waterflows. The quality will be defined in a scale ranging from one to six, with one being the worst quality and six being the best.

In the same idea, different industries require effluents with different water qualities for their purposes. Thus, for the development of the IMWE model the value of water to be taken into consideration will be a function of the industry the flow is required for.

As an example, suppose that there are two industrial actors, A and B. Actor A belongs to an industry that requires an inflow effluent of quality three. In addition, suppose that the actor B belongs to an industry that requires an inflow effluent of quality five. Thus, the waterflow received by A is of lower quality (or lower value) than the one received by industry B.

The definition of the quality of water required by each industry is developed in section 3.1.3.4. This will be a standard classification for all waterflows analysed, depending exclusively on the industry to which the actor receiving the effluent belongs. As stated before, the industrial systems to analyse will include other types of actors inside its boundaries, such as municipal and agriculture applications. The water quality requirements for these applications will also be defined in section 3.1.3.4, according to its purpose (e.g. municipal district heating has a different quality requirement than municipal wastewater treatment). Water quality requirements will range from 1.0 to 5.4 from lower to higher quality, respectively.

In conclusion, the water network of all IS cases will be taken from literature and official references. However, the actual waterflow exchange between the actors will be defined solely by the general requirements according to the industry they belong.

Finally, in order to properly classify the waterflows exchanged between the different actors, it is important to define the control volume to be considered, which is explained in the section below.

## 2.3. Control Volume Characterization

The definition of the control volume of each waterflow is key to properly classify its reuse or recycling level. The control volume defined for each waterflow will include:

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<sup>4</sup> This idea is further developed in section 3.1.

- The water inflow of the organization providing the waterflow (or the supplier)
- The supplier organization
- The water inflow of the company using that water (or the user)
- The user organization

Figure 4 shows an example of two different waterflows analysed with their corresponding control volumes. In this example actor A belongs to an industry that requires an effluent of quality 4, actor B belongs to an industry that requires an effluent quality 1, and actor C to an industry requiring quality 2. The definition and description of actual water quality requirements for each industry is described in section 3.1.3.4.

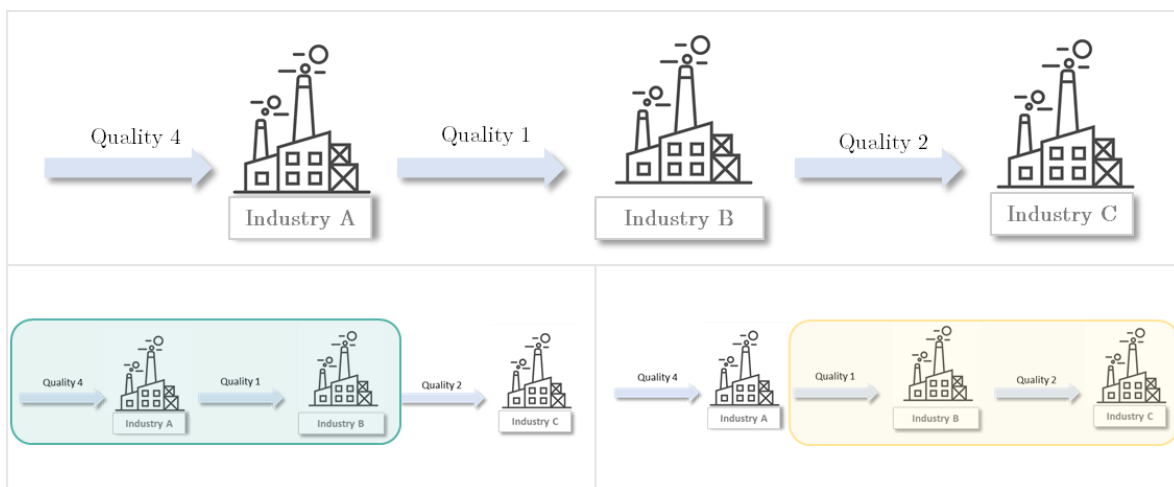


Figure 4. Control volume examples of the ISWE model

The first control volume (at the bottom left) includes (1) a waterflow of quality 4, as the water inflow of the supplier; (2) the industry A, as the supplier; (3) a waterflow of quality 1, as the water inflow of the user; and (4) the industry B, as the user. The second control volume (at the bottom right) includes (1) a waterflow of quality 1, as the water inflow of the supplier; (2) the industry B, as the supplier; (3) a waterflow of quality 2, as the water inflow of the user; and (4) the industry C, as the user.

After defining the control volume for each waterflow it comes the definition of the level of reuse or recycling, by following the procedure shown in Figure 3. Thus, if there is a treatment the waterflow is classified as recycling. Otherwise it is classified as reusing. If it is classified as recycling, the sub-classification level will be defined by the comparison between the water inflows of the supplier (or primary user) and the user (or secondary user).

Moreover, in the example of Figure 4, assume all industries treat its effluents. Thus, all waterflows exchanged are classified as recycling. Moreover, the waterflow exchanged from industry A to B is classified as downcycling, and the one exchanged from industry B to C is



classified as upcycling. On the contrary, assuming there is no treatment, both waterflows are classified as reusing.

There is an additional consideration for defining the control volumes of the waterflow exchanges. There are certain organizations that act only as intermediary facilities between two main actors. They are classified as intermediaries either because they perform water treatment as their only activity, or because they exclusively act as distributors of water, without any other task.

Waterflows received by intermediary organizations are not considered as a circular practice, i.e., nor reuse nor recycling of water. This is because intermediary organizations do not extend the value of the resource by reusing it for its activities, but they act exclusively as a mean for other organizations to receive this waterflow. Moreover, they are not classified as users of the waterflow, but only as a transitory stage of the exchange. Subsequently, intermediaries are skipped in the control volume of the analysis.

Figure 5 represents a control volume example of a waterflow exchange passing through an intermediary organization. In this example, the overall waterflow passes from quality 4 (inflow of the primary user) to quality 2 (inflow of the secondary user). Since the water is treated by the intermediary, the water exchange is classified as downcycling.

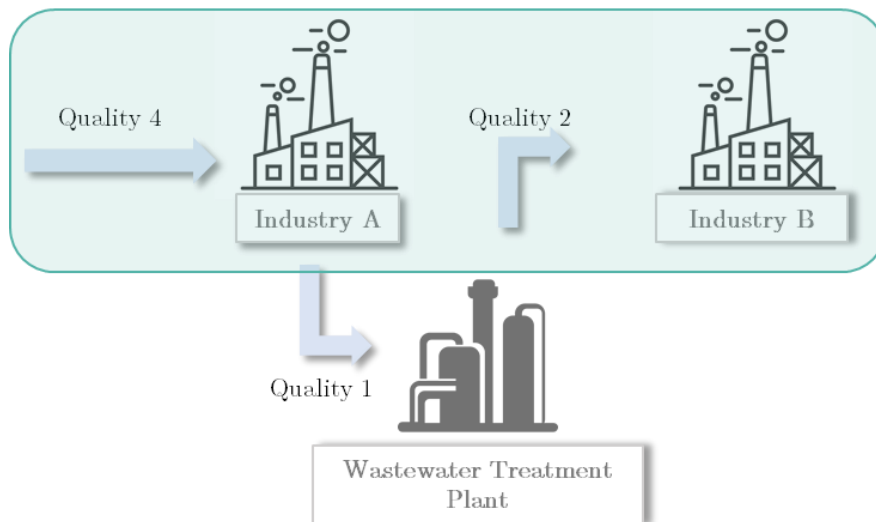


Figure 5. Control volume example with an intermediary organization

Additionally, there are organizations that perform similar activities to intermediaries, however with the difference that they do use the water inflow for some purpose. This is the case, for example, of a plant that performs the treatment of wastewater to produce sludge, which is further used for producing biogas. Even though a wastewater treatment is being performed, the water inflow is being used for an additional purpose different than the treatment. Hence, these organizations are not considered as intermediaries, but as actual users of water.

Figure 6 represents an example of the mentioned situation, taken from the case of Kalundborg Symbiosis analysed in section 3.2.2. In this case, the “wastewater treatment and biogas plant” receives waterflows from different actors. Then it performs water treatment and the resulting by-product is used to produce biogas. Thus, the water treatment is only one of the activities of the organization, and subsequently it is not considered just as an intermediary.

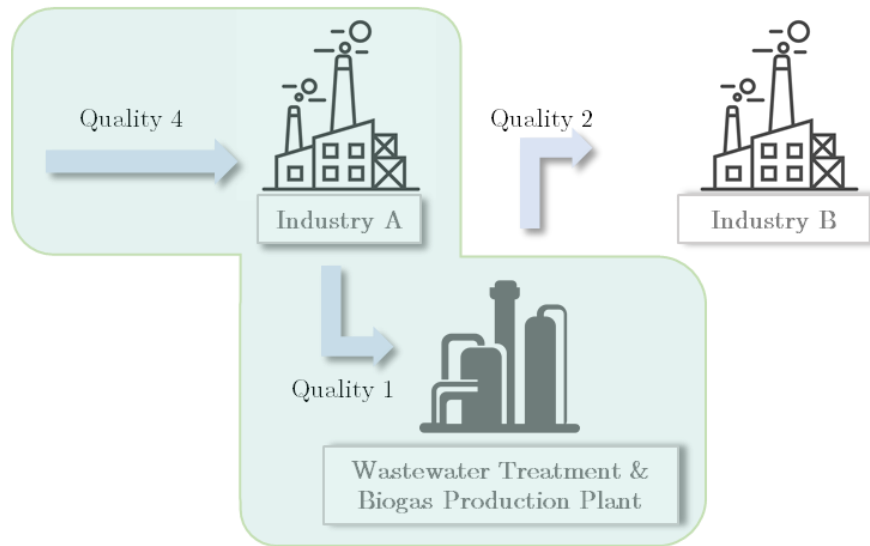


Figure 6. Control volume example with a non-intermediary organization

In addition, waterflows that originate from an intermediary organization are not considered to be reused nor recycled by an actor receiving it, since the intermediary is not a user (and then the actor receiving it is the primary user). The same happens when waterflows are destined to intermediary organizations without any following exchange. In fact, these waterflows are not considered a reuse nor recycling practice since the intermediary organization is not a user of the waterflow (and then they are not the secondary user). These water exchanges are not considered as circular water practices, nor reusing nor recycling.

An example of the previous situation is the effluent provided by the water utility from the Kalundborg Symbiosis case, analysed in section 3.2.2. The utility extracts surface water from the lake and distributes it to other actors, either directly or after previous treatment. In this case, the effluent coming from the utility to an industry is not considered as a circular practice, since it is a waterflow that has not been used by any actor yet.

Concluding, the control volume of waterflows passing through intermediaries (i.e. that water treatment and/or distribution is their only activity) will be defined by avoiding these organizations.

In addition, there will be a clear distinction between the types of organizations that treat water. The waterflow can be treated by an intermediary or a user organization. This treatment

will be distinguished by the letter “M” if the treatment was performed by a municipal application, and with the letter “I” if it was performed by an industrial application.

As stated before, there are intermediary organizations that do not perform any treatment but act as purely distributors. Waterflows passing through these types of organizations will not be distinguished with a letter, since the important information for this model are the users and the potential water treatments, and not the trajectory of the waterflow.

## 2.4. Waterflow Classifications

Summarizing, section 3.1.3.4 provides a detailed methodology to classify the waterflows by their quality, according to the industry they are received. Then, section 3.2 develops a qualitative study of water exchanges in an IS systems, by applying the ISWE model to the waterflow exchanges. Thus, these waterflows are modelled by two main factors, namely the application category of the actors involved, and the *level of reuse/recycling* of the waterflow exchanges between the actors involved. Figure 7 shows the range of classifications to be used in the ISWE model.

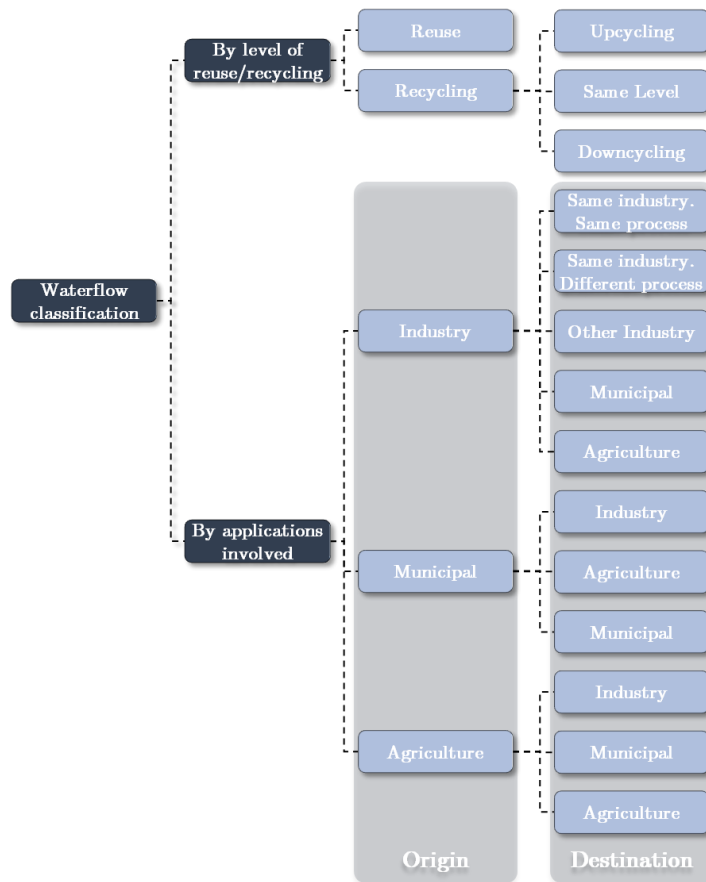


Figure 7. Range of waterflows classifications for the ISWE model

Figure 8 shows an example IS situation. Industry A belongs to an industry that requires water of quality 4.0. Industry B belongs to a different industry that requires water of quality 5.0. The municipal application requires water of quality 3.0. Finally, the agriculture application requires water of quality 3.0. Table 2 summarizes the waterflows exchanges from Figure 8.

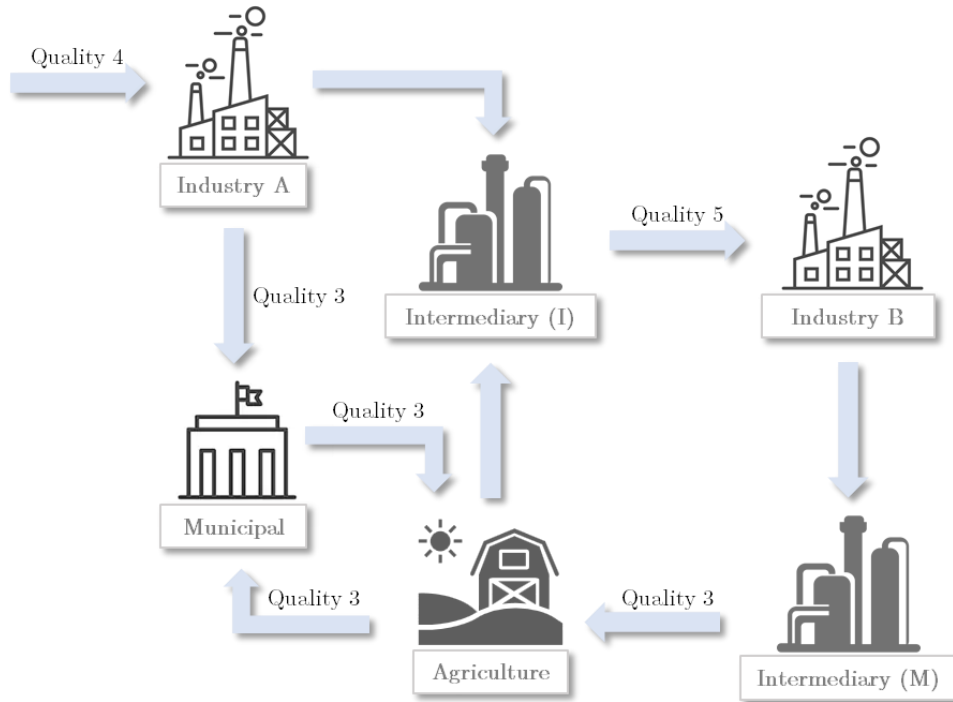


Figure 8. Example of an IS situation

Table 2. Waterflows characterization for the IS of Figure 8

Primary use		Intermediary		Secondary use		Level	
Quality in	User	Actor	Treated?	Quality in	User		
1	4.0	Industry A	N/A	No	3.0	Municipal	Reuse (R)
2	3.0	Municipal	N/A	No	3.0	Agriculture	Reuse (R)
3	4.0	Industry A	Industrial wastewater treatment plant (I)	Yes (I)	5.0	Industry B	Upcycling (U): from lower to higher value
4	3.0	Agriculture	Industrial wastewater treatment plant (I)	Yes (I)	3.0	Municipal	Same level (S): same water value
5	5.0	Industry B	Municipal wastewater treatment plant (M)	Yes (M)	3.0	Agriculture	Downcycling (D): from higher to lower value

## 2.5. Origin/Destination (O/D) Matrixes

The Origin/Destination (O/D) matrixes developed in this model show information about the supplier and the user of the water exchanges, i.e. the two organizations involved in the control volume of each waterflow. These matrixes show one of the classifications of the water exchanges, namely the *application category* of both the *supplier* and the *user*.

According to the ISWE model, the origin industry has three types of industrial destination applications, namely the same industry and same process, same industry but different process, or another industry. For the origins “municipal” and “agriculture” the destinations “same industry/same process” and “same industry/different process” do not apply. For further explanations refer to section 2.1.

The horizontal axis of the O/D matrix represents the origin application (i.e. the supplier or primary user), while the vertical axis represents the destination application (i.e. the user or secondary user). Moreover, it is possible to notice that there are eleven possible O/D waterflow exchanges. Furthermore, for the origin “industry” the destination “industry” refers to a water exchange with “other industry”. Table 3 shows an example O/D matrix of the waterflows in Figure 8.

Table 3. O/D matrix for the IS of Figure 8

Origin/Destination	Same Industry		Industry	Municipal	Agriculture
	Same process	Different process			
Industry			Exchange 3	Exchange 1	Exchange 5
Municipal	N/A	N/A			Exchange 2
Agriculture	N/A	N/A		Exchange 4	

## 2.6. Level and Origin/Destination (L-O/D) Matrixes

The Level-Origin/Destination (L-O/D) matrix developed in this model gather information about both the *value of the waterflow* in study, and also the *application category* of the actors involved. It includes information about the *level of reuse/recycling*, the *supplier*, and the *user* of the water exchanges between organizations. Thus, this matrix complements O/D matrixes by adding information about the reuse/recycling level of the waterflow exchanges.

Additionally, L-O/D matrixes include information about the intermediary organizations performing water treatment activities, for the waterflows passing through these types of organizations.

Each waterflow is represented by a point in the matrix. The colour of the rectangle containing the waterflows represent the category of the supplier of the waterflow (or origin). All waterflows contained in the red rectangle are supplied by an industrial application. Waterflows contained in the blue rectangle are supplied by a municipal application. Finally, waterflows contained in the green rectangle are supplied by an agriculture application. Additionally, the horizontal axis of the matrix represents the category of the user of the waterflow (or destination), and the vertical axis represents the reuse or recycling level of the waterflow.

Figure 9 shows an example L-O/D matrix of the waterflows in Figure 8.

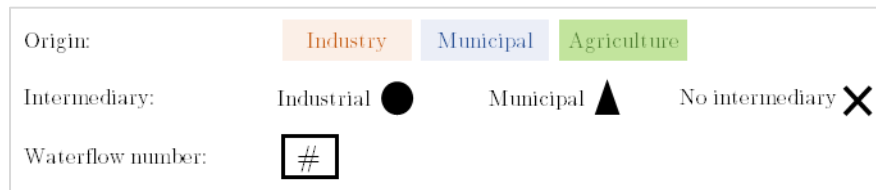
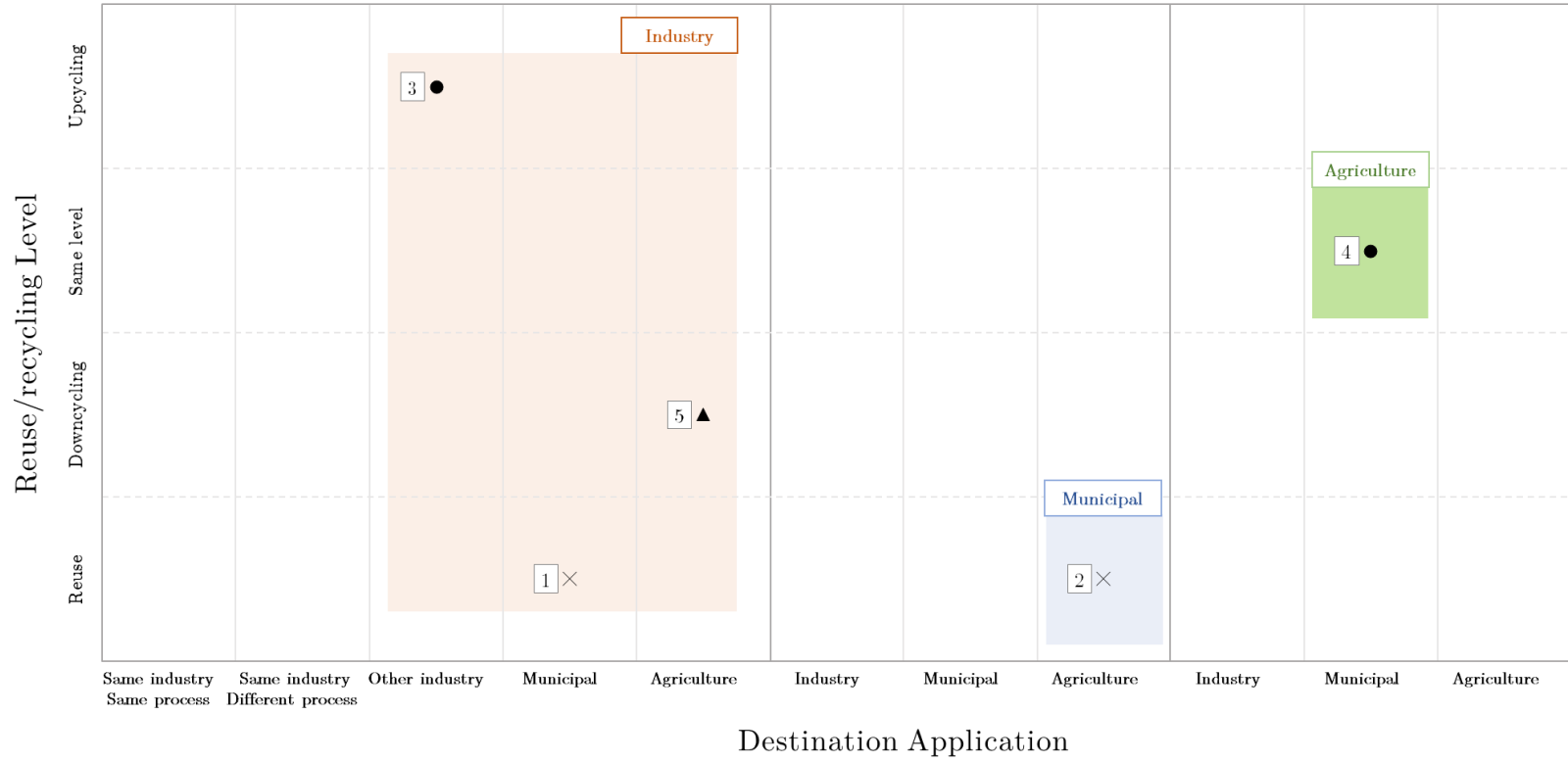


Figure 9. L-O/D matrix for the IS of Figure 8

## 3. Industrial Symbiosis Cases Analysis

This chapter provides a qualitative analysis of circular economy practices in the water network of industrial systems. In particular, it develops a qualitative study on water reuse, treatment, and recycling in the industrial context.

Section 3.1 focuses specifically on water quality and treatments in the industrial context. It presents a detailed description of the different industrial water treatment processes, the different technologies available, and their application level in different industrial sectors.

Section 3.2 focuses on both reusing and recycling practices in the industrial context. It develops a qualitative analysis of circular water practices in different IS cases, by means of the IMWE model presented in chapter 2.

### 3.1. Industrial Wastewater Treatment: Process and Technologies

Industrial wastewater reuse and recycling is a common practice in industrial symbiosis cases, and moreover, in industrial systems in general. Comparing both sustainable practices, their key difference is the treatment (or not) of the wastewater. In fact, recycling implies an extra effort that comes with the treatment process, which can be sustained either by the supplier of the effluent, the user, or an intermediary organization. This effort is not sustained by the organizations performing a direct reuse of the effluent.

As a consequence, in order to reduce the cost and increase the efficiency of the process of recycling, it is necessary to understand how the treatment process is carried on in the industrial context. Section 3.1 provides a detailed description of the treatment process, the technologies available, and how they are applied in the different industrial contexts.

#### 3.1.1. Industrial Wastewater Treatment Process

The first step in any wastewater treatment is the correct characterization of the effluents involved in the process. The two effluents involved in the treatment process are the inflow and the outflow effluents. Their characterization refers to the correct description of their components, explained by several water quality indicators. Thus, two effluents must be characterized, namely the initial and desired waterflows.



The initial characteristics of the waterflow refer to the characterization of the inflow effluent, which is the one to be treated. The desired characteristics of the waterflow refers to the characterization of the outflow effluent, which is the final result of the treatment process. Figure 10 shows a diagram of the treatment process and its correspondent effluents. The characterization of the industrial wastewater effluents is discussed in section 3.1.1.1.



Figure 10. Effluents in a wastewater treatment process

After the correct characterization of the industrial effluents to treat and recycle, it comes the process of the actual treatment of the effluent. This process involves several types of treatment technologies. These separation technologies can be grouped and classified by their nature, which can be physical, biological, chemical, and physicochemical methods. All of them offer different methods for treatment, with advantages and disadvantages of their own. The nature of the different technologies for wastewater treatment is discussed in section 3.1.1.2.

The different separation technologies have been designed and developed in different times throughout history. Some technologies have gained increasing interest over some periods of time, while others gained interest in some others. It is in fact a changing scenario. Furthermore, in the recent years new technologies have been developed in order to treat more complex pollutants, such as refractory pollutants. A brief review of the recent history of technologies is developed in section 3.1.1.3.

Additionally, the different types of technologies are implemented through the different phases of the wastewater treatment process. These phases are primary, secondary, tertiary, mineral removal, and polishing. As a general rule, the more advanced phase reached on the treatment, the greater quality of the outflow effluent.

Subsequently, in a treatment process there are at least two decisions to make: what is the phase to be reached in the treatment process, and what are the technologies to be used in each phase. Furthermore, these decisions are determined at least by the initial and the desired characteristics of the waterflow (in addition to other techno-economical constraints).

A better initial quality and/or lower desired quality of the effluents implies both simpler technologies and a “shorter” treatment process, in terms of the phase reached. On the contrary, lower initial quality and higher desired quality of the effluent implies both more complicated technologies and a greater advancement in the treatment process. A more detailed discussion of the phases of the industrial wastewater treatment is discussed in section 3.1.1.4.

Finally, the advancement of the treatment process defines the actual characteristics of the outflow effluent in terms of quality. Thus, the advancement of the process also define the potential applications for which the treated wastewater can be used. A further analysis of the potential applications for treated wastewater according to its characterization is further discussed in section 3.1.1.5.

#### *3.1.1.1. Characterization of Industrial Wastewater: Technical and Strategic Perspective*

For the effective treatment of industrial wastewater, it is first necessary the correct characterization of the wastewater to be treated, in order to find its best suitable technological solution. This section analyses, from a strategic perspective, the characterization of wastewater for the subsequent implementation of the most suitable technology.

The first step for wastewater characterization is identifying the source of the pollution generation. Identifying the source could allow to take corrective actions to reduce or eliminate the source of pollution. If this is not possible, it is recommended to identify the nature of the pollutant, in order to segregate effluents according to their content and treat them separately according to their specific needs (Ranade and Bhandari, 2014). This will improve the overall efficiency of the water recycling system.

Additionally, one plant using water often performs several different treatment processes, for diverse effluents. This generates a wide variety of water outflows with different pollutant levels, both in quantity and in quality. Thus, it is essential to properly sample the effluents to be treated, in order to strategically design the best suitable wastewater treatment.

According to the classification proposed by Cramwinckel et al. (2017), there are three quality grades of industrial water, namely low-grade, intermediate-grade, and high grade. This is a general rule to cluster different effluents of water into three main categories, defined by their quality characterization. Table 4 presents the water quality parameters for each of the industrial water grades as proposed by the authors.

It is important to state that these limits refer to a general classification that will be used to structure the model proposed in this research, developed by the authors to be used in a global context. The actual limits classification depend on several factors such as the context of each case, the place of discharge, the nature of the industry, and the governmental regulations. For the purposes of this research these will be the characterization applied to the effluents of the model, namely low, intermediate, and high-grade water.

Table 4. Characterization parameters for water grades. Source: Adapted from Cramwinckel et al. (2017).

Parameter	Unit	Low grade	Intermediate grade	High grade
pH	–	6 – 9	6 – 9	> 6
Biological oxygen demand (BOD)	mg/L	10 – 30	n.s.	n.d.
Chemical oxygen demand (COD)	mg/L	100 – 150	70 – 90	< 0,5 mg/L for process water measured as total organic carbon (TOC)
Total nitrogen (TN)	mg/L	10 – 20	1 – 5	n.d.
Total phosphorus (TP)	mg/L	1 – 10	2 – 5	n.d.
Total suspended solids (TSS)	mg/L	10 – 25	5 – 15	0 – 1
Total dissolved solids (TDS)	mg/L	500 – 2.500	100 – 2.500	< 1 – 15
Conductivity	mS/cm	0,75 – 3,5	0,15 – 3,5	0,001 – 0,02
Alkalinity as CaCO <sub>3</sub>	mg/L	n.s.	40 – 100	0 – 50
Calcium hardness as CaCO <sub>3</sub>	mg/L	n.s.	50 – 750	1 – 5
Chlorides	mg/L	50 – 250	50 – 250	n.d.
Sulphates	mg/L	n.s.	0,35	n.d.
Iron (Fe)	mg/L	n.s.	0,2	0,01
Silica	mg/L	n.s.	< 25	0 – 1
Total dissolved oxygen (TDO)	mg/L	n.s.	n.s.	< 0,005
Fecal coliforms	#/100 mL	0	n.s.	Fecal coliforms

Note: mg/L: milligrams/litre; mS/cm: millisiemens/centimetre; mL: millilitre; n.s.: parameters not specified are low due to the treatment applied; n.d.: not detected since parameters must be lower than detection limits.

It can be observed that there are separate independent parameters characterizing wastewater. These parameters mainly include organic components, inorganics, and total dissolved and suspended solids (Ranade and Bhandari, 2014).

The presence of organic compounds in wastewater is measured in terms of biological oxygen demand (BOD), chemical oxygen demand (COD), total oxygen demand (TOD), and total organic carbon (TOC). The BOD represents the total oxygen required by the bacteria for oxidizing the chemicals that can be oxidized by biological means, that is, biodegradable substances such as food organic matter. On the contrary, COD represents the oxygen

requirement for oxidizing all the chemical pollutants in wastewater, including both degradable and non-degradable ones. Subsequently, COD is always higher than BOD.

Even though a complete characterization of the wastewater effluent is always the best, in reality only few parameters are actually measured. Moreover, the deep description and analysis of all available parameters is beyond the scope of this work. For the purposes of this research only the most common parameters for non-toxic industrial wastewater will be briefly described in the following paragraphs, namely BOD, COD and ammoniacal nitrogen ( $\text{NH}_3\text{-N}$ ). Additional and deeply-detailed information can be found in literature (Rice, Baird and Eaton, 2017).

COD is considered a reliable parameter for characterizing industrial effluents. Moreover, in the majority of cases the measurement process does not require expensive chemicals. According to the general rule, the higher the COD value, the more difficult to treat the effluent. Thus, COD measurement becomes a key parameter when deciding the treatment method to be used. On the contrary, BOD measurement is a key parameter to decide whether the nature of the treatment to be used, either biological, chemical, or both. This, in fact, is indicated by the ratio BOD to COD.

Inorganic pollutants generally include heavy metals such as iron, copper, manganese, chromium, zinc, and lead. Additionally, it includes metal pollutants such as arsenic, chromium, and mercury, which can be potentially toxic. Similarly, they can include the presence of ammonia, a key issue for many industrial wastewater treatment methods.

A key parameter for inorganic characterization is the ammoniacal nitrogen ( $\text{NH}_3\text{-N}$ ). This parameter measures the amount of ammonia in wastewater, calculated based on the presence of nitrogen with the potential to transform into ammonia. Ammonia is a toxic pollutant that can both put human lives in danger and also threaten the equilibrium of natural water bodies (Manios, Stentiford and Millner, 2002; Ranade and Bhandari, 2014).

$\text{NH}_3\text{-N}$  removal can be carried out either by biological methods, physicochemical methods, or a combination of both. However, biological methods are usually not effective due to long time requirements with often unsatisfactory performances. The available effective physicochemical technologies for  $\text{NH}_3\text{-N}$  removal include adsorption, membrane filtration, ion exchange, among others, which are described in section 3.1.2.

In case of effective removal of wastewater pollutants with the exception of  $\text{NH}_3\text{-N}$ , the resulting effluent can be successfully used as nitrogenous fertilizer for agricultural applications. In fact, if complemented with phosphate, it further enhances its fertilizing properties (Ranade and Bhandari, 2014).

Summarizing, for the effective strategic design of the overall wastewater treatment, recycle, and reuse practices, it is of paramount importance the organic and inorganic characterization of the effluent, in addition to the correspondent chemical and toxicity analysis.

### *3.1.1.2. Nature of the Separation Methods*

The wastewater treatment (or “separation”) technologies involved in the different phases of the wastewater treatment can be classified by their nature. There are physical, biological, and chemical methods. Moreover, technologies are often a combination of them, such as physicochemical methods. In fact, chemical methods are commonly applied in a combination with physical processes, which is actually the definition of physicochemical methods. The two most important treatment methods are biological and physicochemical methods.

Physical methods are processes using physical properties and/or physical force to separate the pollutant elements from the water. Biological methods are based on degrading the pollutant components by means of microorganisms, bacteria, and other natural organisms. Chemical methods are the ones where the separation process, degradation, and/or removal of pollutant substances is performed by modifying the chemical properties of the effluent. Finally, physicochemical methods are the ones exploiting both physical and chemical properties of the components, chemical reactions, physicochemical interactions, and/or acting at a molecular scale, in order for the pollutant components to dissociate from water and/or degrade.

Physical methods include sand filtration, some membrane separations, and phase separators like oil/water separators (OWS), among others. Biological methods include constructed wetlands, aerobic, and anaerobic treatment, and Membrane Bioreactor (MBR)<sup>5</sup> technologies, among others. Chemical methods include oxidation, reduction, and neutralization, among others. Physicochemical methods include a wide variety of processes such as dissolved air flotation (DAF), coagulation/flocculation, cavitation, some membrane separations, evaporation and crystallization, incineration, oxidation processes, adsorption, ion exchange (IX), and continuous Electrodeionization (CEDI), among others. Further explanation of each one of the mentioned technologies can be found in section 3.1.2.

Among the physicochemical methods there are some separation processes employing both surface forces in addition to chemical and/or electrostatic attraction. These are charge-based separators based on neutralizing the charges present in the solution, appropriate for removing charged bodies and ionic compounds from wastewater. This is the case of coagulation/flocculation, adsorption, ion exchange, and some membrane separators (Ranade and Bhandari, 2014).

### *3.1.1.3. History and Growth of the Separation Methods*

Figure 11 shows research trends in the application of different separation processes on wastewater treatment, considering the number of publications made between 1970 and 2010.

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<sup>5</sup> Membrane Bioreactor (MBR) technology employs simultaneously physical methods (membrane) and biological treatments. For the following sections of this report it will be classified as a purely “biological” method.

The logarithmic scale of the vertical axis allows to graphically separate the technologies in two different zones.

On one hand, Zone I contains adsorption, biological, oxidation, membrane, coagulation, and ion exchange technologies. On the other hand, Zone II contains cavitation and extraction technologies.

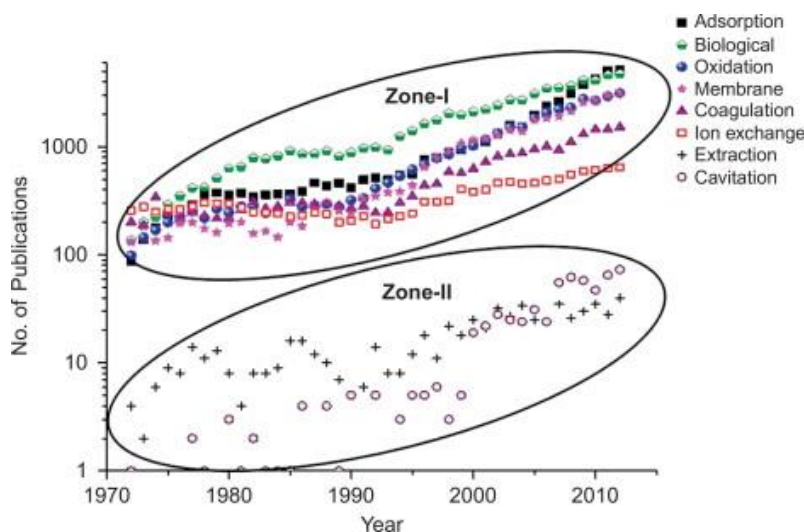


Figure 11. Research trends of various separation technologies. Source: Ranade & Bhandari (2014)

Zone I encompasses well-known and well-established methods for wastewater treatment, which has had continuous research interest both in application and development of the process. Zone II encompasses less common separation technologies for industrial wastewater treatment because of diverse drawbacks.

It is possible to notice that biological methods are the ones with the most research publications over the 40 years studied. Moreover, adsorption has gained notable importance in the first decade of the 2000s. Then, specific physicochemical methods such as oxidation and membrane separation have increased exponentially, at a comparable scale to the one of biological and adsorption technologies.

Even though cavitation is not a recently discovered method, previous to the year 2000 it had an unstable participation on wastewater treatment researches. Even though its participation has increased since then, it still has not gained a notable participation on wastewater treatment applications. In the case of extraction, for example, the main drawback is the selection of the extractant, This selection is characterized by being a challenging decision that can have costly repercussions during its operation and maintenance, in addition to the risk of polluting even more the wastewater to be treated (Ranade and Bhandari, 2014).

Membrane separation technologies have gained considerable interest in the academic world, adding several modifications and developments to this type of treatment over the years of

study. Figure 12 shows the research trends of membranes separation in wastewater treatment applications.

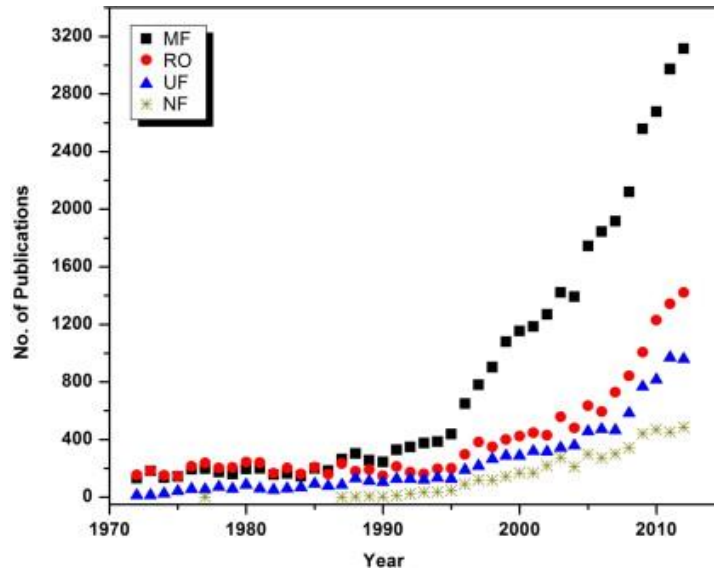


Figure 12. Research trends of membrane separation technologies. Source: Ranade & Bhandari (2014)

It is possible to notice that from 1990 there was an exponential increase of the academic interest on microfiltration (MF), which continued for the next 20 years. This can be explained by the fact this technology is used for removing suspended solids as well as larger molecules, thus making it an extremely flexible, adaptable, and scalable technology.

In addition, both reverse osmosis (RO) and ultrafiltration (UF) started gaining interest sharply after 2005. The former is known to be a crucial technology for effective water recycling, making it a key method for current sustainable practices (Ranade and Bhandari, 2014). This can explain the increased importance of this method, correlated with the increased environmental concerns for general sustainable development. On the contrary, by 2010 nanofiltration (NF) still had not gained a considerable interest comparable to the other membrane separation techniques.

Similarly to membrane processes, biological separation technologies have also gained considerable interest in the academic world. Figure 13 shows the research trends of biological separation processes in wastewater treatment applications.

It can be noticed a greater interest on anaerobic processes in comparison to aerobic ones. According to Ranade & Bhandari (2014) this can be explained by the “increased attention to utilization of waste as a source of energy”. Moreover, the gap between them has further increased over the years. This is related with the previously mentioned idea that the increased interest around a wastewater treatment method is connected with the increased concerns for a sustainable development. In addition, it can also be noticed that MBR technology has gained increased attention, especially after the year 2000.

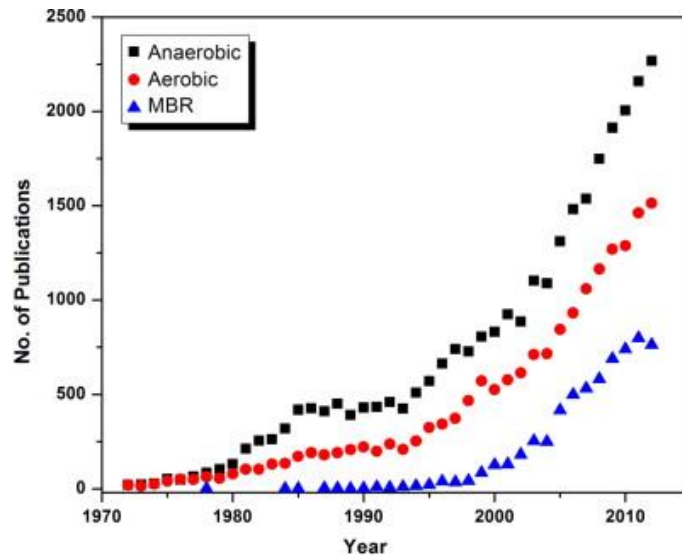


Figure 13. Research trends of biological separation technologies. Source: Ranade & Bhandari (2014)

Figure 14 shows the comparison between the two main wastewater treatments classified by its nature, namely biological and physicochemical methods. This comparison is made on the basis of number of publications (Ranade and Bhandari, 2014). It is possible to notice that based on their number of publications, physicochemical methods have posed a huge majority of contribution to wastewater treatment processes, in terms of application and interest.

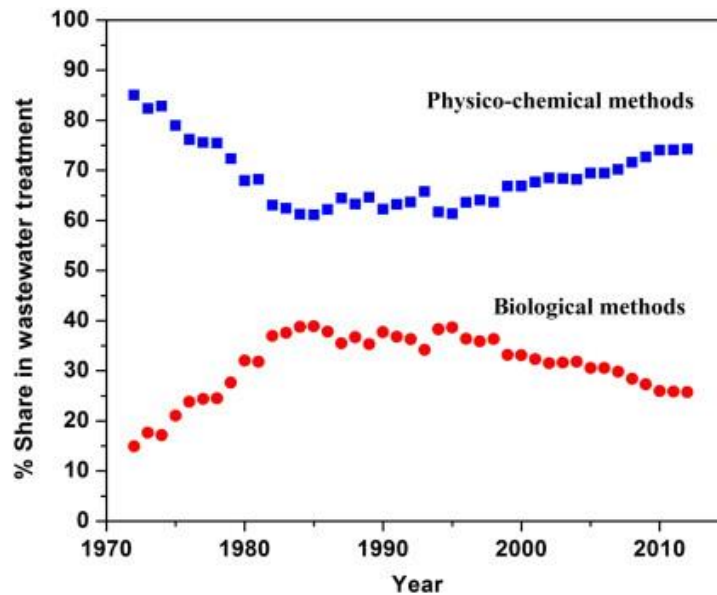


Figure 14. Share of publications on biological/physicochemical methods. Source: Ranade & Bhandari (2014)

By 1970 the difference was an order of magnitude in favour of physicochemical methods. Later, biological methods were able to notoriously increase their contribution prior to the year 1985,



when the ratio between biological and physicochemical methods was around 2:3. This was possible due to improved biological processes and operations. However, in 1995 and later years physicochemical methods regained strength, attributed mainly to the rise of refractory pollutants which are difficult to degrade by means of biological methods (Ranade and Bhandari, 2014)

#### *3.1.1.4. Phases of Industrial Wastewater Treatment Process*

The wastewater treatment process is generally clustered in phases, namely primary<sup>6</sup>, secondary, and tertiary treatments, based on the nature of the process and its outcome. Additionally, after the tertiary treatment there are two additional treatment processes, from now on the 4<sup>th</sup> and 5<sup>th</sup> phases.

It is important to notice that in most literature these two last stages of the treatment are contained into the tertiary treatment. Moreover, often they refer to the tertiary treatment as “tertiary treatment and polishing” or “tertiary and advanced treatment”. However, for the purposes of this work they will be separated as individual steps of the process, namely the 4<sup>th</sup> and 5<sup>th</sup> phases of the wastewater treatment.

In cases where there is a greater chance of human exposure to the water, or if for example an industrial application receiving the treated water requires a higher water quality, a higher treatment level is necessary. This also depends on the composition of the wastewater to be treated, the regulations to which the water stream is subjected, and any other constrain regarding the quality of water required. Moreover, depending on the nature of the effluent and the objectives to meet, one or more separation processes are employed for achieving the desired water quality for discharge, recycling or reuse (Ranade and Bhandari, 2014; EPA, 2018)

Generally, primary treatments are size-based separations using physical and physicochemical methods for basic clean-up. These treatment technologies include phase separators such as oil/water separators (OWS); dissolved air flotation (DAF); coagulation and flocculation; and other methods such as screening, grit removal, sedimentation.

Secondary treatments usually involve biological and/or physicochemical<sup>7</sup> methods capable of removing a great portion of organic compounds and suspended solids from wastewater (Ranade and Bhandari, 2014). These treatment technologies include chemical methods such as neutralization and stabilization; biological methods such as constructed wetlands, aerobic and anaerobic treatments, and membrane separation technologies such as membrane bioreactor

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<sup>6</sup> Primary treatment is also named in literature as “pre-treatment” or “preliminary treatment”

<sup>7</sup> Sometimes in literature the “secondary treatment” is referred to as “biological treatment”, for it mostly comprises biological methods. However, it often comprises additional non-biological methods, such as cavitation (physicochemical).

(MBR); and physicochemical methods such as cavitation. Low-grade water is achieved after secondary treatment.

Tertiary treatments usually involve physical methods of filtration of suspended pollutant particles inside the wastewater. These treatment technologies include sand filtration; and membrane filtration and separation processes such as microfiltration (MF) and ultrafiltration (UF).

The fourth phase of the wastewater treatment involve physicochemical methods with the only aim to remove salts and mineral remains from wastewater. Subsequently, the output of the optimal operation of this stage is demineralized water. These treatment technologies include membrane filtration and separation processes such as nanofiltration (NF) and reverse osmosis (RO); evaporation and crystallization; and incineration. Intermediate-grade water is achieved after the mineral removal phase.

The fifth phase of the wastewater treatment involve physicochemical methods. It is a polishing phase, with the only aim to refine the final output of the treated wastewater by removing remaining toxic and/or harmful organic pollutants to the desired level. The polishing stage consists on the removal of remaining organic compounds from wastewater. However, this concept might also be used as the treatment of residual compounds remaining on unit processes or end-user equipment downstream from a biological treatment.

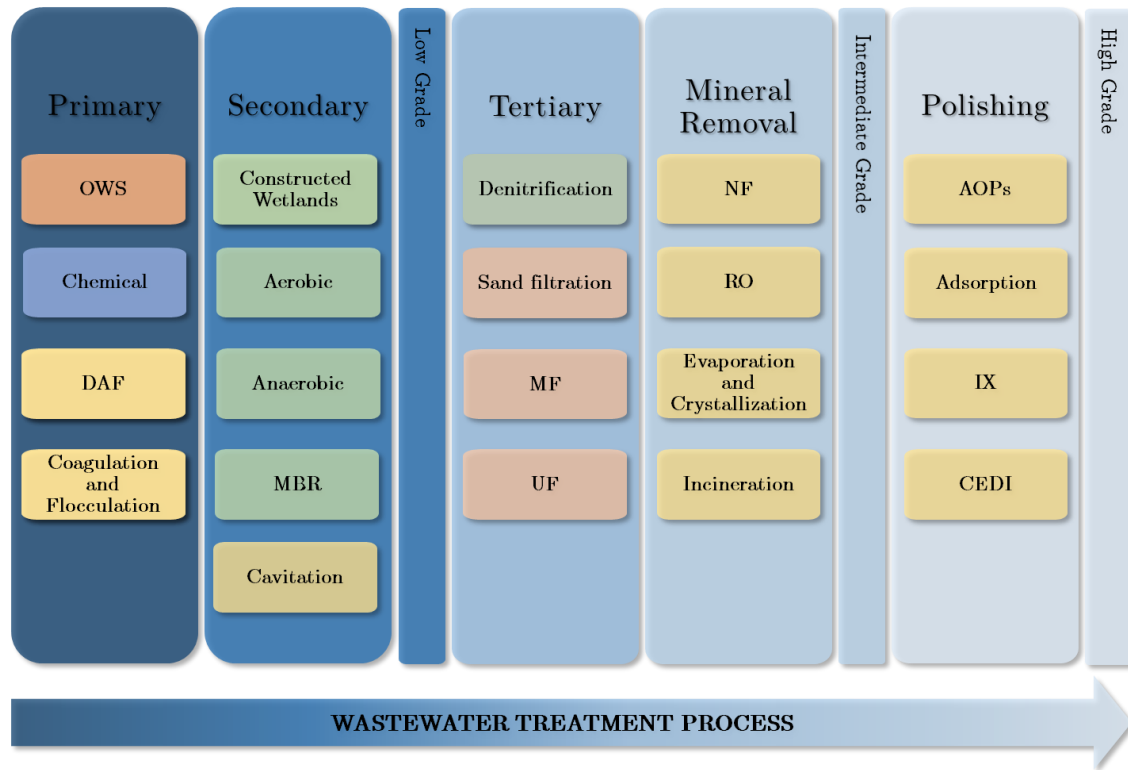
Usually, the organic pollutant compounds trying to be removed in the polishing step are benzene, toluene, and polycyclic aromatic hydrocarbons, among others. According to Ranade & Bhandari (2014) more than 99% removal can be achieved by the end of the wastewater treatment process.

This phase include physicochemical treatment technologies such as adsorption processes; advanced oxidation processes (AOPs) such as Fenton, wet air, ultraviolet (UV), ozone and chlorine dioxide oxidation; activated carbon (AC); ion exchange (IX) processes; and continuous electrodeionization (CEDI). Additionally, there are several niche technologies commercially available for polishing, such as extraction, steam stripping, and magnetic ion exchange. High-grade water is achieved after the polishing phase (Ranade and Bhandari, 2014; Cramwinckel *et al.*, 2017).

It is of paramount importance to state that the treatment process is often not a linear sequence of its phases, but rather a mixed procedure. The phases of the process are only a guide to structure the majority of treatment processes, but it does not represent all cases.

As an example, sometimes secondary treatment is omitted for certain industrial applications, skipping from the primary directly to the tertiary treatment. In other cases, for example, the primary phase is not necessary, thus the process starts directly from the secondary or even tertiary phase. Finally, sometimes the technologies applied are in different order, e.g. first using technologies from tertiary followed by one from the secondary phase.

Figure 15 shows the classification of the previously mentioned separation processes, according to both their nature and phase of the treatment they are usually applied in.



Note: Red: physical methods; blue: chemical methods; yellow: physicochemical methods; green: biological methods

Figure 15. Classification of separation methods according to their nature and phase.

### 3.1.1.5. Applications of the Outflow Effluent

The recommended uses of the various grades of wastewater depend on several factors such as the region it is used, the regulations it is subjected to, among other factors. However, it is possible to reduce the applications for treated wastewater (or recycled water) to certain suggested purposes, in function solely of its grade.

The main objective of primary treatments is to generate the minimum conditions for the operation of the following treatments in the process. Moreover, this stage aims to protect processes, materials, and equipment that are to be used in the following stages, in order to avoid process failure. Thus, the first stage is a pre-treatment process with the objective of preparing the water stream for the following stages. For example there is pH modifications (e.g. neutralization), and suspended solids removal through filtration and clarification, prior to sending the stream to secondary and tertiary treatment (Ranade and Bhandari, 2014).

Table 5. Suggested applications for different water grades. Source: Cramwinckel et al. (2017) and EPA (2018)

Grade of wastewater	Recommended usages	Focused applications
<b>Low grade</b>	Surface irrigation Non-food crop irrigation Restricted landscape impoundments Groundwater recharge of non-potable aquifer Recreational wetlands, wildlife habitat and stream augmentation Flushing Cleaning (vehicles, non-production floors, and similar) Dust control	Municipal applications
<b>Intermediate grade</b>	Industrial cooling, cleaning, and process water purposes Discharges to surface or sub-surface water bodies	Industrial applications
<b>High grade</b>	Boiler-feeding Demineralized water Condenser make-up water (water supplied for example to a steam boiler to compensate for evaporation and leakage losses) Landscape and golf course irrigation Food crop irrigation Unrestricted recreational impoundment Indirect potable reuse (e.g. groundwater recharge of potable aquifer and surface water reservoir augmentation)	Industrial and municipal applications

As stated by Ranade & Bhandari (2014) the primary treatment produce wastewaters that are not suitable for discharge, recycle, nor reuse. Moreover, the US Environmental Protection Agency, EPA (2018), emphasises that the usage of wastewater subjected only to primary treatments is firmly not recommended for any purpose. On the contrary, secondary, tertiary and the following treatment stages entail more advanced separation processes, which generate sufficiently treated water for at least some purposes, such as irrigation and landscape impoundments.

According to the model proposed previously, a low-grade water is achieved after secondary treatment. The suggested applications for low-grade water are surface irrigation; non-food crop irrigation; restricted landscape impoundments; groundwater recharge of non-potable aquifer; wetlands, wildlife habitat and stream augmentation; flushing; cleaning (vehicles, non-production floors, and similar); and dust control. Moreover, low-grade water recycling is mostly focused on municipal applications.

After tertiary treatment and mineral removal, an intermediate-grade water is achieved. The suggested usages for intermediate-grade water are mainly focused industrial uses, such as cooling, cleaning, and process water purposes. Additionally, authorities usually require that water discharged to surface or sub-surface water bodies are at least at intermediate grade. Thus, intermediate-grade water recycling is mostly focused on industrial applications.

After the polishing treatment, a high-grade water is achieved. The suggested industrial usages for high-grade water are boiler-feeding, demineralized water, condenser make-up water (e.g. water supplied to a steam boiler to compensate for evaporation or leakage losses). In addition, high-grade water can be used for landscape and golf course irrigation; food crop irrigation; unrestricted recreational impoundment; and indirect potable reuse such as groundwater recharge of potable aquifer and surface water reservoir augmentation (Cramwinckel *et al.*, 2017; EPA, 2018). Moreover, high-grade water recycling is focused on both industrial and municipal applications.

Table 5 shows the suggested applications for the different grades of water.

According to the treatment process followed by each industry there will be a clear resultant effluent with a defined quality and grade. This will be useful to characterize the effluent required by all types of industrial actors of the cases analysis. This is further developed in section 3.1.3.4. Finally, the treatment process will be used to classify the waterflows for the case studies in section 3.2.

### 3.1.2. Technologies and Methods for Wastewater Treatment

In the area of water and wastewater treatment there is a wide range of commercially available technologies. In fact, identifying all of them is beyond the scope of this work. Moreover, the technologies presented in the following section are not a complete list, nor do they apply to every situation. However, they are some of the most frequently used technologies in the sector of water and wastewater treatment, which are presented in the following section in a complete yet simple fashion.

#### *3.1.2.1. Phase separators: Oil/Water Separator (OWS)*

Phase separators, or Oil/Water Separators (OWS) are wastewater treatment technologies using gravity to split the mixtures of oil with water into their separate phases. The separation occurs due to the different densities between the different components of the mixture, which can be either oil and/or other components, even solid residues.

Usually, OWS are efficient when removing either free oil or larger droplets of emulsified oil (greater than 60  $\mu\text{m}$ ). In addition, and depending on the design of the separator, it may also be possible to remove large solid particles from the mixture.

The most common OWS process consists on oil accumulating at the top of the unit, while solids settle to the bottom of the separator. The oil from the top has to be periodically removed, and depending on its level of contamination, it can be recovered or recycled back into the

process. Settled solids at the bottom are removed from the separator unit. Additionally, chemicals can be added to augment the separation effect and increase the removal efficiency.

The main advantages of OWSs are their simplicity of operation and composition, since they are usually constituted by few moving parts, and the reduced oil load on downstream processes. The main disadvantages of phase separators are their large space requirements (e.g. for the American Petroleum Institute type separator) and the lack of capacity to remove dissolved oil and fine colloidal suspensions (Cramwinckel *et al.*, 2017).

### 3.1.2.2. *Chemical Methods*

According to the UN Statistical Division (1997), chemical treatment refers to the methods used to “effect the complete breakdown of hazardous waste into non-toxic gases or, more frequently, to modify the chemical properties of the waste”.

Applied to wastewater it refers to all types of wastewater treatment where the separation process, degradation, and/or removal of pollutant substances is performed by modifying the chemical properties of the effluent. These contain treatments such as oxidation, reduction, and neutralization of the wastewater.

#### *Neutralization*

Neutralization is a chemical method used as a pre-treatment system before many biological, chemical, and physical treatments. In fact, many of these processes are actually pH dependant. Thus, through the process of neutralization the pH of the solution is adjusted, in order to increase the efficiency of the following processes. Additionally, the pH of discharging effluents often need to be neutralized in order to comply with the regulatory requirements of their context.

This method consists on altering the pH of water through the addition of an acid or base. The choice of the acid or base, the amount, and the process of addition depend on both the target pH and the process requirements. One of the key steps to take prior to the neutralization of any industrial wastewater are the determination of the components causing the alkalinity or acidity of the effluent. This is usually done in laboratory experiments by analysing the titration curves of the effluent.

Moreover, according to Goel *et al.* (2005) the process of neutralization is considered as effective if it complies with three conditions. For the purposes of this work, the third condition is the most important, i.e. that the neutralized wastewater has to have no effect on biological matter, with the purpose of not affecting the following treatments.

### 3.1.2.3. *Dissolved Air Flotation (DAF)*

Dissolved Air Flotation (DAF) is a wastewater treatment technology aimed to clarify water by removing suspended matter like oil or solids. The process consists in dissolving pressurized air in the wastewater to be treated, and subsequently releasing the air at atmospheric pressure in a flotation tank. The released pressurized air forms bubbles that adhere to the suspended matter surface, causing the suspended matter to float to the surface where is removed by a skimming device.

Usually the DAF treatment is complemented with coagulant and/or flocculant elements in order to gather the colloidal particles in bigger clusters, thus making the removal phase easier (Cramwinckel *et al.*, 2017). The addition of coagulant elements gather together bigger clusters of suspended matter, facilitating the adherence of the pressurized bubbles around its surface and enhancing the efficiency and effectiveness of the overall process.

This technology is widely used for treating industrial wastewater effluents, especially for industries containing oil refineries, chemical and petrochemical plants, natural gas processing plants, paper mills, general wastewater treatment plants, and similar.

The main advantage of DAF wastewater treatment processes is that they are able to remove residual oil and fine suspended solids in a single unit operation (usually with the help of coagulants). On the contrary, the main disadvantage is that in order to reach an optimal operation, it requires special efforts to control the water saturated with air, which is not an easy task (Cramwinckel *et al.*, 2017).

### 3.1.2.4. *Coagulation and Flocculation*

Suspended solids in wastewater could be present in the form of a colloidal suspension that will settle very slowly or not at all because the colloidal particles carry surface electrical charges that mutually repel each other. Coagulation is a process aiming to destabilize these suspended particles. This is achieved by adding a coagulation chemical (salts) to water, which reduce, neutralize, or invert the electrical repulsion between particles (Ranade and Bhandari, 2014; Cramwinckel *et al.*, 2017).

With the use of coagulant and flocculant chemicals, the destabilized particles cluster together to form large particles, which are easier to separate from the water by gravity. Thus, coagulation is a charge-based separation method.

One method to convert soluble ions into insoluble salts is the chemical precipitation, which is based in changing the water properties such as pH, temperature, and the chemical reagent concentration. Afterwards, the insoluble salts form flocs and precipitate, which can also be removed by gravity in clarifiers. An example of chemical precipitation is the removal of calcium

ions by forming calcium carbonate at a high pH by using lime or soda-ash (Cramwinckel *et al.*, 2017).

Coagulants can be broadly classified as inorganic and organic. The most commonly used coagulants are shown in Table 6.

Table 6. Example of common coagulants. Source: Ranade and Bhandari (2014 and Cramwinckel *et al.* (2017)

	Inorganic coagulants	Organic coagulants
<b>Commonly used coagulants</b>	Aluminium salts Ferric and ferrous salts Lime	Cationic polymers Anionic and non-ionic polymers
<b>Advantages</b>	Increased cost/effectiveness ratio Adaptable for multiple wastewaters	Near-zero sludge generation Increased efficiency
<b>Disadvantages</b>	High volume of generated sludge Requires more treatment time Sensitivity to pH	Higher costs

Coagulation is usually effective in removing colour, especially from wastewater containing dissolved solids and charged matter. There is a notoriously improved clarity of water, especially compared to the systems where there are no chemicals involved. However, they are often characterized for employing high dosages of chemicals, depending on the water chemistry.

The usage of inorganic coagulants generates high volumes of sludge from chemical reactions, resulting in high cost for sludge disposal. Moreover, inorganic coagulants generally produce smaller flocs that require more time to settle and precipitate. A third disadvantage of inorganic coagulants is that most of them are pH sensitive, thus narrowing the range of pH they are actually effective (Ranade and Bhandari, 2014; Cramwinckel *et al.*, 2017).

Some of the disadvantages of inorganic coagulants can be overcome by using either organic or a formulation of both organic and inorganic coagulants. This is because organic coagulants have several advantages compared to inorganic ones.

Many organic coagulants are known to achieve a near-zero sludge production, almost erasing the sludge disposal problems of inorganic coagulants and reducing significantly the costs of treatment. In addition, organic coagulants such as polydiallyldimethylammonium (PolyDDA) chloride can enhance the coagulation efficiency in some cases. Thus, the formulation of inorganic and organic coagulants can provide a better techno-economically feasible operation in wastewater treatment (Ranade and Bhandari, 2014).

Even though coagulation is one of the most common methods in water and wastewater treatment, this method by itself is generally not a complete solution, and it usually requires additional complementary treatments for its overall effectiveness.



### 3.1.2.5. *Constructed Wetlands*

Constructed wetlands are man-made wetlands created with the intention of treating either wastewater or stormwater runoff. They are artificially engineered systems to treat and remove contaminants from water bodies, by using the natural functions of vegetation, soil, and organisms. Depending on the characteristics of the wastewater to be treated, as well as the properties of the wetland, this system might require additional pre-treatment and/or post-treatment for the effective removal of the pollutants.

Artificial wetlands can be designed to emulate the natural features of wetlands by acting as biofilters and/or removing sediments and pollutants from water, such as heavy metals or other elements. According to Cramwinckel et al. (2017) there are two main types of constructed wetlands, namely subsurface flow wetlands and surface flow wetlands.

The main advantage of constructed wetlands are the fact that they are based on building sustainable green infrastructure, they have a small environmental footprint, and no chemical treatment is involved in the process. On the contrary, their main disadvantage is the large space required for building the necessary infrastructure (Cramwinckel et al., 2017).

### 3.1.2.6. *Aerobic and Anaerobic Treatments*

#### *Aerobic Treatment*

Aerobic biological treatment is a commonly practiced methodology which is simple in its concept and operation. It is a process used to remove the organic fraction from wastewater. This process is based on the biological assimilation of organic matter by the biomass, being its primary aim a high degree of substrate conversion. In addition to the removal of organic substances, the system can be also adapted to enable the removal of nitrogen and phosphorus (Ranade and Bhandari, 2014; Cramwinckel et al., 2017).

In any biological wastewater treatment there are organisms involved, which are invisible to the human eye. Depending on their structures and cellular components, they can be subdivided into bacteria, fungi, plants, and viruses. The bacterial cells can be said to represent “biochemical reactors”, for they oxidize organic compounds by using oxygen. These microorganisms also perform the role of sorbents, binding both organic substances and heavy metals, and subsequently helping their decomposition and/or removal.

According to Ranade & Bhandari (2014) there are certain conditions and aspects to carefully consider for the efficiency of operation of any aerobic process. Among them are the right amount of nutrients concentration, a sufficient oxygen supply for the bacteria, optimal

environmental conditions (e.g. pH and temperature), and an overall appropriate design of the treatment.

Aerobic systems are commonly used when the COD concentration is below 2.000 – 3.000 mg/L. This limit depends on the biodegradability of the effluent and the cost of aeration.

One of the most common aerobic treatments is the conventional activated sludge (CAS) process, dating from as long as 100 years ago. Figure 16 shows an example diagram of the CAS process. This process includes the following steps:

1. Wastewater aeration in the presence of a microbial suspension.
2. Solid-liquid separation following aeration.
3. Discharge of clarified effluent.
4. Disposal of excess biomass and return of remaining biomass to the aeration tank.

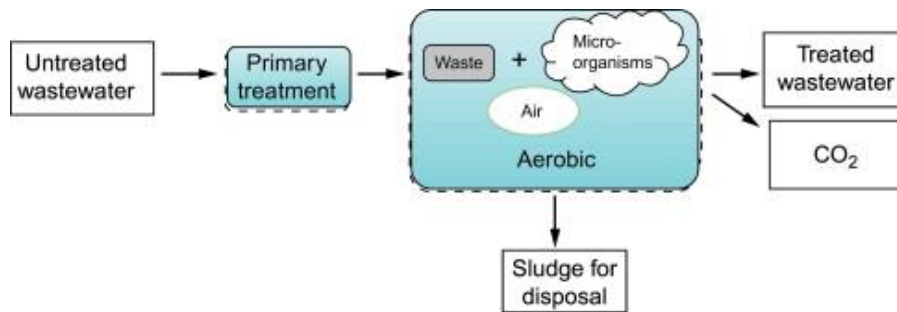


Figure 16. Process diagram of aerobic biological wastewater treatment. Conventional activated sludge (CAS) process. Source: Ranade and Bhandari (2014)

In addition, there are several examples of process variations currently being practiced in different industries. For example, there is the substitution of the infrastructure processing the treatment, such as replacing the re-aeration tanks or contact tanks by aeration tanks. Other process variations include changing the mixing regime, the loading rate, and the flow scheme, which affect the efficiency of oxygen transfer, the kinetics of the process, and the quality of biodegradation, among other factors (Ranade and Bhandari, 2014).

### *Anaerobic Treatment*

Anaerobic biological treatment is primarily used for treating concentrated organic wastewater. This treatment has gained substantial importance due to several factors such as an increase on environmental protection legislation, increasing energy costs, and issues regarding the sludge disposal of aerobic treatments (Ranade and Bhandari, 2014; Cramwinckel *et al.*, 2017).

The anaerobic wastewater treatment process is basically using anaerobic microorganisms to produce a degradation and fermentation of the organic material. As a result of this degradation, the anaerobic sludge generates biogas as a by-product via hydrolysis and acidification (Ranade

and Bhandari, 2014; Cramwinckel *et al.*, 2017). Figure 17 displays a conventional process diagram flow of an anaerobic biological wastewater treatment.

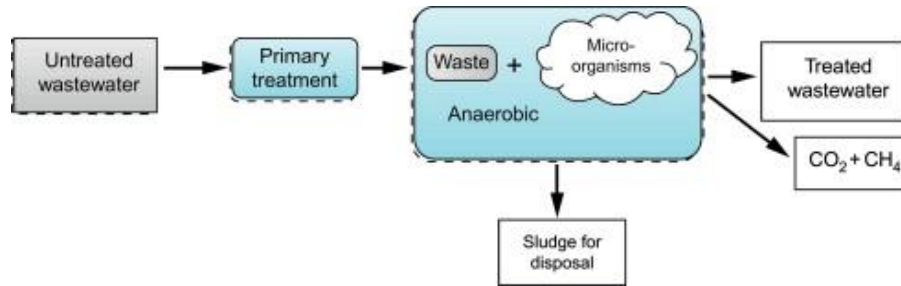


Figure 17. Process diagram of an anaerobic biological wastewater treatment. Source: Ranade and Bhandari (2014)

The biogas produced by the anaerobic treatment is a by-product of the process, and it is used to meet the energy requirements. In addition, the anaerobic fermentation produces methane, alcohols, ketones, organic acids, hydrogen sulphide, and traces of nitrogen, carbon dioxide, and hydrogen.

The efficient and effective operation of the anaerobic treatment depends on the growth of anaerobic microorganisms. This growth is a function of several factors such as the residence time<sup>8</sup>, temperature, redox potential, pH, and nutrient composition, among others. As an example, in the process of anaerobic methane generation at least three groups of microorganisms are involved in the degradation of organic molecules, namely acidogenic bacteria, acetogenic bacteria, and methanogenic bacteria.

First, acidogenesis consists on the degrading performed by the acidogenic bacteria via hydrolysis. This is where biopolymers are hydrolytically degraded to obtain soluble monomers. In second place there is the acetogenesis, where acetogenic bacteria produces acid, and there is a simultaneous generation of hydrogen and carbon dioxide. In third place there is the methanogenesis, where the methanogenic bacteria starts the formation of methane through the reaction of hydrogen with carbon dioxide. In some cases, it might be required a final polishing step after the anaerobic treatment in order to remove the residual fractions of COD, nitrogen and/or phosphorus. This post-treatment can be, for example, an aerobic biological treatment.

A commonly used mode of operation consists in a two-stage operation, namely stage I for acidogenesis and acidogenic bacteria, and stage II for methanogenesis and methanogenic bacteria. Even though a single-stage operation requires a lower initial investment, according to Ranade & Bhandari (2014) the “current trend in anaerobic treatments for highly contaminated wastewater is towards a two-stage process design”.

<sup>8</sup> In this context, the *residence time* refers to a measure of how much time the microorganisms are contained in their growth environment

There are several methods to retain and recycle the biomass that serves as a catalyst for the anaerobic process. The aim of these methods is to decouple the residence times of the liquid substrate and the biomass, and they focus either on internal biomass retention or on external separation and recycling. The main methods are listed in Table 7.

Table 7. Methods for biomass retention and recycling for anaerobic processes. Source: Ranade and Bhandari (2014)

Biomass retention (internal)				Biomass separation and recycling (external)	
Sedimentation by pellet formation	Filtration	Immobilization by adsorption	Immobilization by inclusion or covalent bonding	Sedimentation by chemical or physical separation	Flotation
UASB	Membrane anaerobic reaction system; Rotor-fermenter	Fixed-bed reactor; Anaerobic film reactor; Fluidized-bed reactor; Hybrid concepts		Anaerobic contact process; Centrifugation	

### *Advantages and Disadvantages of Aerobic and Anaerobic Treatments*

The main advantage of biological methods is the low-cost removal of COD compared with other physical and chemical processes. The main disadvantage is the need for effluent polishing, either for aerobic or anaerobic processes.

The main advantages of aerobic treatments are, firstly, that is a simple and known method that has been implemented over a long time. Secondly, the oxidative degradation of carbon substrates provide the energy for microorganisms to propagate and act as the biocatalysts, without requiring energy from other sources. On the contrary, a major disadvantage of aerobic treatments is the considerable amount of biomass (sludge) produced and its subsequent disposal issues (Ranade and Bhandari, 2014; Cramwinckel *et al.*, 2017).

The main advantage of anaerobic in comparison to aerobic treatments is the considerable decrease in the excess biomass formation. According to Ranade & Bhandari (2014), in processes with the same organic load there is as much as 10 times reduction in the sludge produced by anaerobic compared to aerobic processes.

Regarding the process and its effectiveness, there are other advantages of anaerobic treatments such as avoiding the cost and energy-intensive oxygen transfer (no large aerators required), increased bioreactor performances due to the absence of limitations imposed by oxygen transfer, effective removal of heavy-metals through reductive precipitation rather than oxidative precipitation, and reuse of biogas by-product as a source of energy.

The main disadvantage of anaerobic treatments is its increased complexity compared to aerobic methods. The complete degradation chain is intricate and requires a complex design and mixing of various microorganisms. Moreover, the kinetics of the individual steps of the process is still insufficiently understood to this day, because of the complexity of the substrate mixtures and the lack of reliable data. The latter is explained by the fact that data collection is a challenging and time-consuming activity. Subsequently, the anaerobic wastewater treatment has not been studied in a systematic way yet, and currently there is a lack of adequate information for a properly justified design.

### *Combination of Aerobic and Anaerobic Operations*

Each one of the aerobic and anaerobic wastewater treatments have advantages and disadvantages, which make each of them more suitable for certain applications. On one hand aerobic treatment is more appropriate for low-strength wastewaters. On the other hand, anaerobic treatment is more appropriate for high-strength wastewater (Ranade and Bhandari, 2014). In order to exploit the advantages of each type of treatment, there are several applications combining both aerobic and anaerobic treatments.

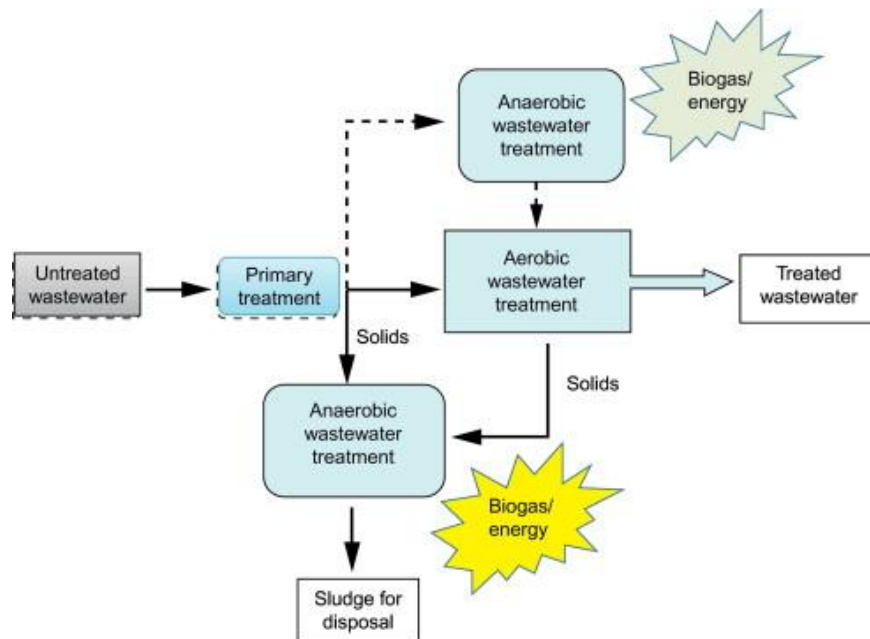


Figure 18. Sequential aerobic/anaerobic process for wastewater treatment. Source: Ranade and Bhandari (2014)

One of the ways to exploit the advantage of both types of treatment is combining them sequentially. This allows to recycle the sludge (external separation of the biomass), which results in a better water quality and a decreased overall sludge formation. In addition, according to Ranade & Bhandari (2014) a sequential operation can help to reduce considerably the amount of nitrogen and the odour issue.

This sequencing methods are especially useful when the wastewater to be treated is composed by a fraction that can only be degraded aerobically, and another that can only be degraded anaerobically. Figure 18 shows an example scheme of the sequential operation of aerobic and anaerobic processes.

In order to improve the efficiency, most designs propose a sequential combination of anaerobic, then aerobic or anaerobic, then aerobic, and finally anaerobic treatments. As Pant & Adholeya (2007) show in their article, such is the case of the typical commercial example of distillery wastewater. This process begins with an anaerobic treatment to produce biogas, followed by an aerobic treatment for meeting wastewater standards, then using an anaerobic process to treat high-strength wastewater, and finally treating low-strength wastewater with an aerobic process (Ranade and Bhandari, 2014).

### 3.1.2.7. *Cavitation*

According to Ranade & Bhandari (2014) many of the conventional wastewater treatment methods use large quantities of chemicals for their process, whose subsequent disposal represents a considerable issue. The cavitation method represents a relatively recent wastewater treatment that is able to remove certain pollutant components of wastewater without the need of large quantities of chemicals.

Refractory compounds are pollutants composed by heat-resistant materials. Subsequently, they are resistant to decomposition by heat, pressure, and/or chemical attacks. In fact, they are organic pollutants in wastewater that are difficult to remove and degrade by using conventional methods of chemical and biological treatment. These are specially present in dye, pigment, and textile wastewaters (Allaby and Allaby, 1991; Ranade and Bhandari, 2014).

Cavitation rises as a solution for degrading these difficult pollutants. It is a recently developed wastewater treatment method consisting in generating extreme conditions by forming, growing, and then collapsing cavities inside the liquid. In fact, these collapsing cavities are able to break down pollutants and organic molecules, representing an optimal solution for degrading refractory compounds that are difficult to remove otherwise.

The phenomenon of cavitation is in fact an event where rapid changes of pressure in a fluid generate the collapsing of the cavities formed in the process, which can generate considerable shock waves. The cavitation process releases significant amounts of energy, while at the same time generating oxidizing agents in the wastewater. Thus, the collapsing cavities generate strong oxidizing conditions due to the production of hydroxyl radicals (OH).

This generates the phenomenon of hydrodynamic and/or sonochemical cavitation, which are successfully employed for destroying the pollutant organic compounds of the mixture. In addition, the impacts of cavitation on organic compounds can be further increased if complemented with other oxidation processes (Ranade and Bhandari, 2014).

Hydrodynamic cavitation refers to the physical effect of cavitation in a liquid, where there is formation of small vapor-filled cavities due to a local pressure decrease followed by their collapse due to the sudden pressure increase. Sonochemical cavitation refers to the chemical effect of cavitation in a liquid, resulting in the initiation or enhancement of the chemical activity in the solution. Hydrodynamic cavitation destabilizes mechanically the organic compounds. Sonochemical cavitation generates a chemical destabilization on the organic compound by a series of radical reactions with the complex organic matter, leading to the final destruction of the pollutants and decolorization of the wastewater (Suslick, 1990; Ranade and Bhandari, 2014; Dular *et al.*, 2018).

The cavitation technology not only offers an effective industrial wastewater treatment by itself, but it can also be complemented and integrated successfully with other conventional methods in order to achieve a complete, techno-economical solution. In fact, there are many hybrid designs where conventional technologies are complemented with cavitation, such as oxidation (AOPs), coagulation, adsorption, ion exchange (IX), membranes, and biological treatments.

The main advantages of cavitation are that it is usually highly effective, especially in treating wastewaters with refractory pollutants and/or having unusually high COD. Additionally, cavitation can be easily combined with other treatments to increase its effectiveness. Moreover, this method can offer substantial economic benefits in comparison to some conventional physicochemical methods.

#### *3.1.2.8. Denitrification*

Wastewater contains nitrogen either in the form of dissolved nitrogen (N) or as suspended solids (SS). Nitrogen can be removed either by biological or physicochemical methods. The method of *denitrification* is the process of removing nitrogen by means of biological methods. Among the physicochemical methods to remove nitrogen there are, for example, chlorination, ammonium stripping, and ion exchange (IX).

Through denitrification it is possible to oxidize ammoniacal nitrogen ( $\text{NH}_3\text{-N}$ ), subsequently reducing the nitrogen content from wastewater. Moreover, the denitrification process contains two main phases. The first phase is the nitrification, where ammonia is oxidized into nitrate under aerobic conditions. The second phase is the actual denitrification, where nitrate is reduced into nitrogen gas under anaerobic conditions (Mori *et al.*, 2003).

#### *3.1.2.9. Sand Filtration*

Sand filtration is a process aimed at removing suspended particles from water. This removal considers a number of sequential mechanisms including straining, flocculation, sedimentation, and surface capture of the pollutants through a sand filter.

Sand filters require periodical backwash to remove accumulated solids, activity which is performed either by water only or by a combination of water and air. The main applications for sand filters are cooling water production, drinking-water preparation, and pre-filtration preceding active carbon (AC) treatments and membranes.

According to Cramwinckel et al. (2017) there are two main types of sand filters used for industrial wastewater treatment, namely continuous filters and batch (or discontinuous) filters. They are mostly subjected to upward flowing and downward flowing, respectively.

On one hand, in continuous filters the polluted sand is removed, rinsed, and then reused continuously without interrupting the filtration process. On the other hand, batch filters are taken out of operation to backwash them, interrupting the filtration operation (Cramwinckel *et al.*, 2017).

The main advantages of the sand filtration technology are that it is cheap and simple in operation. On the contrary, the main disadvantage of is the highly concentrated backwash water discharge and corresponding issues for its disposal.

#### *3.1.2.10. Membrane Filtration and Separation Processes (MF, UF, NF, RO)*

The processes of membrane filtration and separation are based on perm selectivity, which is determined by differences on the transport rate of various components through the membrane. The permeation rate is defined by the structure of the membrane, the size of the permeating component, the properties of the membrane material and permeating component – such as its chemical nature and its electrical charge – and, finally, on the driving force produced by the chemical and/or electrochemical potential gradients.

Membrane-based processes are increasingly being used in wastewater treatment as a method to obtain a high-quality final effluent. In fact, According to Ranade & Bhandari (2014) they are currently being used on a large scale in three different areas:

1. Applications in which the use of membranes is technically feasible, but where they have to compete economically with conventional separation processes. This is the case, for instance, of seawater desalination, where membranes compete with processes like distillation and biological treatment.
2. Applications where alternative techniques are available, but membranes offer a clear advantage, either technical or commercial. This is the case, for instance, of the production and separation of certain food products.
3. Applications where there are not alternative techniques to membrane processes. This is the case, for instance, of some drug delivery systems.



There are different membrane structures and driving forces applications, which have resulted in several different membrane processes that are commercially available. These processes are clustered in conventional processes and recent developments, as shown in Table 8.

Table 8. Conventional and recent technologies for membrane separation processes. Source: Ranade and Bhandari (2014)

	Conventional membrane separation	Recent developments on membrane separation
<b>Membrane filtration and separation technologies</b>	Microfiltration (MF) Ultrafiltration (UF) Nano-filtration (NF) Reverse osmosis (RO)	Membrane Bioreactor (MBR) Pervaporation Membrane distillation Dialysis/electrodialysis Emulsion liquid membranes Hybrid membrane system

Some membrane separation applications include gaseous separations such as O<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CH<sub>4</sub>, Olefin/N<sub>2</sub>, and also liquid separations such as desalination and other applications in the beverage industry. In particular for wastewater treatment, conventional membrane processes have established niche areas for themselves (Ranade and Bhandari, 2014).

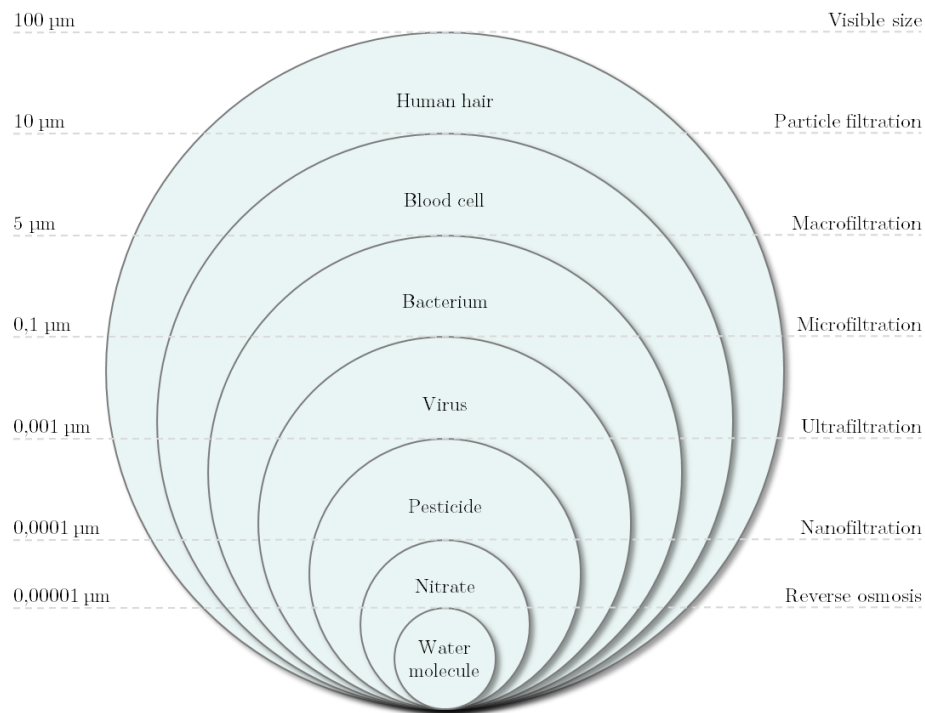


Figure 19. Application areas of filtration techniques according to their scale. Source: Adapted from District Heating Association (Dansk Fjernvarme) (2015)

Regarding the conventional membrane processes, it is common that MF membranes are used for the removal of large size species, while RO membranes are used to obtain highly pure water. Moreover, MF and UF are commonly used as pre-treatment for NF and RO. Additionally, NF and RO are usually followed by a polishing step (e.g. Ion Exchange<sup>9</sup>) (Ranade and Bhandari, 2014; Cramwinckel *et al.*, 2017). Figure 19 shows the different application areas of various filtration techniques depending on their scale.

According to Ranade & Bhandari (2014), membrane processes in comparison with other procedures are generally more energy efficient, easier to operate, and produce higher-quality products. In addition, their environmental impact is relatively low, since they do not require the usage of hazardous chemicals in the processes requiring a discharge or disposal. On the contrary, their main disadvantages are the uncertainty on their long-term reliability, their (common) requirement of extensive pre-treatment, their high risk of destruction due to mechanical fragility, and the high total cost of the process.

Regarding the cost disadvantage it has to be noticed that even though the energy efficiency is high and thus the energy cost is low, this is only a fraction of the overall costs. Other costs of the process include investments such as the cost of the membranes, the cost of additional equipment, pre and post-treatment procedures costs, among others.

### *Ultrafiltration (UF)*

UF membrane processes are based on using pressure to force a liquid through a semipermeable membrane. This process is mainly used for removing suspended solids from water and wastewater, usually as a pre-treatment of NF and RO. However, it can also be used for other treatment processes such as a final filtration stage for deionized water, for eliminating microorganisms in drinking water, for pre-treating demineralized water, among others (Ranade and Bhandari, 2014; Cramwinckel *et al.*, 2017).

UF membranes retain suspended solids and solutes of high molecular weight, while letting pass water and low molecular weight solutes. Moreover, UF membranes are ideal for the removal of colloids, proteins, bacteria, pyrogens, and macromolecules from water. The removal of these solutes from the wastewater will produce a reject stream usually representing 3 – 10% of the inlet flow, which usually have a high concentration of total suspended solids (TSS).

There are several types of UF membranes commercially available, which are aimed to different applications. For example, there are hollow-fibre UF membranes commonly recommended for wastewater with high TSS and low concentration of solvents, oils, and grease. There are also ceramic UF membranes that can be used for streams containing high levels of solvents, oil, and grease.

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<sup>9</sup> Polishing steps such as Ion Exchange and other processes are described in the following sections

The main advantage of UF membrane filtration is that it provides a constantly high quality in terms of removal of particles and microbes. The main disadvantage of these membranes are the high initial capital investment (CAPEX), the inefficiency imposed by fouling<sup>10</sup>, the costs of cleaning and maintaining the membrane surface, and the high cost of replacement of the membrane, among others (Cramwinckel *et al.*, 2017).

### *Nanofiltration (NF)*

Just like UF, NF membrane processes are based on a pressure-driven filtration method. These membranes are typically used after previous pre-treatments like MF or UF. In comparison to RO membranes, they have larger pore size and a higher salt permeability. Their required feed pressure is generally lower compared to RO membranes.

NF processes are mainly used for removing large divalent and trivalent ions, and, in addition, it can be customized for selective ion removal. It can also be used for water softening, removing heavy metals, pesticides and reducing the total dissolved solids.

The main advantages of NF systems are the lower feed pressure required (and thus lower power requirement) than RO systems, and the fact it does not require the addition of sodium ions when used for water softening (unlike base ion exchangers). The main disadvantages of these membranes are the high initial capital investment (CAPEX), its sensitivity to chemical oxidizers, and their extensive pre-treatment requirements (usually MF and UF) (Cramwinckel *et al.*, 2017)

### *Reverse Osmosis (RO)*

RO membrane processes are based on using semi-permeable membranes for wastewater treatment and/or purification. This process requires high feed pressure to push water through the membrane to overcome the osmotic pressure. Feed pressures range from 10 – 60 bar depending on the feed total dissolved solids (TDS), the membrane degree of permeability, and the temperature (lower pressure required for higher water temperature).

During the operation water passes through the RO membrane to produce a purified stream called “permeate”. What remains stuck in the membrane is called the “concentrate”, which is composed by dissolved ions and organics, and it is swept away in the membrane reject stream.

The water-production efficiency of RO membranes is measured as the ratio between what exists the membrane system as permeate and the inlet flow (or feed). This efficiency will

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<sup>10</sup> Fouling is defined as the accumulation of unwanted material on solid surfaces (in this case the membrane surface) with the result of decreasing the efficiency in its functions

mainly depend on variables such as the operating pressure limits of the membrane, the total dissolved solids (TDS) of the feed, and the water feed hardness, among others.

In terms of production efficiency, RO membranes are typically capable of achieving 75 – 90% efficiency when treating groundwater and urban wastewater. For wastewater recycling applications the feed conditions are commonly more challenging, and then the production efficiencies tend to be lower. However, according to Cramwinckel et al. “RO membranes are capable achieving more than 99% removal of dissolved salts from solution”.

The main advantages of RO membrane filtration are that it provides a high removal efficiency of dissolved salts, and it requires a minimum amount of chemicals involved in the process. The main disadvantage of these membranes are the high initial capital investment (CAPEX), inefficiency imposed by fouling, and the costs of cleaning and maintaining the membrane surface (specially disposing high concentration of TDS) (Cramwinckel *et al.*, 2017).

### *MBR*

Recent developments of membrane processes have placed commercially available alternatives to conventional processes. These alternatives offer various wastewater treatment advantages and disadvantages, which can be adapted to the needs of the user. An example of these developments are MBR systems.

MBR systems are the combination of membrane filtration processes with a biological wastewater treatment. These processes have a sequential combination of treatments such as MF or UF membranes followed by an activated-sludge process. Subsequently, it aims to treat wastewater in two stages, treating water biologically while simultaneously separating its biomass physically (Judd and Judd, 2011; Ranade and Bhandari, 2014).

MBR processes are able to remove organic chemicals from the polluted effluents of industrial sources. They do so by utilizing immobilized cells attached to microporous hollow fibres, forming a membrane-attached biofilm-microporous membrane bioreactor (MMBR) for biodegradation applications (Ranade and Bhandari, 2014).

In addition, different engineering designs of MBR membranes are available for different applications. In fact, compared with other types of membrane separations, the engineering principles underlying MBR are mature enough to ensure an acceptable reliability. As stated by Ranade & Bhandari (2014), this reliability in addition with the technological support of the MBR systems are “commercially available to meet the existing and the developing demand”. In fact, these systems are widely used to treat municipal and industrial wastewater. Moreover, they are used to treat a wide range of grades of wastewater and are believed to be installed in over 1.000 sites in Asia (Judd and Judd, 2011; Ranade and Bhandari, 2014).

### 3.1.2.11. *Evaporation and Crystallization*

Evaporation and crystallization are equilibrium-based, thermal separation processes aimed at concentrating wastewater and recovering its clean distillate. The concentrate of the wastewater can be either treated off-site (e.g. through incineration), or crystalized. Moreover, crystallization refers to the process of further concentrating and dewatering the concentrate to finally obtain a solid by-product, namely the “crystallization”. Depending on the process chemistry and operating parameters, the solid by-product may consist on elements that could be almost fully recovered and reused, such as pure salts.

These processes are usually not energy efficient. Subsequently, they are often complemented with pre-treatment processes with high energy efficiency to decrease the load on them. The energy required for the process can be supplied in the form of steam, electricity, or warm water.

The two most common types of evaporators and crystallizers used for wastewater treatment are the falling film and forced circulation units. For enhancing the efficiency of the crystallization water recovery, this process is commonly performed using zero-liquid discharge systems that do not generate aqueous waste.

The main advantages of the evaporation and crystallization processes are the possibility to achieve a zero-liquid discharge generation, the high purity of the distillate obtained which is suitable for reuse, and the potential recovery of valuable salts. On the contrary, the main disadvantages of this methods are the high costs, both as initial capital investments (CAPEX) and also operating costs (due to the elevated energy costs). In addition, often the presence of volatile compounds in the distillate may require separate post-treatment. Moreover, the concentrate or solid waste must be disposed correctly (Cramwinckel *et al.*, 2017).

### 3.1.2.12. *Incineration*

The concept of toxic organics in wastewater refers to synthetic organic compounds such as pesticides, herbicides, and chlorinated hydrocarbons. Wastewater with this type of pollutants is generated when the effluent have contact with manufacturers, people, industries, or other water streams in interaction with these chemicals. Toxic organics are difficult to remove and degrade, and thus they usually remain on wastewater for long periods of time. According to Ranade & Bhandari (2014), incineration raises as the preferable option for eliminating them.

Incineration is a destructive method for wastewater treatment employed to eliminate these toxic organic materials from water. By default, this process raises as an option only when the pollutants are difficult to degrade by biological methods or when physicochemical methods are not economically feasible. In such cases, destructive methods such as thermal incineration and catalytic incineration are the only techno-economically feasible option.

The process of incineration consists on oxidizing the organic material along with some of the inorganic material present in wastewater, by means of subjecting them to extremely high temperatures in the presence of oxygen. Generally, the toxic materials such as pesticides and chlorinated carbons must be subjected to 980 to 1.500 °C. As stated previously, evaporation processes are a suitable complement for enhancing the incineration process performance, separating the concentrated toxic compounds from water. As stated by Ranade & Bhandari (2014), it is always required the treatment of the flue gas by-product, in addition with the proper reuse or disposal of the slag and ash produced during the process.

The main advantage of this method is that it is able to remove highly toxic compounds from the wastewater. The main disadvantages of this process are that it is a highly energy intensive treatment, and it requires the proper technological infrastructure to treat such challenging streams of wastewater. In fact, it is common that the pollutant concentrations and the economics of the process do not justify the size of the incinerator. Moreover, incineration processes often involves a complex design, and involves different chemistry and engineering compared with conventional treatment methods.

Finally, incineration processes should be considered only if there is not any alternative to remove the toxic organic materials from wastewater, and if there is a sufficient load of organics and inorganics for burning.

### 3.1.2.13. *Advanced Oxidation Processes (AOP)*

Advanced Oxidation Processes (AOPs) are used widely in water and wastewater treatment field, especially for refractory pollutants that are difficult to remove with conventional physicochemical methods such as highly toxic and non-biodegradable wastes.

AOPs refer to chemical procedures operating through the generation of hydroxyl radicals (OH) and other oxidant species, with the aim to degrade and remove organic and/or inorganic compounds in wastewater through oxidation reactions. Moreover, the hydroxyl radicals attack the organic molecules by reducing them to carbon dioxide and water, either by abstracting hydrogen atoms from them or by addition to the double bond (Ranade and Bhandari, 2014; Cramwinckel *et al.*, 2017).

There are several methods for generating hydroxyl radicals to generate chemical oxidation reactions. In fact, there is a significant variation in the configuration of catalysts and reactors for the chemical processes applying AOP methods for wastewater treatment. Some of them are Fenton oxidation, wet air oxidation, ozone-based applications, ultraviolet-based applications, chlorine-dioxide-based oxidation, or a combination of some of them.

The main advantages of AOPs are that they require a reduced amount of space in comparison with other chemical and physicochemical wastewater treatment methods. In addition, they often require a lower initial capital investment (CAPEX) compared to other physicochemical

and biological processes. Furthermore, the oxidation products of the treatment are often less complex and can be treated by conventional biological methods.

The main disadvantages of AOPs are that there are often organic compounds which are not affected by hydroxyl radicals, such as acetic, maleic, and oxalic acids, acetone, and chloride derivatives such as chloroform. In such cases the application of AOPs might not be effective nor appropriate. Furthermore, AOPs generally have high operating costs (Ranade and Bhandari, 2014).

### *Fenton Oxidation*

Fenton oxidation is an emerging technology for advanced chemical oxidation wastewater treatment processes. It is commonly used for the removal of highly toxic and non-biodegradable wastes. According to Ranade & Bhandari (2014), this technology is successfully used for industrial wastewater treatment, and specifically effective for black olive and mineral oil wastewaters.

The AOP of the Fenton oxidation consists on the oxidative decomposition and transformation of organic substrates performed by ferrous ion ( $\text{Fe}^{2+}$ ) and hydrogen peroxide or oxygenated water ( $\text{H}_2\text{O}_2$ ) and, known as “Fenton’s Reagent”. The hydroxyl radicals ( $\text{OH}$ ) are produced by Fenton’s Reagent at an acidic pH, environment where they attack the organic molecules, followed by their mineralization into carbon dioxide and water. According to Ranade & Bhandari (2014), the optimal ratio of ferrous ion to oxygenated water is 1:10, where the efficiency of the treatment is maximized.

### *Wet Air Oxidation*

Wet air oxidation is another technology for advanced chemical oxidation wastewater treatment processes. It is commonly used for the removal of toxic, non-degradable and/or slowly degradable substances. According to Ranade & Bhandari (2014), it is successfully used for wastewater with highly concentrated contaminants.

### *Ultraviolet-based Applications (UV, UV/ $\text{H}_2\text{O}_2$ )*

Ultra-violet based technologies are chemical-free methods for wastewater treatment and disinfection. As stated by Cramwinckel et al. (2017), these technologies are “widely used for a number of applications to produce ultra-pure water, ranging from pharmaceuticals to cosmetics, electronics, and general industries”.

Even though they are chemical-free technologies, they are considered chemical processes since they generate chemical reactions having an effect over the pollutant compounds of the wastewater being treated. In fact, these processes are based on increasing the reactivity of the pollutant compounds with the hydroxyl radicals (OH) present in the substance (Cramwinckel *et al.*, 2017).

UV-based applications are mainly focused on removing the organic material from wastewater through emitting irradiation with an artificial UV light source, usually performed by low or medium pressure mercury vapor lamps. As a result, photolysis<sup>11</sup> occurs through the direct absorption of the emitted light (Cramwinckel *et al.*, 2017; The Editors of Encyclopaedia Britannica, 2018).

During the photolysis process, the reactivity of the organic compounds with the hydroxyl radicals is causally related to the structural characteristics of the former, i.e. its aromaticity, its carbon bonding, and its functional groups. On the contrary, inorganic substances usually increase the inefficiencies and delay the removal of organic components. These inorganic components are usually carbonates, bicarbonates, and chlorides.

In order to increase the efficiency of these processes, it is frequent to combine UV photolysis processes with hydrogen peroxide molecules added to the substance, increasing the efficiency of the oxidation process. This aims to generate additional hydrogen atoms from the hydrogen peroxide dissociation, which produces chemical reactions that increase the reduction of the pollutant organic compounds (Cramwinckel *et al.*, 2017).

The main advantage of UV-based AOPs is the minimal chemical addition required for the wastewater treatment. On the contrary, the main disadvantage of this technology is the maintenance and replacement of lamps, which suffer fouling and then require periodical cleaning, and additionally lose efficiency over time.

### *Ozone-based Applications ( $O_3$ , $O_3/UV$ , $O_3/H_2O_2$ , $O_3/H_2O_2/UV$ )*

AOPs based on ozone oxidation are useful to remove organic compounds from wastewater. In addition, they can also be effective in disinfecting and removing colour, odour, and taste from wastewater. Moreover, ozonation has been found to be also effective on the decolorization of textile wastewater.

Ozone ( $O_3$ ) is a powerful oxidant with the capacity to destroy resistant pathogens. Therefore, ozone-based applications are extensively used in wastewater treatment for disinfection purposes. In fact, ozone molecules can react with many organic compounds, particularly those

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<sup>11</sup> Photolysis is defined as a chemical process by which molecules are broken down into smaller units through the absorption of light (The Editors of Encyclopaedia Britannica, 2018).



unsaturated, containing aromatic rings, or heteroatoms (Ranade and Bhandari, 2014; Cramwinckel *et al.*, 2017).

O<sub>3</sub> may react with organic matter through two different mechanisms. The first mechanism consists in O<sub>3</sub> decomposing water to form hydroxyl radicals (OH), thus inducing indirect oxidation. The second mechanism consists on O<sub>3</sub> reacting selectively with some particular functional groups<sup>12</sup> of organic molecules through an electrophilic mechanism called ozonolysis.

As stated previously, different AOP mechanisms can be performed simultaneously or sequentially to increase the efficiency of wastewater treatment. This is a common practice for ozone-based technologies, where the simultaneous addition of H<sub>2</sub>O<sub>2</sub> and/or UV irradiation increase the process efficiency by accelerating the O<sub>3</sub> decomposition and promoting the OH formation. This causes a decreased reaction time in comparison to the process where only one of the AOP methods is applied. The removal efficiency of combined AOP processes is affected by several operation conditions such as the O<sub>3</sub> dose, the contact time, the pH, the H<sub>2</sub>O<sub>2</sub> concentration, and the UV dose.

The main advantage of ozone-based technologies are the disinfection function provided by this technology, attacking both bacteria and viruses, and also the ability to degrade a wide range of organic pollutants. The main disadvantage of this treatment regards the safety issues posed by the method due to the aggressive nature of the chemicals involved in the process (Cramwinckel *et al.*, 2017).

### *Chlorine Dioxide-based Applications*

Chlorine-dioxide-based AOP uses chlorine dioxide solutions to treat wastewater. This compound is used in many industrial wastewater applications as a biocide, including cooling towers, process water, and food processing. In addition, chlorine dioxide can be produced on-site by chemical reactions involving sodium chlorite, hypochlorite, and hydrochloric acid.

The main advantages of this method are that chlorine dioxide is less corrosive than chlorine gas, the compound is not negatively affected by pH, it does not decrease its efficacy over time, and it can be produced on-site. The main disadvantage of chlorine-dioxide-based AOPs is the use and handling of aggressive chemicals when producing the compound for the treatment (Cramwinckel *et al.*, 2017).

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<sup>12</sup> According to Cramwinckel *et al.* (2017) the specific functional groups with which O<sub>3</sub> reacts selectively through ozonolysis are the double bonds and aromatic rings of organic molecules.

### 3.1.2.14. Adsorption

It is first important to define the difference between adsorption and absorption. On one hand, adsorption is defined as the accumulation of the molecular species at the surface of a substance. On the other hand, absorption is defined as the assimilation of molecular species throughout the bulk of the solid or liquid, rather than just remaining in its surface.

Moreover, both are sorption phenomena, but the key difference between them is that adsorption is a superficial phenomenon where each phase remains separated, while in absorption there is mass and volume transfer between both phases (Curiosoando, 2017). The water treatment discussed below refers to the former phenomenon.

According to Ranade & Bhandari (2014), “solid adsorbents have been used since ancient times for various separation/purification applications”. Moreover, they currently find applications in water and wastewater treatment, but also in other industries.

The adsorption is a sorption phenomenon where the substance A (adsorbate), which is present in a fluid phase, is trapped to a surface of a substance B (adsorbent), which is present in a solid phase. There is no mass transfer between the two phases, but rather the adsorbate creates a superficial layer over the adsorbent (Curiosoando, 2017).

This effect is an exothermic phenomenon occurring spontaneously until the adsorbent is saturated. Since it is a superficial phenomenon, the adsorption capacity depends mainly on the exposed surface of the adsorbent.

The adsorption process as a wastewater treatment consists on adding adsorbent substances to water, which adsorb organic and/or inorganic pollutant substances from the wastewater for their subsequent removal. Moreover, wastewater treatment by adsorption is commonly classified as a physicochemical method to treat wastewater, which involves selective attachment of specific molecules in the surface of the adsorbent.

The attraction of a specific molecule is believed to be due to the action of surface forces responsible for the molecule-surface interaction. Moreover, adsorption can be produced for physical phenomena, chemical phenomena, and/or electrostatic attraction.

When adsorption is produced purely by physical phenomena it is defined as physisorption. This is the case, for example, when the adsorbate is attached to the surface of the adsorbent because of the van der Waals forces. When adsorption is produced purely by chemical phenomena it is defined as chemisorption. This is the case, for example, when the adsorbate is attached to the surface of the adsorbent because of the formation of a chemical bond between them (i.e. exchanging electrons between them). When adsorption is produced purely by electrostatic phenomena it is only because both adsorbate and adsorbent are subjected to an attractive forces because of their two unlike electric charges (Ranade and Bhandari, 2014; Curiosoando, 2017)

All physisorption, chemisorption and electrostatic attraction effects work simultaneously and play an important role on the overall adsorption process. The contribution of each one varies according to the nature of the adsorbent (if its synthetic or derived from biomass), the nature of the substrate and surface molecules, the presence of acidic or basic groups on surfaces, and the presence of metal ions, among other factors.

The main applications of adsorption in wastewater treatment are related to odour, colour, acids, metals, and refractory pollutants removal. In order for this treatment to be efficient it is of paramount importance to analyse the specific interactions of pollutants with the surface of the adsorbent substances. For this it is necessary to characterize the effluents of the process, such as the nature of the pollutant substances, its concentration, and the properties of the adsorbent material (Ranade and Bhandari, 2014; Curiosoando, 2017).

Moreover, the performance of the treatment is directly affected by the properties of the adsorbent (specific surface area, porosity, surface polarity, physical shape, among others), the properties of the adsorbate (molecular structure, charge, hydrophobicity, among others), and the properties of the aqueous matrix (pH, temperature, presence of other species in the solution, among others). Therefore, all these parameters must be taken into account when designing the appropriate wastewater treatment for the desired applications (Ranade and Bhandari, 2014; Cramwinckel *et al.*, 2017; Curiosoando, 2017)

In addition, the modification of existing materials and the development and characterization of new materials is a big and current scope of study, with the final aim of recovering valuable components and mitigating environmental concerns about this type of wastewater treatment.

There is a considerable amount of available adsorbents in the market. According to Ranade & Bhandari (2014), the proper selection of the type of adsorbent is usually made based on laboratory analysis and previous experiences. These authors classify adsorbents in two major clusters, as shown in Table 9.

Table 9. Common inorganic and organic adsorbents. Source: Ranade & Bhandari (2014)

	Inorganic adsorbents	Organic adsorbents
<b>Commonly used adsorbents</b>	Zeolites (A, X, Y, ZSM-5, silicalite, ALPO) Oxides (Silica, alumina)	Activated carbon (AC) Polymeric adsorbents Ion exchange resins Biomass-derived adsorbents

Even though the type of adsorbents is small, there is a huge amount of variations of these products commercially available, with difference in their performance, their surface and/or pore properties, their functionalities, and other characteristics. According to Curiosoando (2017), some of the most used adsorbents are activated carbon (organic), oxides like silica or alumina (inorganic), and zeolites (inorganic). Moreover, the selection and design procedure of the adsorbent is similar to that of the ion exchange, discussed in the following sections.

Most of the commercially available adsorbents are distributed in a microcrystalline structure, in order to increase its surface per unit of volume. As an example, activated carbon (AC) is available in surfaces around 1.200 m<sup>2</sup> per gram of product (Curiosoando, 2017).

### *Activated Carbon (AC) Adsorption*

According to Cramwinckel et al. (2017), the AC adsorption is “a well-established process for the removal of organics from wastewater given carbon’s strong affinity to hydrophobic organic compounds even at low concentrations”. Organic pollutants – in addition to other organic substances present in the wastewater – are adsorbed onto the carbon particles, which can be present in several forms such as powder (PAC), granules (GAC), molecular sieves, and carbon fibre.

The adsorption by AC is a process that has been widely used for wastewater treatment, either by itself or associated with other treatment processes such as coagulation and flocculation, membrane filtration, among others.

The main advantages of AC adsorption is the high efficiency of removal of low molecular weight hydrophobic organic compounds. In contrast, its main challenge has to do with the need to replace the activated carbon and thus requiring new sets of adsorbent periodically (Ranade and Bhandari, 2014; Cramwinckel *et al.*, 2017; Curiosoando, 2017).

#### *3.1.2.15. Ion Exchange (IX)*

Ion exchange (IX) is the reversible interchange of ions between a solid, namely the ion exchange resin, and a liquid. It involves counter ion displacement from the resin phase and electrostatic interaction between ionic functional groups.

The conventional ion exchange process depends upon the metathetical exchange of ionic species and the capacity of the resin to exchange ions. According to Ranade & Bhandari (2014) the capacity of the ion exchange resin is a key parameter in the design of the wastewater treatment process.

Even though the use of weak base ion exchange resins is not in accordance with conventional ion exchange mechanisms, it is the optimal type of resin for wastewater treatment applications. These types of resins are able to remove both organic and acidic ionic species, subsequently reducing the COD content greatly. IX resins are typically made from insoluble polymers.

IX technology is commercially used for treating wastewater with different objectives, such as softening water by capturing multivalent cations (e.g. calcium and magnesium capture), specific ion removal applications (e.g. boron removal), and for full demineralization of dilute solutions, where all dissolved inorganic solids are removed from the wastewater. For this last

treatment two different types of resins are used, each one used in order to remove cations and anions, respectively.

Ion exchange media that is saturated – meaning it has all of its capacity used – must be regenerated. In fact, this regeneration is achieved by using a concentrated solution of salt, acid, or base chemicals, and it implies an operation downtime. As stated by Cramwinckel et al. (2017), the “choice of the regeneration chemicals depends on the type of resin used and the type of ions to be removed from the ion exchange resin (Ranade and Bhandari, 2014).

In the case of acid removal, the mechanism consists on the protonation of ionogenic species on the weak base resins by the proton of the acid ( $H^+$ ), followed by the addition of anion to the exchange site through electrostatic interaction (Bhandari, Juvekar and Patwardhan, 1992a, 1992b, 1993; Bhandari, Yonemoto and Juvekar, 2000; Ranade and Bhandari, 2014).

In this case, the regeneration of the resin is done by using base to reverse the reaction. The treatment with a base regenerates the resin in its original free base form. However, the removal of non-ionic and/or organic substances takes place mostly in the surface interaction with the polymer and does not involve ionic interactions as such. In the cation exchange process the typical practice is that ammoniacal nitrogen is removed. In this case, the regeneration of the resin is done by using acid to reverse this reaction.

The design of the ion exchange process requires the appropriate combination of cation and anion exchange resins, for the efficient removal of salts, ionic compounds, and organics, with the final aim of reducing the COD levels. To achieve this, it is necessary the selection of suitable resins for obtaining a high operating capacity while at the same time achieving ease in the regeneration process. Additionally, a high operating capacity results in a lower resin requirement, and easier regeneration implies a lower regeneration consumption and minimizing the waste production.

Finally, according to the model proposed by Ranade & Bhandari (2014) the design of the IX treatment requires a four-step process to achieve an efficient wastewater treatment. The first step involves the appropriate selection of the ion exchange resin. In fact, not all resins are appropriate for any application. The selection of the resin must be related to the defined wastewater treatment objectives, which can be salt, ionic species and/or organics removal, among others. The second step refers to the characterization of the selected resins in terms of capacity, size, and pore size. All of these characteristics will define the pressure drop and the kinetics perspective in the final design.

The third step regards ion exchange breakthrough studies in wastewater treatment, referred by the authors as a key parameter in plant operation. Moreover, the breakthrough curve gives important information regarding the operation of the technology, specifically on the capacity, the potential fouling, and finally the suitability of the resin to be used in the process. The fourth and final step refers to the regeneration studies for the selected resins to be used.

The main advantages of IX-based wastewater treatments are the high percentage of water recovery for wastewater with low TDS concentration, in addition to producing high quality demineralized water and/or ultra-pure water. The main disadvantages are the safety issues and complexity of storing and handling the regenerated chemicals, together with the highly concentrated waste produced by regeneration, which requires disposal efforts to be made (Cramwinckel *et al.*, 2017).

### 3.1.2.16. *Continuous Electro-Deionization (CEDI)*

Continuous Electro-Deionization (CEDI) is a wastewater treatment technology mixing ion exchange resins, ion-selective membranes, and direct current, with the final objective to remove ionized species from water. In addition, CEDI systems reduce the main limitation of ion exchange resins, that is, the release of ions due to the need to change or regenerate the ion exchange resin beds. Subsequently, CEDI systems for wastewater treatment are a self-regenerating and chemical-free technology providing a consistent flow of highly pure deionized water.

This wastewater treatment technology usually consist on a number of cells operating in parallel. Ion-selective membranes allow positive ions to gather around the negative electrode and negative ions to do so around the positive electrode. Additionally, pre-treatment methods such as Reverse Osmosis (RO) are performed prior to CEDI in order to ensure the CEDI stack is not overloaded with highly concentrated salts (Cramwinckel *et al.*, 2017; Evoqua, 2019). Subsequently, CEDI systems separate positive and negative ions from wastewater by employing electromagnetic attraction through direct current.

The main advantages of the CEDI wastewater treatment are that it does not involve chemicals in its operation, and also it does not require an operational downtime for resin regeneration (unlike purely ion exchange technologies). The main disadvantages are its high sensitivity to organics and salt concentration, and that it usually requires an additional complementary pre-treatment for its effective operation, such as Reverse Osmosis (RO) (Cramwinckel *et al.*, 2017).

### 3.1.3. Wastewater Treatment, Recycle, and Reuse by Industrial Sector

Wastewater treatment, reuse, and recycling practices are especially critical for sectors generating considerable volumes of wastewater. However, not all industries are the best suit for wastewater reuse and recycling, nor its wastewater treatment have a noticeable impact. This section aims to identify which are these industrial sectors and how can they be defined.

It is of paramount importance to note the difference between the potential of wastewater reuse and recycling, and the impact of wastewater treatment. For the purposes of this work, the potential and the impact of these practices will be defined as follows.

The potential refers to the feasibility to reuse or recycle wastewater. This feasibility can be explained, for example, because the pollutants concentration is low and/or are easy to remove, because large wastewater volumes produced allow to exploit economies of scale, or any other reason helping the viability of these practices. Reuse and recycle practices are classified as high-potential when wastewater treatment is facilitated due to high produced volumes of wastewater and/or characterized by low concentrations of pollutants. Low potential for reuse and recycle are the opposite situation.

Moreover, the potential for industrial wastewater reuse and recycling is a qualitative assessment of industries considering both their wastewater volume generated and its pollutants concentration, from a very general perspective. The explanation of this potential for some water-intensive industries is developed in the section 3.1.3.1.

On the contrary, the impact refers to the elevated consequences of treating industrial wastewater. Cases with high impact refer to situations where wastewater treatment can be highly beneficial and/or is critical to avoid undesired consequences. Treatments are classified as high impact when an appropriate wastewater treatment could avoid significant health hazard situations, remove highly toxic pollutants, and/or be easily implemented. Low impact treatments are the opposite situation.

Moreover, the impact of industrial wastewater treatment is also a qualitative assessment, but rather focused on its consequences. The explanation of this impact for some water-intensive industries is developed in section 3.1.3.2. Additionally, section 3.1.3.3 presents a brief analysis of a proposed model that gathers both the potential and impact of wastewater treatment, reuse, and recycling.

Finally, different industries have different water quality requirements for their purposes. Subsequently, the technologies and the overall treatment process changes depending on the industry. Some industries require low-grade water, thus only performing primary and/or secondary treatment to wastewater. Others require intermediate or high-grade water, thus requiring an advanced process phase to be reached. Section 3.1.3.4 presents a brief analysis on the diverse treatment processes for different industries, which is the base of the analysis of IS cases of section 3.2.

### 3.1.3.1. *Potential for Wastewater Reuse and Recycling for Various Industrial Sectors*

The potential for industrial water reuse and recycling varies greatly across different industries, and even also inside the same industry. Different industries use a wide variety of water effluents for different purposes. Moreover, even inside the same industry there are different processing units generating waste with a broad range of diverse characteristics.

In fact, Industrial water recycling is governed by different factors such as availability of water, characteristics of the effluent, possibility to recover products from the waste treatment, and the possibility of expansion in the processing units. The latter refers to the relation between effluent volume and pollutant concentration (Panigrahi and Sharma, 2014; Ranade and Bhandari, 2014).

A high volume of wastewater with a low pollutant concentration has the most potential for recycling. On the contrary, low volumes of wastewater with highly concentrated pollutants are more difficult to deal with (Panigrahi and Sharma, 2014). Table 10 shows the wastewater reuse and recycling potential for selected industries, based on these governing factors.

*Table 10. Wastewater reuse and recycling potential for selected industries. Source: Visvanathan and Asano, (2001)*

<b>Low potential</b>	<b>Medium potential</b>	<b>High potential</b>
Explosive	Distillery	Chemical
Paint manufacturing	Food and beverages	Fertilizer
Pesticide	Glass and steel	Oil refining
Rubber	Textile	Petroleum
		Pulp and paper

#### *Petroleum Refining, Petrochemical, and Bulk Chemicals*

Process industries are often characterized by being water intensive industries. Industries like refineries, petrochemical plants, and bulk chemical plants are usually characterized by containing various sources of wastewater, such as desalter effluents, sour water, tank bottom draws, spent caustic, among others. Thus, waterflows inside these process industries form a large network of effluent streams to deal with. Many of these effluents, in fact, are reused and recycled (IPIECA, 2010; Panigrahi and Sharma, 2014)

As an example, many industries are using mathematical modelling to improve the sour water stripping system performance, through changes in its operating conditions and process structure. This allows to decrease the pollutant concentration of the effluents, among other things (such as decreasing water consumption). Thus, through mathematical modelling they are able to achieve an effluent with a low concentration of pollutants



Summarizing, these industries are characterized for requiring high volumes of water for its processes. Additionally, it is possible to decrease the concentration of pollutants from wastewater. Thus, these industries have a high potential for reuse and recycling industrial wastewater.

### *Power Plants (Thermal and Nuclear), Coal Handling, and Other Utilities*

Power plants are one of the largest users of freshwater globally. The major water pollutants from power plants are dissolved solids in cooling water, boiler blowdown, coal drainage, and radioactive material from nuclear power plants (Panigrahi and Sharma, 2014).

Many companies from this industry uses mathematical modelling and online advanced control technology to improve the water reuse and recycling potential. This reduces the water, energy, and coal consumption, while at the same time minimizing the wastewater discharge costs.

Finally, this industry is characterized by requiring high volumes of water, characterized by containing a wide range of concentration of pollutants. Then, the evaluation of high, medium, or low potential for wastewater reuse and recycling will depend on each industrial process the water is used for, defined by its own context.

### *Pulp and Paper*

According to Panigrahi & Sharma (2014) “the paper-making process is one of the most water-intensive industrial production processes”. After the paper constituents are in sludge-shape, it would not be possible to achieve a constituent structure without the physical properties of water.

Additionally, water is unavoidable required for processing natural raw materials such as wood, cellulose vegetable, and fibres, which are the base for fabricating paper. Furthermore, the recycling process of wastepaper is also a water-intensive process. Thus, the pulp and paper industry is characterized by large volumes of water.

As a result, large volumes of water becomes polluted due to the process involved in the industry, involving the water contact with raw materials, by-products, and industrial residues. However, the pollutants are often characterized by being in a low concentration, thus giving this industry a high potential for water reuse and recycling.

### Textiles

Depending on the raw materials used, the textile industry can be classified in three categories, namely cotton, woollen, and synthetic fibres. Overall, the textile industry is characterized by

requiring large quantities of water, and also producing large volumes of wastewater from dyeing and finishing processes (Panigrahi and Sharma, 2014).

The wastewater from dyeing units is habitually characterized by having colour, containing reactive chemicals, and additional non-degrading or slowly degrading materials. The chemicals present are often complex components and/or diverse aerosols. Additionally, given the wide variety of process steps this wastewater usually contains complex mixtures of organic and inorganic materials. Thus, textile wastewater is usually characterized by having concentrated pollutants, with high concentrations of COD and BOD.

Thus, being an industry requiring large quantities of water it could be classified as an industry with high potential for wastewater reuse and recycling. However, the high concentration of pollutants, and thus the complexity on its treatment, makes the industry have a medium potential industry.

### *Food, Beverage and Starch Industry*

Water in the food and beverages industry is used for many purposes. Some of them are transportation, cooling and boiling purposes, conditioning of raw materials, as an ingredient, and as a cleaning agent. Moreover, this industry is characterized by requiring huge amounts of water.

These industries are characterized by requiring high quality of water for their purposes for sanitary reasons. In fact, any water used in this industry containing the slightest organic or bacteriological pollution can imply a serious public health issue. Moreover, most waste from agro-food plants contain high organic and bacteriological pollutants, which often contaminate industrial processes wastewater.

As a result, most of the reused and recycled wastewater coming from this industry is not destined to be used in the same process. Usually process wastewater can be desalinated, and organics can be removed, thus fulfilling water requirements either to be destined for other processes in the same industry, or directly to another industry.

The starch industry is characterized by wastewaters usually polluted by multiple contaminants such as TOC, TDS and TSS. This industry often requires considerable amounts of demineralized and freshwater for its processes, resulting in substantial generation of wastewater.

In conclusion, the food, beverage, and starch industries are characterized by requiring huge volumes of water, and quite strict water quality for their processes. Even though they often produce medium to highly concentrated wastewater, the pollutants are usually organics and/or salts not difficult to degrade and remove. Thus, these industries have a medium potential for wastewater reuse and recycling.

### 3.1.3.2. *Impact of Wastewater Treatment for Various Industrial Sectors*

Industrial sectors characterized by their considerable impact of their wastewater treatment are few. For example, this is the case of all industries related with metal processing, where wastewater polluted by metal compounds can pose significant health hazards to society. Another example of high-impact sectors are the dyes and textiles industries, characterized by wastewater with high contents of organics, toxic pollutants, and colour issues. The last example are food processing industries, characterized by wastewaters that can be easily treated. Table 11 shows the wastewater treatment impact for selected industries, based on these governing factors.

*Table 11. Wastewater treatment impact for selected industries.*

<b>Low impact</b>	<b>High impact</b>
Electricity generation	Chemicals
Machinery	Dyeing
Pulp and paper	Food & beverages
	Mining
	Steel
	Textiles

#### *Metal Processing and Related Industries: Removal of Metals*

Heavy metals are naturally occurring elements present in several domestic, agricultural, medial, technological, and industrial applications. Their toxicity depends on several factors including the dose, the route of exposure, and chemical species. Furthermore, several metallic elements such as copper (Cu), nickel (Ni), chromium (Cr), lead (Pb), mercury (Hg), arsenic (As), and cadmium (Cd), are characterized by their high degree of toxicity and chronic toxicity. These metallic elements are known to induce multiple organ damage at low levels of exposure, damaging human's mental ability, in addition to being considered as human carcinogens (Tchounwou *et al.*, 2012; Ranade and Bhandari, 2014).

Many metallic elements are currently used for different industrial purposes. This poses a great threat for water effluents related to these industries. Moreover, metal degradation and removal from industrial wastewater effluents requires the greatest importance, due to their great significance on public health.

In order to remove metals from wastewater effluents there are several physicochemical methods applied, such as ion exchange, adsorption, membrane filtration, solvent extraction, and precipitation. The cost of operation is a key factor when deciding the technology for removal

(Regel-Rosocka, Cieszyńska and Wísniowski, 2006; Lewis, 2010; Maturana *et al.*, 2011; Chen, Zhong and Fang, 2012; Mungray, Kulkarni and Mungray, 2012; Ranade and Bhandari, 2014).

The complexity of treating effluents coming from metal-related industries is increased by the fact they often contain a mixture of several metallic compounds. Thus, to separate, degrade and/or remove these toxic elements from wastewater to the desired levels is a difficult task. According to Ranade & Bhandari (2014) “a process integration approach by combining various conventional as well as newly developed technologies [...] can help substantially in pollution control and recovery of metals, quite apart from bringing down the cost of operation”.

Ultimately, all industries related with metal processing have the potential to generate wastewater polluted by metal compounds, which can pose significant health hazards to society. Thus, an appropriate wastewater treatment in this industry can have a high impact.

### *Toxic Pollutants and Colour Issues: Dye Wastewater Treatment*

According to Ranade and Bhandari (2014), the dyes and textile industry is one of the most pollutant industries globally, which has led to the closing or shifting of units to emerging economies. This is the case of countries like China, India, and Indonesia (among others), where the majority of international producers have moved their production facilities. On one hand, regulatory barriers have obstructed the opening of new dyestuff manufacturing facilities. On the other hand, manufacturers are continuing to enlarge their production, even adding reactive and specialty dyes.

Usually the dye industry handles different types of dyes, most prominent of which are acid and direct dyes, disperse dyes, sulphur dyes, reactive dyes, and vat dyes, while the dye intermediate industry produces H-acid, vinyl sulfone, and gamma acid as the main products. Reactive dyes are specially characterized by producing large quantities of liquid effluent, in addition to being characterized as refractory compounds that pose several difficulties in their treatment.

Typical raw materials used in the dye industry are organic compounds such as benzene, toluene, aniline, and naphthalene, along with other chemical compounds such as acids, ammonia, sodium hydroxide, and salts (carbonates and sulphates). In addition, some solvents like alcohols are used in the process. Moreover, many components used in the process contain heavy metal compounds, traces of which eventually pollute wastewater effluents.

The dye industry wastewater is usually characterized by high COD levels, ranging from 3.000 to as much as +32.000 mg/L. Additionally, they are also often characterized by high ammoniacal nitrogen (NH<sub>3</sub>-N) levels, with values ranging from 6.000 to 11.000 mg/L. This poses an increased complexity when designing the wastewater treatment methodology to adopt. In fact, there are no general solutions for wastewaters coming from the dye industry,

but rather they depend on the specific characteristics of the effluent (Ranade and Bhandari, 2014).

There are several combinations of physicochemical methods to effectively treat wastewater coming from the dye industry. Some of these are filtration, coagulation, adsorption, and biological methods. For its proper treatment, it is recommended that recoverable components are recovered prior to the wastewater treatment. Activities such as lowering the salts level and recovering by-products can decrease the load on the wastewater treatment, increasing its effectiveness.

However, there are often cases where the wastewater treatment is a complex process. For example, this is the case when there are generation of effluents with high concentrations of  $\text{NH}_3\text{-N}$ . example is the treatment of reactive dyes, which are often characterized as refractory compounds. These effluents are usually difficult to degrade by conventional physicochemical or biological methods and require to be treated separately. According to Ranade & Bhandari (2014), newer methodologies such as AOPs and cavitation are sometimes adequate alternatives to treat such complex effluents.

Finally, appropriate wastewater treatment in this industry can have a high impact, not only to reduce the high pollution content, but also to reduce the water consumption through sustainable practices like water reuse and recycling.

### *Food, Beverages, and Starch Industries*

The food industry is characterized by employing biological methods – in combination with other methods – for treating its wastewater, mainly activated sludge (AS). The main difference between this industry and the chemical industry is that the former is a seasonal industry, hence there is no regular wastewater generation during the year. Additionally, wastewaters differ widely on their volume and the types and concentration of pollutants.

The food industry include industries like brewery and beverages, vegetable-oil producing industries, dairy industry, industries producing milk and milk derivatives, and the starch industry, among others. Oil is the main pollutant of effluents coming from vegetable oil and starch industries, which in fact has to be removed prior to the biological treatment (for example with OWS, in the primary treatment phase). In fact, BOD levels from the food industry are around +400 mg/L - which is already considered slightly high -, while BOD and COD levels from the starch industry are around 10.000 and 20.000 mg/L, respectively. Additionally, the brewery industries generate effluents with a BOD in an order of magnitude higher than the one of the beverage industries.

As stated by Ranade and Bhandari (2014), slaughterhouses and the meat-processing industry belong to a different class, for they produce wastewater effluents containing biological material such as blood with pathogens, hormones, and antibiotics.

Generally, the choice of the biological method to treat the industrial effluents coming from the food industry depends on several factors. The conventional activated sludge (CAS) was the common method for this purpose, specially before the year 2000. However, the increased cost of operations of CAS process, in addition to the high volume of sludge generation, shifted the preferences to anaerobic processes and newer technologies like membrane bioreactors (MBR). Additionally, adsorption methods are commonly used as a polishing process (5<sup>th</sup> phase) for meeting the regulatory standards of effluent discharge (Ranade and Bhandari, 2014).

Lastly, food processing industries are characterized by wastewaters that can be easily treated, usually with conventional methods and without major complexities in the process. Thus, an appropriate wastewater treatment in this industry can have a high impact

### *3.1.3.3. Potential and Impact of Wastewater Treatment, Recycle, and Reuse, by Industrial Sector*

In conclusion, industries can be characterized by both their potential for water reuse and recycling, and also by their wastewater treatment impact. On one hand, industries characterized by a high potential are the ones where wastewater reuse and recycling is a task requiring low techno-economic effort, either because the high volumes of water allow to exploit economies of scale, or because the concentration of pollutants is minimum. On the other hand, industries characterized by a high impact are the ones where the treatment has an important effect on sustainability, i.e. because it prevents dangerous social, environmental, and/or economic threats.

Industries characterized by a high potential and high impact are the ones where reuse and recycling tasks require low techno-economic effort, and also where the treatment is key for preventing dangerous consequences. Thus, high potential/high impact industries are the ones where wastewater reuse and recycling is an “easy” task, and the treatment for wastewater recycling is necessary.

Industries characterized by a low potential and low impact are the ones where reuse and recycling tasks require a high techno-economic effort, and also where the treatment is not as important for it does not pose dangerous consequences in its absence. Thus, low potential/low impact industries are the ones where wastewater reuse and recycling is a “difficult” task, but the treatment for wastewater recycling is not that necessary.

Industries characterized by a low potential and high impact are the ones where reuse and recycling tasks require high techno-economic effort, and also where the treatment is key for

preventing dangerous consequences. Thus, low potential/high impact industries are the ones where wastewater reuse and recycling is a “difficult” task, but the treatment for wastewater recycling is necessary.

Industries characterized by a high potential and low impact are the ones where reuse and recycling tasks require low techno-economic effort, and also where the treatment is not as important for it does not pose dangerous consequences in its absence. Thus, high potential/low impact industries are the ones where wastewater reuse and recycling is an “easy” task, but the treatment for wastewater recycling is not that necessary.

It can be made an analogy to the BCG matrix used for corporate strategy. Figure 20 shows a matrix example for evaluating the potential and impact of wastewater treatment, reuse, and recycling for specific industries, as an analogy to the BCG matrix.

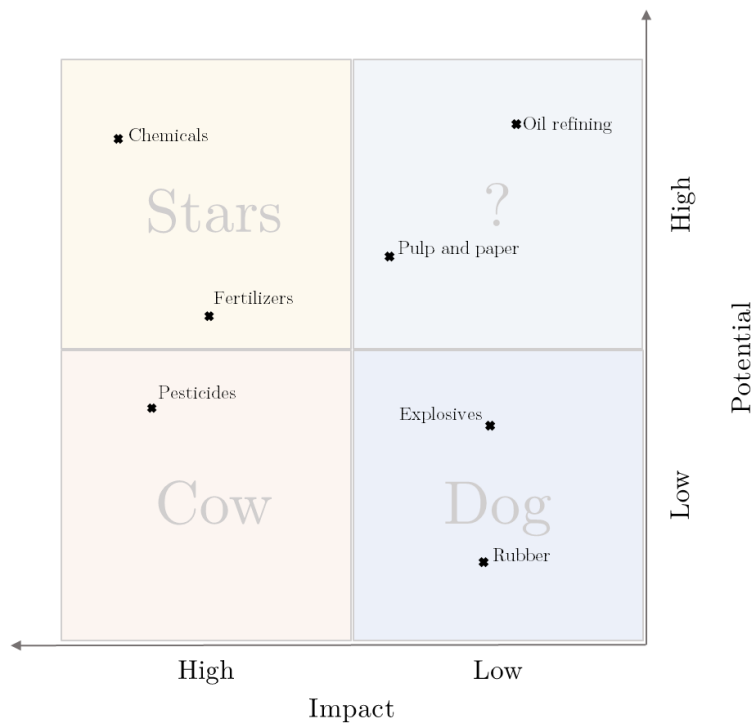


Figure 20. Potential and impact for wastewater treatment, reuse, and recycling, as a BCG matrix

Industries with high impact and high potential would be “stars” because they require a low effort to reuse and recycle wastewater and, additionally, their wastewater treatment is crucial. Therefore, wastewater can be easily reused and recycled. Moreover, these industries require special attention since the reuse and recycling practices are an “easy job”.

On the contrary, industries with low potential and low impact would be “dogs” since they require a great effort to reuse and recycle wastewater and, additionally, their wastewater treatment is not absolutely necessary. Therefore, these industries do not need much interest since the reuse and recycling practices are not easy nor necessary tasks.

Additionally, industries with low potential and high impact would be “cows” since they require a great effort to reuse and recycle wastewater, yet their wastewater treatment is crucial. Therefore, these industries require special attention because, even though the reuse and recycling activities are a difficult task to perform, the wastewater treatment is completely necessary to prevent threatening consequences for society.

Finally, industries with high potential and low impact would be “question marks” since they require a low effort to reuse and recycle wastewater, yet their wastewater treatment is not absolutely necessary. Therefore, these industries must be evaluated case by case. If the wastewater reuse or treatment and recycling is techno-economically feasible, it should be performed. Otherwise, when the treatment is not techno-economically feasible, the possibility to reuse wastewater without any treatment should be evaluated.

#### *3.1.3.4. Wastewater Treatment Process in the Industrial Context*

When deciding which methods to use to treat industrial effluents there are several techno-economic factors to consider. The two main barriers for the different separation methods are the energy consumption and the amount of chemicals required.

On one hand, the choice depends widely on its energy consumption. In fact, the energy used can vary greatly for different methods, ranging from low amounts (e.g. for water transport), to high amounts (e.g. energy for evaporating water). Likewise, producing intermediate-grade water often requires huge amounts of energy, especially when using evaporation methods. Moreover, water authorities usually require at least intermediate grade for water being discharged to natural water bodies, implying a huge energy consumption.

On the other hand, the choice of technology also depends widely on its chemical's consumption. Costly chemicals or high amounts of chemicals required poses a high barrier for certain wastewater treatments.

Summarizing, the wastewater treatment can be considerably costly for industries, especially when there is the need of energy-intensive or chemical-intensive methods for the effective removal of pollutant components.

Table 12 shows the typical wastewater treatment process for different industries and sub-industries, detailing the technology used for each phase of the treatment. This list shows the effort made by each industry to achieve a required quality of recycled wastewater in different types of industries. It also includes the water quality requirements for municipal applications.

It can be noticed that the industries making the effort to obtain a high-grade water are cement, chemicals in general, pharmaceuticals and cosmetics, dyeing, electricity generation, food & beverage in general, dairy, semiconductors, plating, mining, oil and gas, and pulp & paper.



The industries making the effort to obtain an intermediate-grade water are chemical fertilizer, automobile, SCP<sup>13</sup>, CGP<sup>14</sup> and SKP<sup>15</sup> (pulp & paper), cokes, hot mill, blast furnace, col mill (steel), and wool.

The industries making the effort to obtain a low-grade water are petrochemistry, organic chemistry, polymer chemistry, oil & fat (chemicals), desizing, scouring, bleaching (dyeing), vegetable oil, brewery, beverage, starch, daily dishes, confectionary (food & beverages), petroleum refinery, washing/screening and KP<sup>16</sup> (pulp and paper), and synthetic fibre (textile).

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<sup>13</sup> SCP refers to a semi-chemical pulping process, which is a combination of mechanical and chemical pulping.

<sup>14</sup> CGP refers to chemical ground pulping process.

<sup>15</sup> SKP refers to sack kraft paper production process. Sack kraft paper is a porous kraft paper designed for packaging products with high demands for strength and durability.

<sup>16</sup> KP refers to kraft pulping process.

Table 12. Typical treatment process for different industries. Source: Graham (1999), Mori et al. (2003), Danish District Heating Association (2015) Cramwinckel et al. (2017)

Industry	Sub-industry	Primary						Secondary			Tertiary			Min. removal			Polishing									
		Ne	OW	TP	Co	DF	Ch	Ae	An	CW	Dn	Fi	MS	RO	EC	In	Ad	O <sub>3</sub>	UV	CD	IX					
<b>Cement</b>	Cement				█																					
<b>Chemicals</b>	Chemicals (a)		█						█																	█
	Pharmaceuticals (b)					█			█													█	█			
	Petrochemistry	█				█			█		█															
	Organic chemistry	█				█			█		█															
	Polymer chemistry	█							█		█															
	Oil/fat		█			█			█																	
	Chemical fertilizer	█							█																	
<b>Dyeing</b>	Dyeing	█			█	█																				█
	Desizing				█	█																				
	Scouring				█	█	█																			
	Bleaching				█	█	█																			
<b>Electricity Generation</b>	Electr. Generation (c)				█								█	█												█
	Electr. Generation (d)				█										█											█
<b>Food and Beverage</b>	Food & beverage (e)					█			█		█															█
	Dairy					█			█		█			█	█											█
	Vegetable oil		█						█		█															
	Brewery								█		█															
	Beverage								█		█															
	Starch								█		█															
	Daily dishes								█		█															
	Confectionary								█		█															
<b>Machinery</b>	Semiconductor	█			█				█																	█
	Plating	█			█	█	█																			█
	Automobile					█																				

Low grade

Intermediate grade

High grade

Table 12. Typical treatment process in different industries (continuation).

Industry	Sub-industry	Primary						Secondary			Tertiary			Min. removal			Polishing				
		Ne	OW	TP	Co	DF	Ch	Ae	An	CW	Dn	Fi	MS	RO	EC	In	Ad	O <sub>3</sub>	UV	CD	IX
Mining	Mining (f)				■					■			■	■	■						■
	Mining (g)												■	■							■
Municipal	District heating	■							■	■				■	■						
	Potable water		■		■									■	■		■				
	Wastewater treatment																				
Oil and Gas	Oil and gas (h)				■					■			■	■	■						■
	Oil and gas (i)				■				■			■		■							■
	Petroleum refinery		■						■	■				■							
Pulp and Paper	Pulp and paper								■	■			■	■			■	■			
	SCP, CGP				■	■			■							■					
	Washing/screening					■			■												
	KP				■	■															
	SKP								■							■					
Steel	Cokes	■	■						■			■									
	Steel, hot mill		■		■																
	Blast furnace				■							■									
	Col mill	■										■									
Textiles	Synthetic fibre	■			■	■			■												
	Wool				■				■							■					

Note: (a) Without pharmaceuticals; (b): Includes cosmetics; (c), (d), (f), (g), (h), and (i): Different treatment processes for the same industry; (e): Without dairy  
 Treatment methods: Ad: Adsorption (includes Granular Activated Carbon), Ae: Aerobic method, An: Anaerobic method, CD: Chlorine dioxide, Ch: Chemical methods, Co: Coagulation, CW: Constructed wetland, DF: Dissolved air flotation, Dn: Denitrification, EC: Evaporation and crystallization, Fi: Filtration (includes sand filtration), In: Incineration, IX: Ion exchange (includes continuous electrodeionization), MS: Membrane Separation (includes UF, excludes reverse osmosis), Ne: Neutralization, O<sub>3</sub>: Ozonation method, OW: Oil and water separation, RO: Reverse osmosis, TP: Tilted plate interceptor, UV: Ultraviolet method.

The water treatment processes presented in Table 12 provide the baseline to build the water qualities to be used in section 3.2, which are employed to compare the different waterflows of the cases analysis.

The water quality classification will range from 1.0 to 5.4, from lower to higher quality, respectively. Relating this scale to section 3.1.1, water with quality between 1.0 and 3.0 (not inclusive) will be classified as low-grade water. Water with quality between 3.0 and 5.0 (not inclusive) will be classified as intermediate grade water. Finally, water with quality 5.0 or higher will be classified as high-grade water

Table 13 synthesizes the information about the different treatment processes for each industry and shows the quality of water that is required by them, based on Table 12. This is used for the cases analysis in section 3.2. For the easiness of comparison, each industry is classified according to their water quality required. For further details on the methodology of comparison refer to section 2.2.

Industries requiring a low-grade water are the ones requiring primary and/or secondary treatments only. This means, primary treatment from neutralization (Ne) to chemical methods (Ch), ranging from quality 1.0 up to 1.5, and secondary treatment from aerobic (Ae) to constructed wetlands (CW), ranging from quality 2.0 up to 2.2.

This is the case of wastewater treatment (municipal) requiring a quality of 1.0; KP (pulp and paper) requiring 1.4; scouring (dyeing) and bleaching (dyeing) requiring 1.5; oil/fat (chemicals), desizing (dyeing), starch (food and beverage), daily dishes (food and beverage), confectionary (food and beverage), washing/screening (pulp and paper), and synthetic fibre (textiles) requiring a quality 2.0; and petrochemistry (chemicals), organic chemistry (chemicals), polymer chemistry (chemicals), vegetable oil (food and beverage), brewery (food and beverage), beverage (food and beverage), and petroleum refinery (oil and gas) requiring 2.1;

Industries requiring an intermediate grade water are the ones requiring tertiary and/or mineral removal treatments. This means, tertiary treatment from denitrification (Dn) to membrane separation (MS), ranging from quality 3.0 up to 3.2, and salts and mineral removal treatment from reverse osmosis (RO) to incineration (In), ranging from quality 4.0 up to 4.2. This is the case of chemical fertilizer (chemicals) requiring 3.0; cokes (steel), hot mill (steel), blast furnace (steel), and col mill (steel) requiring 3.1; automobile (machinery) requiring 3.2; district heating (municipal) requiring 4.0; and SCP/CGP (pulp and paper), SKP (pulp and paper), and wool (textiles) requiring 4.2.

Industries requiring a high-grade water are the ones requiring polishing treatments. This means, advanced treatments from adsorption (Ad) to ion exchange (IX), ranging from quality 5.0 up to 5.4. This is the case of potable water (municipal) requiring 5.0; dyeing in general, plating (machinery), semiconductor (machinery), and pulp and paper in general, requiring 5.1;

pharmaceuticals (chemical) requiring 5.2; dairy (food and beverages) requiring 5.3; and cement, chemicals in general, electricity generation, food and beverages in general, mining, and oil and gas in general, requiring 5.4

In addition, electric utilities usually receive waterflows for steam generation or for cooling purposes. In fact, these waterflows usually belong to a wide quality range. Water used for steam generation commonly requires high-grade water, while water used for cooling processes often requires low-grade water. Thus, the water quality required by electric utilities will be defined as a range from 2.0 to 5.4 (from low to high-grade water)

As a conservative approach, when a waterflow is received by an electric utility the reference quality will be the lower value of the range, namely 2.0. On the contrary, if it is sent by an electric utility the reference quality will be the higher value of the range, namely 5.4.

Table 13. Quality of water required by selected industries

Industry	Sub-industry	Quality	Grade
<b>Cement</b>	Cement	5.4	High
<b>Chemicals</b>	Chemicals (a)	5.4	High
	Pharmaceuticals (b)	5.2	High
	Petrochemistry/organic/polymer chemistry	2.1	Low
	Oil/fat	2.0	Low
	Chemical fertilizer	3.0	Intermediate
<b>Dyeing</b>	Dyeing	5.1	High
	Desizing	2.0	Low
	Scouring, bleaching	1.5	Low
<b>Electricity Generation</b>	Electr. Generation	2.0 - 5.4	Low - High
<b>Food and Beverage</b>	Food & beverage (c)	5.4	High
	Dairy	5.3	High
	Vegetable oil/brewery/beverage	2.1	Low
	Starch, daily dishes, confectionary	2.0	Low
<b>Machinery</b>	Semiconductor/plating	5.1	High
	Automobile	3.2	Intermediate
<b>Mining</b>	Mining	5.4	High
<b>Municipal</b>	District heating	4.0	Intermediate
	Potable water	5.0	High
	Wastewater treatment	1.0	Low
<b>Oil and Gas</b>	Oil and Gas	5.4	High
	Petroleum Refinery	2.1	Low
<b>Pulp and Paper</b>	Pulp and Paper	5.1	High
	SCP, CGP, SKP	4.2	Intermediate
	Washing/screening	2.0	Low
	KP	1.4	Low
<b>Steel</b>	Cokes, steel hot mill, blast furnace, col mill	3.1	Intermediate
<b>Textiles</b>	Synthetic fibre	2.0	Low
	Wool	4.2	Intermediate

Note: (a): without pharmaceuticals; (b): includes cosmetics; (c): Without dairy; (d) Any industry receiving warm condensate

### 3.1.4. Conclusions on Industrial Wastewater Treatment

The technologies companies choose to treat the desired effluents will depend on their overall water management strategies, the sources of water and wastewater, and the end use for reused or recycled water. The technologies most commonly used include biological treatment and physicochemical treatments such as , membrane filtration, separation processes and chemical oxidation processes (Cramwinckel *et al.*, 2017).

Industrial wastewater treatment, recycling, and reuse is an important theme in today's context, not just to protect the environment from pollution, but also to preserve water resources in order to reduce water stress.

A large number of technologies have been analysed in section 3.1.2. The selection of each technology depends on the desired goals of wastewater treatment: recovery of valuable chemicals from wastewater, possible water recycling and reuse, complying with the statutory norms for discharge into water bodies, and economics of the treatment process. The number and diverse nature of pollutants in wastewater makes the task of selection rather difficult (Ranade and Bhandari, 2014).

The choice of technology depends on the type of wastewater and the quality required for the end use. The end use is defined by the destination of the effluent. If it is an industrial application, it is possible to notice that there is a wide variety of treatment processes depending on the industry the effluent is destined for. In fact, the uses of different grades of water vary widely by industry.

In addition, some applications are more affected by legislation and public opinion than others, which affects hugely the treatment technologies to be used. Such is the case of the food and beverage industry, municipal freshwater production, and agriculture irrigation.

Finally, some industries are key in the reuse, recycling, and treatment process of water. These industries that have a high potential for reuse and recycling, and especially those that the water treatment is key to reduce negative impacts on human health and ecosystems in general, are the ones that require the most attention. Such is the case, for example, of chemical and fertilizers manufacturing industries.

## 3.2. Industrial Symbioses Cases: Qualitative Analysis through the ISWE Model

This section presents a qualitative analysis of the circular practices of water reusing and recycling in the industrial context. Several water exchanges of different cases of industrial symbiosis are analysed.

The industrial classification of each actor involved in the IS cases in study was taken from the official report of the United Nations (2009) “International Standard Industrial Classification of All Economic Activities (ISIC), Rev. 4”.

### 3.2.1. HHG – China

The following case study is centred on an IS occurring northwest of Weifang, a city located in the Shandong province of China. The exchanges analysed are based on data of the year 2014, retrieved from the article developed by Liu, Côté and Zhang (2015) named “Implementing a three-level approach in industrial symbiosis”.

#### 3.2.1.1. *Context of the Case Study*

Weifang is a prefecture-level city located at the centre of the Shandong province, China. This city borders Dongying to the northwest, Zibo to the west, Linyi to the southwest, Rizhao to the south, and Qingdao to the east. To the north it is adjacent to the Laizhou Bay. Figure 21 represents the geographical location of the city in study.

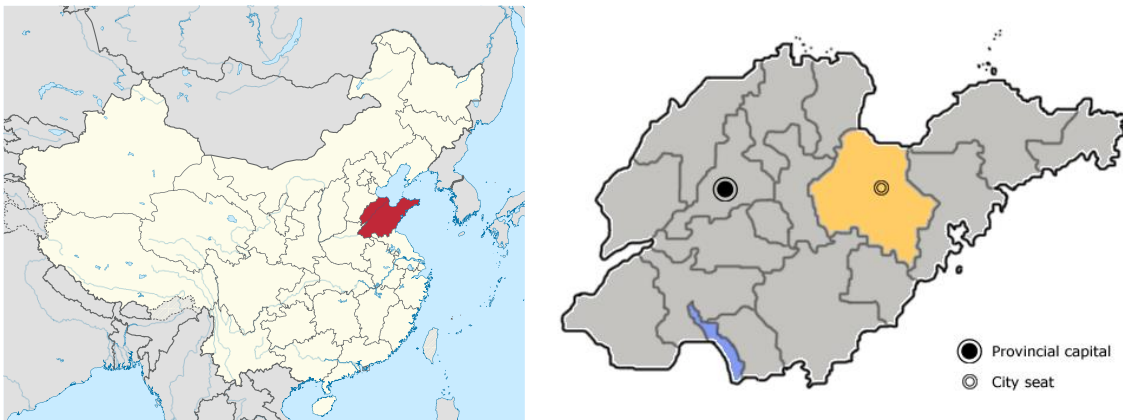


Figure 21. Location of Shandong in China (left) and Weifang in Shandong (right). Source: Wikipedia

In the 1980s many sapphire deposits were discovered in the Changle County of Weifang. It is estimated that huge amounts of this material lays under the region. Moreover, the mining industry of the region prospered in the following years, becoming one of the top sapphire producers in the world.

This case study is based on the Hai Hua Ecological Industry Pilot Zone (HHEIPZ) project. Moreover, the IS analysed is mainly composed by companies from the Hai Hua Group (HHG). For simplicity, this case will be referred to as the latter abbreviation, namely HHG.

The region where the symbiosis is located was first named as Hai Hua Economic Development Area (HHEDA). Later it changed to Weifang Coastal Development Zone (WCDZ), and now is named as Weifang Binhai Economic-Technological Development Area (BEDA). Given the notable success of the companies belonging to HHG, in 2005 the region was designated as a national eco-industrial demonstration area, often called HHEIPZ.

HHG is the largest marine chemical production in China. The IS was first established in 1995 based around the combination of salt and soda organizations, namely the Yangkou salt field and the Weifang soda plant. Nowadays all the companies participating in the IS are somehow connected to HHG, which contains 20 companies. The main products of HHG are soda, crude salt, calcium chloride, bromine, bromide, and silica.

By the year 2014, the main actors involved in water exchanges were the following:

1. Bromine Plant
2. Calcium Chloride Plant
3. Potassium Sulphate Plant
4. Residential Zone
5. Salt Field Plant
6. Sea Farming
7. Soda Plant
8. Thermal Power Plant

### *3.2.1.2. Characterization of the Actors Involved and Intermediaries*

Figure 22 represents the main organizations and the flows involved in the symbiotic exchanges of the HHG case, including energy, water, and material exchanges. Table 14 summarizes the main actors exchanging water in the HHG IS, how they are classified according to their application category, to which industry they belong, and the subsequent water quality they require.

According to Table 13 the water quality required by chemical sub-industries comprise a wide range., from 2.0 to 5.4. Moreover, some actors from this IS case belong to the chemical industry, although their specific sub-industry is not clearly defined. As a conservative



approach, when a waterflow is received by these types of actors the reference quality will be the lower value of the range, namely 2.0. On the contrary, if it is sent by these types of actors, the reference quality will be the higher value of the range, namely 5.4. This is the case of the Bromine Plant, the Calcium Chloride Plant, the Salt Field Plant, and the Soda Plant.

The sea farm of the system belongs to the fishing and aquaculture industry. According to Yeo, Binkowski and Morris (2004), aquaculture usually requires effluents from low to intermediate grade, with a wide range of variation. For this case, it is assumed that the water required by this industry is of quality 3.0.

The Thermal Power Plant belongs to the electric utilities industry. Subsequently, its water quality requirement ranges from 2.0 to 5.4, depending on if it is the primary or secondary user. For further information refer to section 3.1.3.4.

Subsequently, it is possible to notice that the water quality required by the actors of HHG ranges from 2.0 to 5.4, i.e. from low to high-grade water. In addition, there are no intermediaries in this IS case.

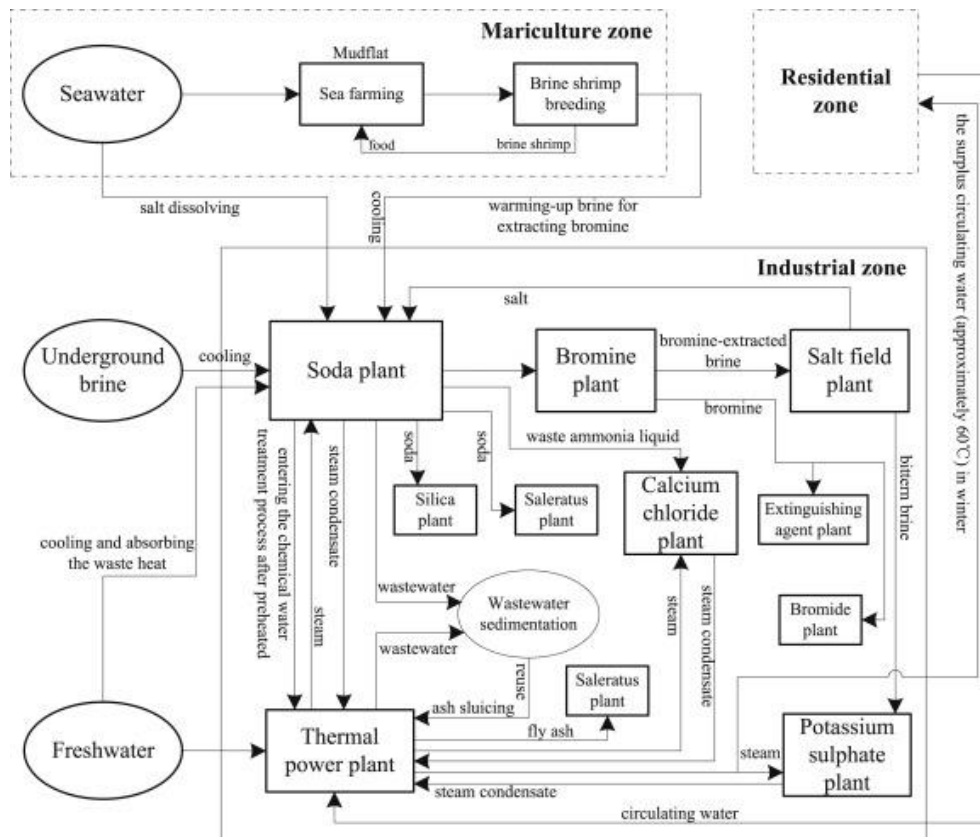


Figure 22. IS network of the HHG case. Source: Liu, Côté and Zhang (2015)

Table 14. Main actors in the water network of the HHG case

Actor	Category	Industry	Quality required
Bromine Plant	Industry	Chemicals manufacturing	2.0 - 5.4
Calcium Chloride Plant	Industry	Chemicals manufacturing	2.0 - 5.4
Potassium Sulphate Plant	Industry	Chemical fertilizer	3.0
Residential Zone	Municipal	District heating	4.0
Salt Field Plant	Industry	Chemicals manufacturing	2.0 - 5.4
Sea Farming	Agriculture	Fishing and aquaculture	3.0
Soda Plant	Industry	Chemicals manufacturing	2.0 - 5.4
Thermal Power Plant	Industry	Electric utilities	2.0 - 5.4

### 3.2.1.3. Characterization of the Waterflows

The waterflows characterizing the HHG symbiosis are represented in

Table 15. The primary users of flows number 1, 2, 5, 7, 8, and 9 belong either to the chemical or to the electric utilities industries. Thus, their required water quality as suppliers is 5.4. The secondary users of flows number 1, 2, 3, 4, 6, 7, and 8 belong either to the chemical or to the electric utilities industries. Thus, their required water quality as users is 2.0. For further information refer to section 3.1.3.4

It can be noticed that none of the waterflows from this case include a water treatment, thus they are classified as reusing. In addition, the quality required by primary users range from intermediate to high-grade water. The water required by secondary users range from low to intermediate grade water.

Table 15. Waterflows characterization of the HHG case

	Primary use		Intermediary		Secondary use		Level
	Quality in	User	Actor	Treated?	Quality in	User	
1	5.4	Bromine Plant	N/A	No	2.0	Salt Field Plant	R
2	5.4	Calcium Chloride Plant	N/A	No	2.0	Thermal Power Plant	R
3	3.0	Potassium Sulphate Plant	N/A	No	2.0	Thermal Power Plant	R
4	4.0	Residential Zone	N/A	No	2.0	Thermal Power Plant	R
5	5.4	Salt Field Plant	N/A	No	3.0	Potassium Sulphate Plant	R
6	3.0	Sea Farming	N/A	No	2.0	Soda Plant	R
7	5.4	Soda Plant	N/A	No	2.0	Bromine Plant	R
8	5.4	Soda Plant	N/A	No	2.0	Thermal Power Plant	R
9	5.4	Thermal Power Plant	N/A	No	4.0	Residential Zone	R

3.2.1.4. *O/D Matrix*

Table 16 represents the O/D matrix for this case.

Agriculture applications are involved in only 1 of the 9 water exchanges in study, only as a supplier. The destination of this waterflow is an industrial application.

Municipal applications are involved in 2 of the 9 water exchanges in study, one as the supplier on the other as the user. The waterflow received by a municipal application comes from an industrial application. On the contrary, the waterflow supplied by a municipal application is destined to an industrial application.

Industrial applications are involved in all water exchanges in study, either as the supplier or as the user. Additionally, 3 of the 8 waterflows received by industrial applications come from the same industry but a different process, and 3 come from a different industry, and the remaining two come from a municipal and an agriculture application, respectively.

Table 16. *O/D matrix of the HHG case*

Origin/Destination	Same Industry		Industry	Municipal	Agriculture
	Same process	Different process			
Industry		1; 5; 7	2; 3; 8	9	
Municipal	N/A	N/A	4		
Agriculture	N/A	N/A	6		

3.2.1.5. *L-O/D Matrix*

Figure 23 represents the L-O/D Matrix of the HHG symbiosis waterflows.

It can be noticed that all waterflows are classified as reusing, and they do not pass through any wastewater treatment organization. Thus, all waterflows required for secondary usage do not require any treatment for they are exchanged directly from supplier to user.

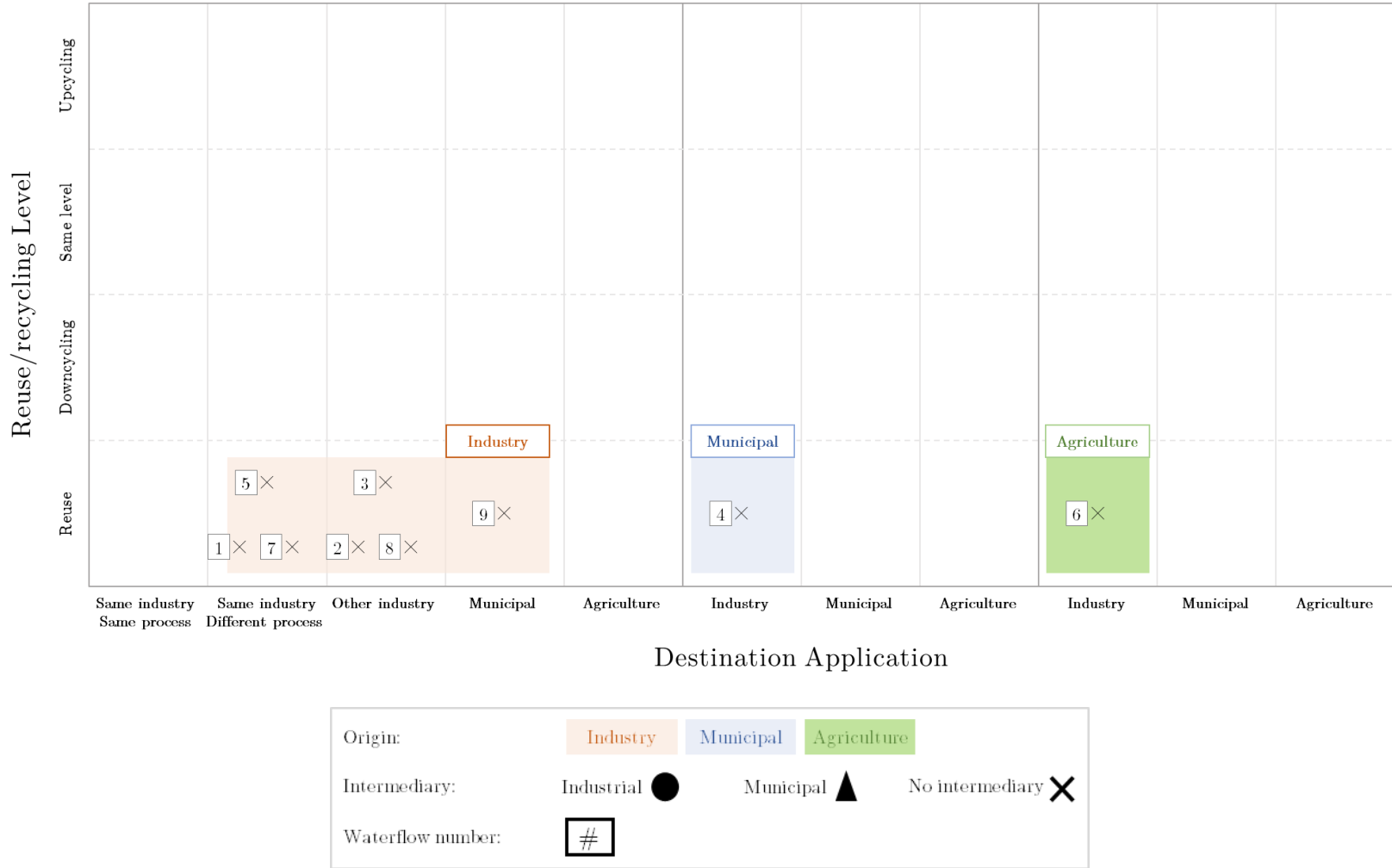


Figure 23. L-O/D matrix of the HHG case

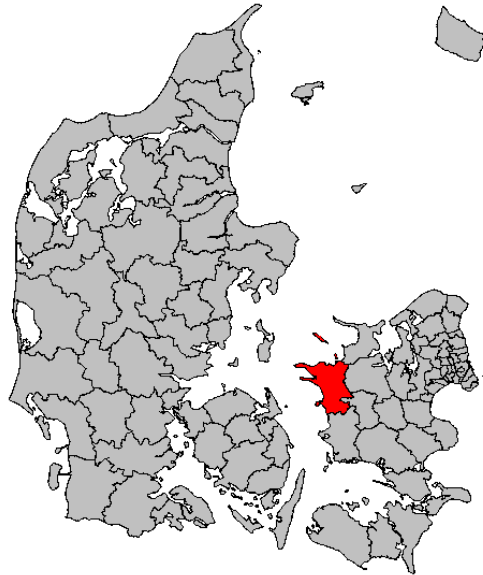
### 3.2.2. Kalundborg – Denmark

The following case study is centred on an IS occurring in the city of Kalundborg in Denmark. The exchanges analysed are based on data from the year 2019, obtained from the official website of the Kalundborg Symbiosis Center (2019).

#### 3.2.2.1. *Context of the Case Study*

Kalundborg is a small harbour city in Denmark. It was first established back in the 12<sup>th</sup> century, and now in the 21<sup>st</sup> century is known around the world as the most prominent example of industrial symbiosis (Roman and Chertow, 2011).

This city is the capital of the municipality with the same name, and it is located in the Kalundborg fjord at the western coast of the biggest Danish island: the Zealand Island. Its population at the beginning of 2019 was 16.370 inhabitants, representing the 33.6% of the entire Kalundborg Municipality population. Figure 24 shows the location of the city in Denmark.



*Figure 24. Location of Kalundborg in Denmark. Source: Wikipedia*

The eco-industrial system at Kalundborg is possibly the most significant example of industrial symbiosis in the academic literature. This symbiotic system has been analysed in literature both as a role model for IS studies and/or developments, and on the contrary, as a unique and isolated phenomenon which is fairly impossible to replicate.

This symbiotic system was first “discovered” in 1989, and its arrangements have been used as the baseline upon which many other industrial symbiosis cases set base. However, its establishment was a long and slow evolutionary process, which started with a water management project in 1961 (Roman and Chertow, 2011; Branson, 2016).

The Kalundborg region of Denmark lacks an adequate supply of freshwater. By the year 1961 a newly built oil refinery from Statoil Company required freshwater for production purposes. Instead of using the valuable groundwater resources of the area, the Kalundborg Municipality built a pipeline to extract freshwater from the surface of Lake Tissø. Statoil ASA financed the project. As stated by Roman and Chertow, this “initial collaboration between the city and business encouraged additional collaborative efforts” (Roman and Chertow, 2011).

Initially, in 1972, there was never a planning of the overall network that would develop in the future. In fact, it just evolved as the different companies surrounding the area started accommodating to one another, collaborating, and generating beneficial exchange relationships with each other. As Roman and Chertow state “it just evolved as a collection of one-to-one deals that made economic sense for participants on all sides” (Roman and Chertow, 2011)

The first symbiotic exchange between industrial applications started in 1972 when Gyproc, a world leader company in plasterboard and other building materials, located its facility in Kalundborg to take advantage of the fuel gas available from Statoil. By this exchange, the company could access to high quality and local raw materials, thus empowering the local economy at a lower price (Roman and Chertow, 2011; Kalundborg Symbiosis Center, 2019).

Over the next decades all the major partners and other surrounding companies spontaneously developed a series of bilateral exchanges, generating a dynamically evolving network of relationships involving exchanges of resources. In fact, the development of the IS has been described as an evolutionary process in which, according to Jacobsen, “a number of independent by-product exchanges have gradually evolved into a complex web of symbiotic interactions[...]” (Jacobsen, 2006; Roman and Chertow, 2011).

By the year 2019, the main partner organizations involved in water exchanges were the following:

1. Equinor (former Statoil)
2. Gyproc
3. Kalundborg Forsyning (Kalundborg Utility)
4. Kalundborg Utility Heat Pump
5. Novo Nordisk A/S
6. Novo Nordisk & Novozymes Landowner’s Association
7. Novozymes A/S
8. Novozymes Wastewater & Biogas
9. Ørsted

3.2.2.2. *Characterization of the Actors Involved and Intermediaries*

Figure 25 represents the main organizations and the flows involved in the symbiotic exchanges in Kalundborg, including energy, water, and materials exchanges. Table 17 summarizes the main actors exchanging water in the Kalundborg IS, how they are classified according to their application category, to which industry they belong, and the subsequent water quality they require.

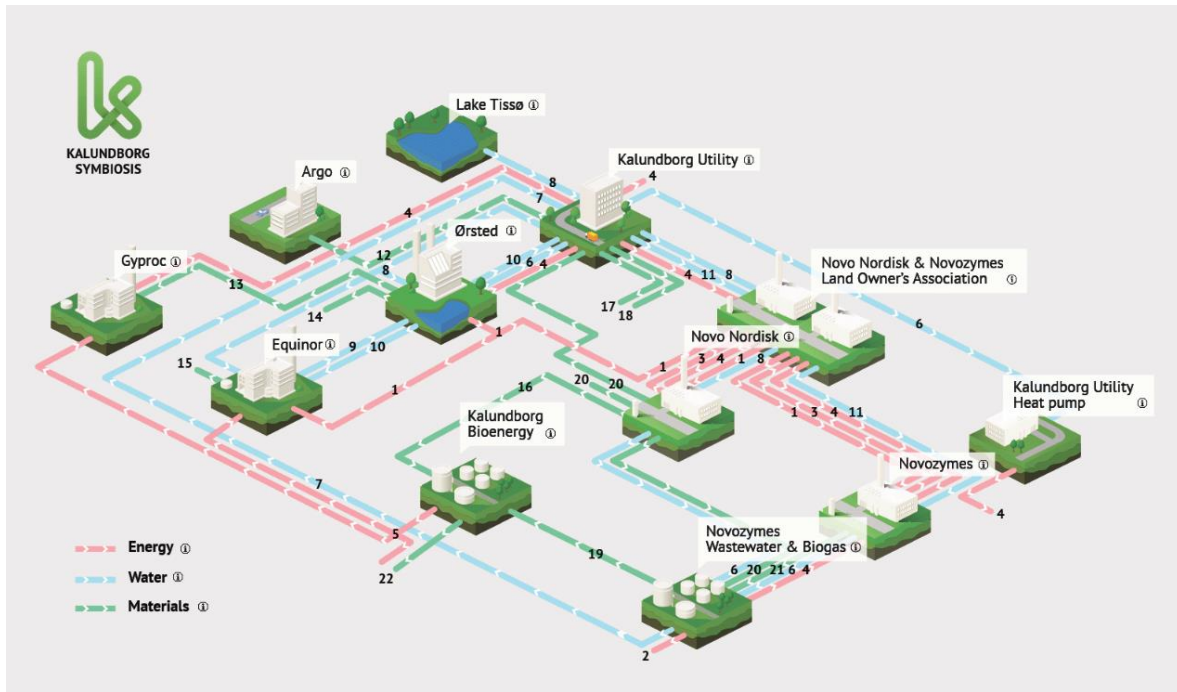


Figure 25. IS network of the Kalundborg case. Source: Kalundborg Symbiosis Center (2019).

Gyproc is a company that produces gypsum, a construction material. Thus, this actor belongs to the industry of building materials manufacturing. According to Eurogypsum (2008), the production process of this material requires high grade water. For this case, it is assumed that the water required by this industry is 5.0.

Novozymes is a company belonging to the biotechnology industry. According to the data provided by the Kalundborg Symbiosis Center (2019), this actor usually requires similar effluents to Novo Nordisk. The only difference is that the ones required by the former company are usually treated, hence, are received in a slightly higher quality (receiving cleaned surface water instead of surface water). Thus, for this case it is assumed that this company requires a higher-grade water in comparison to Novo Nordisk (5.3). Hence, the quality required by this industry is assumed to be 5.4.

Ørsted belongs to the electric utilities industry. Subsequently, its water quality requirement ranges from 2.0 to 5.4, depending on if it is the primary or secondary user. For further information refer to section 3.1.3.4.

Then, it is possible to notice that the water requirements in this case range from a quality 1.0 to 5.4, i.e. from low to high-grade water.

Table 17. Actors involved in water exchanges in Kalundborg

Actor	Category	Industry	Quality required
Equinor	Industry	Oil & gas	5.4
Gyproc	Industry	Building materials	5.0
Kalundborg Forsyning (Kalundborg Utility)	Municipal (M)	Wastewater treatment / District heating	1.0 / 4.0
Kalundborg Utility Heat Pump	Municipal	District heating	4.0
Novo Nordisk	Industry	Pharmaceutical	5.2
Novo Nordisk & Novozymes Landowner's Association	Industry	N/A	N/A
Novozymes	Industry	Biotechnology	5.3
Novozymes Wastewater & Biogas	Industry (I)	Wastewater treatment / Alternative energy	1.0
Ørsted	Industry	Electric utilities	2.0 - 5.4

Kalundborg Forsyning (Kalundborg Utility) has as a primary activity the treatment of the wastewater of the city. Moreover, it aims to treating water as a municipal service. Thus, this organization is considered as a municipal wastewater treatment intermediary (M). For further clarifications refer to section 2.3.

Additionally, it has secondary activities, such as collecting surface water from the Lake Tissø for its following distribution, and also acting as an energy distributor of district heating. Thus, the Kalundborg utility will be considered a municipal wastewater treatment intermediary (M) only when a wastewater treatment is performed. On the contrary, when it acts as an energy distributor it is not considered an intermediary, but as an actor itself (as a secondary user of the district heating).

According to Table 17, the quality required by the utility when acting as a wastewater treatment plant is 4.0, while when it acts as an energy distributor it is 4.0. Moreover, the Kalundborg Utility Heat Pump acts also as an energy distributor. In fact, the flow of wastewater it receives from the utility is used for district heating. Thus, this actor is not considered as an intermediary either.



The actor “Novo Nordisk and Novozymes Landowners’ Association” is a common alliance of both Novozymes and Novo Nordisk, with the purpose to run and maintain the two companies’ common production areas. Moreover, it is classified as an intermediary that do not perform any treatment, but that is just part of the trajectory of the waterflows.

Finally, Novozymes Wastewater & Biogas plant has as a primary activity to handle and treat the wastewater effluents, coming from both Novozymes and Novo Nordisk facilities. Moreover, it aims to treating water for industrial purposes, and not as a municipal service. In fact, the wastewater treatment is used for producing biogas (Novozymes, 2013). Thus, this organization is not considered as an industrial intermediary, however it is considered as an industrial actor that treats water (I). For further clarifications refer to section 2.3.

### 3.2.2.3. Characterization of the Waterflows

The waterflows characterizing the Kalundborg symbiosis are represented in Table 18. The primary users of flows number 8, 9 and 10 belong to the electric utilities industry. Thus, their required water quality as suppliers is 5.4. The secondary users of flow number 1 belongs to the electric utilities industry. Thus, its required water quality as user is 2.0. For further information refer to section 3.1.3.4

Table 18. Waterflows characterization of the Kalundborg case

	Primary use		Intermediary		Secondary use		Level
	Quality in	User	Actor	Treated?	Quality in	User	
1	5.4	Equinor	N/A	No	2.0	Ørsted	R
2	5.0	Gyproc	N/A	No	4.0	Kalundborg Utility	R
3	5.2	Novo Nordisk	Landowner’s Association	No	5.2	Novo Nordisk	R
4	5.2	Novo Nordisk	N/A	No	1.0	Novozymes Wastewater & Biogas	R
5	5.3	Novozymes	Landowner’s Association	No	5.2	Novo Nordisk	R
6	5.3	Novozymes	N/A	No	1.0	Novozymes Wastewater & Biogas	R
7	1.0	Novozymes Wastewater & Biogas	Kalundborg Utility	Yes (I)	4.0	Utility Heat Pump	U
8	5.4	Ørsted	N/A	No	5.4	Equinor	R
9	5.4	Ørsted	N/A	No	4.0	Kalundborg Utility	R
10	5.4	Ørsted	Kalundborg Utility	Yes (M)	4.0	Utility Heat Pump	D

It can be noticed that most of the waterflows contained in this case do not include a water treatment, thus they are classified as reusing (80%). Moreover, the only waterflows that include water treatments are exchanges number 7 and 10, classified as upcycling and downcycling, respectively.

In addition, all waterflows required by the primary users are of high-grade, with the only exception of the waterflow 7. On the opposite, secondary users require from low to high-grade water

3.2.2.4. *O/D Matrix*

Table 19 represents the O/D matrix for this case.

It can be noticed that there are no agriculture applications involved in the water exchanges in study. It can also be noticed that municipal applications are involved in 4 of the 10 water exchanges in study, only as users receiving water from industrial applications.

Industrial applications are involved in all of the water exchanges in study, either as the supplier or as the user. Additionally, 1 of the 6 waterflows received by industrial applications come from the same industry and process, and the remaining 5 are shared between different industries.

Table 19. *O/D matrix of the Kalundborg case*

Origin/Destination	Same Industry		Industry	Municipal	Agriculture
	Same process	Different process			
<b>Industry</b>	3		1; 4; 5; 6; 8	2; 7; 9; 10	
<b>Municipal</b>	N/A	N/A			
<b>Agriculture</b>	N/A	N/A			

3.2.2.5. *L-O/D Matrix*

Figure 26 represents the L-O/D Matrix of the Kalundborg Symbiosis waterflows.

It is possible to notice that when a municipal application is involved (only as user), 2 of the 4 water exchanges are reuse level, 1 as downcycling, and the remaining one is classified as upcycling. On the contrary, when an industrial application is involved either as user or as supplier (i.e. all waterflows), 8 of the 10 water exchanges are reuse level (80%), 1 is classified as downcycling, and the remaining one as upcycling.

There are two waterflows passing through wastewater treatment organizations, both of them passing from an industrial to a municipal application. One of them is treated by a municipal

application and is classified as downcycling. The other one is treated by an industrial application and is classified as upcycling. Moreover, when waterflows are exchanged between the same applications, all of them are characterized as reusing.

Moreover, this case is characterized by high requirements of water quality, both from the primary as well as for the secondary users. Thus, it can be inferred that a water treatment will not be required in between actors if the process using the effluent is not too much polluting. This can explain why most of the waterflows are classified as reusing.

In fact, the only waterflows characterized as recycling are the ones exchanging water as energy, through district heating. All other waterflow do not need treatment to be exchanged between the actors.

Finally, when waterflows are exchanged between different industries, or between the same industry and same process, all 6 waterflows are characterized as reusing.



Figure 26. L-O/D matrix of the Kalundborg case

### 3.2.3. REDA – China

The following case study is centred on the REDA IS occurring in Rizhao, which is a port city of the Shandong province, in the eastern littoral area of China. The exchanges analysed are based on data from the year 2011, from on the article developed by Yu, Han and Cui (2015) named “Evolution of industrial symbiosis in an eco-industrial park in China”.

#### 3.2.3.1. Context of the Case Study

Rizhao is a prefecture-level port city located in southeast of the Shandong province, China. The city faces Korea and Japan across the Yellow Sea to the east. The place where the city is settled nowadays dates from as far as 2070 B.C. It was officially proclaimed a city in 1985, and in 1989 it was named a prefecture-level city within the Shandong province. Figure 27 represents the geographical location of the city in study.

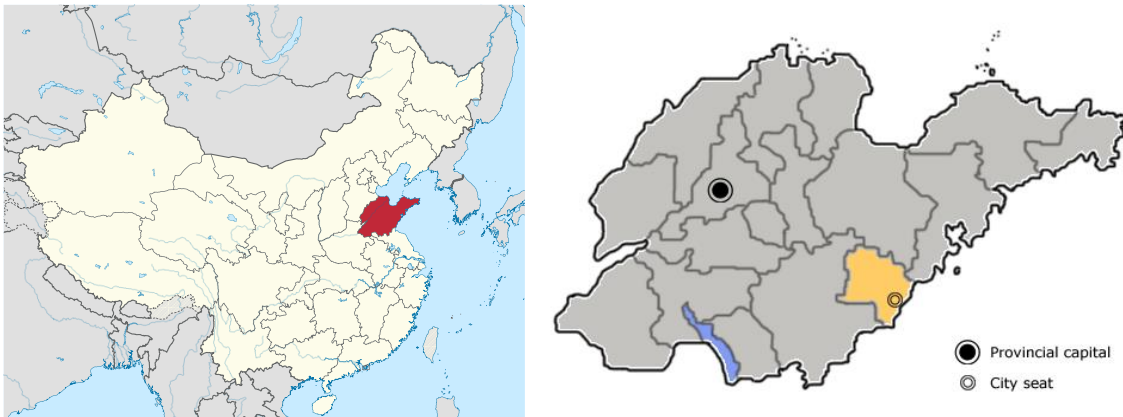


Figure 27. Location of Shandong in China (left) and Rizhao in Shandong (right). Source: Wikipedia

The Rizhao Economic and Technology Development Area, or REDA, is an industrial park located in Rizhao. It is located close to the city port, which is mainly used for coal transportation at national level. It was first established in 1991 in an area of 10 km<sup>2</sup>, which by the year 2003 had expanded to an area of 115 km<sup>2</sup> (Yu, Han and Cui, 2015).

The predecessor of REDA was the Rizhao Export Processing Zone, renamed Rizhao Development Zone in 1992. In the early stages, the main economic activities performed in REDA focused on cement, lubricating oil, and biological pharmaceutical production. By 1994, the industrial output value (IOV) of REDA was around 400 million yuan. By 2011 the IOV was around 55,6 billion yuan. The main industries participating in the IS were cereal oil and food, machinery, pulp and paper, textile, garment, wine, and biochemistry.

By the year 2011, the main organizations involved in water exchanges were the following:

1. Aquaculture Mill
2. Citrate Acid Factory
3. CQ Fertilizer Factory
4. Feed Mill
5. QD Beer Brewery
6. Rizhao Port
7. Rizhao Sewage Treatment Plant (No. 1 & 2)
8. Rizhao Steelworks
9. RW Distillery & Wine
10. SB Fertilizer
11. XL Oil (or BJSW Oil)
12. YG Thermal Power Plant
13. YT Building Material Factory
14. YTSB Pulp and Paper Limited Company
15. YTSB Sewage Treatment Plant

### *3.2.3.2. Characterization of the Actors Involved and Intermediaries*

Figure 28 represents the main organizations and the flows involved in the symbiotic exchanges of the REDA case, including energy, water, and material exchanges. Table 20 summarizes the main actors exchanging water in the REDA IS, how they are classified according to their application category, to which industry they belong, and the subsequent water quality they require.

The aquaculture mill belongs to the fishing and aquaculture industry. According to Yeo, Binkowski and Morris (2004), aquaculture usually requires effluents from low to intermediate grade, with a wide range of variation. Just as in the HHG case, it is assumed that the water required by this industry is of quality 3.0. In addition, it is assumed that the feed mill requires the same quality of effluent.

The Rizhao port is classified as a municipal infrastructure that requires an intermediate grade water. Thus, its quality required is defined on 3.0. Subsequently, it is possible to notice that the water quality required by the actors of REDA ranges from 1.0 to 5.4, i.e. from low to high-grade water.

The Rizhao Sewage Treatment Plant (No. 1 & 2) has as a primary activity the treatment and purification of the wastewater. It aims to treating water as a municipal service. Thus, this organization is considered as a municipal wastewater treatment intermediary (M). For further clarifications refer to section 2.3.

The YTSB Sewage Treatment Plant is a private plant that has as a primary activity the treatment and purification of the wastewater. Moreover, it aims to treating water for industrial purposes, and not as a municipal service. Thus, this organization is considered as an industrial wastewater treatment intermediary (I). For further clarifications refer to section 2.3.

YG Thermal Power Plant belongs to the electric utilities industry. Subsequently, its water quality requirement ranges from 2.0 to 5.4, depending on if it is the primary or secondary user. For further information refer to section 3.1.3.4.

YT Building Material Factory is a company that manufactures construction materials. Thus, this actor belongs to the industry of building materials manufacturing. AS clarified in the Kalundborg case, the production process of building materials will be defined as requiring a high-grade water. For this case, it is assumed that the water required by this industry is 5.0.

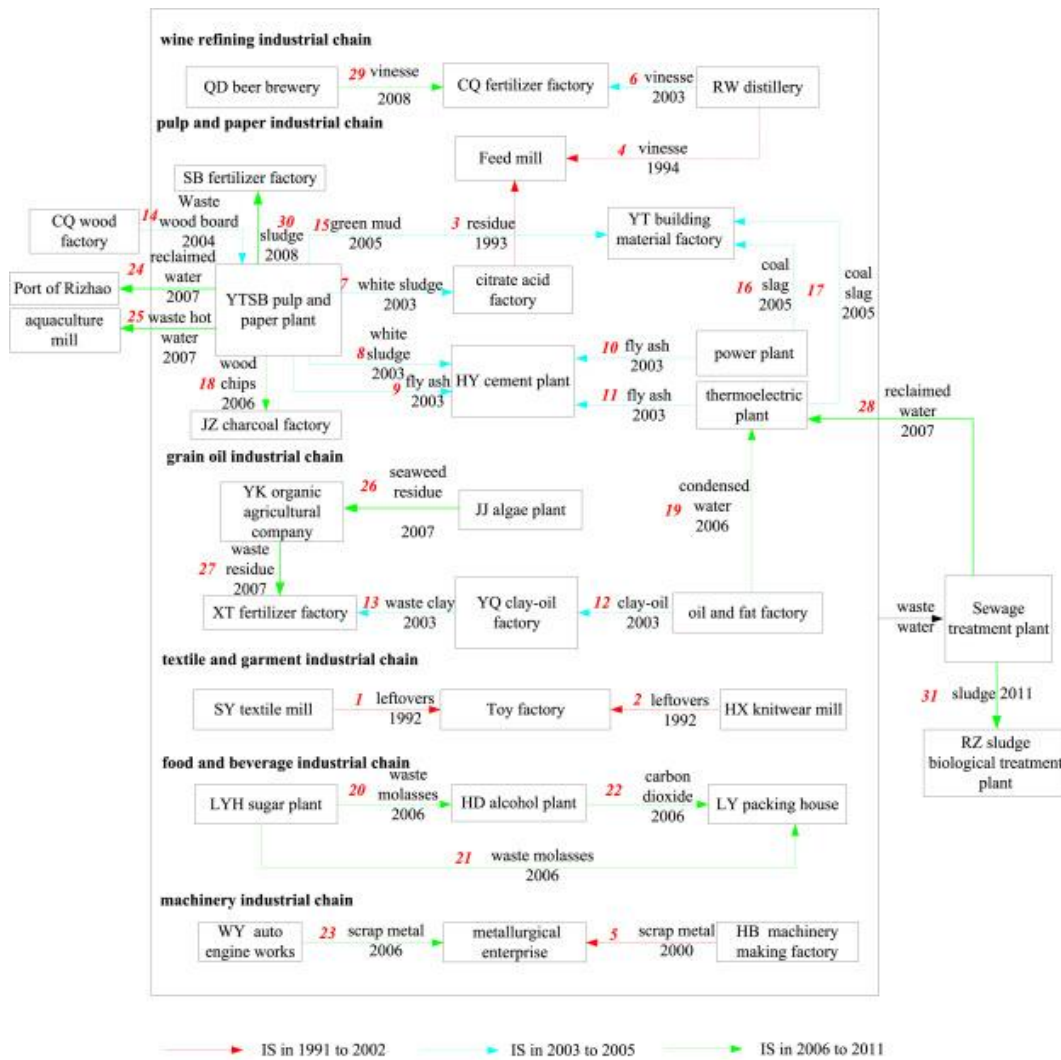


Figure 28. IS network of the REDA case. Source: Yu, Han and Cui (2015)

Table 20. Actors involved in water exchanges in REDA

Actor	Category	Industry	Quality required
Aquaculture Mill	Agriculture	Fishing and aquaculture	3.0
Citrate Acid Factory	Industry	Organic chemistry	2.1
CQ Fertilizer Factory	Industry	Chemical fertilizer	3.0
Feed Mill	Agriculture	Food and beverages	3.0
QD Beer Brewery	Industry	Brewery	2.1
Rizhao Port	Municipal	Transportation and storage	3.0
Rizhao Sewage Treatment Plant (No. 1 & 2)	Municipal (M)	Wastewater treatment	1.0
Rizhao Steelworks	Industry	Steel	3.1
RW Distillery & Wine	Industry	Beverage	2.1
SB Fertilizer	Industry	Chemical fertilizer	3.0
XL Oil (or BJSW Oil)	Industry	Vegetable oil	2.1
YG Thermal Power Plant	Industry	Electric utilities	2.0 - 5.4
YT Building Material Factory	Industry	Building materials	5.0
YTSB Pulp and Paper Limited Company	Industry	Pulp and Paper	5.1
YTSB Sewage Treatment Plant	Industry (I)	Wastewater treatment	1.0

### 3.2.3.3. Characterization of the Waterflows

The waterflows characterizing the REDA symbiosis are represented in Table 21. The primary users of flows number 18, and 19 belong to the electric utilities industry. Thus, their required water quality as suppliers is 5.4. The secondary users of flows number 2, 4, 6, 8, 10, 12, 14, 16, 17, 19, 21, and 25 belong to the electric utilities industry. Thus, their required water quality as users is 2.0. For further information refer to section 3.1.3.4

It can be noticed that 23 out of the 25 waterflows included in this case contain a water treatment, thus they are classified as recycling. Moreover, 15 out of the 23 treated waterflows are classified as downcycling, 1 as same level recycling, and the remaining 7 as upcycling. On the contrary, there are only 2 waterflows classified as reusing.

In addition, the waterflows required by the primary users range from low to high quality. Secondary users require from low to intermediate grade water.



Table 21. Waterflows characterization of the REDA case

	Primary use		Intermediary		Secondary use		Level
	Quality in	User	Actor	Treated?	Quality in	User	
1	2.1	Citrate Acid Factory	Rizhao Sewage Treatment Plant	Yes (M)	3.1	Rizhao Steelworks	U
2	2.1	Citrate Acid Factory	Rizhao Sewage Treatment Plant	Yes (M)	2.0	YG Thermal Power Plant	D
3	3.0	CQ Fertilizer Factory	Rizhao Sewage Treatment Plant	Yes (M)	3.1	Rizhao Steelworks	U
4	3.0	CQ Fertilizer Factory	Rizhao Sewage Treatment Plant	Yes (M)	2.0	YG Thermal Power Plant	D
5	3.0	Feed Mill	Rizhao Sewage Treatment Plant	Yes (M)	3.1	Rizhao Steelworks	U
6	3.0	Feed Mill	Rizhao Sewage Treatment Plant	Yes (M)	2.0	YG Thermal Power Plant	D
7	2.1	QD Beer Brewery	Rizhao Sewage Treatment Plant	Yes (M)	3.1	Rizhao Steelworks	U
8	2.1	QD Beer Brewery	Rizhao Sewage Treatment Plant	Yes (M)	2.0	YG Thermal Power Plant	D
9	3.1	Rizhao Steelworks	Rizhao Sewage Treatment Plant	Yes (M)	3.1	Rizhao Steelworks	S
10	3.1	Rizhao Steelworks	Rizhao Sewage Treatment Plant	Yes (M)	2.0	YG Thermal Power Plant	D
11	2.1	RW Distillery & Wine	Rizhao Sewage Treatment Plant	Yes (M)	3.1	Rizhao Steelworks	U
12	2.1	RW Distillery & Wine	Rizhao Sewage Treatment Plant	Yes (M)	2.0	YG Thermal Power Plant	D
13	3.0	SB Fertilizer	Rizhao Sewage Treatment Plant	Yes (M)	3.1	Rizhao Steelworks	U
14	3.0	SB Fertilizer	Rizhao Sewage Treatment Plant	Yes (M)	2.0	YG Thermal Power Plant	D
15	2.1	XL Oil (or BJSW Oil)	Rizhao Sewage Treatment Plant	Yes (M)	3.1	Rizhao Steelworks	U
16	2.1	XL Oil (or BJSW Oil)	Rizhao Sewage Treatment Plant	Yes (M)	2.0	YG Thermal Power Plant	D
17	2.1	XL Oil (or BJSW Oil)	N/A	No	2.0	YG Thermal Power Plant	R
18	5.4	YG Thermal Power Plant	Rizhao Sewage Treatment Plant	Yes (M)	3.1	Rizhao Steelworks	D
19	5.4	YG Thermal Power Plant	Rizhao Sewage Treatment Plant	Yes (M)	2.0	YG Thermal Power Plant	D

	Primary use		Intermediary		Secondary use		Level
	Quality in	User	Actor	Treated?	Quality in	User	
20	5.0	YT Building Material Factory	Rizhao Sewage Treatment Plant	Yes (M)	3.1	Rizhao Steelworks	D
21	5.0	YT Building Material Factory	Rizhao Sewage Treatment Plant	Yes (M)	2.0	YG Thermal Power Plant	D
22	5.1	YTSB Pulp and Paper	N/A	No	3.0	Aquaculture Mill	R
23	5.1	YTSB Pulp and Paper	YTSB Sewage Treatment Plant	Yes (I)	3.0	Rizhao Port	D
24	5.1	YTSB Pulp and Paper	Rizhao Sewage Treatment Plant	Yes (M)	3.1	Rizhao Steelworks	D
25	5.1	YTSB Pulp and Paper	Rizhao Sewage Treatment Plant	Yes (M)	2.0	YG Thermal Power Plant	D

3.2.3.4. *O/D Matrix*

Table 22 represents the O/D matrix for this case.

Agriculture applications are involved in 3 of the 25 water exchanges in study (12%), either as the supplier or as the user. The only waterflow received by an agriculture application comes from an industrial application. On the contrary, the 2 waterflows supplied by agriculture applications are destined to industries. Municipal applications are involved in only one of the water exchanges, acting as a user receiving water from an industrial application.

Industrial applications are involved in all of the water exchanges in study, either as the supplier or as the user. Additionally, 2 of the 23 waterflows received by industrial applications come from the same industry and same process, 19 are shared between different industries, and the remaining 2 come from agriculture applications.

Table 22. *O/D matrix of the REDA case*

Origin/Destination	Same Industry		Industry	Municipal	Agriculture
	Same process	Different process			
Industry	9; 19		1; 2; 3; 4; 7; 8; 10; 11; 12; 13; 14; 15; 16; 17; 18; 20; 21; 24; 25	23	22
Municipal	N/A	N/A			
Agriculture	N/A	N/A	5; 6;		

3.2.3.5. *L-O/D Matrix*

Figure 29 represents the L-O/D Matrix of the REDA symbiosis waterflows.

When an agriculture application is involved (only as suppliers), the 2 waterflows are classified upcycling and downcycling, respectively. On the contrary, when an industrial application is involved, 2 waterflows are classified as reusing, 14 as downcycling, 1 as same level, and the remaining 6 as upcycling.

There are 23 waterflows passing through wastewater treatment organizations. All of them are destined to industrial organizations, with only one exception destined to a municipal application. Moreover, all treatments are performed by a municipal wastewater treatment application, with the only exception of the waterflow destined to a municipal application. In this case, the treatment is performed by an industrial application.

When waterflows are exchanged between the same type of applications (i.e. industry to industry), 1 of the 21 waterflows is characterized as reusing, 13 as downcycling, 1 as same level, and the remaining 6 as upcycling. On the contrary, when waterflows are exchanged between different applications, 1 of the 4 waterflows is characterized as reusing. 2 as downcycling, and the remaining one as upcycling.

Finally, when waterflows are exchanged between different industries, 1 of the 19 waterflows is characterized as reusing, 12 as downcycling, and the remaining 6 as upcycling. When waterflows are exchanged between the same industry and same process, one waterflow is characterized as downcycling and the other one as same level.



Figure 29. L-O/D matrix of the REDA case

### 3.2.4. SCIP – China

The following case study is centred on an IS occurring on Dalian, a city located in the Liaoning province of China. The exchanges analysed are based on data of the year 2010, retrieved from the article developed by Zhang *et al.*, (2017) named “Life cycle assessment of industrial symbiosis in Songmudao chemical industrial park, Dalian, China”.

#### 3.2.4.1. *Context of the Case Study*

Dalian is a major port city located at the southeast of the Liaoning Province of China. This city is the second largest city in the province, and it is classified as a sub-provincial on administrative status. It is adjacent to the Shandong province at the southwest, and it faces Korea across the Yellow Sea to the east. Nowadays the city is considered as a financial, shipping, and logistics centre for the entire Northeast Asia, mainly used throughout its history by foreign states. Figure 30 represents the geographical location of the city in study.



Figure 30. Location of Liaoning in China (left) and Dalian in Liaoning (right). Source: Wikipedia

The Songmudao Chemical Industrial Park, or SCIP, is a large-scale chemical industry park located in the city of Dalian. Due to the urban expansion, industries had to re-locate, hence creating the industrial park. Moreover, the formation of the new eco-industrial park was due to a combination of several factor, such as the resources combination, the technological development level, the industrial characteristics of the actors, among others.

The basic industrial chain of the park is the synthetic gas chemical industry chain, which includes an ammonia plant, an ammonium nitrate plant, a cement plant, a cogeneration power plant, a fertilizer plant, a soda plant, and a wastewater treatment plant.

The network if the IS is achieved due to material, energy, and water exchanges between the actors. Moreover, the notional hub of the systems is the ammonia plant, acting as the core of the symbiosis.

The SCIP operation is often suggested as a reference for the design, operation, and production of other eco-industrial parks, because of its high economic performance and low generation of environmental pollution (Zhang *et al.*, 2017).

By the year 2010, the main organizations involved in water exchanges were the following:

1. Ammonia Plant
2. Ammonium Nitrate Plant
3. Cogeneration Power Plant
4. Soda Plant

#### *3.2.4.2. Characterization of the Actors Involved and Intermediaries*

Figure 31 represents the main organizations and the flows involved in the symbiotic exchanges of the SCIP case, including energy, water, and material exchanges. Table 23 summarizes the main actors exchanging water in the SCIP IS, how they are classified according to their application category, to which industry they belong, and the subsequent water quality they require.

According to Table 13 the water quality required by chemical sub-industries comprise a wide range., from 2.0 to 5.4. Moreover, some actors from this IS case belong to the chemical industry, although their specific sub-industry is not clearly defined. As a conservative approach, when a waterflow is received by these types of actors the reference quality will be the lower value of the range, namely 2.0. On the contrary, if it is sent by these types of actors, the reference quality will be the higher value of the range, namely 5.4. This is the case of the Ammonia Plant and the Soda Plant.

The Cogeneration Power Plant belongs to the electric utilities industry. Subsequently, its water quality requirement ranges from 2.0 to 5.4, depending on if it is the primary or secondary user. For further information refer to section 3.1.3.4.

It is possible to notice that the water quality required by the actors of SCIP ranges from 2.0 to 5.4, i.e. from low to high-grade water. In addition, there are no intermediaries in this IS case.

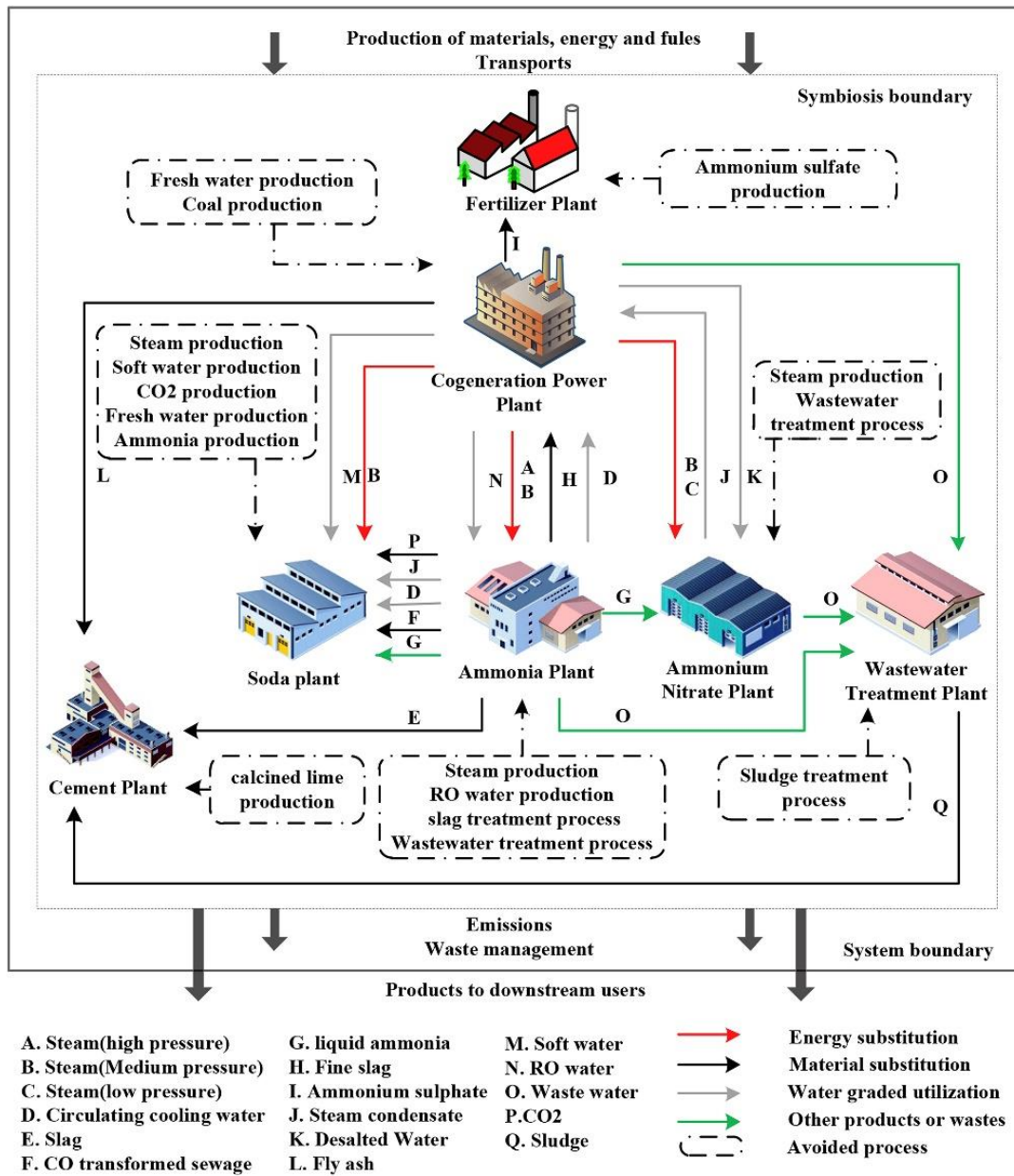


Figure 31. IS network of the SCIP case. Source: Wang et al. (2019)

Table 23. Actors involved in water exchanges in SCIP

Actor	Category	Industry	Quality required
Ammonia Plant	Industry	Chemicals manufacturing	2.0 - 5.4
Ammonium Nitrate Plant	Industry	Chemical fertilizer	3.0
Cogeneration Power Plant	Industry	Electric utilities	2.0 - 5.4
Soda Plant	Industry	Chemicals manufacturing	2.0 - 5.4

### 3.2.4.3. Characterization of the Waterflows

The waterflows characterizing the SCIP symbiosis are represented in Table 24. The primary users of flows number 1, 2, 4, 5, and 6 belong either to the chemical or to the electric utilities industries. Thus, their required water quality as suppliers is 5.4. The secondary users of flows number 1, 2, 3, 4, and 6 belong either to the chemical or to the electric utilities industries. Thus, their required water quality as users is 2.0. For further information refer to section 3.1.3.4.

It can be noticed that none of the waterflows include a water treatment, thus they are classified as reusing. In addition, all waterflows required the primary users range from intermediate to high-grade water. Waterflows required by the secondary users are low-grade water, with the only exception of waterflow number 5 which is intermediate grade.

Table 24. Waterflows characterization of the SCIP case

	Primary use		Intermediary		Secondary use		Level
	Quality in	User	Actor	Treated?	Quality in	User	
1	5.4	Ammonia Plant	N/A	No	2.0	Cogeneration Power Plant	R
2	5.4	Ammonia Plant	N/A	No	2.0	Soda Plant	R
3	3.0	Ammonium Nitrate Plant	N/A	No	2.0	Cogeneration Power Plant	R
4	5.4	Cogeneration Power Plant	N/A	No	2.0	Ammonia Plant	R
5	5.4	Cogeneration Power Plant	N/A	No	3.0	Ammonium Nitrate Plant	R
6	5.4	Cogeneration Power Plant	N/A	No	2.0	Soda Plant	R

### 3.2.4.4. O/D Matrix

Table 25 represents the O/D matrix for this case. It can be noticed that there are no agriculture nor municipal applications involved in the water exchanges in study. On the contrary, industrial applications are involved in all water exchanges in study, both as the supplier and the user. Additionally, 1 of the 6 waterflows received by industrial applications come from the same industry but a different process, and the remaining 5 come from a different industry.

Table 25. O/D matrix of the SCIP case

Origin/Destination	Same Industry		Industry	Municipal	Agriculture
	Same process	Different process			
Industry		2	1; 3; 4; 5; 6		
Municipal	N/A	N/A			
Agriculture	N/A	N/A			



*3.2.4.5. L-O/D Matrix*

Figure 32 represents the L-O/D Matrix of the SCIP symbiosis waterflows. It can be noticed that all waterflows are classified as reusing. Moreover, there are no waterflows passing through intermediary organizations nor receiving treatment.

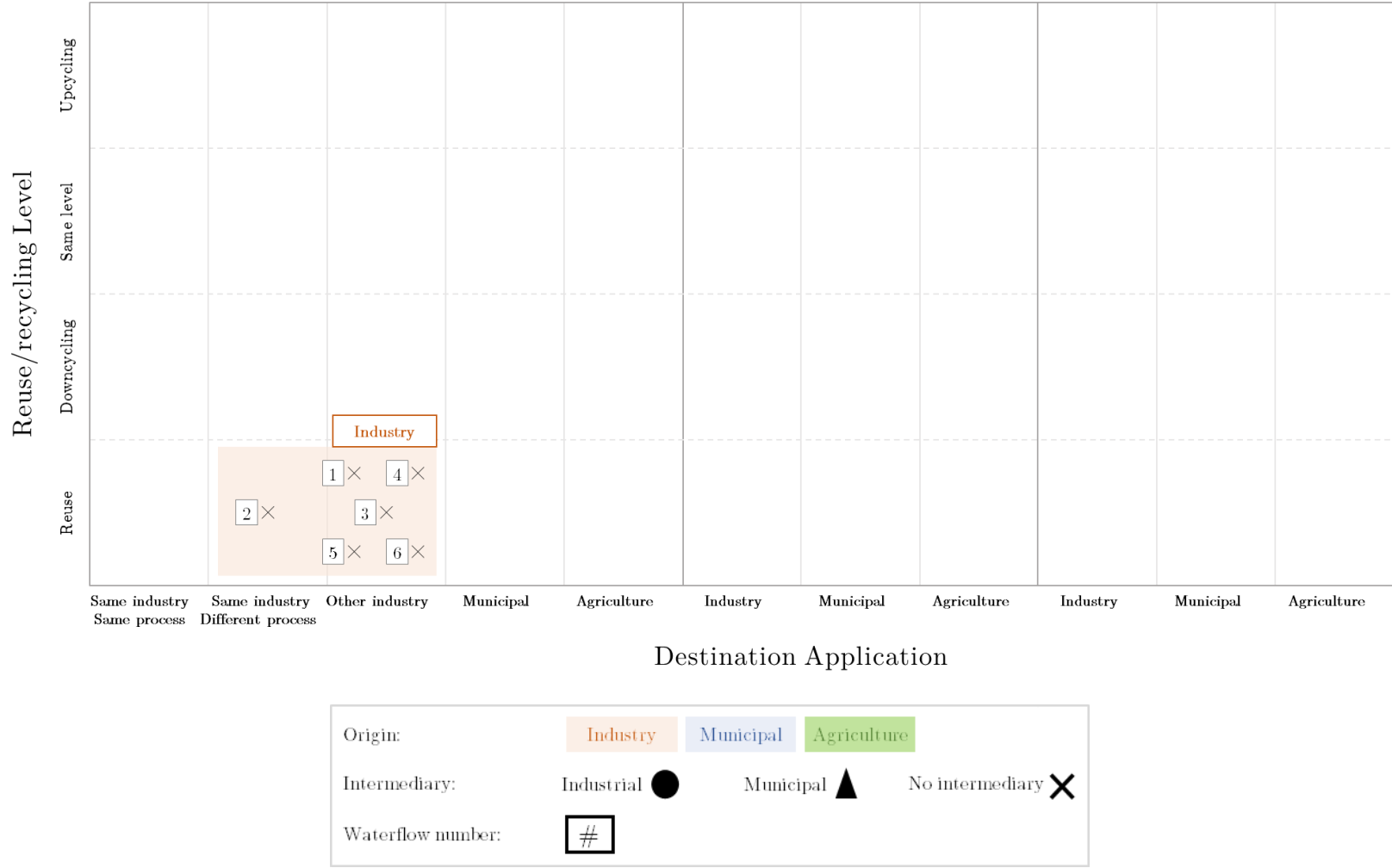


Figure 32. L-O/D matrix of the SCIP case

### 3.2.5. UPM Kymi – Finland

The following case study is centred on an IS occurring in the Kuusankoski neighbourhood, located in the city of Kouvola in Finland. The exchanges analysed are based on data from the year 2005, based on the article written by Pakarinen *et al.* (2010) “Sustainability and industrial symbiosis - The evolution of a Finnish forest industry complex”.

#### 3.2.5.1. *Context of the Case Study*

The UPM Kymi paper mill is located in the city of Kouvola, Finland, around 140 kilometres away from Helsinki (UPM Communication Papers, 2019). This place has been inhabited since the middle ages. However, the enhanced development did not start until the 1870s, when the village at that time became an important railway junction due to the construction of trainlines. With additional developments, this junction became one of the busiest in Finland.

In 1922 the village was separated from the municipality of Valkeala. Later, it was officially established as a city in 1960. In January 2009, the six municipalities of Kouvola, Kuusankoski, Elimäki, Anjalankoski, Valkeala, and Jaala were consolidated, to form the new municipality of Kouvola. Figure 33 shows the location of the city in Finland.

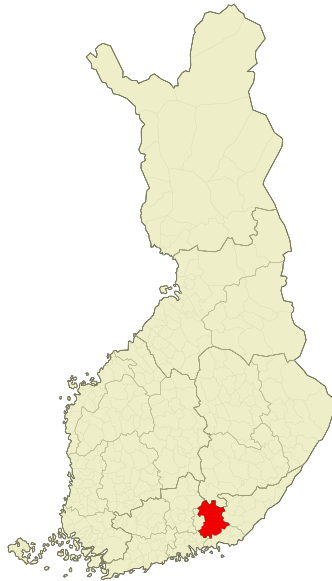


Figure 33. Location of Kouvola in Finland. Source: Wikipedia

Kouvola has also assumed the slogan “Kymijoen kaupunki” - the town of Kymijoki -, referring to the important river of the city and related directly to the name of the IS system analysed.

The Kymi (or Kymijoki) river is located southeast of Finland, at the beginning from lake Päijänne and discharging into the Gulf of Finland.

The paper mill of the case study was founded in 1872 by the River Kymijoki in Kuusankoski and is part of the UPM Kymi integrated mill site. An increasing demand for paper from the Russian markets drove the early growth of the symbiotic exchanges. The exports started and subsequently the production expanded quickly. Additionally, a railway connection was built in 1892 to facilitate the transport of goods for bigger markets (Pakarinen *et al.*, 2010; UPM Communication Papers, 2019).

In 1917 the Finnish declaration of independence from Russia produced a temporary market decline, even more strengthened by the following civil war and the Russian Bolshevik Revolution. Subsequently, in the 1920s production slowly revitalized by exporting to other regions like USA and Western European Countries. The World War II posed a second temporary market decline, taking several years for the market to revive again (Pakarinen *et al.*, 2010).

In the 1950s the industry regained its position. In fact, between the years 1955 and 1971 the production almost doubled, and then between 1971 and 1990 almost doubled again. Moreover, as stated by Pakarinen *et al.*, by the year 1990 “the Kymi pulp and paper mill was the biggest fine paper manufacturer in Europe with a total production of 535.000 tonnes” (Pakarinen *et al.*, 2010).

This case is based on water exchanges surrounding the UPM Kymi paper mill in the year 2005. By this year, the global pulp and paper industry had not yet suffered the consequences of the economic crisis of 2008. Subsequently, the industry still enjoyed of promising numbers in a fast-growing market. In particular for Finland, by the year 2005 around 16% of the total industrial value added came from the pulp and paper production (Statistics Finland, 2008)

By the year 2005, the main organizations involved in water exchanges were the following:

1. Energy Distributor
2. Power Plant

### *3.2.5.2. Characterization of the Actors Involved and Intermediaries*

Figure 34 represents the main organizations and the flows involved in the symbiotic exchanges of the UPM Kymi case, including energy, water, and material exchanges.

The Power Plant belongs to the electric utilities industry. Subsequently, its water quality requirement ranges from 2.0 to 5.4, depending on if it is the primary or secondary user. For further information refer to section 3.1.3.4.

Even though it appears that the water network of the case has many connections between the actors, in fact most effluents are either destined to an intermediary organization – the wastewater treatment plant – or origin from an intermediary organization – the water purification plant. Thus, since they are not connected to each other, most of the waterflows from Figure 34 do not classify as circular practices, for they do not have either a primary or a secondary user.

As a consequence, there is only one waterflow that classified as a circular practice. This waterflow is the district heating sent from the power plant to the energy distributor. In addition, there are no intermediaries in this IS case.

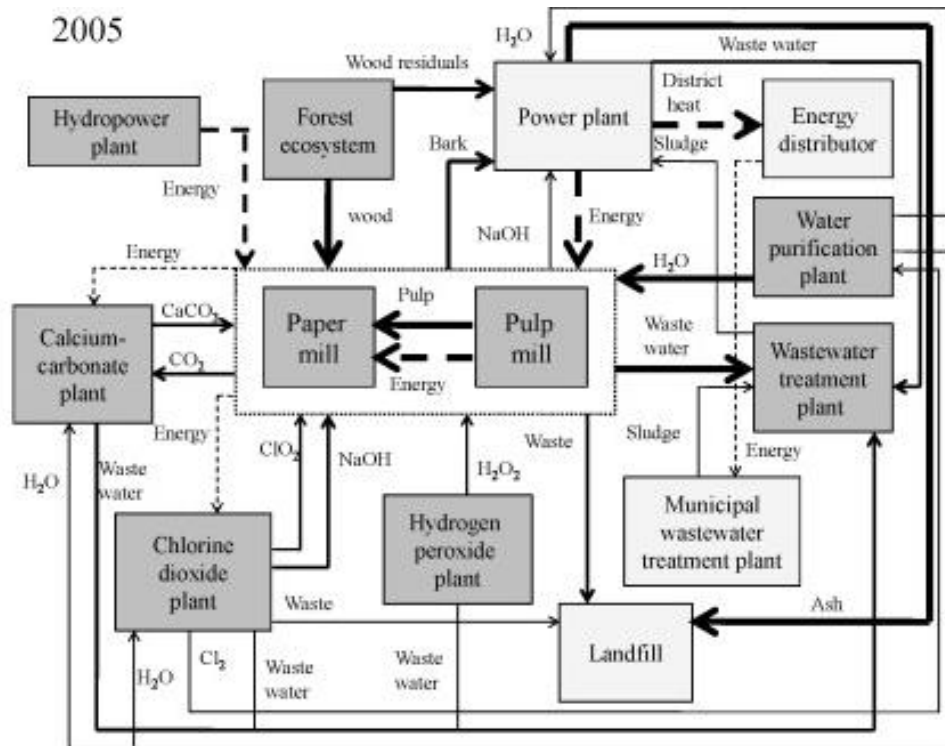


Figure 34. IS network of the UPM Kymi case. Source: Pakarinen et al. (2010)

Table 26 summarizes the main actors exchanging water in the UPM Kymi IS, how they are classified according to their application category, to which industry they belong, and the subsequent water quality they require. It is possible to notice that the water requirements in this case range from a quality 4.0 to 5.4, i.e. from intermediate to high-grade water.

Table 26. Main actors in the water network of the HHG case

Actor	Category	Industry	Quality requirement
Energy Distributor	Municipal	District heating	4.0
Power Plant	Industry	Electric utilities	2.0 - 5.4

### 3.2.5.3. Characterization of the Waterflows

The only waterflow characterizing the water network of the UPM Kymi symbiosis is represented in Table 27. The primary users of the waterflow belongs to the electric utilities industry. Thus, its required water quality as suppliers is 5.4. For further information refer to section 3.1.3.4. It can be noticed that the exchange does not include a water treatment, thus it is classified as reusing. In addition, it can be noticed that the waterflow required by the primary user is high-grade, while the one required by the secondary user is intermediate grade.

Table 27. Waterflows characterization of the UPM Kymi case

	Primary use		Intermediary		Secondary use		Level
	Quality in	User	Actor	Treated?	Quality in	User	
1	5.4	Power Plant	N/A	No	4.0	Energy Distributor	R

### 3.2.5.4. O/D Matrix

Table 28 represents the O/D matrix for this case. It can be noticed that there are no agriculture applications involved in the water exchanges in study. The only waterflow is exchanged from an industrial to a municipal application.

Table 28. O/D matrix of the UPM Kymi case

Origin/Destination	Same Industry		Industry	Municipal	Agriculture
	Same process	Different process			
Industry				1	
Municipal	N/A	N/A			
Agriculture	N/A	N/A			

### 3.2.5.5. L-O/D Matrix

Figure 35 represents the L-O/D Matrix of the UPM Kymi symbiosis waterflow. As seen before, the only waterflow is classified as reusing from an industry to a municipal application. In addition, there are no intermediaries involved.



Figure 35. L-O/D matrix of the UPM Kymi case

### 3.2.6. YEDZ – China

The following case study is centred on an IS occurring northeast of Yongcheng, a city located in the Henan province of China. The exchanges analysed are based on data from the year 2017, from the article developed by Wang *et al.* (2019) named “Life cycle assessment of reduction of environmental impacts via industrial symbiosis in an energy-intensive industrial park in China”.

#### 3.2.6.1. *Context of the Case Study*

Yongcheng is a county-level city at the easternmost part of the Henan province of China. In 2014 it was upgraded to a provincially directly administered city. Moreover, it is surrounded by three other provinces of China, namely Shandong, Jiangsu, and Anhui. This region is well-known by being a coal-rich part of China.

This city is located on the basin of the Huai River, at the easternmost part of the Henan Province. Besides, the Tuo Hui River passes through the urban area of the city. Figure 36 represents the geographical location of the city in study.



Figure 36. Location of Henan in China (left) and Yongcheng in Henan (right). Source: Wang *et al.* (2019)

The Yongcheng Economic Development Zone, or YEDZ, is an energy intensive eco-industrial park composed by several types of industries. Some of them are a cogeneration power plant, a chemical plant producing methanol/ethylene glycol, an electrolytic aluminium and aluminium deep processing plant, ironworks, food, plasterboard factories, and a wastewater treatment plant. The wastewater treatment plant collects and treats domestic and industrial water, including the mining wastewater (pit water) for further purification (Wang *et al.*, 2019).



Some of the industries present in YEDZ are highly energy-intensive, usually with high coal consumption, and thus high pollutant emitters. In fact, China's national standard for energy intensity in eco-industrial parks is surpassed greatly by some of these industries. In particular, the cogeneration power plant surpasses this value over 20 times, which is the highest. Furthermore, the output economic value of YEDZ accounts for 46% of the GDP and 67% energy consumption in the Yongcheng city.

By the year 2017, the main organizations involved in water exchanges were the following:

1. Cogeneration Power Plant
2. Iron Works
3. Methanol/ethylene Glycol Chemical Plant
4. Mining Zone
5. Residential Zone
6. Wastewater Reclamation Plant

### *3.2.6.2. Characterization of the Actors Involved and Intermediaries*

Figure 37 represents the main organizations and the flows involved in the symbiotic exchanges of the YEDZ case, including energy, water, and material exchanges.

The Cogeneration Power Plant belongs to the electric utilities industry. Subsequently, its water quality requirement ranges from 2.0 to 5.4, depending on if it is the primary or secondary user. For further information refer to section 3.1.3.4.

According to Wang *et al.* (2019), the wastewater reclamation plant of the system receives domestic wastewater coming from the residential zone of the city. In addition, it also receives "pit water", which is effluent coming from nearby mining activities. Thus, it is the author includes both a residential zone and a mining industry in the system, for completeness of the analysis.

Furthermore, the case is modelled with the residential zone receiving potable water (of quality 5.0) and providing the resulting effluent to the wastewater reclamation plant. Accordingly, the mining zone is modelled receiving mining water (of quality 5.4) and providing the resulting effluent to the wastewater treatment plant. Thus, the wastewater treatment plant acts as an intermediary between the residential zone and the mining with the rest of the industries in the water network.

Table 29 summarizes the main actors exchanging water in the YEDZ IS, how they are classified according to their application category, to which industry they belong, and the subsequent water quality they require. It is possible to notice that the water requirements in this case range from a quality 1.0 to 5.4, i.e. from low to high-grade water.

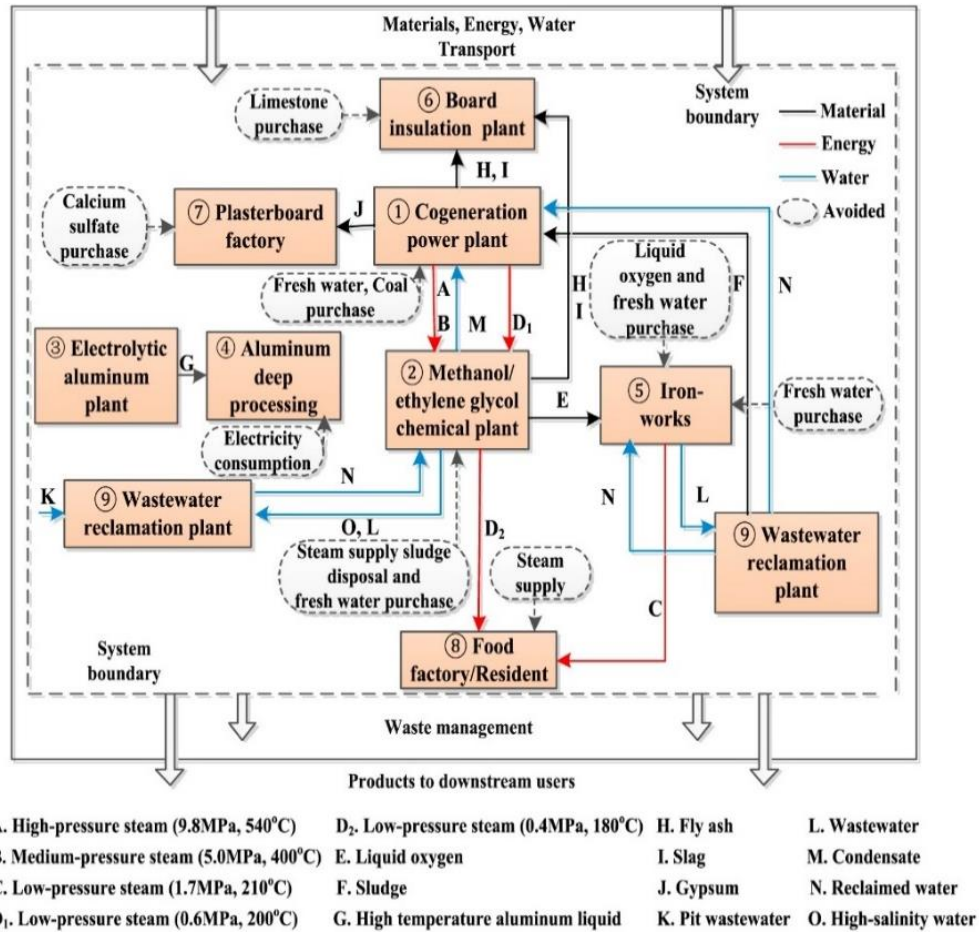


Figure 37. IS network of the YEDZ case. Source: Wang et al. (2019)

Table 29. Actors involved in water exchanges in YEDZ

Actor	Category	Industry	Quality requirement
Cogeneration Power Plant	Industry	Electric utilities	2.0 - 5.4
Iron Works	Industry	Steel	3.1
Methanol/ethylene Glycol Chemical Plant	Industry	Polymer chemistry	2.1
Mining Zone	Industry	Mining	5.4
Residential Zone	Municipal	Potable water	5.0
Wastewater Reclamation Plant	Municipal (M)	Wastewater treatment	1.0

The wastewater reclamation plant has as a primary activity the treatment and purification of the wastewater. Moreover, it aims to treating water as a municipal service. Thus, this organization is considered as a municipal wastewater treatment intermediary (M). For further clarifications refer to section 2.3.

3.2.6.3. *Characterization of the Waterflows*

The waterflows characterizing the YEDZ symbiosis are represented in Table 30. The secondary users of flows number 1, 4, 5, 8, and 10 belong to the electric utilities industry. Thus, their required water quality as users is 2.0. For further information refer to section 3.1.3.4

Table 30. Waterflows characterization of the YEDZ case

	Primary use		Intermediary		Secondary use		Level
	Quality in	User	Actor	Treated?	Quality in	User	
1	3.1	Iron Works	Wastewater Reclamation Plant	Yes (M)	2.0	Cogeneration Power Plant	D
2	3.1	Iron Works	Wastewater Reclamation Plant	Yes (M)	3.1	Iron Works	S
3	3.1	Iron Works	Wastewater Reclamation Plant	Yes (M)	2.1	Methanol/ethylene Glycol Plant	D
4	2.1	Methanol/ethylene Glycol Plant	Wastewater Reclamation Plant	Yes (M)	2.0	Cogeneration Power Plant	D
5	2.1	Methanol/ethylene Glycol Plant	N/A	No	2.0	Cogeneration Power Plant	R
6	2.1	Methanol/ethylene Glycol Plant	Wastewater Reclamation Plant	Yes (M)	3.1	Iron Works	U
7	2.1	Methanol/ethylene Glycol Plant	Wastewater Reclamation Plant	Yes (M)	2.1	Methanol/ethylene Glycol Plant	S
8	5.4	Mining Zone	Wastewater Reclamation Plant	Yes (M)	2.0	Cogeneration Power Plant	D
9	5.4	Mining Zone	Wastewater Reclamation Plant	Yes (M)	3.1	Iron Works	D
10	5.4	Mining Zone	Wastewater Reclamation Plant	Yes (M)	2.1	Methanol/ethylene Glycol Plant	D
11	5.0	Residential Zone	Wastewater Reclamation Plant	Yes (M)	2.0	Cogeneration Power Plant	D
12	5.0	Residential Zone	Wastewater Reclamation Plant	Yes (M)	3.1	Iron Works	D
13	5.0	Residential Zone	Wastewater Reclamation Plant	Yes (M)	2.1	Methanol/ethylene Glycol Plant	D

It can be noticed that most of the waterflows contained in this case include a water treatment, thus they are classified as recycling. Moreover, only 1 of the 13 waterflows is classified as reusing. Of the 12 recycled waterflows, 10 are classified as downcycling, 2 as same level, and 1 as upcycling.

#### 3.2.6.4. O/D Matrix

Table 31 represents the O/D matrix for this case. It can be noticed that there are no agriculture applications involved in the water exchanges in study. Municipal applications are involved in 3 of the 13 water exchanges in study, only as suppliers. In all three of the waterflows supplied by municipal applications the destination are industries,

On the contrary, industrial applications are involved in all of the water exchanges in study, either as the supplier or as the user. In fact, all the destinations of the water exchanges are industries. Moreover, 2 of the 13 waterflows come from the same industry and same process, 8 are shared between different industries, and the remaining 3 come from municipal applications.

Table 31. O/D matrix of the YEDZ case

Origin/Destination	Same Industry		Industry	Municipal	Agriculture
	Same process	Different process			
<b>Industry</b>	2; 7		1; 3; 4; 5; 6; 8; 9; 10		
<b>Municipal</b>	N/A	N/A	11; 12; 13		
<b>Agriculture</b>	N/A	N/A			

#### 3.2.6.5. L-O/D Matrix

Figure 38 represents the L-O/D Matrix of the YEDZ symbiosis waterflows. When a municipal application is involved as supplier, all water exchanges are classified as downcycling. On the contrary, when an industrial application is involved as supplier, 1 of the 10 water exchanges is reuse level, 6 are downcycling, 2 are same level, and the remaining one is upcycling. In addition, all of the waterflows pass through a municipal wastewater treatment intermediary, with the exception of waterflow 5 that is directly transferred for reusing. In all the cases the receiver is an industrial application.

Finally, when waterflows are exchanged between the same industry and same process, both waterflows are characterized as same level. On the contrary, when waterflows are exchanged between different industries, they are mostly downcycled through a municipal intermediary treatment.



Figure 38. L-O/D matrix of the YEDZ case

### 3.2.7. Synthesis of the Cases Analysis

A total of 64 waterflows were characterized qualitatively throughout the six cases studied in the previous section. Table 32 shows the summarized description of these waterflows, ordered by their frequency of occurrence.

Table 32. *Synthesis of the overall cases analysis*

Waterflow type		Frequency	Intermediaries		
O/D	R/R level		Industrial	Municipal	No intermediary
Industry to Other Industry	D	18	0	18	0
Industry to Other Industry	R	15	0	0	15
Industry to Other Industry	U	7	0	7	0
Industry to Same Industry. Different Process	R	4	0	0	4
Industry to Municipal	R	4	0	0	4
Municipal to Industry	D	3	0	3	0
Industry to Same Industry. Same Process	S	3	0	3	0
Industry to Municipal	D	2	1	1	0
Industry to Same Industry. Same Process	D	1	0	1	0
Agriculture to Industry	D	1	0	1	0
Industry to Same Industry. Same Process	R	1	0	0	1
Industry to Agriculture	R	1	0	0	1
Municipal to Industry	R	1	0	0	1
Agriculture to Industry	R	1	0	0	1
Industry to Municipal	U	1	1	0	0
Agriculture to Industry	U	1	0	1	0
Total		64	2	35	27

Most waterflows analysed are classified as downcycling from an industry to another industry (28%). The second and third waterflow types were reusing from an industry to another industry (23%), and upcycling from an industry to another industry (11%). All other waterflow classifications represent 6% or less of the waterflows analysed. In addition, 42% of all

waterflows are classified as reusing, 39% as downcycling, 14% as upcycling, and the remaining 5% as same level.

Upcycling is a practice that requires a greater effort in comparison to other practices like downcycling and reusing. In fact, it means that the water received by the secondary user is of greater quality than the one received by the primary user, thus it needs a greater effort in terms of treatment. Same level and downcycling also requires extra energy and costs to treat the effluent, however it is less than upcycling. On the contrary, reusing avoids the extra effort of treating the effluent, sending it directly to the secondary user.

Even if it is not the highest in frequency, upcycling practices are still a considerable amount. This is explained by the structure of the ISWE model. In fact, none of the upcycled waterflows are transferred directly between the actors, but they rather pass through an intermediary. Moreover, the model neglects the intermediaries between organizations. The job of intermediaries is to treat the wastewater coming from the primary user, to then deliver the treated effluent to the secondary user. All of the 8 upcycling waterflows pass through wastewater treatment intermediaries, 7 through municipal intermediaries and the remaining one through an industrial intermediary.

Accordingly, the effort required to treat the flows between different industries is performed mostly by municipal applications. In fact, municipal applications are in charge of 35 of the 37 intermediary treatment activities (95%), while industrial applications act as intermediaries in only 15% of them. From all water exchanges, 37 required treatment intermediaries (58%), while the remaining 27 were transferred directly (42%).

Most waterflows in the IS cases analysed are exchanged between different industries (63%). This amount surpasses by far the second O/D, which is industry to municipal (11%). It can be concluded that industrial applications are the key actors exchanging water in the IS cases analysed, especially when exchanging with different industries. Moreover, 42% of the waterflows do not require any treatment, which is a sign of efficiency in the circularity of the water networks analysed. In fact, IS are characterized for exploiting the value of waterflows while trying to minimize the treatment required to reuse the water resource. Exploiting the value of water effluents requiring minimum or no treatment is in fact the main advantage of an IS.

On the contrary, most water effluents do require treatment (58%). Most of these exchanges are between actors of different industries, although passing through municipal intermediaries that treat the effluents in order to achieve the necessary quality requirements of the user. Thus, industrial applications are key actors in IS systems, but municipal applications are the ones in charge of recycling the water effluents by performing the intermediary treatment between these industrial actors.

In addition, several waterflows were characterized as upcycling between industries with a municipal treatment intermediary. Thus, adopting a dedicated intermediary (such a municipal actor) to treat the effluent can improve the treatment effectiveness, with the positive result of increasing the quality of the effluent to achieve upcycling.

### 3.3. Conclusions on the Qualitative Analysis of Industrial Symbiosis Cases

Water reuse and recycling practices are a key part of the strategic performance of IS systems. In fact, there are several layers on this issue that must be taken into consideration for the correct development of the system.

Regarding the IS case studies, most waterflows are exchanged between different industries. When a water treatment is required, most of these effluents pass through a municipal intermediary, who is in charge of treating the wastewater before delivering it to the user industry. This shows that there is a critical need for sustained interactions, not only between different industries, but also between industries and municipal actors. This interaction is key for developing sustainable water exchanges that are beneficial for all actors involved.

In addition, the complexity of the water exchange process will be defined by the water quality required by the user (in addition to other important techno-economic constraints). In fact, depending on the application of the effluent different technologies can be used, which vary greatly in energy consumption, overall costs, and effectiveness in the separation and removal of pollutants.

Some users will require more complex treatment processes, while others will require minimum treatment or no treatment at all (i.e. the case of water reusing). Thus, depending on the case, some actors may find convenient to treat its own water, while others would prefer to leave this task for intermediary actors.

Finally, from the qualitative analysis it can be said that there are many variables to consider when designing an appropriate water reuse and recycling network. All of them must be taken into consideration in order to create and develop a sustainable IS system. There are no general rules on how to design the correct water network in an IS, for it majorly depends on the several variables previously mentioned in this chapter. In fact, a techno-economic analysis must be done for each case of interest.

An ideal IS system is the one that achieve a perfect circularity in all of its energy, material, and waterflows. Thus, two things are certain.

First, any waste generated inside the overall system is an inefficiency. This includes all waterflows that are not reused nor recycled between the actors of the system. The goal is, in



fact, to reduce all types of flows coming from the outside of the boundaries of the system, and also the ones going outside.

In the case of UPM Kymi, for example, the water network is an open loop. There is in fact no connection between the companies that are sending water to the wastewater treatment plant, with the ones receiving water from the water purification plant. These are, in fact, two separate water networks in the system.

On one hand, the wastewater treatment plant receives wastewater from industries, treats it until regulation levels, and then performs its subsequent disposal. This generation of waste is an important source of inefficiency in the circularity of the IS system. On the other hand, the water purification plant absorbs water from outside the boundaries of the system, purifies it, and then delivers the resource for the industrial users. The waterflow going inside the boundaries of the IS is another source of inefficiency in the circularity of the system.

Second, the water treatment itself is a misalignment. The treatment process is required because of the quality difference between the desired and the available effluent. Thus, an ideal design of the water network of an IS would be when the outflow effluent of all actors have a direct secondary user, i.e. that has only reusing exchanges.

The HHG and the SCIP cases analysed in sections 3.2.1 and 3.2.4 are both examples of an efficient circular water network, at least from the point of view of the ISWE model. All of the 14 waterflows from these cases are directly reused between different applications, without any treatment in between.

However, a perfect circularity of the water network is often not a reality. Thus, wastewater treatment plants act as the absorbers of the misalignment in the water exchange process. Their aim is to align the resulting effluent quality of a primary user to the effluent quality desired by the secondary user. However, the process requires an effort. The alignment in the circularity of the water network requires energy and economic resources.

As an example of absorber of misalignment, the Kalundborg symbiosis analysed in section 3.2.2 included a wastewater treatment and biogas production plant, which absorbed some of the misalignment of the water network while at the same time recovered material from the waste, increasing the overall circularity of the IS. The overall IS system, however, is characterized by a high circularity in the water network, since only 20% of the waterflows have to be treated and the remaining 80% are transferred directly.

In the case of REDA from section 3.2.3 most waterflows are treated (92%), and only a few are reused (8%). Most treated waterflows are treated through the municipal wastewater treatment plant, showing the importance of this plant for the circularity of the treatment. In fact, this plant is crucial to absorb the misalignments of the water network. In addition, 28% of its waterflows are upcycled by this treatment plant, which implies that the effort made to absorb the inefficiencies and misalignments between the actors is considerable.

A similar situation happens in the case of YEDZ from section 3.2.6, where 92% of the waterflows are treated by a municipal application. In this case, most treated waterflows are downcycling or same level recycling, implying a lesser effort made by the treatment plant in order to absorb the misalignments.

## 4. Water Eco-efficiency Indicators in Industrial Symbioses

The aim of this chapter is to describe indicators that refer to the environmental and economic pillars of sustainability on different IS cases, specifically applied to water resources. Moreover, the idea is to develop quantitative eco-efficiency indicators in order to describe the operation and performance of different IS cases on managing water resources. Thus, this chapter presents a quantitative description of water eco-efficiency in the IS context.

Furthermore, much academic literature has focused on the qualitative description and analysis of IS cases. On the contrary, only few of them are focused on a quantitative analysis of these systems, neither for the individual actors nor the IS system as a whole. However, the present chapter describes several well-documented cases where the data available was enough to measure and describe IS cases through eco-efficiency indicators.

Many waterflows are exchanged between the different actors involved in an IS. Thus, reusing and recycling water are critical practices in the water network of most IS systems. Prior to these waterflow exchanges, there was some wastewater that was discharged to the environment.

In fact, previous to the implementation of the IS there were only standalone facilities operating individually, each one consuming certain quantity of water and discharging the residual water to the environment. The circular economy practice of implementing an IS system provides the possibility to expand the value of the waterflows, exploiting their value at their maximum by giving them – ideally – a closed-loop use. Hence, by reusing and recycling water less water is discharged, produced, extracted from natural bodies, and consumed.

Finally, chapter 4 develops four eco-efficiency indicators with the aim to describe in a quantitative way the water eco-efficiency of IS systems. Data was not available for all the cases analysed in section 3.2, so this chapter included some of these cases and also other additional cases in order to have larger representative sample. The indicator values were taken mostly from literature and lifecycle assessment (LCA) studies. Additionally, a proposed indicator is developed at the end of the chapter.

### 4.1. Materials and Methodology

The data used for developing the following indicators was obtained from different academic references, as shown in Table 33. Most of the references are quantitative and life cycle assessment (LCA) studies analysing specific cases of IS. The LCA method is used to analyse in a complete fashion the environmental impact reduction of a system.

Table 33. Indicators and their respective references

Indicator	Eco-efficiency measurement	References
Avoided direct water discharge	Environmental	Chertow and Lombardi (2005); Dong <i>et al.</i> (2013); Jacobsen (2006); Liu, Côté and Zhang (2015); Wang <i>et al.</i> (2019); Wen <i>et al.</i> (2018); Yu, Han and Cui (2015);
Avoided energy consumption due to water inflow substitution	Environmental	Wang <i>et al.</i> (2019); Zhang <i>et al.</i> (2017)
Economic benefit (EB) due to water inflow substitution	Economic	Wang <i>et al.</i> (2019); Zhang <i>et al.</i> (2017)
Avoided water extraction from natural bodies	Environmental	Berkel <i>et al.</i> (2009); Chertow and Lombardi (2005); Dong <i>et al.</i> (2013); Eckelman and Chertow (2013); Jacobsen (2006); Wang <i>et al.</i> (2019); Wen and Meng (2015); Zhe <i>et al.</i> (2016)

Usually, LCA studies compare the operation in the no-IS scenario with the one in the IS scenario. Moreover, the baseline scenario (or no-IS scenario) is the standalone operation of each water consuming facility of the actors in the system. This reference scenario does not consider the cascade utilization of water, the reuse, nor the recycling of water.

Certain actions undertaken in the baseline scenario are no longer performed in the IS scenario. An example is represented in Figure 39. In the IS scenario the actor A exchanges its outflow effluent with the actor B.

Due to the new water exchange in the IS scenario, actor A avoids discharging directly its effluent for disposal, increasing the circularity of the system by implementing a secondary usage of the resource. In addition, actor B requires less inflow from its original source since it is receiving resources from an additional source (actor A). Subsequently, the avoided actions in the IS scenario are at least two, namely the avoided direct water discharge (from actor A) and the avoided water production (from actor B).

The avoided direct water discharge is the first of the indicators, developed in section 4.2.1. In addition, the direct consequences of the avoided water production are, at least, twofold. First, there is a saving on energy due to the avoided process. Second, there is an economic benefit because of the avoided process. In fact, the result in the IS scenario is requiring less – or no – energy and saving economic resources by avoiding the water production process of the no-IS scenario waterflow. Then, the saved energy and avoided costs due to avoided processes of the no-IS scenario are measured by the indicators from sections 4.2.2 and 4.2.3.

It is important to notice that a water treatment might be required for the exchange to be feasible. If this is the case, the treatment process bears additional energy and economic costs.

In addition, the transportation of the effluent to the secondary user might also bare additional costs to the system. Therefore, an overall energy – and economic – balance must be considered for each case. According to the EPA (2018) usually the energy required to treat and/or transport other sources of water is generally much greater. A proper techno-economic evaluation is required for each case in order to evaluate if there is an overall reduction or not.

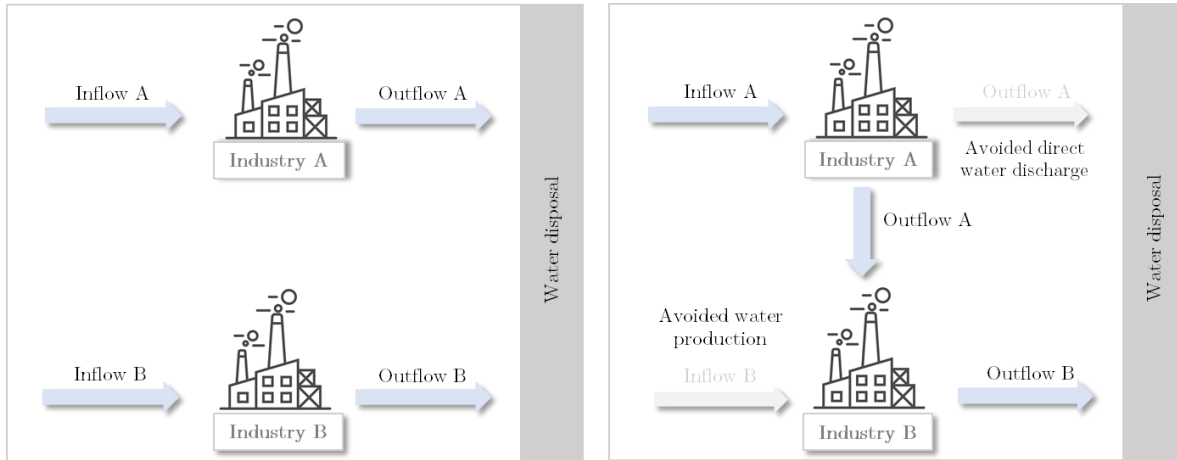


Figure 39. Avoided processes in the IS scenario (right) compared to the no-IS scenario (left)

Another consequence of the new exchanged waterflow in the IS scenario is the potential avoidance of water extraction form natural water bodies. This indicator is further explained in section 4.2.4. In addition, the absolute water consumption is measured by the indicator presented in section 4.2.5.

Some of the indicators require weighting factors in order to be properly valued. Several methods exists for developing factors, although it is still a controversial issue and there is no official consensus on the one to use. For this research, the weighting factors for the calculation of the indicators are the ones used by each one of the consulted references, which are obtained from standardized databases of the zone in study.

In the case of the *avoided primary energy consumption* indicator developed in section 4.2.2, the factors were obtained from two databases, namely the International Life Cycle Inventory Database (Ecoinvent) and the Gabi Basic database. In the case of the *economic benefits* indicator developed in section 4.2.3, the factors regarding the unit price of the resource were obtained from the State Statistical Bureau (2017).

## 4.2. Indicators

### 4.2.1. Avoided Direct Water Discharge

The indicator presented in this section quantifies the avoided direct water discharges due to the implementation of IS. In fact, this indicator measures the circularity increase due to an increase in the rate of reuse and recycling of water through secondary usage. Moreover, this indicator measures the volume of water exchanged between different industries. Thus, this indicator measures the volume of reused and recycled water inside the IS.

Figure 40 represents an example situation of the no-IS scenario compared to the IS scenario. The no-IS scenario is represented by two industries, A and B, in their standalone operation. The IS scenario is represented by these industries in the IS operation, with industry A exchanging its outflow effluent to industry B.

Consequently, the result of the IS scenario is avoiding the direct discharge of the outflow from industry A (in addition to less requirement inflow from industry B, which effect is quantified by the indicators from sections 4.2.2, 4.2.3, and 4.2.4).

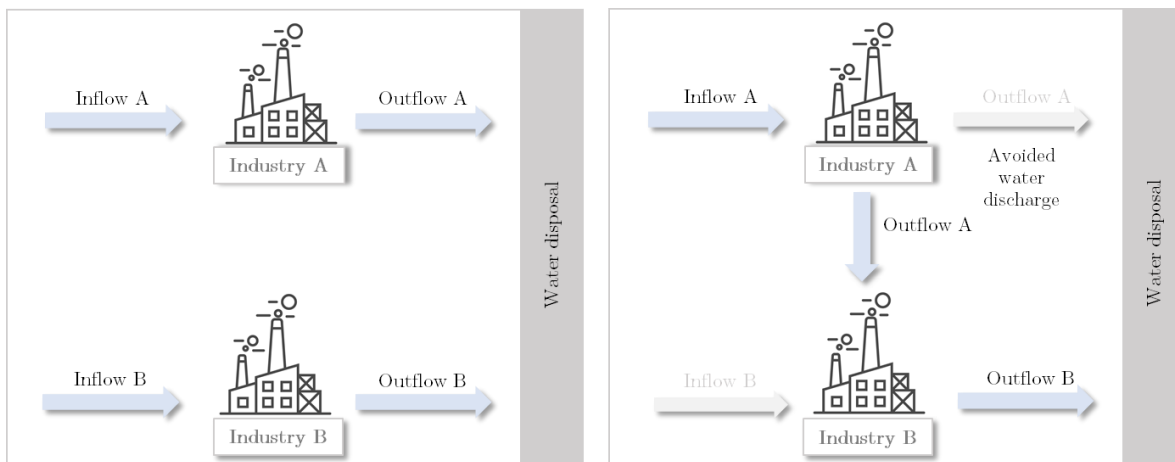


Figure 40. Avoided direct water discharge in the IS scenario (right) compared to the no-IS scenario (left)

Table 34 summarizes the value of the avoided direct discharges indicator for several cases of IS, with the corresponding references they were taken from.

Table 34. Value of the avoided direct water discharge indicator for selected IS cases

IS Case	ML/year	Explanation	Reference
<b>Guayama, Puerto Rico (2005)</b>	5.500	Use of treated wastewater as cooling water at the power station avoids effluent discharge	Chertow and Lombardi (2005)
<b>HHG, China (2014)*</b>	170	Use of warm condensate and cleaned wastewater at the thermal power plant, in addition to other cleaner production initiatives, avoids effluent discharge	Liu, Côté and Zhang (2015)
	40	Use of brine at the potassium sulphate plant, in addition to other cleaner production initiatives, avoids effluent discharge	Liu, Côté and Zhang (2015)
<b>Jinan Iron/Steel Group (JIS), China (2010)</b>	2.000	Use of urban wastewater at the iron and steel plant avoids effluent discharge	Dong <i>et al.</i> (2013)
<b>Kalundborg, Denmark (2002)**</b>	50	Use of warm condensate at the refinery avoids effluent discharge	Jacobsen (2006)
	9	Use of wastewater at the power station avoids effluent discharge	Jacobsen (2006)
	483	Use of cooling water at the power station avoids effluent discharge	Jacobsen (2006)
	100	Use of cleaned wastewater at the power station avoids effluent discharge	Jacobsen (2006)
	23.000	Use of brine at the fish farm avoids effluent discharge	Jacobsen (2006)
<b>REDA, China (2011)*</b>	142	Use of warm condensate at the thermal power plant avoids effluent discharge	Yu, Han and Cui (2015)
	4.000	Use of treated wastewater at the port and the thermal power plant avoids effluent discharge	Yu, Han and Cui (2015)
<b>SCIP, China (2015)*</b>	16	Avoided deionized water discharged into the ocean	Zhang <i>et al.</i> (2017)
	1.247	Avoided treated wastewater discharged into the ocean	Zhang <i>et al.</i> (2017)
	125	Avoided cleaned surface water discharged into the ocean	Zhang <i>et al.</i> (2017)
	1.676	Avoided cooling water discharged into the ocean	Zhang <i>et al.</i> (2017)
<b>TEDA, China (2016)</b>	12.600	Use of treated wastewater at the heat and power plant and the industrial production plants avoids effluent discharge	Wen <i>et al.</i> (2018)
	4.830	Use of warm condensate at heat and power plant avoids effluent discharge	Wen <i>et al.</i> (2018)

IS Case	ML/year	Explanation	Reference
YEDZ, China (2017)*	17.367	Use of treated wastewater at the iron-works plant and the methanol/ethylene glycol chemical plant avoids effluent discharge	Wang <i>et al.</i> (2019)
	4.239	Use of warm condensate at the cogeneration power plant avoids effluent discharge	Wang <i>et al.</i> (2019)

Note: (\*): case analysed in section 3.2; (\*\*): case analysed in section 3.2, but in a different year

#### 4.2.2. Avoided Energy Consumption (AEC) due to Water Inflow

##### Substitution

The indicator presented in this section quantifies the total avoided energy consumption (AEC) due to some actor's water inlet substitution, i.e. a new source of water coming from another actor of the IS. This indicator does not include the energy required for a potential treatment requirement nor the transportation of the resource from primary to secondary user. The energy consumed is calculated based on factors taken from a standardized database of the context of the analysis. The factors of both Campbell and YEDZ cases were obtained from the International Life Cycle Inventory Database (Ecoinvent), while the ones for the SCIP case were obtained from the Gabi Basic database.

The factor used were the ones for water softening and distribution (Campbell), water treatment (Campbell), groundwater extraction (Campbell), desalted water production (SCIP), soft water production (SCIP), wastewater treatment (SCIP), and freshwater production for industrial purposes (SCIP), and freshwater production for industrial purposes (YEDZ). Table 35 summarizes the value of the *AEC due to water inflow substitution* indicator for several cases of IS, with the corresponding references they were taken from. In addition, the value is compared to the total AEC of the IS implementation, integrating the impact of water, energy, and materials exchanges.



Table 35. Value of the avoided energy consumption indicator for selected IS cases

IS Case	Primary energy factor (GJ/ML)	Substituted quantity (ML/y)	AEC (GJ/y)	% of total AEC	Explanation	Reference
<b>Campbell, United States (2013)</b>	9,0	2.800	25.200	0,56%	Primary energy saved due to substituting deionized water production with cleaned wastewater exchange	Eckelman and Chertow (2013)
	2,0	100	200	~0%	Primary energy saved due to substituting deionized water production with warm condensate exchange	Eckelman and Chertow (2013)
	2,0	6.900	13.800	0,31%	Primary energy saved due to substituting groundwater production with cleaned wastewater exchange	Eckelman and Chertow (2013)
	-	-	39.200	0,87%	Total value for Campbell IS	Eckelman and Chertow (2013)
<b>SCIP, China (2015)*</b>	80,7	1.263	101.924	0,75%	Primary energy saved due to substituting desalted water production with desalted water and treated water exchange	Zhang <i>et al.</i> (2017)
	93,6	125	11.700	0,09%	Primary energy saved due to substituting soft water production with soft water exchange	Zhang <i>et al.</i> (2017)
	7,54	1.676	12.637	0,09%	Primary energy saved due to substituting freshwater with cooling water	Zhang <i>et al.</i> (2017)
	7,54	38	287	~0%	Primary energy saved due to substituting freshwater with warm condensate	Zhang <i>et al.</i> (2017)
	40,5	38	1.539	0,01%	Primary energy saved due to avoiding wastewater treatment for substituting freshwater with warm condensate	Zhang <i>et al.</i> (2017)

IS Case	Primary energy factor (GJ/ML)	Substituted quantity (ML/y)	AEC (GJ/y)	% of total AEC	Explanation	Reference
YEDZ, China (2017)*	-	-	128.087	0,94%	Total value for SCIP	Zhang <i>et al.</i> (2017)
	11,4	4.696	53.534	0,57%	Primary energy saved due to substituting freshwater with cleaned wastewater	Wang <i>et al.</i> (2019)
	11,4	17.367	197.984	2,09%	Primary energy saved due to substituting freshwater with wastewater	Wang <i>et al.</i> (2019)
	11,4	4.239	48.325	0,51%	Primary energy saved due to substituting freshwater with warm condensate	Wang <i>et al.</i> (2019)
	-	-	299.843	3,17%	Total value for YEDZ	Wang <i>et al.</i> (2019)

Note: (\*): case analysed in section 3.2

#### 4.2.3. Economic Benefit (EB) due to Water Inflow Substitution

The indicator presented in this section quantifies the total economic benefit (EB) due to some actor's water inlet substitution, i.e. a new source of water coming from another actor of the IS. This indicator is analogous to the *avoided energy consumption due to water inflow substitution*, although from an economic perspective.

The economic benefits are calculated based on the unit price of the resource, which is taken from standardized databases of the context of the analysis. Only the YEDZ IS case had the available data to evaluate this indicator. In this case, the unitary price of cleaned surface water was obtained from the State Statistical Bureau (2017) (Wang *et al.*, 2019).

Table 36 summarizes the value of the *EB due to water inflow substitution* indicator for the YEDZ IS case, with the corresponding reference it was taken from. In addition, the value is compared to the total EB of the IS implementation, integrating the impact of water, energy, and materials exchanges.

Table 36. Value of the economic benefit indicator for the selected IS case

IS Case	Unit price (USD/ML)	Substituted quantity (ML/y)	EB (Thousand USD/y)	% of total AEC	Explanation	Reference
YEDZ, China (2017)*	611,94	4.696	2.874	2,00%	Economic benefit due to the chemical plant substituting freshwater for cleaned wastewater coming from the wastewater treatment plant	Wang <i>et al.</i> (2019)
	611,94	17.367	10.628	7,43%	Economic benefit due to the chemical and steel plants substituting freshwater for wastewater coming from the wastewater treatment plant	Wang <i>et al.</i> (2019)
	611,94	4.239	2.594	1,82%	Economic benefit due to the power plant substituting freshwater for warm condensate coming from the chemical plant	Wang <i>et al.</i> (2019)
	-	-	16.095	11,17%	Total value for YEDZ	Wang <i>et al.</i> (2019)

Note: (\*): case analysed in section 3.2

#### 4.2.4. Avoided Water Extraction from Natural Bodies

The indicator presented in this section quantifies the avoided water extraction from natural bodies due to the implementation of IS.

This indicator is similar to the “avoided direct water discharge” indicator, since the water exchange between two organizations might simultaneously avoid discharges and also reduce the use of water from natural bodies (from the primary and secondary user’s perspective, respectively). Nonetheless, the difference between these indicators is that this one includes only the activities that are explicitly reported to avoid the extraction of water from natural bodies. Moreover, the water discharge indicator regards the perspective from the primary user, while the avoided water extraction the one from the secondary user.

Figure 41 represents an example situation of the no-IS scenario compared to the IS scenario. The no-IS scenario is represented by two industries, A and B, in their standalone operation. The IS scenario is represented by these industries in the IS operation, with industry A

exchanging its outflow effluent to industry B. In fact, it represents the same example situation from Figure 40, although emphasized on the user's perspective.

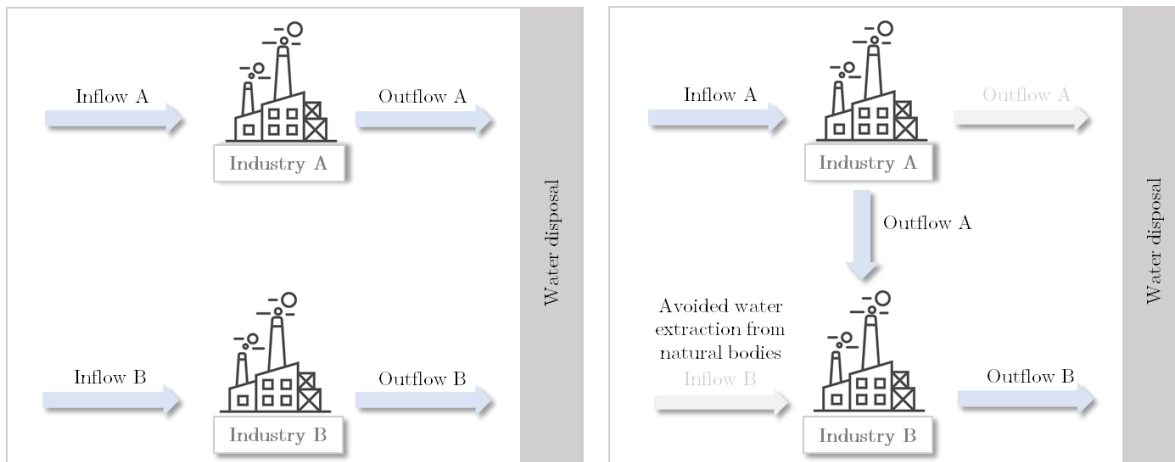


Figure 41. Avoided extraction from natural bodies in the IS scenario (right) compared to the no-IS scenario (left)

Thus, a water inlet coming from a natural water body is replaced with another source of waterflow, aiming to fulfil the same task. As a consequence, the result of the IS scenario is avoiding the water extraction from natural bodies (in addition to avoiding the water discharge and production process, which effect is quantified by the indicators from sections 4.2.1, 4.2.2, and 4.2.30).

It often happens that the waterflow coming from a natural source is replaced with another effluent coming also from a natural water body. As an example, in the IS case of Kalundborg the usage of groundwater at the power plant was slowly replaced over the years with surface water. Thus, the groundwater consumption decreased, implying a positive value of the indicator regarding groundwater. On the contrary, the usage of surface water increased, implying a negative value of the indicator regarding surface water.

Figure 42 shows the water consumption of the Kalundborg power plant for surface and groundwater between 1990 and 2002. It can be noticed that the overall water consumption increased sharply between 1990 and 1994. Moreover, between 1990 and 2002 the overall water consumption increased by 68%, from 440 to 737 ML/year. As a further research topic, the analysis of the water consumption could be compared to the productivity of the plant, in order to evaluate potential returns to scale on the water resource.

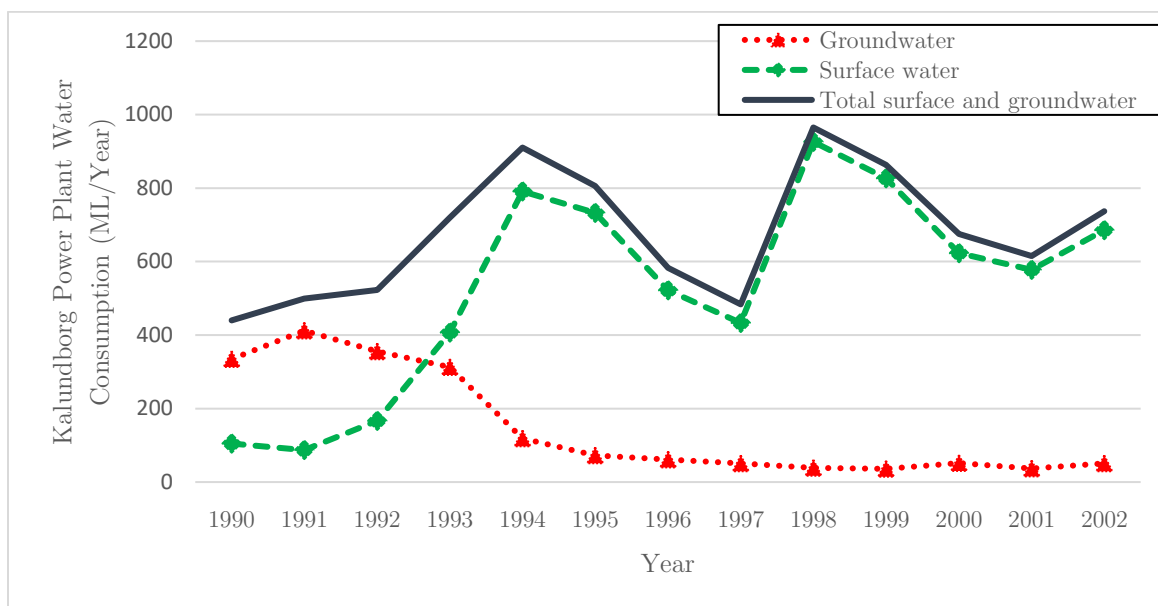


Figure 42. Water consumption of the Kalundborg power plant between 1990 and 2002. Source: Jacobsen (2006)

Summarizing, a positive value of the indicator means that there is a reduction of the water consumed from natural bodies, while a negative value implies there is an increase.

Table 37 summarizes the value of the *avoided water extraction from natural water bodies* indicator for several cases of IS, with the corresponding references they were taken from. In addition, the indicator is used to compare different states over the years of the Kalundborg case, using the baseline scenario of the year 1990.

Table 37. Value of the avoided water extraction from natural water bodies indicator for selected IS cases

IS Case	ML/year	% of water extraction	Explanation	Reference
<b>Campbell, United States (2013)</b>	6.900	N/A	Groundwater saving due to the use of cleaned wastewater at the golf course	Eckelman and Chertow (2013)
<b>Guayama, Puerto Rico (2005)</b>	3.650	N/A	Groundwater saving due to the use of treated wastewater as cooling water at the power station	Berkel <i>et al.</i> (2009)
	5.500	N/A	Total avoided water extraction from natural water bodies due to the use of treated wastewater at the power station	Chertow and Lombardi (2005)
<b>Kalundborg, Denmark (1996, compared to IS of 1990)**</b>	274	82%	Groundwater saving due to the use of surface water at the power plant	Jacobsen (2006)
	(417)	(397%)	Surface water increased consumption due to replacing the use of groundwater at the power plant	Jacobsen (2006)

IS Case	ML/year	% of water extraction	Explanation	Reference
<b>Kalundborg, Denmark (2002, compared to IS of 1990)**</b>	(143)	(33%)	Total avoided (increased) extraction for Kalundborg (1996 vs. 1990)	-
	284	85%	Groundwater saving due to the use of surface water at the power plant	Jacobsen (2006)
	(581)	(553%)	Surface water increased consumption due to replacing the use of groundwater at the power plant	Jacobsen (2006)
<b>Kalundborg, Denmark (2002)**</b>	(297)	(68%)	Total avoided (increased) extraction for Kalundborg (1996 vs. 1990)	
	2.800	N/A	Groundwater saving due to the use of surface water at the refinery	Berkel <i>et al.</i> (2009)
	(2.800)	N/A	Surface water increased consumption due to replacing the use of groundwater at the refinery	Berkel <i>et al.</i> (2009)
	500	N/A	Surface water saving due to the use of cooling water as a heat exchanger at the power station	Berkel <i>et al.</i> (2009)
	9	N/A	Surface water saving due to the use of cleaned wastewater at the power station	Berkel <i>et al.</i> (2009)
	23.000	N/A	Seawater saving due to the use of brine/cooling water at the fish farms	Berkel <i>et al.</i> (2009)
	2.100	N/A	Groundwater saving due to the entire IS operation	Chertow and Lombardi (2005)
	1.200	N/A	Surface water saving due to the entire IS operation	Chertow and Lombardi (2005)
	26.300	N/A	Total avoided extraction of the entire IS operation***	-

Note: (\*\*): case analysed in section 3.2, but in a different year; (\*\*\*) considering groundwater, surface water, and seawater saved at the fish farms negative values are reported in parentheses

#### 4.2.5. Proposed Indicator: Water Reuse/Recycling Rate

This section provides an indicator proposed by the author of this research. The proposed indicator regards the water reuse/recycling rate of the IS. On one hand, there is the water exchanged between the different actors of the IS, measured by the *avoided direct water discharge* indicator from section 4.2.1. On the other hand, there is the water used by each

industry belonging to the IS, measured by the *water consumption of the actors involved*. The proposed indicator compares these two values.

The *water reuse/recycling rate* indicator measures the proportion of water consumed by an actor that comes from water reuse and recycling practices, i.e. that comes from another actor. Hence, the proposed water reuse/recycling rate indicator is the ratio between the avoided direct water discharge and the water consumed by an industry, using the integrated value of the overall IS. Furthermore, the water reuse/recycling rate of the IS is the ratio between the *integrated avoided direct water discharge* and the *integrated water consumption* of the entire IS system.

$$\text{Water reuse/recycling rate} = \left( \frac{\text{Avoided direct water discharge}}{\text{Water consumption}} \right)_{IS \text{ system}}$$

The water consumption accounts all the reported water consumption of the system, either at industrial level or at industrial system level. This value shows a stationary measure of the water consumption of an IS, i.e. not compared to a baseline scenario, but rather from a specific time period (e.g. a year).

Table 38 summarizes the *water consumption* for several cases of IS, with the corresponding references they were taken from. As a complementary value, the ratio between the water consumed and the amount of product produced could be an efficient indicator to measure the water intensiveness of an industrial process, and moreover, of an overall IS. For manufacturing industries, this could be measured in ML per ton of manufactured product. For other industries, it could be measured by the comparison between the water consumed and the economic value of the activity performed (e.g. a service provided).

Table 38. Value of the water consumption indicator for selected IS cases

IS Case	ML/year	Explanation	Reference
<b>DEDA, China (2006)</b>	24.600	Water intake of the entire IS	Zhe <i>et al.</i> (2016)
	34.500	Water intake of the entire IS	Zhe <i>et al.</i> (2016)
<b>Kalundborg, Denmark (2002)**</b>	1.600	Refinery surface water consumption	Jacobsen (2006)
	50	Refinery cooling water consumption	Jacobsen (2006)
	686	Power plant surface water consumption	Jacobsen (2006)
	51	Power plant groundwater consumption	Jacobsen (2006)
	936.000	Power plant seawater consumption	Jacobsen (2006)
	100	Power plant cleaned wastewater consumption	Jacobsen (2006)
	9	Power plant wastewater consumption	Jacobsen (2006)
	483	Power plant cooling water consumption	Jacobsen (2006)

IS Case	ML/year	Explanation	Reference
Suzhou New District (SND), China (2010)	491	Chemical plant surface water consumption	Jacobsen (2006)
	1.900	Chemical plant groundwater consumption	Jacobsen (2006)
	23.000	Fish farm cooling water/brine consumption	Jacobsen (2006)
	2.600	Chemical plant total water intake	Jacobsen (2006)
	1.600	Refinery total water intake	Jacobsen (2006)
	99.240	Fukuda Metal industry freshwater consumption	Wen and Meng (2015)
	36.170	Matsushita Electric Works industry freshwater consumption	Wen and Meng (2015)
	161.000	Baishuo Computer industry freshwater consumption	Wen and Meng (2015)
	277.400	Gold Circuit Electronics industry freshwater consumption	Wen and Meng (2015)
	93.090	Jingpeng Electronic industry freshwater consumption	Wen and Meng (2015)
	110.000	Sony Chemical Electronic industry freshwater consumption	Wen and Meng (2015)
	67.740	Dazhan Circuit industry freshwater consumption	Wen and Meng (2015)
YEDZ, China (2017)*	111.000	Ichia Technology industry freshwater consumption	Wen and Meng (2015)
	9.000	Cogeneration power plant water intake	Wang <i>et al.</i> (2019)
	7.700	Chemical industry water intake	Wang <i>et al.</i> (2019)
	380	Electrolytic aluminium plant water intake	Wang <i>et al.</i> (2019)
	200	Aluminium deep processing plant water intake	Wang <i>et al.</i> (2019)
	4.770	Iron works plant water intake	Wang <i>et al.</i> (2019)
	1.770	Remaining industries' water intake	Wang <i>et al.</i> (2019)
	9,63 ML/kt	Water consumption per ton of product (steel)	Dong <i>et al.</i> (2013)



IS Case	ML/year	Explanation	Reference
<b>Jinan Iron/Steel Group (JIS), China (2000)</b>	3,18 ML/kt	Water consumption per ton of product (steel)	Dong <i>et al.</i> (2013)

Note: (\*): case analysed in section 3.2; (\*\*): case analysed in section 3.2, but in a different year; water consumption per ton of product only applies to manufacturing industries. For its application to other industries, the indicator must be adapted.

Regarding the water reuse/recycling rate indicator, only the YEDZ IS case had the available data to evaluate this indicator. In fact, all the other cases studied did not have either individual data about the actors nor integrated data on the overall IS regarding their water consumption.

The integrated avoided water discharge was taken from the sum of avoided water discharge of the IS. The integrated water consumption was calculated analogously. Table 39 summarizes the value of the *water reuse/recycling rate* indicator for the YEDZ IS case, with the corresponding reference it was taken from.

Table 39. Value of the water reuse/recycling rate indicator for the selected IS case

IS Case	Avoided water discharge (ML/year)	Water consumption (ML/year)	Water reuse/recycling rate	Reference
<b>YEDZ, China (2017)*</b>	21.606	23.820	90,7%	Wang <i>et al.</i> , (2019)

Note: (\*): case analysed in section 3.2

### 4.3. Conclusions on the Quantitative Description of Industrial Symbiosis Cases

It can be concluded that characterizing the eco-efficiency of IS systems through indicators is a complex task. Moreover, the methodology itself imposes several limitations. The main difficulty on the measurement is that it is a data-intensive process. In fact, data available from firms is usually incomplete, unprecise, and/or insufficient due to commercial sensitivity. Thus, most data obtained are merely estimations of the waterflows.

Additionally, data reported from different IS cases usually differ, emphasizing on different types of information depending on the purpose of the study. In fact, often the economic and environmental aspects considered for some IS cases are not considered in others, obfuscating the complete development and subsequent comparison of indicators.

Moreover, the lack of available information on waterflows complicates the development and comparison of indicators from different years, even for the same IS case. Data available for

some year study is often not available for other years, due to the discontinued report on necessary information.

There are multiple reasons for the lack of data availability. Usually, data is obtained from academic studies that focused on a particular year, developing a static analysis of the IS case. Thus, data is often not available for different periods in time.

Additionally, most academic literature focuses on other flows of resources, namely materials and energy, rather than in water exchanges. This is often explained due to the fact that the environmental impact reduction is much more significative for materials and energy exchanges than for water exchanges. For example, in the SCIP case of section 3.2.4 the avoided primary energy consumption due to water exchanges represented only 0,94% of the overall energy saved, while energy and materials exchanged represented the remaining 99,06% (Zhang *et al.*, 2017).

Moreover, regulations on official environmental reporting often does not require the quantitative information on each internal process, but rather an integrated reporting of the overall water measurements of the company. Thus, information about specific data on water consumption and exchanges usually remain as non-public data. The author tried contacting industries directly, however most of them were unwilling or hesitant to share specific information about water usage, treatments, and internal KPIs.

In order to accurately measure the water eco-efficiency of an IS system one must be provided with continuous, detailed, and updated data about waterflows, including both qualitative and especially quantitative information. Furthermore, with the availability of precise and abundant data much more indicators could be developed on this topic.

In addition, the quantitative description given by the indicators is based on a theoretical comparison of the waterflows in the symbiotic scenario, compared to the baseline scenario of no-IS. However, there is a considerable uncertainty in this scenario comparison, given by two reasons.

First, in the absence of symbiotic opportunities the actors might have explored different water saving alternatives, which cannot be measured as an opportunity cost since it is a hypothetical situation. Second, there is a neglected environmental impact of the IS scenario occurring as a result of the water exchanges (e.g. the environmental impact of pumping water between the actors exchanging water) (Pakarinen *et al.*, 2010).

It can be seen that the IS operation allows to re-employ thousands of ML of water per year, by redirecting the flow – that was previously disposed – for reuse and recycle practices. Even though at the end the water exchanged is at least partially disposed by some secondary user, these practices allows to increase the circularity of the system by extending the useful life of the resource. It also allowed to save water resources from natural bodies at the same order of

magnitude. In addition, the avoided water production allows to save energy from tens to hundreds of thousand GJ per year, for each IS case.

## 5. Conclusions and Further Research

Circular economy systems at meso-level, such as IS systems, aim to be in line with sustainable development by means of energy efficiency strategies and sustainable management of resources. In particular for IS systems, their goal is to achieve sustainability through a profitable waste management, which is emphasised in this work through the eco-efficient management of water and wastewater resources.

IS systems are not characterized by a unique, one “fit-all” system model, but rather depend on the context they are developed. However, a common factor is the industrial usage of water for countless purposes. Thus, there is a major importance in the water resources analysis, management, and control in all the phases of the IS system life cycle. However, this is a data-intensive procedure, which poses several difficulties for its correct development.

Data on water resources and water management practices is usually not public. Often there is a great amount of secrecy around industrial water practices. As stated by Branson (2016), “the temporal dimension is obscure, particularly relating to the demise of some projects and [usually] there is scant information about what is actually being transferred from one site to another in the system”. In fact, quantitative information is often difficult to obtain.

On the same path, most quantitative IS studies focus on the physical flows of materials, water, and energy in the overall industrial system, instead of emphasizing in individual system components such as single processes or organizations (Pakarinen *et al.*, 2010). Thus, critical information about the flow of resources is usually not available, especially regarding water exchanges.

In fact, the main limitation of this research was the lack of available data. However, this constraint was overcome through intensive literature review and direct phone interviews to representatives of the IS cases.

Data availability on water practices would be a key tool to assess, compare, and improve both the efficiency and safety of this resource. It would be the first step to apply the necessary regulations in the industrial context at a local, regional, and global level, in order to achieve real circularity in water resources.

Moreover, there would be more data available to replicate good water management practices in the industrial context, and also to regulate and incentivize a proper eco-efficient usage of the resource. Thus, the availability of quantitative information on water management practices in the industrial context becomes a public service for society.

Thus, the quantitative measurement of water resource management is critical to achieve the sustainable usage of the resource in the industrial context. This is key in order to regulate and incentivize the application of circular economy practices on water resources.

According to the analysed cases, water reuse and recycling practices in IS systems, and in industrial systems in general, are a valuable practices to save water resources, reduce pollutants emissions into water bodies, and achieve overall eco-efficient win-win situations for all the actors involved. In fact, local exchanges of water resources among clustered actors can lead to environmental and economic savings on a life cycle basis, which can be seen from the different cases of IS analysed in chapter 4. Moreover, the absolute values of these benefits show how a single IS system can contribute to a significant improvement in terms of sustainable water resources management for a local or regional zone.

Usually water exchanges in IS are mostly driven by the search of a diversified water supply, optimizing the energy efficiency, ensuring the water supply, or a combination of those factors. Overall, IS systems are a powerful approach for reducing wastes generation, pollutants emissions, and improve eco-efficiency in the operation of industrial systems.

In particular, the qualitative modelling from section 3.2 allowed to analyse and compare different contexts where IS cases are developed. It can be concluded that water reuse and recycling practices are a key component for the eco-efficient operation of these systems.

The qualitative analysis allowed to perceive the complexity and increased number of variables playing an important role in the different IS cases. In fact, when analysing the feasibility and potential for water reuse and recycling, and thus a water exchange, there are several variables to take in consideration. First, there should be a correct analysis of the across involved in the exchange, namely the primary and secondary users. Second, there should be a correct quality characterization of the outflow effluent of the supplier. Third, the final purpose of the water effluent should be correctly defined. Moreover, the decision to reuse – without treatment – or recycle – with treatment – the water effluent will depend purely on the difference between the characterization of the outflow effluent of the supplier and the required quality for the final purpose of the user. With the initial characterization of the effluent it is possible to make a first draft of the process to reuse or recycle water in an industrial system.

According to the CE principles, reusing is preferred over recycling. In fact, the main advantage of IS systems is that through the exchange of by-products, in this case process water, they are able to extend the value of the water resources overtime with often minimum or no treatment. In the ideal IS, resources for exchange are transferred directly from primary to secondary user, by using the minimum amount of energy to transport the resource. However, and as shown in the cases from section 3.2, this is often not possible. Recycling poses the great disadvantage of the complexity water treatment processes in comparison to reusing. If a treatment is required, there comes the complex choice of the treatment process, with several decision variables on its own.

The different industrial wastewater treatment process and technologies to employ depend on several factors. The most important are the characterization of the initial effluent, the characteristics of the desired effluent, the pollutant components, the industry it is required for, among other techno-economic constraints.

There are certain actors of the IS that have their own wastewater treatment facility, providing services for water separation and pollutant components removal. However, there are usually municipal applications involved providing the same service. Another decision is through which intermediary will the wastewater treatment process be performed.

Moreover, the effluents coming from the varied actors have different potential for reuse and recycle, and some recycling activities (and thus water treatment) are more important for certain water effluents than for others. This depends purely on the characteristics of the initial effluent.

Hence, in IS and in industrial systems in general the interaction between the different actors is a critical issue. Among these can be found the industry-industry interactions and industry-municipality interactions, which are particularly important, especially if a treatment is required by the user applications.

The quantitative description of chapter 4 allowed to stress the great importance of eco-efficiency measures to be taken. It can be concluded that, if designed correctly, IS systems promote a sustainable circular water management. IS are able to reduce water consumption, save energy, reduce pollution, among many other environmental and economic benefits.

Finally, not all IS are characterized by a circular water network. Some of them are able to exploit and take advantage of an efficient circular model, for example, through implementing wastewater treatment plants to absorb the inefficiencies in the water network. However, it often happens that some are not able to fully exploit the circularity of the IS model, reflected for example in the disconnection between potential primary and secondary users in their water network. This is the case of UPM IS analysed in chapter 3.2.5, where the disconnection between both wastewater treatment plants generated an entirely linear network, not exploiting the potential circularity of the model.

In conclusion, the implementation of an overall sustainable IS system implies taking risks. In order to incentivize these circular practices, more data is required to decrease the information barriers of new entrants. Thus, in order to promote the CE practices at industrial system level, it is of paramount importance to promote and increase the corporate responsibility on detailed environmental reporting, especially regarding the quantitative operation of water networks in IS systems.

## 5.1. Further Research

The ISWE model proposed in chapter 2 has the main limitation of the unknown water quality of the effluents. In fact, in order to give structure to the model, a strong assumption had to be made by classifying the quality required by each actor according to the industry they belong to. Moreover, this quality is the minimum required by an average company of the industry. If the information about the quality of the effluent were available, the model would further increase its precision. Thus, a further research topic could be to analyse an IS case with the specific information about the quality of each effluent.

IS systems are dynamic systems evolving over the years. In fact, some of them have failed to sustain their operations over time, while others appear to remain strong. A further research topic could be to analyse the evolution of IS systems over time, by performing a temporal analysis through the ISWE model. In addition, a correlation and statistical analysis could be made by comparing the water network characteristics and the economic performance of the IS system over the years.

Additionally, most eco-efficiency indicator shown in this research are taken from data available on academic literature. A further research topic could be to add other indicators used by the industries themselves to measure their performance on water management. Moreover, there is the possibility to perform an analysis of potential scale returns on the water resources. Several IS cases could be assessed by measuring their water consumption and comparing this value with the productivity of the organization over time, with the economic value added of the resource, and with other KPIs of interest.

Finally, a further research topic could be to analyse the impact of IS systems implementation regarding water, materials, and energy exchanges. In fact, most of the analysed cases showed that the environmental impact of implementing circular water practices usually was minimum compared to the one of energy a materials exchange. The economic impact of circular water practices was generally higher than the one of energy, however still not comparable to the one of materials nor energy. A complete analysis could be made relating the economic and environmental impacts of these resources exchanges in different IS cases.

## 6. References

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