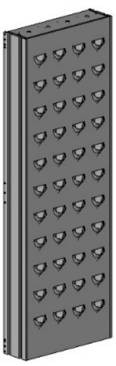
Universitat Politècnica de Catalunya

wetwall

An innovative design concept for the treatment of urban wastewaters



Ph.D. Dissertation

Joana América Castellar da Cunha

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Sustainability program

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For "…those who were seen dancing were thought to be insane by those who could not hear the music…"

Friedrich Nietzsche

Preface

The development of modern society has led to an exploitation of natural capital (especially water), which is reflected in an often bleak urban landscape. Cities are more grey than green. As development continues, land scarcity, overall population growth, and specific demand to live in major cities are leading human society towards a vertical expansion; our cities are becoming taller. In this regard, Nature-based solutions (NBS), such as Living walls (LWs), which can undertake the function of wastewater treatment on empty facades, are promising strategies for climate change mitigation.

The WETWALL is an innovative, environmentally friendly and a gentle way to integrate ecosystem services into the anthropogenic modified milieu. It is a unique multifunctional LW to treat urban wastewaters, such as from urban agriculture or grey wastewaters (GWs) from buildings, for further non potable reuses. The design is modular, can be easily implemented and integrates the features of two well established NBS: constructed WETlands (CWs) and a modular LWs. LWs can improve buildings thermal and energy performance, promote CO_2 sequestration and provide a low impact wastewater treatment. Unlike CWs, which demands great land area, the LWs can be implemented on empty facades. Once installed, they serve and contribute to an aesthetically greener landscape within cities, whilst also providing ecosystem services, ensuring the efficient use of natural resources and reducing diffuse pollution. LW structures can be installed on large surfaces in urban areas where little space is available (Marchi et al., 2015).

The WETWALL encourages the integration of circular economy (CE) into the design process by reusing by-products from local production chains, as filtering substrates. Cork and crushed aerated autoclaved concrete (CAAC) were the selected filter media. Giving a new application to by-products reduces costs, minimizes extraction of non-renewable raw materials, promotes energy savings and reduces CO_2 emissions.

Humanity has already transgressed planetary boundaries regarding changes on global nitrogen (N) and phosphorus (P) cycle, mainly because of the input of reactive compounds into the environment. The WETWALL concept proposes the recovering and reuse of nutrients from wastewaters, giving them a new application. In that sense, substrates and plants can be reused as fertilizers for local urban crops, creating short distances between the provider (WETWALL) and consumers (local agriculture). This can be a sustainable alternative that clearly mitigates the impact caused by the accumulation of N and phosphorus in the environment. Moreover, giving a new application to the "waste" generated by the system reduces the economic cost of the system by subsidising maintenance costs which will encourage the uptake of the technology.

The potential of LWs regarding improving air quality and thermal performances of buildings have been intensely validated in literature. However, our research was mainly focused on the novelty regarding the development of the WETWALL design concept, embracing the water treatment designing (modular Hybrid flow), the proposal of methodologies to select plants and substrates along with technical and environmental requirements. Finally, CE principles were also considered by taking into account the potential interactions between the design and urban environment. As a result, the first article of the thesis titled *"WETWALL" — an innovative design concept for the treatment of wastewater at an urban scale,* was published yet March 2018.

The next phase aimed to evaluate the potential of reusing by-product, such as cork and crushed autoclaved aerated concrete (CAAC), as filter medias. The interactions and main effects of particle size, pH and initial concentration of pollutants (P and N) and contact time were evaluated, at preliminary batch studies in order to further optimize the WETWALL design and make it applicable to real pilot and real scales. As a result, the second article of the thesis titled *"Cork as a sustainable carbon source for nature-based solutions treating hydroponic wastewaters – Preliminary batch studies"* was published on August 2018. The third article of the thesis titled "*Crushed Autoclaved Aerated Concrete (CAAC) a potential reactive filter media to enhance phosphorus removal/recovering in nature-based solutions – preliminary batch studies*" was published on July 2019.

The final phase was focused on the implementation of the prototype. The building process is described and preliminary results, mainly regarding the validation of the innovative hybrid flow, are presented. Further research is needed in order to make feasible the implementation of the WETWALL concept at bigger scales. Indeed, would be interesting to study the effect of the WETWALL design on thermal performances.

Still, the WETWALL design concept has great potential to be successfully implemented in cities. The design is modular and species and substrates are selected in accordance with the implementation area, making it easily adapted to different urban context. Moreover, the novelty of the hybrid flow brings the possibility of treating different urban wastewaters, such as from urban agriculture (HWs) and GWs.

Finally, the relevance of the WETWALL design concept, regarding climate mitigation, is fostered by the sustainable compromise between anthropogenic development and natural habitats, proposed mainly through the replication of natural processes and reusing resources such as water, nutrients, materials and thus, reusing the energy embodied.

List of figures & Tables

OBS: The figures and tables of published/accepted articles are not numbered in this table.

List of acronyms

Nature-Based Solutions	NBS
Constructed Wetlands	CWs
Vertical Garden	VGs
Living Walls	LWs
Circular economy	CE
Horizontal Flow	HF
Vertical Flow	VF
Nitrogen	N
Phosphorus	P
Crushed autoclaved aerated concrete	CAAC
Grey wastewaters	GWs
Hydroponic wastewaters	HWs

Abstract

The development of society has led to a global concern regarding the improvement of resources performance, especially water. The design of nature-based solutions (NBS) for the treatment and reuse of wastewaters, in accordance with circular economy principles (reuse, recycling and reducing) can be a key factor regarding the preservation of natural capital and climate change mitigation. Therefore, WETWALL design concept aims to integrate NBS, such as constructed wetlands (CWs) and living walls (LWs) as an innovative urban wastewater treatment which also can foment others ecosystem services, such as air quality and heat control. These technologies are based on the replication of natural processes and has been used all over the world successfully as wastewater treatments (CWs) and to improve air quality and thermal insulation (LWs). Unlike to CWs, which the implementation demands large area, the LWs structure can be used in blank spaces of facades in urban and rural environments and can undertake the function of wastewater treatment. The performance of LWs have been over studied which regards to thermal and energy performance. Thus, the thesis presents the development of the WETWALL design concept and novelties, mainly regarding its potential for urban wastewaters treatment. Indeed, the modular Hybrid flow is presented and circular economy (CE) principles are considered during the design process, mainly by selecting by-products as filter medias. The filter media selected, cork and CAAC, were studied separately, regarding their ability at enhancing the removal process in NBS, in order to further optimize the design at pilot and real scale. Moreover, the construction and implementation of the WETWALL prototype is presented. Preliminary results regarding the validation of the innovative hybrid flow are discussed. The WETWALL design has great potential to climate change mitigation and adaptation though the establishment of resilient and self-sustaining technological development to treat wastewater in cities where vertical spaces are exponentially growing. However, further research at pilot and real scale are recommended.

Key-words: Green walls, grey wastewater, hydroponic wastewater, hybrid flow, circular economy, nature-based solutions

Graphical abstract

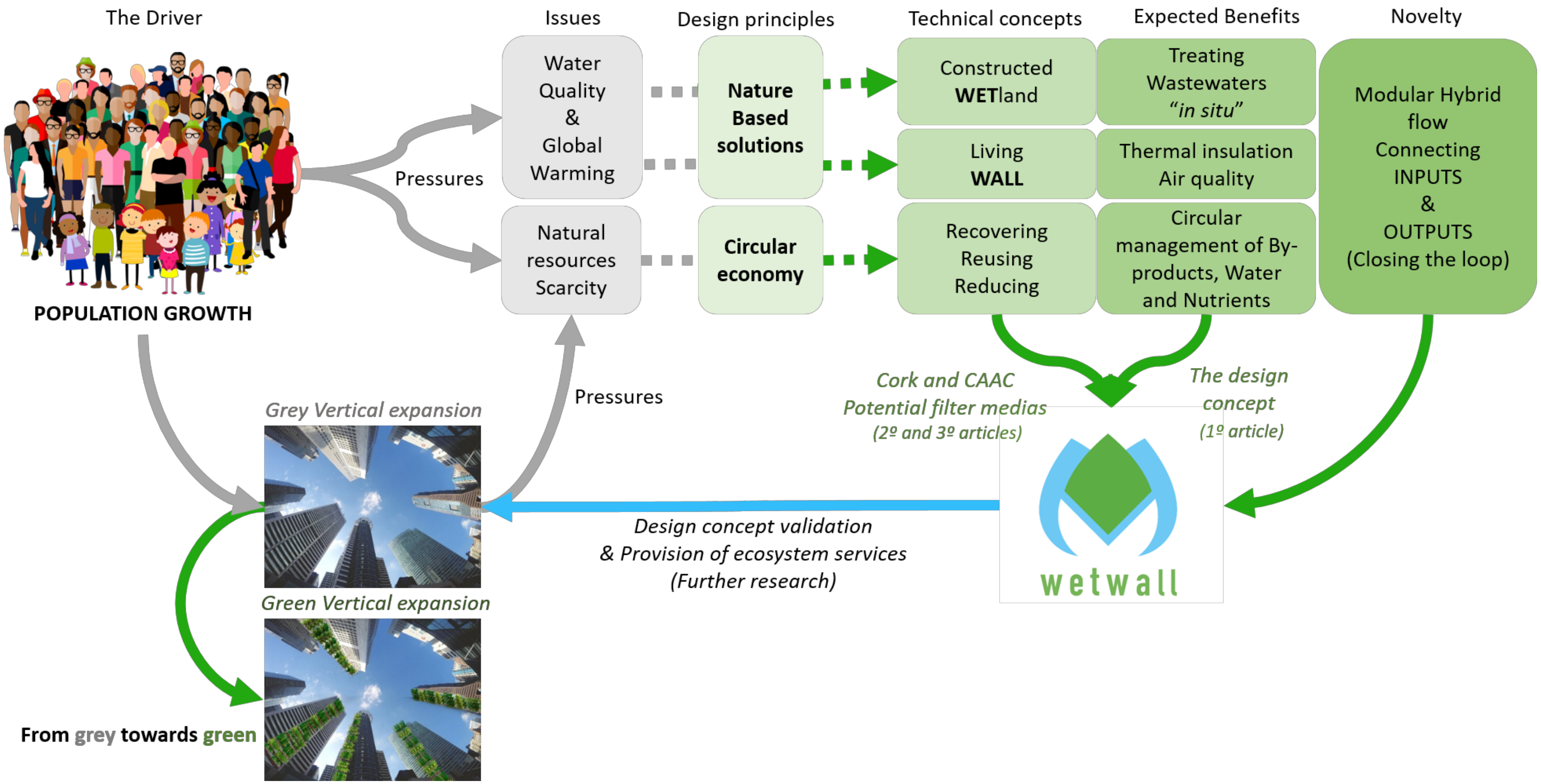


Table of contents

Chapter 1 Introduction

The expansion of modern society has been impacting water resources quality and availability, consequently affecting climate change. Human activities lead to changes in urban landscape, which can cause pressure against natural environment, reduce resilience and limit ecosystem services, including clean water (UNESCO, 2015). It is expected that water demand increases once the world's population is also increasing, which converts the sustainable management of water resources essential to ensure potable water supply (Hadley and Keddington, 2013).

Furthermore, according to RIZWAN et al. (2008) the Urban Heat Island (UHI) is a result of the urbanization and industrialization processes, fact which can lead to significant loss of natural environments and can be considered as one of the biggest issues of 21st century. Moreover, is expected that heat waves will become longer and occur more frequently (Ward et al., 2016). Therefore, technologies that can treat/reuse wastewater and at the same time contribute to minimize the heat island effect can significantly impact on the preservation of natural resources and the mitigation of climate change effects.

In one hand, treatment and further reuse of wastewater is an important strategy to increase the efficiency use of water resources, decrease the competition with drinking water supply, provide freshwater quality, preserve human health and promote ecosystem integrity (WWDR, 2015; European Environment Agency - EEA, 2012; Malik et al., 2015). Reusing wastewater for non-potable purposes directly preserve limited high-quality water resources and is highly efficient and practical, especially in arid regions or developing countries (Li et al., 2009a; WWDR, 2015). Several conventional technologies such as membrane treatment technology (Sonune and Ghate, 2004), reverse osmosis (Sonune and Ghate, 2004), Ion exchange (Sonune and Ghate, 2004), UV light (Gogate and Pandit, 2004) and ozone process (Gogate and Pandit, 2004) have being widely applied to treat wastewaters. However, this treatment has high energy expend and high operation and maintenance costs (Park et al., 2015; Gagnon et al., 2010).

The development of wastewater treatment technologies based on the replication of natural processes has great potential to reconcile human development with the preservation of natural resources. In this scope, NBS can work as an innovative design approach, including the ecosystem process into the human environment and using efficiently natural resources in order to ensure climate adaptation and natural capital preservation. "*The overall aim of green technologies is to maximize the possibility that cities can meet their needs from the natural capital of their own bio-regions in a renewable wa*y" (Zhang, 2013). In this regard, passive wastewater treatments, based on the replication of natural processes, such as CWS, have been used throughout the world to treat several types of wastewater. These technologies have showed to be environment-friendly, economically viable and obtaining good results with regards to the removal of contaminants such as nitrates and phosphorus (P) (Gagnon et al., 2010; Park et al., 2015; Abbassi et al., 2011; Tamiazzo et al., 2015; Park et al., 2008; Park, 2009; Díaz et al., 2010; Winpenny et al., 2010; Babatunde et al., 2008).

On the other hand, LWs have suitable properties for environmental, economic and social benefits not only for buildings, but also for the whole urban areas (Sheweka and Magdy, 2011). LWs can be defined as an ecological engineering technique with an outstanding potential for reconciliation ecology, either by replicating urban (brownfield) or non-urban natural and semi-natural ecosystems (Francis and Lorimer, 2011; Francis, 2010). It is well known that LWs have great potential to improve carbon sequestration, thermal insulation and have the ability to create/preserve ecological biodiverse habitats, facts which can help to mitigate climate change (Victoria State Government and University of Melbourne, 2013; Marchi et al., 2015). According to (Raji et al., 2015) and (Cameron et al., 2014), LWs can provide considerable energy savings, through the reduction of thermal load on buildings and indoor air temperature, facts which can reduce energy expenditure with air conditioned and help to both adaptation and mitigation on the urban heat island issue.

Moreover, to ensure a sustainable development of urban environments the designs should be climate adaptive and based on renewable and recyclable resources (Zhang, 2013; Raji et al., 2015). "*Turning waste into a resource is an essential part of increasing resource efficiency and closing the loop in a circular economy*". Therefore, the principles of CE (reuse, reducing and recycling) need to be considered when designing a climate adaptive NBS.

Therefore, this research aimed to develop a design concept which brings together two well-established NBS, Constructed WETlands and Living WALL. The <u>WETWALL design concept</u> for the treatment of urban wastewaters brings together the prerogatives of removal processes occurring in CWs into a modular LWs structure, which is efficient, but along with the environment conditions.

Unlike to CWs, which construction demands great land area, the LWs are using blank spaces of building walls and facades and can undertake the function of wastewater treatment plant technology and thermal maintenance. Indeed, in the face of the future threats, regarding water and land scarcity, decentralized water infrastructure is an alternative to the traditional centralized systems for implementing sustainable water infrastructure in urban settings. Moreover, the WETWALL design concept encourages the integration of CE mainly by reusing by-products from local production chains, as filtering substrates, recovering nutrients, reclaiming water and suggesting new possible applications to the outputs of the system.

As cited previously in this section, the positive effect of LWs on thermal and energy performance at building scale have extensively been proved in the literature. Hence, it was decided to focus the current research on the novelty of the WETWALL design concept regarding water quality. The research was divided in 3 main parts, regarding the scientific achievements (articles published or accepted). First article brings the state of the art and the novelties of WETWALL design concept, which embraces methods for selection of the main components (plants and substrate), structure developments (innovative hybrid flow), operation strategies and CE analysis are presented (First article). Cork and CAAC were selected as filter media following the methodology described in the first paper. Second and third article were focused on the potential of those by-products, cork and CAAC, with regards, respectively, on its ability to work as an "internal" organic carbon source to enhance denitrification and to recover Pin NBS treating wastewaters.

In regard to follow the above mentioned, putting together the features of NBS such as CWs and LW, bringing CE principles (3R) into the design process has great potential as a sustainable alternative to natural resources preservation and climate change mitigation and adaptation. However, further research on the performance of the WETWALL design concept regarding water quality and thermal insulation is recommended in order to make feasible its implementation at real scales.

Chapter 2 Issue statement

2.1 Water quality

The hydrological cycle keeps the amount of water on earth the same as it was in the past, what is changing is the quality of water in whole environment, which is mainly affected by human, their needs and society development. Human activities in urban areas impact on the natural capital changing the chemistry of freshwater, the temperature of urban streams and reducing urban groundwater supplies (Strungaru et al., 2015). According to Ren et al. (2003) "*rapid urbanization corresponds with rapid degradation of water quality*". Indeed, agriculture is an important source of non-point diffuse water pollution, mainly through leaching of nutrients and pesticides (Oecd, 2013; Eurostat, 2011; UN Water, 2015; Ockenden et al., 2014; Ongley, 1996; Food and agriculture Organization of the United nations (FAO), 2014).

Besides, our planet is nowadays facing the rapid population growth, which is causing a raising of water resources demands and, consequently, impacts on its availability and quality (Gaiser et al., 2008). The scarcity of freshwater is a global concern, the gap between annual freshwater demand and renewable supply is expected to increase till 2030 (UNEP, 2011). It is expected that demand for water increases once the world's population is also increasing, which makes the sustainable management of water resources essential to ensure potable water supply (Hadley and Keddington, 2013). The amount differs for each continent, however the global water withdrawals are about 3,600 cubic kilometres per year, with a 70% corresponding to agriculture withdrawals, followed by industrial and domestic applications (Vorosmarty et al., 2005).

Hence, even when water is abundant, it is a scarce natural source. According to (UNESCO, 2015), "*Disruption of ecosystems through unabated urbanization, inappropriate agricultural practices, deforestation and pollution are among the factors undermining the environment's capacity to provide ecosystem services, including clean water*". Therefore, the growing issues related to water quality and availability has led to global concerns, regarding water management and development of more sustainable practices characterized by an efficient use of water resources and protection of natural ecosystems (WWDR, 2015). In this sense, reclaiming water from wastewaters is needed in order to face the current water scarcity and pollution in our planet (Garnier et al., 2015).

2.2 Urban wastewaters reclaim

Urban wastewaters can contain several pollutants with different concentrations, varying according to previous origin. Therefore, appropriate treatment has to be applied in order to reduce the range of pollution and allow a safe reuse. The thesis is focused in two urban wastewaters, hydroponic wastewaters (HWs) and grey wastewater (GWs), due its important role regarding food security and decentralization of urban water treatment.

Treating, recycling and reusing wastewaters for non-potable purposes is important to ensure an efficient use of water resources and decrease the competition with drinking water supply. It is highly efficient and practical, especially in arid regions or developing countries (Li et al., 2009a; WWDR, 2015; European Environment Agency (EEA), 2012; WWDR, 2015). Moreover, "in situ" recycling wastewater helps to decentralize water management, reducing energy needed to move it through long distances for treatment or pumping groundwater from deep aquifers for human use.

2.2.1 Hydroponic wastewater

Implementation of soilless crops at urban scale is promising with regard to mitigate future threats related to climate change and the exponential increase of food demand, scarcity of local resources such as water and land, and climate change (Alexandratos and Bruinsma, 2012; Whittinghill and Rowe, 2012; dos Santos, 2016; Dimitri et al., 2016). The adoption of soilless agriculture is a sustainable alternative to produce food at an urban scale, since it can be applied in buildings, improving supply chains while reducing transport distance and time of storage (dos Santos, 2016).

HWs are discharged from soilless crops systems, which use different substrates and water as growth media and the nutrient solution can recirculate (closed systems) or can be treated and sporadically discharged into the environment (open systems) (FAO, 2013).

Closed systems usually use is more limited because they carry a large amount of nutrients that can cause excessive nutrient uptake, combined with salinity and pathogens spread (Massa et al., 2010; FAO, 2013; Trejo-tellez and Gomez-Merino, 2012). Therefore, the drained water is usually collected and mixed with freshwater to an accurate nutrient composition and then goes back to the system (Rosberg, 2014). However, normally at the end of the crop season, the water will need to be treated (FAO, 2013), either to be reused or to be discharged into the environment.

In open systems and semi-closed systems, the water is released into the environment, which could cause serious pollution problems like eutrophication, since it has high concentrations of nutrients such as P and N (Park et al., 2015; Gagnon et al., 2010; Park et al., 2008; Bergstrand, 2009; Grewal et al., 2011; Bergstrand, 2009; Massa et al., 2010).

Several authors have shown that soilless crop production represent an important source of non-point pollution, since the wastewaters have a high concentration of nitrates and P and is normally drained and discharged to the environment (Park et al., 2015; Abbassi et al., 2011; Gagnon et al., 2010; Park et al., 2008). According to (Abbassi et al., 2011) "*as a result of the growing adoption of soil-less techniques in the world and due to the pollution potential of this method, treatment of drainage water from such farms represents a great challenge to environmental engineers*". The leaching of N and P can cause several ecological impacts, such as pollution of surface streams and groundwater, eutrophication and loss of biodiversity (UN Water, 2015; Eurostat, 2011; Bergstrand, 2009).

Therefore, the treatment of HWs is important, especially to ensure the safe implementation of soilless crop at urban scale and, thus a sustainable transition for an urban agriculture and food security.

2.2.2 Grey wastewater

There are numerous descriptions of GWs; however, in general is this water characterized as a lightly polluted wastewater discharged from separated devices in buildings (BS 8525-1, 2010; Department of Health Western Australia, 2010; Environment Agency, 2011; Eriksson et al., 2002). The reliability of GWs is due it is a constant water source, contains plenty of nutrients and has a comparatively low concentration of pathogens compared with mixed wastewater and black water. Nevertheless, according to the further utilization, GWs should respect hygienic safety and environmental tolerance (Eriksson et al., 2002).

GWs exhibits with significant variations of water quality dependent on individual user behaviour (Imhof and Mühlemann, 2005). According to the Department of Health Western Australia (2010) GWs may contain high levels of pathogens (bacteria, viruses, protozoa, helminths), suspended solids, organic matter, chemicals derived from soaps, shampoos, dyes, mouthwash, toothpaste, detergents, bleaches, disinfectants, caustic dishwashing powders and other products. Despite the microorganisms cited previously, organic matter and Pare great concerns regarding the safe reuse or discharge of this type of water.

Therefore, it is important to ensure proper treatment of this water before reuse, and to avoid the dangerous consequences on water quality, environment and human health (UN Water, 2015).

2.3 Global warming

During the past 50 years, the "urbanization" phenomena has become faster than ever. Currently 55% of the world's population lives in urban areas and this proportion is expected to increase to 68% by 2050 (UN, 2018). The fast urbanization and exponential growth of world's population lead to changes on cities landscape: **the cities are becoming more grey and taller than green.**

As a consequence, the replacement of vegetation and natural areas with non-natural spaces made of hard and impervious materials, such as concrete, has led to changes on the dynamics of urban ecosystems (Shooshtarian et al., 2018). Changes in urban geometry and use of impervious materials can lead to radiation trapping, ventilation blockage and, **as a consequence an increase of temperatures** (Palme et al., 2016).

Moreover, the rise of global temperatures is intrinsically related to the increase of greenhouse gas emissions, which for instance, is pushed up as the population grows. Currently, is estimated that the anthropogenic activities have incremented 1.0°C of global warming and that Urban Heat Island Effect (UHI) is an important consequence of human intervention on climate change (IPCC, 2018; Palme et al., 2016). The greenhouse emissions are powered either by human basic needs such as food and energy demand or by other requirements such as fuel consumption and industrial purposes.

The most relevant greenhouse gases related to global warming are Carbon Dioxide (CO_2), Methane (CH_4) and Nitrous oxide (N_2O), representing 98% of the emissions monitored by the Kyoto protocol (Marchal et al., 2011). Two third of CO_2 emissions is related to energy demand and fuel combustion, one third of the global warming induced by humans are covered by CH_4 emissions (livestock activities, rice cultivation, biomass burning and waste management), approximately 40% of NO_2 emissions are caused by anthropogenic activities (combustion of fossil fuel, soil changes, fertilisers and industry) (Marchal et al., 2011).

According to IPCC (2018), the global temperatures are estimated to rise up to 1.5°C in the period of 2030 to 2052, if it keep increasing at the current rate. The rise of global temperatures has a straight effect on natural cycles like water and nutrients and changes on ecologic dynamics, both facts can severally limit the ability of natural ecosystems at providing services such as clean water, air and food. If the global temperature rises to 1.5°C, a coastal resources loss is projected, water supply risk will increase and several natural ecosystems will be damaged. On the other hand, reduction in fisheries, aquaculture production and even in yields of maize, rice, wheat is also expected, leading to concerns related food security (IPCC, 2018). In addition, the rise of energy consumption is expected, next to an increase in the frequency of heavy precipitations and droughts. Besides, sea level will rise enhancing flooding risk, ocean temperature and acidity will increase, oxygen levels in oceans will be reduced and direct human health issues associated mainly to vector-borne diseases, such as malaria and dengue fever will also rise (IPCC, 2018).

It is important to highlight that the severity of those impacts is strongly dependent on resilience capacity for each area. This capacity will mainly depend on factors and conditions such as, social and economic empowerment in accordance with environment boundaries, status of natural capital preservation, geographic location (latitude and longitude) and sustainable technological development.

In this regard, NBS such as LWs and CWs have a great potential to increase resilience, mainly by integrating ecosystem services into human environment, increasing natural capital and promoting a self-sustainable cycle of natural sources. In one hand, LWs can help to mitigate global warming, basically, in two ways: mitigating the impact (rise of temperatures) and controlling the driver (CO_2 emissions). First, LWs can mitigate the rise of temperatures and, thus, all the impacts cited previously. LWs are efficient at providing cooling effect (evapotranspiration) and thus, reducing urban temperatures (Pérez-Urrestarazu et al., 2016; Hoelscher et al., 2015; Perini et al., 2011a). Second, LWs can improve air quality by reducing atmospheric CO_2, one of the most important drivers of global warming, and increasing atmospheric O_2 (Charoenkit and Yiemwattana, 2016; Marchi et al., 2015). on the other hand, CWs, a passive wastewater treatment based on the mimicking natural process, have great potential regarding ensuring water supply, in accordance with the preservation of natural capital. More details about LWs and CWS are given in Chapter 3 (Background).

2.4 Natural resources performance

2.4.1 Changes in Nitrogen (N) and Phosphorus (P) cycle. Recovering N and P is needed.

The nature and biodiversity of ecosystems are intrinsically related to the availability of reactive Nitrogen (N_r - all nitrogen compounds except N_2), which is provided mainly by natural processes such as lightning, biomass burning and biological N fixation (Erisman et al., 2011; Erisman et al., 2007).

On the other hand, N has been worldwide recognized as an environment issue (Erisman et al., 2007). The anthropogenic modifications of N cycle are mainly caused by the input of Nr into the natural and semi-natural ecosystems, mainly by N Fixation in agriculture, N_2 fixation by Haber–Bosch process and burning fossil fuels (Butterbach-Bahl et al., 2011; Erisman et al., 2011).

However, the N_r creation is mainly related with the production of synthetic fertilizers (Galloway et al., 2008). In the 20th century, a process to convert gaseous N_2 into synthetic fertilizers, based on Haber–Bosch process, was developed, fact which was important to sustain food demand at this time, according to (Erisman et al., 2007) "*Over 40% of the world's population is here today because of that capability*". According to Rockström et al. (2009), a limit of industrial and agricultural N_2 fixation was fixed to 35 Tg N yr^{-1}. However, N_r from the Haber-Bosch process went from 0 before 1910 to more than 100 Tg N yr^{-1} in 2000, with about 85% used in the production of fertilizers (Galloway et al., 2003), which is over almost 3 times the proposed limit by Rockström et al. (2009). The widely anthropogenic fixation of N_2 and, consequently, the dispersion of N_r by hydrologic and atmospheric transport processes at both, global and local scales, lead to the accumulation of N_r. Therefore, anthropogenic N_r creation ratio is greater than the environmental capacity to remove N_r through denitrification process (Galloway et al., 2003)

This increment of N at regional and global scales can cause several environmental hazards, such as changes in terrestrial, aquatic and marine ecosystems dynamics and, thus, affecting climate change (Rockström et al., 2009). According to (Galloway et al., 2008), the anthropogenic alteration of the N cycle is negatively affecting human and ecosystem health and this effect is expected to increase once the demands for food and energy will also increase. Rockström et al. (2009) estimated that humanity has already transgressed planetary boundaries related to changes in the global N cycle.

Therefore, global strategies to mitigate the N "cascade effect" are extremely important in order to ensure the availability of natural resources, climate change mitigation and food security, in accordance with planetary boundaries. In this sense, reducing the N_r input by recovering N_r, which is already available in the wastewaters, reusing it as fertilizer, can play an important role at closing the N cycle, ensuring a sustainable production of food and reducing anthropogenic pressures on natural resources.

P is a limited resource, an essential nutrient for plants growth and is added into earth mainly by geological natural weathering processes (Lee et al., 2018; Rockström et al., 2009). Natural sources of P have been widely exploited for its use in agriculture (fertilizer) and industry. Moreover, the discharge of wastewaters with high P concentrations and the intense use of P compounds in agriculture (chemical fertilizers) leads to an increase of P loading within ecosystems (Melia et al., 2017). The accumulation of P leads to changes in terrestrial, aquatic and marine ecosystems, mainly by eutrophication and ocean anoxic events. Both process are highly associated to losses on biodiversity and reduction of natural resilience (Rockström et al., 2009; Berg et al., 2006; Karczmarczyk et al., 2014; Renman and Renman, 2012).

One g of P released into water bodies promotes the growth of up to 100 g of algae, enhancing eutrophication of the surface waters (Karczmarczyk et al., 2014). Modelling analysis performed by Rockström et al. (2009) showed a 10 times increase on P inflow into the oceans. For 1000 years, the ocean anoxic fraction could raise to 0.22. Moreover, the author defends that such input of P is not feasible for 1000 years more, when considering the estimative of phosphate natural reserves.

Therefore, recovering P from wastewaters and reusing it is a key strategy regarding the preservation of natural capital, ensuring a sustainable food production and reducing the environmental risk of its accumulation in water bodies and oceans. In this regard, NBS have been rising as a sustainable way to remove and recover P from wastewaters. The NBS promote an efficient use of natural resources, a human well-being and a socially inclusive green growth by replicating natural process and integrating ecosystem services into the human environment (European Commission, 2015a;Garcia-Holguera et al., 2015;Blok and Gremmen, 2016).

2.4.2 Closing the loop is needed

The now widely used production model is based on the 'take-make-dispose' concept, or 'linear' model, where there is no planning for resources reuse or regeneration of the natural systems which are overexploited (Ellen MacArthur Foundation, 2013). The exploitation of raw materials and natural capital is especially intensified in urban areas, due to high population density which lead to high consumption of industrialized products (Tomić and Schneider, 2018).

The cities are responsible for consuming more than 60% of natural resources, for producing 50% of global waste and releasing more than 75% of greenhouse gases (Williams, 2019; Camaren and Swilling, 2012). In 2010, only 40% from the 2.7 billion tons of waste generated in Europe was reused, recycled, or composted and digested, which means that 1,62 billion tons of waste was not reclaimed for European economy (Macarthur, 2013). According to (Zeller et al., 2018), approximately 70% of generated waste is not reused or recycled, fact which explain the current pressures on global raw resources. Therefore, the concept of linear production has been questioned in regard to the optimization of natural resources performance. "*Waste does not exist—products are designed and optimized for a cycle of disassembly and reuse.*" (Macarthur, 2013).

In 2012, the European commission published a manifesto about resource use-efficiency, which started as following: "*In a world with growing pressures on resources and the environment, the EU has no choice but to go for the transition* ***to a resource-efficient and ultimately regenerative circular economy.*** *Our future jobs and competitiveness, as a major importer of resources, are dependent on our ability to get more added value, and achieve overall decoupling,* ***through a systemic change in the use and recovery of resources in the economy****"* (European Commission, 2012).

In 2015, the European commission launched a Proposal for a Directive of the European Parliament and the Council, amending Directive 2008/98/EC on waste and highlighted that "*Waste management in the Union should be improved, with a view to protecting, preserving and improving the quality of the environment, protecting human health, ensuring prudent and rational utilization of natural resources and promoting a more circular economy*" (European commission, 2015). This legislation proposed several priority areas to be addressed in the implementation of CE across different economic sectors. The priority areas are: plastics, food waste, critical raw materials, construction and demolition, biomass and bio-base materials. Moreover, actions addressed to recycling processes (municipal solid, construction and demolition and packaging among others), landfill restrictions, industrial symbiosis and eco-design (Zeller et al., 2018) can play an important role at ensuring the integration of CE principles in the habits of modern society.

In this regard, connecting INPUTS and OUTPUTS from different production chains through promoting the reuse/recycling of waste/by-products are strategies needed in order to promote an efficient and environmental friendly production with high performance and at the same time improves sustainable waste management, energy recovery and climate change mitigation (Jethoo et al., 2012; Corsten et al., 2013). "*Closing the loop between the end of the life of the product and its production enables circulation of resources, materials and products and keeps its energy, material and economic value within the economy for as long as possible*." (Tomić and Schneider, 2018).

Therefore, it can be said that the exponential growth of society has led to a global concern regarding improvements on resources performance through the reuse of by-products and their components, restoring more of their precious material, energy and labour inputs. (Ellen MacArthur Foundation, 2014). Furthermore, environmentally friendly solutions must be in accordance with efficient use of natural resources and energy security supply.

2.5 Population growth, urbanization & vertical growth

According to World Population Prospects (United nations, 2017), the world population in 2100 will be almost twice the population of 2000 (growth rate was calculated dividing population projected for 2100 by population in 2000, and the exactly value is 1.82). More than half of global population is living in urban areas, characterized by a pervasive urbanization process, mainly produced with a clear absence of urban planning (Bhave and Rahate, 2018).

Global world concern regarding food security has leading to the implementation of policies to preserve high quality arable land, fact which is associated with the high costs of horizontal expansion. This issue clearly results in the reduction of land availability, and thus, vertical growth is expected (Lin et al., 2014). Zambon et al. (2019) studied both, vertical and horizontal expansion in large metropolitan areas in Greece. The results showed that intense vertical expansion was correlated to high population growth in large urban areas such as Athens, Salonika, Patras and Iraklio. Zhang et al. (2018) performed a similar study considering East Asian megacities. According to the author, in Seoul during the 1988 to 2015 period, the vertical urban growth dominated the whole city growth behaviour, being present from the centre to peripheral areas and faster between 2002 and 2015.

Vertical building growth can be considered as one of the most important process involving vertical expansion. According to Lin et al. (2014), the vertical expansion in urban areas is reflected by the rise of buildings with different purposes, such as, commercial, residential and industrial. The author also argue that the vertical growth can change not just morphology but as well the functioning of the cities, fact which make it an important factor to be considered in order to ensure a sustainable urban growth.

Due the future treats regarding world population growth, pervasive urbanization process and limited land availability, vertical expansion need to be envisioned and improved. Indeed, cities are key areas regarding climate change, once urban economies are basically consumption nodes based on take and dispose of products and services, fact which lead to great pressures on natural capital (Christis et al., 2019). Therefore, the development of **NBS** which can **undertake urban vertical area** to improve thermal performance, air quality and treat and reuse wastewater, can play an important role regarding the current pressures on water quality, global warming projections and the need to improve natural resources performance and to preserve natural capital.

Chapter 3 Background

3.1 Conventional wastewater treatments

Conventional treatments are usually focused on removing organic matter, solids and nutrients applying physical, chemical and biological processes (Sonune and Ghate, 2004). Different types of wastewater treatment technologies have been established in order to ensure a more efficient treatment process, such as membrane treatment technology, reverse osmosis, ion exchange, UV light and Ozone process (Gogate and Pandit, 2004; Sonune and Ghate, 2004).

3.1.1 Grey wastewater treatments

GWs treatment technologies must be well designed to handle variations of pollutant concentration and to consistently produce effluent with an appropriate and safe quality to meet required standards for reuse (Winward et al., 2007). Choice of treatment process is dependent on two basic factors - source of GWs and further use of treated water.

There are different GWs treatment approaches ranging from simple, low-cost devices that supply GWs directly for final application, such as toilet flushing or irrigation, too costly and high complex advanced treatment processes incorporating sedimentation tanks, bioreactors, filters, pumps and disinfections units (FBR, 2008; NHS - National Services Scotland, 2014). According to type of pollutants removed, treatment processes for GWs could be divided into various levels of requiring treatment process, such as preliminary, primary, secondary, tertiary and advanced.

Preliminary treatment deals with removal of largest components in water which can cause operational problems with following treatment operations. In primary treatment system, the suspended solids or other materials, which could be settled, are removed. Secondary treatment includes removal of floating solids and about 90% of biodegradable organic matters. If the disinfection is not part of secondary treatment, it follows in tertiary treatment when the nutrients and most of BOD are removed. Advanced treatment is usually added if previous treatments were not sufficient or when the water quality has specific high demands (Imhof and Mühlemann, 2005).

Applied treatment technologies are usually physical treatment based on coarse and membrane filtration differing by filter types. For instance, nylon sock with good COD removal (March et al., 2004) and slanted soil with more than 70% chemical and nutrients removal from GWs (Li et al., 2009a). Chemical treatment processes consist of coagulation, flocculation, photo-catalytic oxidation, ion exchange and granular activated carbon (Li et al., 2009a; Lin et al., 2005). There are different biological treatments such as rotating biological contactor (Friedler and Hadari, 2006; Eriksson et al., 2002), or mostly used membrane bioreactors (Lesjean and Gnirss, 2006; Merz et al., 2007) and sequencing batch reactor (Gildemeister et al., 2005). Hybrid technologies are based on the combination of different treatment technologies (physical, chemical and biological) and application of their advantages. The combination of CWs and LWs are a specific type of hybrid systems. Several studies have been proving that CWs have a great potential to treat GWs (Li et al., 2009b; Avery et al., 2007; Comino et al., 2013; Winward et al., 2007).

3.1.2 Hydroponic wastewater treatments

The main purposes for treating HWs are to maintain the quality of the water recirculating in closed systems and to ensure a safe discharge into aquifers recharge when open systems and semi-closed systems are used. Most common HWS treatments include disinfection (pathogens), salinity control, and nutrients control, especially nitrates and phosphates, due they high potential for environmental hazard.

There are several disinfection treatments considered efficient to control water pathogens, mainly used in closed systems, such as heat treatment, ozone, UV radiation, ultrafiltration membranes, microfiltration membranes, slow filter and solar thermal treatment (Rosberg, 2014; FAO, 2013; Bergstrand, 2009; Hultberg et al., 2008; Koide and Satta, 2004). These water disinfection methods can cover a wide range of microorganisms but also have some limitations, for example, UV radiation, heat and ozone can also reduce the beneficial microorganisms (Rosberg, 2014).

To maintain water salinity at an acceptable level in hydroponic systems, electro dialysis, reverse osmosis and Ion exchange have been used (Christie, 2014). According to Park et al. (2015) and Gagnon et al. (2010), ion exchange, electro dialysis and reverse osmosis, are technologies characterized by high operation and maintenance costs.

Hybrid methods, such as CWs and denitrification filters, have demonstrated good results with concerns to removal of nitrates and phosphates in HWs (Park et al., 2015; Gagnon et al., 2010; Park et al., 2008; Park, 2009; Abbassi et al., 2011).

3.2 Nature-based solutions

Transition from grey towards green infrastructure is needed in order to reduce the environmental hazards generated by rapid urbanisation and climate change (Davies and Lafortezza, 2019). According to Francis and Lorimer (2011) "*Reconciling human and non-human use of urban regions to support biological conservation represents a major challenge for the 21st century*".

The implementation of NBS have been increasingly applied as an alternative for the current used technologies, mainly due its great potential to reconcile human development and the preservation of natural capital. The main goals when implementing NBS are to restore ecological flows and increase resilience in cities (Frantzeskaki, 2019).

NBS can be described as an innovative design approach which fosters the integration of ecosystem services and natural processes within the human environment in order to promote an efficient performance of natural resources and climate change adaptation (Blok and Gremmen, 2016; Garcia-Holguera et al., 2015; European Commission, 2015a). Appropriate technologies based on natural processes can enhance the maintenance of ecosystem services such as carbon sequestration and nutrient cycling (Lundholm et al., 2015). According to Blok and Gremmen (2016) "*By using the same design principles as natural entities and systems, and by modelling our technological design on natural principles, biomimicry adheres to a bio inclusive ethics that enables us to resituate our technological design within the ecological limits of the biosphere*."

In one hand, according to Krauze and Wagner (2019) NBS should mimicking nature without manipulating nature process. The authors defend that enabling the implementation of biophysical structures into urban environment, multiplying, enhancing and reviving local processes and native biota already present are the main factors related to "mimicking nature". On the other hand, "Nature manipulation" can be defined as a stimulation of specific processes to achieve a determined goal by introducing external agents, such as exotic species. Moreover, the author highlights that water availability and eco-hydrological interaction between water and biota are key design factors regarding NBS implementation.

In this regard, CWs are passive ecological treatments for wastewater based on the mimicking of biological, chemical and physical process occurring in natural wetlands, which had been implemented worldwide successfully (Winpenny et al., 2010; Babatunde et al., 2008; Vymazal and Březinová, 2015; Avery et al., 2007). LWs have great potential for reconciliation ecology in urban areas once brings up the implementation of sustainable concepts into natural building design and can provide thermal insulation (Francis and Lorimer, 2011; Ragheb et al., 2016; Cheng et al., 2010; Tilley et al., 2012).

3.2.1 Constructed wetlands - types and features

Several studies have been developed and confirmed the CWs high potential to remove a wide range of pollutants such as pesticides (Vymazal and Březinová, 2015), pathogens (Díaz et al., 2010; Gruyer et al., 2013), nutrients (especially nitrates and phosphorus) (Vymazal, 2007; Vymazal, 2013; Gagnon et al., 2010) among others.

CWs are a low cost approach widely used to treat different types of wastewaters and are based on the replication of biological, chemical and physical process, occurring in natural treatment wetlands (Winpenny et al., 2010; Babatunde et al., 2008; Díaz et al., 2010). According to Vymazal and Březinová (2015) "*CW treatment systems are engineered systems that have been designed and constructe*d **to utilize the natural processes** *involving wetland vegetation, soils, and their associated microbial assemblages to assist in treating wastewater*". CWs are environmental-friendly and passive ecological treatments, which could be affordable with low capital and maintenance requirements and contribute to sustainability (Avery et al., 2007).

I n addition, several researchers have demonstrated good results removing nitrates and phosphates and other chemical nutrients from HWs (Park et al., 2015; Gagnon et al., 2010; Abbassi et al., 2011; Park, 2009) and GWs (Avery et al., 2007; Comino et al., 2013; Zhang et al., 2014). CWs, if well designed, can be a feasible alternative to treat HWs and GWs, being even more efficient and less expensive when compared to other conventional treatments, such as membrane filtration, ultrafiltration, ion exchange, reverse osmosis and electro dialysis (Seo et al., 2010; Avery et al., 2007).

Which regards the treatment features, CWs, basically are filter beds filled up with porous media and planted with wetland vegetation in order to treat the wastewater (Canga et al., 2014). According to Shelef et al. (2011) "*water is transferred through the filter media, and contaminants are removed by two major processes: sedimentation and* *biochemical interactions*". Usually, the CWs can be categorized according to their hydrology, mainly regarding the type (surface or subsurface) and the flow direction (vertical and horizontal) Kraiem et al., 2019; Bang et al., 2019; Vymazal and Březinová, 2015). The most known typologies of CWS are surface flow CWs, horizontal subsurface flow CWs and vertical subsurface flow CWs.

CWs with surface flow are mainly based on channels, with substrate to support the plants and roots development and the water are relatively above the substrate level (Vymazal and Březinová, 2015). However, this research is focused on Subsurface flow, mainly because this type of flow reduced the risks associated on human and wildlife contact with pathogens present in the wastewater, since water is not exposed during the treatment process (Kadlec and Wallace, 2000). The subsurface flow type CWs can be divided in two main subcategories: vertical flow (VF) and horizontal flow (HF).

CWs based on a subsurface VF are basically a filtration bed filled up with gravel or sand, planted with macrophytes where the water is fed intermittently in order to ensure the aeration of the bed between batch cycles (Vymazal and Březinová, 2015). In other words, in Subsurface VF the percolates filter bed vertically from the top to the bottom and is collected by perforated pipes (Huang et al., 2016).

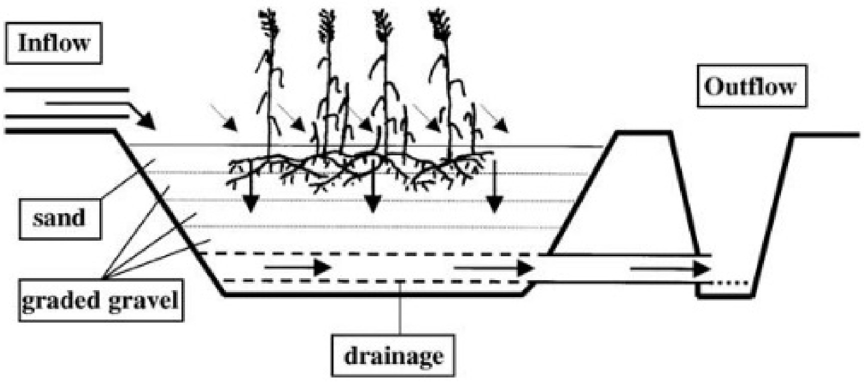


Figure 1 Schematic diagram of an CWs based on Subsurface VF CWs (From Vymazal, 2007; Vymazal, 2001)

CWs based on a subsurface HF usually are gravel, soil or sand filter beds planted with wetland vegetation and continuously fed, where the wastewater flows through the filter bed and under the surface following a horizontal path until reaches the outlet zone (Vymazal and Březinová, 2015; Kadlec and Wallace, 2000).

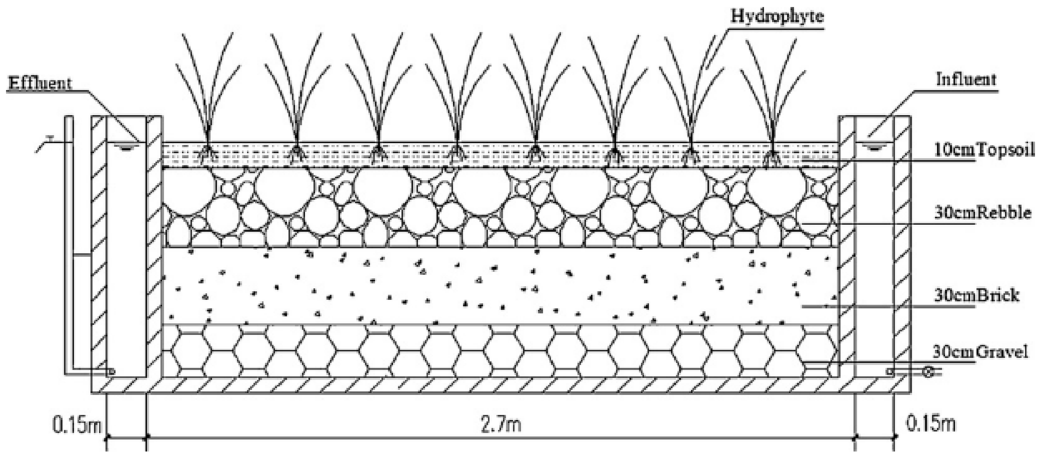


Figure 2 Schematic diagram of an CWs based on Subsurface HF CWs (from Huang et al., 2012)

Hybrids systems, as the combination of horizontal and VF (VF-HF) are probably the most widely used, where the combination of different flows can ensure different redox conditions and thus, enhance the removal of organic matter and nitrification and denitrification process (Vymazal, 2013; Vymazal and Březinová, 2015; Kadlec and Wallace, 2000; Bang et al., 2019).

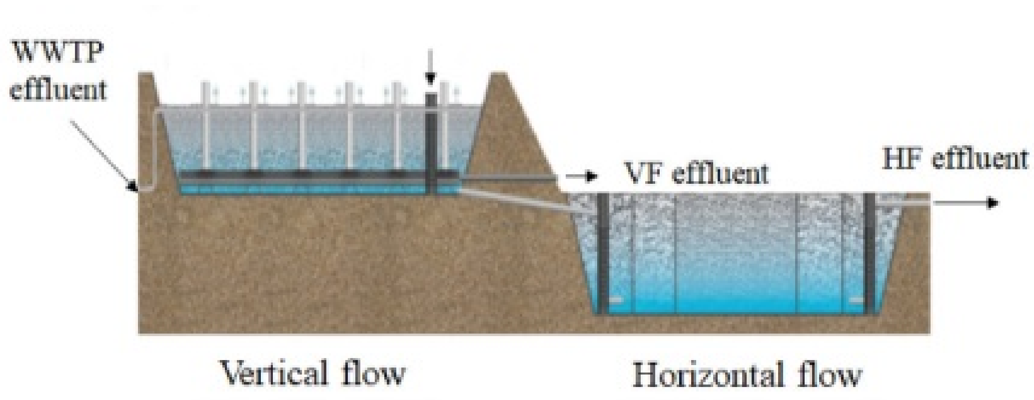


Figure 3 VF-HF hybrid wetland (adapted from Bang et al., 2019)

In such Hybrid systems, the removal of total solid soluble (TSS), organic matter (BOD_5) and nitrification process are attenuated in the VF stage, while in the HF stage denitrification process are favoured by anoxic/anaerobic conditions, if the organic carbon remaining from VF stage is enough to complete the removal of N (Bang et al., 2019). For instance, replicating the rem**oval process occurring in hybrid CWs** in the cities scale can be a sustainable alternative to recovery nutrients from urban wastewaters such as, GWs and HWs.

3.2.2 Vertical Gardens – types and features

Vertical gardens (VG) are aesthetically ecological engineering urban structures with notable potential for **ecology reconciliation in urban areas**, can be installed on large surfaces where little space is available, allows a passive building design along with environmental benefits, not just for the buildings, but for the whole of urban areas (Sheweka and Magdy, 2011; Kontoleon and Eumorfopoulou, 2010; Francis and Lorimer, 2011; Marchi et al., 2015).

Moreover, VGs can preserve ecological biodiversity creating a new profile of urban areas in accordance to nature, mainly by providing ecosystems services such as, CO_2 sequestration, O_2 atmospheric increment, thermal regulation and indirectly favouring energy savings and acoustic comfort (Victoria State Government and University of Melbourne, 2013; Marchi et al., 2015; Natarajan et al., 2015; Coma et al., 2014; Sheweka and Mohamed, 2012).

There are two main typologies of VGs: **green walls and living Walls (LWs)** (Manso and Castro-Gomes, 2015; Kontoleon and Eumorfopoulou, 2010). Green walls are mainly outdoors applied, mostly climbers, are used to cover the building façade directly or indirectly by using external structures to guide the plants growth, such as modular trellis or cable and wire-rope net systems (Perini et al., 2011a; Kontoleon and Eumorfopoulou, 2010). Normally, in this system the plants are rooted at the base of the building straight to the ground or in vessel or planters (Kontoleon and Eumorfopoulou, 2010). LWs can be implemented both, indoor and outdoor. In this system, the plants are not directly contacting on the building façade, since external structures such as pre-vegetated panels, vertical modules, planted blankets, felt layers, planter boxes or steel baskets are used to sustain plants and substrate (Kontoleon and Eumorfopoulou, 2010; Perini et al., 2011b). The main typologies of both greenery systems, Green walls and LWs, can be seen in Figure 4.

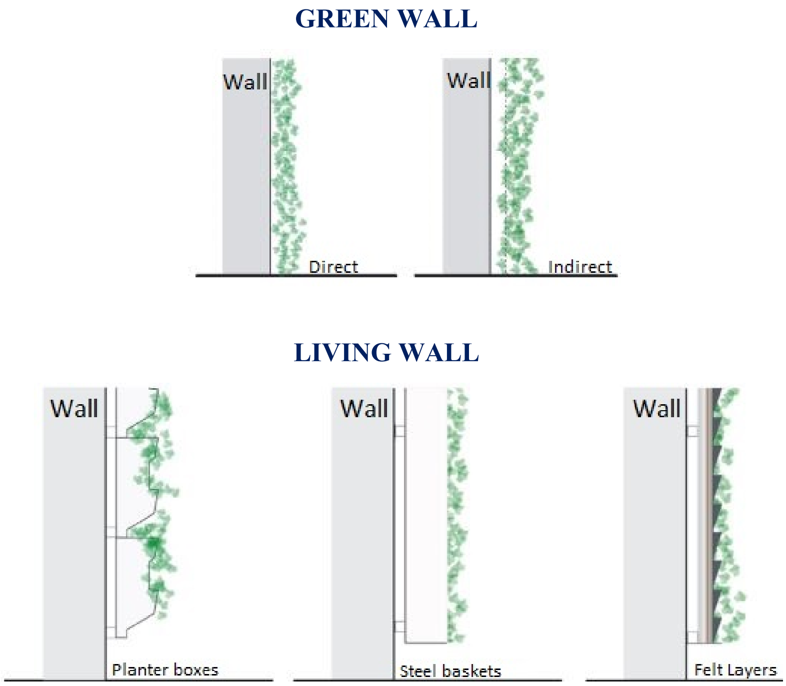


Figure 4 Main typologies of GW and LW greenery systems. (adapted from Perini et al., 2011b)

The thermal regulation provided by VGs can affect energy demands for heating, during winter, and cooling, during summer. The thermal performance of VGs, are mainly regulated by the amount of **solar radiation intercepted (shadow effect), evaporative cooling rates, and wind speed,** all three affecting the heat flux (flow of heat per unit area - Watts per square meter, W/m2), from inside to outside or from outside to inside, depending on the season. In regard to thermal regulation, plant covered surfaces can intercept solar radiation (Shadow effect) which would be absorbed by pavement surfaces (buildings), reducing the warming up of hard surfaces and thus mitigating urban heat effect in urban areas (Perini et al., 2011b; Hoelscher et al., 2015; Cheng et al., 2010; Kontoleon and Eumorfopoulou, 2010; Perez et al., 2011; Carlos, 2015). Moreover, the evaporative cooling and shadow effect can promote the reduction of heat, which usually is re-radiated by artificial hard surfaces.

The **evaporative cooling** is occasioned mainly by evapotranspiration of plants (Green walls and LWs), water evaporated from substrate (LWs) which can cooling the building surface and, for instance, reduce energy requirements for cooling during summer (Cheng et al., 2010; Tilley et al., 2012; Raji et al., 2015; Wong et al., 2010; Pérez-Urrestarazu et al., 2016). The evapotranspiration rates of plants, vegetation coverage and moisture of substrate can directly affect the evaporative cooling performance. Cheng et al. (2010) concluded that the cooling effect provided by the LWs studied, was strongly associated with green coverage and substrate moisture. Cameron et al. (2014) studied Green walls thermal performance and concluded that the evapotranspiration from plants plays a positive role in the reduction of heat loads during the warmest hours of the day. The author showed that the cooling effect provided by an outdoor Green walls lead to a reduction of 3°C during warmest periods, in comparison to a non-vegetated wall, being mainly related to evaporative and shadow cooling.

Interception of solar radiation or shadow effect are mainly affected by vegetation coverage plus others insulation layers when LWs are used, such as substrates, structure and air cavity. The shadow effect can play an important role at regulating heat flux through building façade and thus, regulating energy use. During summer, the shadow normally reduces the incoming of solar energy reducing heat flow from outside to inside the building and thus, energy spends for cooling (Kontoleon and Eumorfopoulou, 2010; Cheng et al., 2010; Tilley et al., 2012). In one hand, results from Coma et al. (2014) highlighted a **reduction up to 14 ºC during summer (July to September) in the external south surface when Green walls were used**, mainly due shadow effect. Indeed, the Green walls seem to reduce the heat flow from outside to inside during warm periods, being the temperature inside the experimental cubicle 1 ºC lower in comparison with the control. On the other hand, the insulation properties of material used to build LWs structure can affect the thermal transmittance and velocity of wind inside the air cavity (Perini et al., 2011b). The experiment of Cheng et al. (2010) showed that the heat flux in presence of LWs modules were significantly lower when comparing to bare walls, during summer. Indeed, the reduction of heat inflow significantly reduced power consumption. Results from Coma et al. (2014) showed that the shadow cooling of Green walls lead to slight reduction in energy consumption (cumulative reduction of energy consumption = 5.5%). Moreover, the shadow effect by vegetated surfaces can be even greater than bare facades naturally shaded. Cameron et al. (2014) found that the cooler effect was significantly greater for Green walls oriented at south, compared to the natural shaded north side without plants, during summer.

Nevertheless, for both systems (Green walls and LWs), plants can play an important role at reflecting solar radiation, working as a solar barrier and therefore, reducing heat flux through building façade (Kontoleon and Eumorfopoulou, 2010). Plants can absorb, reflect and transmit solar radiation, the proportion of each varying across species (Charoenkit and Yiemwattana, 2016). However, most plants can intercept and absorb considerable amounts of solar radiation required for growth and biological process, such as respiration, photosynthesis and tra nspiration (Kontoleon and Eumorfopoulou, 2010). According to Kontoleon and Eumorfopoulou (2010), when a wall is covered by vegetation, the absorption of solar radiation coefficient is estimated to be one third of bare surface. Nevertheless, the relation between dissipated heat and solar radiation absorbed by plants varies according species, but also can highly vary in function of wind speed and air humidity (evapotranspiration) (Charoenkit and Yiemwattana, 2016).

The wind speed can affect the thermal transmittance ($m^2 \cdot K \cdot W^{-1}$) and insulation properties of building façades (Perini et al., 2011b). Despite the VG typology used, the equalization of exterior and interior surface thermal resistance can be affected by the reduction of wind velocity, and thus, regulating energy savings (Perini et al., 2011b). However, the factors affecting the wind speed might vary according to VG typology. When Green walls are implemented on building facades, the wind speed is mainly regulated by vegetation coverage. When LWs or indirect Green walls are used, besides foliage coverage, air cavities (ventilation gap) can also highly affect the wind speed, being the distance between modules and bundling surface extremely important at regulating the thermal transmittance. The air cavity can work as a thermal buffer, reducing heat flux on building envelope mainly through regulating air temperature and wind speed (Raji et al., 2015).

Perini et al. (2011a) investigated the effect of wind speed on LWs and Green walls on thermal performance during summer. The author evidenced that the foliage coverage (Green walls) or plus other insulation layers (LWS), can create a stagnant air layer increasing the thermal resistance of the building facade up to 0.09 $m^2 \cdot K \cdot W^{-1}$. On the other hand, during winter, the air cavity helps to keep the wall surface dry preventing ice damage (Carlos, 2015). Results from Tudiwer and Korjenic (2017) suggested that the increment of air temperature, between LWs and building façade (ventilation gap or air cavity) can lead to lower heat demand during winter.

Other factors related to implementation area or "in situ" factors, such as building façade orientation and thermal properties (thermos physical features and location of insulation layers), also can play an important role on thermal performance of VGs. In this regard, Kontoleon and Eumorfopoulou (2010) compared the thermal performance of bare walls with Green walls, during summer in Greece, under different façade configurations regarding the placement of insulation layers and façade orientations (North, sur, west, east). The authors results showed that both external and internal peak of surface temperatures were lower when Green walls were used in comparison with bare wall. However, differences between external surface temperatures seem to be higher than internal temperatures when comparing both systems (vegetated and non-vegetated), regardless the orientation. These results might suggest that the thermal transmittance was affected as well by the location of built insulation layer.

The placement of insulation layer on the outer (IM) and inner (MI) surface of masonry lead to, respectively, lower peaks of internal and external surface temperature, for both bare and Green walls. The use of MI (insulation configuration) lead to lower demands of energy for both, Bare and Green walls. For instance, the effect of insulation configuration on external cooling have greater effect on energy demands than when considering internal cooling, during summer. In addition, the combination of MI and Green walls showed the lowest energy demands rates regardless the orientation. The effect of Green walls lowering temperatures are more expressive for east and west orientation, regardless the placement of insulation layer. This might be due to the intense solar radiation at this orientation. According to the authors, "*the impact of the orientation of a leaf cover layer on the thermal reduction effect of a building shell depends on the overall intensity of solar radiation*".

Most research on thermal performance of VGs are focused on cooling benefits for tropical, subtropical and Mediterranean climate, and less is known about their effectiveness at insulating buildings during winter and cold weathers (Carlos, 2015; Bolton et al., 2014). The vertical greenery systems thermal performance can vary over different climate seasons. The maximum efficiency is usually reported during summer or in warm climates and, in contrast for winter or cold climates, studies have demonstrated controversial results with regard to cooling/heating effects and energy savings (Raji et al., 2015).

In one hand, simulations suggested that the contribution of south oriented LWs to thermal regulation during winter was not enough to be converted to energy savings (Carlos, 2015). Feng and Hewage (2014) concluded in his study that Green walls are not cost-effective in winter months or cold climatic regions due to the low energy savings performance. (Ottellé et al., 2011) compared the performance of several typologies of VGs (e.g. Green walls - direct and indirect; LWs - planter boxes and felt layers) at Mediterranean weather, with regard to energy savings provided by heating and cooling, and in all cases the energy savings for heating was lower than for cooling. On the other hand, Tudiwer and Korjenic (2017) results showed a great potential of LWs, also south oriented, in reducing heat demand during winter, mainly due to the effect of ventilation gap on the insulation properties of building façade.

During winter and for both systems (Green walls and LWs), the green coverage can work as an extra external insulation layer avoiding the losses of energy from inside to outside. The insulation materials (LWs) and stagnated air layers (Green walls) can slower down the heat transfer between the inside and outside of a building (Ottellé et al., 2011). However, depending on the orientation, the shadow cooling can considerably reduce the heating of building surface, reducing passive heat flow from outside to inside, and possible increasing energy spends for heating. According to Raji et al. (2015) during winter, the shadow cooling, either by plants (green façade) or modules coverage (LWs), can obstruct the passive heat gain through the building leading to heating and energy demand increases. Therefore, studies focused on optimizing heating properties of VG are needed to make feasible its implementation in a worldwide scale.

For instance, **playing with "technical" factors (evaporation, shadow and wind) and "in situ" factors (building façade orientation and insulations properties) can help overcome limitations regarding the thermal performances of VGs during winter or cold climates.**

For example, the **use of evergreen or decidua plants** in accordance with the typology of VG and orientation can help to improve heating performance during winter. Evergreen species can be used for both typologies, Green walls and LWs. The use of evergreen is usually recommended for North orientation, since during winter, the plants can work as an external insulation layer, reducing the heat flow from inside to outside, protecting the façade against snow, rain and wind flow, and contributing to energy savings (Perini et al., 2011a), Perini et al., 2011b, Carlos, 2015).

For Green walls, the use of **deciduous species** can be an option to overcome the increment of heating demands during winter. Deciduous species, usually have no leaves during cold seasons, and thus, can facilitate the solar radiation interception during winter, warming up the building façade (heat flux) (Perini et al., 2011b). Therefore, the use of deciduous species can work very well for Green walls implemented at Mediterranean climates and/or south orientation. Indeed, this practice can provide different aesthetics profiles over the year, from intense green leaves to moderate maze of green and brown stems. Although when LWs typology is used, this practice is not suitable to increase heat absorption, since the modules will still cover the building surface even when the leaves are lost. Thus, the insulation properties of materials and ventilation gap between build façade and modules need to be considered. Indeed, once LWs are implemented cannot be removed, making the even more important orientation where is located. The intensity of cooling effect can vary according to façade orientation (Charoenkit and Yiemwattana, 2016)

Therefore, when LWs are used most important key factors to overcome limitations are selecting proper typology of VG, adequate plants and substrate, locating the modules at the best orientation, taking into consideration façade thermal properties and material and ventilation gaps.

With regard to **air quality**, vegetated covered surfaces can enhance plants uptake of pollutants, such as carbon dioxide (CO_2), Nitrogen dioxide (NO_2), Sulphur dioxide (SO_2), the release of O_2 to atmosphere and the settlement of fine dust particles on plants surface (Perini et al., 2011b; Marchi et al., 2015; Charoenkit and Yiemwattana, 2016). The CO_2 is used for photosynthesis, creating biomass and releasing O_2 while, NO_2 and SO_2 are absorbed and latter transformed to nitrates and sulphate s (Perini et al., 2011b).

However, the efficiency and mechanisms to accumulate carbon can vary across different species. In this regard, Marchi et al. (2015) compared the simulated performance of different perennial species, normally used in VGs, regarding CO_2 sequestration. The simulations showed that the **stocked carbon can vary from 0.14 to 0.99 kgCO$_2$eq m^{-2} of VG per year**, considering respectively, succulent herbaceous species such as *S. spurium* and Mediterranean scrubs such as *R. officinalis*. Therefore, the selection of appropriate plants can play a critical role at enhancing carbon sequestration in urban areas (Charoenkit and Yiemwattana, 2016).

The state of the art, regarding the performance of VGs treating wastewaters is presented further, in the first article of the thesis "*WETWALL - an innovative design concept for the treatment of wastewater at an urban scale*."

3.3 Circular economy

The application of CE strategies has been intensively encouraged worldwide due to its great potential to promote sustainable processes along with environmental boundaries regarding mainly natural resources availability and energy supply security (Petit-boix and Leipold, 2018; Tomić and Schneider, 2018). In this regard, the European commission stated in the EU action plan for the CE that" The *transition to a more circular economy, where the value of products, materials and resources is maintained in the* *economy for as long as possible, and the generation of waste minimised, is an essential contribution to the EU's efforts to develop a sustainable, low carbon, resource efficient and competitive economy*" (European Commission, 2015b). In addition, the CE approaches aim to reduce the impact of urban population growth on natural resources and energy supply, mainly through promoting self-sustainable, low-carbon, competitive and resource efficient process in cities (Tomić and Schneider, 2018).

Nowadays, when the subject is CE the term "*closing the loop*" is always highlighted. When the loop is closed, the life of products and services is increased and its economic value is kept for longer time, enabling the recirculation of resources, such as raw materials, water and energy (Tomić and Schneider, 2018; European Commission, 2015b). Therefore, pressures on natural capital are reduced, either by reducing the demand for raw material and energy (INPUTS) or by reducing the generation of waste (OUTPUTS). "*If cities are to become sustainable, they must reduce their use of all resources and decrease their waste outputs*" (Zhang, 2013).

In this regard, reuse and recycling are two important principles of CE approaches. Therefore, it is important to understand the difference between them, especially regarding the energy and carbon emissions. In one hand, recycling might involve chemical and physical process and human labour inputs, in order to make the material suitable for reuse. According to Williams (2019) the term recycling can be defined as "*resources are reprocessed for the original or other purposes*". Thus, normally process involving recycling material might require energy and CO_2 emissions. On the other hand, reuse can be defined as using something again for the same original purpose or for a totally different one. According to Williams (2019) the term reuse can be defined as "…*resources are used again without any further processing*". According to Jethoo et al. (2012) "*Reusing waste is efficient, as it does not require further processing, thereby not requiring further energy use*."

Petit-boix and Leipold (2018) identified and classified CE initiatives worldwide, according to the geographical area (continent), population size (20.000 to 5.000.000 habitants) and CE features (infrastructure, industries and business, urban planning, social consumption). According to the author, **the reuse of materials** was considered one of the main research lines, embracing a great variability of studies on the validation of new applications. Moreover, it was noticed that different **production chains and systems previously unconnected, were connected** through the interactions favoured by reuse.

Therefore, giving new applications to waste materials or by-products can play an important role at promoting a circular development of modern society. Indeed, it helps to connect different production chains and thus, to create an integrated recycling chain, where the demand for manufacturing and recycling process is reduced. Christis et al. (2019) suggests that reducing activities which requires energy is an efficient strategy to reduce carbon footprint, due to indirectly reduction of fossil fuels consumption.

Therefore, t**he reuse of materials besides helping to reduce the exploitation of raw materials, can also recover embodied energy and reduce CO_2 emissions.** However, the success of circular initiatives (loop actions) is not just a matter of reusing materials. The impact of loop actions can be extremely related to the number of natural resources embraced and production chains connected. In this regard the concept of Eco cycle models (ECM) have been raising. The ECM can be defined as a multi-resource (energy, materials, water), which allows water recycle, reuse of waste material, recovery of energy mainly through integrating looping actions across different natural resources chains (Williams, 2019).

When considering the scope of green buildings, **the design practices must be addressed to reduce energy spends and CO_2 emissions and to promote the reuse and recycle of materials** (Spence and Mulligan, 1995; Jethoo et al., 2012; Satir et al., 2013). In this regard, vertical greenery systems have great potential, not just at bringing ecosystems services into the urban environment, but as well to connect NBS and urban production chains. In one hand, the recycling of materials can be enhanced during the process of design and implementation of VGs in order to optimize the performance of natural resources, recovery of embodied energy and reduce carbon emissions. Few studies have shown the potential of using recycled material for structure of VGs such as polyethylene modules (Azkorra et al., 2015) and recycled PET bottles (Natarajan et al., 2015). Manso et al. (2013) proposed a design based on cork board, which according to the author, besides having low carbon and energy embodied also can contribute to thermal performance of buildings due to its insulation properties.

On the other hand, the reuse of waste materials or by-products as an alternative substrate can be encouraged when LWs typology is used. Several authors have been validating the reuse of materials not just as a substrate, but as well, regarding its ability at recovering different types of pollutants from water. For example, coconut shell (F. Masi et al., 2016), recycled glass beads (Wolcott et al., 2016) and mix of coir fibber and perlite (Prodanovic et al., 2019), have been studied as a potential filtering substrates in LWs treating wastewater. Prodanovic et al. (2017) compared the performance of different by-products such as coir fibber, Rockwool and grow stone (recycled glass) at removing N and Pfrom light GW, in order to validate its reuse in LWs modules. The results showed that coir fibber has great potential for enhancing denitrification process, however clogging effect can be also expected. Recovering and recycling water and nutrients are promising strategies focused in reducing pressures on natural capital and recovering energy and CO_2 emission embodied.

However, the reuse of materials as filtering substrates in LWs is a very recent and an ongoing process. It is possible that the materials already studied in the literature are not the same locally available at a certain implementation area. Indeed, when considering the scope of CE, the local availability of the filtering substrate can be very important in terms of reducing energy and CO_2 emissions involved in the life cycle of LWs treating wastewaters. The proximity of resources and consumer or the called "urban symbiosis" is a key factor to ensure an efficient material cycle and thus a successful implementation of CE actions (Zeller et al., 2018). **Therefore, studies on the performance of by-products as filtering substrates are important in order to facilitate its reuse in LWs and other NBS treating wastewater.**

Chapter 4 – Hypothesis and Goals

4.1 Hypothesis

The development of an **innovative design concept** for **urban wastewater treatment**, which integrates two well established **NBS**, Constructed **WET**land and Living **WALL** together with the principles of circular economy to promote **sustainable technological development** in accordance with the preservation of natural capital and climate change mitigation and adaptation.

4.2 Main and specific Goals

The main goal of the thesis was to develop and present an innovative design concept "WETWALL" for urban wastewater treatment which was based on the following specific goals:

- To present and discuss an innovative and versatile design concept for the treatment of urban wastewaters that can be adapted to different types of urban wastewaters and charges of contaminants: **The modular hybrid flow**, based on **hybrid CWs** and **modular LWs** (First article).
- To determine main design parameters and establish potential limitations and innovations related to the WETWALL design concept, through discussion of **the state of the art in the scope of vertical gardens treating urban wastewaters** (First article).
- Propose a framework to improve the selection for main elements of the WETWALL concept: Plants and Filter media (First article).
- Integrate Circular economy principles into the design process
  - Propose a conceptual analysis of INPUTS and OUTPUTS flow, considering further implementation of the concept WETWALL in cities (First article).
  - Study the performances of potential local by-products (Cork and CAAC) to be used as filtering substrates in NBS treating urban wastewaters (second and third articles)
- Design, develop and build a prototype with scalable automation for water recirculation.
- Analyse the efficiency of WETWALL porotype in regard to phosphorus, nitrogen and organic matter removal.

Chapter 5 The WETWALL Design process

5.1 Overview

The technological features contemplate by the WETWALL design concept are based on the integration of two well established NBS, basically, the structure of modular **LWs**, to support filter medias, water and plants, which are the essential elements of **CWs** for treating wastewaters.

Moreover, the WETWALL design concept brings an innovative application of CE principles (reuse, recycle and reduce), mainly by encouraging the reuse of waste and/or by products as filtering substrates. Indeed, as previously discussed, there is the possibility of using recycled materials for the construction of the modules structure. However, as this topic was not in the scope of the thesis, and thus, further research is recommended, mainly due to its important role regarding the thermal performance at real scale. In addition, the WETWALL design concept bring a conceptual analysis of INPUTS and OUTPUTS flow that can be helpful to detect potential loop actions, to facilitate ecosystem services and thus to “close the loop” in a sustainable and eco-friendly way. More details about the conceptual analysis can be seen in the first article of the thesis and in section 5.4.

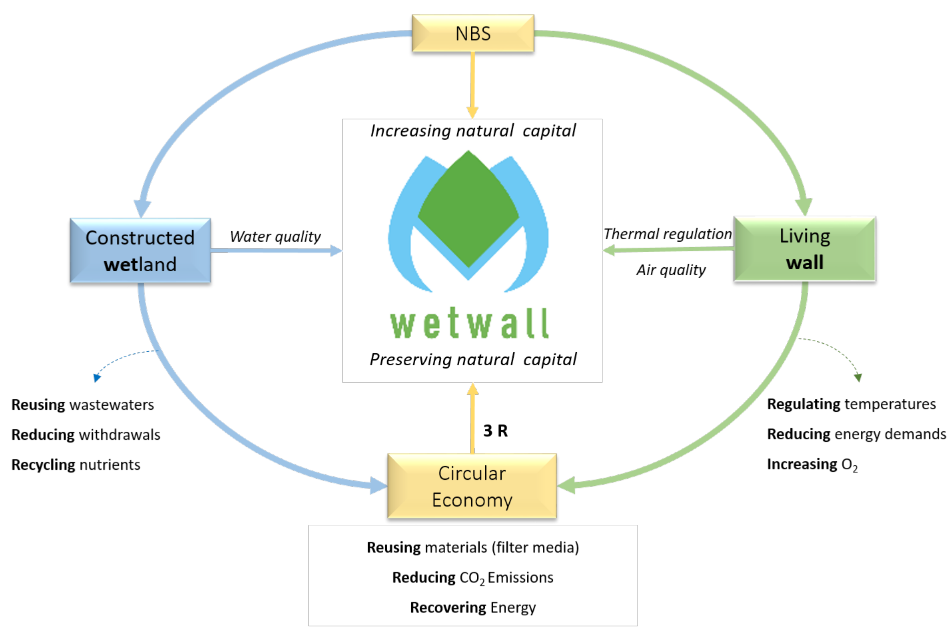


Figure 5 The main technical and principles of the WETWALL design concept.

5.2 Why modular Living walls?

Even though, all VGs systems have the same essential elements (water, plants and substrate) as CWS, LWs have greater potential to incorporate the removal process occurring in CWS when compared to Green walls. Basically, modular LWs is the only typology that allows the interaction between water, plants and substrate, in the role facade (vertical area), resulting in a bigger treatment area when compared with GW that have a limited area for interaction. In contrast when GW (direct/indirect) are implemented, the substrate and the water are allocated just in the bottom of the facade, reducing significantly the treatment area.

Despite plant uptake (bioaccumulation), all removal processes are intrinsically related to the chemical and physical properties of the substrate which can directly favour adsorption and precipitation process and indirectly provide suitable conditions for biofilm growth and thus promote microorganism mediated degradation and (nitrification–denitrification). Therefore, as bigger the area where substrate, water and plants are interacting as higher the efficiency of VGs treating wastewaters.

In regards to thermal performance, LWs seem to be more adaptive to different climates and seasons (summer and winter) than other VGs systems. According to the review performed by (Charoenkit and Yiemwattana, 2016), in the last 10 years, several researches have been highlighting the great potential of LWs at regulating temperatures and thus reducing cooling or heating demands in different climate zones. Indeed, LWs when compared to Green walls, can achieve greater reduction of energy consume for both heating and cooling (Ottellé et al., 2011).

This adaptive capacity of LWs to different seasons and climates might be related to the presence of multiple insulation layers (plants, water, substrate, structure materials) which itself increases thermal resistance and as well to a greater evaporative area where the heat is dissipated through the loss of water by transpiration and evaporation from substrate and plants (Charoenkit and Yiemwattana, 2016). While, Green walls only present one insulation layer (plants), LWs can have multiple layers mainly composed by materials used to build the structure, the water passing through the structure, substrate, plants and for instance air layer, when ventilation gaps are used.

(Perini et al., 2011a) compared thermal performances of LWs and Green walls, during summer. Considering averaged results, LWs showed the lowest external surface temperature

(7.1 ºC) in comparison with direct and indirect GREEN WALLS, being the difference approximately 2.5 ºC. According to the authors the greater thermal behaviour of LWs at cooling down external surface temperatures was attributed to the air insulation layer (air cavity), thermal resistance of material (structure and substrate) and the reduction of wind speed due to foliage coverage.

However, improving thermal performances of VGs during winter and at cold climates can be challenging. In this regard, LWs seem to be more flexible than GREEN WALLS which regards adaptation to colder climates. (Ottellé et al., 2011) showed that the heating benefits provided by LWs are more than three times the direct and indirect greening system, which may be associated to insulation properties of the materials involved. Moreover, several factors can be optimized to improve thermal performance of LWs, since all the components (Water, plants and substrate) are covering the role façade, while for Green walls mainly the plants can play a role in this regard. In LWs, the thermal properties of structure materials can influence solar interception, plant and substrate features can affect directly the evaporation/evapotranspiration and shadow effects as well as solar radiation interception and the presence or absence of air cavities can affect the wind speed and thus the properties of the air insulation layer. For instance, the potential of LWs at being more adaptive to winter and cold climate when compared to GW can be attributed to the possibility of playing with those factors.

According to (Carlos, 2015) the air cavity between LWs and building's façade can reduce wall surface moisture and thus prevents the ice dams during winter. (Tudiwer and Korjenic, 2017) studied the thermal performance of LWs with a ventilation gap (air cavity) between the modules and the building façade. The studies were conducted during winter and the LWs were facing south orientation. Surface temperature of bare walls tended to warm up and cooling down fast, being colder than behind LWs for the most of time. During cold days, both external wall surface and air temperatures, were higher for LWs than for bare walls. Even, during days with higher sun radiation (warmer winter days) the air temperature was higher behind the LWs, than in bare walls surface. The author concluded that the thermal resistance depends on the construction of the module and ventilation gap.

In addition, LWs goes along with a great variety of plants (Perini et al., 2011b) when compared with Green walls. The transmittance, absorption and reflectance of solar radiation and morphological features such leaf area index will vary across species (Charoenkit and Yiemwattana, 2016). The plant morphology can affect foliage coverage and thus solar radiation interception and evaporation rates which can lead to higher or lower evaporative cooling.

In regards to implementation and maintenance costs, LWs are more expansive than Green walls, due to **higher demands of water and nutrients and the requirement of complex design and structure materials** (Perini et al., 2011b). Considering plants and materials, the implementation of direct Green walls system (climber plants) and indirect Green walls (plants and supporting guides), can cost respectively, 30 to 45 € m^{-2} and 40 to 75 € m^{-2} (Perini et al., 2011b). The cost of LWs system can vary from 400 to 1200 € m^{-2}, mainly depending on the vertical design typology, structure material and substrate, being the cheapest and more expansive, respectively, planter box made of HDPE and LWs system based on foam substrate and felt layers (Perini et al., 2011b).

However, the LWs implementation and maintenance cost can be overcome. For example, in the early stage of designing a new building, the modular LWs can replace the insulation out layer normally used (bare wall), and thus compensating part of the implementation cost. Indeed, the potential of LWS at reducing heat and cooling demands can compensate implementation and maintenance costs. Although studies in this field are strongly recommended in order to facilitate the acceptance worldwide.

Moreover, by implementing the WETWALL design concept, the limitations regarding implementation and maintenance costs can be mitigated, basically in three ways. First, by encouraging the use of recycled materials to build LWs modules structure. Second, by promoting the reuse of by-products and/or waste materials from local production chains as filtering substrates. Both initiatives can reduce costs related to the implementation of LWs systems. Third, by reusing and recovering water and nutrients from wastewater, fact which reduces demands for water and fertilizer and thus minimize costs related to maintenance of such systems.

5.3 The process of designing the Hybrid module.

Our first design of the WETWALL treatment were based on a simple modular continuous water flow (Figure 6). The design was mainly conceptual to illustrate a modular structure able to support the essential elements of the treatment (plants, substrate and water) and as well allow a continuous flow of water.

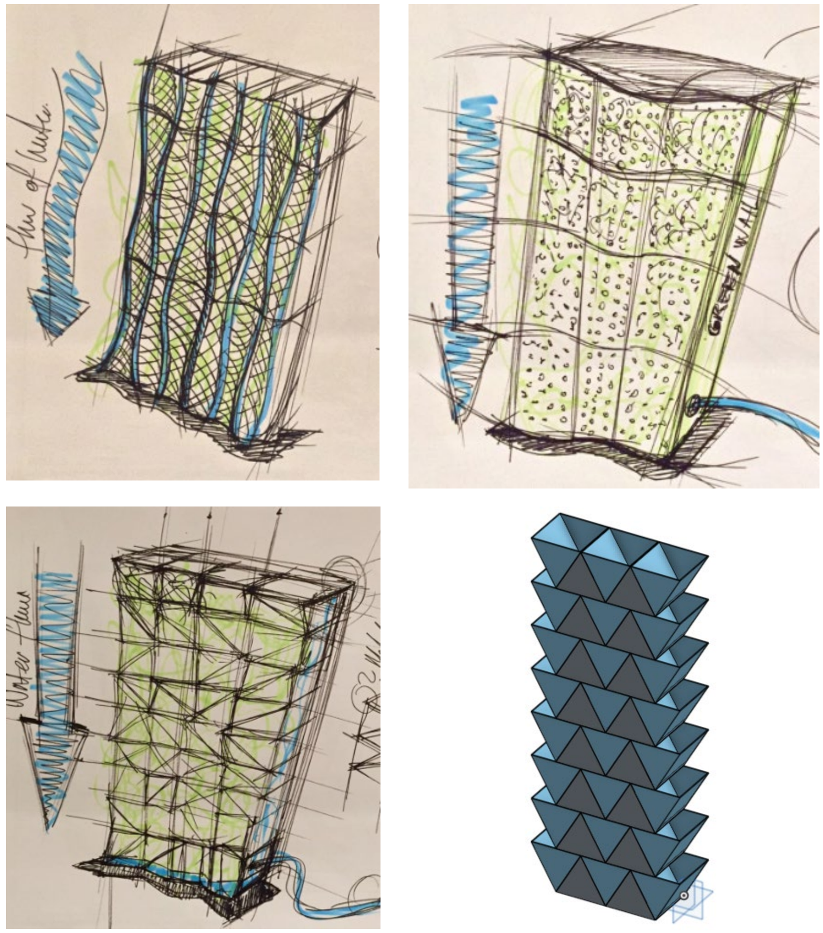


Figure 6 The WETWALL module design. The conceptual modular continuous water flow. (Source: collaboration between Joana Castellar and volunteer and graphic designer Eduardo).

After the initial design, a second evolution was developed, addressing the theme of Do It Yourself (DIY). Cities all over the worlds have been experiencing the rise of DIY urbanism initiatives focused on promoting people engagement, regarding a sustainable and participatory urbanism (Klerk et al., 2013; Sawhney et al., 2015). Therefore, at this stage the WETWALL module design was focused on facilitating the acceptance and participation from all the community members and different stakeholders. Main idea was to develop a simple and replicable design and to encourage the reuse of materials, easily available, such as plastic bottles, wood and cork board (Figure 7).

Figure 7 The WETWALL module design. The integration of Do it yourself approach (Source: collaboration between Joana Castellar and volunteer and graphic designer Eduardo).

Adding DIY approach into the design process enhance the participation from the community, and thus, further acceptance. However, as the WETWALL concept is focused on developing an urban wastewater treatment, such participation was restricted, due to healthy security issues. Therefore, the idea of integrating DIY approach into the WETWALL design concept was declined.

Moving forward, the WETWALL design concept was focused on the development of an innovative hybrid flow in order to enhance the performance of LWs treating urban wastewaters (GWs and HWs). GWs and HWs, can be very different form each other mainly which regards the concentration of N, phosphorus and organic matter. Besides the contaminants loads, also can vary according to the costumer's habits and farmer's practices. HWs are known by having high concentrations of nitrates and low organic matter load (Park et al., 2008). In contrast, the main concern when treating GWs is to remove organic matter, ammonium and phosphorus, due to its high concentrations and thus the potential to cause several environmental hazards.

The concentration of NO_3-N in HWs and GWs can get up to, respectively, 300 mg L^{-1} (Park et al., 2008; Park et al., 2009; Park et al., 2015; Gagnon et al., 2010) and 7 mg L^{-1} (Eriksson et al., 2002). In contrast, the amount of NH_4^+-N seems to be similar for both waters varying from 17-25 mg L^{-1} (Gagnon et al., 2010; Eriksson et al., 2002). On the other hand, the concentration of BOD can reach over than 1000 mg L^{-1} in GWs (Eriksson et al., 2002; Ghaitidak and Yadav, 2013) while can be around 12 mg L^{-1} for HWs (Park et al., 2015) or sometimes the concentration can even be negligible (Huett et al., 2005). In addition, GWs can have approximately 3 times more PO_4-P (highest [PO_4-P] = 170 mg L^{-1} (Eriksson et al., 2002)) than HW (highest [PO_4-P] = 60 mg L^{-1} (Gagnon et al., 2010)).

In this regard, the innovative WETWALL hybrid flow design aims to optimize the recovery of nutrients (N and P) and the reduction of organic load from urban wastewaters, such as wastewaters from household (GW) and from urban agriculture (HWs). Indeed, the hybrid flow brings the possibility of adapting the WETWAL design concept, not just to different types of urban wastewaters, but as well to different loads of contaminants.

The WETWALL modular hybrid flow is inspired on the design and premises of hybrid CWs. The hybrid concept mainly leans on combining different types of CWs in order to enhance the removal of contaminants from wastewaters (Kadlec and Wallace, 2000). The hybrid designs seem to be very adaptive since it has been used to treat different types of effluent such as from septic tank effluent (Li-hua et al., 2006), rural wastewater (Kraiem et al., 2019), sewage wastewater (Bang et al., 2019). In addition, several researches have shown the great potential of hybrid CWs treating GWs (Uddin et al., 2016; Abdel-Shafy and Al-Sulaiman, 2014; Abdel-Shafy et al., 2013). Results of (Park et al., 2015) suggest that a hybrid CWs (HF-HF) can be also used to enhance the removal of N from HW containing high nitrate and low organic carbon. However, there is not much information in literature about the performance of hybrid CWs treating wastewaters discharged from greenhouses (HWs). In general, the studies are focused on the performance of subsurface HF (Abbassi et al., 2011; Gagnon et al., 2010) or subsurface VF (Abbassi et al., 2011) separately.

The most applied hybrid design is based on the combination of sub surface vertical (VF) and horizontal (HF) sub surface flow (for more info about each, VF and HF, please see section 3.2.1) (Bang et al., 2019; Kadlec and Wallace, 2000; Vymazal, 2013). This design is mainly focused on enhancing total N removal, due to individual limitations of each system (VF and HF).

Usually, in HF the nitrification is limited and denitrification is facilitated, due to the anoxic conditions favoured (Kadlec and Wallace, 2000). In contrast, in VF the ammonia-N can be removed by nitrification while denitrification process is restricted, both because of the high oxygenation in the filter bed (Vymazal, 2007). Therefore, combining both systems seem to be a rational way to enhance the removal of total N (Kraiem et al., 2019). In this regard, hybrid systems based on the sequence VF-HF, are designed to enhance the removal of BOD and to facilitate the conversion of ammonia into Nitrate (nitrification) during the first stage (VF), followed by the conversion of nitrates into N2 (HF-denitrification), thus, completing the N cycle and enhancing the total N removal (Vymazal, 2007; Kadlec and Wallace, 2000; Vymazal, 2013; Bang et al., 2019). According to the review made by (Vymazal, 2013) hybrid CWs based on VF-HF sequence were the most efficient at removing NH_4-N and in general hybrid systems are more efficient at reducing total N in the effluent in comparison with single VF or HF design.

Therefore, the design of the WETWALL hybrid flow was focused on developing a module based on the sequence VF-HF (Figure 8 A and B). The VF is separated in several small cylindrical yellow columns in parallel, almost like individual vessels. The HF has cylindrical shape (grey) and its orientation is in parallel with the soil. The water goes through the VF and goes straight to the HF (Figure 8 - A).

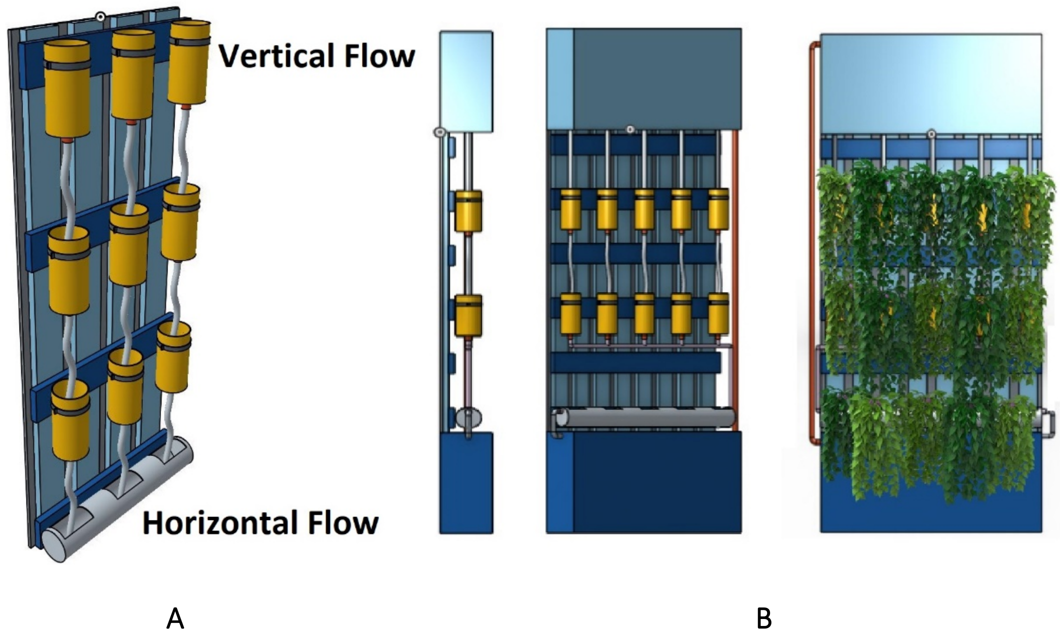


Figure 8 The first insights of the WETWALL **Hybrid** module design (VF-HF) (Source: collaboration between Joana Castellar and volunteer and graphic designer Eduardo).

In Figure 8 – B, some hydraulic improvements can be seen, mainly regarding the water collection and recirculation in the module. There are two deposits (blue boxes), one upper and one down. Basically, the wastewater is collected in the lower reservoir, pumped up (red pipe) and the irrigation is by gravity in order to reduce energy spends. In contrast to the initial design (Figure 8 – A), the water from all VF columns are collected and directed to the Inlet of HF (Figure 8 - B). The water passes through HF almost in a horizontal path from the left to the right till the HF outlet and goes to the lower deposit. The VF plants were allocated in the top of the individual vessels (yellow columns). The main structure was inspired in wood pallets and the VF and HF were fixed by clamps.

Figure 9 brings the first attempt to develop a prototype module focused on the WETWALL hybrid flow (VF-HF). The hydraulics were designed to have 3 replicates of the hybrid flow (VF-HF) in the same module, that's why there were 3 upper water reservoir and 3 lower water reservoirs, instead of just one.

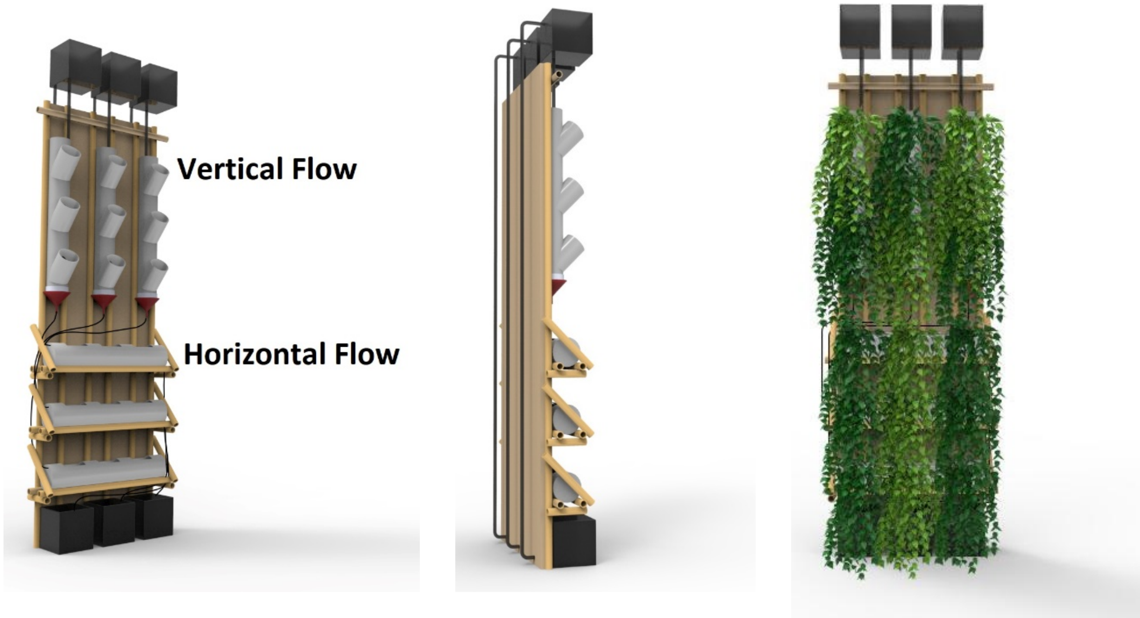
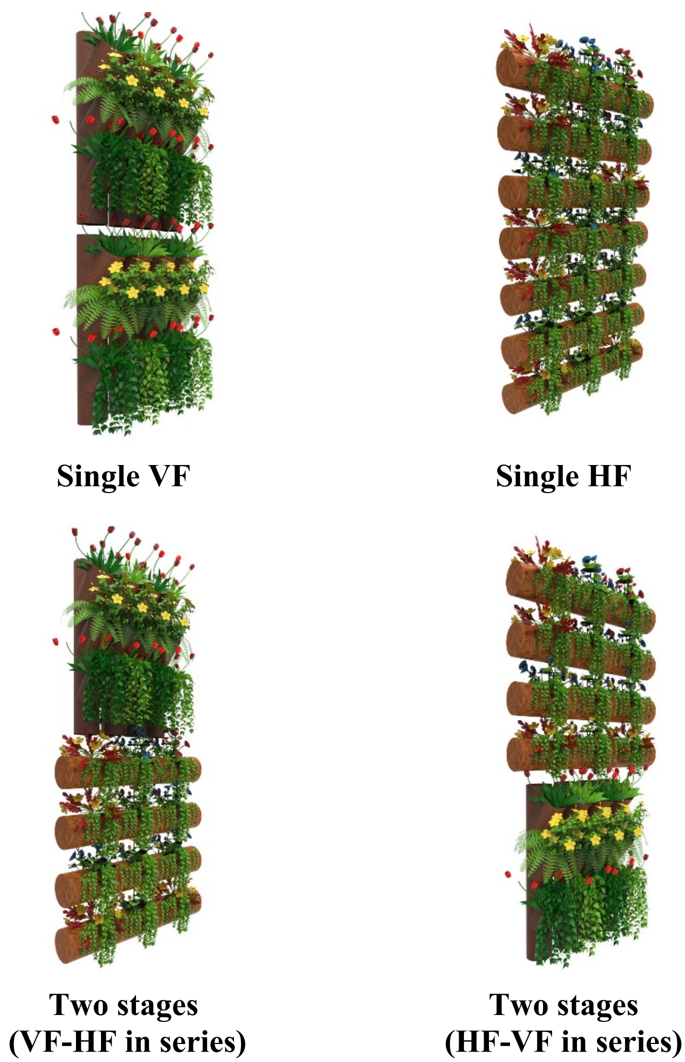


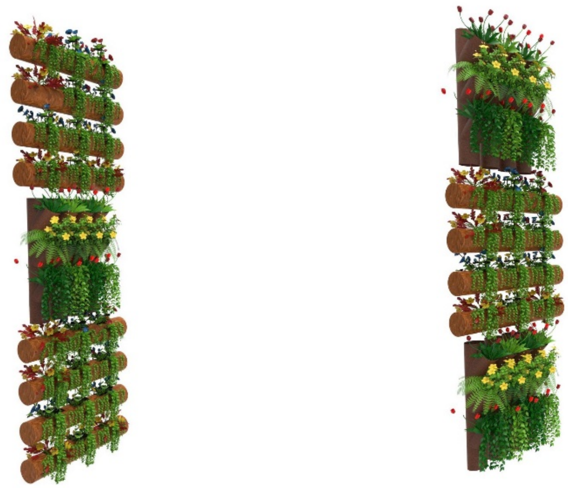
Figure 9 The second WETWALL **Hybrid** module design (VF-HF). Prototype insights. (Source: collaboration between Joana Castellar and volunteer Bart van der Kamp)

Moreover, the design of VF structure was improved. The previously idea of individual vessels was refused in order to improve treatment performance at removing contaminants mainly by increasing the treatment area. On the next improved design, the vertical columns were longer than before. Different from the previously design (Figure 8), the support for the plants were placed all over the treatment column (45º pipes) in order to favour pollutant uptake from plants, biofilm development and aeration of VF. More details on the development of the individual structures of WETWALL VF and HF is presented in the first article of the thesis. In addition, the design of the main structure was inspired in materials such as, *arundo donax* and cork insulation boards. However, although materials are not the focus of this thesis, is important to highlight that organic materials will require special treatments such as water proof resin, in order to guarantee resistance against weathering.

However, having a limited and non-versatile one configuration (VF-HF) did not seem the best decision regarding its adaptation to different contaminants loads, although it is probably the most efficient system, according to literature. Therefore, concerns about the adaptation of the WETWALL concept Hybrid (VF-HF) raised together with new insight. An alternative, for effluents with high concentrations of nitrates and low organic carbon such as HWs, could be a design able to work as well as a two stage sequence HF-VF. During the first stage, the denitrification takes place followed by nitrification and oxidation of organic matter in the second stage (VF) (Vymazal, 2007; Vymazal, 2013). Therefore, limitations on denitrification process due to lack of organic carbon can be reduced. For instance, the concentration of nitrates can increase after VF, due to nitrification. In this case the water will need to return to HF or multi stage design such as HF-VF-HF and VF-HF-VF have been proposed to enhance treatment performances (Vymazal, 2013).

Therefore, the WETWALL design concept took another direction based on the prerogative that adaptation, versatility and flexibility are key factors for ensuring treatment efficiency. The previous idea of a hybrid module (VF-HF) was declined (Figures 8 and 9), being the main concern of the WETWALL design concept to allow single and combined treatments (Figure 10).





Three stages **Three stages**
VF-HF-VF **HF-VF-HF**

Figure 10. The WETWALL hybrid concept. Possible different treatment configurations.

When talking about CWs, the main limitation of implementing **Hybrid systems** is due to the high treatment area demand in comparison to single designs. Moreover, while the implementation of similar treatments, such as CWs, demands large areas, the blank spaces of vertical facades are limited. This is not necessarily a true statement when talking about LWs. The hybrid designs can be a key factor when optimizing the treatment area since combining different stages of treatment (Figure 10), besides not increasing the treatment area also have potential to enhance treatment efficiency by using the same area as a single design.

Next evolution on the design was focused on developing both, VF and HF modules separately in order to facilitate maintenance and the treatment of different load of contaminants and reduce implementation costs. The idea is that the module structure can work as an insulation layer, in new buildings or as ventilated wall in case of existing buildings, and thus, module won't need to be removed and the same module can be used for both VF and HF. Indeed, the treatment structures from VF or HF, can be allocated and reallocated easily inside the module, since they are fixed with clamps into the module as well as all the VF and HF structures were hydraulic independent from each other, and thus maintenance is facilitated. Moreover, different modules can be combined according to the aims of the treatment, in other words, according to the composition of the wastewaters. The modules can be seen in Figure 11.

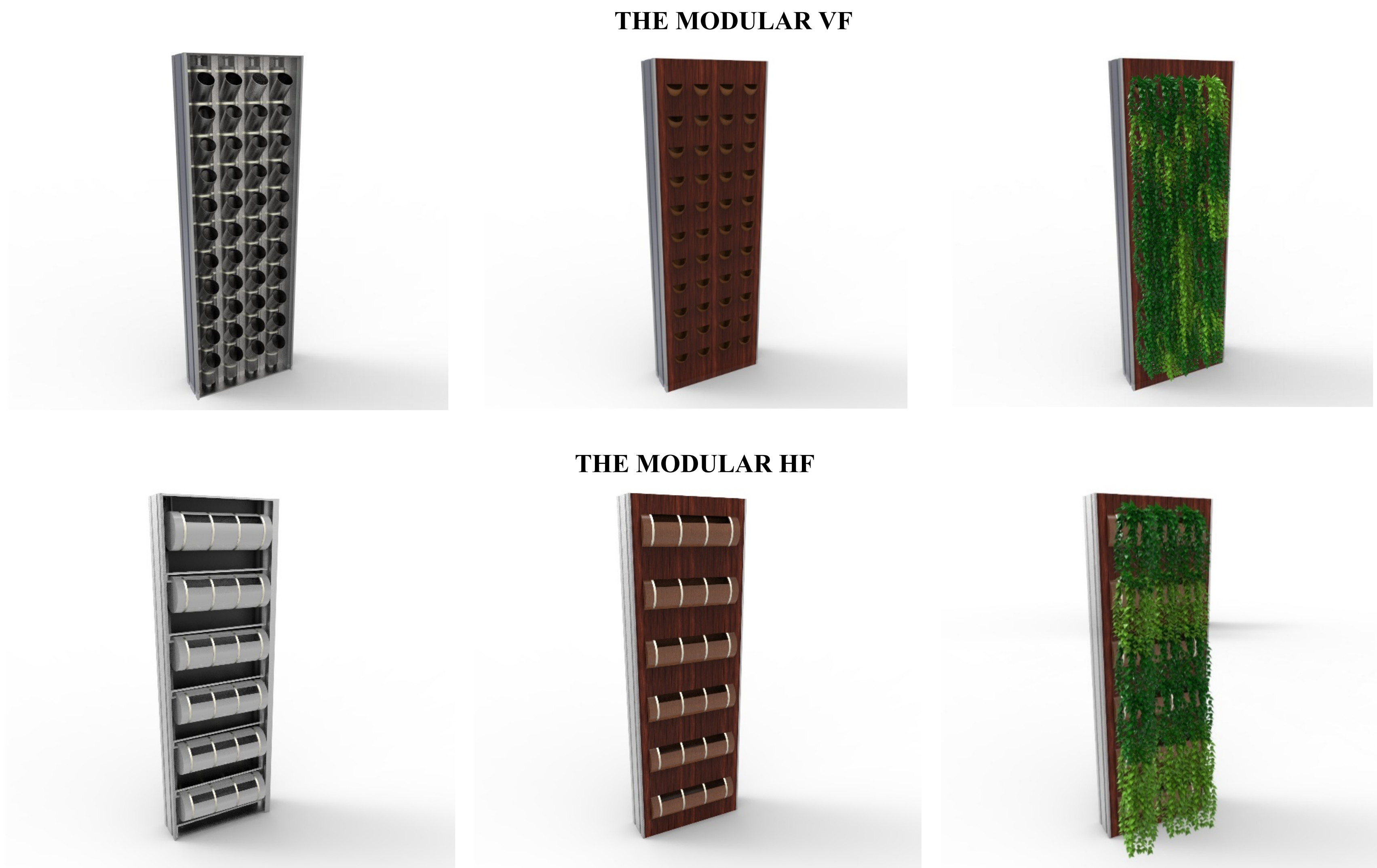


Figure 11 The **WETWALL hybrid concept.** Individual modules for each type of treatment (VF and HF)

5.4 Circular economy and Nature-Based Solutions design: The conceptual analysis

The WETWALL design concept has the potential to connect different production chains mainly by encouraging the reuse by-products as filter medias, recycling materials for module structure and recovering nutrients and water from wastewaters, for further reuses._This concept can promote natural capital preservation and the establishment of resilient and self-sustaining technology in the scope of urban wastewaters treatment. In the scope of LWs design, the integration of CE into the design process can be addressed by connecting the WETWALL design concept with urban and natural environment. For this conceptual analysis it is assumed that natural environment is all natural capital that has not changed by anthropogenic pressures. This connection is fomented mainly by closing the loop of materials, water and nutrients.

Regarding closing the water loop, the WETWALL design concept suggests the "in situ" treatment and reuse of wastewaters, promoting a sustainable recycling of water and nutrients (N and P) and the decentralization of water treatment. At the same time that the contaminants will be transformed and stored in the system (uptake of plants, adsorption of substrates and microbiological degradation), the water treated can be reused in accordance with water quality standards where it is implemented.

Regarding to closing the material cycles, the WETWALL design concept proposes the reuse of waste or by-products from local production chains as potential filtering substrate. The reuse of local waste materials can minimize transport emissions, boots local economy and mitigate the environmental impacts, since minimize the extraction of non-renewable raw materials (Torgal and Jalali, 2011). Several works have been showing the great potential of reusing local products as filtering substrate, such as agave fibber by-product (Vigueras-Cortés et al., 2013), industrial waste materials (Hua et al., 2015) CAAC (Renman and Renman, 2012), cement-based materials (Wang et al., 2014) or wood chips (Sosa-Hernández et al., 2016). In the scope of LWs coir and rock wool (Prodanovic et al., 2017), coconut shell (Fabio Masi et al., 2016) recycled glass beads (Wolcott et al., 2016) have been successfully tested.

In this regard, the WETWALL design concept suggests a 2 times reuse approach, in order to close the nutrient and material loop. First by-products were reused as filtering substrates in order to promote the recovery and further reuse of nutrients (second reuse).

The substrates can stock nutrients removed from the wastewater and be reused as fertilizer for local urban crops, creating short distances between the provider (WETWALL) and consumers (local agriculture). Recovering these nutrients and reusing them instead of keep producing, can be a sustainable way to reduce the impacts caused by the production of chemical fertilizers (Haber-bosh process) and by their accumulation in the environment. Moreover, giving a new application to the system outputs, besides reducing the economic costs by subsidising maintenance costs also may encourage technology acceptance. However, it should be considered that depending on the wastewater treated, the presence of pollutants such as pesticides, heavy metals and pathogens, could represent a challenge on reusing this material as fertilizer.

Another approach regarding closing the material loop is the recycling or reusing material to build the LWs structure (the module from VF and HF structures). Reusing or recycling proper materials can help to reduce the demand for raw materials, closing the cycle of materials and reducing embodied energy and CO_2. Green systems (roofs and walls) should consider materials with less incorporated energy and CO2 emissions (Manso et al., 2013). For example, recycling/reusing waste materials such as bamboo panels, C&D (construction and demolition) or masonry stub foundation, can significantly contribute in reducing energy consumption and CO_2 emission (Jethoo et al., 2012). In the scope of sustainable design of LWs, the use of alternative materials such as cork board, recycled polyethylene and recycled PET bottles have been proposed (Manso et al., 2013; Natarajan et al., 2015; Azkorra et al., 2015).

However, besides recycling and reusing materials, other parameters should be taking into account when selecting material for LWs focused on enhancing thermal and energy performances and reducing environmental hazard. The selection of materials should also take into account simplicity to maintain and install, high durability (resistant to weathering), nontoxicity, low energy and CO_2 emissions embodied, good thermal features (Torgal and Jalali, 2011; Manso et al., 2013). Safety features also need to be considered, such as the materials resistance to fire, although safety requirements will vary according to local legislation. it is strongly recommended further studies focused on improving the selection of materials for LWs structures, due to its important role regarding thermal performance and closing the loop of materials and energy.

The WETWALL design concept has a great potential to transform pollutant gases present in the atmosphere and heat and cold effects in urban environment into ecosystems services such as air quality and thermal comfort (previously discussed in section 3.2.2).

Moreover, considering future threats related to the exponential increment of food demand, scarcity of local resources such as water and land, and climate change, producing food in VGs can be a sustainable alternative. Therefore, the use of agricultural species can be an option for WETWALL design.

However, restrictions and legislation related to the crops irrigation with wastewater must be considered. Indeed, logistic and costs regarding cropping and harvesting can be challenging when implementing the WETWALL design concept for food production. A diagram approaching the conceptual analysis discussed in this section is presented in Figure 12. More information about the conceptual analysis is presented in the first article of the thesis.

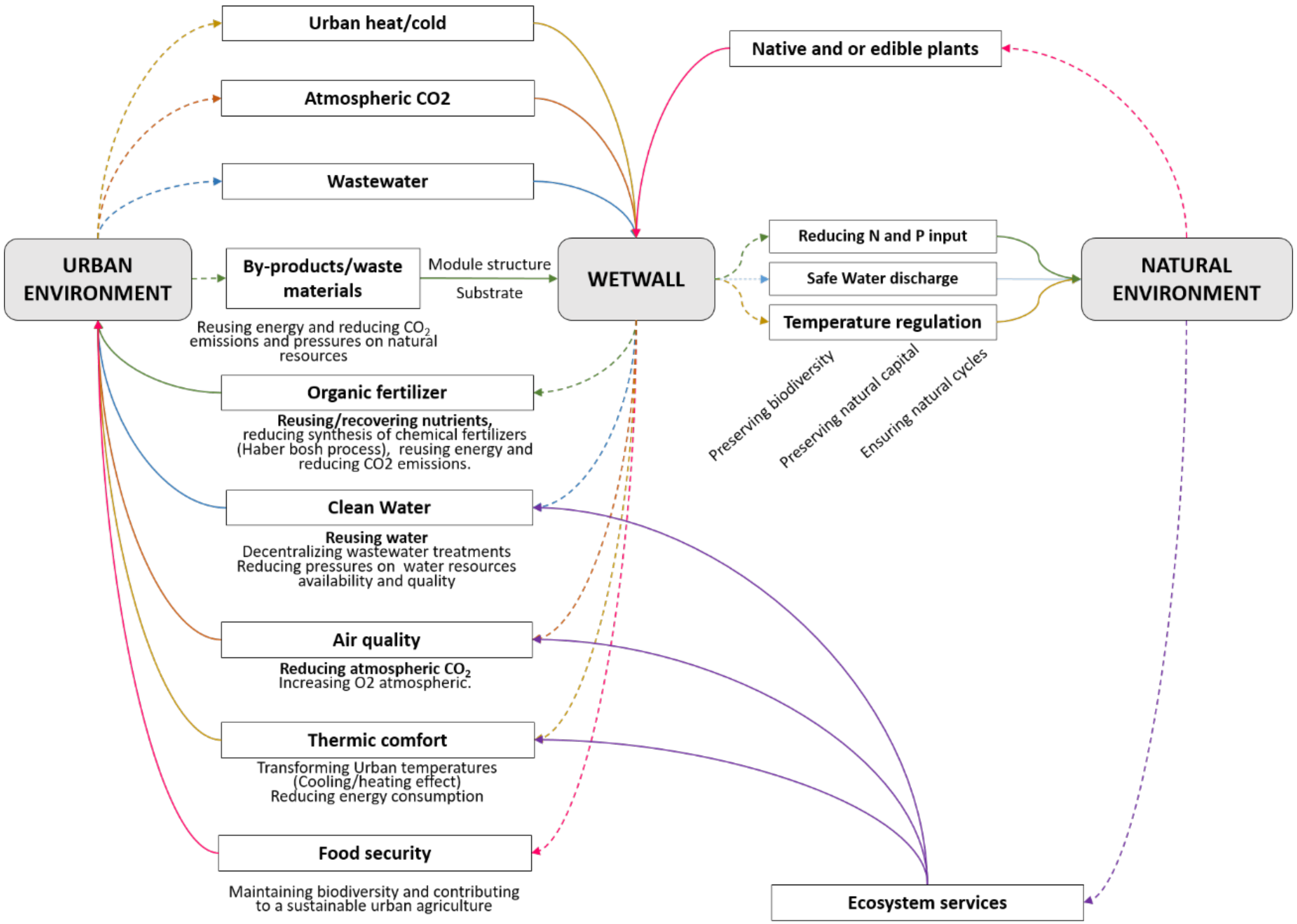


Figure 12 The WETWAL design concept. The conceptual analysis of INPUTS and OUTPUTS.

Chapter 6 First Article

"WETWALL" — an innovative design concept for the treatment of wastewater at an urban scale.

J.A.C. Castellar et al. / Desalination and Water Treatment 109 (2018) 205–220

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"WETWALL" AN INNOVATIVE DESIGN CONCEPT FOR THE TREATMENT OF WASTEWATER AT AN URBAN SCALE

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ABSTRACT

Rising temperatures, increasing food demand and scarcity of water and land resources highlight the importance of promoting the sustainable expansion of agriculture to our urban environment, while preserving water resources. Treating urban wastewaters, such as greywater and hydroponic wastewater, may represent a strategic point for the implementation of urban farming, ensuring food security, reducing pressures on water resources and promoting climate change mitigation. The WETWALL design concept proposes a unique eco-technology for secondary wastewater treatment at an urban scale, which brings the novelty of a living wall hybrid flow. This concept is based on the integration of two established Nature-based solutions (NBS)/ecomimetic designs (ED): constructed wetland and a modular living wall. First presented is an overview about the state of art in the scope of living walls treating wastewater, in order to identify the main design aspects related to the performance of such systems, which mainly concerns the removal of nitrates and phosphates. Secondly, the WETWALL design concept is presented. A scheme regarding the selection of the main components, such as plants and substrate, is proposed, and potential structure developments and operation strategies are discussed. In addition, considering the scope of integrating the circular economy with the design process, potential interactions between this technology and the urban environment are discussed. The main goal of this article is to substantiate the potential of the WETWALL design concept as an innovative wastewater treatment at an urban scale.

Key-words: wastewater, circular economy, living wall, constructed wetland, Nature-based solutions (NBS).

1. BACKGROUND

The development of modern society has led to an exponential urbanization and exploitation of natural capital, causing significant pressures on the availability and quality of natural resources, especially water [1]. Urbanization has a significant impact on the quality of fresh water, and the reduction of urban groundwater supplies. According to Ren et al. (2003) [2], "*rapid urbanization corresponds with rapid degradation of water quality*". In this regard, greywaters (water from several uses such as toilet flushing, batch, hand washing, kitchen sinks, among others), as well as representing about one third of domestic wastewaters, are also considered an important source of pollution, containing high levels of several contaminants, especially, phosphorus and N [3-4].

On the other hand, considering future threats related to the exponential increment of food demand, scarcity of local resources such as water and land, and climate change, the adoption of soilless agriculture has been proposed as a sustainable alternative to produce food at an urban scale [5-9]. According to Komisar et al. (2009) [10], "*Reconnecting cities to their food systems is now emerging as one of the core components of the design of more sustainable urban settlements*". In this regard, hydroponic systems can be applied in buildings, which can improve supply chains while reducing transport distance and time of storage [8]. However, several authors have shown that soilless crop production can represent an important source of non-point pollution, since the wastewater of these systems have a high concentration of nitrates and phosphorus and is normally drained and discharged to the environment [11-14].

According to Rockström et al. (2009) [15], humanity has already transgressed planetary boundaries in relation to changes on the global N cycle. The inputs of reactive N, mainly caused by the production of chemical fertilizers (chemical fixation - Haber-Bosch process), are greater than the environmental capacity to remove reactive N though the denitrification process. This leads to an accumulation of nitrates (NO_3^-) in water and nitrous oxide in the air (N_2O), a process called the N cascade effect [15-18]. On the other hand, anthropogenic input of phosphorus into the environment is mainly caused by agriculture through the application of chemical fertilizers, households and industries in the form of detergents [19]. The accumulation of reactive N and phosphorus may cause several environmental damages such as pollution of groundwater, eutrophication of surface waters, decrease of biodiversity and changes in terrestrial, aquatic and marine systems [15][19-20].

Therefore, technologies, which can promote the treatment and reuse of urban wastewater such as greywater and effluents from soilless crop, may play an important role for the preservation of water resources, mitigation of climate change and promoting a sustainable development of agriculture into the urban environment. According to European Environment Agency (2012) [21] and Malik et al. (2015) [22], treating and promoting the safe reuse of wastewater on a global scale represents a crucial strategy to ensure an efficient use of water resources and decreasing the competition with drinking water supply.

In this scope, ecomimetic designs (ED) and Nature-based solution (NBS) have been considered promising strategies for climate change mitigation. ED and NBS, replicates features of natural systems in order to integrate ecosystem services into the human environment, and thus promote an efficient use of natural resources, a human well-being and a socially inclusive green growth [23-24]. According to Blok and Gremmen (2016) [25], "*By using the same design principles as natural entities and systems, and by modelling our technological design on natural principles, biomimicry adheres to a bio inclusive ethics that enables us to resituate our technological design within the ecological limits of the biosphere*."

Regarding this, constructed wetlands (CWs), a technology based on the replication of biological, chemical and physical processes occurring in natural wetlands have been used throughout the world to treat several types of wastewater. This technology has been efficiently applied to remove nutrients and microorganisms from grey waters [3][26] and hydroponic nutrient rich wastewaters [12-13]. On the other hand, living walls as part of an innovative green infrastructure could provide multiple functions at an urban scale, related to climate change mitigation. Among these functions are the reduction of environment temperatures and the urban heat island effect [27], energy savings [28-29] and improvement of carbon sequestration [30-31].

Moreover, in the face of future threats such as the reduction of land availability and the exponential growth of expected population, NBS, which can take advantage of vertical spaces, can represent a sustainable strategy in the scope of the decentralization of wastewater treatments and climate change mitigation. In addition, several authors have been showing that the implementation of natural ecosystems in vertical spaces of urban environments could represent an important factor in the context of urban resilience [32-34]. Therefore, unlike CWs, which demands great land area, the living walls can be implemented in empty spaces of building walls and facades and can undertake the function of wastewater treatment, improve air quality, to help the mitigation of climate change.

It is well known that microbial degradation, adsorption, plant uptake, sedimentation and precipitation are among the main processes responsible for pollutants removal in CW [35-36]. These processes can be intrinsically related to the substrate by favouring adsorption, providing suitable conditions for biofilm growth to promote microorganism-mediated degradation (nitrification-denitrification) and precipitation of phosphorus (Ca, Mg, Fe and Al). Additionally, the presence of plants can enhance nutrient uptake and the water flow can affect the oxygen conditions in the structures which consequently influences the microbial degradation and precipitation processes. Therefore, when considering the essential elements of constructed wetlands, such as the interaction among substrate, plants, biofilm and water flow also take a place in living walls, it is possible to conclude that the WETWALL design concept could have an interesting role and perform as a wastewater treatment technology as well. In addition, treatment of wastewater by green walls may overcome the biggest limitation related to the implementation of this type of system, which is the high water consumption.

This article presents a theoretical discussion on the innovation presented by the WETWALL design model, as a sustainable building concept to treat urban wastewater. Therefore, this paper presents an overview about living walls treating wastewater in order to determine the main design parameters and its relation with system performance, especially regarding the removal of N and phosphorus. Secondly, the WETWALL design concept is presented in four parts. First, a selection of plant species and substrates to be used. Second, the structure developments are discussed in order to develop a living wall hybrid flow, based on the background of a constructed wetland hybrid flow. Third, operation strategies such as water recirculation and allocation of substrates in the structure. Fourth, to integrate circular economy into the design process, potential interactions between the WETWALL and the urban environment are presented and discussed. To the best of our knowledge, there is no information within the scientific literature about a design of a living wall hybrid flow to enhance the removal of N and phosphates from urban wastewater.

2. STATE OF THE ART

Modular living walls can be defined as "*elements with a specific dimension, which include the growing media where plants can grow. Each element is supported by a* *complementary structure or fixed directly on the vertical surface*" [37]. Modular living walls typology is an appropriate structure for wastewater treatment. The structure allows contact between roots, substrate and water, which are key conditions to provide pollutants removal through plant uptake, substrate adsorption and microbiological degradation. In addition, modular living walls are known as widespread system, mainly because of their easy maintenance, their adaptability to different facades, adaptation to different species and for being environmentally efficient in reducing energy demand, mainly by thermal insulation [37-40]. In this regard, all previous research on the scope of wastewater treatments used modular typology. However, the different studies present a wide variety of structures, substrates, plants and operational factors.

Most of the researchers are focused in living walls performance regarding the treatment of greywaters. There are few studies studying and validating the reuse of wastewater to irrigate Green walls [41] or even integrating Green walls with other treatment systems [42-43]. For example, Elmasry and Haggag (2011) [41] proposed recycling greywater at a school building, using this water as an irrigation source for Green walls. Cameron (2012) [42] proposed an integrated system combining a subsurface flow constructed wetland, living wall and green roof in order to treat greywater. However, no specific sampling was performed in order to assess the contribution of the living walls for the removal of contaminants in this system. Emeric (2009) [43] proposed an integrated household greywater system which combines one initial storage treatment, a living wall, and filter chambers. The living wall was responsible for 24 % of nitrate removal and 44 % of orthophosphate removal and the global efficiency on phosphorus removal reached 95 %.

Sakkas (2013) [44] proposed a living wall for the treatment of greywater based on the replication of a vertical subsurface flow constructed wetland. The living wall was composed by vertical sections (0.57 m) connected to each other. Each section was divided in a merging zone (0.07 m) which is the space for the plant growth, a root zone (0.30 m) filled with expanded clay aggregates and a drainage layer (0.20 m) filled up with foam glass gravel. No data about the practical validation of this system was presented related to pollutants removal. However, the author suggested that the proposed living wall could treat 0.105 m^3/d of domestic greywater on a facade of 4.2 m^2.

Even though the integrated system seems to be a promising alternative, it was decided to focus this overview on wastewater treatments based on living walls systems validated with practical experimentation. In this regard, it was noticed that a couple authors based the living wall design on taking references from similar biological wastewater treatments, such as intermittent biological filter [1], wetlands and storm biofilters [2]. Considering the lack of information in this field, the background provided by such references is important in order to establish the main parameters, which may be used for the improvement of the living wall design as wastewater treatment. On the other hand, a couple of authors focused the design on the development of a GW concept for the treatment of wastewater and tested variables such as filter media, plants and biofilm [3][4]. Furthermore, to understand the influence of design parameters on the removal of nitrates and phosphates and to determine patterns in this matter, the overview is presented in the next section.

2.1.Living walls as wastewater treatments

Svete (2012) [45] developed a system which is mainly based on the adaptation of an intermittent underground biological filter to become a vegetated wall structure for treating greywater. The biggest challenge was the reduction of surface area in comparison with conventional treatment, which can lead to a limitation on the removal of pollutants. Typical intermittent biological filters have larger surface area than filter depth, which is the opposite of the living wall structure, which has bigger filter depth than surface area. To overcome this limitation, the author, as a reference, used design parameters such as aeration and hydraulic retention time. The author design is mainly based on the hypothesis that enhancing the aeration and increasing the retention time may help overcome the issue of limited surface area. Hence, the design proposes the implementation of low volume doses and sequentially feeding, in order to increase retention time and to avoid saturated zones in the filter profile.

The module was filled with lightweight expanded clay aggregates and a drainage section on the bottom was implemented to promote effective drainage. The module was divided in 3 sections: Section A, containing substrates without contact with the atmosphere, enclosed in a plastic liner and plywood walls; Section B and C, where the substrate is in contact with the atmosphere, enclosed by a polyester/PVC geotextile grid and supported by a steel grid. Only section C had plants and all the sections received the same flow frequency and volume doses. Regarding total phosphorus (TP) and total nitrogen (TN) removal, no variations were observed between the sections A, B, C. In fact, Svete (2012) [45] suggests that the diffusion of oxygen from the atmosphere may not significantly influence the aeration of the system and consequently did not influence the nitrification process.

The results showed high removal of TP and TN, in comparison with the expected treatment performance for biological greywater filters in Norway, ranging in the sections respectively, between 69 % - 71 % and 31 % - 34 %. According to Svete (2012) [45] the high removal of TP may be associated to the adsorption capacity of the expanded clay. However, a pattern of nitrate accumulation at 1 m depth was also evident for all the sections. According to the author, "*this is most likely due to suppression of nitrification at the surface of the filter caused by high organic loading*". These results may also suggest that the structure design and operation factors, such as volume dose and frequency of application, lead to limited saturated conditions in the filter bed. This may have a reduced denitrification in the system, promoting the accumulation of nitrates and increasing the nitrification process among depth layers. In addition, the system showed high efficiency removing BOD_5 (95 % - 98 %) which perhaps limited the availability of organic carbon needed for denitrification. This lack of organic carbon availability also may be related to the fact that the filter media is not organic and the exudates of plants roots were not sufficient.

Fowdar et al. (2017) [46] used the background of wetlands and storm biological filters as a reference for the living wall design. The structure designed was mainly based on a planted vertical biological filter (Ø 240 mm columns) filled with substrates (washed sand, coarse sand and gravel), where the greywater percolates vertically. Moreover, Fowdar et al. (2017) [46] proposed a design which integrates a saturation zone in the bottom of the structure in order to improve the removal of nitrates by denitrification, a fact which was the biggest limitation of Svete (2012) [45] design, according to the results mentioned above. The saturation zone proposed by Fowdar et al. (2017) [46] was created by elevating the outlet pipe at 0.16 m and using panels in the bottom of the cylindrical structure, instead of an outlet pipe at 0.30 m and layers of washed sand with carbon, course sand and gravel, which is normally used for stormwater biological filters.

This publication is the first research, which combines different design parameters such as vegetation (climber and non-climbers), saturation zones (standard of stormwater bio filtration and novel design), inflow concentrations (standard and 2x standard) and operation factors such as loading rates (0.11 m/d and low 0.055m/d) and dose frequency (five times per week and a resting period of 2.5 weeks). In addition, the author made infiltration rate tests in order to access the hydraulic performance of the system.

The results showed high biochemical oxygen demand (BOD) removal (96 % - 99 %) for all experimental configurations, however, some treatments showed low removal of TN. For example, *Phragmitis* australis and *Strelitzia* reginae presented TN removal of 7 % and 23 %, respectively, lower than the non-vegetated treatment (control – 36 %). The lower performance of *P. australis* was related to the attachment of aphids. *S. reginae* showed lower development under the system conditions. This result may suggest that the removal by process not related to uptake, such as, adsorption and microbiological degradation are important in these systems. Moreover, plant health and adaptation to the system conditions may influence in its ability on up taking contaminants.

Additionally, it was observed that both species and the non-vegetated treatment showed an accumulation of NOx, suggesting that the denitrification was limited. The denitrification efficiency depends on presence of denitrifying bacteria, carbon availability and under anoxic conditions. In this sense, two aspects should be highlighted. Firstly, the only carbon source was provided by wastewater a fact which associated with a high removal of BOD may lead to a limited availability of organic carbon for denitrification. Secondly, the author suggests a preferential degradation of organic matter in the upper layers and low availability of organic carbon in the bottom-saturated layers where the denitrification is expected to happen. Therefore, the allocation of organic substrate in the saturated layer could help solve the lack of organic carbon required to complete the denitrification process.

The TP removal (%) was lower than TN removal (%), regardless of the configurations used, mainly due to the low capacity of sand on adsorbing phosphorus, a lower phosphorus than nitrogen plant uptake, the release of organic phosphorus from exudates and solid particles of roots and the fact that adsorption of phosphorus is usually temporary. Both, the saturated zone designed by Fowdar et al. (2017) [46] and the standard saturated zone showed good results at removing nitrogen and phosphorus. However, Fowdar et al. (2017) [46], concluded that the design with the novel saturated zone seemed to be more aerobic than the design with standard saturated zone, as the concentration of NH_4-N in the effluent was always lower in the novel design.

In relation to the system operation, some configurations using a low hydraulic loading rate increased TN and TP removal, which according to Fowdar et al. (2017) [46] indicates that increasing retention time promotes further processing of the nutrients. Moreover, ambient temperature influences the infiltration rates, being lower during colder months compared to warmer months. The author attributed this behaviour mainly to the effect of temperature on water viscosity. Moreover, the infiltration rates were also increased by the implementation of one rest period of 2.5 weeks, mainly because of the reduction of substrate moisture and the re-establishment of the macro-pores structure. According to Kadlec and Wallace (2009) [49] and Knowles (2011) [50], resting intervals between loading periods are necessary in order to control the accumulation of solids and to avoid clogging problems.

Masi et al. (2016) [47] proposed the use of a LWs typology for the treatment of greywater in a building. The design consists in 6 pots for each column and 12 pots in a row (12 x 6 pots matrix) planted with several vegetal species. The greywater collected from the building feeds the LWs though perforated pipes and the water flow is carried by gravity to the bottom, where it is collected and reused for garden irrigation. The author compared the influence of coconut and sand, both mixed with LECA (light expanded clay aggregates) on the removal of pollutants.

The LECA with coconut and LECA with sand treatments showed a NH_4^+-N removal of 19.4 % and 70 % respectively. However, a significant increase of Total Kjeldahl nitrogen was also observed in the effluent of coconut treatment, which was probably related to the release of organic nitrogen from the substrate. In addition, the retention time of LECA with coconut was approximately 3 times bigger than LECA with sand, fact which besides favouring the release of organic compounds also may increase saturation among layers, and limit nitrification. In the other hand, the sand treatment showed a higher removal of NH_4^+-N, fact which may be related to lower input of organic nitrogen, once the substrate is mineral, and the aerobic conditions favoured by the use of sand which has higher hydraulic conductivity than coconut. These results highlight the importance of considering the allocation of an appropriate substrate during the design process. In other words, if the main goal of the system is to increase the removal of NH_4^+-N, one alternative could be use just mineral substrates, design structures and operation strategies capable of improving the aeration of the system. No results on nitrates or phosphorus were discussed in this paper.

Wolcott et al. (2016) [48] proposes the design of a modular GW to treat wastewater from beverage manufacturers. The modules were made by aluminium panels (0.61 m × 0.61 m × 0.1 m). Each module was divided in 24 small cells (0.1 m × 0.15 m × 0.1 m) made by packets of fiberglass and filled with substrate. This author compared the performance on the following scenarios: substrate only (S), substrate with plants (S+P), substrate with biofilm (S+B) and substrate with plants and biofilm (S+P+B). The substrate used was recycled glass beads. The modules were continually fed with wastewater with the same flow rate in all scenarios resulting in a 354 m/d hydraulic loading rate (HLR). The HLR proposed by this author was much higher than Fowdar et al. (2017) [46] recommendation of 0.055 m/d and HLR used by Svete (2012) [45] which was 0.67 m/d. According to Wolcott et al. (2016) [48], the increment in the HLR could be achieved by treatment length increase, which could favourably affect detention time. However, no data validated this hypothesis.

The higher and lower removal on phosphorus was, for treatments with substrate (28 %) and treatment with substrate plants and biofilm (12 %), respectively. These results highlight that the removal of phosphorus was mainly related to substrate adsorption. Indeed, a strong limitation on phosphorus removal was directly associated with the development of biofilm due to the loss of specific surface for adsorption. The removal of TN after 24 hours varied between 25 % to 56 % for, S+P+B and S+B, respectively. According to the author, the plants up-take did not seem to play an important role in the removal of nitrogen for this experiment. No data about nitrates and ammonium concentrations were discussed.

2.2 Main research achievements

The previous results above highlight the importance of optimizing removal processes by i) selection of appropriate substrates as well its placement in the system, ii) sustainable hydraulic design, iii) setting the most favourable operation strategies.

Considering that living walls are supposed to run all over the year, it is important to consider strategies to avoid the loss of hydraulic conductivity among the filter bed to ensure the long-term sustainability of the system. The clogging of porous media is mainly caused by suspended solids (mineral and organic), accumulation of organic matter (biofilm) and chemical precipitation [50-51]. In this sense, physical properties of the porous media may play an important role, which regards reducing the problem of clogging and losses in hydraulic conductivity. According to Kadlec and S. D. Wallace (2009) [49] and Knowles (2011) et al. [50] particle diameter, distribution, shape, arrangement and bed total porosity are important parameters, which regard the influence of porous media on the hydraulic conductivity of the system. Therefore, the selection of a proper particle size may play an important role, to ensure the systems hydraulic conductivity.

Smaller particle sizes may favour the development of higher biofilm quantity due to the larger available surface and are more effective in regards of the interception of suspended solids with narrower pore diameters [50]. On the other hand, grain size and hydraulic conductivity increase proportionally, the larger the grain size, the higher the hydraulic conductivity (Fig 2.20 [49]). Therefore, substrates with larger granulometry may avoid hydraulic conductivity loss over time or at least maintain it. However, the use of bigger particle sizes can also lead to a reduction of the adsorption properties of the material, less biofilm surface area and lower retention time. Therefore, the particle size of the substrate must be taken into account to find the best balance between suitable hydraulics and increased biofilm activity and consequent removal processes.

Considering that the adsorption is a temporary and saturated process, the use of substrates, to optimize phosphorus removal by precipitation with Fe, Al, Mg and Ca may be an alternative to overcome the losses of adsorption implied by using bigger particle sizes. On the other hand, couple of designs showed limited total nitrogen removal, mainly related to the denitrification process, suggesting the absence of appropriate anoxic condition and/or availability or organic carbon. Therefore, another strategy to be considered is selecting filter media, not just by its ability to adsorb pollutants but, at the same time, by its ability on providing organic carbon and allocating it to the proper places for enhancing denitrification. Therefore, the use of a mix of organic and mineral materials rich in Ca, Fe Al and Mg to enhance denitrification of nitrogen and precipitation of phosphorus, may be considered a viable alternative to increase the range of removal process in the system. However, according to Masi et al. (2016) [47] results, the use of organic substrate may lead to an increase of Total Kjeldahl Nitrogen. Therefore, studies on the combination of organic and mineral substrates, assessment of proper particle size and its allocation in the system may be an interesting line of research, which relates to enhancing removal of nitrogen and phosphates and reducing issues related to losses on hydraulic conductivity.

On the other hand, Svete (2012) [45] highlights that one of the main concerns related to the performance of these treatments is the lower area available in comparison with other conventional wastewater treatments. This author applied 0.360 m^3/d and the module occupied a vertical area of approx. 2.34 m^2. In the other hand, Fowdar et al. (2017) [46] applied 0.0025 m^3/d (considering HLR of 0.055 m/d) and the module occupied a vertical area of 0.192 m^2. Thus, the relation between hydraulic load and vertical area occupied is 0.153 m^3/m^2d^{-1} [45] and 0.013 $m^3/m^2\ d^{-1}$ [45], respectively. However, the system proposed by Fowdar et al. (2017) [46] showed a maximum TN removal of 92 % while Svete (2012) [45] system showed a TN removal ranging 31 % - 34 %. Therefore, it is possible to conclude that the assessment of optimum hydraulic loading rates may play an important role concerning taking maximum advantage of the vertical space available on urban facades.

Regarding the plants used, Table 1 shows different species that have been used, such as ornamental flowers and climbers [46], agricultural species [45] and ornamentals [47-48]. However, none of the authors described the methodology used for plant selection. According to Raji et al. (2015) [28], living walls can support a large variety of plants, like ferns, small shrubs, and perennial flowers but ornamental species were usually utilized. However, recently the use of native plants has been recommended because of the biodiversity value assigned. Moreover, the use of native species can be an environmental friendly choice mainly for its adaptation related to weather conditions and capacity of reconciling anthropogenic development and natural environment.

All the information discussed above leads to four main concerns in the field of designing living walls optimized for nitrogen and phosphorus removal from wastewater. First, how to ensure desired unsaturated and saturated conditions required for both nitrification and denitrification processes. Second how to enhance nitrogen removal by microbiological means without reducing phosphorus removal by adsorption. Third, how to ensure enough carbon availability to complete denitrification requirements and fourth, how to overcome the issue related with the reduced area available for this kind of treatment.

In this regard, the WETWALL design concept first aims to ensure appropriate conditions for nitrification and denitrification through the development of structures, which replicate the constructed wetland hybrid flow in a modular living wall structure: A novel concept of living wall hybrid flow, which is separated in two independent structures. Second, the WETWALL design concept proposes a methodology for plant and substrate selection and allocation, in order to ensure system efficiency at removing nitrogen and phosphorus. Third, the WETWALL concept design proposes an innovative water recirculation approach, which, besides ensuring an intermittently flow, also increases the retention time through the establishment of treatment cycles; which may be an alternative to overcome the issue related to reduction of treatment area in comparison with conventional treatments.

Table 1. Main design parameters and results on nitrogen and phosphorus removal provided by living wall wastewater treatments.

	AUTHORS			
	Svete [45]	Fowdar et al. [46]	Masi et al. [47]	Wolcott et al. [48]
Wastewater	Greywater	Greywater	Greywater	Brewery wastewater
Irrigation	Drip irrigation: Spray nozzles and timer		Drip irrigation: Timer based solenoid valve and Perforated pipe	Drip irrigation: Perforated pipe (gravity flow)
Plants	Lettuce, marigolds	*Strelitzia* nicolai, *Phormium* spp. Canna *lilies, Strelitzia* reginae, *Lonicera* japonica, *Carex* appressa, *Phragmites* australis, *Vitis* vinifera, *Parthenocissus* tricuspidata, *Pandorea* jasminoides *Billardiera* scandens	*Abelia, Wedelia Portulaca, Alternenthera, Duranta , Hemigraphis*	Golden Pothos*, Epipremnum aureum*
Substrate	lightweight expanded clay	Sand, coarse sand, gravel	Coconut shell, light expanded clay, sand	lightweight expanded clay and recycled glass beads
Operational factors	D: 0.36 m^3/d HLR: 0.67 m/d RT (NaCl): 29880 s	D: standard 0.005 m^3/d Low 0.0025 m^3/d HLR: standard (0.1 m/d) low (0.055 m/d) HRT: standard = 172800 s Low: 345600 s IR: 626.4 m/s - 2170.8 m/s		HLR: 354 m/d
*Ranges of N Removal	NO_3^-:0.2-6.2 mg L^{-1} TN: 31 % - 34 %	TN:7 % - 92 % NOx: 0.001- 4.20 mg L^{-1} NH_3^+: 0.001-0.35 mg L^{-1}	NH_4^+-N: 1-1.9 mg L^{-1} TKN: 5-7.3 mg L^{-1}	TN:25 % - 56 %
*Ranges of P removal	TP (aeration sections): 95 % - 98 %	TP:7 % - 85 % FRP: 8 % - 87%		TP; 12 % - 28 %

* Removal percent (%) or concentration in the effluent (mg L^{-1}). D: doses; HLR: Hydraulic loading rate; HRT: Hydraulic retention time; RT: retention time using tracer; IR: infiltration rate; TN: total nitrogen; TKN: total Kendal nitrogen; NOx: nitrites and nitrates; TP: total phosphorus; FRP: filterable reactive phosphorus

3. WETWALL DESIGN

There is no terminology to define living walls as wastewater treatment. Therefore, the terminology of WETWALL was proposed, since the design concept is mainly based on the combination of a constructed WETland hybrid flow with a modular living WALL structure, creating an innovative living wall hybrid flow. The design proposed by Fowdar et al. (2017) [46], intend to promote anoxic and aerobic conditions as well. However, the author design aims to promote these different conditions in the same structure by elevating the outlet and creating a saturated layer at the bottom of the vertical pipe used as a support for plants and substrate. For the best of our knowledge there is no similar living wall, in the scope of wastewater treatment, that integrates two separated types of treatment in a modular living wall.

In addition, to the best of our knowledge, a design concept for living walls treating wastewaters which proposes a selection methodology for plants and substrates, as well the integration of circular economy principles into the design process, does not exist in the current literature. Therefore, in this section, the methodology to select plants and substrates, the living wall hybrid flow, the operation strategies and the integration of circular economy principles into the design concept, are presented and described.

3.1 Plant selection

The plants can play an important role in the scope of living walls treating wastewaters not just by direct pollutant uptake or promoting microbial activity, but also in ensuring the acceptation and implementation of this kind of technology in urban areas. However, due to the novelty of this research field, there is no methodology available to select the plants. Most of the authors used ornamental [46-48] or crop species [45] in their works. However, no parameters of selection were discussed. Therefore, the WETWALL design concept brings several prerogatives for the selection of plants which mainly takes into account 3 keys aspects: adaptation to the system, ecosystem services and social acceptance.

Moreover, the results of Wang et al. (2014) [52] suggest that the use of 3 to 4 different plant species in constructed wetlands may increase the removal of total N in wastewater. In addition, the use of more than one species may avoid issues related to pests and phytodiseases, once increases the biodiversity of the system. Therefore, the WETWALL design concept proposes the selection of a minimum of 3 native species according to the following prerogatives (see Table 2.):

a. **Adaptation:** A candidate species must be adaptable to the system conditions such as weather, high moisture, limited space for root development (modular structure), high solar incidence, and tolerance to high concentrations of contaminants (salts, nitrates, phosphates among others – depending on the type of wastewater to be treated). Species must be resistant or not susceptible to existing diseases and plagues in the implementation area.

b. **Ecosystem services:** The species must be capable of providing ecosystem services such as uptake of contaminants and high evapotranspiration rates, to ensure high performance in cleaning the water and providing the cooling effect. Moreover, the ability of the species, regarding the ability of sequestering carbon and reducing GHG emissions gases, must be taken into account to increase air quality and reduce the greenhouse effects.

c. **Social Acceptance**: Considering the acceptance of society, the species selected should provide a social benefit, as for example medicinal properties, agriculture value and good aesthetic appearance. On the other hand, the use of agricultural species can be an option, however, restrictions and legislation related to the irrigation of crops with wastewater must be considered. Indeed, species with a good aesthetic appearance provide welfare and acceptance, regardless of the technical knowledge on the subject, a fact which is important considering large scale acceptance and implementation.

Table 2. WETWALL design concept - Prerogatives for the selection of native species.

(a)Adaptation	(b) Ecosystem services	(c) Social Acceptance
Adaptable to weather changes	High uptake of nitrates and phosphates	Medicinal plants
Tolerant to high moisture	High evapotranspiration	Agriculture species
Tolerant to high solar radiation	Carbon sequestration	Aesthetics appearance
Restricted roots grown		
Tolerant to high concentrations of contaminants		
Resistance to diseases and plagues		

It is expected that plant selection success will depend on the information available and on the number of prerogatives filled (Table 2.). Moreover, the allocation of plants should also consider their solar radiance tolerance so that species with a higher solar tolerance should be allocated in the upper sections of the system. The A and B prerogatives are related to the system performance, treating water and providing thermal insulation. The C prerogative aims to promote the integration of technology with the urban environment, anticipating possible issues regarding social acceptance. In addition, the C prerogative brings the circular economy principle of connecting production chains. However, in this particular case, connecting a wastewater treatment (WETWALL design concept) with other production chains, such as food sector, pharmaceutical and landscape industry.

3.2 Substrate selection

The selection of appropriate substrates and their location in the system is fundamental to guarantee the efficiency of the treatment based on the replication of natural processes. Growing media for modular living walls systems is usually based on a mix of lightweight substrate with granular material [37] while the commonly used filter media in CWs are sand and gravel [53]. In the scope of living walls treating wastewater, most authors have been using substrates such as gravel, sand and lightweight expanded clay, which are materials frequently, used in similar biological treatments such as biological filters and constructed wetlands [45-48]. However, considering the novelty of this field, it is important to establish adequate criteria for appropriate filter media selection, to ensure system hydraulic operation and pollutant removal efficiency.

The main requirements of living walls, regarding substrates, are related to light weightiness, water retention and capacity to support plant growth. The substrate, besides being support for plant growth, must be lightweight in order to reduce the total weight of the structure and to facilitate the implementation in external facades. Finally, the water retention capacity plays an important role for plants maintaining and incrementing the cooling effect by water evaporation. On the other hand, substrates ability on pollutants removal from wastewater is mainly related to exchange, adsorption, precipitation and complexation [35]. However, in the scope of constructed wetlands, usually the selection of substrates must prioritize good hydraulic behaviour and adsorption ability, in order to avoid clogging and enhancing pollutants removal by adsorption [54].

In the scope of living wall for wastewater treatment, Sakkas (2013) [44] suggested the use of expanded clay aggregate (ECA) and glass foam gravel as substrate based on the following criteria: high water treatment efficiency, low weight/bulk density, low environmental burden and good structural behaviour. However, that selection is contradictory, since the production of ECA demands high energy, which leads to a high environmental burden and not much is known about the adsorption properties of recycled foam glass gravel. Prodanovic et al. (2017) [55] selected organic and mineral materials based on physical and chemical properties such as weight, water retention, capacity for nutrients adsorption, porosity, sustainability and local availability. However, none of the papers discussed in the state of the art proposes selection criteria, they only deal about the features of the substrate selected or describe the parameters used [45-48]. None of the authors considered the parameters such as organic carbon, Fe, Al, Mg and Ca in the selection procedure. Considering that, the adsorption of materials usually reduces with time [53], and that uptake varies according to species and physiologic stages, these features can play an important role at providing conditions to increase the range of removal processes, such as denitrification and phosphorus precipitation.

The removal of nitrogen is mainly performed by microorganisms through denitrification and microbiological degradation, processes which are highly dependent on anoxic conditions and organic carbon availability [36][56]. Moreover, taking CW as a reference, it is possible to predict that the precipitation and adsorption of phosphorus are higher under saturated conditions because of the low fluctuation in redox potential [35]. Therefore, the selection of materials rich in Fe, Al, Mg, Ca and organic carbon and its allocation under anoxic zones could increase phosphorous removal by precipitation and nitrogen removal by microbiological degradation in living wall systems.

In addition, the use of waste materials as filter media is an alternative to reduce cost, minimize extraction of non-renewable raw materials, promote energy saving and reduce the generation of waste and CO_2 emissions [57-58]. A couple of authors proposed the use of waste materials as substrates in living walls for wastewater treatments [47-48], however not as a part of the selection process, where the substrate needs to fulfil a series of parameters in a certain order. In that sense, the WETWALL design concept proposes a selection, which is mainly based on selecting local waste, with good hydraulic conductivity, light weightiness, high adsorption of contaminants, potential to release organic carbon (denitrification) and rich in Fe, Al, Ca and Mg (precipitation). Water retention capacity was not considered, since the design concept suggests water recirculation as an alternative to overcome the limitation regarding the area available (facades). More details about the water recirculation proposed by the design concept will be discussed in the section 3.4.

However, the selection of a material, which can fit in all the criteria mentioned above, was not considered feasible. Therefore, the selection process is focused in selecting one organic to ensure organic carbon availability so that the denitrification process takes place and one mineral material to potentiate the adsorption and precipitation of phosphorus.

Considering the information mentioned above, the selection process is based on tree stages (see Table 3):

a. Pre-Selection. Contact public and/or private institutions responsible for waste management in the area. Do an inventory of potential waste materials available considering the following criteria: organic and mineral materials, light weightiness, free of pollutants (heavy metals, pesticides and herbicides, among others), low energy and CO_2 emissions embodied. Particle size is smaller than 20mm (recommended for constructed wetlands [54]). As the selection of filter media aims to improve microbiological and precipitation removals, this may reduce the infiltration rate among time. Thus, it is recommended to use a homogeneous distribution of particle size in the layers and diameter bigger than 1 mm. The allocation of filter media in the treatment will depend on each system. In the WETWALL, the allocation of filter media is done considering the goal for each designed water flow, in order to ensure appropriate conditions for nitrogen and phosphorus removal. The allocation of filter media will be discussed in the sections 3.3.1 and 3.3.2.

b. Materials Characterization. The characterization can be done based on available literature information or laboratory analysis. The main parameters suggested are hydraulics (hydraulic conductivity m/s or infiltration rate mm/h), concentration of Fe, Al, Ca and Mg, C:N ratio and adsorption ability (NO_3^--N, PO_4^{+3}-P),

c. Final selection. This stage aims to compare the characteristics of each material in order to optimize the selection. The comparison must be between materials with same origin (mineral or organic). The goal is to select materials by comparison, considering the following parameters: good hydraulic behaviour, capable to release organic carbon and to enhance precipitation of phosphorus and high adsorption of nitrates and phosphates. First, regarding the hydraulic operation, organic and mineral materials with the highest infiltration rate (mm/h) or hydraulic conductivity (m/s) should be selected in order to reduce risk of clogging and reduce maintenance costs. With regards to phosphorus removal by precipitation, the concentration of Fe, Al Ca, Mg of mineral materials should be highest as well.

In order to select a material with potential on releasing organic carbon, the C:N ratio should be considered**.** The recommended C:N ratios may vary depending on the type of system, type of wastewater and organic source. For example, Hang et al. (2016) [59] recommended C:N ratios of at least 4:5 and 1.8:3.0 for constructed wetlands and bio reactor, respectively. Park et al. (2008) [14] results showed the maximum removal of nitrogen at 2 C:N ratio. Considering the novelty of living walls in the scope of treating wastewater, materials with a minimum C:N ratio of 2:1 is suggested.

Regarding the removal of contaminants by adsorption, the comparison should select organic and mineral materials with highest adsorption of nitrates and phosphates. However, it is important to highlight that these are flexible parameters, considering that, for example, the material with the highest adsorption of nitrates may not be the material with highest phosphates adsorption. Therefore, each filter media organic and mineral, must fulfil at least one of the flexible parameters (adsorption of NO_3^--N and/or PO_4^{3-}P) as long as the other material fulfil the remaining flexible parameters.

Table 3. WETWALL design concept - Stages and parameters suggested for the selection of filter media.

		Selection parameters	
Selection stages	**Parameters**	**Filter media A**	**Filter media B**
a	Waste origin	Organic	Mineral
	Lightweight	YES	YES
	Pollutants	NO	NO
	Diameter	1<Ø<20	1<Ø<20
	Energy and CO_2 embodied	Lowest	Lowest
b and c	Infiltration rate (mm/h) or hydraulic conductivity (m/s)	Highest	Highest
	Organic carbon (C:N)	Minimum 2:1	
	Fe, Al, Ca and Mg (mg g^{-1})		Highest
	[1]Adsorption of NO_3^--N	Highest	Highest
	[1]Adsorption of PO_4^{3-}-P	Highest	Highest

[1]Flexible parameters: means that Filter media A and B does not necessary need to fulfil both parameters at the same time.

3.3 Innovative living wall hybrid flow

Hydroponic wastewater and greywaters have different characteristics (Table 4). On one hand, hydroponic wastewater has high concentrations of nitrates and ammonium and low organic matter while greywaters have a high concentration of organic matter and phosphates and a low concentration of nitrates. Therefore, in order to design a system, which, can cope with a bigger range of urban wastewater types, a hybrid flow is proposed for the Living wall. The design is based mainly on the prerogatives of a constructed wetlands subsurface hybrid flow.

Table 4. Typical composition of hydroponic wastewater and greywaters (adapted from [5][6][7][8][9][10][11][12])

	Hydroponic wastewater		Greywater	
	Min	Max	Min	Max
Compounds	*mg L^-1*			
NO_3^--N	10	414	0	5
NH_4^+-N	0.8	36	0.03	25
PO_4^{-3}-P	0.8	60	4	68
BOD	9	12	90	200

NO_3^--N: Nitrate-Nitrogen. NH_4^+-N: Ammonia-Nitrogen. PO_4^{-3}-P- Phosphate-Phosphorus. BOD: Biological oxygen demand.

Hybrid systems include the advantage of combining Horizontal (HF) and vertical flows (VF), providing different redox environments, which can significantly improve the conditions needed for nitrification and denitrification processes, adsorption and precipitation of phosphorus and removal of organic matter. The VF brings aerobic conditions needed to remove ammonia-N by nitrification/volatilization and BOD by bacterial oxidation, while horizontal flow bring anaerobic conditions which increases the removal of nitrogen, through the denitrification and precipitation of phosphorus [35][56]. According to Vymazal (2007) [35] HF systems have higher potential to promote adsorption and precipitation of phosphorus because of the low fluctuation in redox potential (anaerobic conditions) while the aerobic conditions of vertical-flow systems may cause desorption and release of phosphorus.

Therefore, the main goal of the Living wall hybrid flow is the enhancement of aerobic conditions of VF and anoxic conditions through the HF, in order to enhance the contaminants removal from urban wastewater such as, greywater and from hydroponic wastewater. For the treatment of greywater, the vertical flow aims to remove BOD (biological oxidation), while the horizontal flow aims to remove phosphates (precipitations and adsorption). On the other hand, for the treatment of hydroponic wastewater, the vertical flow aims to remove ammonium, while the horizontal flow aims to remove nitrates (denitrification) and phosphates (precipitations and adsorption). It is important to highlight that the proposed hybrid flow is a design concept based mainly on the oxygen conditions. However, other aspects such as, pH, biofilm and temperature, among others, may influence the removal process as well.

3.3.1 Subsurface vertical flow

Subsurface vertical flow consists of a planted bed filled with porous media, where the wastewater flows vertically [56][64]. Several methods have been proposed in order to improve the aeration of subsurface flow [65-66]. However, artificial aeration usually requires energy inputs and additional costs [65]. Therefore, in the WETWALL concept, the vertical subsurface flow was designed to enhance the aeration of the bed during the gravity drainage to tackle the removal of BOD, the nitrification of ammonium and the uptake processes by the plants to remove nitrogen and phosphorus. The main considered hypotheses were the following ones (see Figure 1.):

a. **Vertical drainage** (Figure 1 – a_1 and a_2): The inlet (Figure 1 - a_1) and outlet (Figure 1 - a_2) are located at different levels in order to promote vertical drainage.

b. **Irrigation and overflow control** (Figure 1 – b_1 and b_2): Drip irrigation is recommended in order to provide a homogeneous distribution of the flow among time and to avoid saturation on the first layers of substrate. The Vertical flow can be feed by compensate drippers or perforated pipe. The main advantage of using compensate drippers is the constant flow rate, however the dripper can be easily clogged by solids particles, fact which will depend on the type of wastewater to be treated and on the secondary treatment used to remove total solids (Figure 1 – b_1). Also compensate dripper requires a minimum water pressure, fact which may be a limitation if the system is operating by gravity flow. In the other hand, the flow rate of perforated pipes varies according with the hydraulic head, however clogging is not such a big concern for thi type of irrigation. Therefore, the type of drip irrigation will depend on two main aspects: The presence or absence of previously treatment to remove total solids and if the system will work by gravity flow or under pressured flow. A cascade overflow control is allocated along the vertical flow in order to avoid saturated layers and to collect the overflow in cases of extreme rainfall (Figure 1 – b_2). The overflow is discharged to the lower water reservoir.

c. **Main structure features** (Figure 1 – c_1, c_2 and c_3): The main structure of the vertical flow is a filter column built from a cylindrical pipe (Figure 1 – c_1). Additional pipes installed at 45 degrees in order to support the plants and promote a passive diffusion of oxygen to the media (Figure 1 – c_2). Moreover, the distribution of plants among the column aims to enhance the contact of roots with the wastewater (Figure 1 – c_3), to facilitate the uptake of contaminants.

d. Filter media allocation (Figure 1 – d_1,d_2 and d_3): Since the main goal of VF is to reduce the organic load by oxidative processes and increase nitrification process, it is suggested the use of mineral substrates to avoid the increment of organic load by the substrate. The mineral filter media is allocated all over the vertical flow (Figure 1 – d_1, d_2 and d_3). It is recommended to use tree particle sizes distributed in tree layers in order to enhance retention time and avoid saturation of the upper layers. The length of each layer will depend on the height of the treatment column. Particle size of upper layers larger must be smaller than the lower layers.

e. Water collection and system maintenance (Figure 1 – e_1 and e_2): this layer aims to avoid clogging and favours the drainage (Figure 1 – e_1). It is suggested the use of gravel with diameter ranging from 10 mm to 16 mm. An external filter is allocated in the bottom in order to reduce the flow of sediments to the next treatment stage and to facilitate the maintenance of the system (Figure 1 – e_2). This filter can be easily removed in case of system maintenance. It is expected that the reduction of the sediments flow will also reduce the potential of clogging in the inlet of horizontal flow.

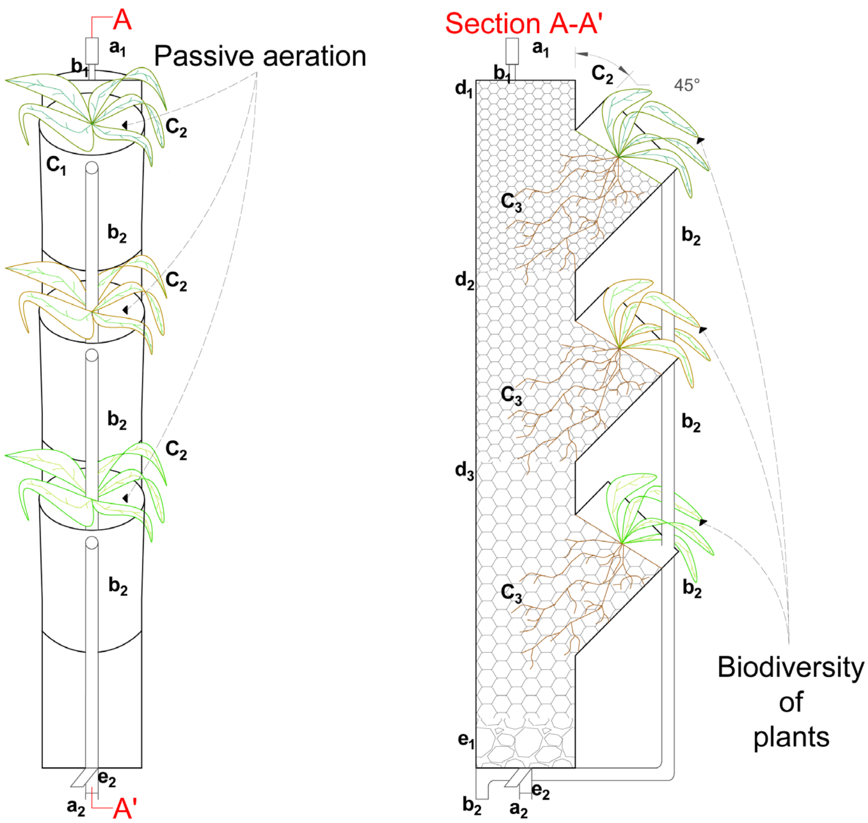

Figure 1. WETWALL – Vertical flow design. a: Vertical drainage (a_1: INLET. a_2: OUTLET). b: Irrigation and overflow control (b_1: drip irrigation – compensate drippers. b_2: cascade water level control). c: Main structure features (c_1: filter column. c_2: plants support and passive aeration, c_3: roots contact with filter media and water). d: Filter media allocation (d_1, d_2 and d_3: Layers of mineral substrate). e: Water collection and system maintenance (e_1: Drainage layer. e_2: external filter).

3.3.2 Subsurface horizontal flow

In subsurface horizontal flow, the wastewater pass through substrate and go under the surface of the bed in a horizontal path, until it reaches the outlet zone, where it is collected for further recirculation or discharge [13]. Therefore, the WETWALL horizontal subsurface flow is designed to provide anoxic conditions among the filter bed and, therefore, enhance the removal of nitrogen by denitrification and phosphorus by precipitation. The main compounds and structures are explained below (see figure 2.):

a. **Main structure functions** (Figure 2 – a_1, a_2, a_3 and a_4): The main structure of the horizontal flow is cylindrical with a slope of 1 % (Figure 2). The inlet position is higher than the outlet (Figure 2 – a_2). Therefore, besides providing anoxic conditions at a

certain height, the design also gives a margin for water rise by capillarity, whilst avoiding dead zones. Moreover, there is a water level control, which is located at the same height as the inlet, to avoid overflow in case of rainfall (Figure 2 – a_3). The plants are located all over the bed in order to increase the uptake of contaminants, mainly by the contact of roots with the subsurface flow, as well as capillarity in the upper layers (Figure 2 – a_4).

b. **Filter media allocation** (Figure 2 – b_1, b_2 and b_3): The allocation of the substrates is divided into 3 main layers. Usually in Horizontal sub-surface flow wetlands, the clogging of the INLET area causes a great reduction of hydraulic conductivity of the bed [49]. Therefore, the design suggests the implementation of an INLET layer (Figure 2 – b_1) filled with gravel (10 mm < Ø > 16 mm) in order to minimize inlet clogging effects. On the other hand, horizontal flows require large amounts of organic carbon to promote denitrification and at the same time are quite efficient for the adsorption and precipitation of phosphorus [35]. Therefore, a layer composed by a mix (1:1) of mineral media rich in Fe, Al, Cal and Mg with organic media (Figure 2 – b_2), is proposed. In addition, as the WETWALL design concept aims to increase removal processes, such as microbiological degradation of nitrogen and precipitation of phosphorus, which may lead to accumulation of solid particles, an OUTLET layer filled with gravel (10 mm < Ø > 16 mm) is proposed (Figure 2. b_3).

c. **Water collection and system drainage** (Figure 2. – c_1 and c_2): The wastewater is collected by an inverted T-pipe perforated, which is allocated at the end of the horizontal flow (Figure 2 – section A-A'). A drainage pipe is located at the bottom of the horizontal flow, in order to facilitate the system's full drainage in case of maintenance (Figure 2 – c_1). External filters are suggested in order to facilitate the maintenance and as well avoid clogging by reducing the sediments flow through treatment cycles (Figure 2 – c2).

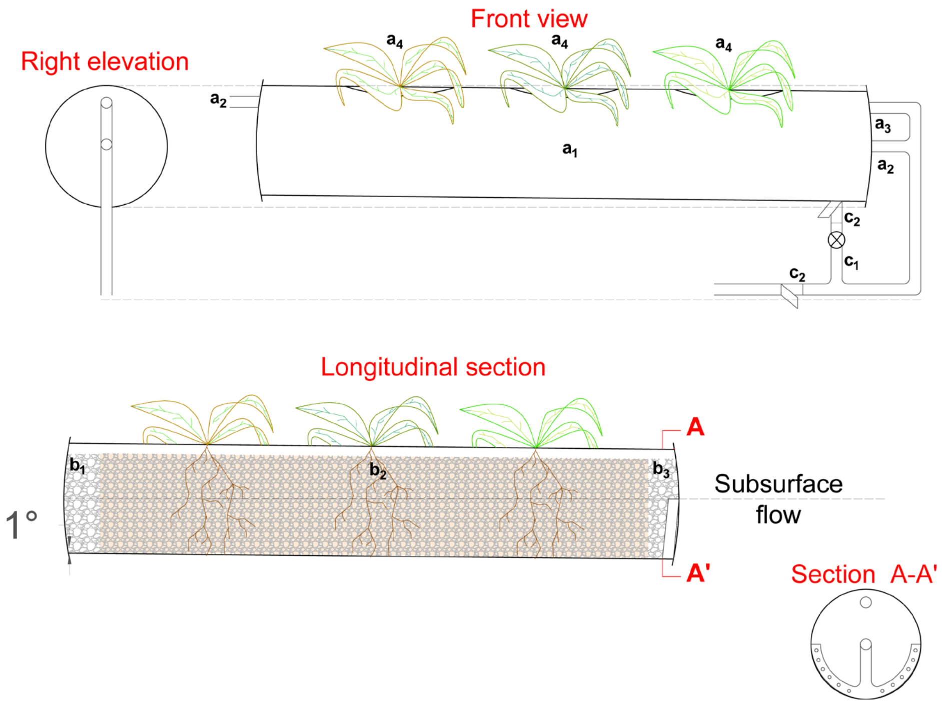

Figure 2. WETWALL – Horizontal flow design. a: Main structure functions (a_1: main structure. a_2: INLET and OUTLET. a_3: water level control. a_4: plants location). b**:** filter media location (b_1: INLET layer – gravel. b_2: Mix of mineral and organic media (1:1). b_3: OUTLET layer – gravel.). **c:** Water collection and system maintenance (Section A-A': water collection pipe. c_1: drainage. c_2: external filters).

3.4 Operations strategies and challenges

The implementation of NBS, such as CWs, is unfeasible at urban scale, mainly because of its large area requirement [64]. In this regard, the WETWALL design concept aims to give the urban environment a NBS, which can undertake available spaces of facades. However, one of the main concerns related to the efficiency of living walls treating wastewater at an urban scale, is the limitation regarding area available for its implementation. While the implementation of similar treatments, such as constructed wetlands, demands large areas, the blank spaces of vertical facades are limited.

Therefore, the WETWALL design concept proposes the recirculation of water in order to enhance the removal of nutrients through increasing the contact time between wastewater and the treatment surface. According to Wu et al. (2014) [64] water recirculation in vertical-flows and hybrid CWs enhances the interactions between pollutants and microorganisms, which can increase treatment performance, as well as reducing the area requirement. However, the energy spent for pumping and influent load must be considered as possible limitations. Therefore, the use of two tanks (lower and upper) is proposed in order to minimizes the operating time of the pump and save energy during the water recirculation. The pump only works the necessary time to raise the water to the upper tank and remains off until all the water flows through the system by gravity and a new water cycle starts.

On the other hand, vertical flow CW must be intermittently fed to promote the drainage and diffusion of oxygen into the bed, providing suitable conditions for the nitrification process [36]. The intermittent flow is ensured by the establishment of “resting periods” between cycles of treatment to ensure the full drainage and passive aeration of the vertical flow bed.

In addition, an integrated overflow control is proposed in order to facilitate the collection of rainwater. The overflow control of both, Vertical and horizontal treatments (sections 3.3.2 and 3.3.2), are connected to the lower reservoir. The rainwater collected can be stored for further reuses.

Moreover, the WETWALL design concept brings the possibility of performing different configurations of water recirculation, which may play an important role, especially considering the adaptation of the system to different types of urban wastewater and different pollutants loading. Treatments using separate structures which can be combined differently were not found in the literature. All the papers discussed in the state of the art present one single main structure where the wastewater is treated. In this regard, the WETWALL design concept, can run as a hybrid flow (Figure 3. VF-HF, HF-VF, VF-HF and HF-VF, VF and HF) or just vertical flow (Figure 3. VF) or just horizontal flow (Figure 3. HF).

However, a couple considerations regarding the WETWALL operation are important. First, it is expected that the number of treatment cycles will influence the treatment performance, once the contact time between wastewater and treatment surface increases. Second, the hydraulic load will influence the number of viable treatment cycles per day. Considering the same initial flow rate during the hole cycle (compensate drippers), the treatment cycle will be as long as the hydraulic load increases. Hence, accessing the optimum initial flow rate and hydraulic load is important to adapt the system to real scale, where a certain amount of wastewater is produced per day. Third, different resting periods between cycles may influence the system efficiency as well, mainly regarding the aeration of the vertical flow. Fourth, it is expected that the number of treatment cycles needed will be higher as loading rates of contaminants increases. Fifth, the hydraulic conductivity of the system will decrease with time affecting the retention time, fact which may influence treatment efficiency as well. Sixth, it is expected that the treatment configuration (Figure

3), as well as the number of modules will variate in accordance to treated wastewater features (pollutant loading) and the hydraulic load.

Therefore, to ensure the validation of the WETWALL design concept and its implementations at real scale, further research on the relation between treatment configurations (Figure 3), number of cycles, hydraulic load, hydraulic conductivity, resting periods and pollutant loadings is needed.

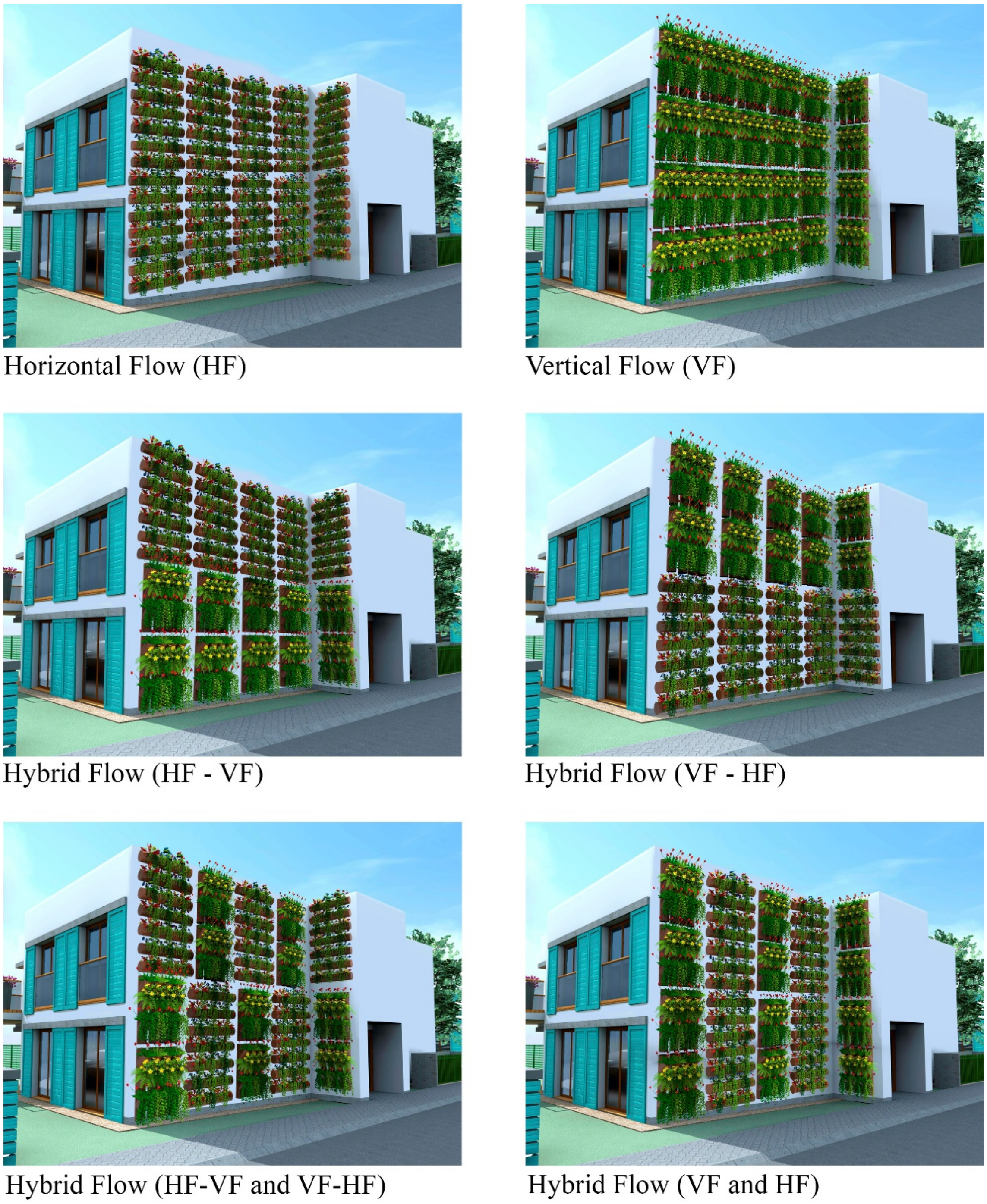

Figure 3. The WETWALL design concept – possible treatment configurations.

3.5 WETWALL and Circular economy

In general, the production models currently widely used is based on the concept of ‘take-make-dispose’ or ‘linear’ model, in which the reuse of materials is not a concern, since the economic efficiency is achieved using raw resources and exploiting natural environments [67-68]. Currently the concept of linear production has been questioned, in order to rethink the optimization of waste management, through the integration of production chains.

In 2012, the European commission published a manifesto about resource use-efficiency, which started as following: “*In a world with growing pressures on resources and the environment, the EU has no choice but to go for the transition to a resource-efficient and ultimately regenerative circular economy*” [69]. In this sense, the development of systems based on the principles of circular economy (reuse, recycling and reducing), plays an important role regarding the promotion of the efficient use of resources, reducing environmental costs, conserving raw materials, mitigating global warming, reducing greenhouse emissions and providing energy savings [57][68].

It is important to highlight that integrating technological development and the circular economy is more than just reusing materials. Moreover, considering the scope of water treatment designs, the initiatives are mainly focused on the efficiency of technological features and system performances. Technologies are developed primarily as individual systems and no account is taken of the interaction between them and the operating environment where they are introduced.

Green walls provide a number of benefits; environmental, economic and social. Not just for the buildings, but for all urban areas. Several authors have been showing the positive impact of promoting the reconciliation of the urban environment and natural habitats, with regards to promoting biodiversity, increasing the resilience ability of the cities and climate change mitigation [24][33-34]. The potential interactions between green technologies and the environment may represent an important role, regarding closing the “cycle” and promoting a sustainable technological development. Therefore, integrating circular economy into the WETWALL concept design, it was considered as part of the design process, the determination of possible interactions between the technology and the environment, which will be applied. Therefore, four main interactions are discussed below (see Figure 4):

a. **Reusing Wastewater ➔ Recycling water and nutrients** (Figure 4-a): Irrigating with wastewater a living wall may overcome the biggest limitation, concerning the implementation of these green technologies at an urban scale: high water demand. An important step, that will redound in an increase of the social acceptance and integrating natural habitats into urban environment.

Moreover, the treatment of wastewater for further reuse aims to promote a sustainable recycling of water and nutrients (N and P), at an urban scale. Additionally, the contaminants (high concentrations of N and P) will be transformed and stored in the system (uptake of plants, adsorption of substrates and microbiological degradation), and the water treated can be reused in accordance with international water quality standards. According to European Environment Agency (2012) [21], reusing wastewater is an important strategy to increase the efficient use of water resources and to decrease the use of drinking water for activities that don't demand drinking quality standards. Moreover, treating and promoting a safe reuse of wastewater "*in situ*", can be considered a sustainable alternative which promotes energy saving and the decentralization of wastewater treatment.

b. Reusing waste materials ➔ Recycling organic fertilizer (Figure 4-b): The main goal of selecting local waste/sub products as substrate (Section 3.2) is to promote the integration of local production chains, reduce withdrawal of raw material and to provide a sustainable alternative for waste management at an urban scale. The reuse/recycling of local materials are important strategies with regards to climate change mitigation, minimizing extraction of no-renewable raw materials, promoting energy saving and reducing the generation of waste and CO_2 emissions [57-58][70]. The research of Manso et al. (2015) [37] shows that several authors have been using natural/recycled materials and integrating water recovery systems in order to provide a sustainable implementation of this kind of technology at an urban scale.

In addition, the WETWALL brings the innovative concept of recovering nutrients from urban wastewaters and giving them a new application. Humanity has already transgressed planetary boundaries regarding changes on global nitrogen and phosphorus cycle mainly because of the input of reactive compounds into the environment [14]. Hence, recovering these nutrients, reusing them instead of keep producing, can be a sustainable way to reduce the impacts caused by their presence and accumulation in the environment. Therefore, once the treatment requires maintenance, the substrates and plants can be reused as fertilizer for urban crops, reducing manufacturing process (Haber-Bosch) and lowering distances between providers and consumers. Moreover, adding an economic value to the waste produced by the treatment may reduce maintenance costs and increase social acceptance. However, it should be considered that depending on the wastewater treated, the presence of contaminants such as pesticides, heavy metals and pathogens, might represent a challenge on reusing this material as fertilizer.

c. Reusing air pollutants ➔ providing Air quality ➔ Reducing greenhouse effect (Figure 4 – c): According to Szulejko et al. (2017) [71], the highest level of global warming was achieved in 2015, mainly due the increment of greenhouse gas emissions. In this regard, living walls are able to create a new profile of urban areas in accordance to nature, improving air quality, mainly through reducing pollutant gaseous levels, absorbing fine dust particles and increasing atmospheric oxygen [30][72][40]. The research developed by Marchi et al. (2015) [30] provided evidence of carbon sequestration promoted by living walls. The author's results showed that "*CO_2 uptake by plant biomass of 0.44–3.18kg CO_2eqm^{-2} of vertical garden per year*". Therefore, the WETWALL design concept aims to promote the reuse of pollutant gaseous present in the atmosphere, in order to improve air quality and reduce the greenhouse effect. However, it is important to highlight that the performance of such system is intrinsically related to the capacity of plants at up taking CO_2 and other pollutant gases.

d. Reducing urban heat (summer)/heat losses (winter) ➔ Reducing energy expenditure (Figure 4 – d): Living walls as a part of innovative green infrastructure can provide multiple functions in the scope of thermal maintenance and energy savings [72][31][29]. Vertical greening systems are efficient at providing cooling and heating effects on the building's surface, which can significantly increase energy savings for buildings and the urban environment. The evapotranspiration of plants and substrate provides the cooling effect on the building's surface, which is very important during summer. While during winter, the surface covered by the plants can work as an external insulation layer to avoid heat loss [73][28]. The reduction of indoor temperatures during summer leads to a reduction in the use of air conditioning and increases energy savings [28]. Results of Stec, Paassen, and Maziarz (2005) [74] showed that the use of certain plants inside a facade cavity can reduce energy requirement for air-conditioning systems by 20 %. On the other hand, results from Tudiwer et al. (2017) [39] suggest the use of the greening system on building facades, leads to a lower heat demand during winter. However, it is important to highlight that each greening system has different performances regarding cooling and heating effects, which will also depend on the plants ability at evapotranspiration, substrates transpiration, structure materials, orientation and weather conditions of each local area.

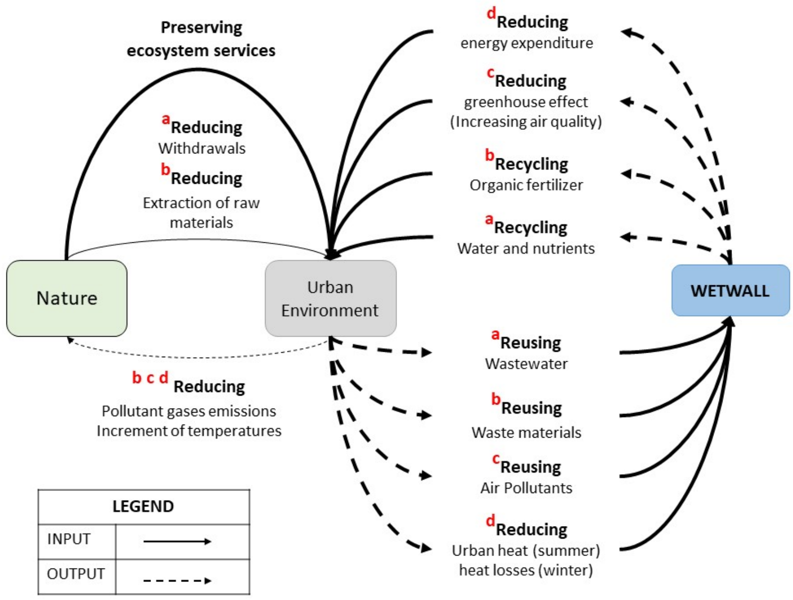

Figure 4. Integration of circular economy principles of reusing, recycling and reducing into the design process. The letters are in accordance with the de interactions discussed previously in this section.

4. CONCLUSIONS

Currently, the number of studies on the performance of living walls treating urban wastewater has been increasing. Mainly because of their potential for decentralizing wastewater treatments and their properties that can provide thermal insulation, both facts which may have a positive impact on climate change adaptation. However, it was observed that a wide diversity related to design parameters for living walls, such as structures, operational factors, plants and substrates, are hindering the establishment of standards. Indeed, operational factors such as hydraulic loading rates and retention time seem to be dependent on each design. Hence, the assessment of optimum operational factors is crucial to ensure high pollutants removal and an efficient use of vertical spaces.

The removal of nitrogen and phosphorus in these systems are mainly related to microbiological degradation, plant uptake and filter media adsorption. In this sense, it was noticed that the development of biofilm is an advantage for nitrogen removal by microbiological process. On the other hand, the biofilm development was also associated with the decrease in the adsorption of phosphorus. This fact highlights the importance of selecting the appropriate substrates and plants, as well as their allocation, in order to ensure optimum conditions for adsorption, microbiological degradation and plant uptake. Some systems showed limitations on the nitrogen removal, related to low availability of carbon and/or limitation on saturated or un-saturated conditions. Therefore, the design should favour the requirements for microbiological degradation of nitrogen, which are aerobic for nitrification and anoxic conditions with availability of organic carbon for denitrification.

In this regard, the WETWALL design concept proposes a novel design in the scope of living walls as wastewater treatment, which brings a living wall hybrid flow that is mainly based on the integration of constructed wetlands hybrid flow into a modular living wall structure. This design aims to provide saturated and non-saturated conditions at the same time, in order to enhance nitrification and denitrification. Furthermore, a selection procedure of plants and substrates which aims to enhance the removal of contaminants, thermal maintenance, good hydraulic conductivity performance and social acceptance, is proposed. The selection of substrates highlights the importance of selecting organic and mineral materials, in order to provide sustainable conditions for denitrification and precipitation of phosphorus. The allocation and proportion of these materials in the system can be as important as selecting the appropriate materials. Moreover, it is suggested that water recirculation, in accordance with an intermittent flow, could be an alternative to overcome the issue related with the area available to the treatment.

In addition, the design concept proposed in this article highlights the importance of taking into account the potential interactions between the technology and the urban environment by ensuring a sustainable recycling of natural resources. It can be said that integrating technological development and the urban environment by the replication of natural processes, reusing and recycling resources (water, nutrients and materials), is an important part of achieving the reconciliation between anthropogenic development and natural habitats and, thereafter, climate change mitigation. This article was a theoretical discussion on the innovation proposed by the WETWALL design concept, however, further research on its validation and its adaptation to real scale is needed.

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Chapter 7 Second Article

Cork as a sustainable carbon source for nature-based solutions treating hydroponic wastewaters – Preliminary batch studies

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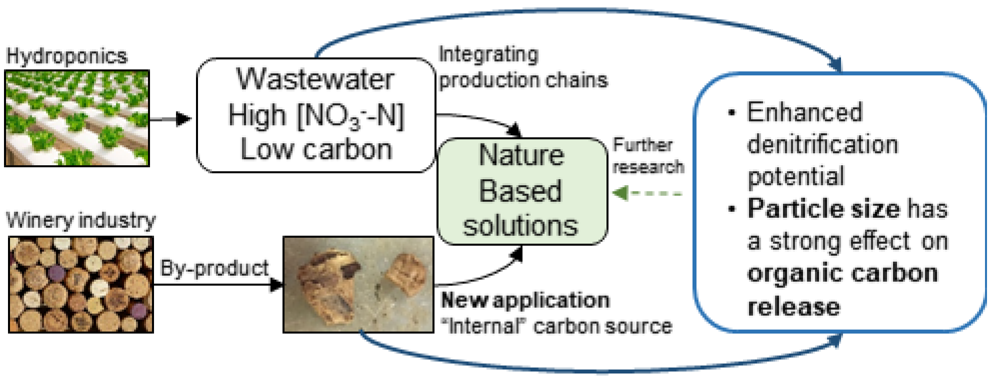

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CORK AS A SUSTAINABLE CARBON SOURCE FOR NATURE-BASED SOLUTIONS TREATING HYDROPONIC WASTEWATERS – PRELIMINARY BATCH STUDIES

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Abstract

Reusing by-products is an important strategy to ensure the preservation of natural capital and climate change mitigation. This study aimed at evaluating the potential of cork granulates, a by-product of winery industry, as an organic carbon (OC) source for the treatment of hydroponic wastewaters. First, chemical characterization was performed and discussed. Secondly, batch studies were performed using synthetic hydroponic wastewater to understand the role of particle size (PS), pH and contact time (CT) on the release of OC. The suberin is the major compound, representing more than 50%. It was noticed that a variance on the content of suberin across species, within the same species and depending on the extraction part (belly, cork and back) could be expected. More than 60% of the sample is composed by carbon while less than 1% was nitrogen (high C:N ratio), indicating a low risk of releasing organic nitrogen. The statistical results suggested that the main effect of PS on the release of OC is greater than both, CT and pH. The chemical release of OC gets slower with time, being this effect greater as the PS increase. Moreover, estimations showed that using the 4 mm PS, the amount of water treated would be twice the amount if the 8 mm PS had been used. The PS seems to play an important role at design nature-based solutions (NBS) focused on denitrification. The surface response methodology indicates a significant negative interaction between CT and PS suggesting that the mathematical model could be used for further optimization studies. The reuse of organic by-products as filter media seems to be an economic and environmentally friendly alternative to enhance denitrification in NBS, while preserving natural capital. However, further real scale and long-term experiments are needed to validate cork`s potential as an “internal” OC source for NBS.

Keywords: wastewater, denitrification, reusing, by-products, particle size, contact time.

1. INTRODUCTION

In the past years, the use of urban and soilless agriculture is becoming more common to supply the ever-increasing food demand and to deal with water and land scarcity, increasing the risk of water pollution. Wastewater from soilless agriculture, besides having high concentration of nitrates and phosphates is usually drained and discharged to the environment without proper treatment (Prystay and Lo, 2001). The leaching of N and P causes several environmental impacts such as, groundwater pollution, eutrophication of surface waters and ecosystem biodiversity losses. Therefore, the treatment of wastewaters generated by soilless agriculture is a must as it may play an important future role, with regards of ensuring food security, sustainable management of water resources and environmental protection, once this type of agriculture is implemented, both in urban and rural environments.

Conventional treatments such as reverse osmosis and ion exchange membranes were highly efficient, although have high maintenance and operation costs (Koide and Satta, 2004; Gagnon et al., 2010; Park et al., 2015). Therefore, NBS, namely, constructed wetlands (CWs) and biofilters, may represent a sustainable and low-cost alternative for the removal of nitrogen from hydroponic wastewaters before discharge (Park et al., 2008; Gagnon et al., 2010; Abbassi et al., 2011; Park et al., 2015).

However, nitrogen removal from hydroponic wastewaters by NBS can be a challenge, since this water is known to have high concentration of nitrates and, at the same time, low carbon content (Prystay and Lo, 2001). The availability of carbon is one of the main limiting factors regarding the efficiency of biological denitrification (Vymazal, 2007; Mutsvangwa and Matope, 2017). According to Mutsvangwa and Matope (2017) wastewaters with low carbon to nitrogen ratio, usually require an external carbon source to achieve denitrification. However, the use of external carbon sources such as, methanol, ethanol, acetic acid and fructose besides increasing operational costs can cause negative environmental impacts (Park et al., 2008).

Therefore, alternative organic materials such as, plant biomass (Wen et al., 2010; Zhang et al., 2014), flower straws (Chang et al., 2016) and plant pruning (Park et al., 2008) have been proposed as external carbon sources to enhance denitrification in NBS, mainly because of their low cost, availability and renewable biomass. In addition, in the past 5 years, authors have shown the potential of roots exudates as a carbon source for denitrification in CWs (Zhai et al., 2013; Chen et al., 2016; Wu et al., 2017).

Moreover, some authors have suggested the use of organic filter media to enhance denitrification, such as, woodchip bioreactors (Nordström and Herbert, 2017), green walls built with coconut fibber and light expanded clay (Masi et al., 2016) and green walls with Coco coir (Prodanovic et al., 2017). Results of Prodanovic et al. (2017) indicated that biological processes are enhanced by the addition of organic filter media. The use of coco coir increased the retention time and the availability of OC, enhancing the microbiological removal process. On the other hand, the use of organic substrates can lead to an accumulation of total nitrogen in the effluent. The study of Masi et al. (2016) showed an increment of total Kjeldahl nitrogen when using coconut fibber and light expanded clay mixed, possibly due to the increment of retention time, which favours the release of organic compounds, such as organic nitrogen.

Nevertheless, reusing organic by-products, as filter media transforms, what was once an external source, into an integrated part of the system, reducing operational costs while preserving natural capital. In this regard, cork granulated seems to have potential to be used as a sustainable "internal" organic source for the treatment of hydroponic wastewaters.

Cork granulates by-product is generated from several operations of wine industry and is considered as a natural, renewable and biodegradable raw material (Olivella et al., 2011a; Sierra-Pérez, 2016). The cork oak trees are planted, the bark is stripped for the first time when tree is 20 to 25 years old. The next stripping is carried out every 9 to 12 years, with an expected productive life from 100 to 300 years depending on the tree's health (Jové, 2011; Olivella et al., 2013a). More than 80% of the world`s cork is produced in Europe, being the annual production about 340.000 ton (Olivella et al., 2011a). However, the cork waste generated is around 50.000 ton (Olivella et al., 2011a), which represents approximately 15 % of waste in relation to the total cork extracted.

Moreover, several researchers have shown the potential of cork to remove emergent pollutants such as, polycyclic aromatic hydrocarbons (Olivella et al., 2011a, 2011b, 2013a), phenanthrene (Olivella et al., 2013b), methyl orange (Krika and Benlahbib, 2015), ofloxacin (Crespo-Alonso et al., 2013), Biphentrin (Domingues et al., 2005) ibuprofen, carbamazepine and clofibric acid (Dordio et al., 2011) or heavy metals (Pintor et al., 2012). On the other hand, not much is known about the behaviour of cork regarding the release of OC and its potential to enhance denitrification in NBS.

The main goal of this paper was to investigate the potential of granulated cork as an OC source. The chemical release of OC can play an important role regarding the establishment of biofilm in natural wastewater treatments. Moreover, the chemical OC released by the substrate can enhance denitrification process while reducing the use of external carbon sources and thus, ensuring a long-term performance on pollutant removal, reducing operation costs and environmental hazard. The granulated cork was characterized (PZC, FTIR, chemical and elemental constitution) and batch studies were performed using synthetic hydroponic wastewater in order to understand the role of PS, pH and CT on the release of OC.

2. MATERIALS AND METHODS

2.1 Synthetic Hydroponic Wastewater

The composition of hydroponic wastewaters varies depending on the crops, type of fertilizers used for the nutritive solution, frequency of application, time of the year and type of system (closed or open). A literature research was made to establish a reliable range of contaminants to guide the preparation of synthetic hydroponic water (Table 1).

The compounds used to prepare the solution were potassium Nitrate (KNO_3), calcium chloride dihydrate ($CaCl_2*2H_2O$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), sodium hydroxide (NaOH), magnesium sulphate heptahydrate ($MgSO_4$*7H2O) and zinc sulphate heptahydrate ($ZnSO_4*7H_20$). The hygroscopic compounds were dried at 105ºC for 4 hours and all compounds were mixed with tap water. When it was necessary, the water was stored in a freezer at 10°C in order to avoid losses of N- ammoniacal by volatilization. However, the water was not stored for more than 3 days. The wastewater was prepared five times during the experiment to provide the same initial concentrations of contaminants for all the treatments. All data and the standard deviation can be seen in Table 1.

Table 1. Composition of hydroponic synthetic wastewater (Adapted from Prystay and Lo, 2001; Koide and Satta, 2004; Huett et al., 2005; Taylor et al., 2006; Park et al., 2009; Gagnon et al., 2010; Gruyer et al., 2013; Dunets et al., 2015; Park et al., 2015).

		Synthetic Hydroponic wastewater	**Literature RANGE**	
Compounds	**Unit**	Average (^{a}SD ±)	Min	Max
N total	*mg L^{-1}*	70.89 ± 1.1	2.8	122.0
NO_3^--N	*mg L^{-1}*	66.28 ± 1.0	10.0	414.0
NH_4^+-N	*mg L^{-1}*	4.61 ± 1.4	0.8	36.7
PO_4^{-3}-P	*mg L^{-1}*	11.01 ± 3.3	0.7	99.3
$^bK^+$	*mg L^{-1}*	189.18	13.0	459.0
$^bNa^+$	*mg L^{-1}*	83.00	83.0	108.0
$^bCa^{2+}$	*mg L^{-1}*	123.52	21.0	295.0
$^bMg^{2+}$	*mg L^{-1}*	90.00	10.0	105.0
$^bCl^-$	*mg L^{-1}*	41.00	3.9	80.0
$^bZn^{2+}$	*mg L^{-1}*	0.50	0.03	1.4
pH		9.6 ± 0.08	5.5	7.3
^{c}EC	dS m^{-1}	2.2 ± 0.05	1.3	2.3
^{d}SAR	meq L^{-1}	1.96	1.8	2.0

[a] Statistical deviation (SD) was performed using IBM SPSS. [b] Concentration calculated by the amount of compound used (same for all water prepared). [c]Electrical conductivity. [d] SAR: The Sodium Adsorption Rate was calculated based on (Pescod,1992). To determine the literature range, the SAR was calculated considering the values of Na^+, Ca^{2+} and Mg^{2+} found in the following papers: Koide and Satta, 2004; Park et al., 2009.

2.2 Cork preparation

For the present study, the "cork-wood" granulates extracted from the cork oak trees (Q. *suber*) were used. "Cork-wood" is a raw material with high density, which is not appropriate for the production of wine stoppers. This material does not go through any disinfection method (boiling process) and normally is reused raw as organic fertilizer. "Cork-wood" is a mixture of the denser part of the cork, which has part of the back of the cork bark (woody part), part of the belly (innermost part) and the one that is understood by cork. The cork used for this study was provided by the Catalan Cork Institute (ICSURO). The cork was washed 3 times with demineralized water, dried for 48 hours at 105°C and sieved to obtain PS of 4 mm and 8 mm.

2.3 Cork characterization

A Fourier Transform Infrared Spectroscopy (FTIR) test was performed using Cary 630 FTIR according to the internal protocol PNTM 7.5-54 by triplicates (Ortega-Fernández et al., 2006; Prades et al., 2010; Miranda et al., 2013). Chemical constitution analysis methods have previously been described by Jové et al. (2011). The elemental analysis of C, H, N and O were performed with 4 samples (replicates), using elemental analyser EuroVector EuroEA3000 equipped for analysis of CHNS.

The determination of PZC for each PS of cork (4 mm and 8 mm) was based on the immersion technique (adapted from Fiol and Villaescusa, 2009; Hafshejani et al., 2016). The pH value at the PZC was determined by adding 250 ml 0.1 M NaCl solution into a series of 500 ml plastic flaks. The initial pH of the aqueous solutions was adjusted in the range of 1-10 by the addition of HCl (0,5-1M) or NaOH (0,5-1M). After the pH adjustment, 15 grams of cork were added to each flask and the suspension was shaken for 24 hours, at 40 rpm and 22 ± 1◦C. The solution was finally filtered on 0.45 mm cellulose acetate membrane filter and the final pH was measured using digital pH meter (Metrhom) standardized by NBS buffers. The experiment was performed in triplicates. The variation of pH (ΔpH = initial pH – final pH) was plotted versus initial pH.

2.4 Batch studies

The batch studies were carried out at the Department of Bioscience - Aarhus University (Denmark). To evaluate the effect of PS and pH on the release of OC, the following experimental design was performed: Factor PS (levels 4 mm and 8 mm) and Factor pH (levels 3, 5, 7 and 9). The Kinetics experimental design considered PS as factors (levels 4 mm and 8 mm) and CT (levels 0.5, 1, 3, 12 and 24 hours). All the experiments were performed in triplicates. Blank samples, without cork, were used as control.

The initial composition of the synthetic hydroponic wastewater was constant during the entire experiment (Table 1). Plastic flasks (250 ml) were used to mix the synthetic water and the cork granulate (PS 4 mm and 8 mm). Each flask was filled with five grams of cork and 50 ml of synthetic hydroponic wastewater, resulting in an adsorbent dosage of 100 g of cork per L $^{-1}$. The temperature during the batch essays was constant, approximately 20°C (± 1°C).

2.4.1 Effect of PS and pH on the release of OC

The initial pH of synthetic hydroponic wastewater (SHW) was adjusted to different pH values (3, 5, 7, and 9) either with HCl (0,5-1 M) or NaOH (0,5-1 M) and the SHW was characterized in order to know if initial concentrations were in accordance with the expected range (Table 1). Initial values of OC were considered to be zero. The adsorbent dosage of 100 g L^{-1} was achieved adding the desired amount of adsorbent and aqueous solution into plastic flasks (250 mL). The suspensions were shaken at 40 rpm at 20±1°C during 24 hours. The solutions were filtered and the final pH of filtered samples was measured using a HACH digital probe and the non-purgeable organic carbon (NPOC) was measured.

A factorial ANOVA (4 x 2) was performed in order to analyse main effects and interaction for significance of 4 mm and 8 mm PS and pH 3, 5, 7 and 9 on the release of OC. Post Hoc test (Tukey HSD 5%) were carried out just for the pH independent variable (more than 2 levels) in order to determine the significance of the differences between the means across the levels.

2.4.2 Kinetics

Kinetic experiments were conducted under pH 7, normally based in hydroponic wastewaters (Table 1), by varying the CT: 0.5, 1, 3, 12, 24 hours following the methods previously described. After the pre-established CT, the samples were filtered using a cellulose membrane filter, and non-purgeable organic carbon (NPOC) analysis were performed.

A factorial ANOVA (5 x 2) was performed to analyse the effect of PS (4 mm and 8 mm) and CT (0.5, 1, 3, 12 and 24 hours) on the release of OC. Post Hoc test (multiple comparisons – Tukey HSD 5%) were carried out just for the CT (more than 2 levels) to determine the significance of the differences between the means across the levels. In order to determine the specific relationships between both independent variables (PS and CT) across levels, an analysis of simple effects was conducted, using general linear model.

2.4.3 OC indicators

In order to analyse the data from the batch studies, 3 indicators are proposed. The description of the indicators can be seen below.

$$OC_I = NPOC_f * V$$

OC_I (mg) = mass balance or the mass of OC released. Where, $NPOC_f$ is the final concentration of non-purgeable organic carbon (mg L^{-1}) and V is aqueous volume of the sample (L).

$$OC_{II} = {}^{OC_I}/_{M}$$

OC_{II} (mg of OC / g of cork) = The amount of OC released per gram of cork. Where M is the mass of cork in the samples (g) (adapted from Crespo-Alonso et al., 2013; Hafshejani et al., 2016)

$$OC_{III} = {}^{OC_I * 100}/_{MC_i}$$

OC_{III} (%) = % of OC released related to total OC in the sample. Where MC_i is the initial mass of OC in the sample (mg). For MC_i calculation the initial mass of cork (mg) and the elemental analysis of carbon (%) were considered. The elemental analysis performed showed that 66 % of the cork mass of samples was composed by carbon, regardless the PS (following the methodology described in section 2.2 – cork characterization).

2.4.4 Statistics

As mentioned before, for both experimental stages an ANOVA factorial analysis was carried out using the software IBM SPSS Statistics (version 23), in order to understand the main effects of PS, CT and pH on the chemical release of OC. Only the indicator OC_I was used for statistical analysis.

Moreover, the effects on each factor have been individually analysed by a "trial and error" approach. Therefore, for the kinetic studies, the design of the needed experiments was carried out using Design Expert® (Design-Experts Software Version 7.0). The DoE technique allows verifying whether or not there is a synergistic effect between the variables on the final response (Montgomery, 2007; Formosa et al., 2012), and which parameters can influence the release of OC to a greater extent. The objective was to quantify the results according to the PS and CT, which are related to the kinetics. On this manner, a desirable OC_I can be obtained by varying the parameters under study (i.e.: PS and/or CT). The statistic approach was a response surface methodology (RSM), specifically a historical data to further perform an optimization process by using the results previously obtained. The analysis of DoE results is based on the analysis of variance (ANOVA) (Montgomery, 2007).

3. Results and Discussion

3.1 Characterization of cork

In the following subsections the results from the analysis performed to characterize the cork samples will be presented and discussed.

3.1.1 FTIR

Cork is mainly composed by suberin and lignin (Miranda et al., 2013). Based on the FTIR spectra (Figure 1), most characteristic absorption bands were between 2800 and 3000 cm-1, corresponding to the link C-H of suberin (Cordeiro et al., 1998), similar to other previous results (Miranda et al., 2013).

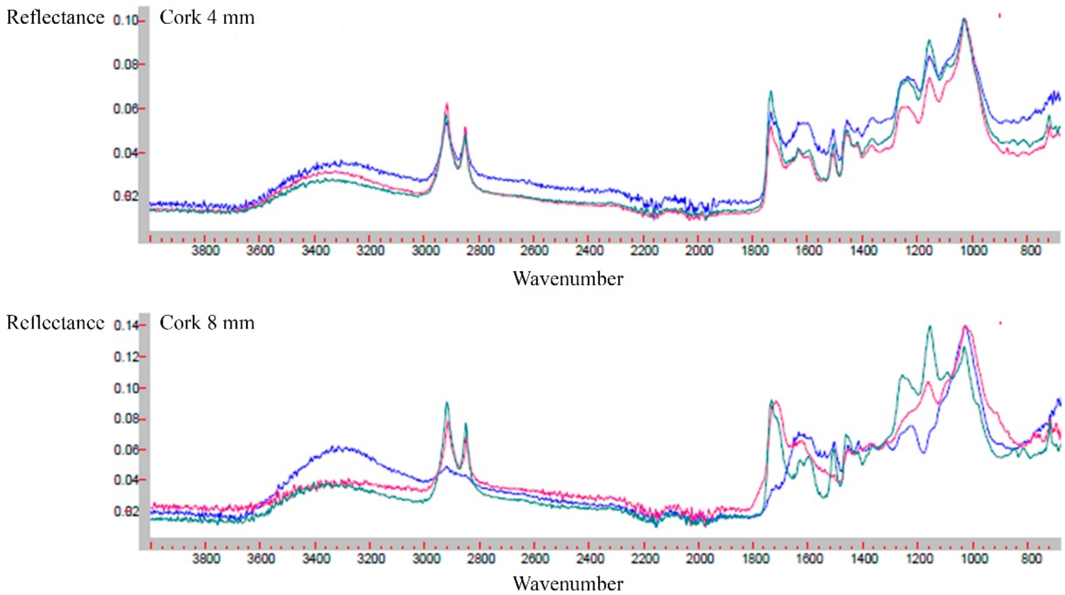

Fig. 1. FTIR results - cork granulate Quercus suber.

The analysed samples showed other bands at 1738, 1630 and 1605 cm-1 corresponding respectively to the C = O bond of suberin and aliphatic acids, C = C bonds of suberin and lignin. Bands from 1600 to 1125 and 1087 to 1035 cm-1 were related, respectively, to different bonds of lignin and C-O bonds of polysaccharides (cellulose + hemicellulose) (Marques et al., 1994). As can be seen in Figure 1, both PS (4 mm and 8 mm) showed similar behaviour regarding their bands and peaks.

The heterogeneity of the samples can be explained by some differences between replicates.

3.1.2 Chemical constitution.

The suberin was the major chemical compound, representing 51.3 % of the total composition (Table 2). Together, suberin and lignin represented 65.4 % of the total chemical composition of cork (Q. *suber*) analysed in this present study. Other authors showed similar results, where the suberin plus lignin of Q. *suber* ranged from 69.8 % - 70.1% (Table 2.). The lignin contents in Q. *suber* presented by Olivella et al. (2011a, 2011b) were, respectively, 2.2 and 1.8 times higher than the lignin content of Q. *suber* on our present study. The Q. *suber* content of suberin showed by Olivella et al. (2011a, 2011b) and by the present study, were respectively, 1.35, 1.54 and 1.8 times higher than Q. *cerris* (Olivella et al., 2011b). Those results suggest that might be a variance in the chemical constitution of cork within species and between species.

Table 2. Chemical composition of cork granulates.

	Species		*Extraction part		
Chemical compounds (%)	Q. *Cerris*	Q. *Suber*	Cork	Belly	Back
Suberin	[2]28.5	[1]51.3 (± 0.2) [2]44.1 [3]38.5	[4]34.4 – 48.7 [5]33.5 – 48.7	[4]33.5 – 53.1	[4]21.1 – 40.7 [5]21.1-40.7
Total lignin	[2]28.1	[1]14.1 (± 0.6) [2]25.7 [3]31.6	[4]14.6 - 25.3 [5]13.4 - 31	[4]14.9-31	[4]18.9 – 28 [5]23.9 – 27.9
Suberin + Lignin	[2]56.6	[1]65.4 [2]69.8 [3]70.1	[4]54.4-71 [5]54.7 – 71.4	[4]55 – 69.8	[4]41.6 – 64 [5]49 – 64.6

* Range: lower and the highest results from different origin area for each extraction part.[1]Results of the present study. The Standard deviation was calculated with triplicates using the software IBM SPSS (values in brackets). [2]Adapted from Olivella et al., 2011b. [3]Adapted from Olivella et al., 2011a. [4]Adapted from Jové et al., 2011. [5]Adapted from Olivella et al., 2013a.

The variations within the same species might be related with the extraction part (belly, back and cork). As can be seen in Table 2, the content of suberin tends to be higher in the belly and cork than in the back part, fact that is in accordance with Jové et al. (2011). The samples of the present study are a mixture of back layer (woody part), belly (innermost part) and the one that is understood by cork, while the samples of Olivella et al. (2011a, 2011b) were just composed by the belly layer. Therefore, the higher content of suberin in our study in comparison with other works could be explained by the heterogeneity of our cork sources.

This heterogeneous composition confers cork a unique characteristic and makes it a very interesting natural material to investigate (Olivella et al., 2013a). However, not much is known about the influence of the chemical composition of cork on the release of OC.

3.1.3 Elemental analysis

In our samples, carbon was the main element, representing 61.7 % of the total mass of the sample, a similar result obtained from other authors (Olivella et al., 2011b), and can correspond to the ranges of cork and belly (extraction parts) founded in literature (Table 3).

The proportion of material coming from belly and cork layers of our samples might be greater than the back layer, justifying the previously mentioned highest content of suberin. In fact, the content of carbon from Q. *cerris* is slightly lower than the results from Q. *suber*, which might be related to the lower content of suberin mentioned in the previously section (Table 3).

Table 3. Elemental composition of cork granulates.

	Species		*Extraction part		
Elements (%)	***Q. Cerris***	***Q. Suber***	***Cork***	***Belly***	***Back***
Carbon (C)	[2]50.7	[1]61.7 (± 0.97) [2]61	[3]58.5 – 63.1	[3]60.2 – 62.5	[3]51.5 – 59.7
Hydrogen (H)	[2]7.3	[1]7.7 (± 0.2) [2]8.7	[3]7.1 - 8	[3]6.8 - 9	[3]6.6 – 7.3
Nitrogen (N)	[2]1.73	[1]0.68 (± 0.05) [2]1.7	[3]1.3 – 2.1	[3]1.3 – 3.1	[3]1.2 - 2
Oxygen (O)	[2]31.4	[1]29.8 (± 1.14) [2]22.57	[3]26.8 – 36.1	[3]28.4 – 36.1	[3]31-42

* The range: lower and the highest results from different origin area for each extraction part.[1]Results of the cork granulated used for this study (Q. *Suber*). The Standard deviation was calculated with triplicates using the software IBM SPSS (values in brackets). [2]Adapted from Olivella et al. 2011b [3] Adapted from Olivella et al. 2013b

The organic nitrogen composition might be an issue to be considered in the scope of selecting organic by-products as substrates on NBS for water treatment. The results of Masi et al. (2016) showed an increase of total Kjeldahl nitrogen, which was probably related to the release of organic nitrogen from the substrate (coconut fibber). The organic nitrogen released will be mineralized, and eventually, will change to mineral forms, such as ammonium, nitrates and nitrites. Moreover, the release of greenhouse gases such as CO_2 and N_2O can be increased when organic filter media is used. The increment of organic C and N can lead to higher greenhouse gases emissions in CWs and denitrification process can increase N_2O emissions (Gentile et al., 2008; Maucieri et al. 2017).

Therefore, the nitrogen released from the substrate needs to be addressed during the design of such technologies. In our study, the nitrogen content of cork samples represented less than 1% and was lower than all results founded in the literature (Table 3), suggesting a low risk regarding the release of organic nitrogen.

3.1.4 PZC

The PZC can be defined as the pH value in which the surface of the biosorbent has zero charge (or the same number of positive and negative charges). Biosorbent surface net charge plays an important role in the sorption/desorption processes, and to explain protonation / deprotonation behaviour in the aqueous medium. As can be seen in Figure 2, performing the immersion technique, the PZC from granulated cork were between pH 5.5 and 5.8, respectively, to PS 8 mm and 4mm.

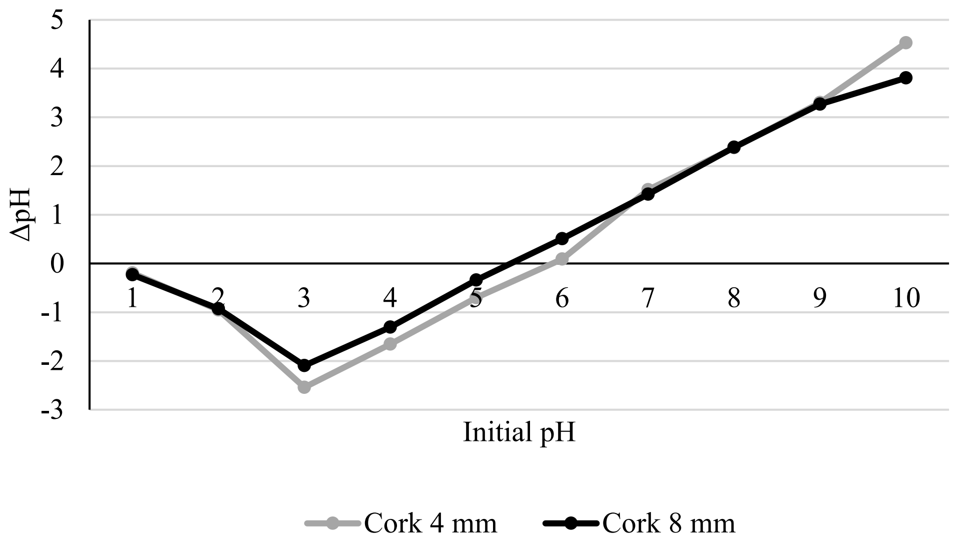

Fig. 2. Point of zero charge of cork (4 mm and 8 mm).

Above pH 6, the surface of the samples is negatively charged, mainly because of the presence of phenolic -OH or carboxylic groups (-COOH). However, the results of Fiol and Villaescusa (2009) showed a PZC of around pH 3,5 regardless the methodology used.

As previously mentioned (section 3.1) the chemical composition of cork might vary according the species and the extracted part and, therefore, different chemical compositions might lead to different behaviour of protonation / deprotonation process that can influence the PZC.

3.2 Effect of PS and pH on the release of organic carbon

The extractives of cork include several organic compounds such as waxes, triterpenes, fatty acids, glycerides, phenols and polyphenols. The pH influences the chemical speciation, the diffusion rate of solutes, the dissociation of sorbent functional groups and the sorbent surface charge (Rahmani et al., 2010; Glestanifar et al., 2016). It is assumed that the PS affects the release of OC, since it is directly related to surface area, although this effect might vary according to the initial wastewater pH.

The results indicated that the null hypothesis can be rejected for PS ($F(1,16) = 293 > 4.49$, $p = 0.05$) and pH ($F(3,16) = 9.61 > 3.24$, $p = 0.05$), indicating the existence of main effects. On the other hand, there was insufficient evidence to reject the null hypothesis of interaction effect ($F(3,16) = 2.66 < 3.24$, $p = 0.05$). Therefore, the main effects of PS and pH are discussed below (Figure 3.).

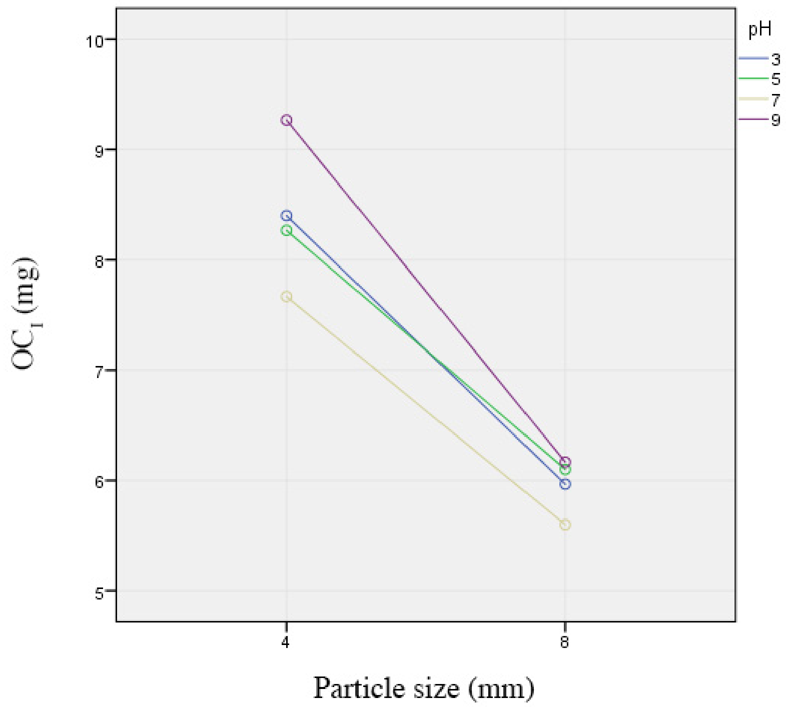

Fig. 3. Effect of PS and pH on the release of OC (mg).

Regardless of the pH, as the PS is smaller the higher the release of OC, due to more available surface area. Regarding the effect of pH, the release was not affected from pH 3 to 7, but a significant effect was obtained from pH 7 to 9 (Tukey HSD, 5%), with higher release at pH=9, perhaps due to the deprotonation of phenolic –(OH) or carboxylic groups (–COOH) at pH 8-9. No significant interaction effect was obtained (p=0.083). The main effect of PS (95% of the variance) is stronger than the main effect of pH (64% of the variance).

Moreover, 95% of the variance on the release of OC can be attributed to the PS, while 64 % was explained by the variance of initial pH, fact, which, suggest that the main effect of PS is stronger than pH. Therefore, comparing each PS across levels of pH, separately, the pH did not affect the release of OC for PS 8 mm. On the other hand, for PS 4 mm, the differences between pH 3-7 and 7-9 were statistically different, decreasing and increasing, respectively. These results might indicate that as lower the PS as greater can be the effect of pH on the release of OC.

3.3 Kinetics

The null hypothesis can be rejected for PS ($F(1,20) = 931.33 > 4.35$, $p = 0.05$) and CT ($F(4,20) = 232.93 > 2.87$, $p = 0.05$), indicating the existence of main effects of CT and PS on the release of OC. The results showed significant effect of PS and CT on the release of OC, increasing with smaller PS ($p<0.05$) regardless the CT. Indeed, the mass of carbon released by PS 4 mm was two times higher than the release of OC by PS 8 mm for all CT, except for CT 3 hours which was 1.7 time higher. This may indicate the presence of a possible inverse exponential relationship between PS and release of OC.

The post hoc tests (Tukey HSD, 5%) indicate that the multiple comparisons across levels of CT were significant, increasing the release of OC when the CT increases, regardless the PS (Figure 4).

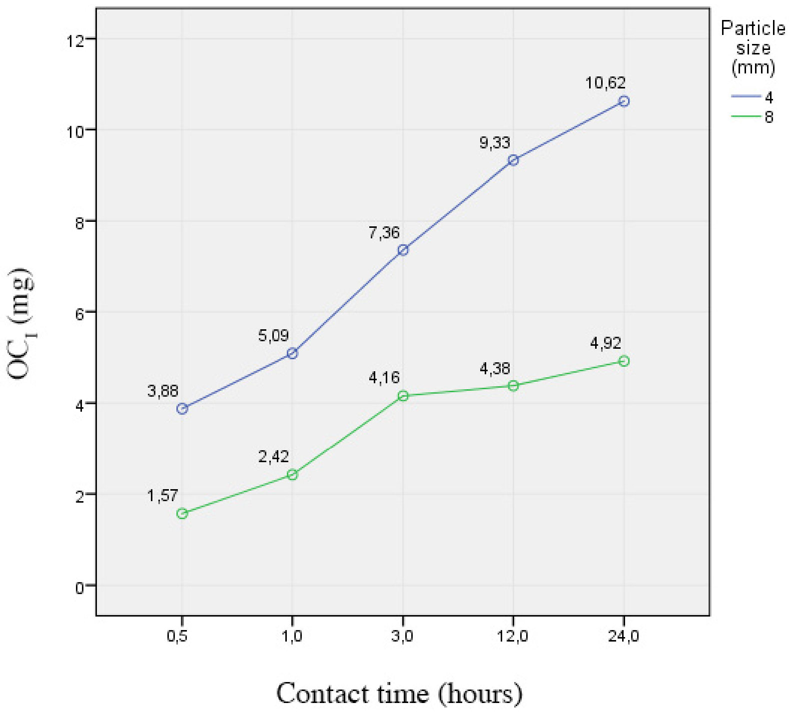

Fig. 4. Effect of CT and PS on the release of OC. Fig. 4. Effect of CT and PS on the release of OC.

An interaction effect was noticed on the release of OC ($PS*CT - F(4,20) = 28.87 > 2.87$, $p = 0.05$). All eta squared ($\eta 2$) were greater than 0.14, indicating that both, main and the interaction effects, are representing great influence on the release of OC. However, while the main effects of PS and CT represents 98% of the release of OC, the interaction effect between then represents 85%, suggesting that the main effects of PS and CT are slightly greater than the interaction effect.

The pairwise comparison results showed no significant differences on the release of OC in the periods, 3-12 hours and 12-24 hours, for PS 8 mm. However, the release of OC after 24 hours was significantly higher than after 3 hours. Moreover, there was significant differences between all the means across CT, for PS 4 mm. These results indicate that in the period of 3-12 hours and 12-24 hours the release of OC was influenced by PS and/or that there is an interaction between the independent variables. This result might indicate that the CT may have a stronger effect on PS 4 mm than on PS 8 mm, in other words, with smaller PS the effect of CT is higher on the release of OC.

Considering the mass of carbon released after 24 hours as the total released, it is possible to conclude that approximately 32 % and 11 % of total carbon released took place during the 3 to 24 hours period, respectively for PS 4 mm and PS 8 mm. On the other hand, more than 70% of the released OC occurred during the first 3 hours, for both PS. Therefore, the release of OC might get slower when the CT increases. In addition, this effect might be stronger with the increase of PS. Considering that the specific surface area and PS are inversely related, the surface area might have an effect not just on the amount of carbon released but also at which speed the release of carbon takes place.

Table 4 summarizes the results following the RSM obtained using the software Design Expert® for the best fitted model. Both factors (PS and CT) present significant effect on the response (OC_I) in the range of the study. In this case, the best fitted model is a response surface reduced cubic model which presents interaction between the factors under study (PS and CT) with a p-value<0.05. In addition, there is a cubic interaction (see factor CT^2PS and p-vales<0.05 in Table 4). Besides, a quadratic and a cubic effect on the response is presented for the CT factor in the range of the study.

Table 4. ANOVA for Response Surface Reduced Cubic Model.

Factors	Sum of squares	[a]df	Mean square	F-value	[b]cv	[c]ρ-value
Model	225.73	6	37.62	329.91	2.60	$\rho < 0.05$
PS	5.10	1	5.10	44.72	4.35	$\rho < 0.05$
CT	41.45	1	41.45	363.47	4.35	$\rho < 0.05$
PS*CT	11.57	1	11.57	101.47	4.35	$\rho < 0.05$
CT^2	8.95	1	8.95	78.49	4.35	$\rho < 0.05$
CT^2PS	0.99	1	0.99	8.66	4.35	$\rho < 0.05$
CT^3	12.45	1	12.45	109.23	4.35	$\rho < 0.05$
Lack of Fit	0.33	3	0.11	0.99	3.10	$\rho > 0.05$
Pure Error	2.29	20	0.11	-	-	-
Total	228.36	29	-	-	-	-

[a]df = Degrees of freedon. [b] Critical value of F distribution. [c]$\rho < 0.05$ = significant. $\rho > 0.05$ = not significant

PS factor does not fit in the proper manner when is in quadratic and/or cubic function, for that reason these terms where discarded on the final equation. In addition, it should have been emphasized that the lack of fit is not significant. Consequently, there is only a 0.01% chance that the model occurs due to noise.

All the results derived from the modification of any of the controllable variables can be translated into a predictive mathematical model. This model can quantitatively predict the response within the operating range of controllable variables. It can also give some suitable formulations when a certain response is required. The model only incorporates the statistically significant factors and interactions. Therefore, the mathematical model can be written by the following equation:

$$OC_1(mg\cdot) = 5.471 + 2.137 \times CT - 0.506 \times PS - 0.069 \times CT \times PS - 0.163 \times CT^2 + 0.002 \times CT^2 \times PS + 0.004 \times CT^3$$

Figure 5 presents the surface plot obtained for OC_I. An increase of PS or CT lead to a decrease of OC_I. When both factors are increased their combined effect is found to be lower than the expected form considering the sum of each factor separately. Therefore, it can be concluded that there is significant negative interaction between both factors: as higher the PS the lower the response of OC_I, as we previously explained.

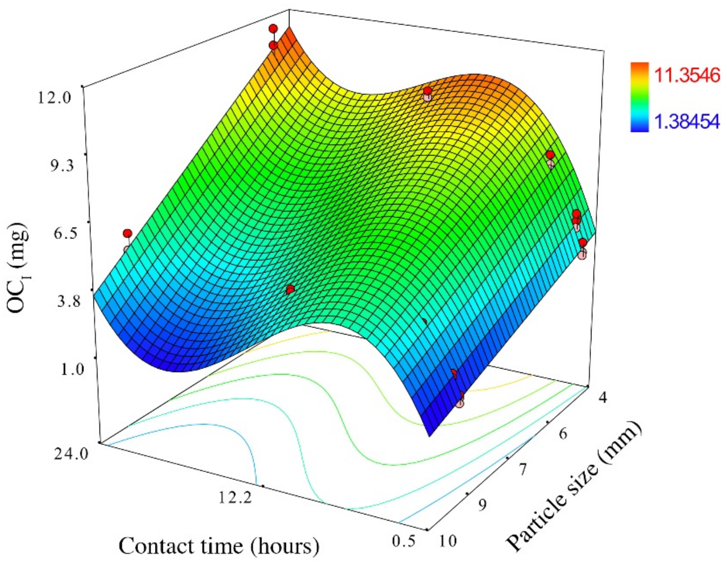

Fig. 5. Kinetics - response surface plot.

3.4 Cork as an organic carbon source for denitrification.

The potential of cork as a carbon source for denitrification was estimated by calculating the amount of carbon released (g) and the amount of water that could be treated in a hypothetical batch biofilter during 24 hours. For those calculations, the following assumptions were considered: theoretical stoichiometry for denitrification was considered as 1 g of OC per g nitrate-N (Zhai et al., 2013); two hypothetical batch biofilters with unknown dimensions and a volume of 1 m^3 filled up with each PS of cork (4 mm and 8 mm); the mass of cork for each batch biofilter was calculated considering the density of cork as 123 Kg /m^3 and 125 Kg /m^3 for, respectively, 8 mm and 4 mm PS (Source: internal data from ICSURO). Moreover, the averages of OC_{II} in mg of OC released / g of cork (section 2.3.3) at 24 hours were used for the calculations. The composition of hydroponic wastewater to be treated can be seen in Table 1 and temperature was considered to be the same at lab conditions (sections 2.3).

Therefore, the chemical release of OC, would be approximately 265 g (PS 4mm) and 120 g (PS 8 mm) after 24 hours. If one considers that all the OC released is consumed by the denitrification process it means that 3.9 m^3 and 1.8 m^3 of hydroponic wastewater could be treated, using PS 4 mm and 8 mm, respectively.

It is well known that PS is a crucial parameter when NBS are designed for wastewater treatment. The PS besides influencing the hydraulics of the system will also affect the performance of contaminants removal by adsorption, complexation and precipitation, as well as the microbiological process; since it influences the biofilm density and growth (Vymazal, 2007). The results mentioned above showed that by using a 4 mm PS, the amount of water treated after 24 hours of batch treatment was more than 2 times that for 8 mm PS. Moreover, results of Capodici et al. (2014) showed that the PS might have a greater influence on OC release than the total OC content itself. The author compared several materials, including cork. Cork presented the lowest result regarding the release of OC, even though it had the highest total OC content. Fact, which were related to its biggest PS of cork in comparison with the other materials. Moreover, the kinetics results of our study highlighted that OC release from cork granulate decreases with time, and this effect is stronger when the PS increase. Therefore, the effect of PS on the release of OC should be considered when NBS treatments are designed using cork as filter media and OC source to enhance denitrification.

In one hand, the chemical release of OC_{III} was less than 1% of the total content of carbon after 24 hours, for both PS, suggesting that cork could be suitable for a long-term carbon organic source (Figure 6). On the other hand, as mentioned before (section 3.3), the release of OC gets slower with time, fact which could be a limitation regarding cork long-term efficiency as carbon source. In the present study, after 24 hours, for PS 4 mm and 8 mm respectively, 2.12 and 0.98 mg of OC was released per g of cork. Capodici et al. (2014) results showed that, after 50 hours a peak of carbon release was reached being 5.6 mg of OC / g of cork. After 50 hours the increment of carbon released was slower and linear.

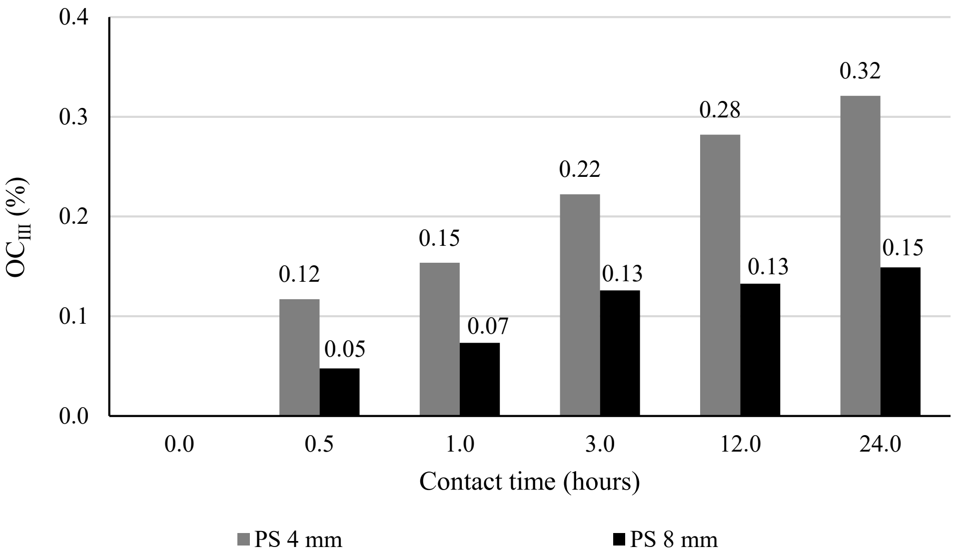

Fig. 6. Effect of CT and PS on the release of OC (%)

Those results suggest that even though the OC release gets slower with time it keeps taking place, fact which highlight the importance of models to predict it.

However, it is important to consider that the performance of cork as carbon source will be influenced by real scale features such as, type of treatment (bio filters, CWs, green walls and others), design and operational factors (flow type, saturated or unsaturated conditions, retention time, hydraulic and pollutants load, among others), cork features (chemical composition) and environmental conditions (temperature, pH). Therefore, further studies on long-term efficiency of cork as an OC source are needed.

3.5 An issue to be regarded: Phenolic compounds release

Several phenolic compounds are persistent pollutants with high toxicity even at low concentrations (Villegas et al., 2016), and their accumulation in the environment can lead to biodiversity loss and to increase human health risk (Sun el at. 2015; Stefanakis and Thullner, 2016; Villegas et al., 2016).

Phenolic compounds were not measured in the present study, although this potential issue needs to be addressed once the use of cork as filter media in NBS may lead to an increase of biorecalcitrants (phenolic compounds) in the effluent. For example, the cork boiling water, which is acquired after the raw cork granulate is boiled up to 1.5 hours, have high organic load of biorecalcitrant compounds, resulting in an increase of chemical oxygen demand and total phenolic compounds (TPC) concentration (Gomes et al., 2018). Moreover, the TPC of the cork boiling water can vary from 1.0-3.5 g/L, which is substantially high when compared to the toxicity range for phenolic compounds which is 0.009 – 0.025 g/L (Kulkarni and Kaware, 2013; Gomes et al., 2018).

In this regard, NBS, such as CWs, have been proposed as an economic and environmentally friendly treatment to remove phenolic compounds from wastewaters (Kurzbaum et al., 2010; Stefanakis and Thullner, 2016; Gomes et al., 2018). The main removal mechanisms of phenolic compounds taking place in CWs are sorption, phytoremediation (plant uptake) and volatilization, although biodegradation seem to be the key removal process of phenolic compounds in this type of treatment (Imfeld et al., 2009; Stefanakis and Thullner, 2016; Gomes et al., 2018).

In one hand, biodegradation of phenolic compounds taking place in NBS could overcome the issue related to the release of phenolics by cork. The results from Kurzbaum et al. (2010) showed that in a subsurface flow CW, most of phenolic compounds removal was due to bacterial colonization of roots and gravel bed, while abiotic processes like evaporation and adsorption were considered negligible. Gomes et al. (2018), studied the removal of phenolic compounds from cork boiled water using a horizontal subsurface flow CWs (lab scale). The removal achieved was higher than conventional biological treatment, suggesting the great potential of this type of treatment regarding the removal of phenolic compounds released by cork. However, both authors used conventional substrates like gravel (Kurzbaum et al., 2010) and light expanded clay (Gomes et al., 2018), while not much is known about the increment of phenolic compounds when cork is used as substrate in NBS treating wastewaters.

On the other hand, Calheiros et al. (2018) studied micro biodiversity of treatment wetland treating winery wastewater using cork stoppers as substrate (granulate 3-7 mm), what means a double load of phenolic compounds, since winery wastewaters have high concentration of polyphenols. The author results showed that the gender *Pseudomonas spp*. and *Bacillus spp.* were dominant and most important they were able to survive in such conditions. According to Nair et al. (2008) *Pseudomonas spp*. and *Bacillus spp*. are efficient at biodegrading phenolic compounds. This might suggest that despite the toxic effect of phenolic compounds on microbial communities, the expected release of phenolic compounds from cork could be compensated by biodegradation occurring in NBS such as CWs.

However, three aspects need to be highlighted. First, biodegradation of phenolic compounds is a complex process. Besides depending on the composition and structure of the phenolic compounds is also strongly affected by environmental conditions such as pH, temperature and dissolved oxygen (Zhao et al., 2018). Secondly, cork is a heterogenic material regarding its chemical constitution. As was discussed previously (Section 3.1.2), the chemical constitution of cork might vary according with the species and extraction part, fact which might influence the types of phenolic compounds released. Thirdly, depending on the stage of cork acquirement (raw cork or after boiling process) the chemical properties will be certainly different. Perhaps, the reuse of cork granulates generated during the production of stoppers or even the stoppers themselves, would be a saver alternative, since both passed by boiling process which extracts most of phenolic compounds.

Therefore, the release of phenolic compounds needs to be considered, when design NBS using cork as substrate and “internal” OC source. Moreover, laboratory and real scale studies focused on understanding and overcoming this limitation are recommended to ensure safe reuse of cork as substrate in NBS.

4. CONCLUSIONS

The main compound and element of cork are Suberin and carbon, representing respectively, more than 50% and 60% of the sample composition. Also, when comparing the results with other researches, it was noticed that might be a variance on the content of suberin across species, within the same species and depending on the extraction part (Belly, cork and back). Furthermore, the lignin content seems to vary within Q. *sube*r specie. However, no statistical analysis was performed to validate this hypothesis. Nevertheless, as not much is known about the influence of the chemical composition of cork on the release of OC, further researches on it might facilitate standards to ensure an efficient performance of cork as carbon source in accordance with its chemical constitution.

The PZC of cork was between pH 5 and 6, which was different than the result founded in literature (3.5). This difference was attributed to the variance of cork chemical composition which might lead to different behaviour of protonation / deprotonation.

As smaller the PS granulometry the higher is the OC released, regardless the pH or CT. Regarding the pH main effect, the results suggest that as lower the PS as stronger the effect of pH on the release of OC. The kinetics results showed that as the CT increases the release of OC is increased as well, regardless the PS. However, an interaction effect between PS and CT was noticed, indicating that as smaller the PS becomes the higher the effect of CT has on the release of OC. In addition, more than 70 % of the carbon released took place during the first 3 hours for both PS, indicating that the release of OC might get slower as CT increases. Those results highlight the effect of surface area affects the amount carbon released and as well the velocity that the carbon is released.

When using cork as carbon source of NBS treating wastewater, the effect of PS on the release of OC can play an important role at designing such systems. Estimations showed that the amount of water treated by using PS 4mm was more than 2 times that would be for PS 8 mm, considering that all carbon released would be consumed by denitrification. In this regard, the results of surface response methodology indicate that optimization could be performed to facilitate the design of technologies considering the interaction between PS and CT at releasing OC.

Using cork as a source of carbon for denitrification seems to be a promising alternative to reduce costs and environmental hazard of NBS treating wastewaters with low carbon content and high nitrates. By using organic substrates, the development of microbiota also might be facilitated and thus, microbiological removal process. However, this practice might lead to losses of hydraulic conductivity and adsorption surface area, fact that can influence treatment efficiency. Indeed, at real scale and long-term conditions cork behaviour at releasing OC will be affected by external factor (type of treatment, design and operation factors, cork features and environmental conditions).

The release of phenol compounds by cork can be a restriction for using the material as filter media in NBS. However, the biodegradation of such compounds seems to be efficient in NBS, fact which could help overcome this restriction. Indeed, using cork granulate acquired after boiling process might reduce the risk of releasing phenolic compounds in NBS treating wastewaters.

Validating the use of cork as a carbon source for denitrification at real and long-term scales can be an interesting line of research. Furthermore, the effect of such practice on the release of greenhouse gases and phenolic compounds also should be considered. Nerveless, the reuse of organic by-products as filter media seems to be an environmental and economic friendly alternative to enhance denitrification in NBS. This approach can help preserve natural capital, reduce the dependency of external inputs, treatment costs, increase self-efficiency, all of it leading to a sustainable technological development in the scope of wastewater treatments.

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Chapter 8 Third article

Crushed Autoclaved Aerated Concrete (CAAC) a potential reactive filter media to enhance phosphorus removal/recovering in nature-based solutions – preliminary batch studies

J.A.C. Castellar et al. / Water 11,7 (2019) 267–276

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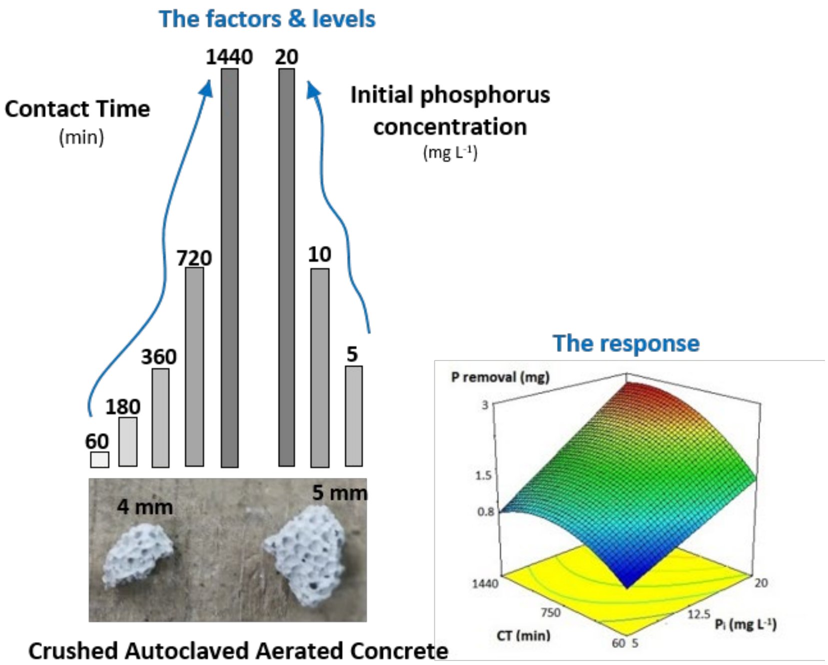

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Crushed Autoclaved Aerated Concrete (CAAC), a Potential Reactive Filter Medium for Enhancing Phosphorus Removal in Nature-Based Solutions - Preliminary Batch Studies

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Abstract: Phosphorus (P) is a limited resource and can promote eutrophication of water streams and acidification of oceans when discharged. Crushed autoclaved aerated concrete (CAAC), a by-product from demolition, has shown great potential for recovering P. The potential of CAAC to be used in nature-based solutions as a P-reactive filter medium was evaluated by performing preliminary batch essays. Here, we evaluated the interactions and main effects of the initial concentration of P (P_i; 5, 10 or 20 mg L^{-1}), particle size (PS; 4 or 5 mm) and contact time (CT; 60, 180, 360, 720 and 1440 min) upon the removal. We performed physical and chemical characterization to understand the removal processes. Data collected were fitted in adsorption kinetic models. The statistical analysis showed a significant interaction between CT and P_i, with the combination of its main effects stronger on P removal than each one separately. Intriguingly, we noticed that the higher the concentration of P_i, the faster and higher the removal of P. Contrary to expectations, PS 5 mm showed higher removal rates than PS 4 mm, indicating that besides adsorption, other unidentified chemical processes are in place. Further studies using columns/pilots with real wastewater are recommended for a future follow-up.

1. Introduction

Phosphorus (P) is a limited resource and an essential nutrient for the growth of plants, and it is found on Earth, mainly by geological natural weathering processes [1,2]. P from nature sources has been widely exploited for its use in agriculture (fertilizer) and industry. Moreover, the discharge of wastewaters with high concentrations of P and the intense use of P compounds in agriculture (chemical fertilizers) has led to an increase of P loading within ecosystems [3].

The accumulation of P leads to changes in terrestrial, aquatic and marine ecosystems, by eutrophication and ocean anoxic events; both processes are associated with loss of biodiversity and thus a reduction of natural resilience [1,4–6]. According to Karczmarczyk et al. [6], 1 g of P released into water bodies promotes the growth of up to 100 g of algae, enhancing eutrophication of surface water. Modelling analysis performed by Rockström et al. [1] has shown that P inflow into oceans will increase 10 times in the next 1000 years, leading to extreme anoxic conditions. Moreover, the author suggests that such an input of P is not feasible for more than 1000 years, considering the estimated amount of phosphate natural reserves.

In this regard, nature-based solutions (NBS) have been rising as a sustainable way to both remove and recovery P from wastewaters. NBS promote an efficient use of natural resources, human well-being and a socially inclusive green growth by replicating natural process and integrating ecosystem services into the human environment [7–9]. Several authors have demonstrated that NBS, such as constructed wetlands (CWs) and biological filter beds are environmentally friendly and efficient at removing P from water [5,6,10–12]. In such systems, the filter medium plays an important role at recovering P, mainly by promoting absorption and precipitation processes [5,13,14]. Therefore, studies on the efficiency of reactive filter mediums for recovering P are important for enhancing the ability of NBS at removing P from wastewaters.

The reuse of byproducts as reactive filter mediums is an important strategy regarding the connection of production chains and technological development in the scope of wastewater treatment. Such approaches promote a circular economy, an efficient use of resources and preservation of natural capital, mainly by reducing withdrawal of raw materials and water. Therefore, reusing tobermorite-rich waste, such as the scrap granulate generated from the production of crushed autoclaved aerated concrete (CAAC) or from the demolition of facilities built with this material, can be an interesting approach regarding recovery of P from wastewaters [4,5]. In addition, reusing this material also helps to promote the reuse of energy and to preserve natural capital, as concrete is embedded with high energy and raw material [15].

CAAC is a highly available building material used worldwide, mainly for masonry, insulation or structure reinforcement (lintels and roof/floor and wall panels) [5,6]. Several authors have demonstrated the potential of reusing CAAC for P removal [5,6,10,14–16]. For instance, estimations have shown that approximately 590 kg or 1.2 m^3 of CAAC would be required to treat wastewater for one year from a household of five persons [5]. This is an impressive result considering that a CW requires a minimum of 2 m^2/person [17].

For P removal, the potential processes promoted by CAAC are adsorption of P, chemical precipitation of P with calcium cations (Ca^{+2}) and the formation of Ca-P–silicates aggregates, as the major compound of tobermorite is ($Ca_5Si_6O_{16}(OH)_2{\cdot}H_2O$), a calcium silicate hydrate (CSH) known for its high content of calcium and silicate [5,15,16]. Furthermore, physical properties of CAAC, such as its high specific surface (30 to 81 m^2 g^{-1}) and low density (275 to 400 kg m^{-3}) [5,10,18], highlight the great potential of this material for P adsorption as compared to sand or gravel, the usual filter mediums used in CWs. In addition, CACC seems to have a great potential for recovering P for further reuse (fertilizer and industrial purposes). The product generated by using tobermorite-rich waste compounds to recover P from water has the promise to meet the requirements of the industry (phosphate rock substitute) and fertilizing features [19]. The total P in the mineral content varies from 11% to 13%, which is comparable to phosphate rock (apatite) with a 14% total P content. Therefore, for sustainability and maintaining policies of circular economy, CAAC can be considered as an accessible and environmentally-friendly reactive medium with a high potential for NBS.

However, several factors, such as adsorbent dosage (g L^{-1}), pH, contact time (CT) and P initial concentration (P_i; mg L^{-1}) can influence the efficiency of materials based on calcium silicate hydrates, such as CAAC. Comparing the performance of a CSH ($CaO_3Si{\cdot}H_2O$) with $Ca(OH)_2$ and $CaCl_2$ at removing and recovering P has shown that the P removal efficiency varies from 1.2% up to 96% when varying the adsorbent dosage from 10 g L^{-1} to 20 g L^{-1} for CSH, while $CaCl_2$ removed only 49% of P [2]. Further experiments have also shown that CHS (P removal = 80%) perform better performance at removing P than $CaCl_2$ (P removal = 65%) [16]. Indeed, the lower P removal promoted by $CaCl_2$ is probably due to variations of pH, which affect the available ion species as well as the solubility of the products formed [16]. These results highlight that both the effect of the adsorbent dosage and the pH might play an important role in P removal processes of such materials.

In addition, P_i can play an important role in the performance of CSH-based materials, such as CAAC, with respect to P removal. The performance of autoclaved aerated concrete (AAC) at removing P under different P_i, as assessed by isotherm experiments, revealed that the P sorption increased as P_i increased [6]. A similar tendency was observed when using recycled crushed concrete: P removal increased linearly as P_i increased [15]. The authors suggest that, at higher P_i, other processes beside adsorption can take place, such as complexation and precipitation [15]. Considering that P_i can vary across different types of wastewaters, understanding the role of P_i with respect to the P removal potential provided by CAAC can play an important role for upscaling NBS for treatment of real wastewaters. Moreover, the PS not only influences the hydraulic design of NBS used for treating wastewaters but can also affect the sorption capacity of the material, mainly due to its effect on the specific surface available for sorption. As a general rule, the smaller the PS, the higher the specific surface and thus the higher the sorption capacity.

To the best of our knowledge, there is no information within the scientific literature about a study that correlates the effects of P_i, particle size (PS) and CT on the removal of P by CAAC. Therefore, due to the important roles of P_i, PS and CT on the removal of P, we tested this in preliminary batch studies. In this regard, our main goal was to investigate the interactions and main effects of P_i, PS and CT on the P removal promoted by CAAC. We have now obtained a model from the batch preliminary studies which helps to clarify the roles of P_i and PS and CT and to facilitate further optimization. The information about the effects and interactions between those factors can be expected to facilitate the further use of CAAC as filter medium in NBS for treating wastewaters rich in P. Finally, in order to better understand the removal of P provided by CAAC, we discuss possible P removal processes that occur when CAAC is used as a filter medium, based on the literature. Further validation of the model, both in the laboratory and on a real scale, is now recommended.

2. Materials and Methods

2.1. Adsorbent Preparation

During the process of building with CAAC, the blocks usually need to be cut in order to fit the design. Therefore, the tested material was supplied as 30 kg blocks, which were to be discarded by the company YTONG (https://www.ytong.es). Blocks were manually crushed and sieved using a mechanical sieve to obtain a PS of either 4 mm or 5 mm [15]. The sample was homogenized and quartered to a 1/16 splits to achieve representative subsamples. Afterwards, the material was washed three times with Milli-Q water to eliminate small particles (dust).

2.2. Chemical and Physical Characterization of the Adsorbent

Initial analysis of the specific surface area was performed following the BET single point method, with a Micrometrics Tristar 3000 porosimeter, and density was determined with helium pycnometer.

X-ray diffraction (XRD) initial analysis were performed with a Bragg Brentano Siemens D-500 powder diffractometer with Cu Kα radiation for a qualitative analysis of the crystalline phases. X-ray fluorescence (XRF) initial semi-quantitative analysis was conducted with a Philips PW2400 X-ray sequential spectrophotometer.

Initial analyses of Fourier-transform infrared spectroscopy (FTIR) were performed to evaluate chemical changes in the adsorbent, and to determine the correlation with potential chemical processes involving P removal. FTIR was performed by attenuated total reflectance (ATR) by using a FT-IR Spectrum TwoTM (Perkin Elmer, Walthan, Massachusetts, USA), with a working range from 400 to 4000 cm^{-1}.

2.3. Kinetic Bath Studies

2.3.1. General Information

Kinetic batch studies were carried out at the Department of Bioscience—Aarhus University (Denmark). The experimental design was based on the following factors and levels: P_i, 5, 10 or 20 mg L^{-1}; PS, 4 or 5 mm; and CT, 60, 180, 360, 720 and 1440 min.

Preliminary tests were performed using the conventional methodology for kinetics experiments [20]. Samples were placed in individual flasks, filtered and analyzed [20]. Unexpected and apparently conflicting results were obtained for P removal rates across CT; namely, the removal rate of P was greater at lower CT than at higher CT. In addition, significant differences between repetitions were also noticed, which can likely be attributed to the chemical heterogeneity of the material. Further, as the chemical composition of concrete blocks can vary across material surface and depth, putting each sample into an individual flack might lead to differences in P removal rates, related to the chemical heterogeneity of the absorbent rather than to the variables (PS, P_i and CT), reducing the reliability of the experiment.

The following method was used to reduce the effect of material heterogeneity on the removal of P and to ensure a reliable experimental design. The P solutions were prepared using KH_2PO_4 and tap water, to maintain the buffer capacity of the solution and to mimic real conditions (tap water characteristics can be seen in https://www.aarhusvand.dk). P_i represents the typical concentration of P in real wastewaters, which can vary from 5 to 10 mg L^{-1} and up to 20 or 30 mg L^{-1} in extreme cases [20]. All experiments were performed in triplicate.

For each treatment (P_i5PS4; P_i5PS5; P_i10PS4; P_i10PS5; P_i20PS4; P_i20PS5), three glass bottles were settled up, each one representing one repetition. Each crystal bottle (repetition) was filled up with the 0.2 L of the correspondent P_i solution, and 10 g of adsorbent was added, resulting in an adsorbent dosage of 50 g L^{-1}.

Experiments were conducted under constant room temperature (20 °C ± 1 °C). Aliquots were shaken at 20 rpm (20 °C ± 1 °C), and at each pre-established CT (60, 180, 360, 720 and 1440 min), 0.5 mL of supernatant solution were sampled for P analysis and pH was measured. P analyses were performed according to the ascorbic acid method [21] using a Shimadzu UV-1800 spectrophotometer. Results were adjusted taking into account the amount of P used for each sampling time. Indeed, the amount of P taken represented less than 0.3% of the mass of P (mg) in the samples for all CT. These variations were not considered significant as they were within the expected error (0.5%).

2.3.2. Phosphorus Removal Indicators

All calculations were made in triplicate. The P removal indicators were:

$$mP_{(t)} = [P]_{(t)} \times V_{(t)} \tag{1}$$

where $mP_{(t)}$ (mg) is the mass of P removed at a certain time, $[P]_{(t)}$ is the concentration of P (mg L^{-1}) in function of sampling time and $V_{(t)}$ is the volume (L) at the sampling time, discounting the volume of aliquots taken for sampling (which is accumulative);

$$q_{(t)} = \frac{mP_{(i)} - mP_{(f)}}{M} \tag{2}$$

where $q_{(t)}$ (mg g^{-1}) is the mass of P (mg) removed per gram of CAAC at certain time (adapted from [22]), $mP_{(i)}$ and $mP_{(f)}$ are the initial and final mass of P (mg) in the aqueous solution, respectively, and M is the mass of adsorbent (CAAC). Both, $mP_{(i)}$ and $mP_{(f)}$ were calculated using $mP_{(t)}$;

$$P_{\%} = \frac{mP_{(f)} \times 100}{mP_{(i)}} \quad (3)$$

where $P\%$ is the percent of P removed at a certain time. $mP_{(i)}$ and $mP_{(f)}$ were described previously.

2.3.3. Statistics

The interactions and main effects of the variables were analyzed by running split-plot ANOVA (repeated measures) and two-way ANOVA. The software used was SPSS version 23 (International Business Machines corporation – IBM, Armonk, New York, USA). For statistical purposes, P removal was calculated using $mP_{(t)}$ (mg). First, a split-plot ANOVA (repeated measures) were performed in order to determine the within and between variables effects (CT, P_i, PS). CT was the dependent variable measured in mg of P removed at five levels (60, 180, 360, 720 and 1440 min). The independent variables were: P_i with three levels (5, 10 and 20 mg L^{-1}) and PS with two levels (4 and 5 mm). Indeed, tests of normality (Skewness & Kurtosis z-values and Shapiro-Wilk), homogeneity (Levene's test), sphericity (Mauchly´s test), Bonferroni adjustment for multiple comparisons and post-hoc test were applied [23].

Second, a factorial two-way ANOVA was performed, to analyze in detail the main effects of P_i (5, 10 and 20 mg L^{-1}), PS (2, 4 and 5 mm), CT (60, 180, 360, 720 and 1440 min) and the interaction of P_i and PS with CT. Bonferroni adjustment for multiple comparisons and a post-hoc test were applied in order to determine the significance of the differences between the means across levels [23].

Finally, the conducted experiments were analyzed using Design Expert® Version 7.0 (Statease, Minneapolis, Minnesota, USA) and the use of Design of Experiments (DoEs) to optimize the experimental method [24]. The response surface methodology (RSM) was performed (historical data), in order to further perform an optimization process by using previously obtained results. The DoE methodology is based on the analysis of variance (ANOVA) and allows validation of whether or not there is a synergistic effect between the variables on the final response [23,24]. In this manner, a desirable phosphorous removal (P removal) can be achieved by varying the parameters under study (i.e., P_i and/or CT). Further, DoE allows the user to evaluate which parameters can influence the phosphorous removal (P removal) to a greater extent.

2.3.4. Kinetic Models

In addition to allowing the estimation of sorption rates and constants, kinetic models can also give a suitable expression of the possible processes involved in the removal of pollutants.

Therefore, to elucidate the sorption process occurring within the time, the pseudo-first order (PFO) and pseudo-second order (PSO) kinetic models were selected to fit the experimental data acquired. The following non-linearized equations were applied (adapted from [25–27]):

$$\text{PFO: } q_{(t)} = q_{(e)}(1 - e^{-k_1 t}) \quad (4)$$

$$\text{PSO: } q_{(t)} = \frac{tK_2 q_{(e)}{}^2}{1 + tK_2 q_{(e)}} \quad (5)$$

where $q_{(t)}$ (mg g^{-1}) is the amount of P removed at a certain time (t) per gram of CAAC and $q_{(e)}$ (mg g^{-1}) is the amount of P removed at equilibrium per gram of CAAC. The constants K_1 (min^{-1}), K_2 (g·mg^{-1} min^{-1}) are the rate constant of PFO and PSO, respectively. All the fitting calculations were performed using MATLAB R2017b.

A least-squares non-linear regression method was applied [26–28]. The $q_{(e)}$ obtained were termed $q_{(e)cal}$. The $q_{(e)}$ experimental ($q_{(e)exp}$) represents the amount of P removed per gram of adsorbent at equilibrium, which might not be the last sample. Therefore, to estimate the equilibrium time, one-way ANOVA was performed. Equilibrium was assumed when there were no statistical differences between CT; this was termed CTANOVA. Note that while $q_{(e)exp}$ is equal to $q_{(CTANOVA)exp}$, it was decided to call it $q_{(e)exp}$; $q_{(e)exp}$ was calculated using the indicator (2), as previously described (Section 2.3.3).

Besides calculating the squared correlation coefficient (R2) for each model, the method of Marquardt's percent standard deviation (MPSD) was also applied, in order to compare the fitted data (adapted from [28,29]):

$$MPSD = \sqrt{\frac{1}{n_m - n_p} \sum_{i=1}^{n} \left(\frac{q_{t,i,exp} - q_{t,i,calc}}{q_{t,i,exp}} \right)^2} \quad (6)$$

where the terms "*exp*" and "*calc*" represent the experimental data acquired with the kinetic essays and the data calculated by fitting the experimental data into the PSF and PSO models, respectively.

3. Results and Discussion

3.1. Physical and Chemical Properties of the Adsorbent (CAAC)

The density of CAAC was found to be 2.51 g cm^{-3} and 2.46 g cm^{-3} for PS 4 and 5 mm, respectively. The specific surfaces for PS 4 mm and 5 mm were 12.35 m^2 g^{-1} (± 0.10) and 11.82 (± 0.11), respectively. The density and specific surfaces do not seem to vary between PS. However, previous results have shown that the specific surface of similar materials was more than twice the values determined here, with around 30 m^2 g^{-1} when the PS varied from 2 to 5 mm [5], from 1 to 6 mm [6] and from 2 to 4 mm [14]. As a general rule, the lower the PS, the higher the specific surface. Nevertheless, we noticed the opposite trend when we compared the values determined by Damrongsiri [18] and Bao et al. [10].

The latter indicates that PS is not the only thing that affects the specific surface of CAAC. For instance, the aeration method applied during the production of CAAC can vary according to each company's protocols, affecting the porosity and specific surface of the material. In general, CAAC blocks are aerated with aluminum powder and autoclaved under specific pressure during a certain amount of time [5]. It is possible that variations related to the type of powder, pressure and duration of the aeration process affect the final specific surface and porosity of the material. The PS and specific surface are extremely important parameters for proper hydraulic design and for predicting sorption performance when NBS are used to remove P. Therefore, recommending general design standards can be challenging when CAAC is used as a filter medium, mainly due to its heterogeneity regarding the relation between specific surface and PS.

The initial FTIR analysis showed a strong peak around 968 cm^{-1} (Figure 1), which according to Fang et al. [30] represents the "antisymmetric stretching vibration of Si-O-Si". The expressive peak of Si-O highlights the presence of tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot H_2O$), which has been determined to be the main component of this type of cement [5,15,16].

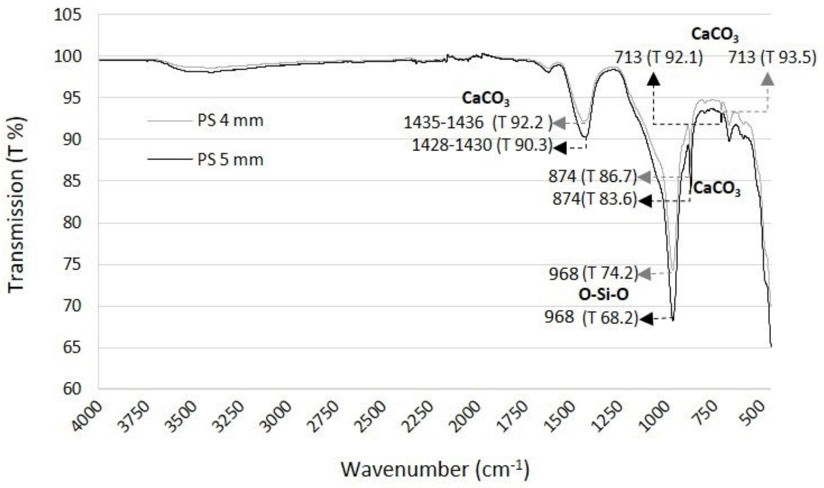


Figure 1. Main functional groups of the CAAC studied (results of FTIR)

We observed a broad band at 1430 cm^{-1} and sharp peaks at 874 cm^{-1} and 713 cm^{-1} (Figure 1), indicating the presence of calcium carbonates [30–32]. Previous results from Kiefer et al. have shown a calcium carbonate spectrum with similar bands and peaks, at 1390 cm^{-1}, 871 cm^{-1} and 712 cm^{-1} [32]. Indeed, Fang et al. [30] analyzed a similar calcium silicate with the same band, at 1430 cm^{-1}, which according to the authors indicates the great potential of the material for releasing Ca^{2+} and OH^{-}. This indicates that the presence of calcium carbonates in the CAAC that we studied might lead to precipitation and crystallization of P with Ca. The PS 5 mm showed slightly lower transmission for all peaks as compared to PS 4 mm, which might indicate a tendency for having higher contents of the compounds described previously.

About 70% of the chemical composition of the CAAC under study is CaO and SiO_2 (Table 1). Similar results were found in the literature, for instance, with a content of Ca and Si were 194 g kg^{-1} and 232 g kg^{-1}, respectively, and for which CaO and SiO_2 together represented more than 70% of the material composition [5,6,10].

Table 1. The chemical composition of CAAC (Results of XRF).

Chemical Compound	Current Study		Literature
	PS 4 mm	PS 5 mm	
SiO_2 (%)	47.46	46.88	[1,2,3,4] 44.8–57.0
CaO (%)	26.53	26.95	[1,2,3,4] 24.9–27.6
Al_2O_3 (%)	3.28	3.28	[1,2,3,4] 1.95–16.06
Fe_2O_3 (%)	1.18	1.18	[1,2,3] 1.0–4.2
K_2O (%)	0.74	0.74	[4] 0.7
MgO (%)	0.65	0.64	[2,4] 0.5–0.6

[1] Renman and Renman [5]: PS 2–5 mm. [2] Karczmarczyk et al. [6]: PS 1–6 mm. [3] Chen et al. [33]: PS 5–9 mm. [4] Hartmann et al. [31]: 5–20 µm.

For both PS values (4 mm or 5 mm), quartz (SiO_2; PDF-01-083-0539), tobermorite ($Ca_{2.25}Si_3O_{7.5}(OH)_{1.5}\cdot H_2O$; PDF-01-083-1520), calcite ($CaCO_3$; PDF-01-072-1937) and anhydrite ($CaSO_4$; PDF-01-072-0916) were identified as the main crystalline phases (XRD analysis), which is in accordance with previous studies [5,31]. According to Hartmann et al. [31], the main components of aerated concrete are tobermorite, quartz and calcite (given in order of importance). It should be emphasized that three additional small peaks were detected only in PS 5 mm (23.5°, 27.8°, 30.22°, 48.10°, 51.11°). Those peaks can be attributed to the presence of Ca, Al and Si compounds, such as albite ($K_{0.2}Na_{0.8}AlSi_3O_8$; PDF-01-083-2215), wollastonite ($CaSiO_3$; PDF-01-072-2284) and calcium aluminum oxide ($Ca_5Al_6O_{14}$; PDF-00-011-0357).

3.2. Kinetics Batch Experiments

3.2.1. Interactions and Main Effects of P_i, PS and CT

This section aims to identify and discuss the interactions and main effect of Pi, PS and CT on the removal of P at the laboratory scale, mainly due to the importance of these variables for designing NBS for treating rich P wastewaters. On one hand, P_i and PS values can affect the CT needed to achieve the removal equilibrium [20]. Therefore, understanding the interactions and main effects of PS, P_i and CT, by performing kinetic studies, can be useful to predict the efficiency of the material within time in accordance to the PS and P_i. On the other hand, batch studies are usually focused on the sorption performance of material, even though other removal processes can also occur. With regard to the material properties, several factors can influence the sorption performance, such as PS and specific surface, chemical composition (functional groups) and surface charging. However, at the same time, P_i can influence the types of processes that occur with respect to P removal. For example, Deng and Wheatley [15] have suggested that at higher P_i, other processes beside adsorption, such as complexation and precipitation, can occur. Therefore, understanding the main effects of P_i and PS can clarify the role of each of these variables on the P removal process. In other words, accessing the variable has a stronger effect on P removal might also give indications about the prevalent removal process occurring, and thus facilitate further optimization when upscaling the experiment.

First, the interactions and main effects of Pi, PS and CT were analyzed using split-plot ANOVA (repeated measures). Data were considered to be approximately normally distributed. The Shewness and Kurtosis z-values were between −1.40 and 1.40, and the Shapiro-Wilk test significance were above 0.01. The Mauchly's sphericity test showed a significance above 0.05, and therefore sphericity was assumed. The following assumptions can also be made. Time had a significant main effect on P removal ($F(4, 48)$

$= 2390.544$, $p < 0.001$, $\eta p^2 = 0.995$); in other words, P removal was moderated by CT. A significant interaction occurred between CT and P_i ($F(8, 48) = 310.758$, $p < 0.001$, $\eta p^2 = 0.981$) and CT and PS ($F(4, 48) = 5.215$, $p < 0.001$, $\eta p^2 = 0.303$), in terms of removal of P, which means that the time effect was moderated by both P_i and PS. However, the interactions between CT and P_i seems to be stronger than between CT and PS, as 98% and 30% of P removal can be explained by these interactions, respectively.

The Levene's test showed significance above 0.01 for all CT values (60, 180, 360, 720 and 1440 min). Therefore, for between-subject's effects tests, the error variance of the dependent variable was considered equal across groups. The results showed a significant main effect P_i of ($F(2, 12) = 2688.878$, $p < 0.001$, $\eta p^2 = 0.998$) and PS on the removal of P ($F(1, 12) = 100.789$, $p < 0.001$, $\eta p^2 = 0.894$). Further, there was a significant interaction between P_i and PS regarding the removal of P ($F(2,12) = 17.206$, $p < 0.001$, $\eta p^2 = 0.741$) (Figure 2).

However, this interaction may be related to the absence of significant differences between PS when P_i was equal to 5 mg L^{-1}, while for P_i equal to 10 and 20 mg L^{-1}, the differences across levels of P were significant. Thus, the magnitude of the differences between levels of PS across levels of P_i were different (Figure 2), causing the interaction. Indeed, the main effects of PS might be stronger as P_i increases.

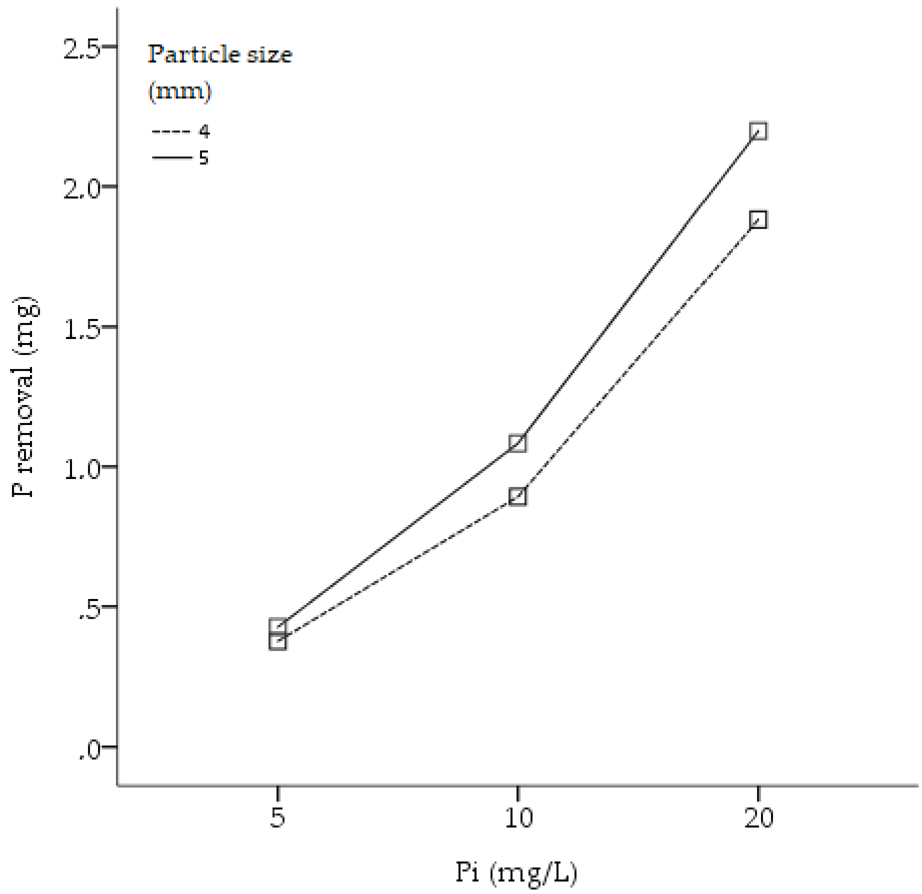


Figure 2. Interaction between P_i and PS.

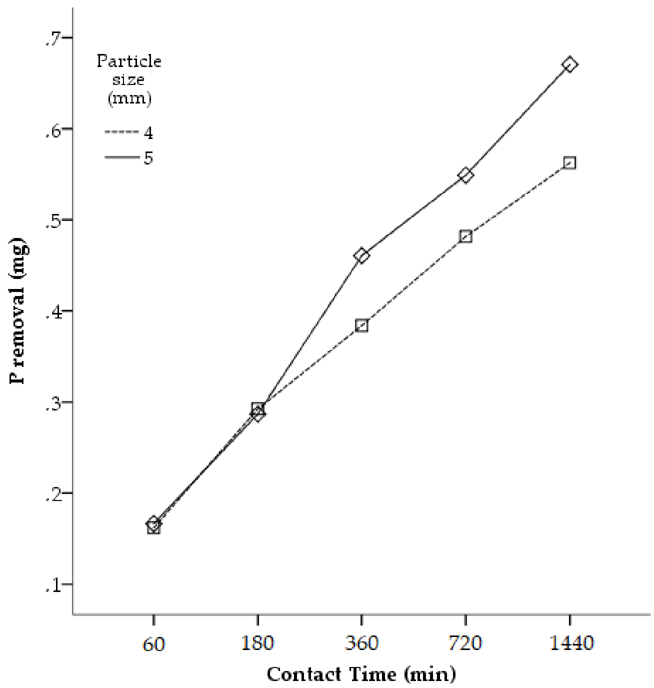
The three-way interaction between CT, P_i and PS was not significant in terms of P removal ($F(8, 48) = 1.328$, $p = 0.253$, $\eta p2 = 0.181$). Therefore, a factorial two-way ANOVA was performed to understand in detail the main effects of P_i and PS and as well their interactions with CT (Table 2).

Table 2. Two-way ANOVA. Results regarding P removal (mg).

P_i (mg L^{-1})	Factors	df	F	α	ηp^2	PS (mm)	Factors	df	F	α	ηp^2
5	CT	4	263.855	<0.01	0.981	4	CT	4	395.825	<0.01	0.981
	PS	1	25.903	<0.01	0.564		P_i	2	2332.852	<0.01	0.994
	CT x PS	4	4.895	<0.01	0.495		CT x P_i	8	56.205	<0.01	0.937
10	CT	4	442.058	<0.01	0.989	5	CT	4	1192.745	<0.01	0.994
	PS	1	124.721	<0.01	0.862		P_i	2	7985.244	<0.01	0.998
	CT x PS	4	1.071	0.40	0.176		CT x P_i	8	143.770	<0.01	0.975
20	CT	4	595.938	<0.01	0.992						
	PS	1	149.948	<0.01	0.882						
	CT x PS	4	0.978	0.44	0.164						

Df: degrees of freedom; α: significance (Tukey 95%): ηp^2: partial Eta squared.

Furthermore, an interaction between PS and CT was observed when P_i was equal to 5 mg L^{-1} (Table 2), which was probably related to the fact that during the first 3 h, differences between PS were not significant (Figure 3a). However, no significant interactions occurred when P_i varied from 10 to 20 mg L^{-1}, which are the mean differences significant for all CT (Figure 3b). The results presented for the interactions between PS with P_i, were likely related to the differences between levels of PS across levels of P_i, which were generated mainly by the absence of significant differences between PS during the first 3 h (CT: 180 min) when P_i was equal to 5 mg L^{-1}, as previously stated. The interactions between PS x P_i and PS x CT can be explained by an absence of differences of one of three levels (P_i—5 mg L^{-1}) and two of five levels (CT, 60 min and 180 min), respectively. For further studies, we would strongly recommend to increase the number of samples during the first 3 h for P_i equal or lower than 5 mg L^{-1}.



(a)

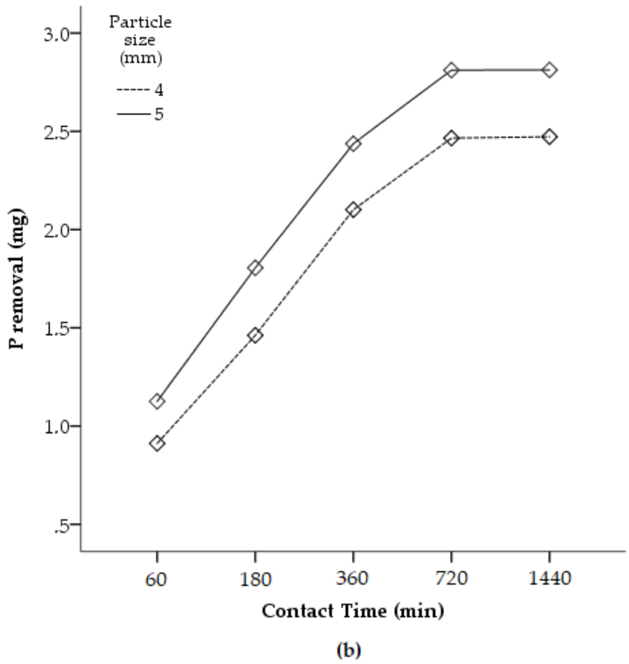


Figure 3. Effects of PS P_i and CT on the removal of P. (**a**) P_i: 5 mg L^{-1}; (**b**) P_i: 20 mg L^{-1}.

The interaction between CT and P_i was significant, regardless of PS, with more than 90% of the variation of P removal explained by this interaction. In other words, the combination of CT and P_i generates a stronger effect on the removal of P than each one separately.

More than 95% of variability on the removal of P can be related to CT, irrespective of which variable is being analyzed. A main effect of PS on the removal of P was evident, regardless of the initial P_i. However, 56, 86 and 88% of the variation can be explained by PS for P_i equal to 5, 10 and 20 mg L^{-1}, respectively. The removal increment provided by PS 5 mm when P_i was equal to 20 mg L^{-1} was 1.6 to 3.2 times higher when P_i equal to 10 and 5 mg L^{-1}, respectively, suggesting that the main effects of PS might be stronger as the P_i increases.

Contrary to what was expected, PS 5 mm removed more P than PS 4 mm in all the cases, except when P_i was equal to 5 mg L^{-1} at CT 60 and 180 min, at which time no differences between PS were observed. P removal depends on chemical and physical properties of the adsorbent [20]; however, there were no differences between PS regarding specific surface. Thus, it is possible that the heterogeneity of the material regarding its chemical composition led to an increment of the P removal process, which is not dependent on specific surface or PS. For instance, chemical precipitation with Ca^{2+} and the formation of Ca–P–silicates aggregates can occur, as the CAAC studied is mainly made of tobermorite and calcite (Section 3.1). Several researchers have shown positive correlations between the chemical composition of filter material and the P sorption process, related mainly to the presence of Al, Fe and Ca [34–37].

The differences between P_i across the levels of CT were significant, with P_i 5 and 20 mg L^{-1} responsible for the lowest and highest P removal rates, respectively. The study of Deng and Wheatley [15] also showed a linear increment of P removal as the P_i increased (from 5 to 30 mg L^{-1}). By compared the relationship between P sorption performance of different materials by varying P_i (mg L^{-1}), Cucarella and Renman [20] found an exponential tendency: increasing P_i correlates with a higher sorption of P, as this interaction is stronger with increasing P_i. At higher concentrations of P, besides adsorption, other removal process such as complexation and precipitation took place, resulting in higher P removal rates [15,20].

Moreover, when P_i was 10 and 20 mg L^{-1}, for both PS 4 mm and 5 mm, the pairwise comparison and post-hoc showed no significant differences between CT 720 and 1440 min. Thus, the equilibrium was most likely reached between 720 min and 1440 min (Figure 4). In contrast, the same is not observed however for P_i 5 mg L^{-1} once the differences between all CT were significant, indicating that the equilibrium was not reached until 1440 min of CT (Figure 4).

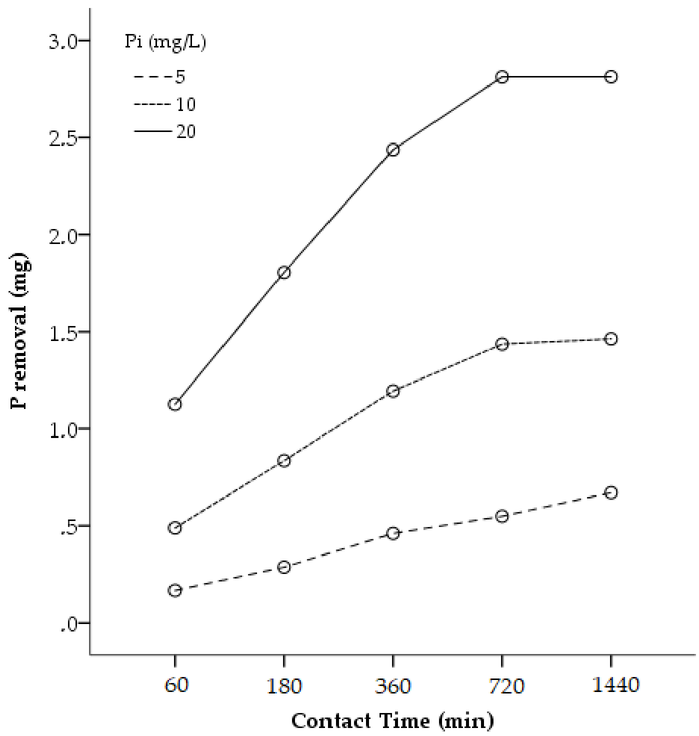


Figure 4. Effect of CT and P_i on the removal of P (results of PS 5 mm).

The experiment of Deng and Wheatley [15] also showed that equilibrium was reached between 720 min and 1440 min for P_i 15 mg L^{-1}, while the results of Renman and Renman [5] showed that when P_i was equal to 5 mg L^{-1}, 1440 min were needed to reach 100% of removal. Therefore, P_i seems to play an important role regarding the equilibrium. Indeed, there is a tendency that the higher the P_i, the faster equilibrium is reached, and vice versa.

Results of this study showed that with P_i 20 mg L^{-1} and PS 5 mm (P_i20PS5), more than 60% of P removal occurred during the first 320 min, with less than 10% of removal after this period. In contrast, with P_i 5 mg L^{-1} and PS 5 mm (P_i5PS5), 40% of P was removed by 320 min, and approximately 20% was removed between 320 min and 1440 min. Karczmarczyk et al. [6] had similar results, with 70% of P removed during the first 600 min and over 20% in the first 5 min. Indeed, Deng and Wheatley [15] showed a substantial removal of P between 60 min and 900 min, with more than 90% removed by 720 min. The processes of P removal needed to reach equilibrium are complex and are basically composed by fast sorption reactions in the beginning followed by slow processes, for instance that of intra-particle diffusion [20]. Therefore, taking into account the experimental conditions presented here as well as those previously published, a tendency can be appreciated: the larger the P_i, the faster and more efficient the removal of P.

Moreover, a proportional relation between P_i and total P removed was evident. The removal of P provided by P_i20PS5 was approximately four-times that of P_i5PS5. The total P removed by P_i20PS5 was approximately two times that of P_i10PS5. Finally, P_i10PS5 removed twice as much as P_i5PS5. The same relation was identified when PS 4 mm was used. Therefore, for the current experimental conditions, the removal of P is proportionally related to the P_i. In other words, if the P_i increases two or four times, it can be expected that the removal of P also will follow this proportional increment, regardless of PS.

The standard analysis of variance (ANOVA) was also conducted for P removal considering the initial 30 aliquots (using historical data design). The factors under study consist on P_i of 5, 10 and 20 mg L^{-1}; PS of 4 and 5 mm; and CT of 1, 3, 6, 12 and 24 h. The response under evaluation was P removal in mg.

Hence, a response surface–reduced quadratic model was obtained. As the interaction between P_i and CT was noticed, a quadratic term for CT presented a significant effect on the response, in the range of study. The results obtained from the modification of any of the controllable variables can be translated into a predictive mathematical model. The obtained model can quantitatively predict the response in the range of study. As was mentioned above, the mathematical model only presents the statistically significant factors and interactions (i.e., p-value < 0.05). Therefore, the mathematical is depicted by the following equation:

$$\text{P removal (mg)} = 1.333 + 0.083P_i + 0.186PS + 0.107CT + 0.003P_i \times CT + 0.004 \times CT^2 \quad (7)$$

Figure 5 shows the surface plot obtained for P removal. An increase of P_i leads to an increase of P removal. Meanwhile, an increase of CT leads to an increase of P removal in a different manner because of the quadratic term in the equation.

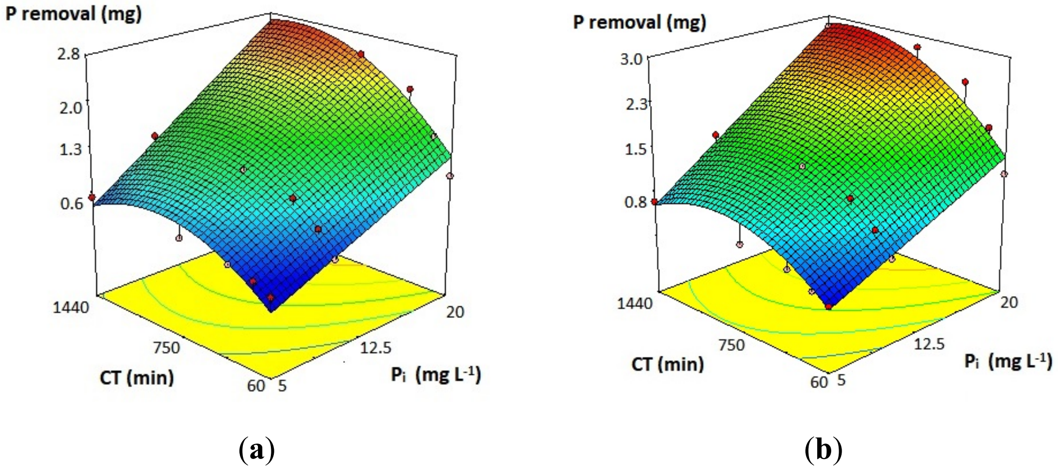


Figure 5. Response surface plot for P removal. (**a**): PS 4 mm; (**b**): PS 5 mm. Adapted from Design Expert® software (version 7.0, Statease, Minneapolis, Minnesota, USA).

Further, it is remarkable that an increase of both factors at the same time led to a higher effect than expected by considering the sum of each factor separately. This additional effect can be attributed to the positive interaction between them.

3.2.2. Potential Removal Process

Regarding P removal, several compounds formed can be expected, such as calcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$), octacalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$) and hydroxyapatite ($Ca_5(PO_4)_3OH$) [3,15,35,38]). However, several factors can affect the formation and longevity of calcium phosphates, such as pH, P_i and Ca^{2+} availability [19].

The pH influences the availability of phosphates formed and the solubility of products formed with Ca. For example, hydroxyapatite is the most common Ca-P precipitate, which is normally formed at high pH (above 10), while calcium phosphate dihydrate and octacalcium phosphate are expected at lower pH [3]. In the pH range of the present study (7 to 8.5), H_2PO_4 and HPO_4 were expected, which can form $Ca(H_2PO_4)_2$, a highly soluble product, and $CaHPO_4$; a less soluble form of Ca-P [39]. Thus, the removal of P by precipitation with Ca^{2+} might not be a predominant process, mainly due to the solubility of the products formed. However, precipitation might be an intermediate process.

Conflictive results can be found in the literature regarding the effect of pH on the removal of P. Several authors have suggested that P removal can be favored by acid pH [15,40]. Deng and Wheatley [15] suggested that, at an acidic pH, material is positively charged and therefore binds negative orthophosphates and acidic forms of P ($H_2PO_4^-$ and HPO_4^{2-}). In contrast, functional groups dissociate at high pH, generating negative ions and thus reducing adsorption due the limited interactions of phosphate anions with the adsorbent surface [40]. In contrast, phosphate removal can be enhanced by an increased pH, as the released Ca^{2+} probably triggers crystallization of calcium phosphate compounds [19,38,41]. Wang et al. [42] have suggested that the release of Ca^{2+}, Al^{3+} and OH^- ions lead to precipitation when cement-based material is used to recover P. Further studies should thus consider the determination of the point of zero charge of the adsorbent in order to clarify the range of pH at which the sorbent is negatively or positively charged.

In the present study, a pH increment and release of Ca^{2+} within time was expected, due to the presence of calcite ($CaCO_3$) (Section 3.1). In this regard, ANOVA results showed a significant increase of pH with time, varying from 7 to 8.5. Calcite can react with H^+ ($CaCO_3 + H^+ = Ca^{2+} + CO_2 + H_2O$), or for instance cement hydration products like calcium hydroxide, which can be dissolved ($Ca(OH)_2 = Ca^{2+} + 2OH$) [18].

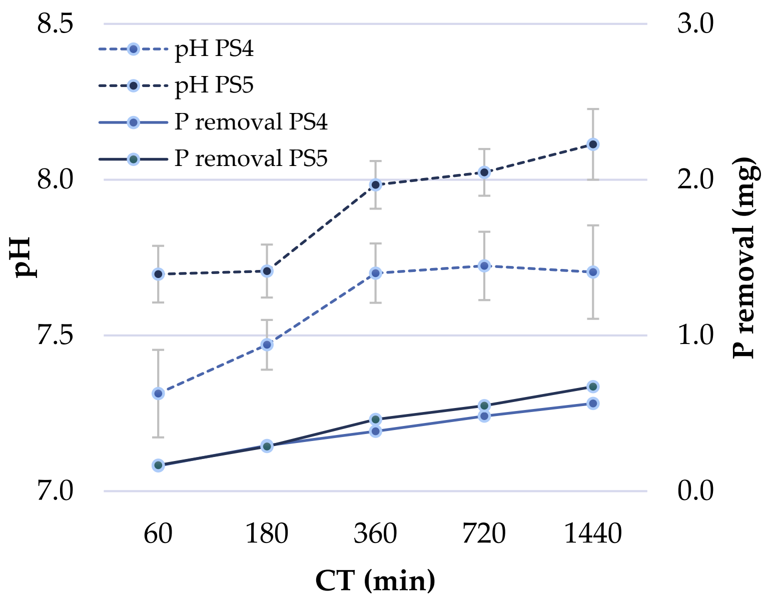
On one hand, the increment of effluent pH might become a limitation on using this material, as it can lead to loss of aquatic fauna biodiversity as well as to carbonation inhibition. In this regard, Nilsson et al. [14] studied a material called "sorbulite", which is manufactured from autoclaved aerated concrete (AAC). The main goal was to remove several contaminants from wastewater, including P, and to minimize the pH increment or even reduce the pH. The results showed a reduction from a pH of 9.1 to 8.9, which is still higher than the range of pH registered in the present study (7.0–8.5) at approximately the same P_i (10 mg L^{-1}). This suggests that the material used in the present study might have a low environmental risk with respect to the effects of higher pH on losses of aquatic fauna biodiversity.

On the other hand, the carbonate inhibition should not be an issue in the range of pH of the present study regarding the removal of P, as CO_3^{2-} formation becomes significant at pH values above 9.0. However, carbonation inhibition can be more likely as P_i increases, due to the P_i effect on pH increment, considering that the pH reached equilibrium very quickly when Pi was 5 mg L^{-1}, which was only after 180 min. In contrast, the pH kept increasing after 1440 min when P_i was 10 and 20 mg L^{-1}. In this regard, Okano et al. [16] results showed a pH increment of up to 8.9 in just 20 min when P_i was 90 mg L^{-1} (approximately calculated considering authors data: 392 mg KH_2PO_4 L^{-1}). Although, the author stated that free Ca^{2+} reacted rather preferably with HPO_4^{2-} rather than CO_3^{2-}, even at this range of pH where carbonate inhibition is expected, and the reasons remained unclear. For instance, the carbonation process can be moderated by P_i when pH is lower than 9. In addition, the current results suggest that P_i can influence either the release of Ca (as higher P_i as higher release of Ca^{2+}), the increment of pH (as higher P_i as higher the increment of pH).

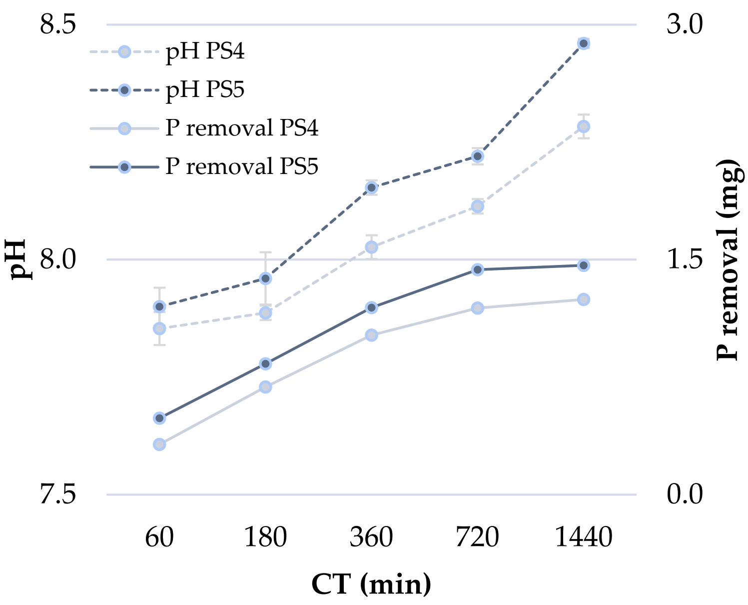
Moreover, when P_i was 20 and 10 mg L^{-1}, P removal reached equilibrium after 720 min, and no pH equilibrium was reached (Figure 6). The fact that the pH continued to increase after P removal reached equilibrium might indicate that free Ca^{2+} was probably being released and not reacting with P. When P_i was 5 mg L^{-1}, the pH reached equilibrium after 180 min, while P removal did not reach equilibrium until 1440 min (Figure 6). This might suggest that, after pH equilibrium, the release of free Ca^{2+} was most likely the "limiting factor", indicating that other removal process, besides precipitation of Ca-P, were taking place.

Okano et al. [16] studied an amorphous CSH and concluded that precipitation of P with free Ca^{2+} cannot be considered as the prevailing mechanism for P removal. They suggest that the formation of Ca–P–silicates ion aggregates is likely to occur by binding of triple cations

($[Ca^{2+}\text{-}(HPO_4)^{2+}\text{-}Ca^{2+}]^{2+}$) with the negatively-charged surface. For instance, two mechanisms can lead to a negatively charged surface, which indirectly favors the formation of Ca-P-silicates. When Ca^{2+} and Si are released, the surface acquires negative electrical charges [16]. Ca^{2+} release might increase as calcium phosphate are formed, as free calcium is removed from the aqueous solution, pushing the equilibrium.


8.5
8.0
7.5
7.0
pH
3.0
2.0
1.0
0.0
P removal (mg)
pH PS4
pH PS5
P removal PS4
P removal PS5
60
180
360
720
1440
CT (min)

(a)


8.5
8.0
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pH
3.0
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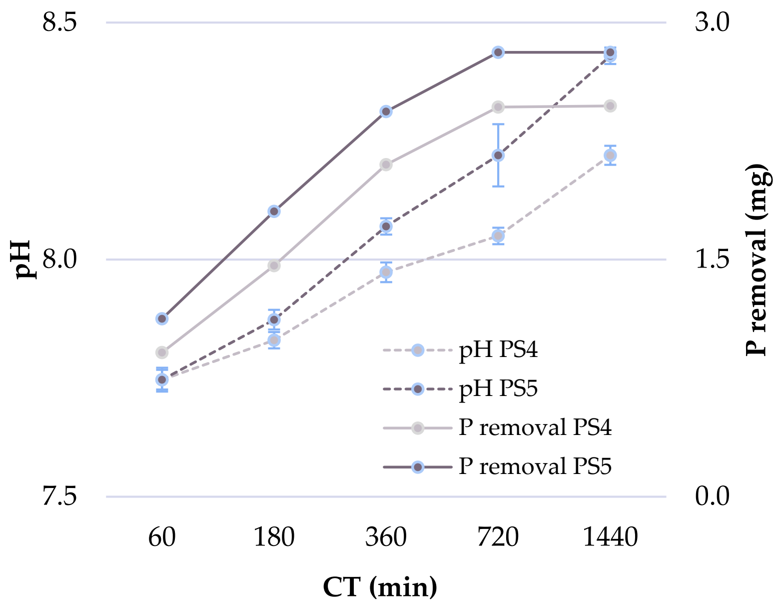
P removal (mg)
pH PS4
pH PS5
P removal PS4
P removal PS5
60
180
360
720
1440
CT (min)

(b)



(c)

Figure 6. Kinetics of P removal (mg) and pH. (**a**) P_i 5 mg L^{-1}; (**b**) P_i 10 mg L^{-1}; (**c**) P_i 20 mg L^{-1}.

The combination of higher values of both P_i concentration (20 mg L^{-1}) and PS (5 mm) leading to better P removal rates can be attributed to two main theories, based on the previous publications (as discussed also above). First, considering that the specific surface was very similar for both PS values (Section 3.1), the chemical constitution seems to play an important role at P removal rates. Initial FTIR analyses of PS 5 mm showed lower transmission for all peaks as compared to PS 4 mm, which could for instance indicate higher amounts of calcium carbonates and silicates. In regard to PS, 5 mm showed higher values of pH in comparison with 4 mm, which might be related to the presence of wollastonite only in PS 5 mm. The dissolution of wollastonite can lead to an increment of pH in the aqueous solutions [43]. Moreover, wollastonite ($CaSiO_3$), is a calcium meta-silicate known for its great performance at removing P [44,45]. According to simulations performed by Herrmann et al. [46], wollastonite can play an important role of providing Ca^{2+} and OH^- for PO_4 precipitation. Moreover, P adsorption can also be related to, either by ion or surface exchange [47].

Second, higher P_i and PS values likely lead to faster and higher rates of Ca^{2+} release, which reacts and forms high/medium soluble calcium phosphates products ($Ca(H_2PO_4)_2$ and $CaHPO_4$), thus removing free calcium for a certain time, pushing the equilibrium and leading to a negatively charged surface of the absorbent. Therefore, at the experimental pH (which was lower than 8.5), the precipitation of Ca-P is likely to be an intermediate process that leads to sorption of triple Ca-P cations and perhaps also the formation of Ca-P–silicates ion aggregates.

Further studies focused on the main effects and interactions between pH and P_i are recommended to clarify the removal processes of P that have occurred to ensure an efficient and safe application of CAAC as a filter medium in NBS for treating wastewaters—in other words, to ensure high removal rates of P, and to avoid carbonation inhibition and environmental hazards due to the expected increase of pH (effluent).

3.2.3. Removal Rates

The phosphorus removal rate presented by Renman and Renman [5] was 57 mg of P g^{-1} of CAAC considering a P_i of 10 mg of P L^{-1}, whereas the one from Karczmarczyk et al. [6] was lower than 20 mg g^{-1} for P_i concentrations lower than 200 mg L^{-1}. According to the chemical compositions and physical properties (PS and specific surface), the material used by both authors seems to be very similar. In this regard, the adsorbent dosage (g mL^{-1}) can play an important role when comparing the performance of experiments focused on P removal. According to Cucarella and Renman [20], higher material-to-solution ratio (grams of adsorbent: ml of solution) generally leads to an increment of P removed by the material. How many grams of adsorbent per liter of P solutions was used in these previous batch experiments is unclear. Therefore, we would recommend that, in the future, the adsorbent dosage used is reported, to make it possible to compare studies.

In an apparent conflict to our results, Deng and Wheatley [15] showed a P removal rate (0.75 mg of P g^{-1} of adsorbent) twice the maximum rate observed in our study (0.3 mg of P g^{-1} adsorbent) using a similar P_i (15 mg L^{-1}) and similar material. This result is even more unexpected considering that the authors used less than half the adsorbent dosage (20 mg L^{-1}) than we used in our study (50 g L^{-1}). Such a significant difference regarding the P removal rate can be attributed to differences in experimental constants, such as pH and agitation velocity (rpm). For instance, the experiments performed by Deng and Wheatley [15] were carried out at pH 5, while ours were in a pH range of 7.0 to 8.5; as discussed above, the removal of P can be strongly affected by pH.

In addition, even though the authors used a similar PS (2 to 5 mm), samples were agitated at 180 rpm, as compared to 20 rpm in the present study. The higher agitation rate might lead to mechanically generating smaller particles, thereby increasing the specific surface available for adsorption of P as well as increasing P removal rates. According to Cucarella and Renman [20], stirring the aliquots over 100 rpm alters the physical properties and lead to

overestimation of results. Moreover, 180 rpm is far from a real operational conditions of NBS. Thus, it is not possible to compare the results of the current study with those of Deng and Wheatley [15], mainly due to differences regarding pH range, adsorbent dosage (g L^{-1}) and agitation velocity (rpm). In this regard, we would recommend keeping both the pH range and the agitation rate as close as possible to real conditions whenever the aim is to use the results for upscaling experiments.

3.2.4. Kinetic Models

The kinetic models, PFO and PSO, were used to fit the experimental data. The $q_{(e)calc}$ values obtained from PFO were closer to $q_{(e)exp}$ than the ones obtained from PSO. Nevertheless, such comparisons have limitations, due mainly to the calculation procedure of $q_{(e)exp}$. Namely, when calculating $q_{(e)exp}$, defining an equilibrium point becomes a subjective matter. The supposed equilibrium point is defined either visually (sorption graph) or when a specific slope in the curve is reached.

Based on this study, we would suggest applying a one-way ANOVA to define the sampling point, which represents the equilibrium, and then to calculate $q_{(e)exp}$ (Section 2.3.4). However, it must be highlighted that ANOVA tests for significance consider only the mean difference between sample points, and therefore the results give a lower bound for CT at which $q_{(e)exp}$ is achieved. In contrast, the $q_{(e)calc}$ (non-linear regression models) is determined by evaluating the function at its limit when time tends to infinity. Thus, $q_{(e)exp}$ and $q_{(e)calc}$, are not easily comparable, as one uses a specific time, whereas in the other the equilibrium time tends to infinity. Hence, the equilibrium $q_{(t)}$ from regression models was obtained using ANOVA ($q_{(CTANOVA)calc}$).

As can be seen in Table 3, $q_{(CTANOVA)calc}$ is always lower than $q_{(e)calc}$ (PFO and PSO) and $q_{(e)exp}$, indicating that the equilibrium of the models takes place after the CT defined by ANOVA. The latter makes sense considering that, as discussed in Section 3.2.1, no equilibrium was achieved for P_i 5 mg L^{-1} until 1440 min, and for P_i 10 and 20 mg L^{-1} the equilibrium was reached between 720 min and 1440 min. Furthermore, this stresses the fact that the CT obtained from one-way ANOVA are indeed conservative (lower bounded).

Table 3. Results of kinetic models fit (PFO and PSO).

Factors		Experimental		PFO					PSO				
PS	P_i	$q_{(e)exp}$	[1]CTANOVA	$q_{(e)calc}$	[2]$q_{(CTANOVA)calc}$	K_1	R^2	MPSD	$q_{(e)calc}$	$q_{(CTANOVA)calc}$	K_2	R^2	MPSD
4	5	0.056	1440	0.053	0.053	4.12×10^{-3}	0.954	0.173	0.063	0.055	7.68×10^{-2}	0.991	0.078
4	10	0.119	720	0.124	0.120	4.64×10^{-3}	0.999	0.038	0.146	0.116	3.67×10^{-2}	0.986	0.077
4	20	0.246	720	0.246	0.242	5.65×10^{-3}	0.969	0.137	0.280	0.236	2.62×10^{-2}	0.976	0.074
5	5	0.067	1440	0.065	0.064	3.36×10^{-3}	0.970	0.175	0.079	0.066	4.58×10^{-2}	0.988	0.107
5	10	0.143	720	0.145	0.142	5.13×10^{-3}	0.980	0.126	0.167	0.137	3.83×10^{-2}	0.984	0.061
5	20	0.281	720	0.278	0.275	6.54×10^{-3}	0.965	0.123	0.313	0.270	2.82×10^{-2}	0.982	0.053

Units: PS (mm), P_i (mg L^{-1}), $q_{(e)}$ (mg g^{-1}), K_1 (min^{-1}) K_2 (mg/g min). [1]CTANOVA: CT of equilibrium (min) determined by using one-way ANOVA. [2]$q_{(CTANOVA)}$ was obtained by evaluating the nonlinear regression model at the contact time from ANOVA (CTANOVA).

When calculating the percentage that $q_{(CTANOVA)calc}$ represents in relation to $q_{(e)cal}$ ($\%_{equilibrium\ reached} = \frac{(q_{(CTANOVA)calc} \times 100)}{q_{(e)calc}}$) , it becomes clear that for PFO, the equilibrium was closer to the sampling point defined by ANOVA than for PSO. For all treatments of PFO, 96% to 99% of the equilibrium was reached at the ANOVA experimental equilibrium point, while for PSO this range varied from 79% to 87% across treatments. When executing the same procedure and immediately comparing $q_{(e)exp}$ with $q_{(e)calc}$ ($\%_{equilibrium\ reached} = \frac{(q_{(e)exp} \times 100)}{q_{(e)calc}}$), the percentage ranges increased, indicating that the equilibrium was either getting closer, or had even been reached for some of the treatments of PFO for which the values were higher than 100%. The latter facts also highlight that the equilibrium is reached faster for PFO than PSO.

The comparison of $q_{(e)exp}$ with $q_{(e)calc}$ only indicates how close $q_{(e)calc}$ was to the sample equilibrium point, but does not provide a good validation for the fitting of the model. One-way ANOVA determines the time (CTANOVA) at which the equilibrium point for $q_{(e)exp}$ is reached. Thus, we believe it is more robust to compare $q_{(e)exp}$ with $q_{(CTANOVA)calc}$. The comparison is performed for the same CT and provides a better understanding of the validity of the model.

In this regard, the $q_{(CTANOVA)calc}$ values for both models (PFO and PSO) were very close to $q_{(e)exp}$. Indeed, considering R^2 and MPSD, the PSO fitted slightly better the experimental data when compared to PFO, (Table 3 and Figure 7). For all treatments, the correlation coefficient proved to be higher in PSO except for the PS4 P_i10 treatment, for which R^2 was 1.3% below the PFO model fit for the same treatment. With similar results, a lower MPSD was obtained for the PSO model except for PS4 P_i10, which presented an increase of (2.6%) with respect to PFO model for the same treatment.

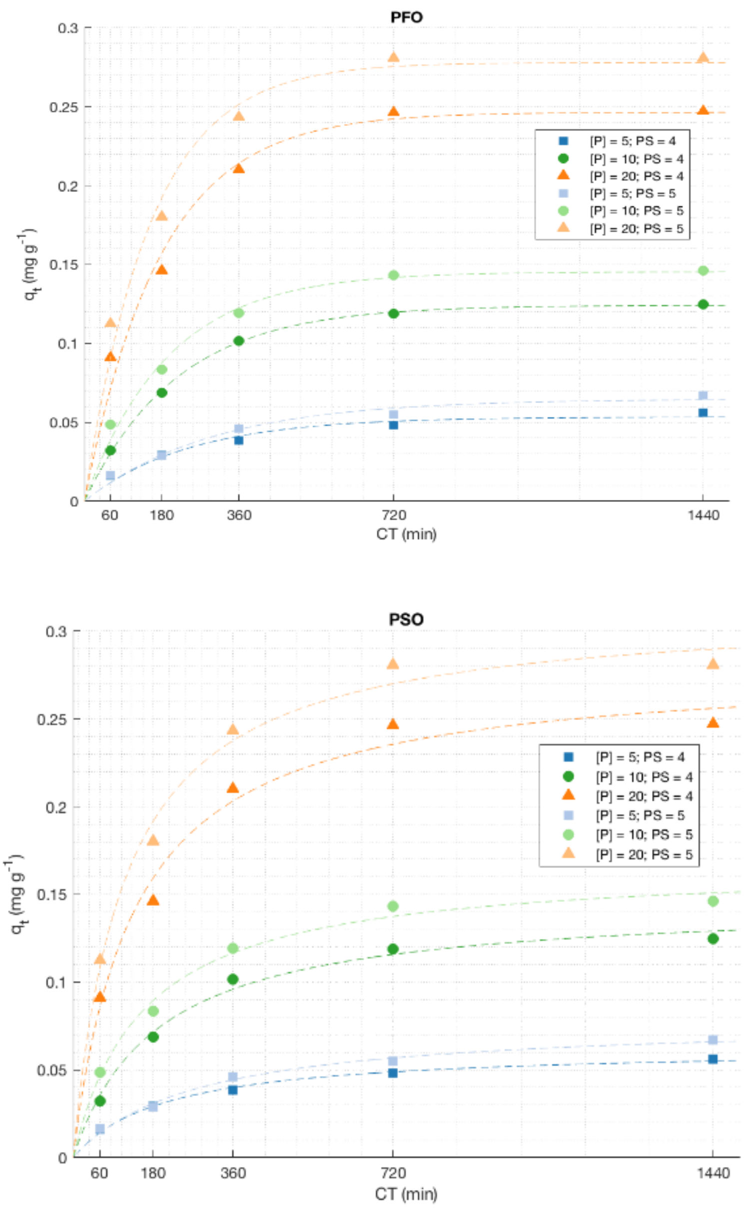


Figure 7. Non-linear kinetic fitting (PFO and PSO). Dashed lines represents the kinetic model regression.

Similar results can be found in the literature, with PSO providing a better fit for experimental data regarding the sorption of P using similar materials, such as sorbulite [14], recycled crushed concrete [15], CAAC [5] and crystalline CSH or crystallized tobermorite [48]. As previously discussed, either adsorption and/or precipitation and formation of Ca–P–silicates can be involved in P removal. Hence, it can be assumed that the best fit of PSO is associated to chemical sorption rate-limitation regarding the sharing and/or exchanging of electrons between sorbent and sorbate [25].

4. Conclusions

As expected, initial FTIR analyses confirmed the presence of calcium carbonates and Si-O group, indicating the presence of tobermorite, which was later confirmed by XRD analysis.

The two-way ANOVA showed a significant main effect of CT, P_i and PS on the removal of P, with the removal of P moderated by these variables. In contrast to expectations, samples with PS 5 mm removed more P than those with PS4 mm. The latter was related to the heterogeneity of the material regarding its chemical composition. Further, the presence of certain Ca, Al, Si compounds only in the PS 5 mm samples might have led to greater P removal rates due to processes that are not dependent on specific surfaces (such as chemical precipitation with Ca^{2+} and the formation of Ca–P–silicate aggregates).

The equilibrium and the efficiency of removal seems to be dependent on P_i. Specifically, the higher the P_i, the faster the equilibrium was reached, and the higher the removal rate of P. We noticed that if the P_i increased two to four times, the removal of P also followed a similar proportional increment, regardless of the PS.

In addition, P_i seem to play an important role in moderating P removal. It is likely that P_i can affect Ca^{2+} release and thus regulate the precipitation process as well as the indirect sorption by influencing the negative charging of adsorbent surface. Moreover, the results suggest that higher P_i leads to higher increases of pH, which might affect the solubility of Ca-P precipitates.

When comparing the P removal rates with those given in the literature, the current results seem to be lower; this apparent conflict can however be attributed to differences regarding experimental conditions as well as the heterogeneity of concrete based materials, such as CAAC.

The PSO fitted better with the experimental data, which was in accordance with previous studies. However, we did not consider that the usual comparison of $q_{(e)exp}$ with $q_{(e)calc}$ is a feasible way to determine the quality of the fit: $q_{(e)exp}$ occurs at a "known time", determined by one-way ANOVA, while $q_{(e)calc}$, occurs after or before this known time (CT_{ANOVA}), making it impossible to compare these values. Therefore, it can be said that such comparisons have limitations regarding the validation of the model`s fit, mainly due to the fact that only give an idea about how closer $q_{(e)calc}$ was to the equilibrium point sampled (ANOVA CTANOVA). In this respect, we propose comparing $q_{(CTANOVA)calc}$ with $q_{(e)exp}$ to validate the model fit, which shows how the model responds at the equilibrium point determined by one-way ANOVA. Nonetheless, an improved methodology for determining the $q_{(e)exp}$ needs to be developed in order to make its comparison with $q_{(e)calc}$ more accurate.

In sum, reusing waste materials or by-products, such as CAAC, in the scope of water treatments is important with respect to integrating water management and circular economy, promoting natural capital preservation and climate change mitigation. However, due to the importance of P_i and pH regarding the removal of P when using CAAC, further studies at real-scale which allow these parameters to be co-related are recommended in order to optimize the removal of P in NBS.

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Chapter 9 WETWALL prototype

9.1 Optimizing the prototype design

The first attempt of building the WETWALL was based on the idea of developing a hybrid module (design previously presented on Figure 8) where both VF and HF were working together. As can be seen in Figure 13, all the “wastewater” is collected and stored in one deposit and distributed thought the VF and HF. Thus, in order to validate the performance of the prototype at improving water quality, 3 modules were needed in order to have enough replicates for statistical analysis. Therefore, it was noticed that couple hydraulic and design improvements were required in order to optimize the area and amount of materials needed to build the prototype and its replicates.

Figure 13 The First WETWALL **Hybrid** module (VF-HF).

Moving further, the design process was focused on building one module containing 3 replicates of the hybrid flow (VF-HF). This phase was developed in collaboration with a final work to get the Architecture and Edification Technical degree from the UPC. The student was responsible for finding sustainable solutions in order to develop the structure and fixations for the Hybrid Prototype module (the design was previously presented - Figure 9).

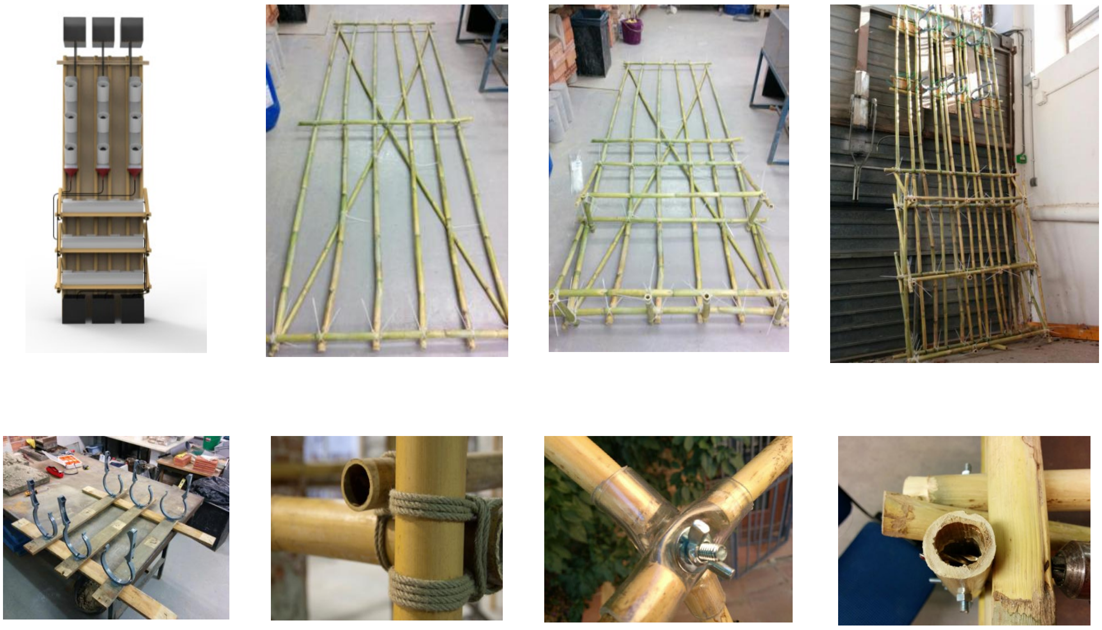


Figure 14. The second WETWALL **Hybrid** module (VF-HF). The prototype first attemps

During the process of building the prototype structure a lot of struggle was faced mainly regarding connecting the *arundo donax* structure, thus several types of fixations were tested (Figure 14). Indeed, safety and durability of the structure when implementing outdoors was questioned. Together with the rise of this technical concerns, the idea of building a prototype which only can be tested on treatment configuration (VF-HF) was also questioned (as discussed previously in section 5.3).

Therefore, first the design of the prototype was improved in order to make the WETWALL prototype more versatile, specially allowing tests of different treatment configurations (Figure 15). As discussed previously (Section 5.3), testing different configuration can play an important role on the adaptation of the WETWALL design concept to different types of urban waters with different pollutant loads. In contrast to the previous design which allowed just one hybrid treatment configuration (VF-HF: Figure 15 – A➔B➔C➔D➔E), the final design of the prototype allowed for several treatment configurations:

- Figure 15 - A ➔ B ➔ C_1➔ D ➔ E ➔ A ➔ B ➔ C ➔ C_2 (The hybrid flow HF-VF)
- Figure 15 – A ➔ B ➔ C ➔ C_2 (single VF)
- Figure 15 – A ➔ B ➔ C_1 ➔ D ➔ E (single HF)

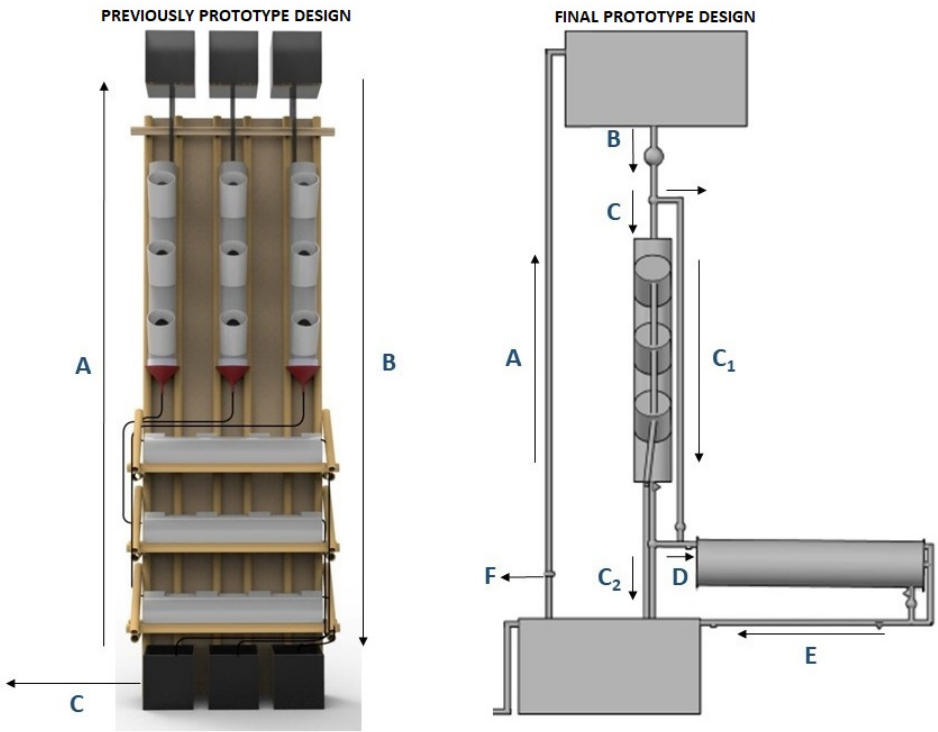


Figure 15. The design optimization of the WETWALL prototype - The treatment versatility (different configurations)

This design also allowed playing with the number of cycles for each treatment (VF or HF) separately or combining them. Indeed, instead of discharging the water from the lower water deposit (Figure 15 – C), there was the possibility of pumping the water out (Figure 15 – F). The final design proposed the direct fixation of treatment structures (VF and HF) into the wall, excluding the module, due to limitations regarding budget for the construction of the prototype.

All the past experience described before, also allowed some hydraulic improvements in order to facilitate the collection of data, either regarding water flow measurement or water sampling. Indeed, the prototype design also focused on facilitating the external maintenance of the system in case of clogging. In this regard, as can be seen in Figure 16, several hydraulic components were added into the design. The 3-Way valves control the establishment of the treatment configurations. One of the 2-Way valves (allocated between the upper deposit and HF) aim to adjust the water flow entering in the HF.

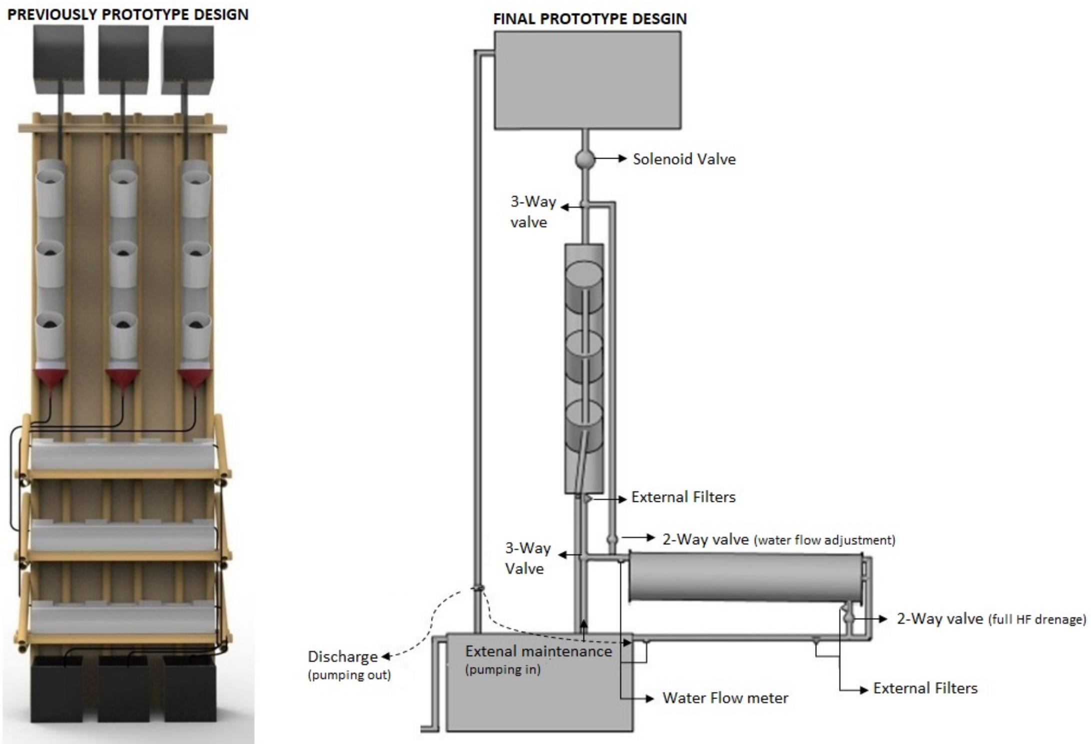


Figure 16 The design optimization of the WETWALL prototype – Hydraulic improvements.

Different water flows lead to different resilience time of the treatment, an important parameter regarding the performance at removing contaminates from water. Other 2-Way valve (allocated in the bottom of the HF), aim to facilitate the maintenance of the HF in case of full drainage is required. In order to facilitate the calculation such as, water flow, hydric balance and the mass of contaminants removed for each treatment (VF/HF), two flow meters were allocated, one after the VF and other after the HF.

External filters were placed in strategic points to avoid sediment flow through treatments structures (VF/HF) and cycles. Indeed, the filter can be cleaned from outside, fact which facilitates the long term maintenance. One connection which allowed using the same pipe for different purposes was added to the main pipe (pumps up the water). The pipe can be used to pump out the "treated" (discharging) water and as well to pump in water in order to solve clogging issues in the end of VF and HF. It can be said that the maintenance of the system was made by applying external pressure of water.

As the system will be implemented outdoors, some hydraulic improvements regarding its adaptation to extreme climatic events, such as rainfall were carried out. Therefore, water level controls were added into the prototype design (Figure 17). More details about the "cascade "water level control for both, the VF and the HF were presented in the first article of the thesis.

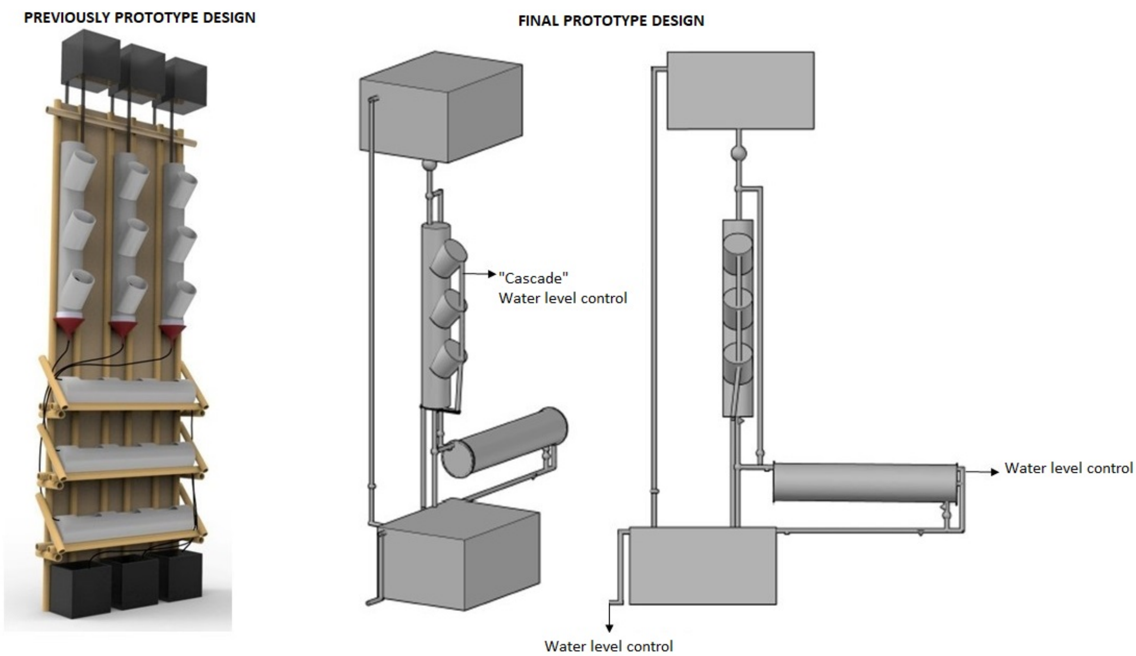


Figure 17 The design optimization of the WETWALL prototype – Adaptation to outdoors conditions (Water level control).

9.2 The Building process

In order to integrate the circular economy principles into the prototype implementation, the reuse of materials was encouraged. Thanks to UNESCO Chair on Sustainability, several materials from the LIFE_REAGRITECH completed project were reused. In this case, pumps, solenoid valves, flow meters, floaters, cables, automation and electrical components were collected and reused (Figure 18). In the research scope, the reuse of materials from ended projects should be considered when design new systems, in order to close the loop regarding materials.

The remaining materials required were acquired thanks to GICITED (UPC research group), thanks to an internal call from the UPC, which subsided materials for ongoing R+I+D projects. These funds were mainly used to buy hydraulic components such as, manual valves (2-way and 3-way), external filters, water reservoirs, pipe connections and drippers (Figure 18), beside tools and fixation components like the clamps and scrolls (Figure 18).

The building process of the WETWALL prototype was divided in 4 main parts: The treatment structures (VF and HF), the “in situ” implementation (hydraulics, electrics, plants), the substrate and the plants. During wall stages of the building process, AUTOCAD plans were developed in order to guide the building process and to ensure the further replicability of the WETWALL design concept.

Figure 18 WETWALL Prototype - Materials

9.2.1 The structures of the WETWALL Hybrid flow (VF and HF)

The treatment structures were built in the Escuela Politécnica Superior de Edificación de Barcelona (EPSEB –UPC). The vertical and horizontal flow structures were built separately as can be seen in Figure 19.

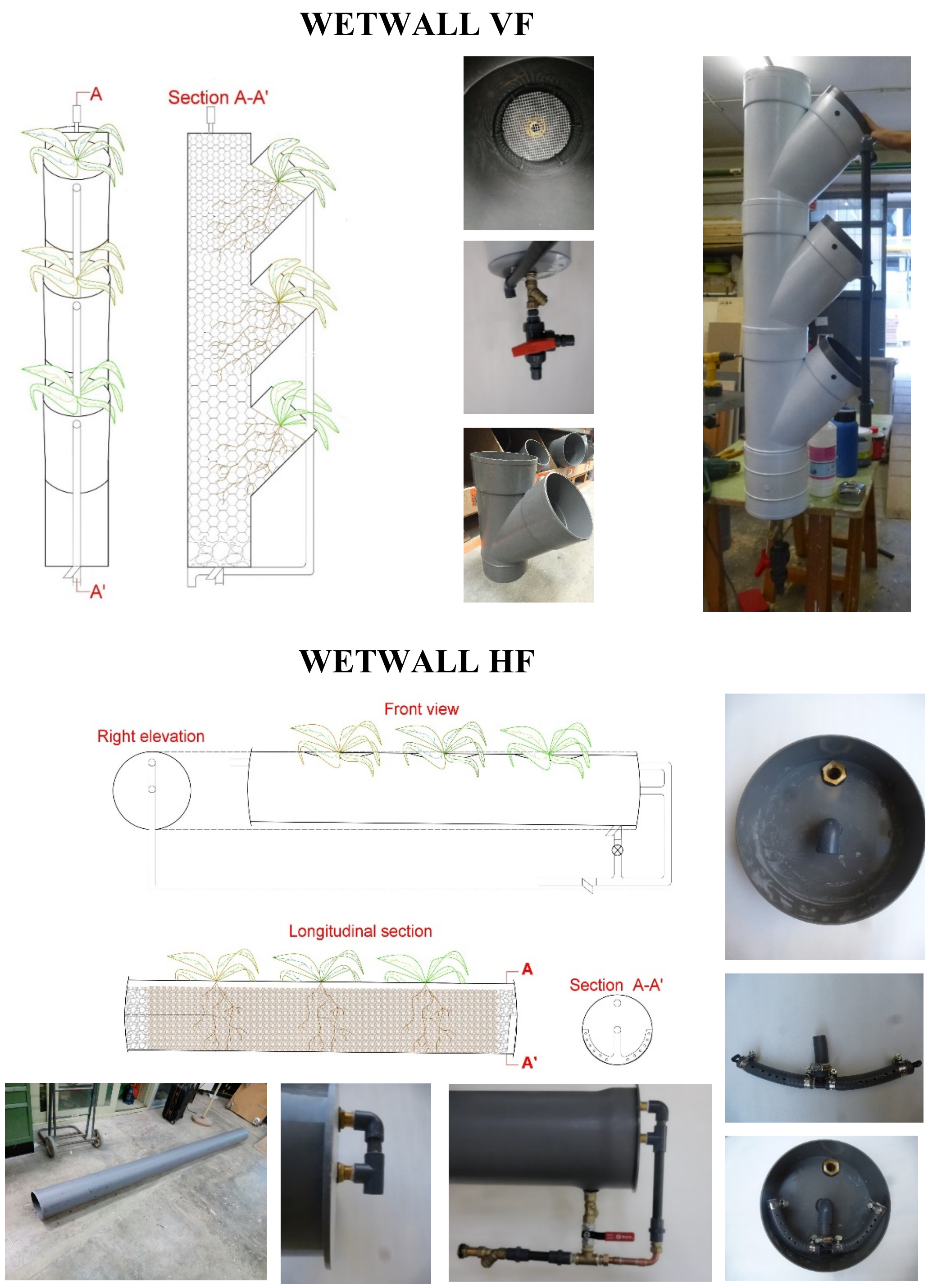


Figure 19 The building process of VF and HF structures.

9.2.2 The prototype implementation

Two identical modules were implemented in order to further validate the replicability of the WETWALL hybrid flow. First, the main structures (VF, HF and water reservoirs) were allocated and fixed in the wall according to the AUTOCAD plan (Figure 20). For the fixation of VF and HF, clamps and metal “L square were used. The upper water reservoir was fixed using metal “L” squares and steel bar.

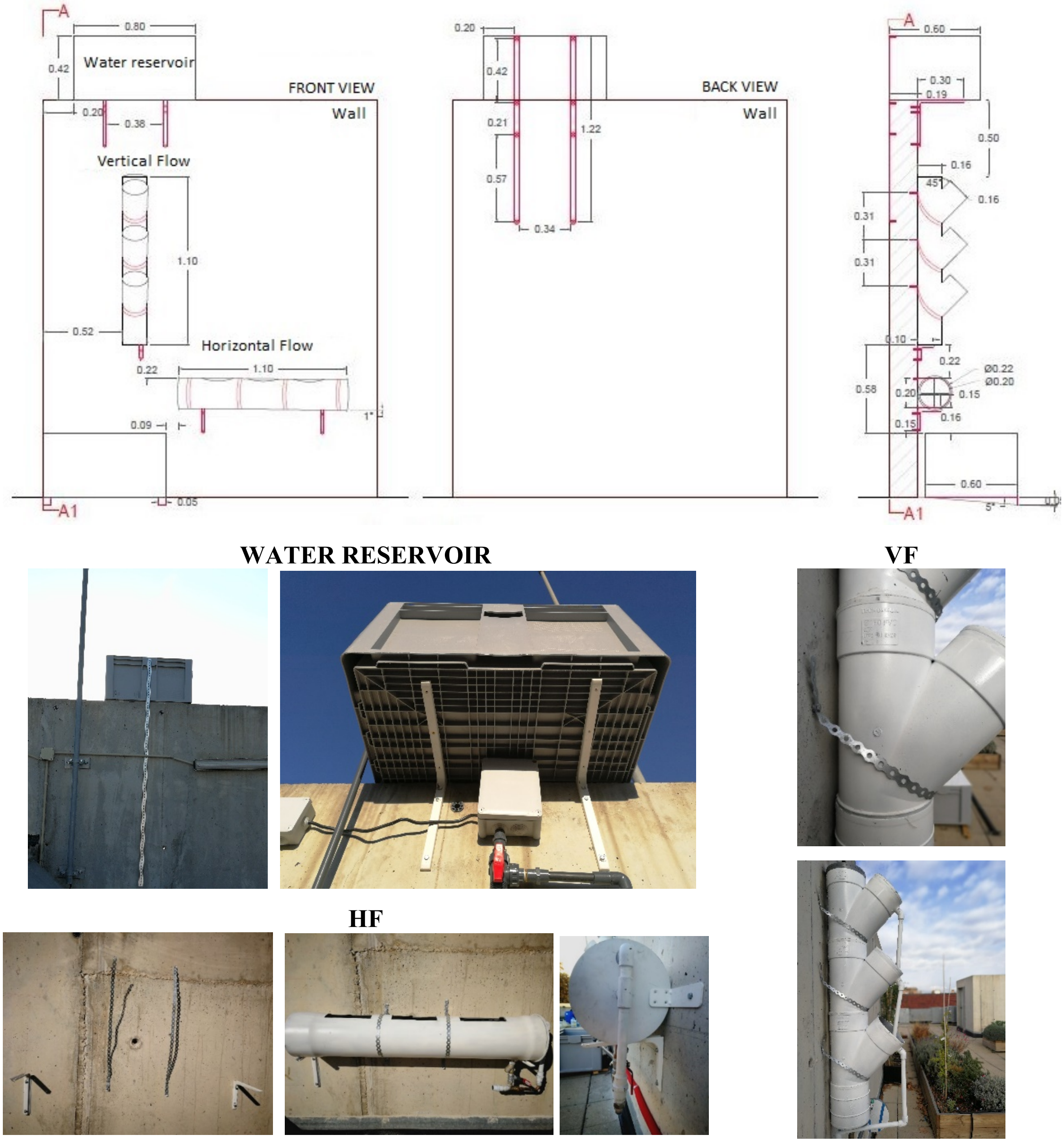


Figure 20 The WETWALL prototype – Fixation and allocation of the main structures (VF, HF and water reservoirs)

Second, electric plan was developed in order to ensure the operation of pumps, solenoids valves and floaters (Figure 21). The electrical planning allowed the prototype operation in an automatic or manual mode. More details about the electric operation can be seen in Figure 21. More information about the automation will be given in the next section.

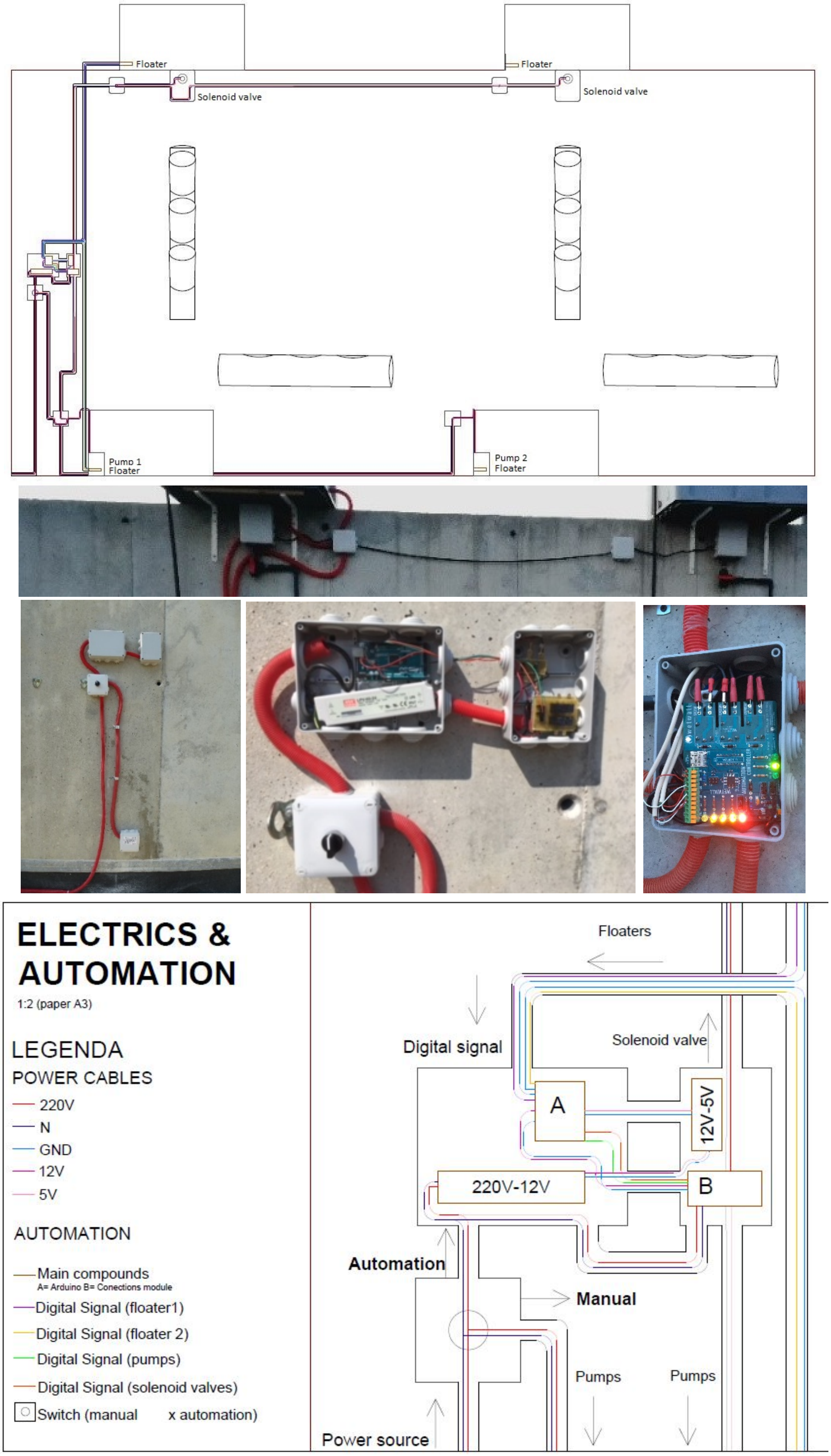


Figure 21. The WETWALL prototype - Electrical planning and construction.

Third, the hydraulic components were implemented in accordance with the AUTOCAD planning (Figure 22 and 23).

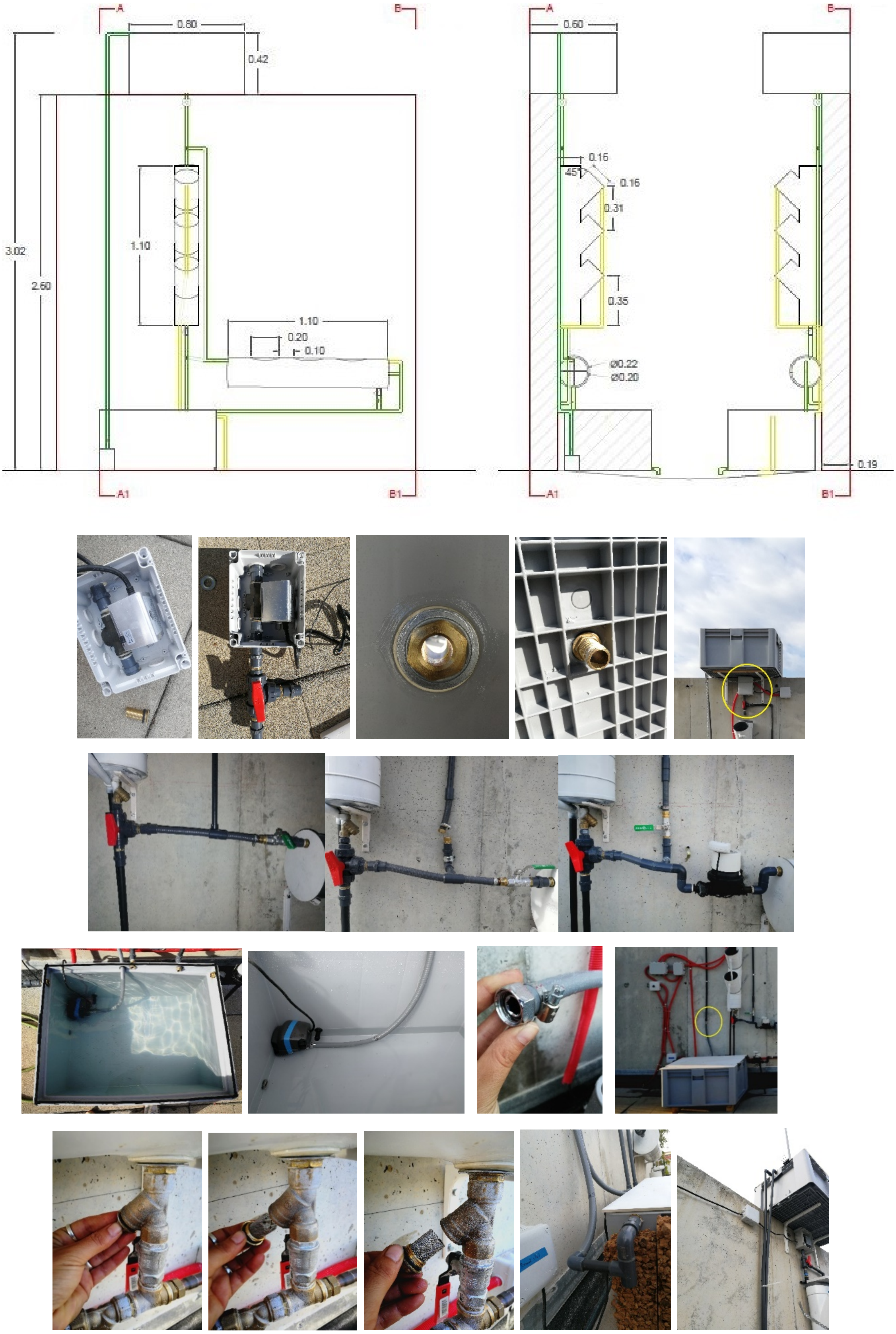


Figure 22. The WETWALL prototype – Hydraulic implementation.

During the building process a By-pass was added in order to facilitate counting the litres of water without passing it through the VF or HF (Figure 23 – A➔B➔C_1➔

C2).

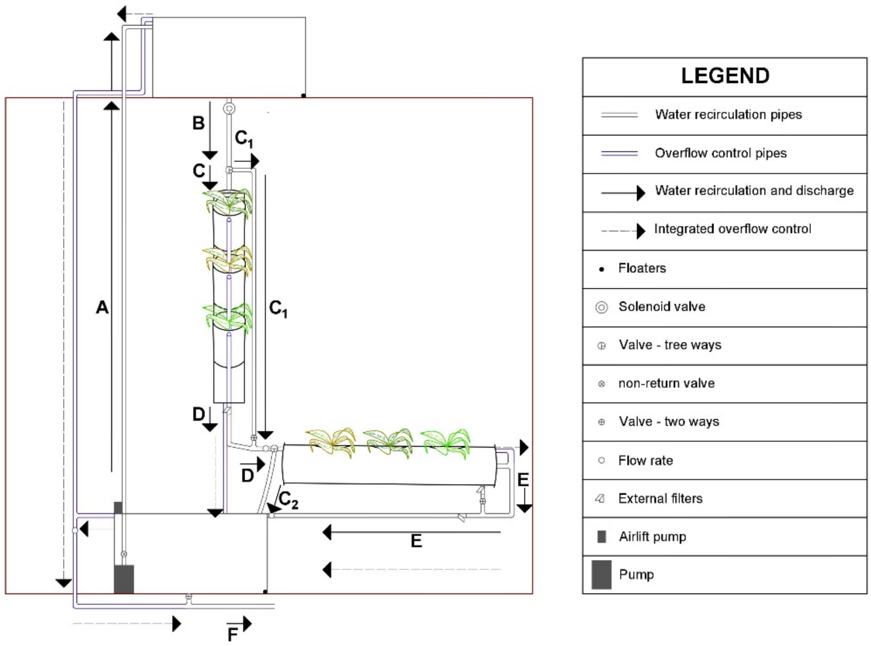


Figure 23 The main hydraulic components of the WETWALL prototype and the possible hydraulic routes, including the bypass (letter From A to F).

The building process started on September, 2017 and finished in January, 2018. A resume of the Prototype building process can be seen in Figure 24.

Figure 24 The WETWALL prototype – Resume of the Implementation.

9.2.3 Substrate (Filter media)

The substrates, CAAC and cork, were selected according to the parameters described in the first article of the thesis. Information about its chemical and physical characteristics can be seen in the second and third articles of the thesis. The cork granulates and CAAC blocks were donate respectively by the Catalan Cork Institute and the company YTONG S.A. In total, approximately 20 kilograms of CAAC were manually crushed. Both CAAC and cork were homogenized, quartered to a 1/16 split and mechanical sieved in order to obtain the required particle sizes. The main procedures regarding the preparation of filter medias can be seen in Figure 25. The filter media allocation, the amount and diameter of each material (CAAC, cork and gravel) and density for each layer can be seen in Figure 26.

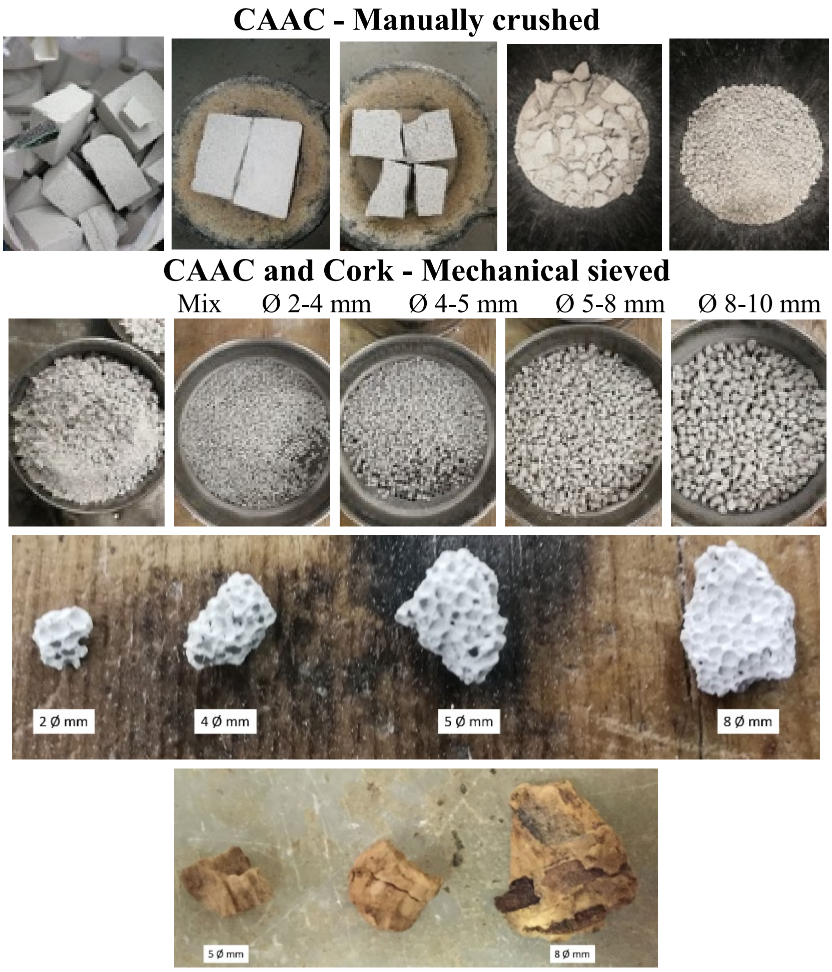
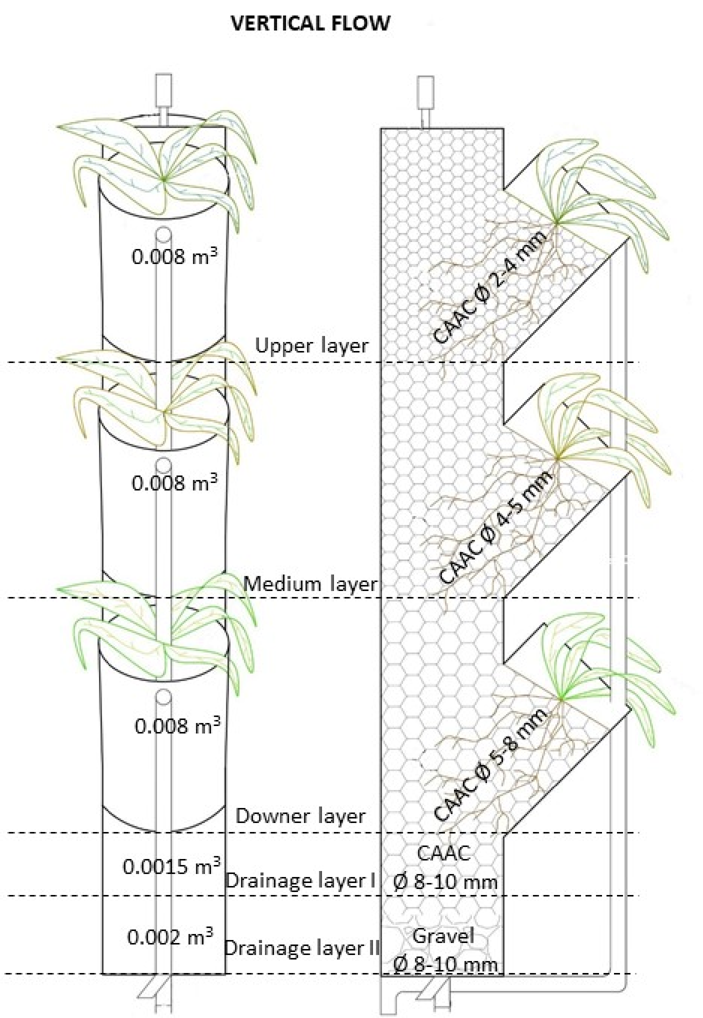
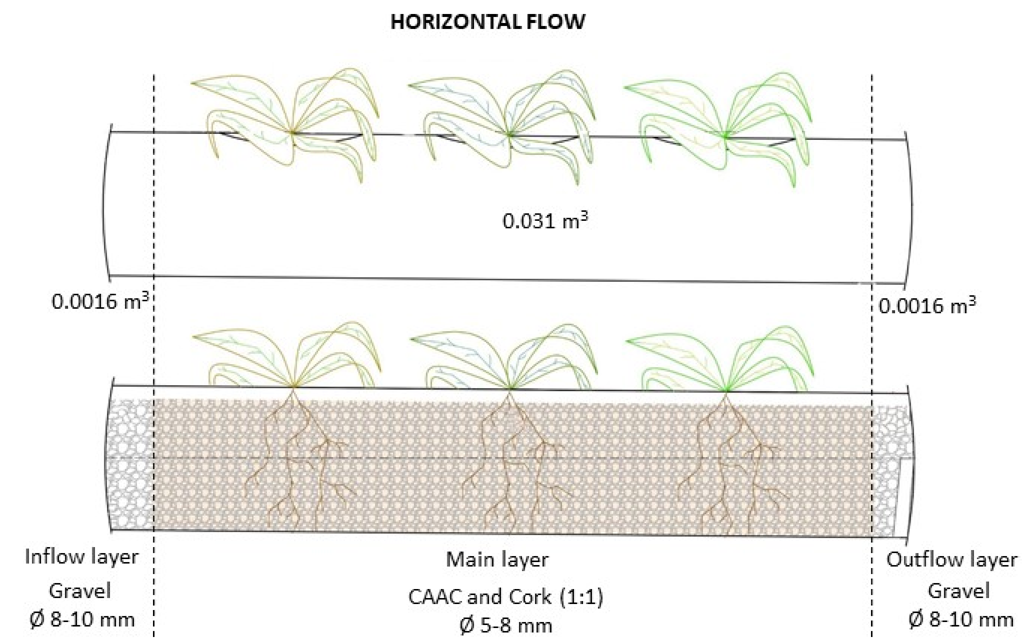


Figure 25 Main procedures for substrates preparation.





	VERTICAL FLOW			HORIZONTAL FLOW	
	MODULE 1	MODULE 2		MODULE 1	MODULE 2
Layers	^{1}Kg/Kg m^{-3}		Layers	^{1}Kg/Kg m^{-3}	
Upper	1.36/170	1.50/188	Inflow	2.25/1408	2.23/1393
Medium	1.736/217	1.72/215	Main	3.56/113	3.64/116
Downer	1.73/216	1.84/231	Outflow	2.25/1408	2.23/1395
Drainage I	0.36/237	0.35/235			
Drainage II	3.04/1520	2.23/1113			

[1]Density (Kg/Kg m^{-3}) = amount of substrate (kg)/ volume occupied (m^{-3}).

Figure 26 Allocation of filter medias (CAAC and Cork)

9.2.4 Plants

The plants were selected in accordance with the premises described in the first article of the thesis. Three different species were selected for each treatment (VF and HF) in order to increase biodiversity and resistance to phyto diseases and plagues attack. Moreover, considering the novelty on the scope of LWs treating wastewaters, the use of different species is a great way and necessary to improve its adaptation to the WETWALL design and operation features and to increase the uptake of pollutants.

For the VF, 3 native species from the Mediterranean and normally recommended to VGs, such as *Salvia officinalis, Helycrisum italicum* and *Santolina chamaecyparissus*, were selected. All 3 native species are tolerant to drought and salty conditions, resist high solar incidence and have aromatic and medicinal properties as an economic and social added value.

Access to uptake features of species that already are used in VGs could be strategic and could increase the range of species to be used for the WETWALL design concept. However, no information was found in the literature about their performance at removing contaminants from wastewater.

For the HF, cosmopolitan (adapted to different weather) species *Berula erecta, Iris pseudacorus and Juncus effusus,* were selected. Those species resist flooded conditions and are tolerant to high solar incidence or partial shade. *Juncus* and *Iris* are native species from natural wetlands. Several investigations have been proving the great performance of those species at removing emergent (pesticides and pharmaceutical compounds) and nutrients (N and P) from wastewaters, either directly (uptaking and bioaccumulation) or indirectly (roots exudates and biofilm) (Schultze-nobre et al., 2015; Zhai et al., 2013; Lv et al., 2016; Saad et al., 2016; Calheiros et al., 2018; Salvato and Borin, 2010; Lyu et al., 2018; Lyu et al., 2018; Xu et al., 2017; Lv et al., 2017).

The roots growth for all species can vary from 5 to 50 cm, which is a good length considering the available space for each design (VF and HF). Details for all selected species and planting process can be seen in Figure 27 and 28, respectively for VF and HF. The plants were planted on February, 2018.

Figure 27 Species selected and planting process of VF for the WETWALL prototype.

Figure 28 Species selected and planting process of HF for WETWALL prototype.

9.3 Automation

9.3.1 The code Logic

WETWALL water recirculation was automated, enabling an accurate characterisation of the system with repeatable timings and consistent conditions. The main goals of the automation were:

i. Modules work in parallel and synchronized.
ii. To be scalable.
iii. Intermittently feed of the vertical and horizontal treatments allowing, if necessary, adjustments to enhance retention time.
iv. Ensure resting periods between treatment cycles in order to aerate the VF.

For that matter, two flotation water sensors have been placed at the minimum capacity line of the bottom and top tanks. They serve as inputs to control a water pump at the bottom tank as well as an on-off valve located at the drain port of the top tank. Both, pump and valve operated synchronously to WETWALL loading (water is pumped up) and discharging dynamics (water passes through the VF and HF by gravity).

The system is solved with a state machine structure, where three states have been identified and three more state transitions determine the duration of the cycle: Pumping - Discharging - Idling (Figure 29). In that manner, input (minimum water level floaters) and output (pump and valve) define a logic behaviour that has been implemented using electronics.

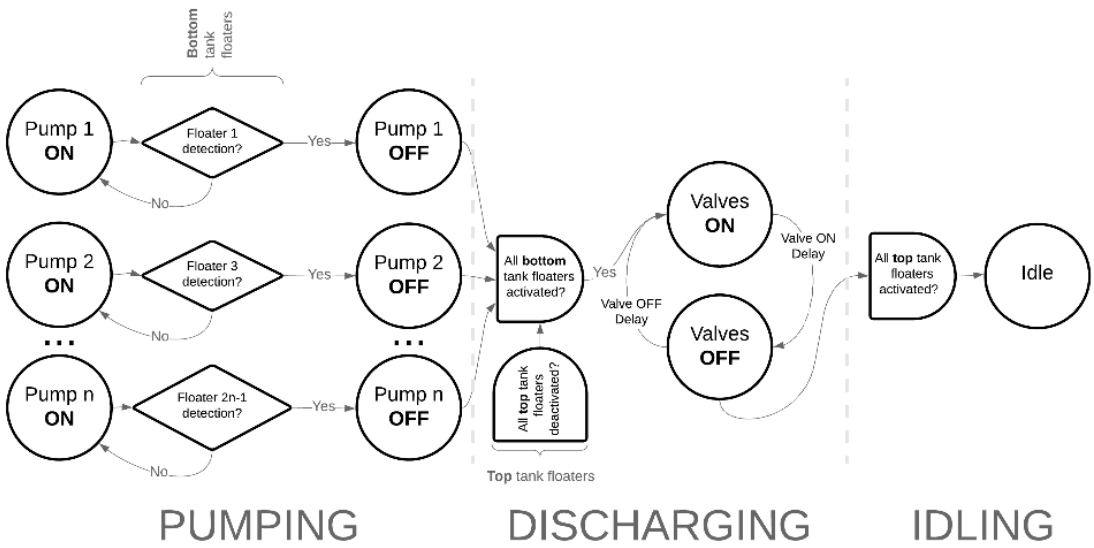


Figure 29. The WETWALL automation – The states of the logic (diagram).

The modules work in parallel. Each pump stops when its corresponding bottom tank is empty, although all valves start discharging at the same moment. In its simplified form, the system depends only on the floater inputs and operates on the pump and valve outputs as follows: with water on all bottom tanks and no water on the top ones, pumping starts. Pumping on each tank continues until there is a signal from either bottom tank floater. Individual pumps will remain pumping until all water on the system is located on the top tanks. Next, discharging shall begin, opening all valves at once. After water has flooded the system and finally discharged onto the bottom tanks (with no remaining water on the top tanks), the valves close and WETWALL logic enters an idle. The process is able to start again with as many iterations as desired (treatment cycles).

The logic was developed to be scalable. Featuring only two floater sensors for a minimum water level (on top and bottom tanks), the number of treatments between water reservoirs can be as many as desired, thus, the logic can be implemented regardless the high of the building or house. Indeed, more parallel treatments can be added (pumps, valves and floaters). In summary, the logic is scalable in both directions vertically and/or horizontally (Figure 30).

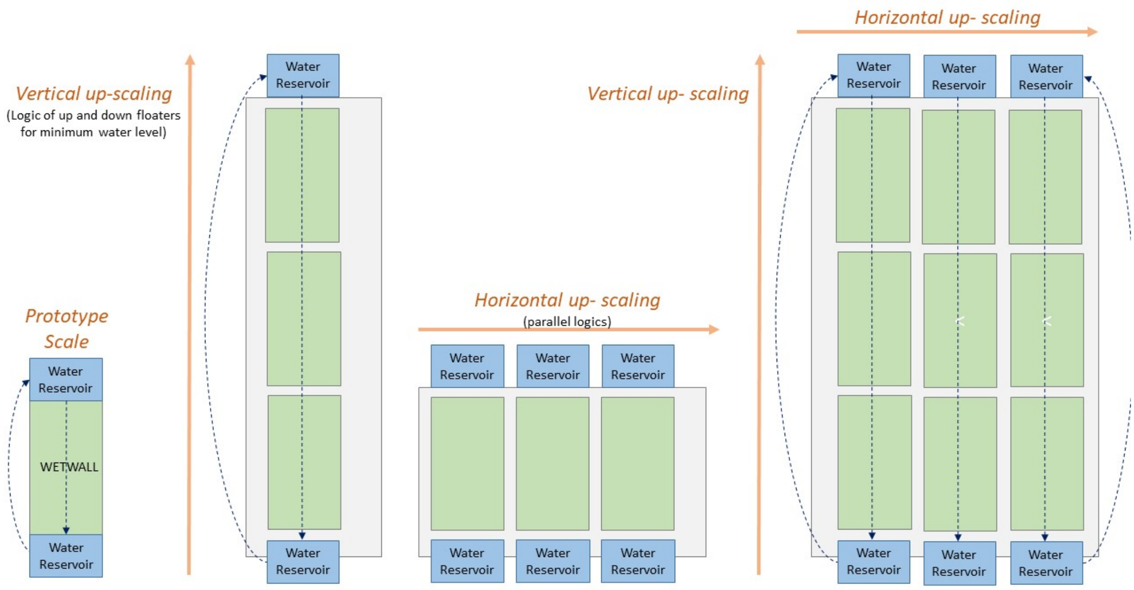


Figure 30 The WETWALL automation - The scalable logic for water recirculation.

The practical implementation of the previously described logic has shed light on inconsistencies in floater triggering. Due to water oscillations caused by the pump action, top floaters tended to provided double or triple activations in a short period of time. To cater for this issue, a configurable delay was added to the code, so that only the first input in a time frame activated the next state.

The concept of intermittent flow was introduced. Instead of leaving the valves fully open during the complete discharge cycle, smaller cycles of open-close where launched in order to enhance the retention time of VF and HF. Overall, the treatment cycle is conceived so that the whole process repeats every 24 hours. Doing so, the discharge duration and the idling state shall be adjusted to fulfil the appropriate duration. A frequency of 1 cycle per day ensures enough idling time to restore the system primarily by aeration of the vertical treatment.

9.3.2 Hardware

The physical implementation of the WETWALL Logic lead to the design, manufacture and testing of a custom electronic printed circuit board. The Board developed can run up to two WETWALL modules in parallel (Figure 31).

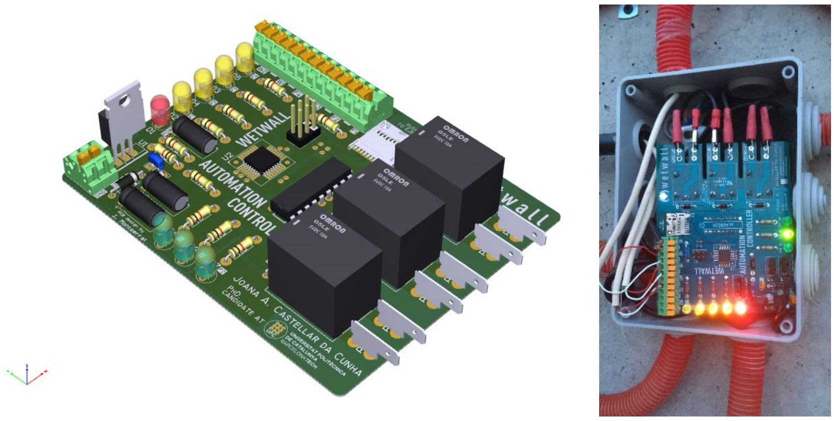


Figure 31 The WETWALL automation - Hardware design (3D) and implementation.

Centred around a 8-bit microcontroller, the system was able to perform the logic implemented as a modified state machine. Delay modules for the idling state and to compensate for multiple floater triggering were added to the microcontroller firmware, providing 4 inputs and 3 outputs, that operated on the mains rated pumps and valves by means of transistor current amplifiers and relays. The power to the board came from two rectified, down-converted and regulated 12 and 5 volt supplies, on a separate off-the-shelf module. Since the electrical connections and hardware needed to be water resistant, they were mounted on electrical boxes, isolated from rainfall, splashing and moisture.

The logic was thoroughly tested, cycle time duration and accuracy was also logged and finally proofed on the in situ system, validating that the installation was fully adaptable and scalable. However, further validation of logic up-scaling is recommended, in order to facilitate the implementation and acceptation of WETWALL design concept at different scales (houses and building).

9.4 First results from prototype operation

One sampling campaign was performed on October, 2018. During the start of the operation from January till September, the plants of the prototype were maintained alive just with tap water, in order to avoid saturating the system before sampling. During this period, automation and hydraulic tests were performed in order to test and improve the system operation. In addition, the prototype was inoculated by using real wastewater and water from the lake of Ciutadella Park. The inoculation was performed 3 times, during this period, once every 3 months.

During the sampling campaign (October 2018), water and substrate samples were collected in order to evaluate the potential of the WETWALL hybrid flow, mainly regarding the removal of phosphorus, N and organic matter. In this section, the experimental design and preliminary results is presented.

9.4.1 Experimental setup

The main goals for the sampling campaign were to verify the replicability of the WETWALL hybrid flow (two modules) and to evaluate the effect of number of treatment cycles in the water quality. For the campaign, synthetic GW was prepared, due to absence of real GW supply in the building where the WETWALL was installed. The following chemicals were used to prepare the synthetic GW (SGW): Potassium Nitrate (KNO_3), Di-Ammonium sulphate ($(NH_4)_2SO_4$)), Di-potassium phosphate (K_2HPO_4), Glucose ($C_6H_{12}O_6$). The initial concentrations of BOD, NH_4-N, NO_3-N and PO_4-P were, respectively, 30, 10, 10 and 10 mg L^{-1}, being considered a light GW (Butler et al., 1995, Casanova et al., 2001, Eriksson et al., 2002, Racek, 2016). However, the values of NH_4-N, NO_3-N were higher than normally found in light GW.

Defining the experimental hydraulic load was challenging due to the great variability regarding GW consumption. For example, the average consumption of GW per person in Barcelona is 120 L (Shapiro, 2014) while in England and Wales is around 150 L. Therefore, the hydraulic load was defined to be 135 L, in order to represent the GW consumed by one person per day. The GW was recirculated once per day according to the following stages:

A. **SGW preparation:** SGW is prepared in the lower reservoir (first day of WETWALL operation. During the fallower days the SGW is recollected in the lower reservoir.

B. **Checking the Hydraulic load** (Figure 32 Soft blue/dashed line): The water is pumped up (upper reservoir) and goes down via bypass, and is discharged again into the lower reservoir. This stage can occur in the beginning (1º day) and between treatment cycles (following days or treatment cycles).

C. **Treatment cycles - Charging** (Figure 32 Dark blue/full line): SGW is pumped to the upper reservoir

D. **Treatment cycles - Discharging** (Figure 32 soft blue/full line): SWG in discharged intermittently (solenoid valve open 3 min and close 15 min) goes trought VF followed by HF and is discharged in the lower deposit.

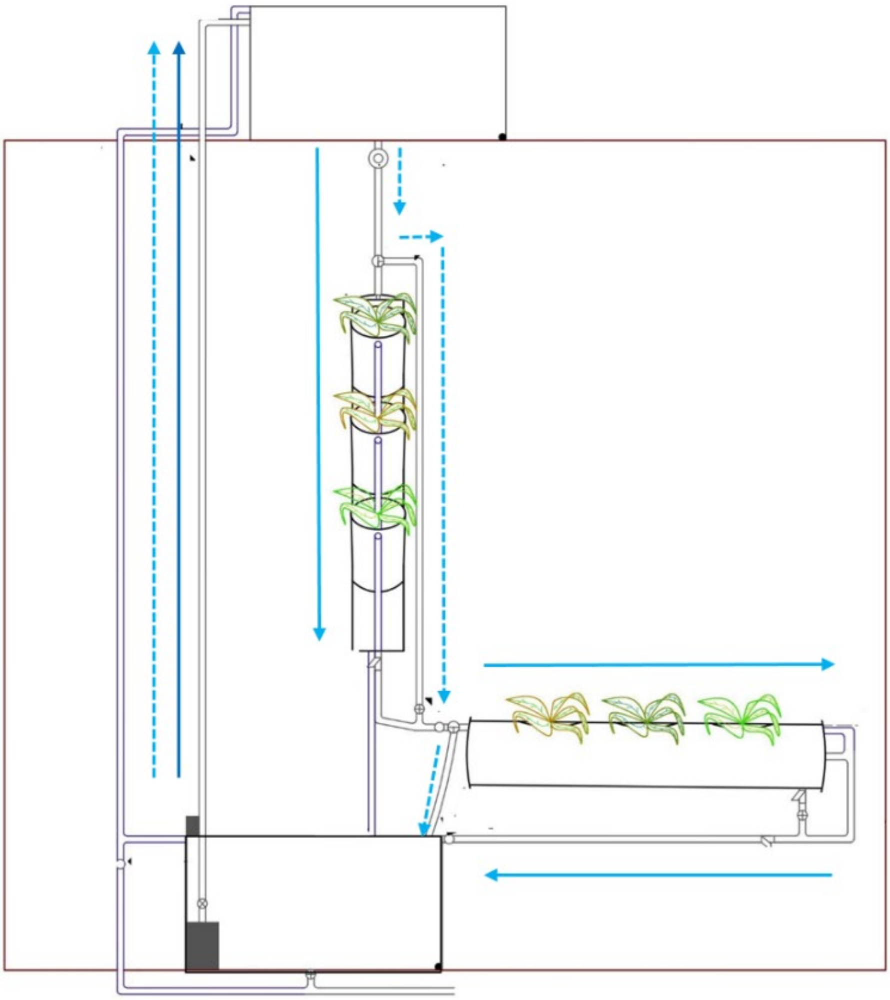


Figure 32 The WETWALL prototype operation (one treatment cycle – one day). Soft blue/Dashed line: Bypass (flowmeter); Dark blue/full line: Charging; Soft ¡ blue/full line: Discharging.

One treatment cycle took approximately 24 hours. About 1 hour is needed to prepare the synthetic GW (1º day) and to check the hydraulic load (by-pass) and charge the upper reservoir. Moving forward, 21 hours was required to complete the discharge, considering the intermittently feed previously mentioned. Finally, approximately 2 hours of resting period (between treatment cycles) Is expected that the duration of the treatment cycle will be lower as the recirculation goes on, due to reduction of the hydraulic load.

The initial load of BOD (30 mg L^{-1}), the hydraulic load (135 L), the treatment area of the WETWALL VF (Ø of the Column = 160 mm ➔ ($\pi * R^2$) ➔ 0,020 m^2) and global removal of BOD in CWs-VF (40 g/m²/d) were the considered parameters to calculate the number of treatment cycles (days) required to clean up the GW (Figure 33).

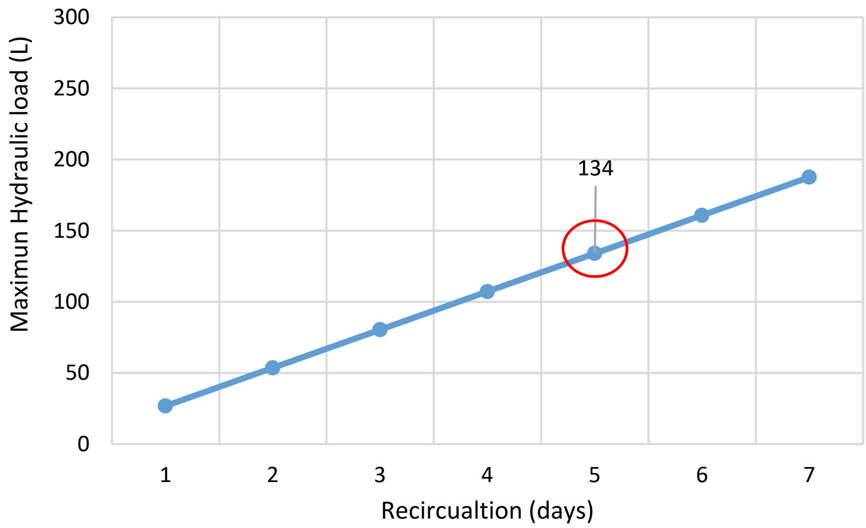


Figure 33. Maximum hydraulic load versus recirculation days required (estimation).

It was estimated that five days were required to remove 100 % of the BOD. However, due to lack of financial support to complete more campaigns, the water samples were collected just after first and second day of recirculation. The water was sampled in 3 points, every day: Initial (Figure 34 – A), After the VF (Figure 34 – B) and After the HF (Figure 34 – C). The balance of the mass was calculated by multiplying the concentration of the pollutant by the amount of water passed by the Flow meter or by-pass (L). The removal of pollutants was calculated as percent of mass removed in relation the respective input of mass. The average of the two modules were considered as final results. The data collected was not enough to perform statistical analysis.

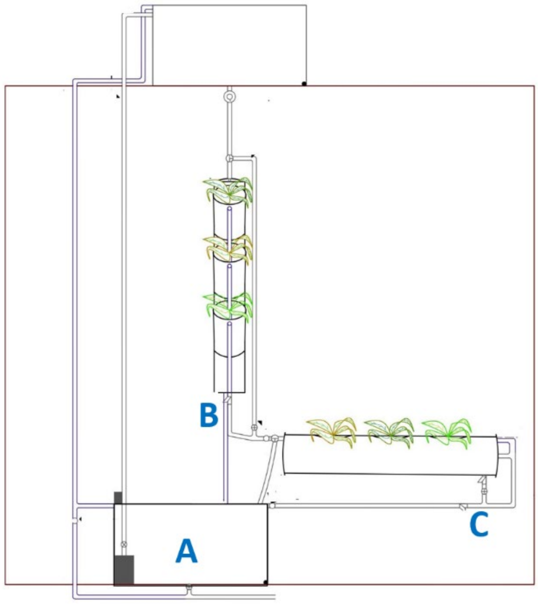


Figure 34. WETWALL prototype – Sampling points.

9.4.2 Water quality performance

In order to evaluate the replicability of the WETWALL hybrid flow (VF-HF), the global efficiency of the two modules were contrasted. In this case, the global efficiency was considered to be the total removal of contaminants after 2 days of recirculation. Thus, samples from point A - day 1 and point C – day 2, were considered for the calculations (Figure 34). As can be seen in Figure 35, both WETWALL modules presented similar results regarding the removal of pollutants.

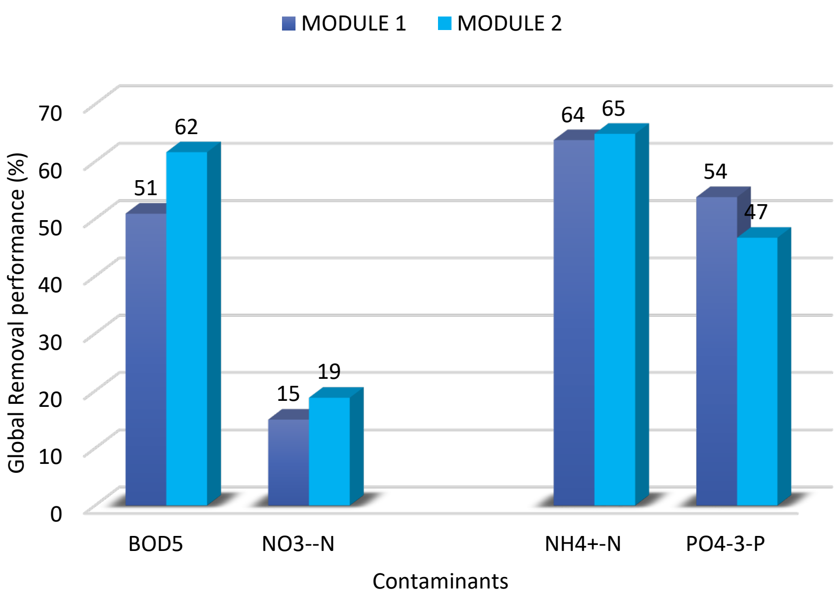


Figure 35 Comparison of WETWALL modules regarding the removal of BOD, NO_3-N. NH_4-N and PO_4-P.

The removal of PO_4-P varied between modules from 47 % to 54 %. The BOD and NH_4-N removal rates were the greatest, getting up to 60%, while the removal rate of NO_3-N was the lowest, being less than 20%, regardless the module. The low removal of N-nitrate may be associated with 3 factors. First, the retention time probably was not enough to complete denitrification processes. Second, it could be possible that there were limitations regarding the availability of organic carbon to complete the denitrification. In this regard, perhaps the carbon released from the cork granulate was not enough for denitrification. In fact, a high BOD removal (upper to 60%) was observed, that might have limited the denitrification performance in the HF.

Third, the high removal rates of NH_4^+ -N might lead to an increase on the NO_3-N load, and the system was not able to compensate this load increment. The load increment of any contaminants by itself pushes the systems performance to the limit. The performance of any treatment can be severally limited when the load increment is associated with limitations regarding the conditions required to complete the removal process (two factors explained above).

Couple strategies regarding the optimization of **retention time and the lack of organic carbon**, to overcome limitations at removing N are presented below.

As resting periods between cycles are important to promote the aeration of VF and thus, ensure proper conditions for nitrification, reducing the hydraulic load and adjusting the intermittently feed (open-close cycles) might help stablishing a longer retention time to enhance denitrification in the HF.as well as increment the duration of resting periods between treatment cycles (days).

The initial organic load can be increased, when working with synthetic GW. However, controlling initial loads is not feasible when working with real GW. Thus, in both cases, for synthetic or real GW, changing the treatment sequence from VF-HF to HF-VF or even HF-VF-HF can help to optimize the availability of organic carbon required for the denitrification.

Those alternative configurations, beginning with HF, allows the treatment to take advantage of the organic carbon already present in the water (BOD). However, depending on the initial GWs characteristics, additional stages in the VF might be required in order to remove the remaining BOD and to convert NH_4^+-N into NO_3^-—N. Indeed, depending on the standards regarding maximum concentrations of NO_3—N allowed to reuse or discharge the treated wastewater, additional stages in the HF also might be required, due to the increment of N load after VF (always expected).

The global efficiency of the Hybrid flow within time/number of treatment cycles (1 cycle per day) was calculated considering the average of the two modules. The sampling points were A and C (Figure 34). The removal was calculated considering the total area occupied by VF and HF, the longitudinal section instead of transversal area, normally used for similar treatments (e.g. CWs). For instance, calculating the removal efficiency related to the area occupied by the modules (Longitudinal area) can help further designing optimization. The removal of P (phosphate) and N (nitrate and ammonium) took place mostly in the first day (Figure 36).

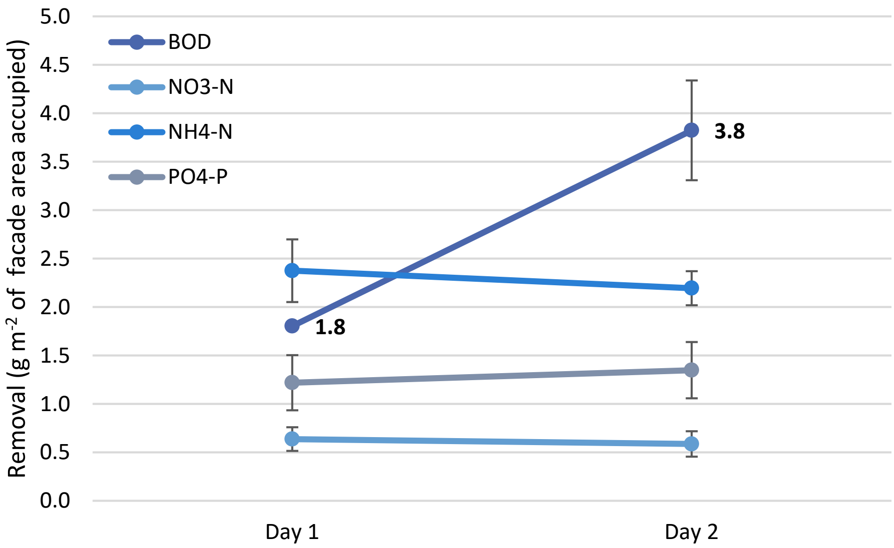


Figure 36 The global removal of BOD, NO3-N. NH4-N and PO4-P within treatment cycles. (Day 1 – first treatment cycle; Day 2 – recirculation, second treatment cycle). Obs: the area considered represent the sum of the longitudinal area of VF and HF.

In contrast, the removal of BOD doubled on the second day of treatment (Figure 36). Approximately 2 g of BOD was removed per m^2 of WETWALL (Hybrid module) per day, which is 20 times lower than the global efficiency of Vertical CWs (40 g m^{-2} day). However, it is important to highlight that such comparison is not feasible, mainly by inconsistences regarding the area referred. The area used as reference for vertical CW is related to the horizontal treatment occupation (transversal area). In contrast the area occupied by the WETWALL module is related to the total vertical area occupied, considering both, VF and HF (longitudinal area).

Previously, estimation were carried out showing that 5 treatment cycles (5 days) would be required to totally remove the BOD, fact which seem to be in accordance with the results obtained, since the BOD removal went upper to 50% after two treatment cycles (day 1 and day 2). Unfortunately, two sampling points (days) and duplicates (two modules) are not enough to make a reliable regression and thus, to estimate the removal rate expected after 5 days of recirculation.

Therefore, in order to verify the feasibility of the estimation, the removal performance of the WETWAL hybrid module (g m^2 day) was calculated taking as reference the transversal area of the VF $(\pi * R^2)$, in order to make it comparable with CWs. The removal of BOD varied from 36 (day 1) g m^{-2} per day to 39 (day 2) g m^{-2} per day, which is very similar to the global efficiency of Vertical CWs (40 g m^2 per day).

Due to the novelty of this field it is important to obtain results, regarding hydraulics and pollutants removal, useful for further design optimization (related to longitudinal area) and as well comparable to similar treatments such as CWs (related to transversal area).

In order to verify the potential removal processes occurring in each treatment, samples were collected in points A, B and C (Figure 34) during the first day. Unfortunately, it was not possible to calculate the mass balance for day 2 for each treatment (VF and HF), due to operation issues related to the flowmeter allocated between the VF and HF. Nevertheless, as previously stated, the VF was designed to enhance the removal of BOD and NH4-N. In this regard, the VF was responsible for more than 60% of the NH_4-N (Figure 37).

In addition, as was expected, the BOD and NH_4-N removal were more expressive in the VF than in HF (Figure 37). About to 26% of the BOD was removed in the VF while only 1% was removed in the HF (Figure 37). The P removal was more efficient in the VF than the HF, being respectively, 33% against only 12% (Figure 37). For instance, the higher removal of P can be associated to the higher amount (higher surface) of CAAC in the VF, which was twice the amount of CAAC in the HF.

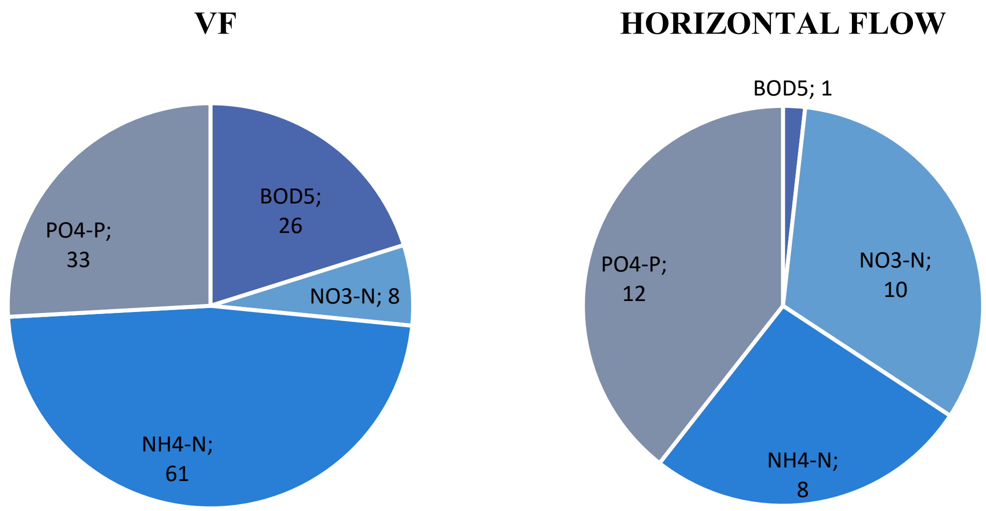


Figure 37. Representability of contaminants removal for each treatment (VF and HF) after one treatment cycle (day 1).

The HF was designed mainly to enhance the denitrification process. However, only 10% of nitrates were removed in the HF (Figure 37). More than 60% of the initial NH_4-N was converted into Nitrates in the VF, fact which might have increased the TN load getting into the HF. Nevertheless, there was no increment of Nitrates in the effluent in comparison with the influent. Thus, denitrification was happening, despite the increment of TN load. As commented previously, the load increment associated with lack of organic carbon and low retention time possible might have restricted the HF performance regarding denitrification.

Moreover, the composition of the biofilm can play an important role when NBS are focused on enhancing denitrification process. Therefore, the biofilm of the substrate was analysed in order to quantify the number of genetic copies per gram of biofilm **(16S)**, the number of denitrifying bacteria related transformation of nitrite (NO_2) into nitric oxide (NO_x) **(nirS)** and denitrifying bacteria related nitrous oxide (N_2O) conversion into Nitrogen gas (N_2) **(nosZ)**. The methods and protocols were based on the following articles (He et al., 2014; Chon et al., 2011). As can be seen in Table 1, the VF, showed higher presence of total bacterial community (16S) when compared with HF. For instance, this may be related to treatment sequence (VF-HF). The VF might have a greater opportunity of developing the microbiological community, since it is the first stage of the treatment, and thus, carry higher load and biodiversity regarding microorganisms.

Table 1 Characterization of the biofilm present in the substrates of the WETWALL hybrid flow (VF and HF).

	VF	HF
	[a]gc/g	
[b]nirS	4,37E+07	2,88E+07
[c]nosZ	1,51E+05	7,63E+04
nirS + nosZ	4,38E+07	2,89E+07
[d]16S	1,24E+14	7,31E+13

[a] Number of genetic copies per gram of biofilm. [B] Denitrifying bacteria ($NO_2 \rightarrow NO_x$). [C] Denitrifying bacteria ($N_2O \rightarrow N_2$)

Unexpected results regarding the denitrifying bacteria were noticed. The VF presented higher quantity of denitrifying bacteria (Table 1. nirS + nosZ) when compared to HF, indicating possibly, the presence of saturated zones along the VF column. However, when comparing the relative abundance of nirS bacteria in comparison with the total number of bacteria, the HF showed a greater rate than VF (Figure 38). Nevertheless, the nitrate removed was probably converted into NOx and the transformation into N_2 was not taking place, due to low relative abundance of nosZ. Probably, only 3 inoculations with real wastewater might have not been enough to ensure a good development of microbiologic community.

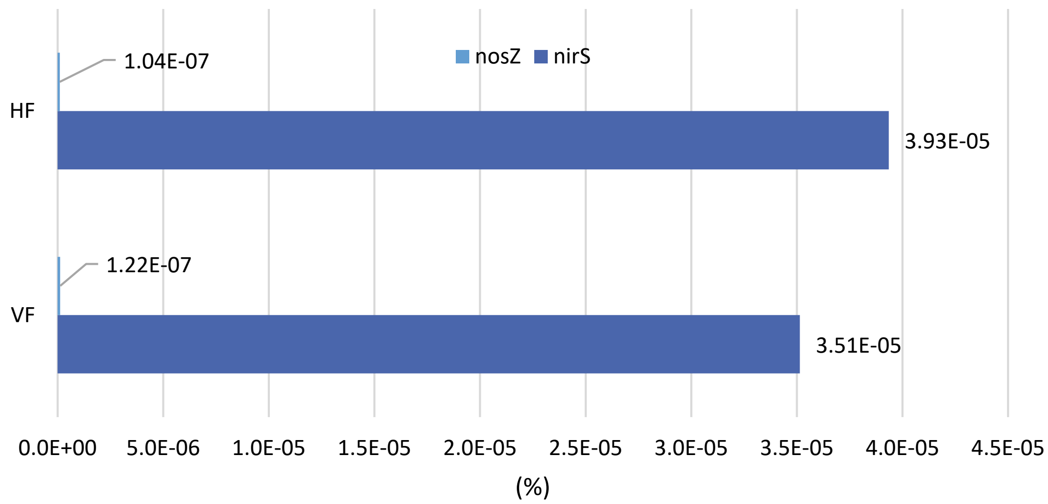


Figure 38. Relative abundance of denitrifies bacteria compared to total bacteria present in the WETWALL hybrid prototype.

Chapter 11 Conclusions & Further Research

In this chapter couple conclusions, not published in the articles, will be presented. The researchers on LWS treating urban wastewaters has been increasing in the past years, mainly because due its potential to become one multifunctional NBS, which can embrace, water treatment, thermal regulation and air quality.

It was observed a wide diversity related to design parameters such as structures, operational factors, plants and substrates, which are hindering the establishment of standards. In this regard, the WETWALL proposes a design concept aiming to facilitate the requirements for microbiological degradation of N, which are aerobic for nitrification and anoxic conditions with availability of organic carbon for denitrification. Preliminary result of the prototype highlighted the importance of defining a proper load of TN in accordance with retention time and availability of organic carbon. In addition, when working with synthetic wastewaters, proper inoculation procedure needs to be carried out in order to ensure the development of the denitrifying bacteria. Therefore, the assessment of optimum operational factors is crucial to ensure high pollutants removal and an efficient use of vertical spaces for treating urban wastewaters.

Nevertheless, the main innovation of the WETWALL design concept is the modular hybrid flow which can be combined differentially. The possibility of settling different treatment sequences can be very important at adapting the concept to different scales, different types of urban wastewater and different loads of contaminants. Even that the concept was not fully verified, the preliminary results showed a great potential to be further improved.

Therefore, it is strongly recommended further studies to validate the WETWAL design concept in regards to the treatment of urban wastewaters and as well as its performance at providing other potential ecosystem services such as improvement of air quality and thermal regulation.

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"it takes strength to dream and realize that the road goes beyond what you see"

Los hermanos

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