Politecnico di Torino

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# Valorisation of agricultural waste for the treatment of agro-food wastewater

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*A te sorella mia, che sei sempre stata al mio fianco.*
*A te che mi hai aiutata, sostenuta e supportata.*
*A te che sei sempre stata il mio esempio e la mia guida.*
*Non potrei avere sorella migliore di te.*

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# ABSTRACT

This study investigated the relationship between variations in pH and electrical conductivity (EC) with the degradation of total organic carbon (TOC) and total nitrogen (TN) in agro-industrial effluents, specifically apple boiling water and digestate derived from apple boiling water subjected to dark fermentation. Substrates partly composed of agricultural waste, such as ground corn cobs and hazelnut shells, were used. These substrates were tested in two 28-day batch tests and three column tests, two lasting 6 hours and one 12 days, in contact with the agro-industrial effluents to determine the optimal substrate for their degradation. The results showed that corn cobs were unsuitable for this purpose, whereas hazelnut shells achieved over 90% TOC degradation from the digestate and more than 40% from the apple boiling water. TN degradation exceeded 80% in the digestate and reached 100% in the apple boiling water. These findings demonstrate that hazelnut shells can significantly reduce organic matter, achieving levels below the standards set by Italian Decree D.M. 185/2003.

# 1. Introduction

Groundwater constitutes 99% of the world's liquid freshwater resources, making it a vital resource for nearly 50% of the world's drinking water production, 50% of its river base flow, and approximately 40% of its food production [1]. Groundwater has been overused in the last century due to increased industrial and agricultural demand, which together account for 69% of groundwater usage. About 21 of the 37 largest aquifers in the world have already run out of water [2]. Managed Aquifer Recharge (MAR) is one of the most effective methods for the recharging of groundwater.

Wastewater generated by various human activities is another significant water type, which requires treatment, recovery, and reuse. To remove contaminants from wastewater, researchers are increasingly turning to adsorbents derived from waste biomass, such as agricultural residues, instead of relying on synthetic materials. These biomass-based adsorbents are abundant, cost-effective, easy to produce, and environmentally friendly, making them an attractive alternative to becoming waste. As a result, their application in wastewater treatment has gained considerable attention [3].

## 1.1. Thesis Objectives

The objective of this study is to compare the efficiency of two types of agricultural waste, corn cobs and hazelnut shells, in treating two distinct agro-industrial wastewaters with a high DOM content: the apple water from boiling process, and the digestate from dark fermentation process. The evaluation is based on two batch tests and three column leaching tests to determine which agricultural waste is more suitable for incorporation into a SAT system, enabling the reuse of these wastewaters for agricultural irrigation in compliance with M.D. 185/2003.

## 1.2. Managed Aquifer Recharge (MAR)

Managed Aquifer Recharge (MAR), also known as Artificial Groundwater Recharge, is a globally implemented strategy aimed at preventing groundwater depletion and recovering, securing, and maintaining adequate groundwater volumes with sufficient quality for drinking water supplies. It involves the artificial infiltration of surface water from lakes or rivers into groundwater systems. The main goals of a MAR system are [4]:

- to store surplus water during wet seasons for use during dry periods;
- to establish a water treatment barrier that enhances water quality for future specific applications;
- to create a hydraulic barrier to prevent seawater intrusion, especially in coastal areas;
- to assist with flood control.

Since the 1970s, MAR has grown in significance, and future water management plans that guarantee groundwater availability and quality will probably depend heavily on it [5]. More than half of the MAR systems in Europe use surface water spreading. These systems include bank filtration (Figure 1), which uses lake or river water for infiltration and then extraction via wells, or infiltration basins, which reroute surface water into artificial basins and allow it to infiltrate into groundwater systems through a sandy filtration layer [2].

Even though MAR implementation is becoming more popular, it has proven difficult to choose MAR locations and techniques based on local conditions and qualities. This is because they depend on many interrelated factors, such as [2]:

- availability of source water for recharge;
- types of subsurface soil for source water infiltration;
- capacity of aquifers to store and extract enough water;
- quality of source water;
- capacity of particular MARs to remove pollutants;
- cost of implementation projects.

There are also elements that can have an impact on the MAR's ability to infiltrate and remove contaminants, like the site's hydraulic conductivity, soil texture, mineral content, and source water chemistry. For example, the infiltration rate is influenced by geologic architecture and soil texture. Therefore, the soil hydrology is generally used to evaluate the suitability of MAR for the rate of infiltration. Surface water pollutants can be eliminated through photolysis [6], while in soil they can be eliminated through physicochemical filtration, solute precipitation, sorption, and biodegradation. The hydraulic conductivity or texture of the soil may have an indirect impact on the water treatment capacity of MAR since sorption and biodegradation rely on the hydraulic residence time in the system. Groundwater pollution may increase because of contaminant precursor transformation, redox fluctuation, and the desorption of pollutants from contaminated subsoil due to various factors [2]. As a result, it's critical to choose a location with the right soil properties to enable rapid infiltration and storage of huge amounts of water while also providing enough residence time for the removal of contaminants.

However, Managed aquifer recharge is a popular groundwater management technique due to its low implementation costs, low evaporation loss when compared to surface reservoirs, and capacity to absorb large amounts of water from various sources, such as river or stream waters, treated municipal wastewater, and urban and agricultural runoff.

Moreover, MAR reduces turbidity during the artificial infiltration process and naturally removes suspended organic and inorganic impurities. Filtration, straining, (ad-)sorption, and biological degradation control the process, which may serve as a (pre-)treatment stage in the creation of drinking water [1]. The natural purification processes that occur during the infiltration process result in the complete or partial retention of nutrients, natural organic matter (NOM), metals, or organic pollutants within the subsurface. For high-molecular-weight NOM, removal efficiencies can be up to 87%; however, MAR is less successful for low-molecular-weight NOM [7]. Additionally, MAR serves as a stabilizing stage, lowering temperature fluctuations and contaminant concentrations while also improving the taste of the water.

In the literature there are different MAR designs (Figure 1) that help infiltrate water or remove pollutants. Some examples are [2]:

a) Aquifer storage and recovery (ASR): injection of freshwater into aquifer using wells for later recovery by using the same wells.
b) Aquifer storage transport and recovery (ASTR): injection of freshwater into aquifer using wells for later recovery by using a different well.
c) Dune filtration: water infiltrates through dunes for later collection from a pond at a lower elevation.
d) Soil aquifer treatment (SAT): partially treated wastewater infiltrated into a shallow aquifer through the vadose and saturated zone. This argument is discussed in detail in paragraph 1.2.2
e) Percolation tanks: recharge basins are designed to collect flow from transient streams during the rainy seasons.
f) Recharge release: temporary or permanent dam on the ephemeral stream that allows draining stored water when required.
g) Bank filtration: groundwater pumping near streams to enhance infiltration and improve surface water quality.
h) Infiltration pond: shallow facilities to provide temporary water storage and facilitate infiltration.

However, securing land suitable for MAR is often difficult, and limited land resources can hinder the implementation of many MAR projects. An emerging strategy to improve aquifer recharge is to utilize agricultural land for MAR, known as Agricultural Managed Aquifer Recharge (Ag-MAR).

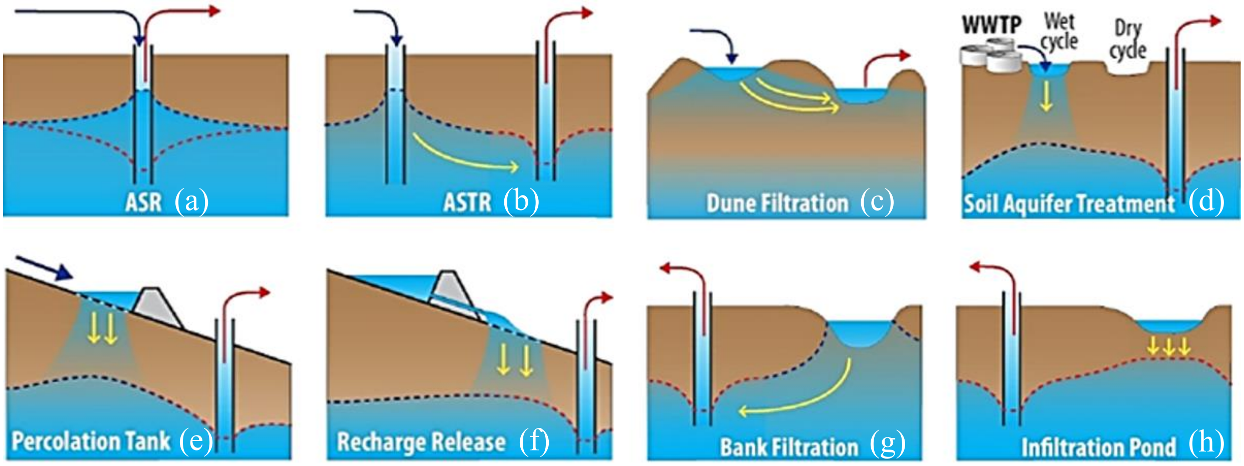


*Figure 1. Types of Managed Aquifer Recharge [2]*

### 1.2.1. Agricultural managed aquifer recharge (Ag-MAR)

Ag-MAR can be applied to large agricultural areas during times when crops are not being cultivated or are in a dormant state, such as winter for deciduous orchards like almonds, pomegranates, and pistachios [8]. This approach allows agricultural plots to act as temporary infiltration sites, thus avoiding the need to dedicate land exclusively for MAR and reducing land competition, particularly in urban settings.

Despite its potential, Ag-MAR's effectiveness is influenced by several factors [4]:

- Flooding can harm root health, leading to reduced nutrient uptake and lower crop yields.
- Enhanced artificial recharge can cause groundwater contamination, as higher water flows may carry agricultural fertilizers, pesticides, and herbicides through the vadose zone.

Additional considerations include water availability for recharge, necessary infrastructure, soil properties, groundwater quality impacts, water law regulations, and financial costs.

Table 1 shows the benefits and drawbacks of the MAR system, compared to the Ag-MAR system.

*Table 1. Benefits and drawbacks of MAR and Ag-MAR [4]*

| | **Benefits** | **Drawbacks** |
|---|---|---|
| **MAR** | Provides relief for stressed aquifers | Lack of land resources (major drawback) |
| | Constitutes both a treatment and hydraulic barrier | Infiltration basins have a small footprint (smaller area for groundwater recharge compared to agricultural fields) |
| **Ag-MAR** | Temporal utilization of farmland → additional surface area designated towards aquifer recharge | Prolonged waterlogged conditions for crops |
| | Minimal damage to crop's health and yield | Groundwater contamination and soil erosion |

Ag-MAR represents a broad approach to managed aquifer recharge, incorporating various techniques to enhance groundwater resources. Among these techniques, Soil Aquifer Treatment (SAT) stands out as a specific application of MAR, designed with the purpose of treating wastewater through natural soil filtration processes. This distinction highlights how SAT is not separate from MAR but rather a specialized form with a clear focus on effluent treatment, which will be explored further in the paragraph below.

### 1.2.2. Soil Aquifer Treatment (SAT)

Soil aquifer treatment is a method of artificial recharge of groundwater by infiltrating the stormwater or wastewater treatment plant effluent from the basin surface under a cycle of alternate wetting and drying phases. To restore depleted groundwater, the pre-treated wastewater infiltrates through the unsaturated soil zone into an aquifer; this passage further improves the quality of the feed water thanks to filtration, adsorption, and biological processes that take place in the unsaturated soil zone.

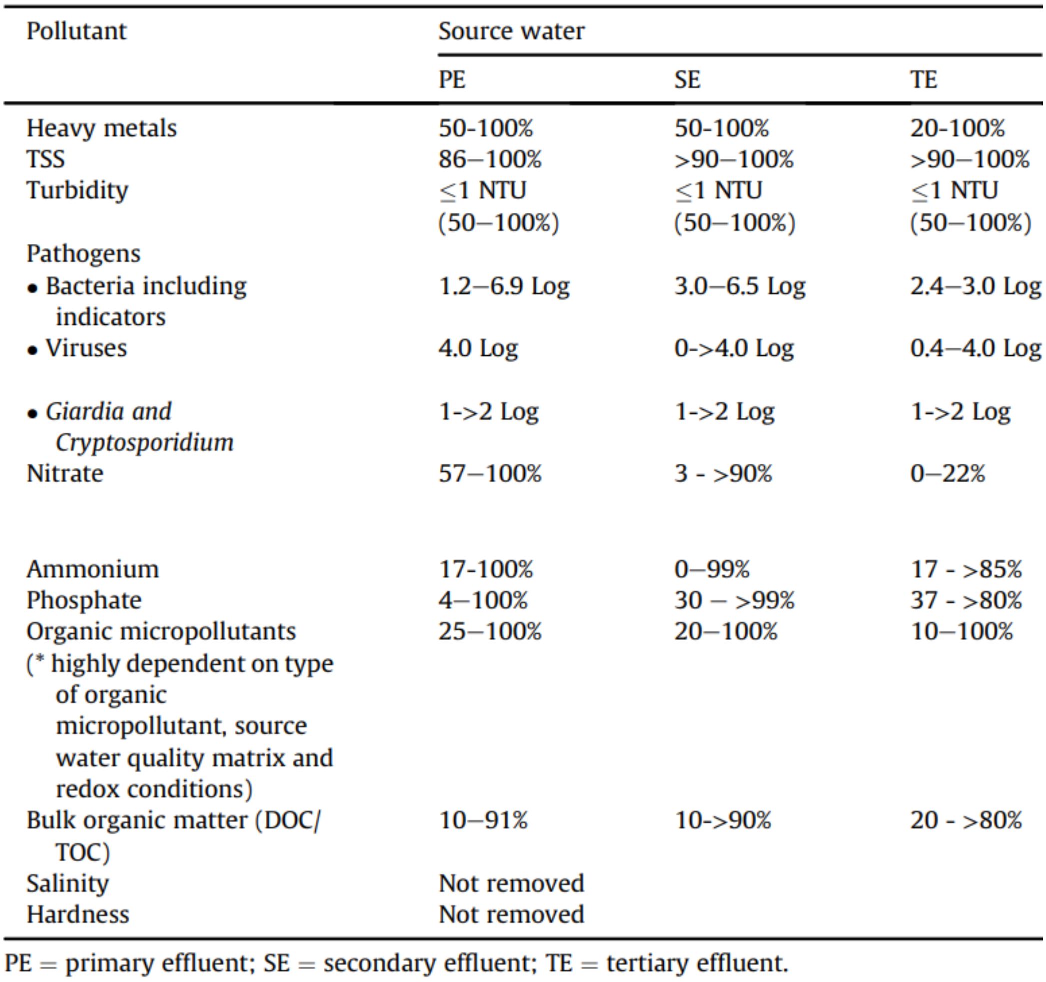
The three main benefits of SAT are enhanced water quality, restoration of groundwater levels in depleted aquifers, and the likelihood of partially treated wastewater being stored in the aquifer for later use. Furthermore, it can be utilized in conjunction with other saltwater interference barrier systems to create a barrier system in coastal zones [9].

The efficacy of the SAT system in eliminating contaminants is contingent upon various elements, such as the quality of the source water, the hydrogeological characteristics of the area, and the operational parameters employed. With careful site selection and thoughtful component design, including pre- and post-treatment, the performance of the SAT system can be further enhanced.

A properly built and maintained SAT system produces treated water that satisfies different quality standards for unrestricted irrigation or other applications. Organic materials, nitrogen species, and pathogens are the main entities linked to SAT. Furthermore, SAT has superior efficacy in nitrogen removal through nitrification and de-nitrification processes [10]. The unsaturated zone serves as a platform for biological and physicochemical interactions that lead to a large reduction in the characteristics of wastewater, including total suspended solids (TSS), pathogens, nutrients, and heavy metals before reaching the aquifer [9]. Most of the microbiological activity in SAT basins takes place in the topsoil layer, where the conditions for water, nutrients, and oxygen are most favourable. Soil column and field studies have determined that biological degradation plays a key role in reducing organic carbon content [9]. This process is complemented by mechanical filtration, which removes suspended organic matter in the upper few centimetres of the soil, where a surface-clogging layer tends to develop.

Table 2 presents some representative values for the removal efficiencies of SAT in eliminating various selected pollutants, as gathered from different literature sources.

*Table 2. Indicative removal efficiency of typical pollutants during SAT [11]*



| Pollutant | Source water | | |
|---|---|---|---|
| | PE | SE | TE |
| Heavy metals | 50-100% | 50-100% | 20-100% |
| TSS | 86–100% | >90–100% | >90–100% |
| Turbidity | ≤1 NTU (50–100%) | ≤1 NTU (50–100%) | ≤1 NTU (50–100%) |
| Pathogens | | | |
| • Bacteria including indicators | 1.2–6.9 Log | 3.0–6.5 Log | 2.4–3.0 Log |
| • Viruses | 4.0 Log | 0->4.0 Log | 0.4–4.0 Log |
| • *Giardia and Cryptosporidium* | 1->2 Log | 1->2 Log | 1->2 Log |
| Nitrate | 57–100% | 3 - >90% | 0–22% |
| Ammonium | 17-100% | 0–99% | 17 - >85% |
| Phosphate | 4–100% | 30 – >99% | 37 - >80% |
| Organic micropollutants (* highly dependent on type of organic micropollutant, source water quality matrix and redox conditions) | 25–100% | 20–100% | 10–100% |
| Bulk organic matter (DOC/TOC) | 10–91% | 10->90% | 20 - >80% |
| Salinity | Not removed | | |
| Hardness | Not removed | | |

PE = primary effluent; SE = secondary effluent; TE = tertiary effluent.

The main advantages of the SAT system include the following [11]:

- SAT enhances the physical, chemical, and microbial quality of source water during its passage through the soil by removing particles, microorganisms, heavy metals, nitrogen, bulk organic matter, and organic micropollutants (OMPs) across different SAT zones (interface, vadose zone, and saturated zone).
- It offers seasonal and long-term water storage without the common issues found in surface storage reservoirs, such as evaporative losses, external re-contamination of stored water, and algal growth.
- SAT serves as both an environmental and psychological barrier, increasing public acceptance of reclaimed water and promoting water recycling and reuse.
- It can also function as part of a saltwater intrusion barrier system in coastal aquifers.
- SAT can be integrated with other conventional and advanced wastewater treatment systems to produce water of the desired quality for specific uses. In this way, SAT can either replace or complement other treatment processes by providing a reliable barrier, ultimately reducing the overall costs of wastewater treatment and water reuse.

The SAT system also has several limitations, including the following [11]:

- The effectiveness of SAT is highly site-specific, relying on favourable local hydrogeological conditions, particularly permeability, which means it may not be suitable for all locations.
- Under reducing conditions, there is a risk of aquifer material leaching, which can lead to increased concentrations of iron, manganese, arsenic, or fluoride in the extracted water.
- One of the major concerns is the potential clogging of infiltration basins, wells, and aquifers due to the accumulation of suspended matter or chemical precipitation, especially if the system is not properly designed, operated, and maintained, or if pre-treatment is insufficient.
- SAT may provide limited protection against certain contaminants, like persistent OMPs, and there is a risk of aquifer contamination if the system is poorly designed, or pre-treatment is inadequate.
- The system offers limited operational control, making its performance difficult to predict; it requires thorough monitoring and regulation to prevent potential hazards.
- SAT may require a large amount of land for spreading basins, which may not be available.
- In winter, the infiltration rates in SAT basins decline, partly due to lower microbial activity because of cooler temperatures during this season. So, the decomposition of organic matter slows down, leading to a buildup of organic material in the topsoil layer that hinders infiltration [4].

However, there are different types of SAT models [12] with distinct mechanisms at natural sites, visible in Figure 2:

a) Reverse river bank filtration: water is pumped from an aquifer back towards a river, instead of naturally flowing from the river to the aquifer, as in a traditional river bank filtration.

b) Subsurface drainage: infiltration of water into the soil, where it is collected by a network of subsurface drains. These drains can either carry the treated water to a treatment facility or discharge it, depending on the level of treatment required. This method is typically used in agricultural fields.

c) Multiple SAT wells: water is infiltrated through multiple wells, which increases the area of interaction between water and soil, enhancing the treatment process. The water may be injected into one well and extracted from another to ensure thorough filtration through the soil.

d) Circled SAT wells: SAT wells are arranged in a circular pattern to optimize the infiltration and extraction processes, ensuring a more uniform distribution of water through the aquifer.

e) River bank filtration with single SAT well: a single SAT well is placed near a riverbank. Water infiltrates from the river into the surrounding soil, and reaches the well, where it is extracted.

f) River bank filtration with either side SAT wells: SAT wells are placed on both sides of the river. Water infiltrates through the riverbanks on either side, with each well acting as a point of extraction. This increases the area of infiltration and enhances the treatment process by allowing more extensive interaction between the water and the soil.

Each of these models offers different advantages and can be selected based on specific site conditions, water quality goals, and the volume of water to be treated.

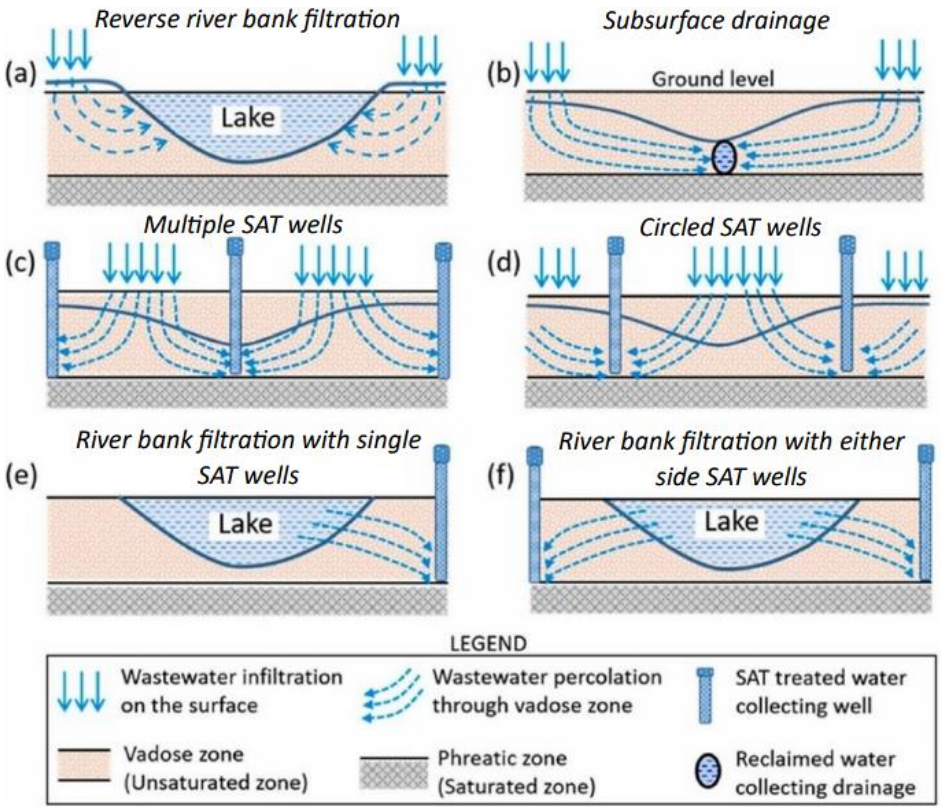


*Figure 2. Types of SAT model for treating the wastewater and stormwater [12]*

#### *1.2.2.1. Feasibility analysis and design of SAT system*

The characteristics of the medium, such as the geology, soil type, and hydrogeological variables, determine a field-site SAT system's treatment capability. Understanding the treatment potential thus requires an understanding of the hydrogeological dynamics and physical structure of the vadose zones, which control the effectiveness of contaminant removal [12]. Once SAT is selected as a potential technology to meet the objectives, a comprehensive feasibility study should be conducted, analysing technical, economic, institutional, legal, social, and environmental factors [11].

The design of SAT systems should consider the following factors [13]:

- pre-treatment requirements (level of wastewater treatment);
- infiltration (hydraulic loading) rate;
- land requirements (accounting for the wet/dry cycle);
- number of wells (production capacity per well);
- spacing between wells;

- distance of the wells from the infiltration pond or injection well;
- pumping rate (which influences groundwater flow and velocity);
- proportion of native groundwater in reclaimed water (%);
- water quality produced by the SAT system;
- any necessary post-treatment;
- operation and maintenance needs, including monitoring.

Therefore, the performance of SAT systems is influenced by various factors, with infiltration rates being a key parameter. The infiltration velocity and aquifer treatment can vary depending on the quality of wastewater and the type of SAT system, the soil type and permeability, the surface clogging material (related to the type of wastewater effluents applied), the pond depth, and the duration of wetting/drying cycles [13].

The proper selection of a site with suitable hydrogeological conditions is the first crucial step in the feasibility analysis and design of SAT systems. Achieving this requires a thorough site investigation, including test pits, boreholes, infiltration tests, groundwater wells, and analyses of groundwater quality and soil samples. The key hydrogeological factors to consider in designing SAT systems include [13,14]:

- physical and hydraulic boundaries of the aquifer and its degree of confinement;
- hydrogeological properties of the aquifer and the overlying formations;
- hydraulic gradient in the aquifer, as well as the groundwater flow direction and velocity;
- depth to the aquifer or piezometric surface;
- quality of the groundwater;
- aquifer's mineralogy and permeability.

Table 3 below summarizes the conditions for various parameters across the three stages of SAT: infiltration interface, soil percolation, and groundwater transport.

*Table 3. Comparison of Typical SAT Zones [13]*

| **Process/Parameter** | **Infiltration Interface** | **Soil – Percolation** | **Groundwater Transport** |
|---|---|---|---|
| Treatment mechanisms | Filtration, Biodegradation | Biodegradation, Adsorption | Biodegradation, Adsorption, Dilution |
| Transport | Saturated | Unsaturated | Saturated |
| Residence time | Minutes | Hours to days | Months to years |
| Travel distance | Centimetres | 3 – 30 m | Variable |
| Mixing | No | No | Yes (regional G.W.) |
| Oxygen supply | Recharge water | Unsaturated zone | Regional G.W. |
| Biodegradable organic carbon availability | Excess | Excess/Limiting | Limiting |
| Redox conditions | Aerobic | Aerobic to anoxic | Anoxic to aerobic |

The residence time is the main parameter governing the quality of SAT effluents. Sewage water should travel a sufficient distance through the soil aquifer, and the retention time in the SAT system should be long enough to achieve the desired water quality. While a general guideline suggests 100 meters of underground travel and a one-month retention time, the actual requirements vary based on the quality of the sewage effluent, the soil types in the vadose zone and aquifer, the depth of the groundwater, and the desired quality of the treated water [13]. Although most water quality improvements occur within the top 1 meter of soil, longer travel distances are beneficial as they provide more thorough removal of microorganisms and additional polishing treatment.

When the hydraulic loading rate is high, more effluents are infiltrated at once, allowing for longer relaxation periods and greater oxygen introduction into the soil. However, infiltrating a larger amount of organic matter at once can potentially hinder biological activity in the upper layers. The extended relaxation time that facilitates oxygen introduction is a key mechanism in this process [13].

The breakdown of nitrogen compounds, organic matter, and various other pollutants is the primary focus in SAT processes. These degradation processes predominantly involve redox-sensitive reactions, where the simultaneous presence of terminal electron acceptors (preferably $O_2$ and $NO_3$ in SAT) and electron donors (organic carbon and $NH_4$) plays a crucial role in determining water treatment quality [15]. Effective SAT management should maintain adequate aerobic conditions to ensure significant organic removal while also establishing suboxic conditions necessary for the denitrification process [16].

SAT systems operate intermittently through wetting and drying cycles in infiltration basins to prevent prolonged oxygen-deficient conditions in the SAT vadose zone. The impact of the duration and management of these wetting and drying cycles on the quality of infiltrated water is vital for the efficiency of SAT [15].

To enhance SAT management, it is essential to frequently sample soil pore water for chemical analysis. However, this intensive sampling process is both time-consuming and costly. As an alternative, studies have demonstrated that in situ monitoring of redox potential ($E_h$) at a high temporal resolution, along with additional parameters like gaseous $O_2$, soil temperature (T), and soil water content ($\theta$), can significantly improve the management of SAT and MAR systems [15]. Despite this, $E_h$ measurements are primarily used qualitatively, which limits the ability to accurately identify the dominant redox reactions and their rates [17].

In 2023, Turkeltaub did some studies on the relationship between gaseous $O_2$ and redox potential in a SAT system [15]. His three main conclusions were the following:

- When gaseous $O_2$ is present, aerobic conditions dominate, maintaining high positive $E_h$ values. As the levels of gaseous $O_2$ decrease, $E_h$ conditions also drop, shifting towards negative values [18]. However, the relationship between gaseous $O_2$ and $E_h$ weakens with increasing depth, suggesting that gaseous $O_2$ has less influence on $E_h$ conditions at greater depths within the SAT vadose zone.

- The study found a negative correlation between seasonal changes, such as monthly average temperature and redox potential ($E_h$). However, fluctuations in soil temperature showed weak correlations with different $E_h$ components.
- The relationships between the $\theta$ components and $E_h$ components show that during periods when $\theta$ is higher, $E_h$ conditions are high and positive. However, under wetter conditions, increased microbial activity should lead to a decrease in $E_h$ to negative values. This discrepancy might be explained by the low microbial activity at deeper depths, which allows $E_h$ conditions to remain positive [16]. This insight could be valuable for understanding the degradation processes of total organic carbon (TOC) and total nitrogen (TN), as $E_h$ plays a crucial role in these transformations.

#### *1.2.2.2. Agricultural Soil Aquifer Treatment (Ag-SAT)*

A new approach to MAR being investigated involves the off-season flooding of agricultural land, referred to as agricultural MAR or Ag-MAR. This method repurposes agricultural fields as temporary infiltration basins during their dormant periods, thereby enhancing land use for groundwater recharge without the need to dedicate specific areas solely for MAR. As space for SAT becomes scarce and the availability of treated wastewater (TWW) rises, agricultural SAT, or Ag-SAT, merges SAT with Ag-MAR [4]. Ag-SAT involves flooding agricultural land during the off-season with TWW to recharge groundwater, which can then be reused. This approach not only offers alternative sites for SAT where infiltration space is limited but also allows the TWW to potentially supply nutrients to the fields during flooding.

The temporary use of agricultural land is usually inexpensive, provided it doesn't significantly disrupt its primary function. A low-cost and eco-friendly method can be achieved by deliberately flooding Ag-SAT sites during the off-season and reusing the recharged water for local irrigation. Additionally, distributing the reclaimed water regionally for off-site irrigation is also a feasible option. Farms that already use flooded irrigation may be well-suited for Ag-SAT, especially if the aquifer below is conducive to recharge and the soil is deep and permeable. In such cases, flooding during the growing season could also be viable. Furthermore, there may be financial incentives for farmers and landowners to use Ag-SAT because it requires very little special infrastructure.

An example of Ag-SAT layout is displayed in Figure 3.

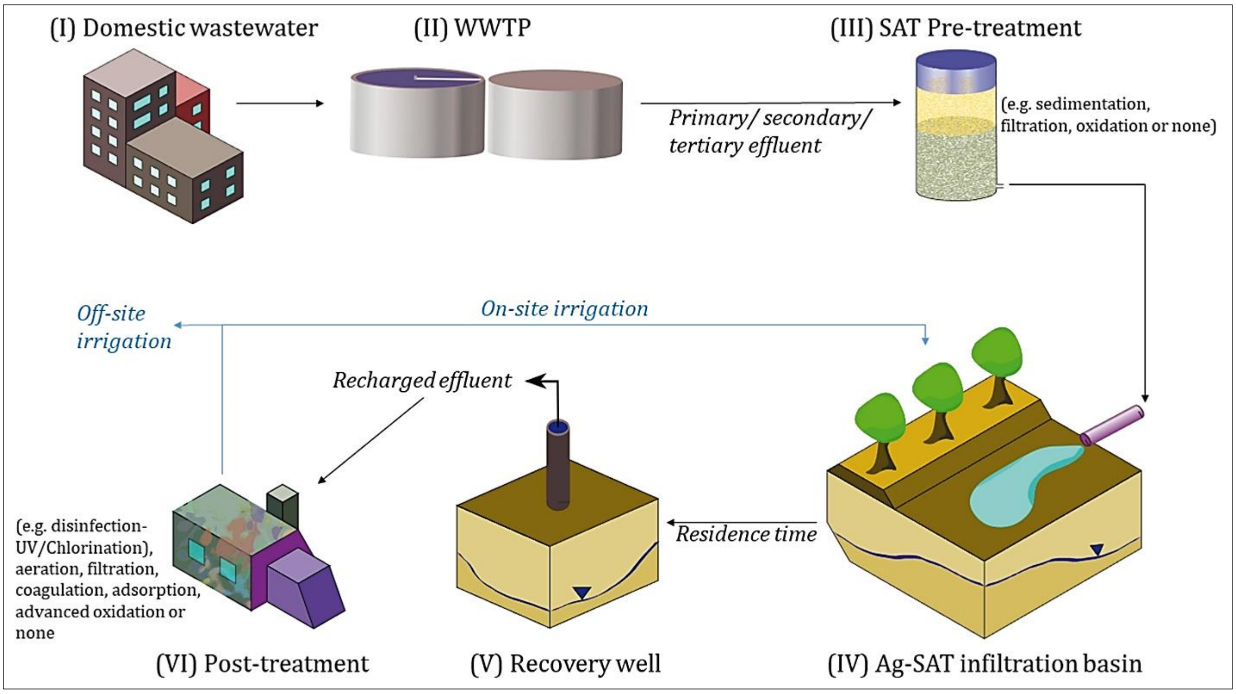


*Figure 3. Schematic of agricultural soil aquifer treatment (Ag-SAT) process stages [4]*

The process is the following:

I. Raw wastewater is produced from domestic facilities.
II. The wastewater is sent to a wastewater treatment plant (WWTP) for initial processing.
III. The treated effluent undergoes SAT pre-treatment, which includes sedimentation, mechanical filtration, and oxidation. Disinfection methods like chlorination or UV are avoided at this stage because biochemical filtration is crucial.
IV. The pre-treated effluent is applied to agricultural fields designed for SAT (Ag-SAT fields) during the off-season through surface spreading or flooding.
V. After a period of infiltration, the recharged water is extracted using recovery wells.
VI. The reclaimed water is further treated as needed based on its intended use. For example, in the Shafdan system, no additional disinfection is required post-treatment since the water quality after SAT is deemed suitable for unrestricted irrigation [19]. Ultimately, the treated water is distributed for unlimited irrigation. The main operational difference between Ag-SAT and traditional SAT lies in the location, which may involve additional specific considerations.

Employing treated wastewater (TWW) for Ag-SAT offers various advantages but also introduces potential risks and concerns. The benefits of Ag-SAT are the following [4]:

- Reduced pressure on freshwater resources, particularly in agriculture, which accounts for 70% of global freshwater consumption.

- Enhanced water security and increased availability of irrigation water through the recharge of treated wastewater.
- Recycling of nutrients and organic matter into soils, such as carbon, nitrogen, and phosphorus, from the compounds in treated wastewater, thereby decreasing the need for fertilizers.
- Improved soil characteristics, including texture and fertility, which leads to higher crop yields and the possibility of cultivating a wider range of crops, especially in arid and semi-arid regions.

The risks and concerns of an Ag-SAT system are [4]:

- Pharmaceutical compounds in treated wastewater (TWW) can be absorbed by crops through their roots. Sandy soils used in SAT basins pose a higher risk for the accumulation of these compounds.
- Over time, the repeated use of TWW can lead to the formation of a clogging layer, which reduces the soil's ability to absorb water. In SAT systems, this buildup could prolong waterlogged conditions for crops, posing a significant risk.
- The development of hydrophobicity, or soil water repellency, can result from TWW use. This condition affects the even distribution of moisture and the soil's wetting rate, leading to uneven water and nutrient availability in the crop root zone. It also decreases infiltration rates, potentially increasing runoff and erosion on the soil surface, negatively impacting agricultural productivity.

Various issues and their implications have been studied, such as water quality, effects on soil properties, plant health, and soil condition. For instance, salinity, sodicity, and boron toxicity are notable concerns [4]. In Ag-SAT, agricultural fields are inundated with treated wastewater (TWW) that might not meet the highest standards of tertiary treatment currently advised.

Both the crop needs and the needs for water quality treatment must be considered when choosing a site for a crop in order to increase the likelihood that an Ag-SAT project will be successful.

## 1.3. Agricultural waste

The quality of the environment directly affects the ability to sustain life on Earth. Water sources are increasingly scarce, and those that remain are often contaminated with various pollutants. Heavy metals and dyes polluting water resources can lead to the degradation of biological and chemical systems. Agricultural waste offers advantages due to its diverse sources, low cost, and renewable nature. When these wastes are repurposed into valuable products like environmental adsorbents for pollutant removal, biochar (BC), composts, and natural fertilizers, they can be a valuable resource. This approach is preferable to burning the waste in open fields, which causes environmental issues such as air pollution and soil erosion. Converting waste into useful compounds is a crucial area of scientific research [20].

The unregulated discharge of industrial effluents into waterways led to a rise in pollutant levels, which rapidly altered the ecosystem's composition and adversely affected the health of humans, plants, and animals. The most common environmental pollutants are organic and inorganic, both of which are released into the environment through human activities and natural processes. Organic contaminants include substances like pesticides, chlorophenols, phenolic compounds, nitro compounds, dyes, and polyaromatic organometallic compounds, while toxic ions such as Cr, Pb, As, and Hg are examples of inorganic pollutants [20]. Inorganic pollutants are generally persistent and can have harmful effects, including genotoxic, teratogenic, carcinogenic, and mutagenic impacts, even at low concentrations. In contrast, organic pollutants are primarily human-made, frequently used as intermediates, fuel additives, and industrial solvents. Many manufactured products, such as paints, adhesives, fuels, and plastics, contain hazardous organic compounds.

Various species have demonstrated the ability to remove both organic and inorganic contaminants using different materials, including [20]:

- Industrial wastes (such as dried activated sludge, fly ash, coal fly ash, waste tires, and silica gel);
- Soil and mineral substances (such as montmorillonite clay, river sediment, hematite, zeolite, and bentonite);
- Agricultural wastes (such as rice husk, sugarcane bagasse, and peanut husk).

Additionally, processed agricultural waste offers several advantages, including being a renewable natural resource, widely available, cost-effective, capable of producing selective adsorption effluent, and easy to regenerate.

Recently, agricultural production has tripled due to expanded farmland, the technological advancements of the Green Revolution, and rapid population growth. This rise in global production has intensified environmental pressures, negatively impacted natural resources and jeopardized ecological sustainability and public health. Agriculture contributes 21% of global greenhouse gas emissions [21]. As a key sector in the bioeconomy, agriculture generates the largest amount of biomass compared to other biological industries. This presents a significant opportunity for transforming plant waste into high-value byproducts such as bioenergy, bioproducts, animal feed, and food. Agricultural wastes can be utilized to produce a range of products such as biochemicals, biofuels, and biomaterials through various biological, chemical, and physical processes.

Agricultural wastes can be integrated into soil and groundwater treatment (SAT) systems to improve water management. Using these wastes as infiltration materials or as additives in SAT processes can enhance the soil purification capacity and optimize the aquifer recharge process.

Recent research [22] emphasizes choosing suitable solid carbon sources for biofilter media that offer sustainability, long-term availability, and reactivity. These sources should have lower potential for pollution replacement, improved hydrodynamic properties, and consistent nitrate removal efficiency.

In 2019, Özkaraova explored the potential of using tea factory waste and hazelnut husk, two major organic wastes in Turkey, as carbon sources for denitrification bioreactors [22]. Turkey is the world's leading hazelnut producer and the fifth-largest tea producer. Between 2008 and 2018, annual hazelnut production ranged from 420,000 to 800,791 tons, reaching 515,000 tons in 2018. The husk constitutes about two-thirds of the hazelnut's wet weight. For tea production, the quantity of wet tea leaves harvested increased from 1,100,257 tons in 2008 to 1,500,000 tons in 2018. At the end of the production process, black tea constitutes roughly 20% of the fresh tea leaves processed. In this study, three main activities were undertaken:

- Leaching tests were performed to evaluate the dissolution levels of nitrate, nitrite, ammonia, and total organic carbon (TOC).
- Batch experiments were conducted to assess how effectively different organic wastes stimulate denitrification and their impact on nitrate removal at various doses.
- Column experiments were executed to examine the long-term availability of carbon and the efficiency of nitrate removal over extended periods.

Both types of waste were air-dried and screened to a size below 4 mm. For the leaching experiments, dry samples were used, while saturated samples were employed in batch and column experiments to eliminate trapped oxygen, then stored at temperatures below 4°C. Elemental analyses were performed on finely powdered samples, with details of the composition and properties provided in Table 4.

*Table 4. Elemental composition and some properties of organic residues used in the study [22]*

| **Organic residues** | **Elemental composition, % (Standard deviation)** | | | | **Density (g cm$^{-3}$)** | **Porosity (%)** |
|---|---|---|---|---|---|---|
| | **C** | **H** | **N** | **S** | | |
| Hazelnut husk | 42.10 (1.31) | 5.66 (0.26) | 1.21 (0.04) | 0.24 (0.08) | 0.56 | 84 |
| Tea factory waste | 48.17 (1.31) | 6.57 (0.03) | 2.72 (0.09) | 0.22 (0.004) | 0.70 | 74 |

The conclusions obtained from this study were the following:

- Initial results from the batch experiments indicated that both substrates facilitated the denitrification process without requiring inoculation.
- The zero-order kinetic model revealed that nitrate removal rates were dependent on carbon availability and the proportion of organic substrate used.
- For hazelnut husk, conditions were carbon-limited, while tea waste had higher carbon abundance.
- The highest nitrate removal rates were achieved with 100% hazelnut husk and 40% tea factory waste, with half-lives of approximately 4 days for hazelnut husk and 6 days for tea factory waste.
- Gene enumeration indicated a greater presence of denitrifying bacteria in the flasks with hazelnut husk compared to those with tea factory waste.
- Due to the high leaching potential of tea factory waste, control measures such as pre- and post-treatment might be necessary, like pre-washing or reusing outlet water at nutrient-limited sites.
- Long-term column experiments showed that the release of organic carbon and nitrogen compounds did not negatively impact nitrate removal under continuous flow conditions.
- There were much shorter half-lives and nearly absent nitrate levels throughout.

## 1.4. Legislation

### 1.4.1. International legislation

There are various laws and regulations around the world that pertain to soil aquifer treatment (SAT) and related environmental management practices.

One of the international regulations is “Sustainable Development Goals (SDGs)” from 2015 [23]. This standard promotes sustainable development globally, including water management and environmental protection. SDG 6 (“Clean Water and Sanitation”) and SDG 15 (“Life on Land”) provide frameworks for sustainable water use and soil management, which are relevant to SAT practices. Another international regulation is “World Health Organization (WHO) Guidelines for Drinking-Water Quality” [24] originally passed in 1983. This law sets international standards for water quality, including guidelines for the safety of water used in drinking and irrigation. It provides standards for the quality of treated water that could be used after SAT processes.

The main laws of North America about SAT are divided between the United States and Canada. The first one relies on the “Environmental Protection Agency (EPA)” [25], which develops on two fronts:

- The “Safe Drinking Water Act (SDWA)” from 1974 protects public health by regulating the nation's public drinking water supply. It ensures that any treated water from SAT systems meets safety standards for drinking.
- The “Clean Water Act (CWA)” from 1972 regulates discharges of pollutants into U.S. waters and sets quality standards for surface waters. It affects how the water used in SAT is managed and monitored.

Instead, Canada's legislation relies on “Guidelines for Canadian Drinking Water Quality” [26] from 1968, which establish standards for drinking water quality across Canada. It ensures that water treated through SAT systems meets national safety standards.

Australia's legislation is based on “Australian Guidelines for Water Recycling” [27] from 2006, where the objective is to provide guidelines for the safe recycling of water, including treated wastewater. This law is relevant to SAT because it guides the use of recycled water in various applications, including irrigation.

Another continent with important water regulations is Asia. China relies on the “Water Pollution Prevention and Control Law of the People's Republic of China” [28], originally passed in 1984, with significant revisions in 2008 and 2017. It aims at regulating the discharge of pollutants into water bodies and protecting water quality. Therefore, it influences how treated wastewater is managed and used in SAT systems. Another country is India, where the main law is “National Water Policy”, ultimately perfected in 2012 (the earlier version was in 1987), which provides a framework for water management and conservation in India.

The European laws and regulations concerning soil and aquifer treatment (SAT) do not directly address SAT as a specific process but include rules and directives that govern related aspects such as water quality, waste management, and environmental protection. Some relevant European regulations are:

- "Water Framework Directive" (2000/60/EC): establishes a framework for the protection of inland surface waters, transitional waters, coastal waters, and groundwater. It aims to ensure the long-term protection of water quality and achieve good status for all water bodies. It provides guidelines for groundwater management, including the use of artificial recharge methods like SAT.
- "Groundwater Directive" (2006/118/EC): focuses on the protection of groundwater against pollution and deterioration. It complements the Water Framework Directive by setting out measures to prevent and control groundwater pollution. It establishes standards and regulations for groundwater quality that are relevant to the effectiveness of SAT systems.
- Directive 2008/98/EC on Waste ("Waste Framework Directive"): sets the basic concepts and definitions related to waste management and recycling. It aims to reduce the negative impacts of waste on the environment and human health. It may influence how agricultural and other wastes used in SAT are managed and disposed of.
- Directive 91/676/EEC on the Protection of Waters Against Pollution Caused by Nitrates from Agricultural Sources (Nitrates Directive): aims to reduce water pollution caused by nitrates from agricultural activities, thereby improving water quality. It addresses the impact of agricultural runoff on water bodies, which can be relevant to the design and operation of SAT systems.
- Directive 2006/7/EC on the Management of Bathing Water Quality: ensures the high quality of water at bathing sites to protect public health and the environment. It provides standards for water quality that could influence the treated water used in SAT systems.

Another important law is the Regulation (EU) 2020/741, which is the former refers to agricultural reuse only. The regulation establishes stringent standards for water quality, monitoring, and risk management. It outlines the obligations of wastewater treatment operators, setting out specific requirements for the levels of microorganisms and chemical contaminants allowed in the reclaimed water. The regulation also mandates the implementation of a risk management plan by the operators, which includes identifying potential risks to human health and the environment and taking preventive measures to mitigate those risks. Additionally, EU 2020/741 encourages Member States to promote the reuse of treated wastewater to address water scarcity and reduce the demand for freshwater resources. The regulation aims to create a uniform framework across the EU, ensuring that treated wastewater used for agricultural purposes meets high safety and quality standards, thus facilitating its acceptance and use across different regions.

There are then ISO standards that offer guidelines and requirements that can influence various aspects of SAT systems, from environmental management and process quality to water safety and sample analysis. The most important are the following:

- ISO 14001:2015 – Environmental Management Systems: provides a framework for improving environmental performance through effective management and monitoring of environmental practices. It helps organizations manage the environmental impacts of their operations, including water treatment and waste management.
- ISO 9001:2015 – Quality Management Systems: establishes criteria for a quality management system to help organizations ensure their products and services meet customer expectations and regulatory requirements. It ensures that processes and treatments, including those for water, are performed according to strict quality standards.
- ISO 16075-1:2015 – Guidelines for the Safe Use of Treated Wastewater: provides guidelines for the safe reuse of treated wastewater, particularly for irrigation purposes. It concerns practices related to the reuse of treated water, which may include water recovered through SAT.
- ISO 10500:2012 – Quality of Drinking Water: establishes requirements for the quality of drinking water to ensure safety and health. It provides criteria for the quality of treated water that might be recovered through SAT and intended for human consumption.
- ISO 11969:2016 – Water – Determination of Total Organic Carbon (TOC) Content: defines the method for determining the total organic carbon content in water. It is essential for monitoring the organic carbon content in treated water and the SAT process.
- ISO 5667-1:2006 – Water Quality – Sampling – Part 1: Guidance on the Design of Sampling Programs: provides guidelines for the design of sampling programs and the preservation of water samples for analysis. It is crucial for ensuring that water samples used in SAT processes are collected and preserved correctly for accurate analysis.

### 1.4.2. Italian legislation

In Italy, SAT and related groundwater management practices are governed by a combination of national and regional laws, environmental regulations, and technical standards. Key legal frameworks include:

- Legislative Decree 152/2006 ("Environmental Code"): this is the primary environmental legislation in Italy, which includes provisions on water management, groundwater protection, and the regulation of wastewater treatment and reuse. It sets out the general principles for environmental protection, including water resources.
- Legislative Decree 31/2001: this decree transposes European Directive 98/83/EC on the quality of water intended for human consumption into Italian law. It includes regulations related to the safety and quality of water, which could be relevant to SAT operations, especially when treated wastewater is used.

- Ministerial Decree 185/2003 (Table 5): this decree regulates the reuse of wastewater in Italy, setting the standards and guidelines for using treated wastewater for irrigation and industrial purposes. The decree is essential for SAT practices when using reclaimed water.
- Regional Laws and Regulations: various Italian regions have additional regulations governing water management and groundwater protection, which can impact the implementation of SAT projects. Regional authorities may set specific rules regarding land use, water rights, and environmental protection that must be considered.

In Italy, Ministerial Decree 185/2003 sets forth the minimum quality standards for reuse of industrial wastewater for irrigation, civil and industrial purposes (Table 5). It aims to ensure that reclaimed water is safe and environmentally sustainable while promoting the efficient use of water resources. The decree specifies the maximum allowable concentrations of pollutants, including nitrogen, phosphorus, and pathogens, in treated wastewater. These standards are designed to protect public health and the environment. It outlines different quality classes for reclaimed water, depending on its intended use, with stricter standards for more sensitive applications. It mandates that wastewater must undergo specific treatment processes to meet the quality standards set for various reuse applications. Operators of wastewater treatment facilities are required to regularly monitor the quality of treated wastewater and report on compliance with the established standards. This regulation aligns with broader European and international efforts to enhance water reuse and sustainability in the face of growing water demands and environmental concerns.

However, it is crucial to emphasize that current Italian legislation explicitly prohibits the recharge of aquifers with treated wastewater. This restriction is established under the Legislative Decree No. 152/2006, which outlines the environmental regulations for water protection. Furthermore, the use of treated wastewater for irrigation is permitted only within the “limits of crop requirements”, meaning that any application must avoid excess water that could lead to infiltration and potential contamination of groundwater resources. This careful regulation underscores Italy's commitment to protecting water quality while addressing agricultural needs.

*Table 5. Limit values for wastewater at the outlet of the recovery plant (D.M. 185/2003) [29]*

| | **Parameter** | **Unit of measurement** | **Limit value** |
|---|---|---|---|
| Chemico-physical parameters | pH | - | 6 - 9,5 |
| | SAR | - | 10 |
| | Coarse particles | - | Absent |
| | TSS | mg/L | 10 |
| | $BOD_5$ | $mgO_2/L$ | 20 |
| | COD | $mgO_2/L$ | 100 |
| | $P_{TOT}$ | mgP/L | 2 |
| | $N_{TOT}$ | mgN/L | 15 |
| | $NH_4^+$ | $mgNH_4/L$ | 2 |
| | Electric conductivity | μS/cm | 3000 |

|  | **Parameter** | **Unit of measurement** | **Limit value** |
|---|---|---|---|
|  | Al | mg/L | 1 |
|  | As | mg/L | 0,02 |
|  | Ba | mg/L | 10 |
|  | Be | mg/L | 0,1 |
|  | Bo | mg/L | 1 |
|  | Cd | mg/L | 0,005 |
|  | Co | mg/L | 0,05 |
|  | $Cr_{TOT}$ | mg/L | 0,1 |
|  | Cromo VI | mg/L | 0,005 |
|  | Fe | mg/L | 2 |
|  | Mn | mg/L | 0,2 |
|  | Hg | mg/L | 0,001 |
|  | Ni | mg/L | 0,2 |
|  | Pb | mg/L | 0,1 |
|  | Cu | mg/L | 1 |
|  | Se | mg/L | 0,01 |
|  | Sn | mg/L | 3 |
|  | TI | mg/L | 0,001 |
|  | V | mg/L | 0,1 |
|  | Zn | mg/L | 0,5 |
|  | Total cyanides (as CN) | mg/L | 0,05 |
|  | Sulphides | mg$H_2S$/L | 0,5 |
|  | Sulphites | mg$SO_3$/L | 0,5 |
|  | Sulphates | mg$SO_4$/L | 500 |
|  | Active Chlorine | mg/L | 0,2 |
|  | Chlorides | mgCl/L | 250 |
|  | Fluorides | mgF/L | 1,5 |
|  | Fat & animal/vegetal oils | mg/L | 10 |
|  | Mineral oils | mg/L | 0,05 |
|  | Total phenols | mg/L | 0,1 |
|  | Pentachlorophenol | mg/L | 0,003 |
|  | Total aldehydes | mg/L | 0,5 |
|  | Tetrachloroethylene, trichloroethylene (sum of concentrations of specific parameters) | mg/L | 0,01 |
|  | Total chlorinated solvents | mg/L | 0,04 |
|  | Trihalomethanes (sum of concentrations) | mg/L | 0,03 |
|  | Total aromatic organic solvents | mg/L | 0,01 |
|  | Benzene | mg/L | 0,001 |
|  | Benzo(a)pyrene | mg/L | 0,00001 |
|  | Total nitrogenous organic solvents | mg/L | 0,01 |
|  | Total surfactants | mg/L | 0,5 |
|  | Chlorinated pesticides (each) | mg/L | 0,0001 |
|  | Phosphorus pesticides (each) | mg/L | 0,0001 |
|  | Other pesticides (total) | mg/L | 0,5 |
| Microbiological parameters | Escherichia Coli | UFC/100mL | 10 (80% of the samples) 100 max puntual value |
|  | Salmonella |  | Absent |

# 2. Materials and methods

## 2.1. Materials

The materials used in this study are divided in two categories: wastewaters and agricultural wastes. The first category is further divided into two types:

- Apple boiling water from jam production plant.
- Digestate from apple boiling water subjected to dark fermentation.

The agricultural wastes used were corn cobs, and hazelnut shells, mixed with sand to create different types of substrates.

### 2.1.1. Apple boiling water from jam production plant

The apple boiling water came from a jam production plant, and it had been frozen before starting the study to conserve its properties. At the beginning of each test, the wastewater was thawed, then centrifuged and diluted. For the first two batch tests, the apple boiling water was diluted at different values to create various samples, each of which has been characterized. The dilution chosen for every test was 1:65 to obtain an effluent with initial TOC of 165±30 ppm, like the one of the digestate. This similarity was necessary to compare the results obtained from the study of apple water and digestate.

### 2.1.2. Digestate from apple boiling water subjected to dark fermentation

The digestate studied originated from residual apple boiling water subjected to "dark fermentation", a process that produces biohydrogen in complete darkness, produced by DISAT of the Polytechnic of Turin as part of the NODES project. This residue is being used by DISAFA (Department of Agricultural, Forestry, and Food Sciences of University of Turin) in fertigation trials to advance the concept of a circular economy.

The digestate was initially frozen, then thawed before each test and centrifuged, similar to the apple boiling water. Subsequently, it was diluted for characterization purposes. The chosen dilution was 1:40, with an initial TOC of 160±30 ppm.

### 2.1.3. Substrates

The materials used were corn cobs, hazelnut shells, Dorsilit 8 sand, and Dorsilit 5 sand. Of these, corn cobs were used only in the first batch test and the sand Dorsilit 5 was used only in the column tests.

#### 2.1.3.1. *Corn cobs*

The corn cobs used in this study came from the agricultural company "La cicogna" at Cavallerleone. Corn cobs were used in two different granular forms: 300 µm and 400 µm.

Corn cobs were mixed with Dorsilit 8 sand to create one type of substrate, and they were also mixed with hazelnut shells and Dorsilit 8 sand to create another type of substrate. Different percentages of corn cobs were analysed for substrate characterization, but the selected percentage was 10% by weight of corn cobs, with the remaining portion consisting of D8 sand, which had an initial TOC of 100.8 ppm. In the substrate containing the mix with hazelnut shells, the total mix was also 10% by weight, with corn cobs making up 5% by weight and hazelnut shells making up the other 5%, while the remaining portion was D8 sand.

The substrates containing corn cobs were analysed only in the first batch test due to the results obtained from it. This agricultural waste was set aside, and subsequent tests focused on the substrate made with hazelnut shells. Nevertheless, corn cobs were initially chosen as they are a by-product of sweet corn processing, widely produced in the food industry, and are considered one of the most abundant forms of agricultural waste. Corn cobs are rich in cellulose and hemicellulose, along with other carbohydrates. The corn plant itself is composed of about 60% to 70% starch, while the corn cob, a waste component, contains a significant amount of cellulosic biomass, making up roughly 30% of the plant's total biomass [30]. Specifically, corn cobs consist of approximately 41% cellulose, 36% hemicellulose, 16% lignin, and 7% water content, along with other essential components [30].

#### 2.1.3.2. *Hazelnut shells*

The hazelnut shells used in this study came from some agricultural industries. Like corn cobs, they were also used in two granular forms but divided in two ranges: 180-400 µm, and 400-800 µm. To create the substrates at 10% by weight, a 5% of each range was add to the 90% of D8 sand.

Hazelnut shells is another by-product of the food industry, which are produced in large quantities in different countries. In 2019-2020, the global production of hazelnuts was approximately 528,070 tons, with about 67% (353,897 tons) being shells [31]. Hazelnut shells are primarily used as fuel due to their calorific value, which is similar to that of wood. In fact, hazelnut shells are also chemically comparable to wood, as they are composed mainly of lignocellulosic polymers, including lignin, cellulose, and hemicellulose. Another potential use for untreated hazelnut shells, given its chemical makeup, is as an adsorbent. Unmodified hazelnut shells have been utilized for the adsorptive removal of copper ions from water, as well as for the removal of dyes and chlorophenols. Modified hazelnut shells, either as activated carbon or chemically treated, have been shown to effectively remove lead, cadmium, zinc, copper, uranium (VI), arsenic (III), chromium (VI), etc. [31]. After pollutants have been adsorbed, the loaded material can be directly used as fuel, bypassing the often-challenging processes of regeneration and disposal of the used adsorbent. Additionally, hazelnut shells can be converted into activated carbon through appropriate thermal treatment.

This research aimed to develop a novel adsorbent comprising hazelnut shells and to assess its effectiveness in removing DOM from agro-industrial wastewater. Substrates made from hazelnut shells were characterized at various weight percentages, with the selected 10% being used for all subsequent tests. Its initial TOC was 14.81 ppm.

### 2.1.3.3. Dorsilit 8 sand

Dorsilit 8 sand, commercialized by Dorfner (Germany), is a type of sand with distinct properties for specific applications in construction and engineering. It has a uniform particle size distribution (Figure 4), which makes it suitable for applications requiring specific grain size. The sand main component is high-quality quartz grains. This composition ensures strength and durability in its applications. Due to its specific grain texture and size, Dorsilit 8 sand is well-suited for filtration purposes. Therefore, this sand was used in all the tests as substrate mixed with the two agricultural wastes to create different types of filters.

*Table 6. Dorsilit 8 sand characteristics [32]*

| **SAND CHARACTERISTICS** | |
|---|---|
| Grain dimension (mm) | 0.3-0.8 |
| Bulk density (g/cm$^3$) | 2.65 |
| Apparent density (g/cm$^3$) | 1.4-1.5 |
| $SiO_2$ %m/m | 97.9 |
| $Fe_2O_3$ %m/m | 0.02 |
| $Al_2O_3$ %m/m | 0.47 |
| $TiO_2$ %m/m | 0.03 |

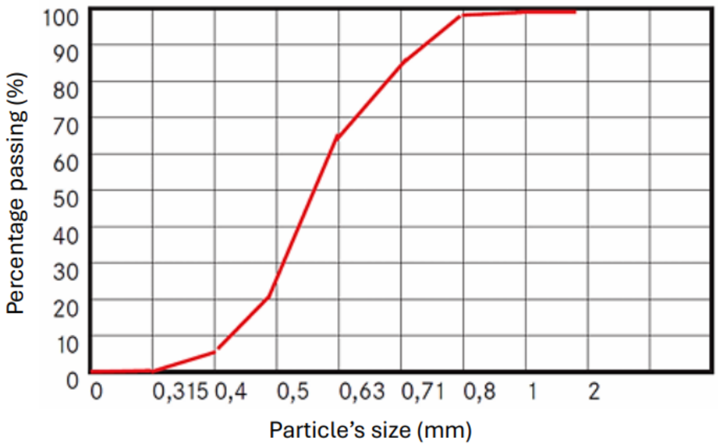


*Figure 4. Granulometric curve of Dorsilit 8 [32]*

#### 2.1.3.4. Dorsilit 5 sand

Dorsilit 5 is a type of sand that is specifically designed and processed for use in various construction and engineering applications. Similar to Dorsilit 8 sand, this is primarily composed of high-quality quartz grains. Due to its micro-rough surface texture, Dorsilit 5 sand has excellent filtration properties. This makes it suitable for use in water filtration systems where efficient removal of particles is required. Therefore, Dorsilit 5 sand was used in the column tests as a filter at the top and at the bottom of every column.

The sand, regardless of type, was washed multiple times with water to eliminate dust, soluble salts, and surface impurities. Then it was treated by soaking in a 100 mM NaOH solution to remove organic impurities and other substances adsorbed onto its surface. After the NaOH treatment, the sand was thoroughly rinsed with deionized water to ensure all residual NaOH and released impurities were removed. Finally, the sand was dried in an oven at a controlled temperature, typically between 60°C and 105°C, to eliminate any remaining moisture before it was used in testing. This process ensured that the sand was clean and consistent, minimizing the potential impact of contaminants on the test results.

*Table 7. Dorsilit 5 sand characteristics [33]*

| **SAND CHARACTERISTICS** | |
|---|---|
| Grain dimension (mm) | 1-2.2 |
| Bulk density (g/cm$^3$) | 2.7 |
| Apparent density (g/cm$^3$) | 1.5 |
| $SiO_2$ %m/m | 98 |

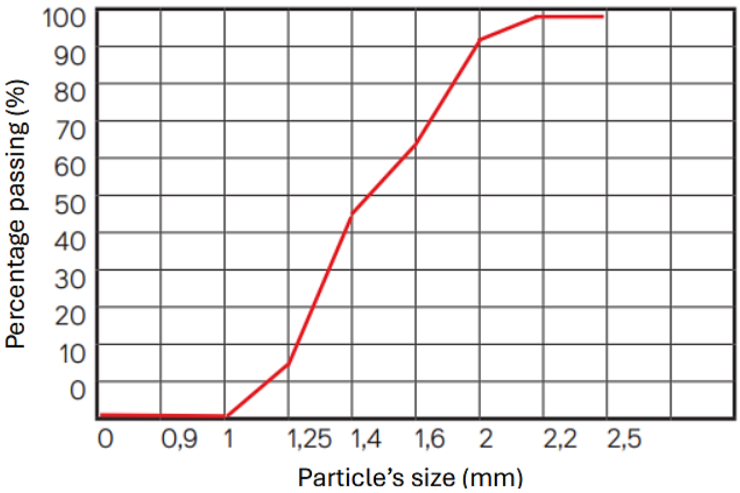


*Figure 5. Granulometric curve of Dorsilit 5 [33]*

## 2.2. Methods

The tests performed in this study were two batch tests and three column tests. However, before their application it was necessary the characterization of the two effluents and of the various type of substrates.

### 2.2.1. Effluent characterization

#### *2.2.1.1. Batch test 1: digestate characterization*

The digestate was initially frozen, but after thawing, approximately 40 ml were placed in 3 Falcon tubes under a fume hood due to the odour of the digestate. These tubes were then introduced into a centrifuge at 6500 rpm for 10 minutes (program 02) to separate the solid residues from the liquid solution (Figure 6).

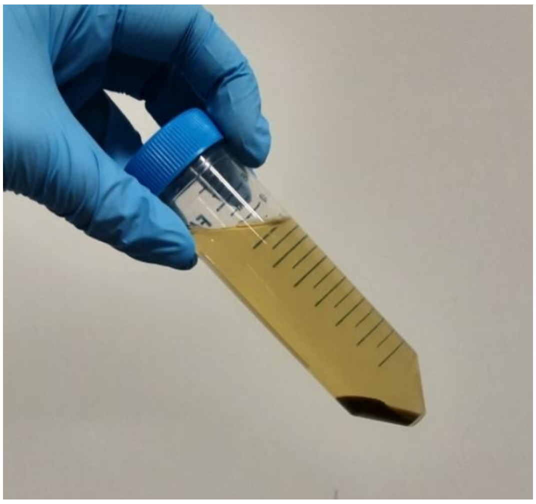


*Figure 6. Falcon tube containing centrifuged digestate*

Subsequently, the liquid phase was distributed in different quantities into vials (Figure 7) for the analysis of various dilutions of the effluent in terms of pH, TOC and TN. These two last characterizations were carried out using the TOC instrument, which provides average values of total organic carbon (TOC), inorganic carbon (IC), total carbon (TC), and total nitrogen (TN) for each sample. These average values were recorded in an Excel sheet to generate characterization curves at different dilutions for each parameter, called calibration curve.

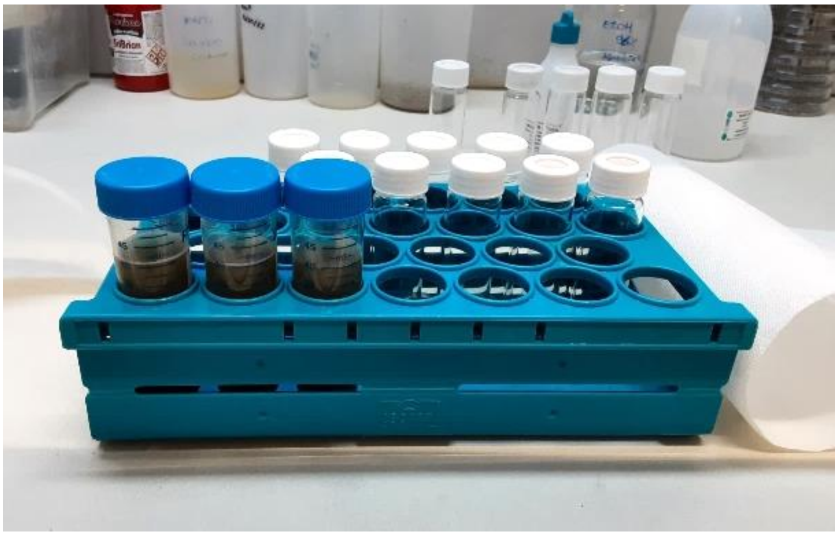


*Figure 7. Falcon tubes and vials used for the characterization of the digestate*

The initial dilution was 1:40 in 200 ml of solution, with the dilutions made using digestate and deionized water. For this first sample, the amount of digestate was calculated using a simple proportion, resulting in a required quantity of 5 ml. From this initial dilution, subsequent dilution of 1:1000 was prepared, with a total volume of 200 ml, applying the dissolution law. Further dilutions were derived from this second solution, with a total volume of 100 ml: 1:5000, 1:4000, 1:3000, 1:2000, 1:800, 1:400, 1:200, and 1:100.

One of the parameters analysed was the pH, which was measured both before (pH = 5.12) and after (pH = 5.13) centrifugation, as well as for each dilution. Another parameter was the TOC content, which was measured only after the centrifugation process.

After analysing all the results, the chosen dilution of the digestate for all the tests was 1:40, with a TOC content of 169.6 ppm.

#### *2.2.1.2. Batch test 2: apple boiling water and digestate characterization*

For the second batch test, the apple boiling water was analysed simultaneously with the digestate, which always maintained a 1:40 dilution, making it necessary to characterize the apple water and re-characterize the digestate in terms of TOC and TN.

To compare the results of the two effluents, a dilution of the apple boiling water was sought such that the TOC content was nearly the same as that of the digestate. This dilution was determined by interpolation and was found to be 1:65, resulting in a TOC of 165.3 ppm for the apple boiling water and 162.5 ppm for the digestate diluted at 1:40 ratio. To better study these two effluents, calibration curves of TOC and TN were obtained for both using different dilutions: 1:500, 1:300, 1:250, 1:200, 1:100, 1:65, 1:40, and 1:25.

### 2.2.2. Substrates characterization

The substrates studied were created by mixing the two agricultural wastes (Figure 8) with D8 sand. So, the substrates analysed were three:

- Corn cobs with D8 sand (CC);
- Hazelnut shells with D8 sand (HS);
- Mix of corn cobs and hazelnut shells with D8 sand (CC + HS).

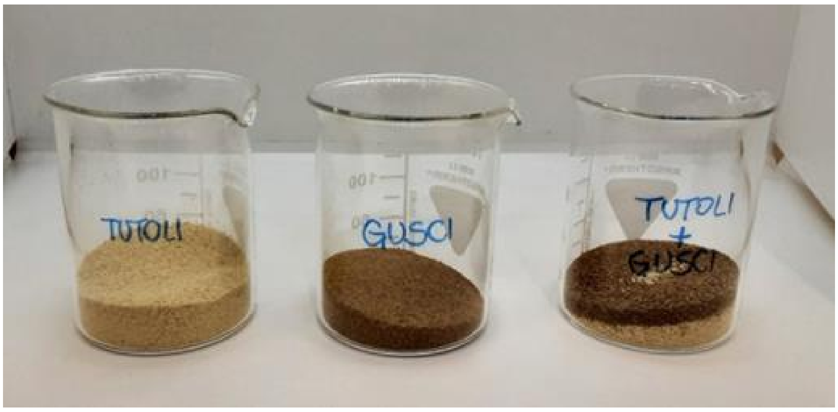


*Figure 8. Corn cobs on the left, hazelnut shells in the centre, and the mix of both on the right*

The weight percentages of each agricultural waste used were 2%, 5%, 10%, 20%, and 100% (Figure 9), with each substrate having a total weight of 50 g. These percentages were selected to characterize the agricultural wastes and identify the optimal configuration for use in the tests.

*Figure 9. Weight percentages of the substrate composed of the mix of corn cobs and hazelnut shells*

The characterization of each substrate was performed by measuring the pH and electrical conductivity (EC) of each sample using the suspension method:

- 1:10 ratio with 40 ml of deionized water for EC measurement;
- 1:5 ratio with 25 ml of 10 mM $CaCl_2$ for pH measurement.

The samples were placed in Falcon tubes, mixed for 1 hour (Figure 10), and then centrifuged at 6500 rpm for 10 minutes before measuring the two parameters, to avoid damaging the instrument probes with suspended particles. After measuring pH and EC, approximately 40 ml of the liquid samples were injected into vials to determine the TOC and TN content of the different substrate percentages.

*Figure 10. Mixing of samples in Falcon tubes for 1 hour*

Another defined property of the substrates is the bulk density, measured by determining the volume difference in a graduated cylinder filled with deionized water (Figure 11). A starting volume of 60 ml of deionized water was set, and a mass of substrate was then added. The bulk density was calculated by dividing the mass of the substrate by the difference in water volume indicated on the graduated cylinder, resulting in a measurement in g/cm$^3$.

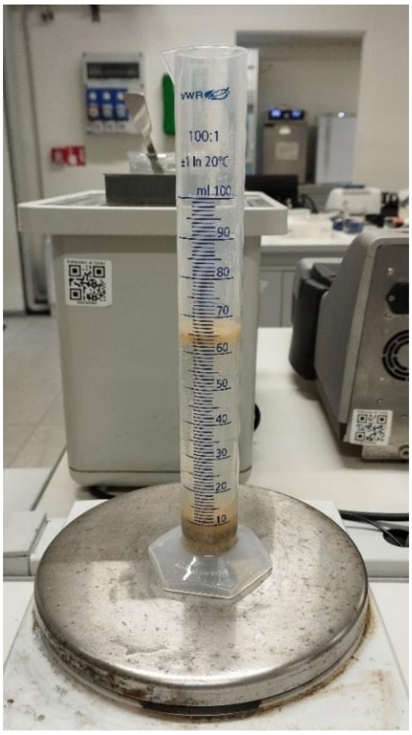


*Figure 11. Graduated cylinder used for measuring bulk density*

A 10% by weight proportion of agricultural waste relative to the D8 sand was chosen, resulting in substrate samples with a total weight of 200 g to use them in the first batch test.

### 2.2.3. Batch tests

A batch test is a laboratory procedure used to evaluate the behaviour or properties of a material or substance under controlled conditions. In these tests, a fixed amount of substrate was placed in a container, along with a controlled volume of digestate for the first test, and then apple water and digestate separately for the second test. The mixture was then left to react for a specified period of time.

This test was used to assess the effectiveness of treatment processes for removing contaminants from the effluents, providing preliminary data on the interactions between substrates and effluents and optimizing conditions for larger-scale experiments.

#### *2.2.3.1. Batch test 1: digestate*

This initial test focused on analysing the digestate in comparison to all the substrates described in paragraph 2.2.2. The samples were prepared with a substrate-to-effluent ratio of 1:25. Sampling was conducted on days 8, 14, 21, and 27, with the samples kept at a constant temperature of 25°C throughout the duration of the test in a thermostatically controlled oven.

Based on the date of sampling, a total of 21 samples were created:

- 4 samples for each substrate, consisting of 2 g of substrate in 50 ml of 1:40 digestate;
- 4 samples of D8 sand, consisting of 2 g of sand in 50 ml of 1:40 digestate;
- 5 blanks, one for each substrate (CC, HS, CC + HS) and one for the sand consisting of 10 g of substrate in 250 ml of deionized water, and one for the 1:40 digestate (250 ml).

In experimental testing, blanks (or blank samples) serve as control samples to account for any potential contamination or interference arising from the test procedure itself. They contain all components of the test samples except for the specific substance being investigated. In this batch test, one blank contained only the 1:40 digestate, while the other blanks included only the substrates mixed with deionized water, without the digestate. By comparing the results of the test samples to these blanks, it was possible to determine whether any observed effects were attributable to the test material itself rather than to procedural artifacts.

The parameters analysed in this test were pH, EC, TOC, and TN. Before measuring these parameters, the samples were transferred into Falcon tubes and centrifuged at 8000 rpm for 15 minutes (program 05) to separate the liquid phase from the solid phase and to prevent damage to the instruments.

Additionally, biochemical oxygen demand (BOD) was studied in parallel with the test using a VELP Respirometric Sensor system. This system measures the oxygen consumption of the sample over a set period by tracking the reduction in oxygen levels within the sample bottles. The respirometric sensor continuously monitors changes in oxygen concentration or pressure resulting from microbial respiration. Data on the rate of oxygen consumption is collected and used to calculate the BOD. Measurements are taken over a specified duration, typically 5 days ($BOD_5$), and the resulting BOD value indicates the amount of organic matter present in the sample. A higher BOD value reflects a greater concentration of biodegradable organic material.

The test was set to run for 30 days, with sampling every 6 hours, a scale range of 4000 mg/L, and a temperature of 25°C. Consequently, the samples were maintained in the thermostatically controlled oven alongside the batch test samples (Figure 12). They included one liquid sample with 25 ml of 1:40 digestate, which was kept in agitation throughout the measurement period, and three solid samples, one for each substrate, each consisting of 100 g of substrate mixed with 10 g of 1:40 digestate (10% by weight). To absorb the $CO_2$ generated within the bottles during the degradation, KOH tablets were placed in the air space just beneath the cap.

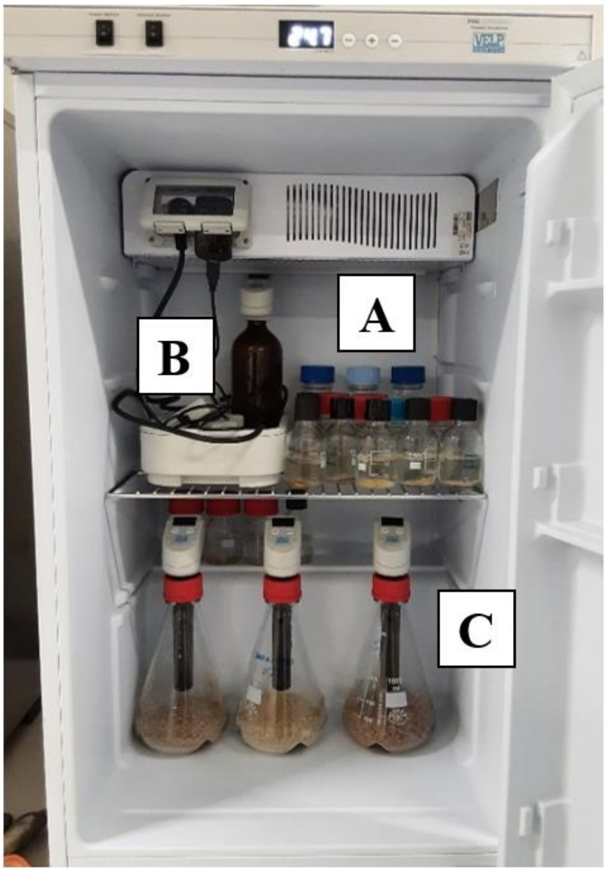


*Figure 12. Batch test samples (A), BOD sample in the liquid phase (B), and BOD samples in the solid phase (C) in the thermostatically controlled oven*

After analysing the results from the initial batch test, a second test was conducted, this time focusing on a shorter duration. Sampling was performed on days 1, 2, 3, 4, and 5, with measurements of pH, EC, TOC, and TN. For this test, new samples were prepared in the same manner as the previous ones, and the digestate was re-characterized at different dilution levels to establish a more accurate correlation between the substrates and the digestate.

#### 2.2.3.2. *Batch test 2: apple boiling water and digestate*

Based on the results from the initial batch test, the focus was shifted to a single substrate: the one made from hazelnut shells, compared against only D8 sand. Additionally, alongside the 1:40 digestate, the apple boiling water diluted to 1:65 was also analysed, with the dilution factor derived from the characterization of the two effluents.

The parameters measured were the same as in the initial batch test: pH, EC, TOC, and TN. However, the sampling days differed from those in the previous test and were set to days 1, 4, 10, 14, 21, 23, and 28. For this second batch, the BOD was not analysed again.

An error in the initial batch test was the composition of the blanks. Specifically, they contained 10 g of substrate in 250 ml of deionized water, resulting in a substrate-to-effluent ratio of 1:25. However, during each sampling, approximately 50 ml of deionized water was removed, altering this ratio. Therefore, for the second batch test, the blanks were prepared in individual bottles to maintain the 1:25 ratio consistently, ensuring more accurate and meaningful results.

All the samples (Figure 13) were kept in a thermostatically controlled oven to maintain a temperature of 25°C throughout the entire duration of the test.

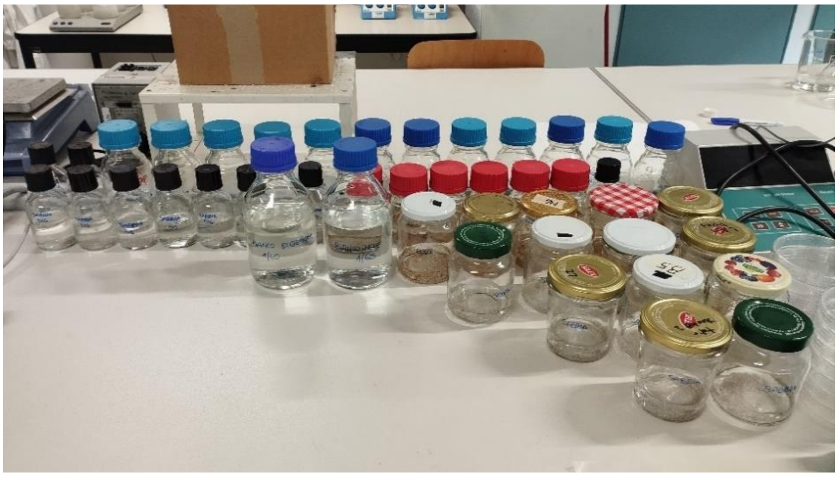


*Figure 13. All samples for batch test 2*

Table 8 summarizes the characteristics of the two batch tests, as described in the preceding sections.

*Table 8. Characteristics of the two batch tests*

| **Test** | **Effluent** | **Substrate** | **Duration (days)** | **Sampling intervals (days)** | **Parameters monitored** |
|---|---|---|---|---|---|
| Batch test 1 | 1:40 Digestate | D8 sand, Corn cobs (CC), Hazelnut shells (HS), Mix of Corn cobs and Hazelnut shells (CC + HS) | 27 | 1, 2, 3, 4, 5, 8, 14, 21, 27 | pH, EC, TOC, TN, $BOD_5$ |
| Batch test 2 | 1:65 Apple water<br>1:40 Digestate | D8 sand, Hazelnut shells (HS) | 28 | 1, 4, 10, 14, 21, 23, 28 | pH, EC, TOC, TN |

### 2.2.4. Column leaching tests

Column tests are a type of laboratory experiment used primarily in environmental engineering and hydrogeology to study the behaviour of fluids and dissolved substances as they move through porous media, such as soil or sediment. These tests are performed using a column, a vertical tube filled with a soil sample or other porous material, through which a fluid is passed under controlled conditions. Column tests allow for the observation of chemical reactions between the fluid and the soil, including biodegradation, precipitation, or dissolution, providing insights into the rates and extents of these reactions. The data from column tests give information about effective remediation techniques for contaminated sites, ensuring that the methods chosen are appropriate for the specific conditions of the site.

In this study, three types of column tests were conducted: continuous flow test, intermittent flow test, and test at a medium pH.

#### *2.2.4.1. Continuous column leaching test*

The continuous column test was conducted by analysing two parallel columns filled with the hazelnut shells substrate, one was permeated with apple boiling water, and the other with digestate. At the end of the test, both columns were flushed and refilled, this time with D8 sand instead of the hazelnut shell substrate, to compare the different behaviours of the two substrates in terms of filtration and degradation of the effluents.

The selected columns were made of glass with an internal diameter of 4 cm. The packing length consisted of approximately 17 cm of substrate, including about 1 cm of D5 sand above and below the substrate to prevent clogging in the connected tubing. Approximately 280 g of hazelnut shell substrate (320 g of D8 sand) was placed in each column, and the planned flow rate for the test was 1 ml/min. Consequently, the inlet flow velocity was 0.08 cm/min.

Once the flow rate was determined, the speed of the peristaltic pump was set to 26 rpm. The transit times through the tubing and column caps were then calculated. The final preparation step involved packing the columns from the bottom up under unsaturated conditions to prevent the hazelnut shells from layering at the surface of the water. The substrate was moistened to 5% water content to ensure that as much material as possible could be transferred from the beaker into the columns.

Once the columns were prepared, they were flushed with deionized water for approximately 24 hours at 6 rpm, from top to bottom, to achieve an outflow that could be analysed using a spectrophotometer. However, the spectrophotometric analyses yielded no significant results, due to an high turbidity of the outlets, leading to the decision to pursue alternative analyses. Therefore, the parameters studied during the test included pH, EC, TOC, and TN.

Before conducting the test, the two columns were characterized using potassium bromide (KBr) as a tracer. Although bromophenol could have been used as an alternative, it was likely to adhere to the hazelnut shells, so KBr was chosen instead. KBr was used at a molar mass greater than 1 mM to ensure that its electrical conductivity (898 µS/cm for hazelnut shell columns and 1000 µS/cm for D8 sand columns) was distinct from that of the column outflow. This was necessary to avoid a negligible delta, which would render the measurements non-significant and unanalysable, similar to the issues encountered with the spectrophotometer.

Characterizing the columns is a crucial step that allows for the determination of their pore volume (PV). This volume represents the capacity of the column to hold and transport fluids, indicating how much fluid the column can contain and how this fluid interacts with the substrate. By understanding the pore volume, it can be assessed flow dynamics, contaminant transport, and the overall efficiency of the column.

The tracing of the hazelnut shell columns lasted 4.25 hours, consisting of 2.25 hours of KBr injection followed by 2 hours of deionized water flushing (Figure 14). For the sand columns, the process lasted a total of 6 hours, with 3 hours dedicated to KBr injection. These periods of time were necessary to obtain a constant values plateau for each column before injecting deionized water.

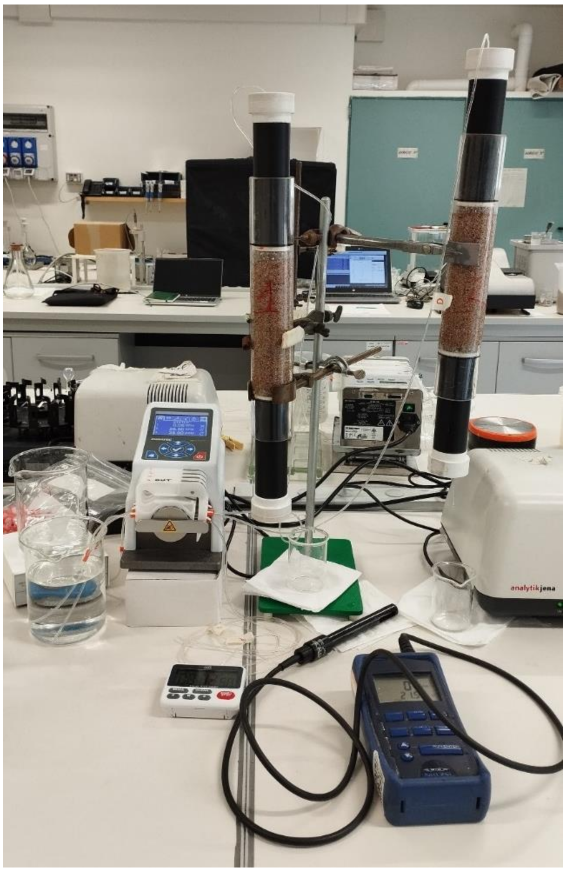


*Figure 14. Organization of the workspace for the continuous column test: hazelnut shell columns*

The column leaching test lasted 6 hours, with 3 hours dedicated to injecting apple boiling water (1:65) into Column 1 and digestate (1:40) into Column 2. Every 15 minutes, pH and EC were measured for both the inlet and outlet samples. Additionally, TOC and TN were analysed for the inlet and outlet effluents, but the samples were diluted to a 1:3 ratio in 30 ml total volume before analysis. However, TOC and TN measurements for the inlet effluents were only conducted for the first 3 hours of the test, including the initial time (t = 0), resulting in a total of 4 inlet measurements. For each parameter, the Breakthrough Curve was determined by calculating the ratio of the outlet value to the inlet value. For TOC and TN, the inlet value was the average of the 4 measurements taken every hour.

After the test was completed, the columns were extruded from top to bottom, in 1 cm increments (Figure 15). Each sample was weighed and then left to dry for 3 days. After drying, the samples were weighed again to determine the moisture content profile of the columns. Additionally, the most significant layers were selected, and the total solid carbon (solid TC) was determined for these layers, creating another profile.

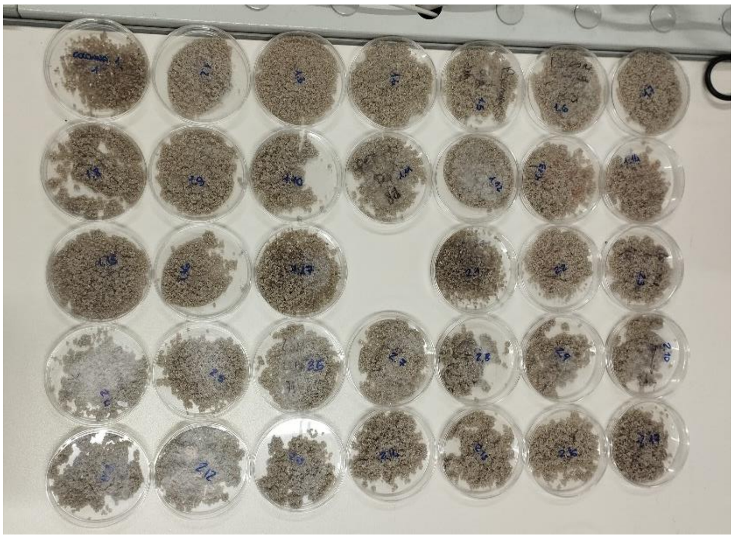


*Figure 15. Samples obtained from the extrusion of the two columns*

### *2.2.4.2. Intermittent column leaching test*

The intermittent column leaching test was conducted using only the hazelnut shell substrate, but for both effluents (Figure 16). The columns had the same characteristics as those used in the continuous leaching test, and the column tracing followed the same procedures as described in the previous paragraph.

The test involved 24 hours of flooding followed by 72 hours of gravity-driven drainage, repeated three times to resemble the wet and dry cycle of a SAT system. During the 24-hour flooding periods, pH, EC, and oxidation-reduction potential (ORP) were measured at specific intervals: 1, 2, 3, 5, 7, 13, 19, and 24 hours. Additionally, samples for TOC and TN were collected and diluted at 1:3 in 30 ml of deionized water.

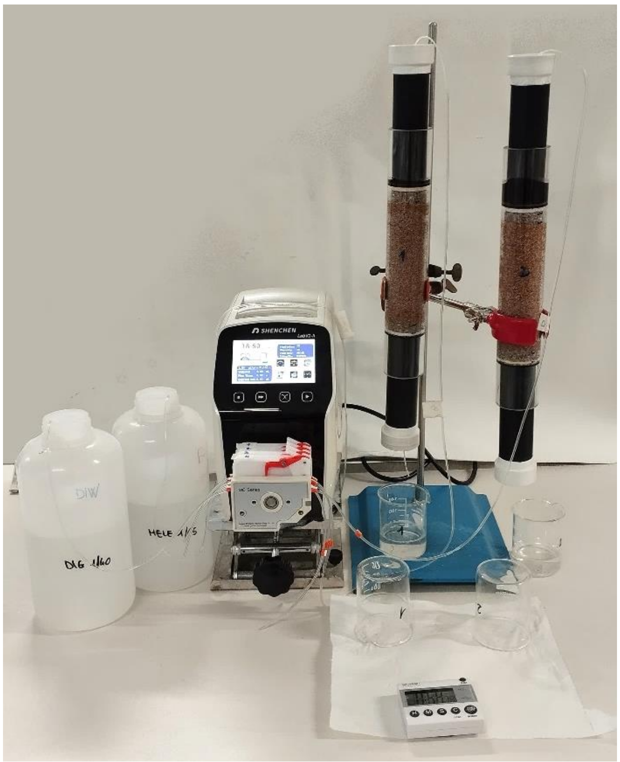


*Figure 16. Organization of the workspace for the intermittent column leaching test*

As with the previous test, at the end the columns were extruded, and the moisture content profile and solid TC profile were determined for the two columns.

#### 2.2.4.3. Column leaching test at average pH

To gain a better understanding of the behaviour of hazelnut shells, a column test was conducted where the pH of the two influents was adjusted to 5.5, a midpoint between the pH of the digestate and the apple boiling water. This approach allowed to determine whether the differences observed in previous tests between the apple water and digestate were solely due to the distinct characteristics of the two influents or if they were also influenced by their interaction with the hazelnut shells.

To achieve an intermediate pH between the digestate and the apple boiling water, these influents were diluted not with deionized water as previously done, but with an acetate buffer at pH 5.5. This buffer was prepared using sodium acetate and acetic acid at final concentrations of 8.9 mM and 1 mM, respectively. The buffer was injected into the columns prior to the test, ensuring that they were already at the desired pH, thus allowing for more meaningful results.

The test lasted 6 hours, just like the continuous test, with pH, EC, TOC, and TN measured every 15 minutes at both the inlet and outlet. TOC and TN were measured at the inlet only every hour during the first 3 hours of effluent injection, with samples diluted at a 1:3 ratio, following the same procedure as in the continuous test. The 3-hour injection of deionized water after the effluent was replaced by the injection of the buffer.

After the test, the two columns were extruded, and the profiles of water content and solid TC were obtained.

Table 9 summarizes the characteristics of the three column leaching tests, as described in the preceding sections.

*Table 9. Characteristics of the three column leaching tests*

| **Test** | **Injected effluent** | **Substrate** | **Duration (hours)** | **Sampling intervals** | **Parameters monitored** |
|---|---|---|---|---|---|
| Continuous column leaching test | 1:65 Apple water<br>1:40 Digestate | D8 sand, Hazelnut shells (HS) | 6 | Every 15 minutes | pH, EC, TOC (1:3), TN (1:3) |
| Intermittent column leaching test | 1:65 Apple water<br>1:40 Digestate | Hazelnut shells (HS) | 216 | 1, 2, 3, 5, 7, 13, 19, 24 h of the 24 h of flooding | pH, EC, ORP, TOC (1:3), TN (1:3) |
| Column leaching test at average pH | 1:65 Apple water + Acetate buffer<br>1:40 Digestate + Acetate buffer | Hazelnut shells (HS) | 6 | Every 15 minutes | pH, EC, TOC (1:3), TN (1:3) |

# 3. Results and discussion

In the following paragraphs, the results obtained from the batch tests and the column leaching tests are reported, beginning with the characterization of the effluents and the substrates.

## 3.1. Effluents characterization

### 3.1.1. Batch test 1: calibration curves

The characterization of the digestate was performed starting with the pH analysis of the different prepared dilutions, ranging from a 1:1000 dilution (pH = 5.47) to a 1:5000 dilution (pH = 5.78), the trend of which is shown in Figure 17.

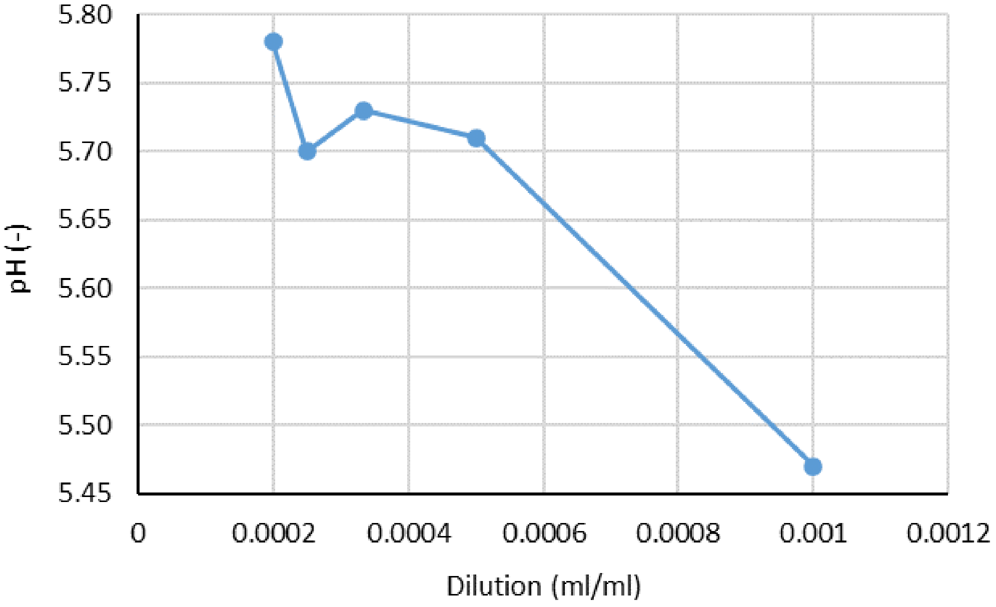


*Figure 17. pH trend of the digestate at different dilutions*

It can be observed from Figure 17 that as the dilution relative to the digestate becomes more concentrated, the pH shows a slight trend toward becoming more acidic. Conversely, as the digestate is further diluted with deionized water, the pH tends to shift slightly towards being more basic. Consequently, the digestate obtained from the dark fermentation of apple boiling water has an acidic pH compared to deionized water. However, the variation is minimal, indicating that the pH essentially remains unchanged.

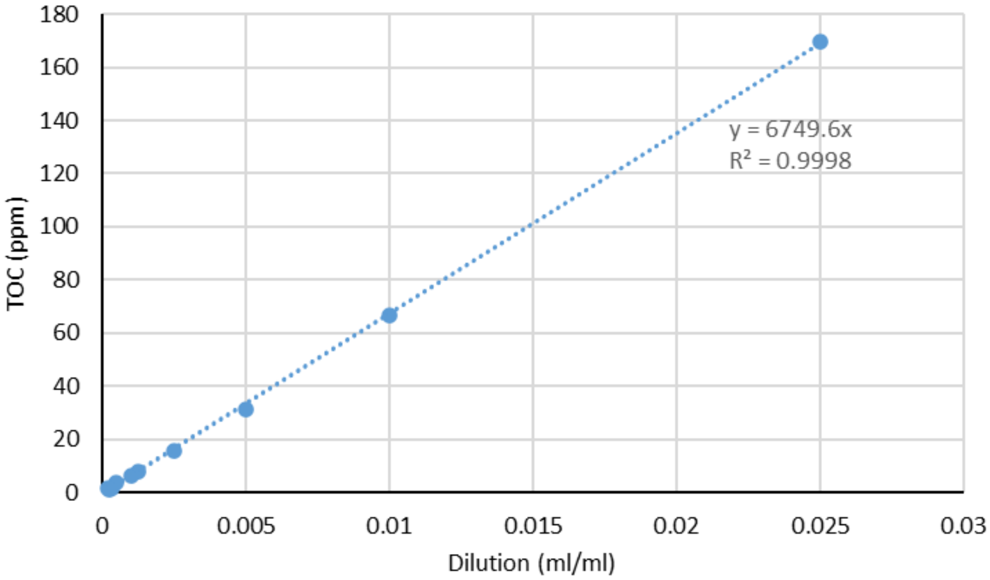


*Figure 18. Calibration curve of TOC of the digestate at different dilutions*

Figure 18 shows that the TOC content of the low-concentration dilutions was too low for a meaningful analysis. Therefore, the dilutions with higher concentrations of digestate were analysed. However, this curve shows an $R^2$ value close to one, indicating that the data fit well with a linear interpolation.

Ultimately, the concentration of digestate chosen for all tests in this project was 1:40, with an initial TOC of 169.6 ppm. This parameter was recalculated for each batch test to ensure meaningful results. The first batch test was conducted over both long and short terms, with TOC contents of 160.7 ppm and 158 ppm, respectively.

The third parameter analysed was the total nitrogen (TN) content, for which a calibration curve was obtained using only the high-concentration dilutions, visible in Figure 19. For TN, the curve was not forced through the origin, allowing for an $R^2$ value closer to one. This approach was chosen because it acknowledges that even in the absence of TN, there may be other factors that could affect the measurement, leading to a more accurate representation of the relationship between concentration and response.

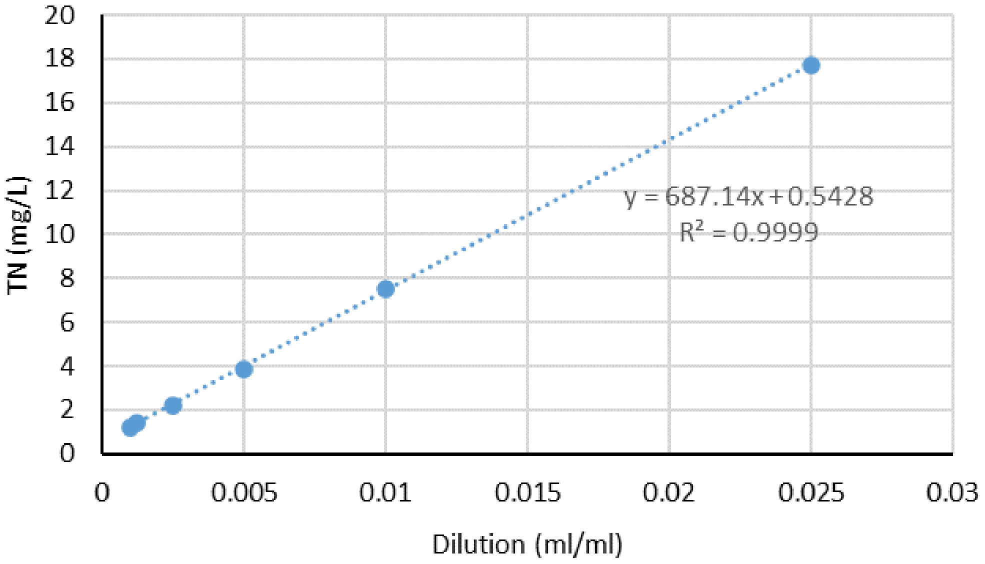


*Figure 19. Calibration curve of TN of the digestate*

The TN content of the digestate diluted to 1:40 was 17.71 mg/L. This parameter was also measured for each batch test to ensure meaningful results. For the long-term phase of batch test 1, the TN content was 17.41 mg/L, while for the short-term phase it was 5.688 mg/L. This discrepancy was likely due to an incorrect dilution in the short-term test; therefore, the TN value of 17.41 mg/L from the long-term test was used for both phases of the first batch test.

### 3.1.2. Batch test 2: calibration curves

For the second batch test, the characterization of the digestate was repeated in terms of TOC and TN, and the apple boiling water was also characterized. The calibration curves for these two parameters are shown below.

Figure 20 shows the TOC calibration curve for various dilutions, ranging from 1:500 to 1:25. The 1:25 dilution was calculated only for the apple boiling water and not for the digestate, because it was not necessary for its characterization.

Based on the TOC values obtained from the characterization of the first batch test, a dilution of 1:65 was calculated for the apple boiling water to achieve a TOC content comparable to that of the digestate. The actual TOC value for the 1:65 dilution of the apple boiling water was 165.3 ppm, compared to 162.5 ppm for the digestate at a 1:40 dilution. Given the similar values obtained, this dilution was used for the apple boiling water in all subsequent tests.

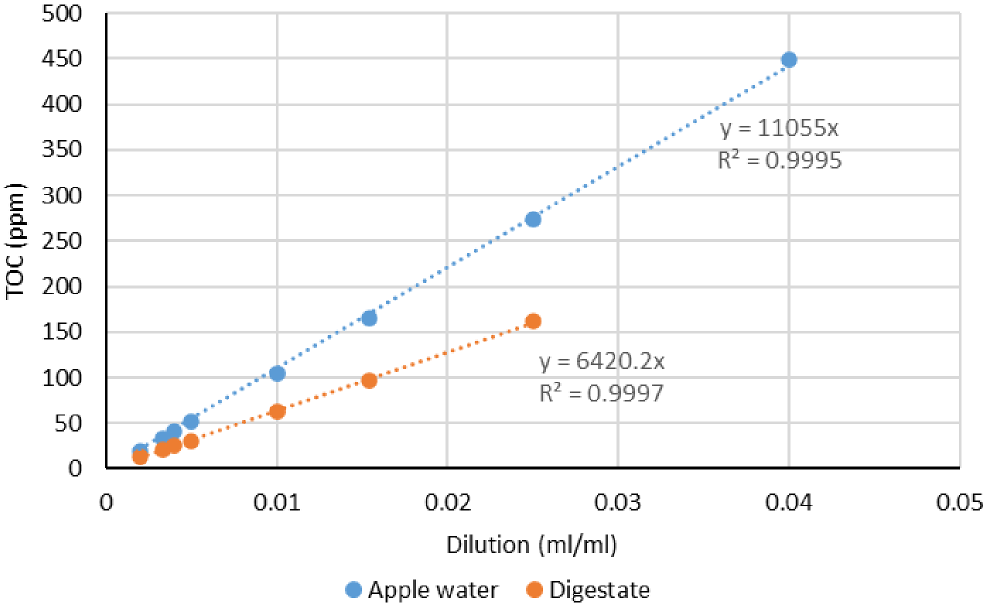


*Figure 20. Calibration curves of TOC of the apple boiling water and the digestate*

From Figure 20, it can be observed that the apple boiling water has a higher TOC content compared to the digestate. This difference can be explained by the chemical and biological processes each sample has undergone. The apple boiling water, rich in soluble organic compounds leached from the apples, contains a higher amount of organic carbon. These compounds are relatively intact and have not undergone significant degradation. In contrast, the digestate has been subjected to dark fermentation, a type of anaerobic digestion where microorganisms break down organic matter. This microbial activity consumes a significant portion of the organic carbon present, resulting in a lower TOC content. The presence of these microorganisms in the digestate leads to the decomposition of complex organic molecules into simpler compounds, which decreases the overall TOC. Therefore, the higher TOC in the apple boiling water compared to the digestate reflects the impact of fermentation processes on organic carbon content.

Figure 21 illustrates the characterization of total nitrogen (TN), revealing a trend that contrasts with the TOC content. Specifically, the digestate exhibits a higher TN concentration compared to the apple boiling water. This difference in TN levels is significant, reflecting the higher nitrogen content typical of digestate due to its nature as a byproduct of organic matter decomposition.

This opposing trend between TN and TOC suggests distinct compositional characteristics and processing effects in the two types of samples. The elevated TN in the digestate indicates its role as a nutrient-rich material, whereas the lower TOC reflects the breakdown of organic matter during fermentation. On the other hand, the higher TOC in the apple boiling water indicates a higher preservation of organic carbon, which is consistent with its less processed nature. A higher TN content can be beneficial in certain contexts, especially for agricultural and nutrient purposes, but it must be managed properly to avoid potential negative environmental impacts.

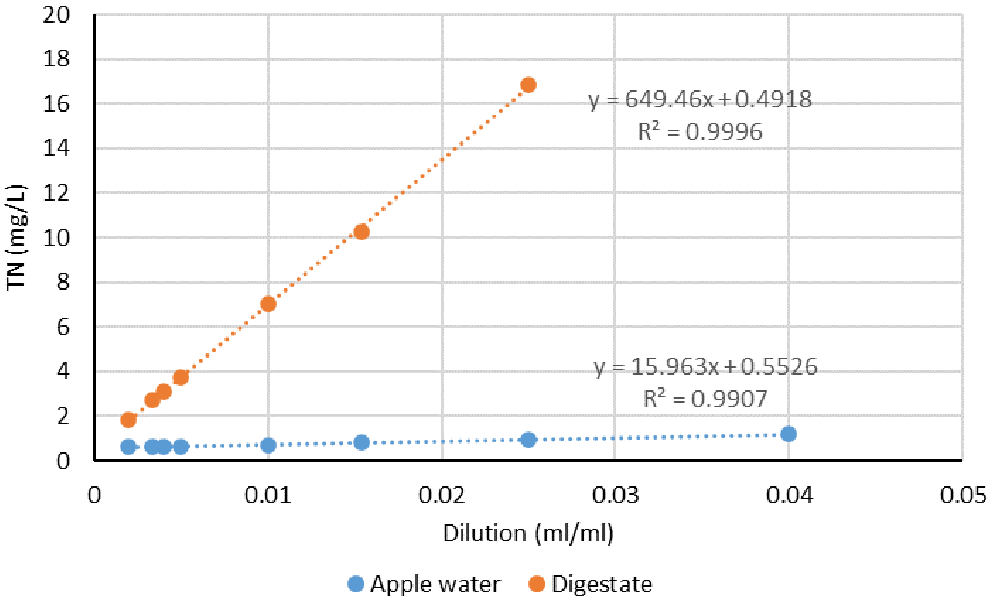


*Figure 21. Calibration curves of TN of the apple boiling water and the digestate*

The TN content was measured as 0.8243 mg/L in apple boiling water diluted at a 1:65 ratio, whereas it was significantly higher at 16.85 mg/L in digestate diluted at a 1:40 ratio.

## 3.2. Substrates characterization

The characterization of the substrates included measuring the pH and electrical conductivity (EC) of various proportions of agricultural waste relative to D8 sand, assessing the bulk density of these different proportions, and determining the calibration curves for TOC and TN content.

### 3.2.1. pH and electrical conductivity

The pH and electrical conductivity were measured using two separate probes inserted into different samples according to the suspension method, as described in paragraph 2.2.2.

Only the substrates containing agricultural waste were characterized, while the D8 sand was used only as a component to complete the substrates.

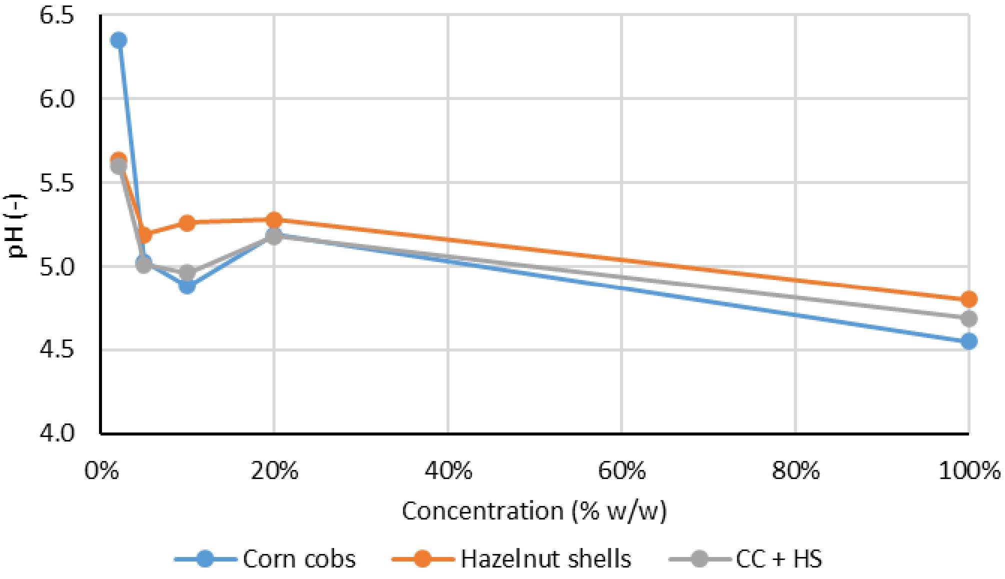


*Figure 22. pH trend of the three substrates at different weight percentages*

Figure 22 illustrates a trend of decreasing pH with increasing concentrations of agricultural waste in the substrate. This observation aligns with the theoretical understanding that agricultural wastes often contain organic acids and other acidic compounds that contribute to the acidification of the substrate. As the proportion of agricultural waste rises, these acidic substances become more prevalent, leading to a lower pH.

Additionally, even at lower percentages of agricultural waste, an acidification is observed. This effect can be attributed to the inherent acidity of agricultural residues, which, despite their lower concentration, still exert a significant influence on the overall pH of the substrate. This relationship underscores the impact of organic waste composition on substrate acidity and highlights the importance of managing pH levels in substrates containing agricultural materials for optimal performance in various applications, such as soil conditioning or composting.

To examine an extreme scenario, characterized by acidic pH, a concentration of 10% by weight of agricultural waste was selected for the three substrates. Under these conditions, the corn cobs substrate had a pH of 4.88, the hazelnut shells showed a pH of 5.26, and the mixed substrate recorded a pH of 4.96. A 100% by weight concentration of agricultural waste was not chosen due to the risk of clogging in subsequent column tests. By selecting the 10% concentration, the study addresses a critical scenario of pH acidification while avoiding potential operational issues that could arise from higher concentrations. This approach ensures that the impact of agricultural waste on substrate acidity is assessed without compromising the integrity and functionality of the testing process.

The second parameter analysed for the various proportions of agricultural waste was the electrical conductivity (EC), as illustrated in Figure 23.

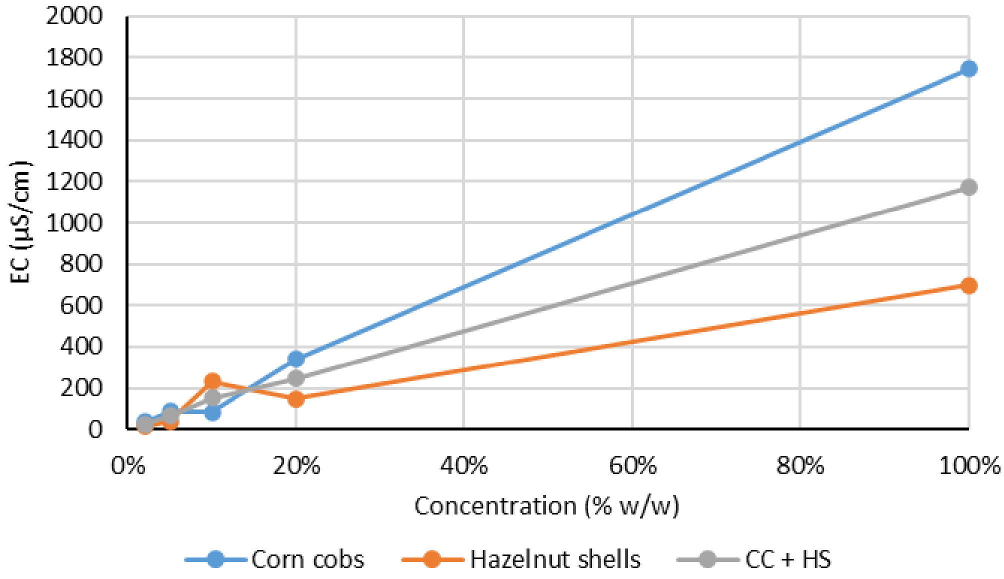


*Figure 23. EC trend of the three substrates at different weight percentages*

Electrical conductivity exhibits a behaviour opposite to that of pH. As the concentration of agricultural waste in the substrate increases, the electrical conductivity also rises. This is because agricultural wastes often contain soluble salts and ionic compounds that enhance the substrate's ability to conduct electricity. Furthermore, at lower concentrations, a difference in EC is observed between the types of agricultural waste. Specifically, corn cobs have a lower EC compared to hazelnut shells, which have a slightly higher

EC. This difference is attributed to the varying levels of soluble salts and ionic substances in these materials. This variation in EC between different types of waste underscores the impact of the specific composition of agricultural residues on the overall electrical conductivity of the substrate. The intermediate EC value observed in substrates containing a mix of both types of agricultural waste reflects the combined ionic contributions from each material. Thus, the EC of the substrate is influenced not only by the concentration of agricultural waste but also by the ionic characteristics of the waste types used.

Corn cobs are primarily composed of silica ($SiO_2$), potassium (K), calcium (Ca), and magnesium (Mg) [34]. Silica is less ionic and therefore does not significantly increase the concentration of free ions. Potassium is a mineral that can contribute to an increase in EC; however, its quantity is relatively low compared to other minerals richer in salts. Calcium and magnesium are present in moderate amounts and can influence EC, although not to a degree that would drastically alter conductivity. As a result, corn cobs tend to have a neutral or slightly alkaline effect on the substrate's pH, as they do not contain large amounts of acidic compounds. On the other hand, they contribute moderately to EC, but their effect is limited due to their relatively low content of soluble salts.

Hazelnut shells are primarily composed of calcium (Ca), magnesium (Mg), and silica ($SiO_2$) [35]. Calcium can significantly contribute to an increase in EC as it is a cation that raises the concentration of free ions in the substrate. Magnesium is present in higher amounts, further enhancing EC. Silica, on the other hand, is present in less significant quantities relative to calcium and magnesium in terms of its impact on EC. As a result, hazelnut shells tend to have a neutral or slightly alkaline effect on the substrate's pH, like corn cobs. However, the presence of calcium can make the substrate slightly more alkaline if the concentration of hazelnut shells is high. Additionally, the presence of calcium and magnesium in hazelnut shells significantly increases the substrate's EC. Nevertheless, even though the EC of hazelnut shells increases with their concentration in the substrate, it remains lower than that of corn cobs. This suggests that hazelnut shells release fewer conductive ions or that these ions are less mobile compared to those released by corn cobs.

For the EC study, the optimal percentage of agricultural waste was determined to be 10%. This percentage ensures that the electrical conductivity remains within a manageable range, which is crucial for evaluating the impact of agricultural wastes. At 10% concentration, corn cobs exhibited an EC of 83 μS/cm, hazelnut shells had an EC of 230 μS/cm, and the mixture of both resulted in an EC of 151 μS/cm.

### 3.2.1. Bulk density

Another parameter that was determined as the percentage of agricultural waste varied is the bulk density, as shown in Figure 24. The bulk density decreases as the content of agricultural waste increases because agricultural wastes generally have a lower density compared to the sand or other base materials in the substrate.

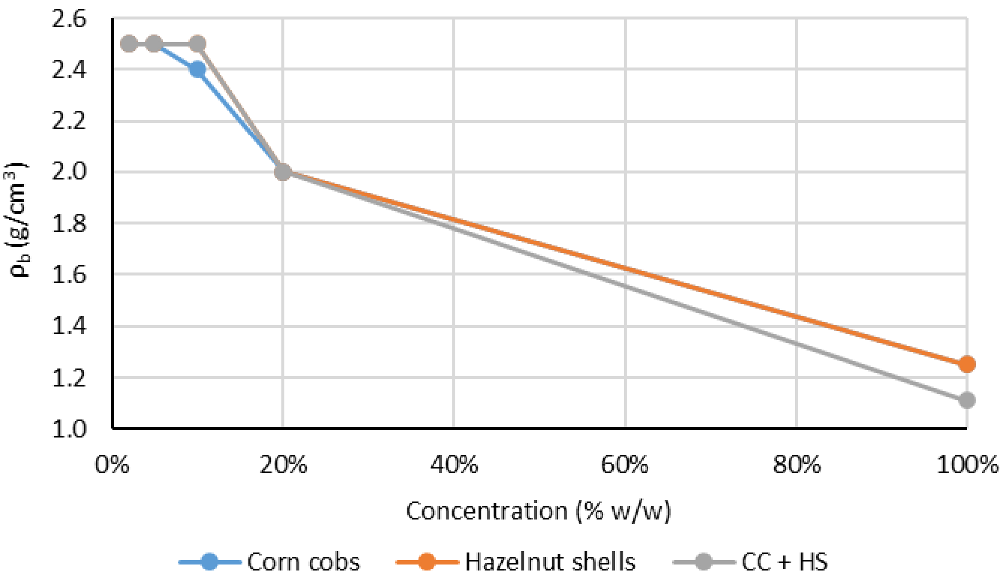


*Figure 24. Bulk density ($\rho_b$) trend of the three substrates at different weight percentages*

These wastes often contain more organic matter, which is less compact and has a more porous structure. As the proportion of agricultural waste rises, the overall bulk density of the substrate is reduced due to the lighter and more fibrous nature of the waste materials. This decrease in density can also be attributed to the increased air space within the substrate, as the irregular shapes and sizes of the agricultural waste particles prevent tight packing, further contributing to a lower bulk density.

For a SAT system, a decrease in bulk density with a higher content of agricultural waste can be beneficial:

- Lower bulk density typically indicates higher porosity, which enhances the infiltration rate and water movement through the soil.
- With higher porosity, the SAT system can retain more water and allow it to percolate slowly through the substrate. This slower percolation allows for better filtration of contaminants, as the water has more contact time with the soil matrix.
- A lower bulk density reduces the risk of soil compaction, which can impede water infiltration and lead to poor performance in a SAT system. With less compaction, the substrate remains more effective in treating water over time.

Therefore, using 10% by weight of agricultural waste allows for the examination of a critical scenario with higher bulk density, enabling the analysis of the most challenging conditions for filtration and degradation in the soil. At a 10% concentration, the bulk density of corn cobs was 2.4 g/cm$^3$, whereas it was 2.5 g/cm$^3$ for both hazelnut shells and the mixture of the two agricultural wastes.

### 3.2.2. TOC and TN

The final parameters analysed were TOC and TN contents as the percentage of agricultural waste in the substrate varied. These two parameters were only analysed for the single agricultural waste substrates and not for their mix.

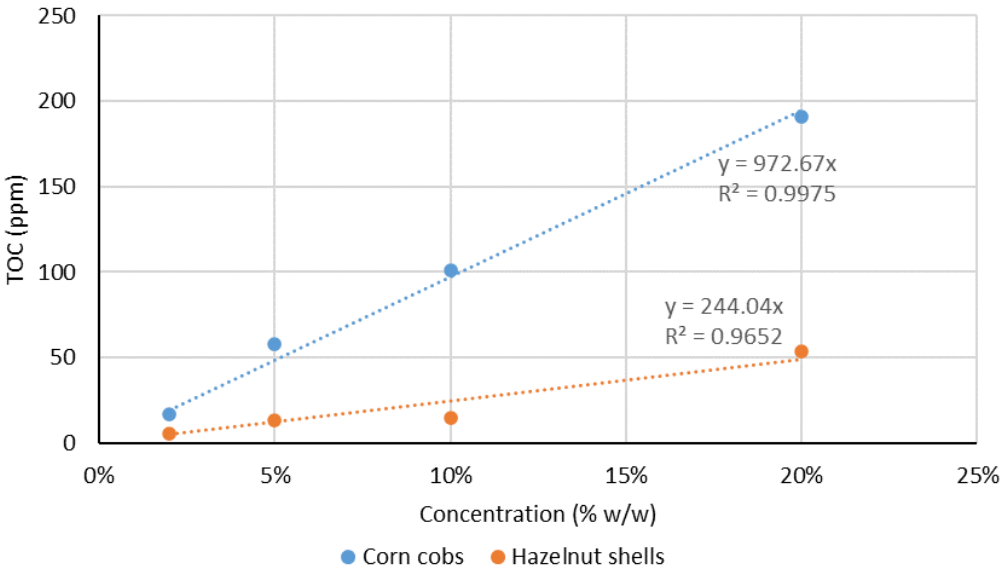


*Figure 25. TOC trend of the corn cobs and hazelnut shells substrates at different weight percentages*

From Figure 25, a good linear interpolation is obtained for corn cobs, but the fit is less optimal for hazelnut shells. This may be due to imperfect dilution or variations in the TOC content of hazelnut shells depending on their quantity. The organic carbon content in hazelnut shells can be more variable due to differences in the chemical composition and the degree of processing or degradation. Hazelnut shells primarily consist of cellulose, hemicellulose, and lignin, which can vary in organic carbon content based on factors such as the nut variety and growth conditions. In contrast, corn cobs have a more consistent composition with higher cellulose content and relatively uniform levels of organic carbon, resulting in more stable TOC values.

Additionally, the TOC content of hazelnut shells is generally lower than that of corn cobs. Corn cobs tend to have a higher percentage of organic matter and higher levels of organic carbon due to their higher sugar and starch content. Hazelnut shells, on the other hand, contain more lignin, which is less readily measured as TOC. The TOC content at 10% concentration was 100.8 ppm for corn cobs, while it was 14.81 ppm for hazelnut shells.

The second parameter quoted is the TN content at different percentages of the two agricultural wastes, reported in Figure 26.

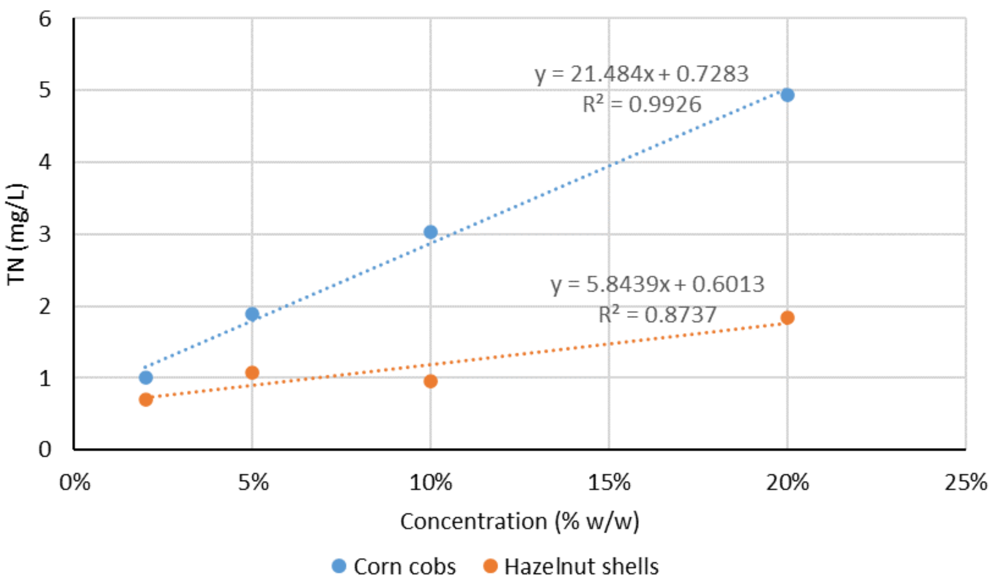


*Figure 26. TN trend of the corn cobs and hazelnut shells substrates at different weight percentages*

The trend in TN is like that of TOC for both types of agricultural waste, but the TN values are lower compared to TOC content. Additionally, a better linear interpolation is observed for corn cobs compared to hazelnut shells.

At a 10% concentration, the TN content was 3.038 mg/L for corn cobs, whereas it was 0.9509 mg/L for hazelnut shells. Table X summarizes the parameters obtained from the characterization of the substrates at 10% by weight.

*Table 10. Characteristics of substrates at 10% by weight*

| **10% w/w** | **pH (-)** | **EC (µS/cm)** | **$\rho_b$ (g/cm$^3$)** | **TOC (ppm)** | **TN (mg/L)** |
|---|---|---|---|---|---|
| Corn cobs | 4.88 | 83 | 2.4 | 100.8 | 3.038 |
| Hazelnut shells | 5.26 | 230 | 2.5 | 14.81 | 0.9509 |
| CC + HS | 4.96 | 151 | 2.5 | - | - |

## 3.3. Batch tests

The parameters analysed in the batch test included pH, EC, TOC and TN. Each of these parameters is explained in the following paragraphs.

### 3.3.1. Batch test 1: digestate

#### *3.3.1.1. pH and electrical conductivity*

Before measuring pH and EC, the samples (50 ml) were transferred into Falcon tubes and centrifuged at 8000 rpm for 15 minutes. After centrifugation, the probes were inserted into the Falcon tubes to measure the parameters. The pH measurements of the samples and the blanks are shown in Figure 27.

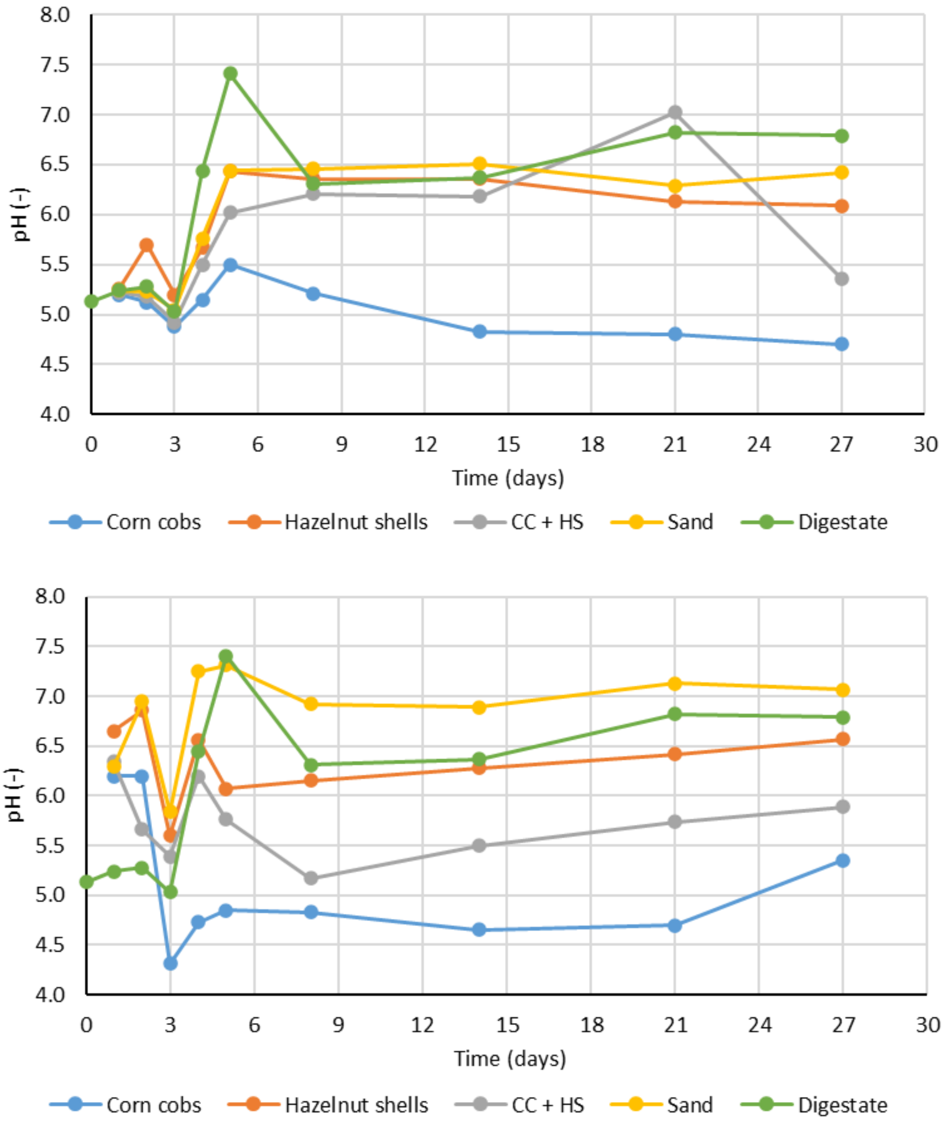


*Figure 27. pH trend of the samples (top) and the blanks (bottom)*

As observed in the first graph of Figure 27, the pH undergoes significant changes during the initial days of the test. It decreases slightly, reaching its lowest point by the third day, and then gradually increases, stabilizing around the fifth day. However, the pH of the substrate composed of corn cobs is an exception, because it experiences a second drop, returning to a more acidic level after this period. This pattern suggests that most substrates reach a point of equilibrium where pH fluctuations become minimal. The initial acidification might be attributed to microbial activity or the breakdown of organic materials, which releases acidic compounds. The subsequent increase and stabilization could indicate the buffering capacity of the medium or the depletion of readily degradable materials. The corn cobs substrate's unique behaviour could be due to its specific composition, leading to continued fermentation or microbial processes that lower the pH even after the initial stabilization.

Another substrate with a particular behaviour is the mix of corn cobs and hazelnut shells. This substrate shows a distinctive pattern: the pH rises sharply on the 21st day (pH = 7.02) and then returns to acidic conditions by the 27th day (pH = 5.36). This sudden increase in pH might suggest a phase of intense microbial activity or a temporary chemical reaction that disrupts the pH balance. It could indicate a brief period of accelerated decomposition or the production of basic compounds that temporarily neutralize the acidity. Following this, the return to a more acidic pH could result from continued decomposition of organic materials or the production of acids by microorganisms.

Alternatively, there could have been a measurement error on the 21st day, where the pH of the mix should not have increased, but rather continued decreasing, maintaining a consistent downward trend. This analysis is supported by the control samples. Specifically, the pH of the mix has been increasing steadily since the eighth day, indicating a potential anomaly in the 21st-day measurement. Furthermore, the corn cobs also exhibit a rising pH trend during the final days of the test. These control samples provide a useful point of reference, highlighting that the expected behaviour for the mix would have been a continued pH decrease rather than an unexpected increase. The consistency in the upward pH trends observed in both the mix and the corn cobs suggests that the anomaly on the 21st day may indeed be due to a measurement error.

Another important aspect to consider is that the digestate had a pH of 5.13 on day 0. According to D.M. 185/03 (Table 5), the acceptable pH range for effluents exiting the treatment facility is between 6 and 9.5. Consequently, this effluent must undergo alkalinization before being applied to the soil in a SAT system.

The electrical conductivity (EC) shown in Figure 28 reflects the theoretical concept outlined in paragraph 3.2.1, which posits a correlation between pH acidification and increased electrical conductivity. Indeed, the EC in the graph exhibits a trend that is almost the opposite of the pH trend. Additionally, it can be observed that substrates with a more basic pH exhibit lower EC compared to those with a more acidic pH, which show higher EC values. This perfectly aligns with the well-established relationship between pH and EC.

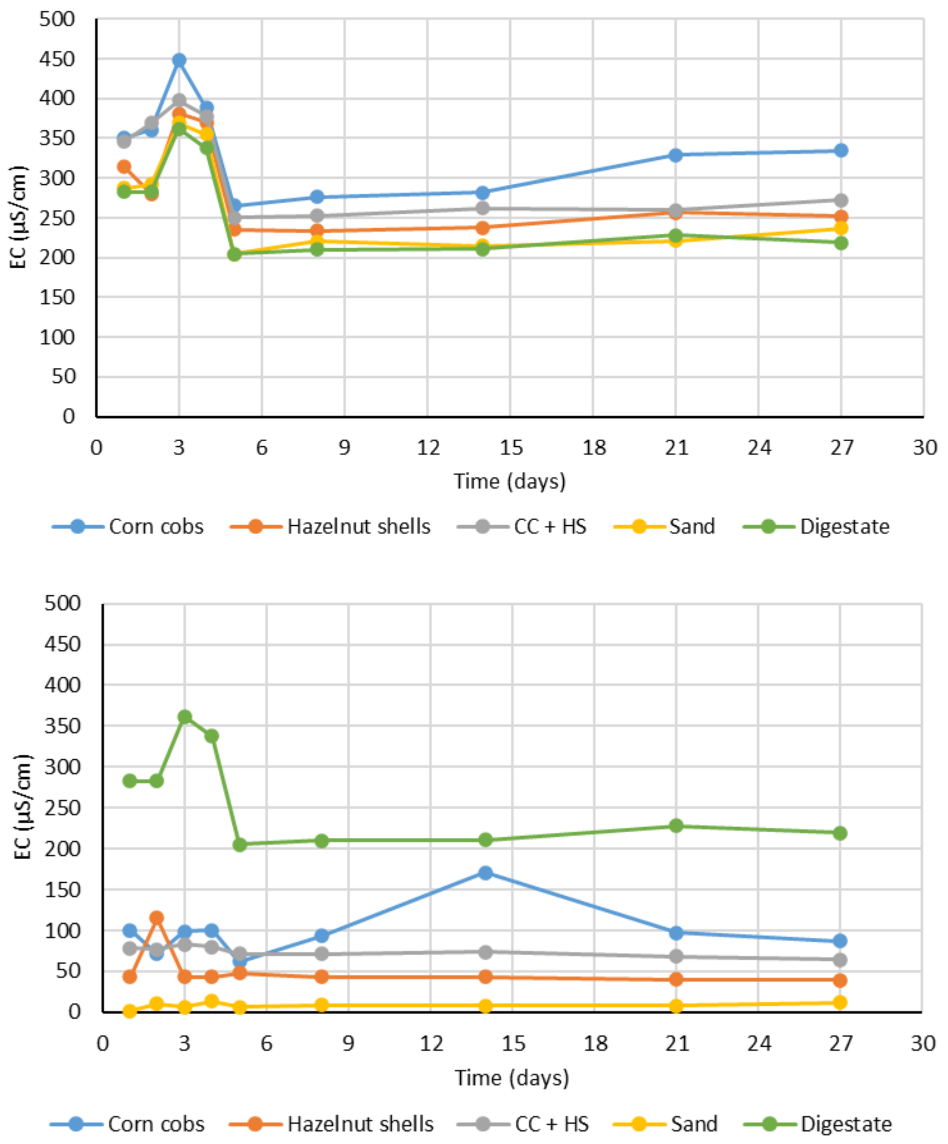


*Figure 28. EC trend of the samples (top) and the blanks (bottom)*

The digestate has a lower EC compared to all other samples; however, among the control samples, it shows the highest EC. This indicates that the ions from the substrates and digestate are combined in a way that affects their conductivity. Specifically, the corn cobs exhibit higher conductivity than the mix, followed by hazelnut shells, and finally sand, consistent with the trends observed in the control samples.

Additionally, the EC of the digestate complies with the limit set by D.M. 185/03, which is 3000 µS/cm.

#### *3.3.1.2. Biological Oxygen Demand*

After 4 days, the BOD measurement exceeded the scale limit of 4000 mg/L in two of the three solid samples: the substrate made from corn cobs (BOD = 4994 mg/L) and the substrate made from a mix of cobs and shells (BOD = 5361 mg/L). The substrate made from hazelnut shells was the only one to maintain a BOD below the scale limit (BOD = 1977 mg/L). To prevent exceeding the scale limit, new substrates were prepared with a 2% by weight concentration of corn cobs and the mix with hazelnut shells, instead of the previous 10% by weight, for a total of 100 g. The $BOD_5$ analysis of the 2% by weight substrates revealed the following results: 2144 mg/L for corn cobs, 1405 mg/L for the mixed substrate, 406 mg/L for hazelnut shells, and 273 mg/L for the digestate alone.

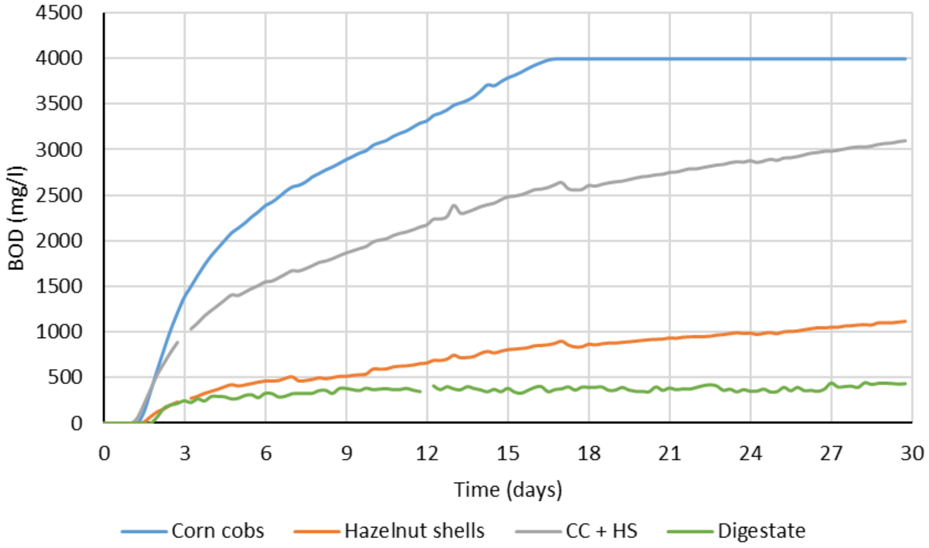


*Figure 29. Solid BOD of substrates 2% by weight*

As shown in Figure 29, the $BOD_5$ results, particularly for corn cobs and the mixed substrate, are significantly higher than the limits established by Italian Decree D.M. 185/03, which sets the maximum allowable concentration at 20 mg/L. These elevated $BOD_5$ levels reflect a high organic load in the tested substrates, posing potential environmental risks if not properly treated before discharge.

Additionally, the corn cobs reached the upper limit of 4000 mg/L by the end of the 16th day, highlighting their continued high organic load throughout the test period. This elevated $BOD_5$ concentration suggests that corn cobs may not be effective in reducing organic matter in the effluents and could pose a significant challenge for biodegradation. Such high levels of $BOD_5$ indicate an increased demand for oxygen during the breakdown of organic substances, which can strain aquatic environments if discharged untreated. Effective treatment and substrate selection are critical to achieving compliance with regulatory standards and preventing negative environmental impacts.

The analysis of TOC and TN degradation allowed for the identification of the optimal substrate for a large-scale SAT system.

#### 3.3.1.3. TOC and TN

Figure 30 illustrates the trend of TOC in the digestate both when in contact with the substrates and on its own (green line). Additionally, it shows the decomposition of TOC within the digestate. On day 0, the digestate had a TOC of 158 ppm, which exceeds the limit of 10 mg/L set by D.M. 185/03. During the first four days of the test, TOC levels increased, followed by a sharp decline on the fifth day, indicating effective decomposition starting from day 5.

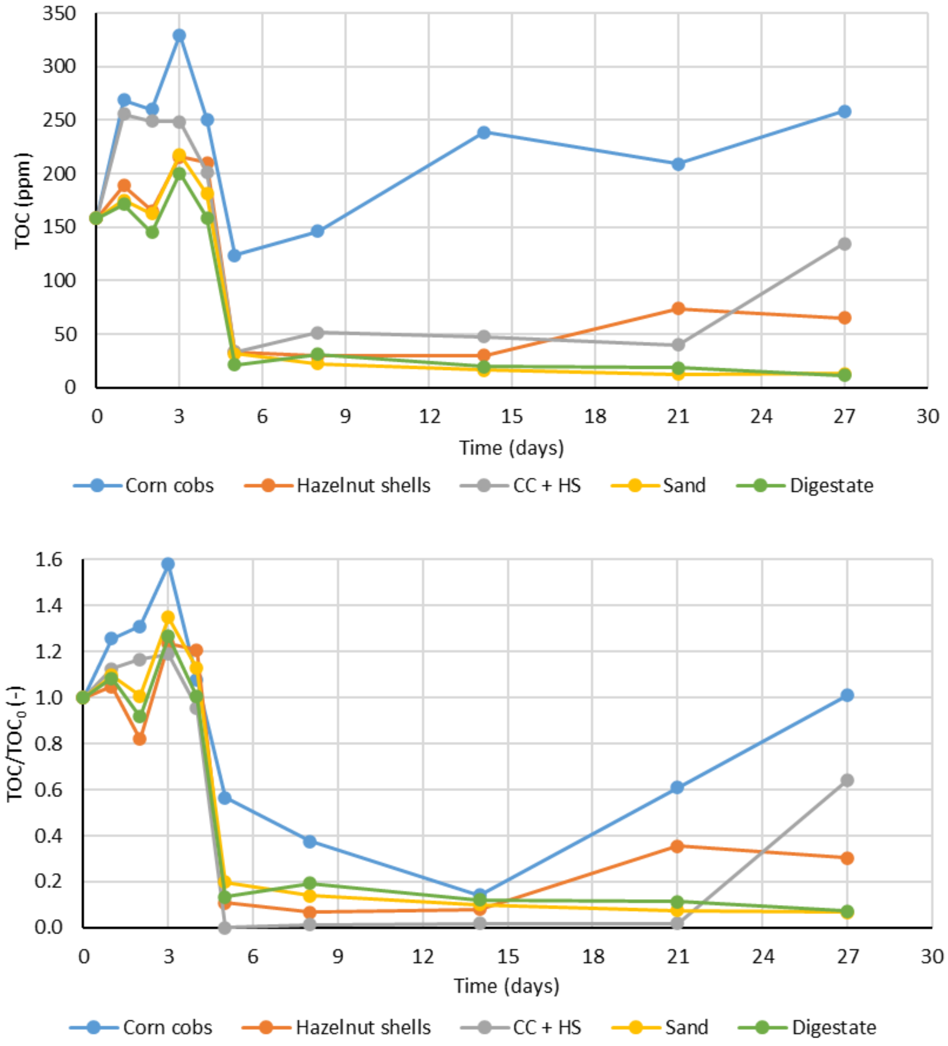


*Figure 30. TOC trend (top) and TOC degradation (bottom) in batch test 1*

The initial increase in TOC across all samples indicates the breakdown of organic materials, leading to the release of carbon-rich compounds. The subsequent sharp decrease on the fifth day suggests the onset of more advanced stages of microbial decomposition, where these compounds are further metabolized, resulting in lower TOC levels.

Corn cobs have again a particular behaviour, because they have a higher TOC levels compared to the other combinations. This suggests that the corn cobs release a larger quantity of organic compounds into the digestate, potentially due to its specific composition and higher organic content. While the TOC in the corn cobs alone declines toward the end of the test, due to the consumption of organic matter, the digestate stimulates further release of carbon-rich substances, leading to a higher TOC in the combined sample.

The mix shows an increase in TOC on the final day of the test, due to the presence of corn cobs in the substrate. In contrast, the hazelnut shells maintain a relatively constant TOC from the fifth day onward, with only a slight increase in the last few days. This suggests that the corn cobs are the primary contributors to the late-stage TOC rise in the mix. While the hazelnut shells exhibit minimal changes, the corn cobs' influence becomes more pronounced towards the end of the testing period, indicating their significant role in organic carbon release within the substrate.

The most efficient degradation of TOC in the digestate at the end of the test occurs in the substrate composed of D8 sand (93.29%), followed by hazelnut shells (69.72%) and the mix (35.91%). However, the degradation process starts from the fifth day, with a degradation of 100% from the mix, 89.03% from hazelnut shells, 80.06% from D8 sand and 43.41% from corn cobs. This indicates that for rapid degradation, the best options are the mix of corn cobs and hazelnut shells or the hazelnut shells substrate alone. However, if the wastewater remains in the SAT system for more than 5 days, the optimal choices are the sand and hazelnut shells substrates. In the absence of information regarding the duration of effluents in the system, the best solutions for TOC degradation are the hazelnut shell substrate and the D8 sand, as they perform well in TOC degradation across both short and long durations.

The trends and degradation of TN are shown in Figure 31, displaying a pattern very similar to that of TOC. Additionally, the TN concentration in the digestate exceeds the limit set by D.M. 185/03, which is 15 mg/L, with an initial value of 17.41 mg/L on day zero.

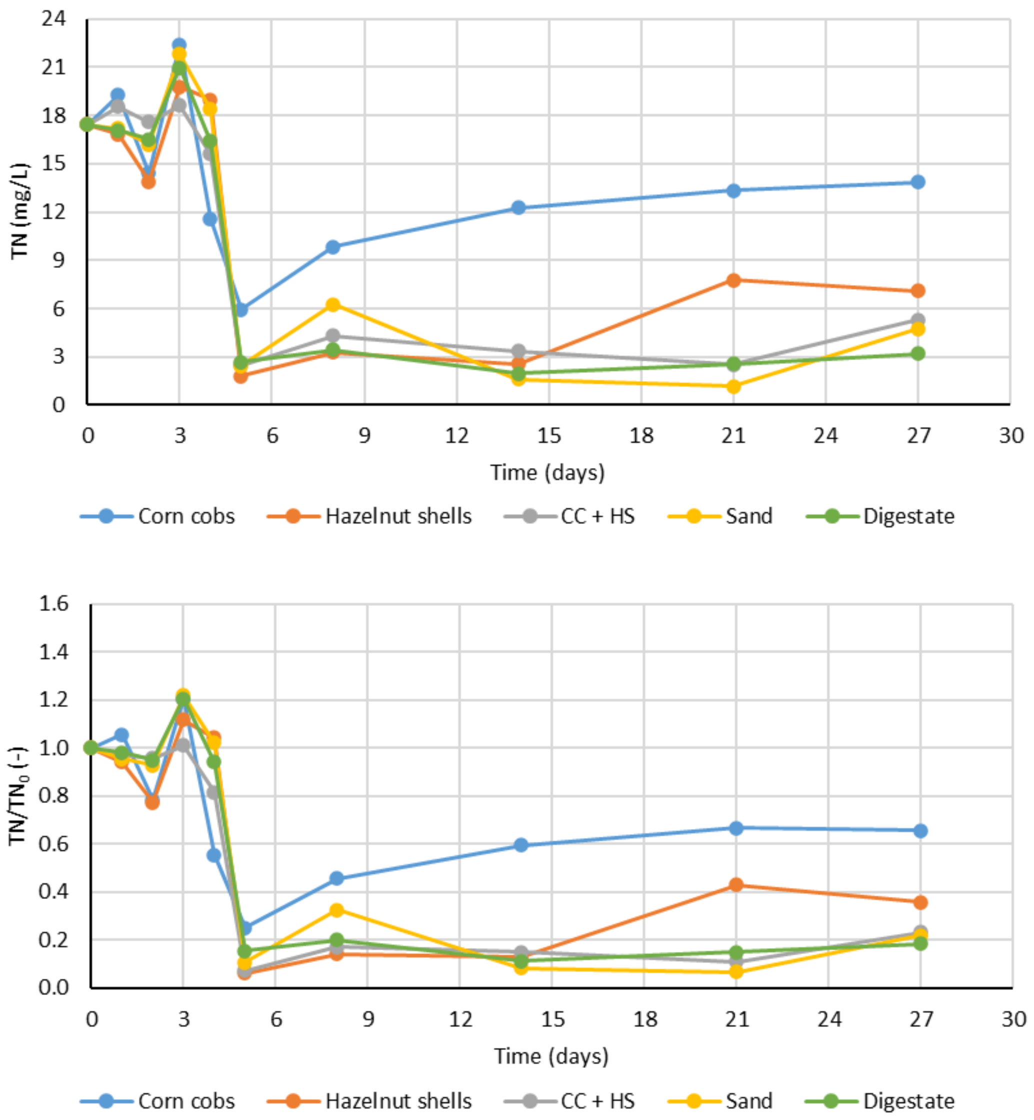


*Figure 31. TN trend (top) and TN degradation (bottom) in batch test 1*

On the twenty-seventh day, the most effective substrates for total nitrogen degradation were sand (78.26%) and the mixed substrate (76.78%), followed closely by hazelnut shells (64.36%). However, the degradation process began as early as the fifth day, with hazelnut shells leading (93.93%), followed by the mixed substrate (92.95%), sand (89.49%), and lastly, the corn cob substrate (75.12%). Therefore, the hazelnut shells substrate and the sand are the optimal choices for TN degradation, like for the TOC degradation.

Based on the results of the initial batch test, the study proceeded with only two substrates: sand and hazelnut shells. Both substrates demonstrated positive outcomes for the degradation processes, while corn cobs proved to be suboptimal. The mixed substrate produced good results, which can be attributed solely to the presence of hazelnut shells.

### 3.3.2. Batch test 2: apple boiling water and digestate

The second batch test analysed both the digestate and apple boiling water in parallel, using only the two substrates selected from the first batch test: sand and hazelnut shells. The parameters measured were the same as in the previous test, namely pH, EC, TOC, and TN, except $BOD_5$.

#### *3.3.2.1. pH and electrical conductivity*

The pH behaviour of the digestate (Figure 32) in this test closely resembles that observed in the first test, but with a notable difference in the initial days: it no longer becomes more acidic. This change could be attributed to the freezing and thawing process to which the digestate was subjected.

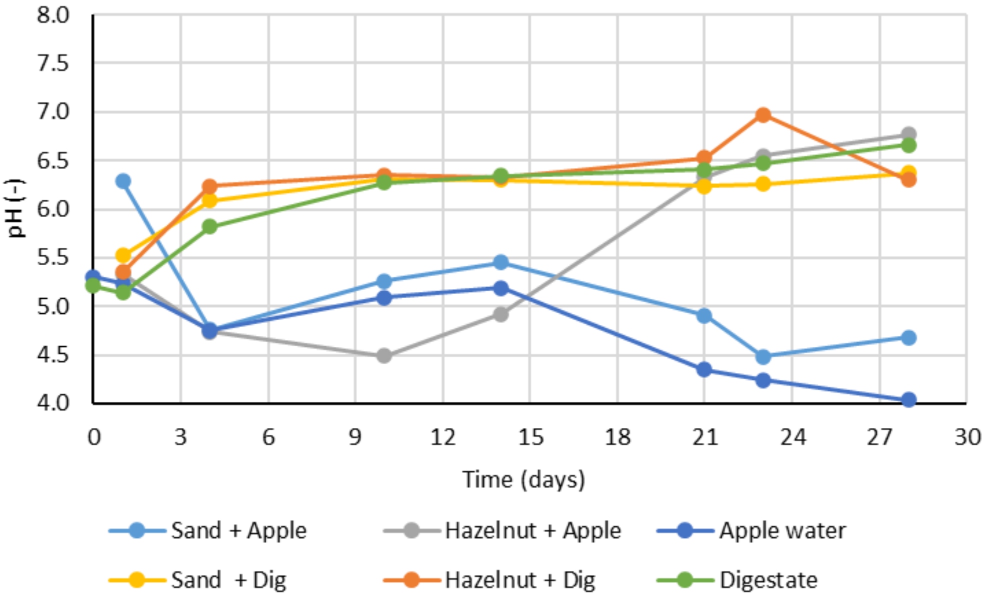


*Figure 32. pH trend of the apple boiling water and the digestate in each substrate over time*

When the digestate is frozen and then thawed, several physical and chemical changes occur. Freezing causes the formation of ice crystals, which disrupt cell structures and alter the composition and activity of the microorganisms in the digestate. Upon thawing, these changes result in a stabilization or even a reduction in the production of acidic byproducts, which are typically responsible for lowering the pH. Furthermore, the freeze-thaw cycle impacts the solubility and mobility of various compounds in the digestate, affecting its interaction with the substrates. As a result, the acidification process observed in the first test is diminished or altered, leading to the observed lack of pH decrease during the initial days of this test. This highlights how pre-treatment conditions like freezing and thawing can significantly influence the chemical behaviour and degradation processes of digestates.

Regarding the apple boiling water, its pH becomes acidic, even when in contact with sand, though the acidification is less pronounced compared to when it is alone. Conversely, when the apple boiling water interacts with hazelnut shells, the pH begins to increase after the tenth day, eventually stabilizing towards the end of the test. These pH changes in the apple boiling water can be attributed to the interactions between the water and the substrates. When in contact with sand, the apple boiling water continues to acidify due to the limited buffering capacity of the sand which does not significantly neutralize the acids produced. In contrast, the interaction with hazelnut shells seems to have a buffering effect. Initially, the presence of hazelnut shells might not neutralize the acids as effectively, but over time, their decomposition or chemical interactions result in the release of basic compounds or changes in the substrate that increase the pH. By the end of the test, this buffering effect led to a near stabilization of the pH, reflecting the dynamic equilibrium reached between the acidification processes and the neutralizing capacity of the hazelnut shells.

Electrical conductivity is shown in Figure 33, where a distinct contrast between the digestate and apple boiling water is evident. Specifically, when the digestate's conductivity decreases midway through the test, the conductivity of the apple boiling water increases.

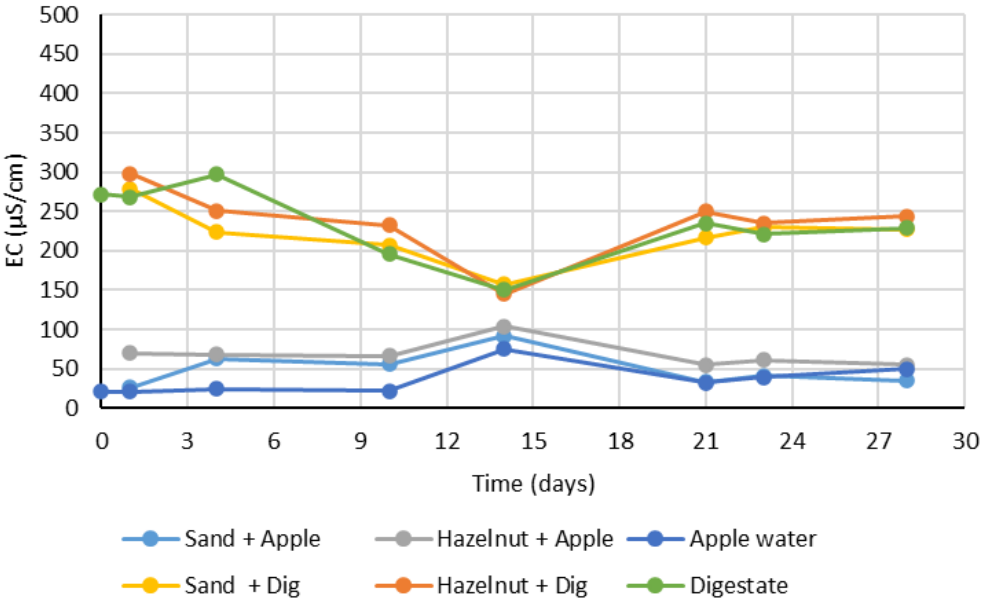


*Figure 33. EC trend of the apple boiling water and the digestate in each substrate over time*

The substrates exhibit a pattern closely mirroring the behaviour of the effluents they interact with, indicating that they do not significantly influence changes in electrical conductivity. This suggests that the variations in conductivity are primarily driven by the properties of the digestate and apple boiling water, rather than the substrates themselves. Additionally, the trend observed in the digestate seams delayed compared to the first batch test, because the minimum pH occurs at the fourteenth day instead of the fifth day, reflecting the impact of freezing and thawing on the behaviour of the digestate in this second batch test.

The contrasting behaviour in EC between the digestate and apple boiling water is influenced by their different chemical interactions and processes. Initially, the digestate’s EC decreases over time due to changes in ionic composition or chemical reactions within the sample. Conversely, the apple boiling water's EC increases as it interacts with substrates or undergoes compositional changes.

In the second half of the test, this pattern reverses: the digestate’s EC starts to increase again, while the EC of the apple boiling water begins to decrease. This shift suggests that after the initial phase, the digestate releases additional ions or experiences reduced buffering effects, leading to increased EC. At the same time, the apple boiling water’s EC decreases due to the consumption or precipitation of ions or other changes in its interaction with substrates.

The lack of correlation between pH and EC can be attributed to several factors. Electrical conductivity measures the ability of a solution to conduct electricity, which depends on the concentration and type of ions present, while pH measures the concentration of hydrogen ions ($H^+$). Variations in other ionic species, the presence of non-ionic substances, and the interaction with substrates can affect EC without significantly altering pH. Additionally, buffering capacity of the substrates, complex biological or chemical processes, and potential measurement errors can contribute to this lack of correlation.

#### *3.3.2.2. TOC and TN*

Figure 34 displays the trends and degradation of TOC for both the digestate and apple boiling water. The TOC trend for the digestate shows a much more pronounced decrease over time compared to the apple boiling water. Furthermore, the digestate also maintains lower TOC values overall.

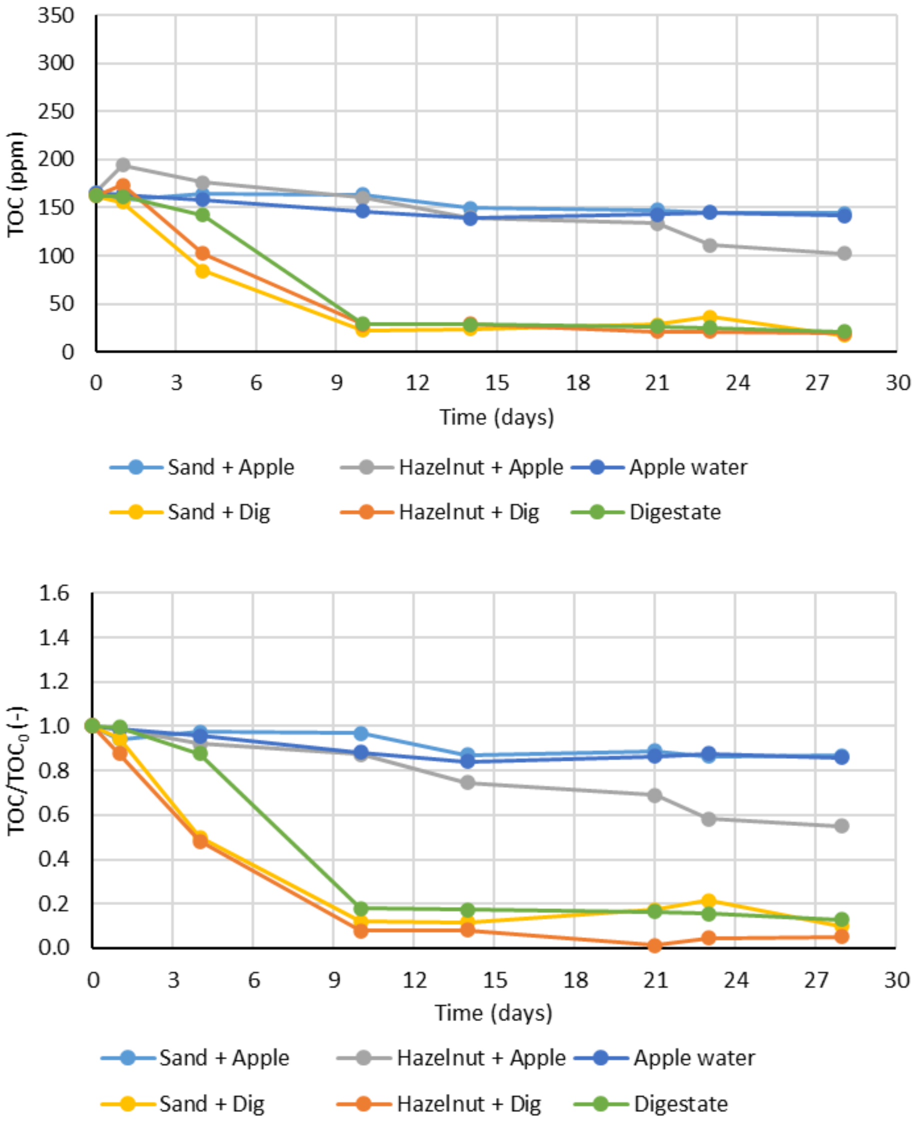


*Figure 34. TOC trend (top) and TOC degradation (bottom) in batch test 2*

The most effective degradation of TOC for the digestate is observed from the tenth day forward. In contrast, the apple boiling water does not show a particularly efficient degradation on any specific day. Notably, the substrate that performs best in terms of TOC degradation for both types of effluents is the one composed of hazelnut shells, with a degradation of 98.84% for the digestate and 44.92% for the apple boiling water, compared to the natural degradation of the two effluents alone, which is 87.09% for the digestate and 14.22% for the apple boiling water. This indicates that while the digestate achieves more effective TOC reduction over time, the apple boiling water's degradation process is less consistent, but still improved by the hazelnut shells substrate.

Compared to the first test, the peak of TOC degradation shifts from the fifth day to the tenth day in this second test. This change is attributed to the freezing and thawing of the effluents prior to the test. This shift underscores how pre-treatment conditions, such as freezing and thawing, can significantly impact the timing and effectiveness of degradation processes, as already explained in the paragraph 3.3.2.1.

Figure 35 shows the trend and degradation of TN. The apple boiling water has significantly lower TN compared to the digestate and complies with the D.M. 185/03 regulations. The TN value of apple boiling water is low (TN = 0.8243 mg/L), with near-complete decomposition observed from the first day when in contact with hazelnut shells. Without substrate interaction, degradation would have ceased by the fourth day of the test (26.58%). In contrast, the digestate starts with higher TN value (16.85 mg/L) that decrease over time, although it rises slightly toward the end of the test.

By the end of the test, TN degradation in the digestate (51.80%) improves when it interacts with hazelnut shells (80.44%), demonstrating that substrate interaction plays a crucial role in enhancing the breakdown of nitrogen compounds. This indicates that while the digestate initially had a higher TN, the presence of effective substrates can significantly boost its degradation efficiency.

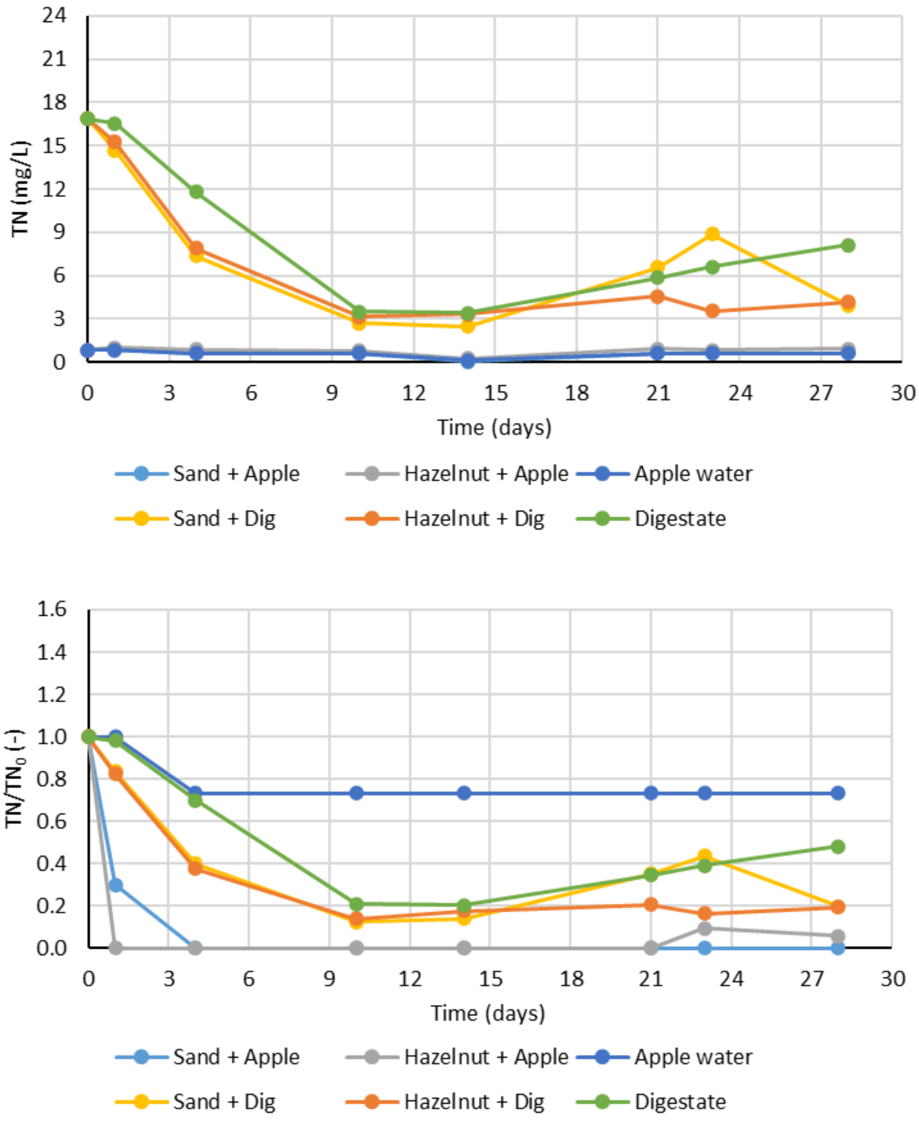


*Figure 35. TN trend (top) and TN degradation (bottom) in batch test 2*

### 3.4. Batch test considerations

The second batch test reveals that the freezing and thawing process significantly affects the timing of degradation. This alteration shifts the optimal degradation period from the fifth day to the tenth day, indicating that temperature fluctuations can influence the rate at which substrates degrade organic materials.

Despite this shift, the substrate composed of 10% by weight hazelnut shells consistently proves to be the most effective for both digestate and apple boiling water throughout the test period. This suggests that hazelnut shells provide a robust and reliable solution for optimizing the degradation of organic compounds, even when external factors like freezing and thawing are introduced. The persistent efficacy of this substrate highlights its potential for practical applications in large-scale treatment systems where such variables are common.

## 3.5. Column leaching tests

To evaluate the potential application of the substrate as a filtering material in a real-world SAT system, column tests were conducted. These tests are detailed in the following sections.

### 3.5.1. Continuous column leaching test

Each column test was conducted only after the columns were characterized by injecting KBr to determine their pore volume. The parameters measured during each column test included pH, EC, TOC, and TN, as was done for the batch tests. Additionally, other parameters studied were the profile of solid TC and of water content of each column.

#### *3.5.1.1. Columns of hazelnut shells*

Figure 36 shows the breakthrough curves of the first two columns composed of the hazelnut shells substrate. The pore volume was determined by analysing the breakthrough curve, which was derived from the ratio of the electrical conductivity measured at the outlet to that measured at the inlet, sampled every 15 minutes.

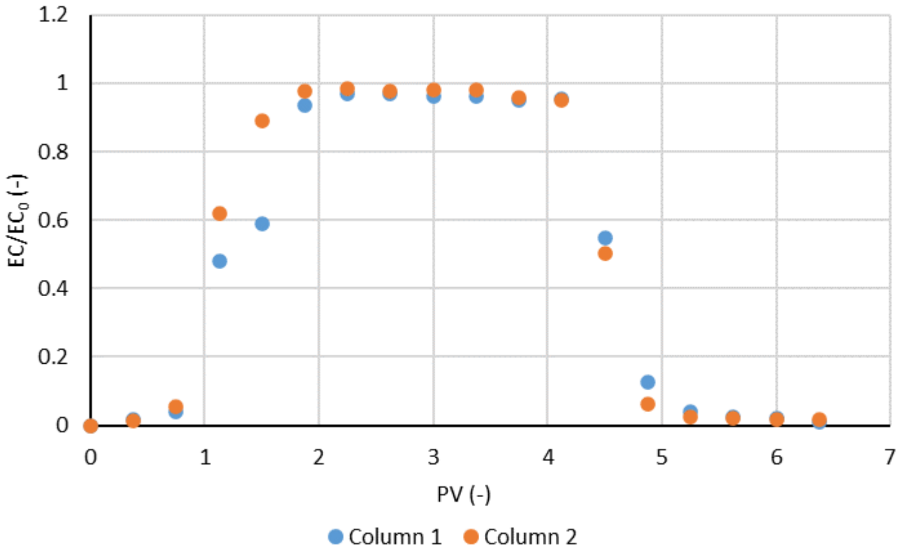


*Figure 36. Breakthrough curves from EC measurements of the two columns of hazelnut shells*

The pore volume for the first column was approximately 45 minutes, while for the second column it was 40 minutes, making them quite similar. Based on this value, it was possible to determine the duration of the effluent injection for this column test, which was set at 5PV. Given a PV of 40 minutes for both columns, the injection time was approximated to 3 hours, followed by 3 hours (180 minutes) of deionized water.

Figure 37 shows the trend of the pH at the inlet and outlet of the columns, measured every 15 minutes. In Column 1, apple boiling water at a 1:65 ratio was injected, while in Column 2, digestate at a 1:40 ratio was used. After 180 minutes, deionized water was injected, but the parameters continued to be measured on the effluents, even though they were no longer being injected, to obtain the graph of the inlet pH over 360 minutes.

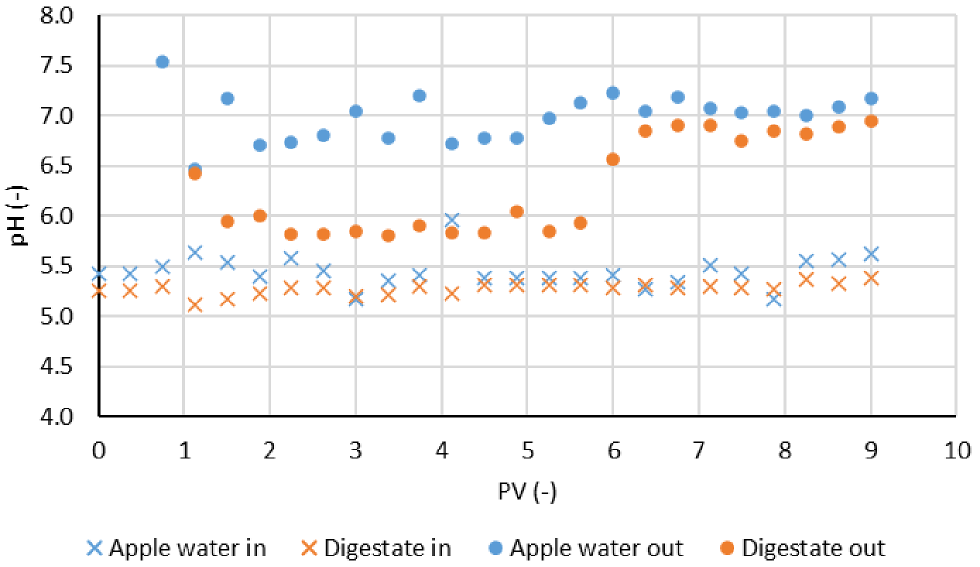


*Figure 37. pH trend of effluents entering (X) and exiting (Circles) the columns of hazelnut shells*

Comparing the two graphs, it is evident that the pH of the effluents is altered as they pass through the hazelnut shell substrate. In the case of the digestate, the pH increases slightly, reflecting a minor interaction between the substrate and the effluent. However, for the apple boiling water, a more significant change is observed, with the pH increasing from an average of 5.5 at the inlet to 6.9 at the outlet. This indicates that the hazelnut shell substrate has a stronger buffering effect on the apple water, due to differences in the chemical composition of the two effluents.

Another parameter analysed was the EC of the effluents at the inlet and outlet of the columns (Figure 38). This parameter was not significantly affected by the effluents passing through the substrate. In fact, the digestate reached the inlet value after about 2PV, whereas the apple water had such a low EC that it was difficult to precisely identify the effluent breakthrough point based on this graph. However, the presence of hazelnut shells slightly enriched the apple boiling water, leading to a modest increase in its EC.

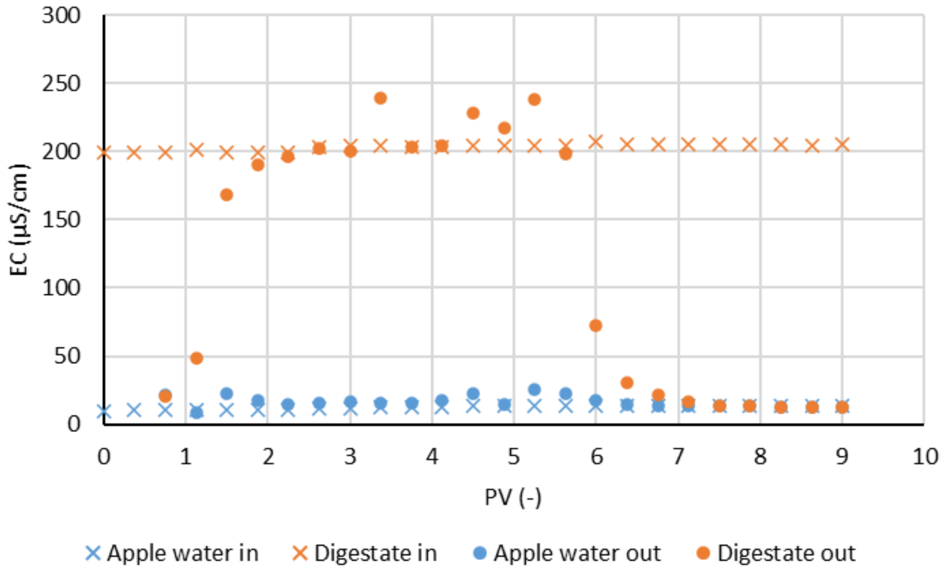


*Figure 38. EC trend of effluents entering (X) and exiting (Circles) the columns of hazelnut shells*

The first deionized water samples (after 180 minutes) exhibited greater variability compared to earlier ones, likely due to sampling challenges. Since the sand has a much lower EC than the other substrates analysed in this study, this variability is not attributable to the deionized water itself, but rather the instrument. The probe needed to be inserted into a very small volume of liquid, making it difficult to ensure meaningful results.

Figure 39 shows the degradation of TOC at the column outlet. The samples collected were diluted with deionized water at a ratio of 1:3 in 30 ml of total volume before being analysed for TOC.

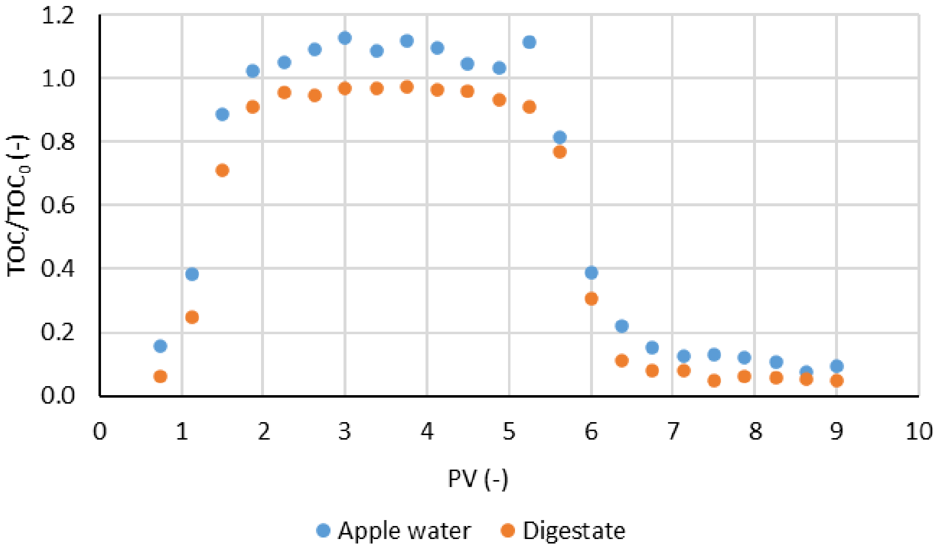


*Figure 39. Breakthrough curves of TOC of the apple boiling water and the digestate from the columns of hazelnut shells*

The graph indicates that the TOC from the digestate is almost fully eluted from the column, as the ratio approaches unity, with a TOC degradation of 3.95% at the end of the 3 hours of injection of the wastewater in the substrate.

In contrast, the apple boiling water shows a higher TOC output. This behaviour can be attributed to the hazelnut shells, which is also observed in Figure 34. In the early days of Batch test 2, apple boiling water with hazelnut shells had a higher TOC compared to apple boiling water alone. Therefore, this column test confirms that the hazelnut shells contribute to additional organic material, which impacts the overall TOC levels in the effluent.

Figure 40 illustrates the degradation of TN for the two effluents exiting the hazelnut shells substrate.

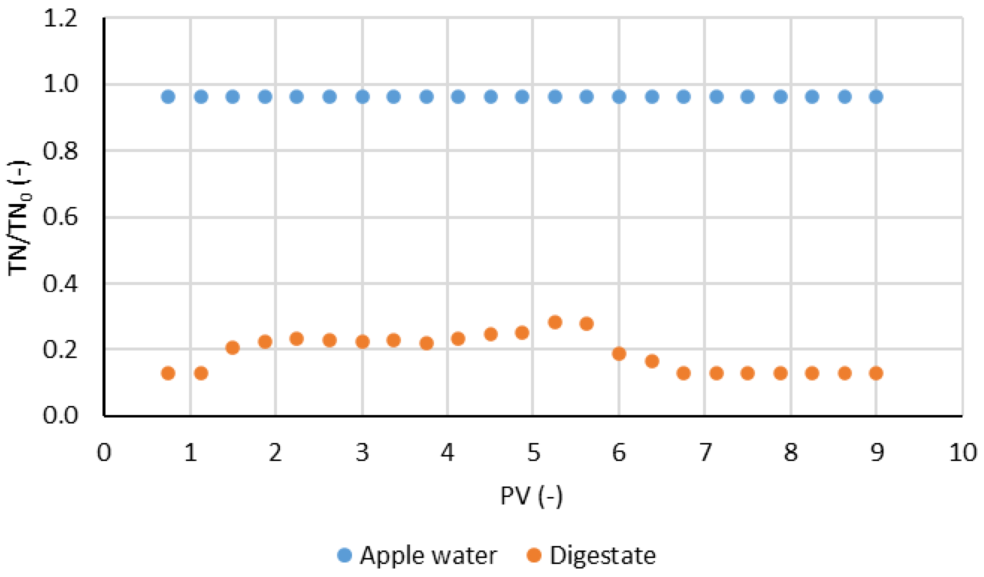


*Figure 40. Breakthrough curves of TN of the apple boiling water and the digestate from the columns of hazelnut shells*

The TN in the apple boiling water is so low that it remains unchanged by the substrate, with a consistently low value of 0.6052 mg/L. In contrast, the digestate starts with a higher TN concentration at the inlet, averaging 4.6 mg/L. This TN is partially removed by the substrate, resulting in a reduced average value of 0.97 mg/L at the outlet. This reduction indicates that the hazelnut shells substrate has some capacity to filter out TN from the digestate, with an average TN degradation of 77.80%, but it is not significantly impacting the TN levels of the apple boiling water due to its already low initial concentration, with an average TN degradation of 3.72%.

Figure 41 shows the water content profile of the two columns, determined at the end of the test. The water content in both columns aligns with the expected results, with the highest amount of water found at the bottom of the column, indicating effective downward infiltration. The middle layer shows a higher water content compared to other layers because it was the last centimetre removed from the column and therefore contained the most material. The first and last layers consist of 5G sand, the coarser type of sand used.

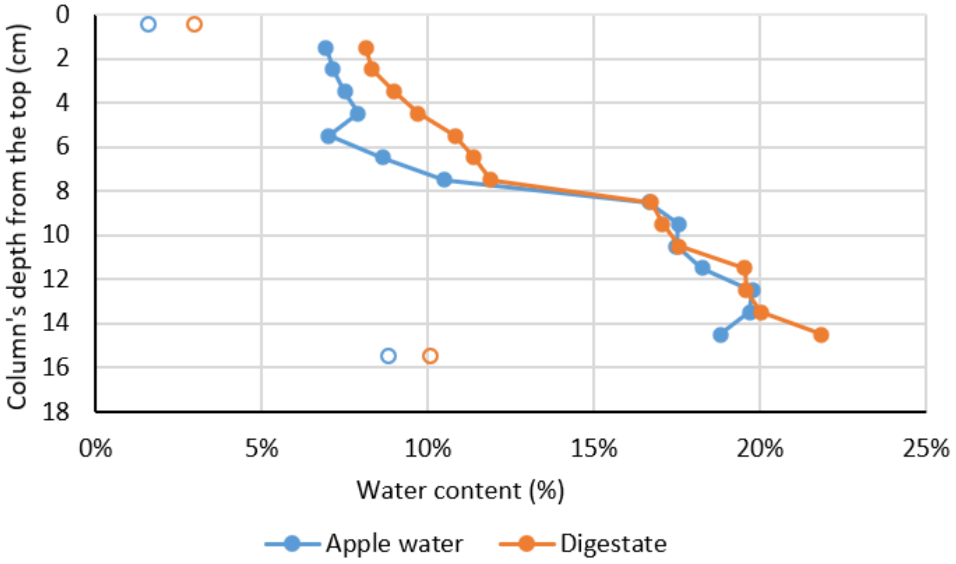


*Figure 41. Water content profile of the two columns of hazelnut shells*

Figure 42 presents the profile of solid TC (total carbon) content of the hazelnut shells columns. The profiles are quite similar for both columns, as the values are generally very low. The layer with the highest content is the second one, located just below the 5G sand layer. The digestate releases a maximum solid TC content of 8.062%, while the apple water releases 6.586%. This suggests that the substrate effectively filters out solid TC, with the highest concentration occurring in the layer immediately beneath the coarser sand, indicating the substrate's efficiency in removing this substance.

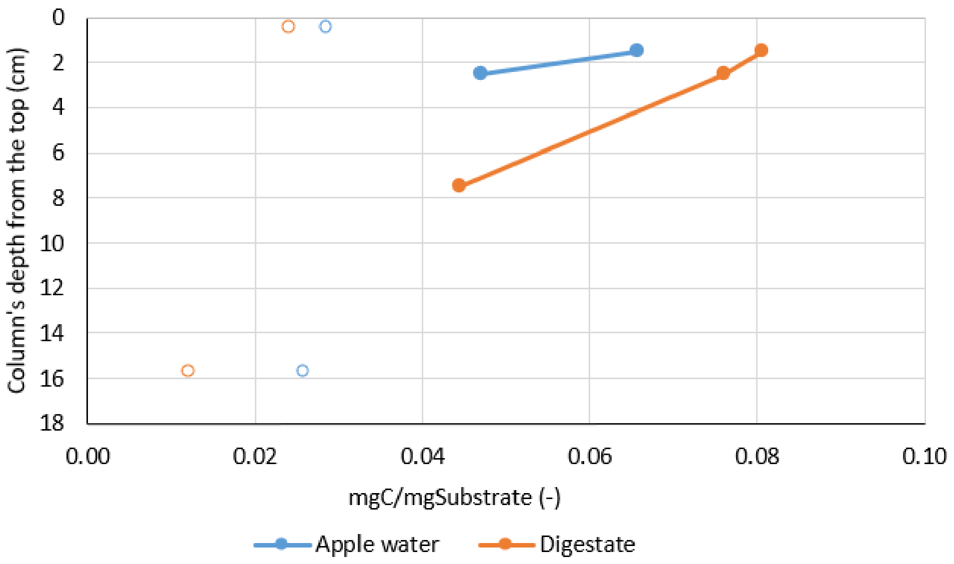


*Figure 42. Solid TC profile of the two columns of hazelnut shells*

The results obtained from the hazelnut shells columns are promising for both effluents. The columns slightly increase the pH, do not significantly alter the electrical conductivity, and effectively degrade the TN, particularly for the digestate. Additionally, the water content and solid TC profiles are optimal for a filtration system. The only potential drawback may be the degradation of TOC. However, according to the batch tests, it should simply require more than 6 hours for the digestate and in particular for the apple boiling water.

#### *3.5.1.2. Columns of D8 sand*

The continuous column leaching test was repeated using the substrate composed solely of Dorsilit 8 sand. As with the previous columns, the pore volume was determined by the ratio of EC at the outlet to the EC at the inlet of KBr. For the sand columns, the pore volume was achieved at approximately 45 minutes for both.

Figure 43 illustrates the pH levels at the inlet and outlet of the D8 sand substrate. For the digestate, there is no significant change in pH. Once the system reaches a plateau of stable values, the pH at the outlet (pH = 5.54) is nearly the same as at the inlet (pH = 5.42).

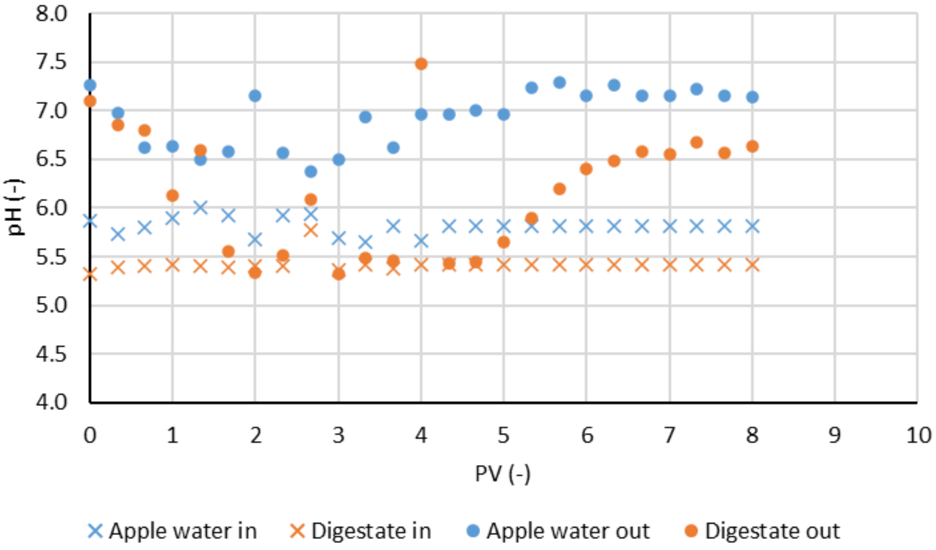


*Figure 43. pH trend of effluents entering (X) and exiting (Circles) the columns of sand*

In contrast, the apple water experiences a slight increase in pH, indicating a mild alkalinization as it passes through the sand substrate. One possible reason is the dissolution of basic or alkaline substances from the sand, which increases the pH of the water. Additionally, the interaction between the water and the sand may lead to the exchange of hydrogen ions for more alkaline ions, further contributing to the increase in pH.

This process indicates that the sand substrate has a mild buffering capacity, which influences the acidity of the effluent. However, the hazelnut shell substrate had a more pronounced effect on the pH of the apple boiling water, visible in Figure 37.

Figure 44 shows the variation in electrical conductivity (EC) from inlet to outlet of the apple boiling water and the digestate through D8 sand.

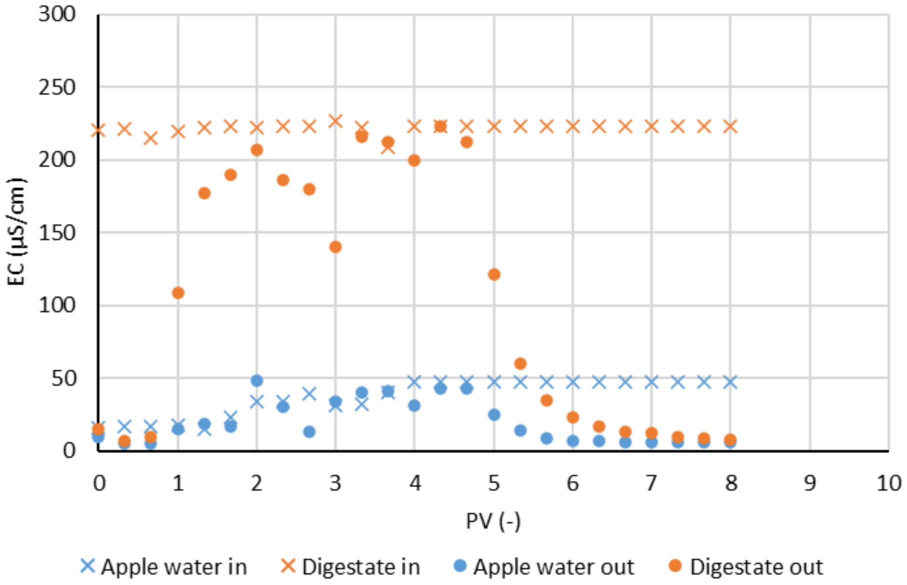


*Figure 44. EC trend of effluents entering (X) and exiting (Circles) the columns of sand*

There is a noticeable pattern of repeated increases and decreases in the EC at the outlet. This fluctuation may be due to minor clogging phenomena, which can cause temporary loss of ions in the effluent. Alternatively, it could reflect the challenges associated with sampling in a very small volume, leading to inconsistent results.

Additionally, variations in EC could also be attributed to changes in the flow rate or the interaction between the effluent and the sand substrate, which affects the ion concentration measured. Despite this, the EC at the outlet of both the digestate and apple boiling water nearly reaches the inlet value, demonstrating that there are times when all the ions contributing to the EC are eluted from the columns. However, the inlet values are never exceeded, suggesting that the D8 sand does not release significant additional ions into the outlet solutions.

Figure 45 shows the degradation of TOC for the two effluents after passing through the D8 sand substrate. The behaviour of TOC through the sand is very similar to that observed with hazelnut shells when analysed over the short term of the first two columns. However, results from the second batch test reveal that, over the long term, sand is less effective than hazelnut shells in TOC degradation.

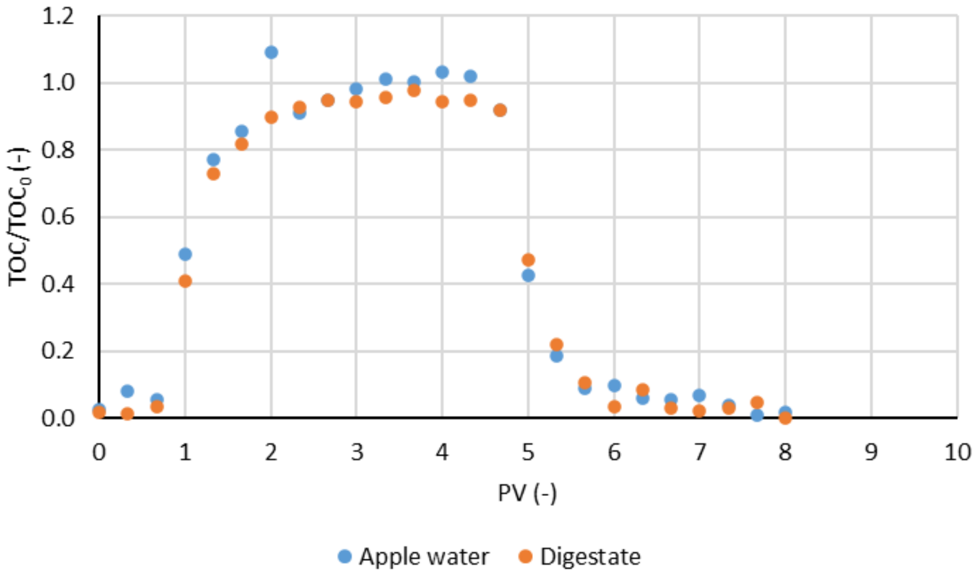


*Figure 45. Breakthrough curves of TOC of the apple boiling water and the digestate from the columns of sand*

An interesting aspect is the TOC release from the apple boiling water; it surpasses the initial value slightly later compared to the hazelnut shells and in a smaller amount. This delayed release and smaller quantity are attributed to the lower organic content in the sand compared to the hazelnut shells, which means that the sand has less capacity to adsorb or react with the organic substances present in the apple boiling water. Therefore, although hazelnut shells initially contribute some organic content to the apple boiling water, they ultimately serve as a more effective filter than D8 sand in terms of TOC degradation over time.

Figure 46 shows the degradation of TN of the apple boiling water and the digestate through D8 sand. The degradation of TN is similar to that observed with hazelnut shells for apple boiling water, as it consistently maintains a very low value of 0.6052 mg/L. This suggests that the sand substrate does not significantly affect the TN concentration in apple boiling water, like the hazelnut shells.

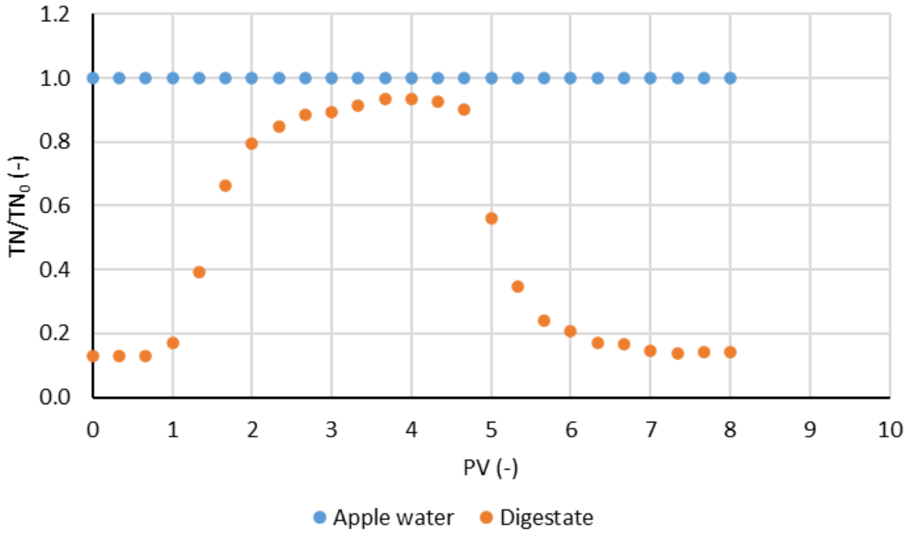


*Figure 46. Breakthrough curves of TN of the apple boiling water and the digestate from the columns of sand*

In contrast, at the end of the first three hours the digestate shows a much lower level of TN degradation (6.46%) compared to the one with the hazelnut shells (75.38%). The TN concentration decreases slightly from a maximum of 4.72 mg/L at the inlet to 4.63 mg/L at the outlet. This indicates that the sand substrate has limited capacity for reducing TN in the digestate, suggesting that it is less effective at removing nitrogen compounds compared to hazelnut shells.

The water content profile (Figure 47) of the sand columns aligns the expected results, with the highest water content found at the bottom of the column. As with previous observations, the central layer retains more water, likely because it was the last layer removed, leading to greater material accumulation. However, the water content in the D8 sand columns is lower than that of the hazelnut shells, due to the latter's higher capacity to adsorb water compared to sand.

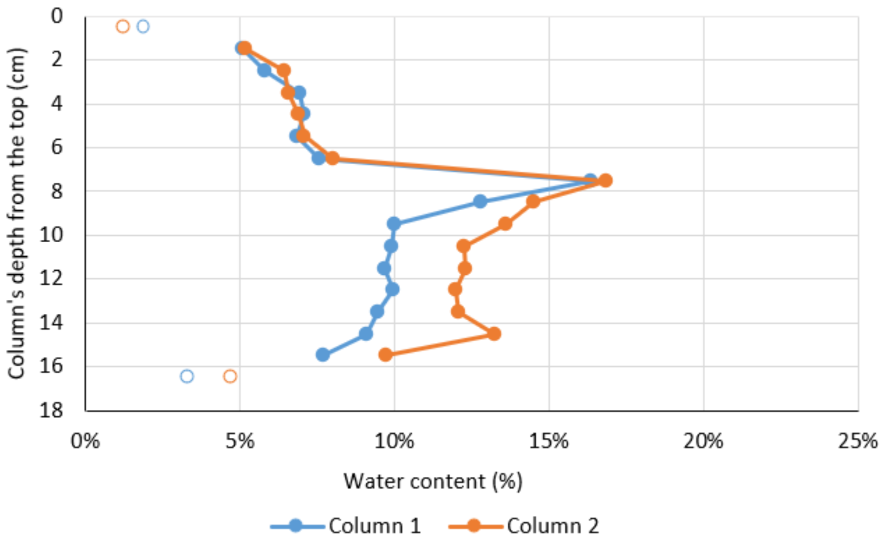


*Figure 47. Water content profile of the two columns of sand*

The profile of solid TC (Figure 48) content does not aligns with the expected results, showing consistently low concentrations throughout the entire columns. This suggests that D8 sand is not an optimal filter for organic matter.

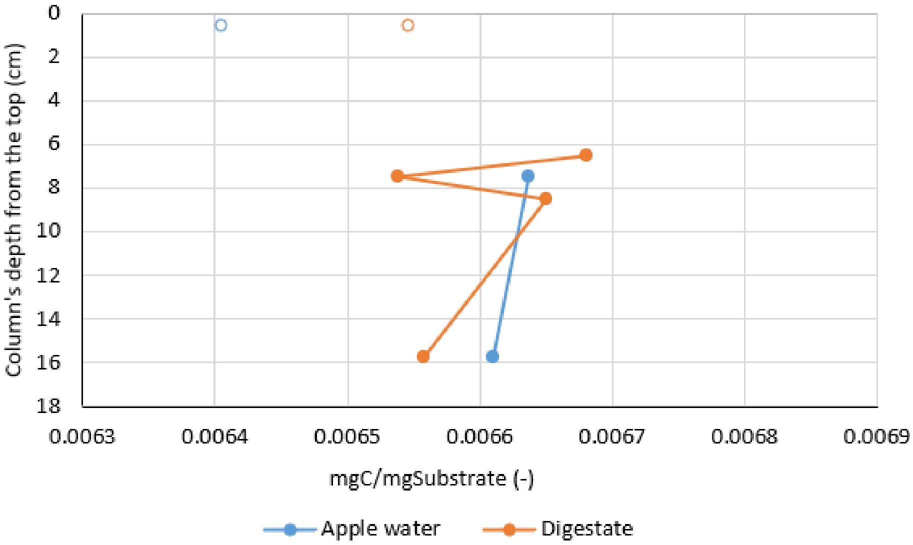


*Figure 48. Solid TC profile of the two columns of sand*

In conclusion, the D8 sand substrate is not optimal for filtering organic matter such as TOC and TN. Unlike the hazelnut shells substrate, the sand does not induce significant alkalinization of the pH, but like the hazelnut shells, the electrical conductivity remains nearly the same as the inlet value. Therefore, when comparing these results to those from the hazelnut shells test, it is evident that the most effective filter is the substrate composed of 10% by weight of hazelnut shells.

### 3.5.2. Intermittent column leaching test

In this column test, the three flooding periods of the two effluents were examined, each lasting 24 hours. The parameters measured included pH, EC, ORP (oxidation-reduction potential), TOC, and TN. Trends were analysed over the total 216-hour period.

The only substrate used for this test was the one composed of hazelnut shells at 10% by weight and the PV of each column was about 55 minutes.

In the third flooding phase, the first three measurements of pH, EC and ORP were taken using a multiparameter instrument rather than individual devices for each parameter. This change in methodology could have led to slight variations in the results for these initial measurements. The use of a multiparameter probe often integrates several sensors into one unit, which can introduce minor differences in calibration and sensitivity compared to dedicated instruments. These small discrepancies may arise due to differences in response time, sensor precision, or environmental factors that multiparametric devices handle differently from single-parameter tools. Consequently, the comparability of these early measurements with the others could be slightly affected.

The pH trend is shown in Figure 49, with the variation in apple boiling water displayed in blue and the digestate in orange.

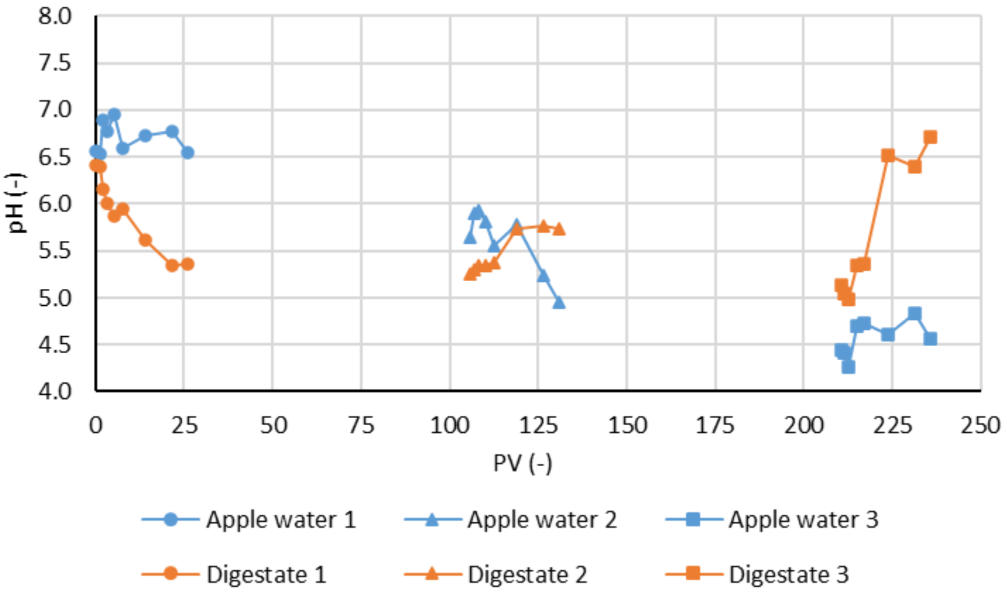


*Figure 49. pH trend monitored in the three floodings*

For the apple boiling water passing through the hazelnut shells substrate, a noticeable decrease in pH occurs with each flooding event. This progressive drop in pH can be attributed to several factors, including the interaction between the organic acids in the apple water and the hazelnut shells, as well as microbial activity within the substrate. Organic materials often undergo decomposition and fermentation when exposed to water, leading to the release of acidic byproducts. As these compounds accumulate over time, they contribute to the overall acidification of the system. Additionally, the buffering capacity of the hazelnut shells seams gradually reduced with each successive flooding, further amplifying the pH decline. This pattern suggests a dynamic interaction between the effluent and substrate, where both chemical and biological processes drive the observed pH changes.

The results from the second batch test (paragraph 3.3.2.1) showed that the pH of the apple boiling water with hazelnut shells initially follows a decreasing trend over the first few days, as observed in this test. However, after that initial drop, the pH begins to rise again.

When considering each individual flooding event, it is evident that the pH trends do not vary significantly, except for the second flooding, which shows a noticeable acidification toward the end. This specific behaviour during the second flooding could be linked to a delayed release of acidic compounds or enhanced microbial activity triggered by the renewed water exposure. The relatively stable pH in the other floodings suggests that the system has reached a sort of equilibrium, where the interaction between the effluent and the substrate stabilizes. The second flooding's deviation might indicate a temporary imbalance, potentially due to accumulated organic material or shifts in microbial communities, which momentarily lowers the pH before stabilizing again in subsequent floodings.

For the digestate, an opposite behaviour is observed, where with each flooding, the pH starts at an increasingly lower level but ends at a higher point than the previous flooding. This suggests that the digestate undergoes a complex chemical and biological interaction with the substrate. The initial decrease in pH with each flooding could be due to the release of acidic compounds, possibly resulting from the breakdown of organic material or microbial activity. However, the subsequent rise in pH indicates that, over time, the system is generating alkaline byproducts, such as ammonia, from the digestion of nitrogen-rich compounds. This pattern of decreasing starting pH followed by an increase suggests that the digestate's buffering capacity and microbial processes are evolving with each cycle, leading to a more alkaline environment as the flooding progresses.

Considering that there were three days of gravity drainage between each flooding, during which oxygen likely entered the column, this could explain the observed pH behaviour. The oxygen influx between floodings would have promoted aerobic microbial activity, which can influence the chemical environment within the column. In the case of the digestate, aerobic conditions may have led to the oxidation of organic matter, resulting in the initial pH drop at the start of each flooding. As the flooding progressed and oxygen levels decreased, anaerobic processes may have become dominant again, leading to the production of alkaline byproducts, such as ammonia, which could explain the pH increase toward the end of each flooding cycle.

By analysing the total nitrogen data, it can be assessed whether nitrogen compounds are being transformed or consumed in a way that supports the proposed chemical and biological processes.

Electrical conductivity is shown in Figure 50. The apple boiling water exhibits no significant changes as the floodings progress. Initially, the conductivity is higher at the start of each flooding event, but it then decreases and stabilizes at a nearly constant level after the first 6 hours. For the digestate, a decrease in electrical conductivity is observed with each flooding, which aligns with the pH trends.

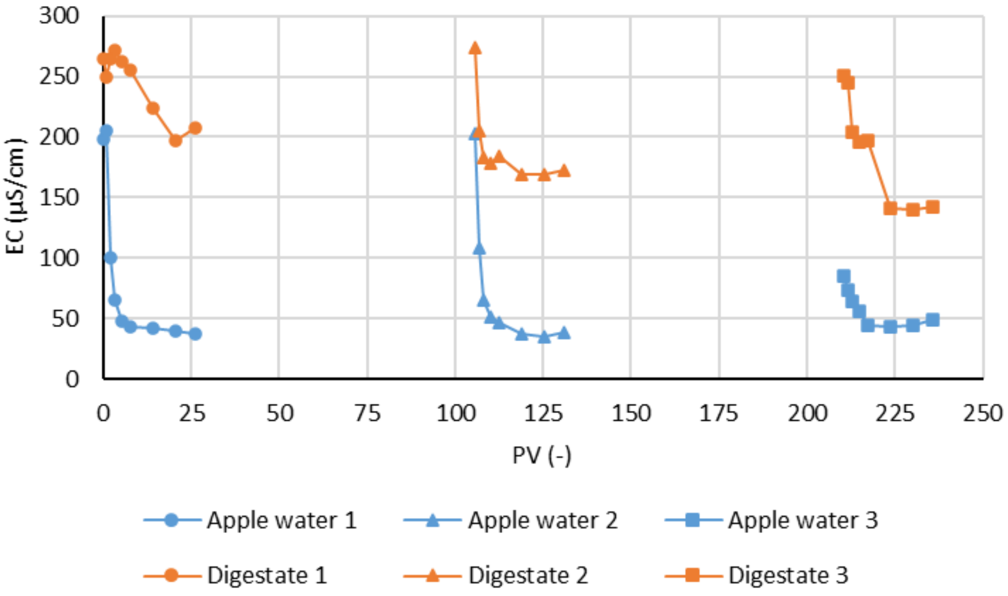


*Figure 50. EC trend monitored in the three floodings*

The higher electrical conductivity of the apple boiling water at the beginning of each flooding can be attributed to the fact that, after the three-day gravity drainage period, the column is refilled with fresh effluent that contains dissolved salts and other electrolytes. Initially, this fresh effluent introduces a higher concentration of ionic species, which results in increased conductivity. As the flooding progresses, the introduction of fresh effluent causes a temporary spike in conductivity, but this is followed by a gradual dilution and mixing with the substrate and any residual solution from previous floodings. Over time, as the effluent interacts with the substrate and undergoes dilution, the conductivity levels stabilize.

For apple boiling water, the stable EC despite pH changes suggests that ionic concentration is relatively constant over time.

For the digestate, as the flooding progresses, the dilution effect and the potential consumption or transformation of ionic compounds by microbial activity or chemical processes lead to a lower EC. This is consistent with the observed pH behaviour, where the initial drop in pH could be associated with the release of acidic components, which might also affect the ion concentration. Over time, as alkaline byproducts accumulate and microbial activity changes, the pH increases, and the overall ionic strength of the digestate decreases, resulting in a lower EC. This correlation suggests that both pH and EC are influenced by the dynamic chemical and biological processes occurring within the digestate during the flooding cycles.

Figure 51 shows the trend of oxidation-reduction potential (ORP). For the apple boiling water, ORP increases with each flooding event. In contrast, for the digestate, ORP rises during the second flooding but decreases during the third flooding.

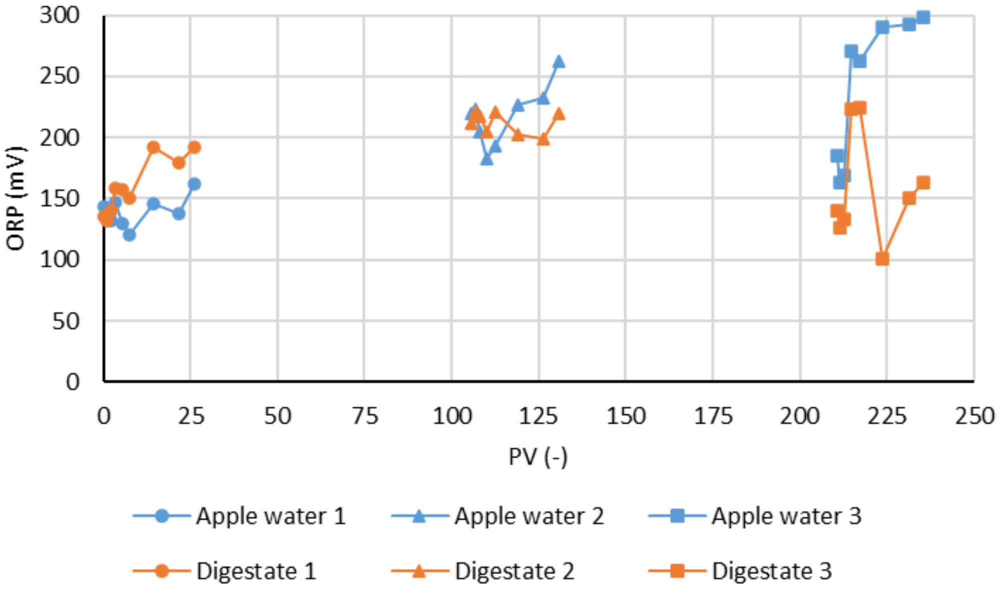


*Figure 51. ORP trend monitored in the three floodings*

The increase in ORP for the apple boiling water suggests a progressively more oxidizing environment, likely due to the continuous introduction of fresh effluent and the possible oxidation of organic compounds. This indicates that the apple boiling water is becoming more capable of accepting electrons over time. This increase is consistent with the pH behaviour, as the environment becomes more acidic, which often correlates with higher ORP values due to increased oxidation potential. Furthermore, increasing ORP with stable EC aligns with a more oxidizing environment without significant changes in ionic content.

For the digestate, the initial rise in ORP during the second flooding could be related to the temporary increase in oxidative conditions or the oxidation of certain compounds. The subsequent decrease in ORP during the third flooding may indicate a shift towards more reducing conditions, possibly due to changes in microbial activity or the accumulation of reduced compounds as the flooding progresses.

Figure 52 illustrates the degradation of TOC for each flooding event. The first and last apple water flooding are quite similar in terms of TOC degradation. Both show a slight increase beyond the initial level, after which the first flooding remains almost constant, while the third drops slightly below the initial value. In contrast, the second flooding starts with a much higher TOC level, which decreases after the second hour, ending slightly below the initial value after 24 hours. Therefore, the third flooding shows a slightly greater TOC degradation compared to the other two.

As for the digestate, TOC degradation increases significantly after the 13th hour during the third flooding. However, by the end of the 24-hour period, the most significant degradation occurs during the second flooding.

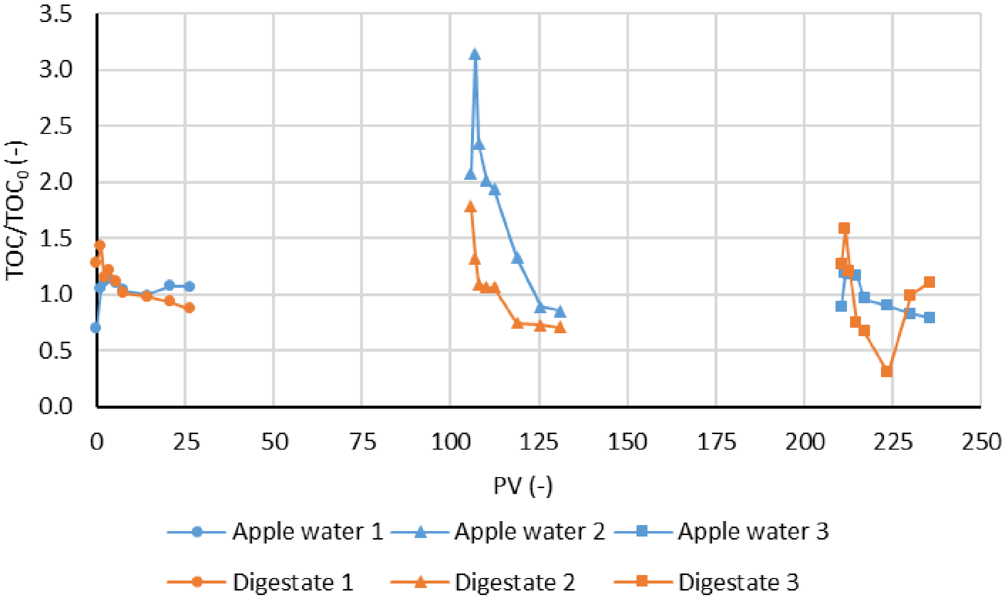


*Figure 52. Degradation of TOC from the three floodings*

In the case of the first and third apple boiling water floodings, TOC levels initially exhibit a slight increase. This might be attributed to the initial release of organic compounds from the hazelnut shells or other trapped organic matter in the substrate. After this brief rise, TOC levels in the first flooding stabilize, suggesting that the microbial degradation rate is in equilibrium with the TOC release. However, in the third flooding, the TOC levels decrease slightly below the initial value, indicating a greater degree of degradation (21.10%). This could be due to the cumulative adaptation of microbial communities over the previous cycles, making them more efficient at processing the organic carbon present in the apple water.

In contrast, the second flooding shows a much higher initial TOC concentration, which then declines after the second hour and stabilizes just below the initial level after 24 hours. This could be explained by a buildup of organic carbon from the first flooding that was not fully degraded during the drainage period, leading to a higher starting TOC concentration. As the microorganisms become more active, they degrade the TOC over time, resulting in a significant reduction.

The overall trend suggests that microbial communities may become progressively more efficient at degrading TOC across successive floodings, but this effect varies depending on the initial organic load and other environmental factors like oxygen availability.

Digestate, being a more nutrient-rich and complex effluent compared to apple water, shows a different TOC degradation pattern. The TOC degradation becomes more pronounced after the 13th hour in the third flooding (69.94%), due to delayed microbial activity from freezing and thawing the two effluents. However, by the end of the 24-hour cycle, the second flooding still shows the highest overall TOC degradation (29.38%). This might be because the microbial communities were better adapted to the nutrient-rich conditions during the second flooding, leading to faster and more complete breakdown of the digestate's organic content.

In summary, the substrate composition, the intervals between flooding, and the nature of the effluents (apple boiling water vs. digestate) all influence the TOC degradation patterns observed in these tests.

In relation to the degradation of TN, as shown in Figure 53, the trends for apple boiling water are quite consistent across all three flooding events, while the digestate shows some alterations.

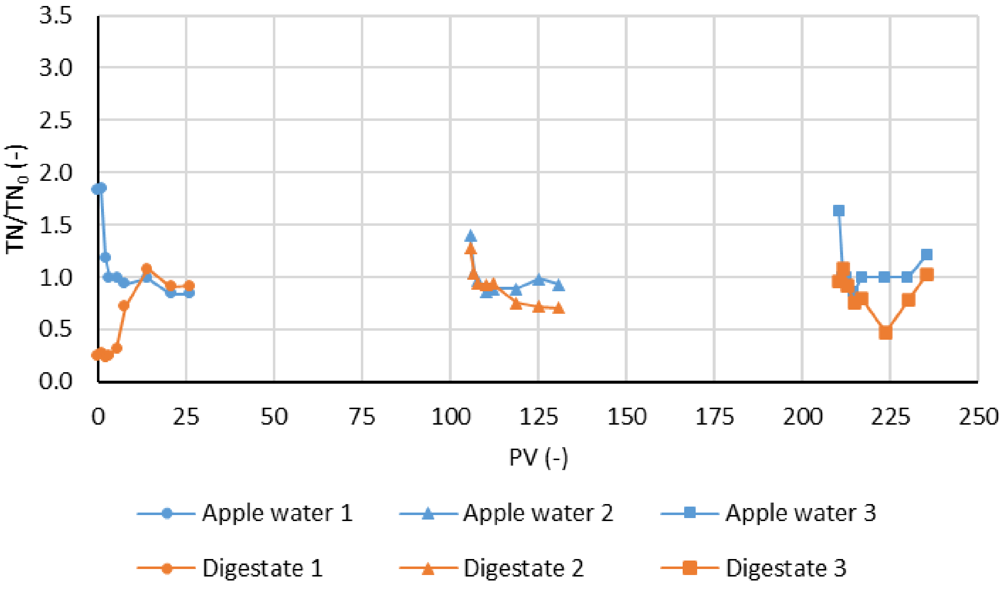


*Figure 53. Degradation of TN from the three floodings*

For the apple boiling water, in each flooding the TN content begins at levels higher than the initial concentration ($C_0$), indicating that nitrogen compounds are released into the solution at the start of each flooding. This could be due to the leaching of nitrogen-containing compounds from the substrate, particularly from the hazelnut shells, which might release organic nitrogen as they degrade.

As the flooding progresses, the TN content gradually decreases, ultimately reaching levels just below the initial concentration for the first two floodings, whit the first flooding having a better TN degradation of 15.86%. This suggests that nitrogen is being removed from the system, likely through microbial processes such as nitrification or denitrification. These microbial processes are influenced by the oxygen availability in the substrate, which can fluctuate due to the flow and drainage conditions.

The third flooding shows a slightly different behaviour, as the TN content ends just above the initial concentration. This deviation could indicate that after repeated flooding cycles, the microbial communities and the substrate have reached a state where nitrogen release exceeds its removal. A possible explanation is that the microbial communities may have exhausted their ability to remove nitrogen as efficiently as in the first two floodings, leading to an accumulation of TN. Another option is that after successive floodings, the hazelnut shells may start to break down more significantly, releasing additional nitrogen into the solution.

The decrease in pH across the floodings could have several impacts on the content of TN of the apple boiling water:

- Nitrifying bacteria become less effective, resulting in slower TN degradation.
- More nitrogen remains in the ammonium form, which is less likely to be removed from the water, particularly during the third flooding.
- Acidic conditions can enhance the breakdown of organic matter, including nitrogen-containing compounds from the hazelnut shells, releasing more nitrogen into the water.

This could explain why the third flooding ends with TN levels slightly above the initial concentration, as the combination of lower pH and repeated flooding may lead to a buildup of nitrogen that is not efficiently removed.

The digestate, in the initial hours of flooding, significantly contributes to the TN concentration, resulting in levels that rise to the unit value by the thirteenth hour. After this peak, TN levels begin to decrease slightly, indicating that microbial processes are actively degrading the nitrogen compounds present in the digestate.

The second flooding starts with TN levels slightly above the unit, reflecting residual nitrogen from the previous cycle and potentially more nitrogen being released from the digestate. Over time, the TN concentration decreases significantly, reaching optimal degradation levels by the end of the 24 hours (29.31%).

The third flooding shows the best TN degradation around the thirteenth hour (52.40%) but ends slightly above the unit after 24 hours. This could suggest that, while the microbial activity peaks earlier in this cycle, it eventually plateaus, leading to a slight accumulation of TN by the end of the period. The microbial communities may reach a saturation point where they can no longer process nitrogen as efficiently, resulting in the remaining TN in the solution. This higher TN concentration is consistent with the more alkaline pH observed towards the end of each flooding event. This supports the hypothesis that as flooding progresses and oxygen levels decrease, anaerobic processes become more dominant, leading to the production of alkaline byproducts, such as ammonia, which explains the increase in pH towards the end of each flooding cycle.

As with the other column tests, water content and solid TC profiles were obtained from the extrusion of the columns, which are shown in Figure 54 and Figure 55, respectively.

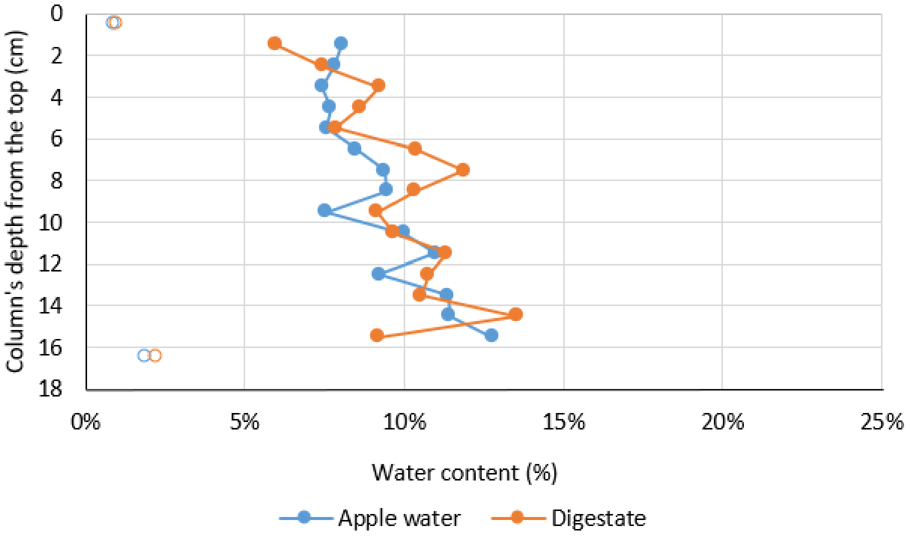


*Figure 54. Water content profile of the two columns of hazelnut shells after the floodings*

The water content is lower compared to the previous two tests, due to the 3-day drainage period the columns underwent before extrusion. Despite this, the profile remains consistent with expected results, showing higher water content at the bottom of the columns.

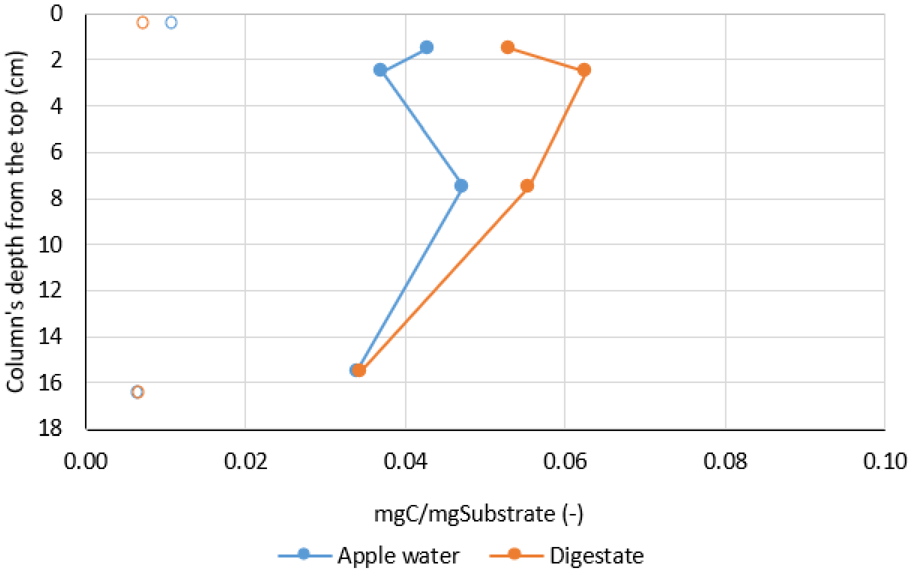


*Figure 55. Solid TC profile of the two columns of hazelnut shells after the floodings*

The solid TC content also aligns with the expected results, showing a higher concentration at the top of the column. Also, the TC content is slightly lower compared to the hazelnut shells columns from the previous test, due to the 3-day drainage period, which reduced the amount of carbon retained in the substrate.

The intermittent column leaching test demonstrates the important role of drainage of a SAT system, substrate composition, and microbial adaptation in the degradation of organic matter and nitrogen. While the microbial communities become more efficient over time, the overall degradation capacity may be limited by repeated cycles, suggesting that alternating flooding and drainage periods help optimize nutrient removal in such systems.

### 3.5.3. Column leaching test at average pH

Testing at a pH between that of apple boiling water and digestate offers the opportunity to identify an optimal balance for organic carbon and nitrogen degradation. It could help optimize microbial activity, simulate real-world conditions, and provide insights into how the substrate interacts with effluents of different pH levels, ultimately improving the design and efficiency of treatment systems.

Choosing a pH of 5.5 for the column test balances between the acidic nature of apple boiling water and the digestate. This test might help in understanding the release patterns of organic carbon and nitrogen from the hazelnut shells and D8 sand mixture.

As agreed, the incoming pH, shown at the top of Figure 56, remained constant throughout the test at 5.7 for the apple boiling water and 5.6 for the digestate.

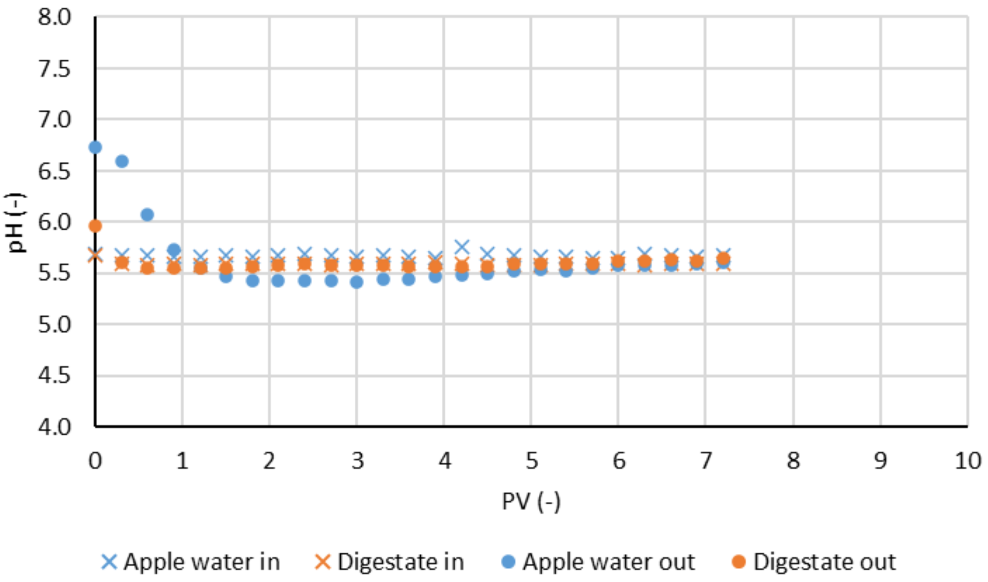


*Figure 56. pH trend of the effluents diluted with a buffer entering (top) and exiting (bottom) the columns*

The outflow pH reaches the initial value after one hour for the apple boiling water and after 15 minutes for the digestate. For this test, it was not possible to determine the pore volume due to time constraints.

However, an average pore volume was estimated by taking the mean of the continuous test with hazelnut shells (40 minutes) and the intermittent test (55 minutes), resulting in an average approximated to 50 minutes. It is possible that the digestate exited before compared to the apple boiling water because the second column (used for the digestate) was flushed with deionized water for a longer time before the test. Consequently, the first column still contained residual elements from the hazelnut shells, which had already been flushed out of the second column. Additionally, the chemical interactions between the apple boiling water and the substrate residues may have differed from those with the digestate.

Another important result obtained from this test is that when the pH is kept constant at 5.5, the buffering capacity of the hazelnut shells seams insufficient to alter the outflow pH of the apple boiling water. This suggests that the external buffering system is strong enough to prevent any fluctuations in pH. The shells' alkalizing potential is unable to overcome the force of the system maintaining the pH. While the shells would naturally influence pH balance at the outlet (Figure 37), this effect is "blocked" when the pH is held at a fixed value at the inlet.

Figure 57 shows the trend of EC at the inlet and outlet of the columns for both effluents with the buffer. In this test, the EC at the inlet significantly increased with the use of the buffer, rising from a maximum of 250 µS/cm in the previous test (Figure 38) to a maximum of 650 µS/cm in this test. This substantial increase in EC can be attributed to the introduction of the buffer solution, which has a higher ionic concentration compared to the previous conditions. After completing the injection phase of 3 hours, the effluents were set aside, and this cessation of flow could have led to the sedimentation of some ions in the $C_0$.

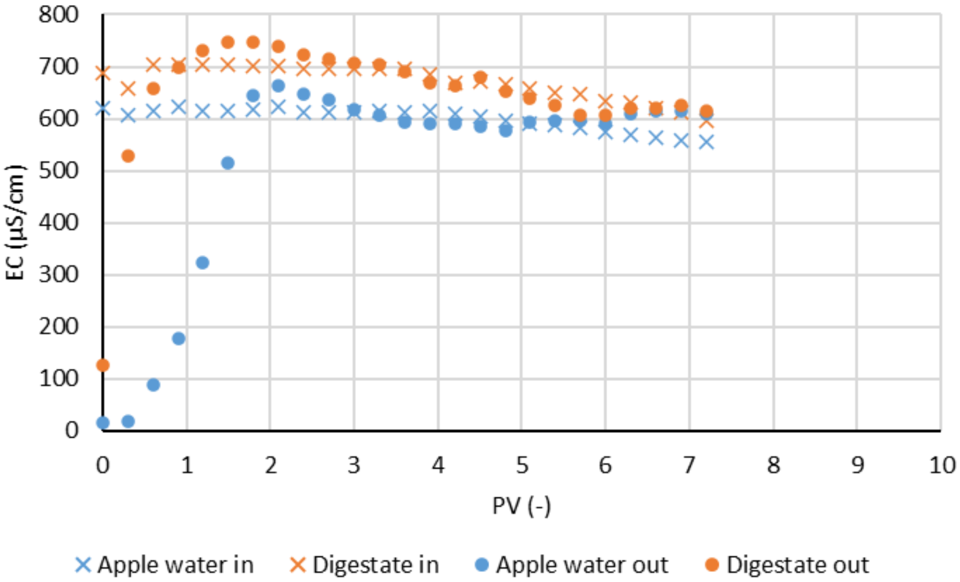


*Figure 57. EC trend of the effluents diluted with a buffer entering (top) and exiting (bottom) the columns*

The EC at the outlet reaches and exceeds the inlet EC for both effluents within the first 2 hours, before decreasing to a constant value after approximately 2 theoretical PV. Maintaining a constant pH results in a nearly stable EC profile, free from sudden fluctuations, unlike the variations observed in the other tests. Even though the pH is maintained at a constant level, the EC of the inlet effluents tends to decrease slightly over time. This happens because as ions from the buffer or effluent interact with the substrate, some ions may be adsorbed or exchanged, leading to a gradual decrease in the overall ionic concentration of the solution.

Figure 58 shows the degradation of TOC. Compared to the first column test with hazelnut shells, the apple boiling water exiting the column has a slightly lower TOC content, although the degradation is still above unity. While for the digestate, the TOC degradation seems to be slightly worse than the continuous column leaching test (Figure 39).

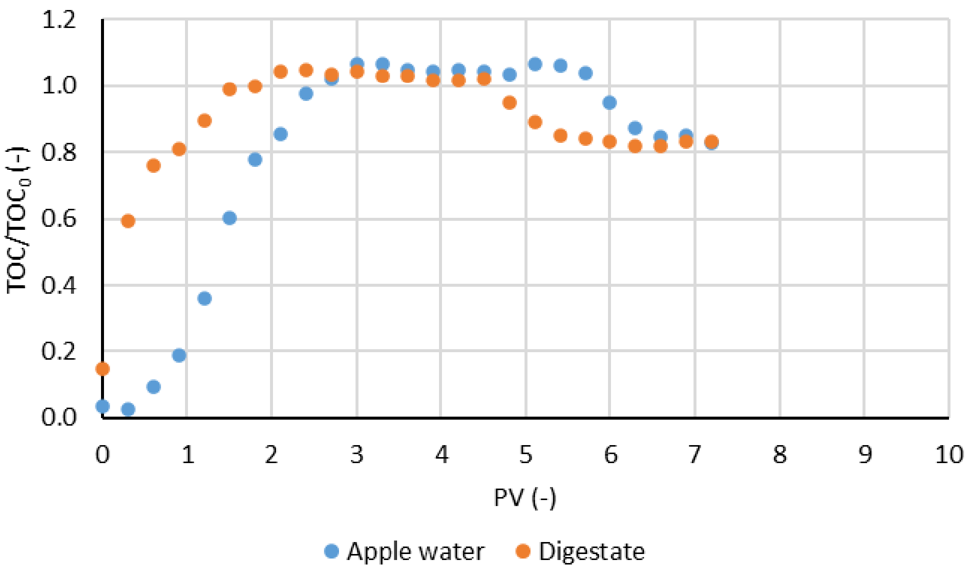


*Figure 58. Degradation of TOC of the apple boiling water and the digestate diluted with a buffer*

The TOC content was higher in this test, likely due to the presence of the buffer. In the first column test, the preparation and dilution of digestate without a buffer may have caused the loss of some organic compounds that are unstable under variable pH conditions. The use of a buffer may have better preserved these compounds, leading to a higher TOC content.

Maintaining a more constant pH might lead to improved stability in the degradation process of TOC:

- A stable pH can facilitate more consistent conditions for the microbial and chemical processes involved in TOC degradation.

- A more stable pH can optimize the efficiency of complex chemical reactions, possibly leading to a more complete breakdown of organic materials and a reduction in TOC.
- Maintaining a stable pH ensures that microbial communities remain active and effective in degrading organic carbon. Consistent microbial activity can lead to more effective degradation of TOC, as evidenced by the lower TOC content in the output.
- Fluctuating pH levels can create inhibitory conditions for both chemical and biological processes. By maintaining a stable pH, encountering such inhibitory conditions is reduced, promoting more efficient TOC degradation.
- A stable pH allows for more predictable and controlled degradation processes. This predictability helps in optimizing the performance of the column and achieving desired degradation outcomes. The observed lower TOC content despite degradation being above unity indicates that the process is being controlled more effectively under stable pH conditions.

Another particular aspect of the two outlets is that during the last 3 hours of injection, when deionized water and buffer were introduced into the columns, the TOC ratio did not return to zero, as observed in other column tests. A possible explanation is that the hazelnut shells may have released organic compounds under specific chemical conditions, such as a constant pH of 5.5. These compounds could have contributed to the measured TOC even in the absence of an external supply of organic matter.

Focusing on the hazelnut shells, they appear to influence TOC degradation differently depending on the type of effluent. For apple water, a pH of 5.5 may be more favourable for degradation, while for digestate, which may contain more complex or different compounds, a pH of 5.5 might not be as optimal. The behaviour of the hazelnut shells in relation to a pH of 5.5 suggests that the substrate plays an active role in modulating TOC degradation.

From these results, it can be understood that while TOC degradation in apple boiling water is more efficient at a more alkaline pH, a more acid pH would be preferable for digestate. This conclusion can be drawn by comparing the pH (Figure 37) and TOC degradation (Figure 39) from the first column test with the pH (Figure 56) and TOC degradation (Figure 58) from this test at an average pH.

The degradation of TN is shown in Figure 59. Once again, apple water had a very low content, equal to 0.6052 mg/L both in inflow and outflow, and thus was not significantly affected by the hazelnut shells and not displayed in the graph. Conversely, the assertion that a more acidic pH benefits TOC degradation in digestate can also be applied to TN degradation. This is evident when comparing the first column test (Figure 40) with Figure 59, where the $TN/TN_0$ ratio for digestate is significantly higher in the latter.

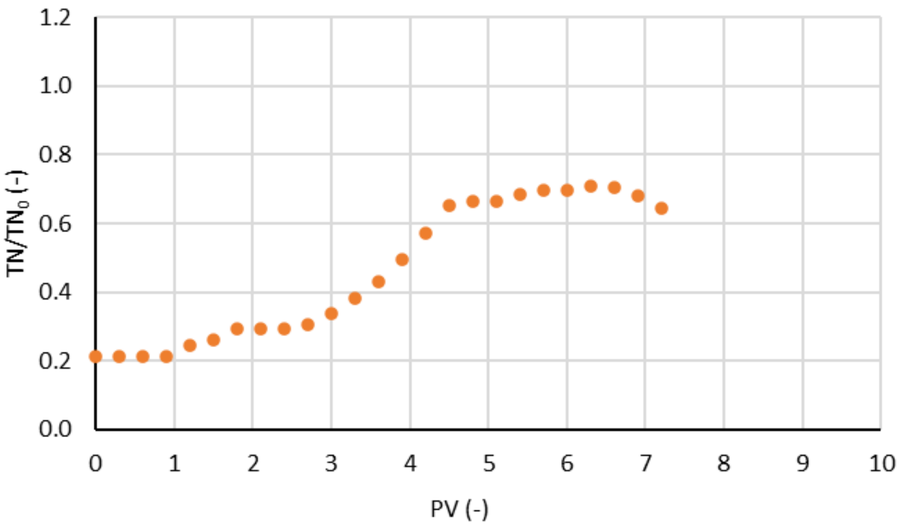


*Figure 59. Degradation of TN of the digestate diluted with a buffer*

An interesting aspect is that the maximum TN concentration is reached during the 3 hours of deionized water and buffer injection, rather than during the injection of the two diluted effluents, which were also buffered. This indicates that the hazelnut shells are more effective at retaining or interacting with nitrogen compounds under certain conditions. The presence of the buffer, combined with the deionized water, could be creating an environment that favours the release or stabilization of nitrogen compounds, leading to a higher TN concentration.

As with the other column tests, at the end of this experiment, profiles of water content (Figure 60) and solid TC (Figure 61) for the two columns were also assessed.

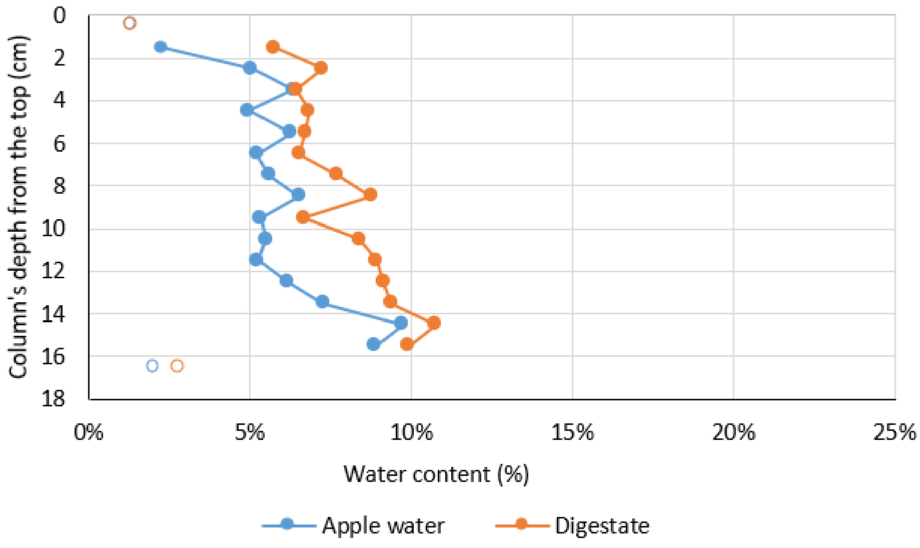


*Figure 60. Water content profile of the two columns of hazelnut shells flooded with buffer*

The water content aligns with the expected results, showing a higher water content at the bottom of the columns. However, the solid TC appears to increase slightly towards the bottom of the columns. Despite this, the values of solid TC remain quite low and thus are not significant.

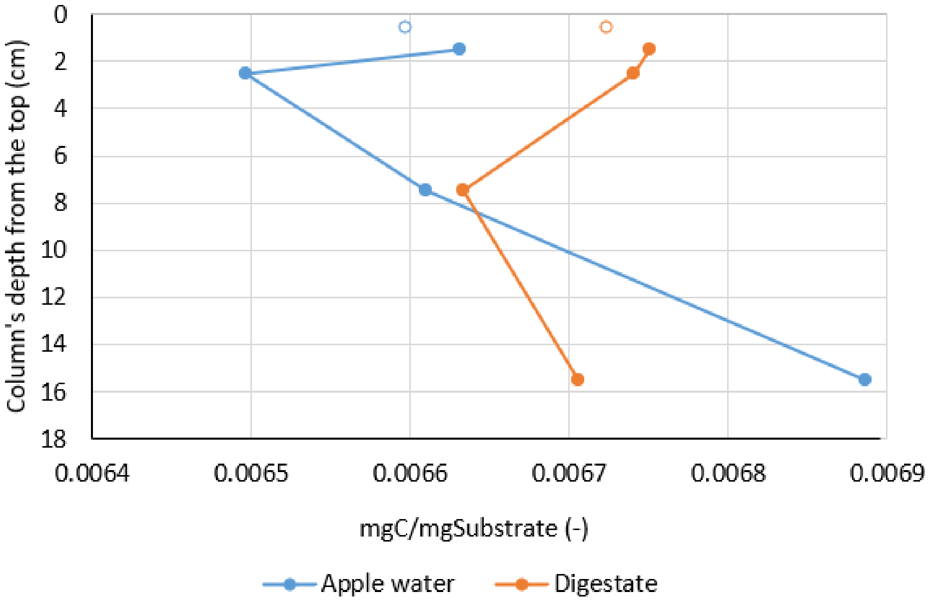


*Figure 61. Solid TC profile of the two columns of hazelnut shells flooded with buffer*

From this last column test, the results obtained are the following:

- For apple boiling water, a more alkaline pH enhances TOC degradation, while for digestate, a more acidic pH is better for increased degradation of both TOC and TN.
- For digestate, the higher $TN/TN_0$ ratio observed during the injection of deionized water and buffer, compared to the first column test, suggests that these conditions enhance the release or stabilization of TN. Meanwhile, the TN in the digestate may be consumed or retained in the substrate during its injection, due to the buffer's effect on modifying the column conditions.
- Hazelnut shells impact the degradation of TOC and TN differently depending on the type of effluent. A pH of 5.5 is beneficial for apple water but may not be optimal for digestate. This indicates that hazelnut shells play an active role in modulating the degradation of carbon and nitrogen, and that chemical conditions, such as pH, are crucial for optimizing these processes.
- Experimental conditions, including pH and the type of effluent, significantly affect degradation efficiency, suggesting that adjusting these factors is essential for optimizing treatment outcomes.

# 4. Conclusion

After completing all the tests, several conclusions have been drawn, as detailed below:

- The first batch test demonstrated an inverse relationship between pH and EC. As pH decreased, EC values increased, indicating that a lower pH is associated with a higher concentration of ions in the solution. This suggests that as the solution becomes more acidic, the ionic strength increases, leading to higher EC measurements.
- Corn cobs were found to be suboptimal for degradation processes in the first batch test, while the mixed substrate, which included corn cobs, showed good results primarily due to the presence of hazelnut shells. The hazelnut shells substrate consistently outperformed others in terms of TOC and TN degradation.
- The freezing and thawing process significantly affected the timing of degradation. In the second batch test, the optimal degradation period shifted from the fifth day to the tenth day, indicating that temperature fluctuations impact substrate performance.
- While D8 sand demonstrated good results in TOC degradation in the second batch and column tests, it was less effective compared to hazelnut shells. D8 sand showed a lower capacity to adsorb or react with organic substances, resulting in less effective degradation.
- The D8 sand substrate exhibited mild buffering capacity, influencing the acidity of the effluent. In contrast, hazelnut shells had a more pronounced effect on the pH of the apple boiling water.
- In the second column test, the TN degradation showed that microbial activity peaked earlier in the third flooding cycle, but eventually plateaued, leading to a slight accumulation of TN. This was consistent with higher pH levels at the end of each flooding event, showing how important it is to study correlations with pH.

Therefore, a substrate composed of 10% by weight hazelnut shells proves to be an optimal choice for enhancing a SAT (Soil Aquifer Treatment) system designed to filter agro-industrial wastewater with high DOM. This substrate significantly improves degradation and filtration performance. However, these results provide a solid foundation for further exploration.

Future research should focus on exploring and evaluating a range of substrate combinations to identify the most effective mixtures for optimizing SAT systems. This includes experimenting with various materials and ratios to enhance the filtration and degradation of different types of agro-industrial wastewater. Additionally, refining test conditions, such as flow rates, temperature, and pH levels, will better simulate real-world scenarios and improve treatment performance. Extending contact times between wastewater and substrates may also provide further insights into how prolonged interactions affect degradation efficiency. By systematically investigating these factors, researchers can develop more robust and adaptable SAT systems tailored to diverse wastewater profiles and treatment requirements.

# List of Figures

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