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## Application of a Hybrid Adsorption–Biodegradation System for Treating Algerian Landfill Leachate

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## **List of Abbreviations**

**AC:** Activated Carbon

**AOP:** Advanced Oxidation Processes

**ASP:** Activated Sludge Process

**BET:** Brunauer–Emmett–Teller

**BOD:** Biochemical Oxygen Demand

**CNI:** Color Number Index

**COD:** Chemical Oxygen Demand

**FTIR:** Fourier Transform Infrared Spectroscopy

**GIS:** Geographic Information Systems

**MCDA:** Multi-Criteria Decision Analysis

**MBR:** Membrane Bioreactor

**MSW:** Municipal Solid Waste

**OD:** Optical Density

**OM:** Organic Matter

**ORP:** Oxidation-Reduction Potential

**pH<sub>pzc</sub>:** pH at the Point of Zero Charge

**SBR:** Sequencing Batch Reactor

**TOC:** Total Organic Carbon

**TVA:** Total Volatile Acids

**VFA:** Volatile Fatty Acids

**XOC:** Xenobiotic Organic Compounds

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# Introduction

The global increase in population and industrial activity has led to a sharp rise in municipal solid waste (MSW) generation, expected to reach 3.4 billion tons annually by 2050 (Kaza et al., 2018). To manage this waste, landfilling remains the most common method of disposal due to its low cost and ease of implementation (Vaverková, 2019; Laner et al., 2012). However, this practice produces landfill leachate, a highly contaminated liquid formed as water infiltrates waste and dissolves organic, inorganic, and microbial compounds (Renou et al., 2008). If not properly treated, leachate poses significant risks to soil, groundwater, and public health (Kulikowska & Klimiuk, 2008; Amara et al., 2021). Its complex composition, variable over time, and high pollutant load make it particularly difficult to treat using conventional approaches.

In Algeria, landfilling continues to dominate solid waste management, with more than 90% of municipal waste directed to controlled or uncontrolled sites (GIZ & SWEEP-Net, 2014). The landfill of Batna, located in Chaâba, receives waste from several surrounding municipalities but faces notable operational challenges, including incomplete infrastructure and limited leachate collection and treatment (Haddad & Aouachria, 2020; Sefouhi et al., 2010a). As a result, large volumes of untreated leachate are either reinjected or allowed to infiltrate the environment. These limitations highlight the urgent need for low-cost, efficient, and sustainable treatment strategies that can address the complex nature of leachate under local constraints.

A variety of technologies have been developed for the treatment of landfill leachate, including biological, chemical, and physical processes (Vaverková, 2019). Adsorption using activated carbon remains a commonly applied method due to its operational simplicity and capacity to remove a broad range of contaminants. However, as a non-destructive process, it merely transfers pollutants to a solid phase and can generate secondary pollution upon adsorbent saturation.

Conversely, biological treatment degrades contaminants through microbial action and offers a sustainable and cost-effective solution. Yet, its efficiency is often compromised by leachate toxicity and fluctuating composition (Kulikowska & Klimiuk, 2008). The inherent limitations of each technique, when applied separately, justify the development of hybrid systems. In this context, the integration of adsorption and biological degradation offers a synergistic solution. In the present study, activated carbon was synthesized from green agricultural waste, providing a renewable, low-cost adsorbent. Indigenous bacterial strains isolated from the leachate were co-immobilized with the carbon within alginate beads. This system was engineered to promote efficient treatment by combining the immediate pollutant uptake

capacity of activated carbon with the longer-term biodegradation potential of the microbial community.

The aim of this study was to evaluate a hybrid treatment system for landfill leachate collected from the landfill of Batna, combining adsorption and biological processes. The specific objectives were to:

- Produce activated carbon from green agricultural residues and characterize its physicochemical properties.
- Assess the pollutant removal performance of the physicochemical (adsorption), biological, and hybrid systems.
- Compare the effectiveness of all systems in reducing the leachate's pollutant load and improving its quality.

This thesis is structured into five parts:

- Part 1 presents the general context, outlines the research problem, and defines the study objectives.
- Part 2 is a bibliographic review covering six key topics: the concept and management of landfills, the formation and characteristics of leachate, adsorption as a treatment process, the preparation and properties of activated carbon, biological treatment methods, and the principles and potential of hybrid systems combining both approaches.
- Part 3 describes the materials and methods used for the preparation and characterization of activated carbon, as well as for the implementation of physicochemical, biological, and hybrid treatment systems.
- Part 4 presents and discusses the experimental results obtained.
- Part 5 offers a general conclusion and proposes directions for future research.

# Literature Review

# 1. Landfills

## 1.1 Overview

The continual growth of the world population, industrial production, and global trade over the past few decades has been accompanied by a noticeable increase in municipal and industrial waste. In 2002, a population of 6.2 billion individuals (U.S. Census Bureau, 2021a) generated approximately 0.68 billion tonnes of municipal solid waste (MSW) (Hoornweg & Bhada-Tata, 2012). Less than two decades later, in 2018, 2.01 billion tonnes of waste were generated (Kaza et al., 2018) by 7.6 billion people (U.S. Census Bureau, 2021b). Projections estimate that by 2050, annual global waste generation will reach 3.4 billion tonnes (Kaza et al., 2018). Fig. 1 shows regional projections of waste generation per year, measured in millions of tonnes.

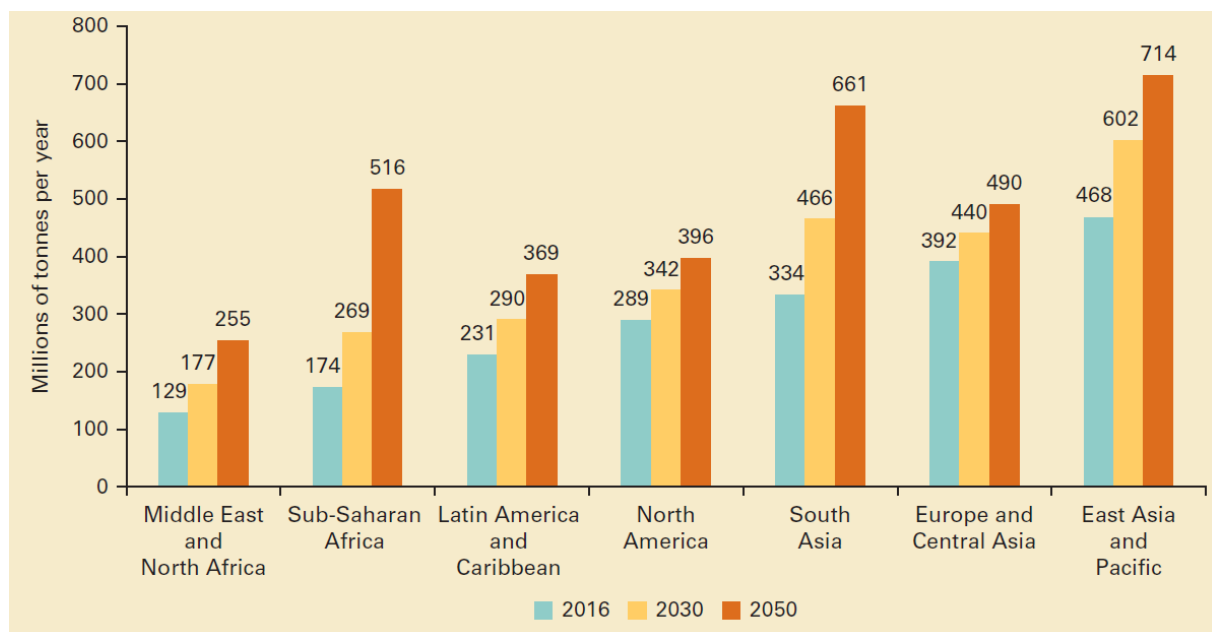


Fig. 1. Projected waste generation, by region (millions of tonnes/year) (World Bank, 2018)

The management of this waste is paramount, with major implications for public health, ecological preservation, sustainable development, and the circular economy (Vaverková, 2019). Various methods have been and continue to be used by countries to address this challenge, including incineration, open dumping, composting, and landfilling (World Bank, 2018) (Fig. 2). Among these, landfilling is the most widely adopted, primarily due to its relatively low cost and minimal technical requirements (Vaverková, 2019).

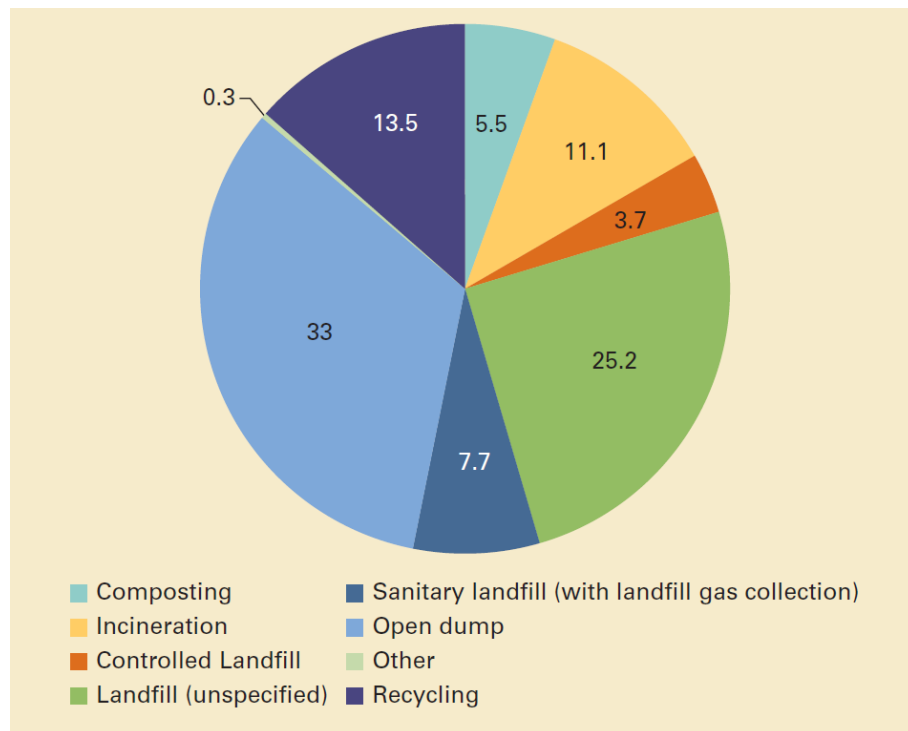


Fig. 2. Global treatment and disposal of waste (percent) (World Bank, 2018).

At the national level, Algeria produced 11.1 million tonnes of MSW in 2021 (National Waste Agency, 2022). The composition of this waste varies, with organic matter accounting for more than half, while the remainder consists of materials such as glass, plastic, textiles, and others (GIZ & SWEEP-Net, 2014) (Fig. 3).

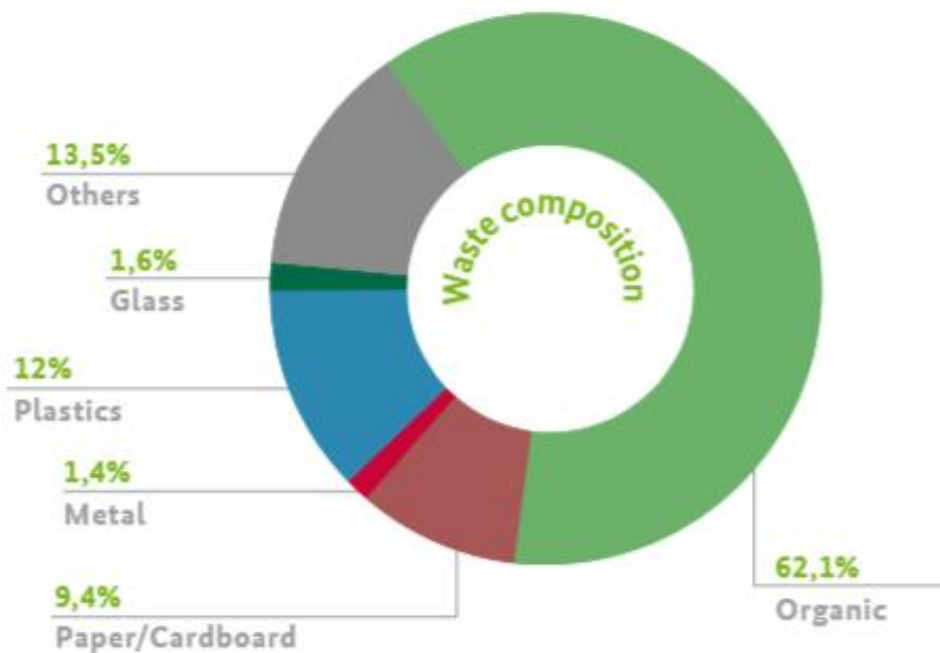


Fig. 3. Municipal solid waste composition in Algeria (2012) (GIZ & SWEEP-Net, 2014).



Despite efforts to promote recycling and move toward a more circular waste management system, progress remains limited. As of 2012, landfilling was still the dominant method of disposal, with 30–35% of waste directed to controlled or technical landfills and 60–65% to open dumps, which are often considered a form of uncontrolled landfilling. In contrast, composting and recycling accounted for only 1% and 7% respectively, while incineration and other methods represented 5–10% (GIZ & SWEEP-Net, 2014) (Table 1). These figures highlight the central role landfilling continues to play in Algeria’s waste management system, underscoring the need for a deeper examination of its definition, types, and environmental impacts.

Table 1. Waste Processing Methods in Algeria and Their Percentages (2012) (GIZ & SWEEP-Net, 2014).

<b>Waste processing method</b>	<b>Percentage</b>
<b>Composting</b>	1%
<b>Recycling</b>	7%
<b>Landfills (technical and controlled)</b>	30-35%
<b>Open dumps</b>	60-65%
<b>Other (incineration, ...)</b>	5-10%

## 1.2 Definition

A landfill is an area of land where waste is buried under layers of earth (Oxford University Press, n.d.). According to the American Society of Civil Engineers (1959), landfilling is a controlled process carried out at designated sites, where MSW is deposited in clearly defined layers, with each layer compacted and covered with soil before the next is placed. Landfilling is considered easier and cheaper than most other waste treatment methods and remains the only method suitable for treating all types of waste (Vaverková, 2019). Although its use has declined in recent years, particularly in developed countries (Vaverková, 2019), landfilling continues to be the most widely adopted method in many parts of the world (Laner et al., 2012).

## 1.3 Types of landfills

Landfills are generally classified into three types based on the nature of the waste they receive and the permeability coefficient (K) of the underlying soil (Table 2). This coefficient determines how easily pollutants can percolate through the substrate (Bentetifa, 2012), and is closely related to the type of waste being disposed of. The three commonly recognized types of landfills are:

- **Hazardous waste landfills (class 1):** intended for dangerous and toxic waste, such as treated and stabilized special industrial waste, and fly ash from incineration plants.
- **Non-hazardous waste landfills (class 2):** for municipal and similar waste, including household garbage, bulky items, green waste, and ordinary non-hazardous industrial waste.
- **Inert waste landfills (class 3):** used for inert materials such as excavation waste, rubble, and debris from construction companies, public works, or household DIY activities (Bougueraa, 2021).

Table 2. Landfill Types, Accepted Waste, Soil Permeability, and Site Characteristics (European Council, 1999).

<b>Landfill Type</b>	<b>Accepted Waste</b>	<b>Soil Permeability (K)</b>	<b>Thickness</b>	<b>Site Characterization</b>
<b>Hazardous</b>	Special/hazardous waste	$K \leq 1.0 \times 10^{-9}$ m/s	5 meters	<ul style="list-style-type: none"> <li>- Fully impermeable site</li> <li>- Sealed base layer</li> <li>- Cells direct flow to low point</li> <li>- Perimeter blocks surface water</li> <li>- Sloped cover for runoff</li> </ul>
<b>Non-Hazardous</b>	Household and similar waste	$K \leq 1.0 \times 10^{-9}$ m/s	1 meter	<ul style="list-style-type: none"> <li>- Semi-impermeable site</li> <li>- Partial leachate treatment</li> <li>- Controlled moderate infiltration</li> <li>- Groundwater pollution protection</li> </ul>
<b>Inert</b>	Inert materials	$K \leq 1.0 \times 10^{-7}$ m/s	1 meter	<ul style="list-style-type: none"> <li>- Permeable site</li> <li>- Rapid leachate migration risks groundwater pollution</li> </ul>

## 1.4 Landfill Site Selection and Design

Effective landfill site selection and design are crucial for minimizing environmental impacts and ensuring safe long-term waste disposal. Key considerations include environmental protection, public health, and operational efficiency (Molleta et al., 2009).

### 1.4.1 Site Selection Criteria

The selection of a landfill site involves several factors:

- **Distance from Populated Areas:** Sites should be located at least 200 meters away from residential areas and public spaces to reduce health risks (Molleta et al., 2009).
- **Hydrogeological Suitability:** Sites must have favorable geological conditions, such as low permeability soils and deep groundwater tables, to prevent leachate contamination (Elkhrachy et al., 2023).
- **Avoidance of Risk Zones:** Locations prone to floods, landslides, or subsidence should be avoided (Rogaume, 2006).
- **Environmental and Cultural Protection:** Landfills must not interfere with ecologically sensitive or culturally significant areas (Rogaume, 2006).

Advanced tools such as Geographic Information Systems (GIS) and Multi-Criteria Decision Analysis (MCDA) are commonly used to integrate site selection criteria systematically, as demonstrated by Elkhrachy et al. (2023), who applied GIS-based MCDA to identify suitable landfill sites in Najran City, Saudi Arabia, evaluating factors like land use, water proximity, and soil type.

### 1.4.2 Landfill Design Elements

Modern sanitary landfills include several engineered features to enhance safety and performance (Elkhrachy et al., 2023). Fig. 4 illustrates the main structural components of a typical engineered landfill, including the liner system, leachate collection network and gas capture wells.

- **Liner Systems:** Composite liners made of clay and synthetic materials prevent leachate leakage (Elkhrachy et al., 2023).
- **Leachate Collection and Treatment:** Drainage pipes at the base collect contaminated water for treatment, protecting surrounding soils and groundwater (Addou, 2009).

- **Gas Capture Systems:** Methane-rich landfill gas is collected through wells and either flared or used for energy production (Addou, 2009).
- **Surface Cover:** Once full, landfills are sealed with protective layers and vegetation to reduce infiltration and emissions (Waste Today, 2021).

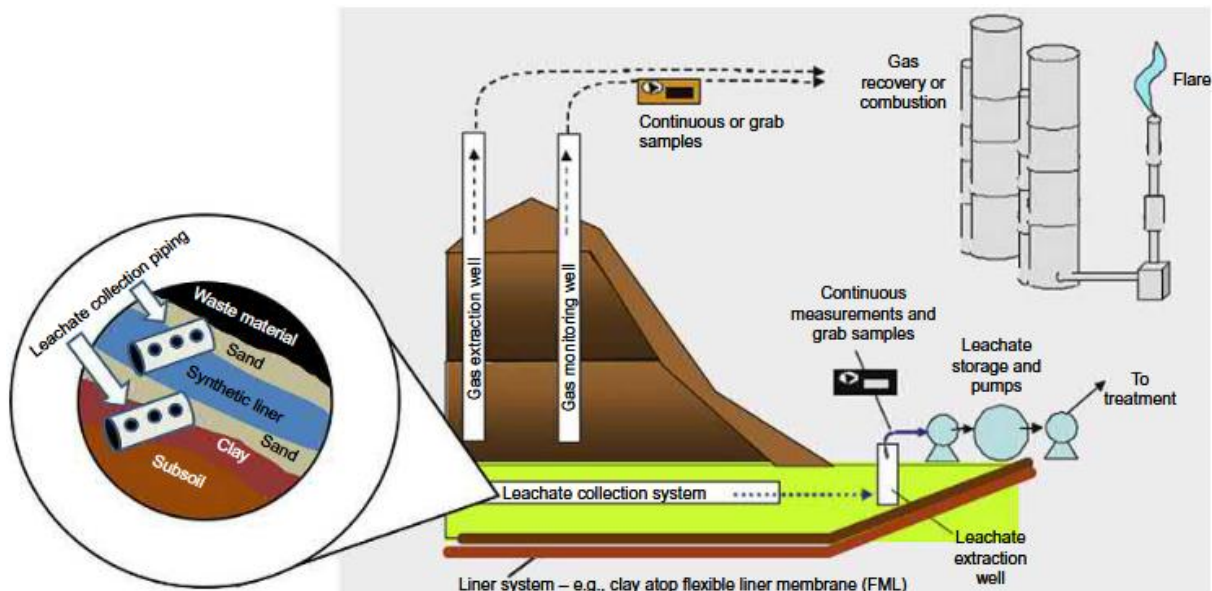


Fig. 4. Modern landfill design with liner, leachate collection, and gas capture systems (Letcher & Vallero, 2019).

A coordinated design is essential since each component—liner, leachate, and gas systems—directly impacts the others (Waste Today, 2021).

### 1.5 Landfill degradation process

According to Letcher and Vallero (2019), the stabilization of waste in landfills occurs in a series of overlapping microbial-driven phases. These phases reflect shifts in environmental conditions within the landfill and directly influence gas production, leachate composition, and overall waste decomposition rates. Fig. 5 illustrates these sequential phases, highlighting the associated chemical changes and environmental transitions.

- **Phase I: Initial Adjustment**

Immediately after waste placement, aerobic conditions dominate due to the presence of oxygen in void spaces. Aerobic microorganisms begin breaking down readily degradable organic matter, consuming oxygen and producing heat, carbon dioxide, and water. This phase is short-lived as oxygen is quickly depleted.

- **Phase II: Transition**

As oxygen becomes scarce, facultative and anaerobic bacteria begin to outcompete aerobic microbes. Alternative electron acceptors like nitrates and sulfates are used, leading to the formation of reduced compounds. This phase marks the shift from aerobic to anaerobic conditions.

- **Phase III: Acid Formation**

Hydrolysis and fermentation of complex organic matter result in the accumulation of volatile fatty acids (VFAs), lowering the pH of the leachate. This acidic environment mobilizes metals and increases chemical oxygen demand (COD) in the leachate. High biological activity by acidogenic bacteria defines this phase.

- **Phase IV: Methane Fermentation**

Methanogenic archaea metabolize VFAs into methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ). As acids are consumed, the pH begins to rise, and the leachate becomes less chemically aggressive. This is the longest phase, characterized by significant biogas production and ongoing waste mass reduction.

- **Phase V: Final Maturation**

With most biodegradable material exhausted, microbial activity slows. Methane production declines, and oxygen may gradually re-enter the system, increasing redox potential. Remaining organic matter is converted into stable, humic-like substances. Long-term stabilization occurs as the landfill becomes more inert.

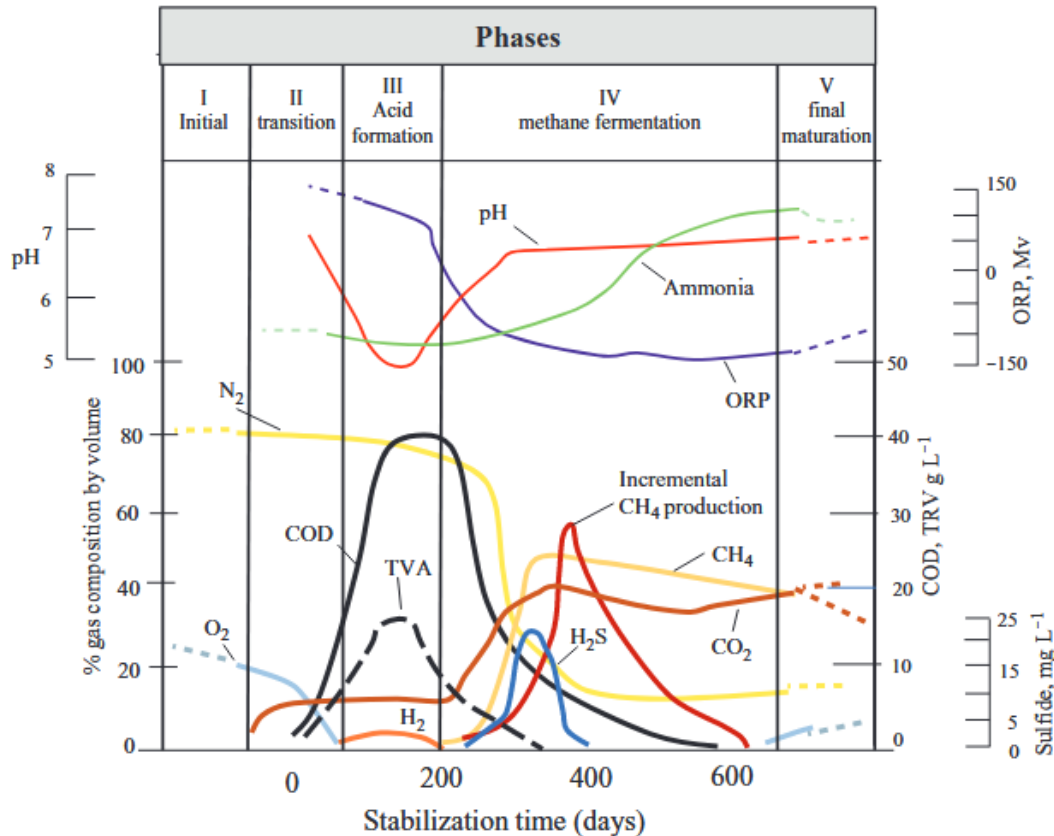


Fig. 5. Phases of landfill waste degradation, showing changes in compound release and environmental conditions (Letcher & Vallero, 2019).

## 1.6 Environmental impact

According to Chihaoui (2017), when landfills are mismanaged, they can lead to five major environmental impacts:

- **Impacts on Soil**

The establishment of landfill sites and related infrastructure—such as clearing and excavation—can alter local ecosystems by disturbing the food chain, reshaping landforms, and removing vegetation. These changes increase surface runoff, which may accelerate soil erosion in the surrounding areas (Chihaoui, 2017).

- **Impacts on Water Resources**

Poorly managed landfills pose a risk of contaminating groundwater through leachate infiltration, especially during rainfall events. This can result in waterborne diseases such as cholera and typhoid (Amara et al., 2021). Groundwater contamination may also occur due to accidental ruptures or chemical degradation of the underlying geomembrane, which is meant to

ensure impermeability. These protective liners are typically made from materials such as high-density polyethylene, polyvinyl chloride, or ethylene propylene diene monomer (Belghali & Dries, 2017).

- **Biogas Pollution**

Biogas, primarily composed of methane and carbon dioxide (CH<sub>4</sub> and CO<sub>2</sub>), may also contain trace amounts of nitrogen, hydrogen, ammonia, carbon monoxide, and sulfur compounds like hydrogen sulfide and mercaptans (Ngô & Régent, 2008; Doucet, 2022). Methane is highly flammable and contributes significantly to greenhouse gas emissions (Lamraoui, 2015). Exposure to biogas can irritate the eyes and respiratory system, and prolonged exposure has been linked to cardiovascular, hepatic, and neurological disorders, as well as cancer and congenital defects (Chihaoui, 2017). In addition, biogas emissions and combustion create strong, unpleasant odors that are exacerbated by seasonal changes and wind patterns (Belghali & Dries, 2017).

- **Leachate Contamination**

Rainwater percolating through waste materials generates leachate—an effluent comparable in pollution load to highly contaminated municipal and industrial wastewater (Wage et al., 2020). Leachate may escape from the site, threatening nearby vegetation, wildlife, and human health—particularly if the landfill is situated near a groundwater source used for drinking water (Mohammedi, 2016).

- **Proliferation of Disease Vectors**

Landfills attract scavengers such as gulls, crows, rodents, and insects, drawn by food waste and the heat generated by fermentation (ranging from 35°C to 80°C). These species can carry pathogens that threaten nearby communities with potential epidemics. Additionally, they may damage local crops and spread infectious diseases (Amara et al., 2021).

## **2. Leachate**

### **2.1 Definition**

Leachate refers to any liquid that percolates through waste material and is either released from or remains within a landfill (European Council, 1999). It originates mainly from rainwater infiltrating the waste layers, but also includes moisture already present in the waste and liquids produced by biochemical reactions within it (Renou et al., 2008). As it moves through the landfill, this liquid becomes loaded with various organic and inorganic substances, both dissolved and in suspension, along with microbial content. The generation of leachate is influenced by several factors, including the type of waste, the landfill design and operation—such as compaction and waste height—and the interactions between water and waste. These interactions involve complex biological and physico-chemical mechanisms (Kulikowska & Klimiuk, 2008).

### **2.2 Leachate formation**

The formation of leachate in landfills results from the interaction between deposited waste and various sources of water, leading to the mobilization of soluble and particulate substances. Three primary water sources contribute to leachate generation: (1) the moisture originally present in the waste at the time of disposal, (2) water released during the microbial decomposition of organic matter, and (3) rainwater infiltration through the landfill cover—by far the dominant contributor (Teffahi & Djettene, 2017; Berkani, 2016). These mechanisms are visually summarized in Fig. 6, which provides a schematic representation of how leachate is formed within a landfill system.



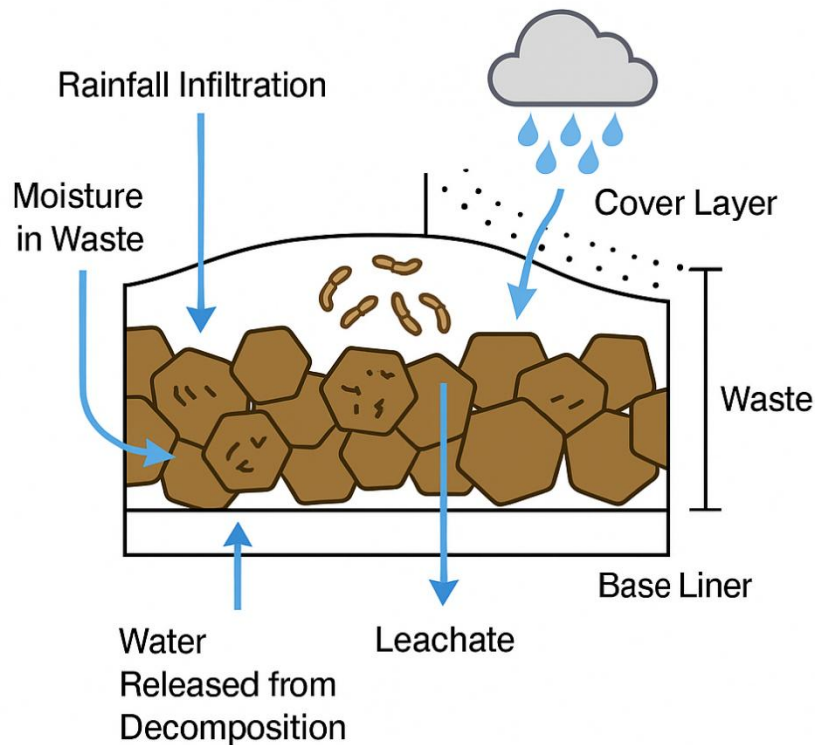


Fig. 6. Schematic representation of leachate formation in a landfill (Illustrated by the author).

The decomposition of organic matter is a dynamic and long-term process that spans several years. It depends on the type and quantity of waste deposited, as well as its biodegradability. During this process, microbial activity breaks down organic compounds, releasing both metabolic by-products and additional water that adds to the leachate volume (Teffahi & Djettene, 2017; Berkani, 2016). This internal water production is particularly significant during the early and intermediate phases of waste degradation.

Rainfall infiltration plays a critical role, especially in open or poorly covered landfills. Precipitation that reaches the waste body either percolates into the mass or runs off the surface, depending on the intensity of rainfall, site topography, slope, and the nature of surface vegetation (Teffahi & Djettene, 2017). When infiltration occurs, the water mobilizes both soluble organic and inorganic compounds, carrying them through the waste matrix and out of the landfill as leachate. Over time, accumulated rainfall and the continuous input of biodegradable waste result in progressively more complex leachate profiles.

The landfill's age is also a fundamental factor in leachate formation. As waste decomposes and compacts over time, its permeability and chemical reactivity change. These alterations influence how much water can infiltrate and how easily it can interact with buried materials (Laceb & Meziani, 2013). Older landfills may produce less leachate in volume, but the chemical characteristics often shift toward more stabilized, persistent compounds.

Additionally, the physical and operational characteristics of the landfill—such as compaction levels, cell height, surface area, and covering systems—affect water retention and movement within the landfill body (Teffahi & Djettene, 2017). Biological activity, particularly from bacteria and fungi, contributes to the transformation of waste and the solubilization of organic matter, further enriching the leachate with both organic and inorganic constituents (Teffahi & Djettene, 2017).

### **2.3 Leachate composition**

The composition of leachate is a direct consequence of the complex interactions involved in its formation. As water percolates through the waste, it dissolves, mobilizes, and transports a wide range of contaminants, resulting in a heterogeneous and highly variable effluent. This variability depends on several factors, including the age of the landfill, the nature and degree of waste decomposition, the composition and moisture content of the waste, infiltration rates, and climatic conditions (Trabelsi, 2011)

Although leachate composition is highly site-specific, it can generally be characterized by four main groups of pollutants (Trabelsi, 2011)

- **Organic Matter**

The organic fraction of leachate consists of both biodegradable and non-biodegradable compounds. Biodegradable organics include VFAs, which accumulate during the acidogenic phase of waste degradation and can represent up to 95% of the total organic carbon (Trabelsi, 2011). More stable compounds, such as fulvic- and humic-like substances, appear during later stages of decomposition and are more resistant to biological breakdown (Kjeldsen et al., 2002). Organic matter is typically measured by parameters such as COD and Total Organic Carbon (TOC) (Kjeldsen et al., 2002).

- **Inorganic Macrocomponents**

Leachate also contains a wide range of inorganic macroelements resulting from the dissolution of minerals and salts. Common ions include calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), sodium ( $\text{Na}^{+}$ ), potassium ( $\text{K}^{+}$ ), ammonium ( $\text{NH}_4^{+}$ ), iron ( $\text{Fe}^{2+}$ ), manganese ( $\text{Mn}^{2+}$ ), chloride ( $\text{Cl}^{-}$ ), sulfate ( $\text{SO}_4^{2-}$ ), and bicarbonate ( $\text{HCO}_3^{-}$ ) (Trabelsi, 2011). These components affect the ionic strength and pH of leachate and can influence treatment performance and environmental impact.

- **Heavy Metals**

Heavy metals are present in leachate in trace concentrations but pose a significant environmental risk due to their toxicity, persistence, and potential for bioaccumulation. Metals commonly detected include cadmium ( $\text{Cd}^{2+}$ ), chromium ( $\text{Cr}^{3+}$ ), copper ( $\text{Cu}^{2+}$ ), lead ( $\text{Pb}^{2+}$ ), nickel ( $\text{Ni}^{2+}$ ), and zinc ( $\text{Zn}^{2+}$ ) (Kjeldsen et al., 2002). Other studies have also reported arsenic, cobalt, and mercury in small quantities (Trabelsi, 2011). The concentration and mobility of these metals depend on several factors, including pH, redox potential, and the presence of organic complexing agents.

- **Xenobiotic Organic Compounds (XOCs)**

Xenobiotic organic compounds originate from anthropogenic sources such as household and industrial chemicals. These substances include aromatic hydrocarbons, phenols, chlorinated aliphatics, pesticides, plasticizers, and other synthetic organic compounds, usually found at concentrations below 1 mg/L (Kjeldsen et al., 2002). Despite their low concentrations, XOCs are of particular concern due to their potential toxicity, persistence, and resistance to conventional biological treatment.

- **Microorganisms**

Leachate is also biologically active, containing various microorganisms originating from the waste mass. These include bacteria, fungi, and viruses that either participate in the degradation of organic matter or are simply mobilized within the leachate flow (Teffahi & Djettene, 2017; Berkani, 2016). While some microbes play beneficial roles in natural attenuation processes, others may contribute to pathogenic risks if leachate contaminates nearby soil or water bodies.

The composition of leachate significantly varies depending on the age of the landfill. There are three distinct types of leachate, each with unique chemical and biological properties. The characteristics of leachates depending on their age are summarized in Table 3, which highlights the changes in the concentration of key pollutants such as organic compounds (indicated by COD) and ammonia ( $\text{NH}_3$ ) over time.

Table 3. Classification of Landfill Leachates (Vaverková, 2019)

Parameter	Young Leachate	Medium Leachate	Old leachate
Landfill age (years)	<1	1-5	>5
pH	<6.5	6.5-7.5	>7.5

Table 3 (continued)

Parameter	Young Leachate	Medium Leachate	Old leachate
COD (g O <sub>2</sub> .dm <sup>-3</sup> )	>15	3.0-15	<3.0
BOD <sub>5</sub> /COD	0.5-1	0.1-0.5	<0.1
TOC/COD	<0.3	0.3-0.5	>0.5
NH <sub>3</sub> -N (mg.dm <sup>-3</sup> )	<400	400	>400
Heavy metals (mg.dm <sup>-3</sup> )	>2.0	<2.0	<2.0

## 2.4 Leachate treatment methods

Landfill leachate treatment encompasses a diverse array of technologies, each tailored to address the complex and variable composition of leachate. These methods aim to meet stringent environmental regulations and ensure the safe discharge or reuse of treated effluent. The primary treatment approaches include biological processes, physicochemical methods, membrane filtration, advanced oxidation processes (AOPs), and natural systems (Vaverková, 2019).

### • Biological Treatment

Biological processes leverage microbial activity to degrade organic pollutants within leachate. Common methods encompass activated sludge systems, aerobic and anaerobic lagoons, and membrane bioreactors (MBRs). MBRs, in particular, integrate biological degradation with membrane filtration, achieving high removal efficiencies for biochemical oxygen demand (BOD) and COD, while producing a clarified effluent suitable for discharge or further treatment (Kurniawan et al., 2010). The effectiveness of biological treatments can be influenced by factors such as leachate composition, temperature, and retention time (Kurniawan et al., 2006).

### • Physicochemical Methods

Physicochemical treatments are pivotal for removing suspended solids, heavy metals, and refractory organic compounds. Key techniques include:

- **Coagulation-Flocculation:** Involves adding coagulants to destabilize colloidal particles, followed by flocculants to aggregate them for removal. This method effectively reduces turbidity and certain organic pollutants (Kurniawan et al., 2006).

- **Chemical Precipitation:** Targets the removal of heavy metals by converting them into insoluble compounds that can be separated from the leachate.
- **Adsorption:** Utilizes materials like activated carbon to adsorb organic and inorganic pollutants, offering a versatile treatment option. Adsorption is particularly effective for removing non-biodegradable organic contaminants and trace metals, and it is frequently used in combination with other methods to achieve higher treatment efficiencies (Kurniawan et al., 2006).
- **Air Stripping:** Removes volatile compounds, such as ammonia, by transferring them from the liquid phase to the gas phase through aeration (Kurniawan et al., 2006).

While these methods are effective, they may require subsequent treatments to address residual contaminants and manage generated sludge.

- **Membrane Filtration**

Membrane technologies offer high-efficiency separation processes, crucial for achieving advanced treatment goals:

- **Microfiltration and Ultrafiltration:** Remove suspended solids, bacteria, and some viruses, serving as effective pre-treatment steps (Wang & Qiao, 2024).
- **Nanofiltration:** Targets divalent ions and larger organic molecules, reducing hardness and specific contaminants (Wang & Qiao, 2024).
- **Reverse Osmosis:** Provides the highest removal efficiency, eliminating a broad spectrum of dissolved solids, including salts and small organic molecules (Wang & Qiao, 2024).

Despite their effectiveness, membrane processes face challenges like fouling, high operational costs, and the need for concentrate management.

- **Advanced Oxidation Processes (AOPs)**

AOPs are employed to degrade persistent organic pollutants through the generation of highly reactive species:

- **Fenton and Photo-Fenton Reactions:** Utilize hydrogen peroxide and iron catalysts, with or without UV light, to produce hydroxyl radicals that oxidize organic contaminants (Kurniawan et al., 2010).

- **Ozonation:** Applies ozone gas to oxidize and break down complex organic molecules, effectively reducing color and COD levels (Kurniawan et al., 2010).
- **Photocatalysis:** Employs catalysts like titanium dioxide under UV light to initiate oxidation reactions, targeting a wide range of pollutants (Kurniawan et al., 2010).
- **Electrochemical Oxidation:** Involves the application of electric current to oxidize contaminants directly at the electrode surface or indirectly through generated oxidants (Kurniawan et al., 2010).

These processes are particularly effective for treating non-biodegradable and toxic compounds but may involve high energy consumption and operational costs.

- **Natural Treatment Systems**

Constructed wetlands represent a sustainable approach, mimicking natural processes to treat leachate:

- **Surface Flow Wetlands:** Leachate flows over a vegetated surface, allowing for sedimentation and microbial degradation (Kurniawan et al., 2006).
- **Subsurface Flow Wetlands:** Leachate passes through a porous medium beneath the surface, promoting filtration and biological treatment (Kurniawan et al., 2006).

These systems are cost-effective and environmentally friendly but may require significant land area and longer retention times to achieve desired treatment levels.

- **Integrated Treatment Approaches**

Given the complexity of landfill leachate, combining multiple treatment methods often yields superior results. For instance, integrating biological treatment with membrane filtration or coupling physicochemical methods with AOPs can enhance overall efficiency and address a broader range of contaminants (Kurniawan et al., 2006). Such hybrid systems are tailored to meet specific treatment objectives and regulatory requirements.

### 3. Adsorption

#### 3.1 Definition

Adsorption is a surface phenomenon in which molecules, ions, or atoms from a fluid phase (liquid or gas) accumulate on the surface of a solid or liquid material, known as the adsorbent (Worch, 2012). This process results from unbalanced surface forces acting on the outermost atoms of solids, creating high-energy sites capable of attracting and retaining species from the surrounding environment (Faust & Aly, 1987). The materials that become attached to the surface are referred to as adsorbates, and this attachment can occur through either physical interactions (e.g., Van der Waals forces) or chemical bonding (Pourhakkak et al., 2021). A general representation of the adsorption process is shown in Fig. 7.

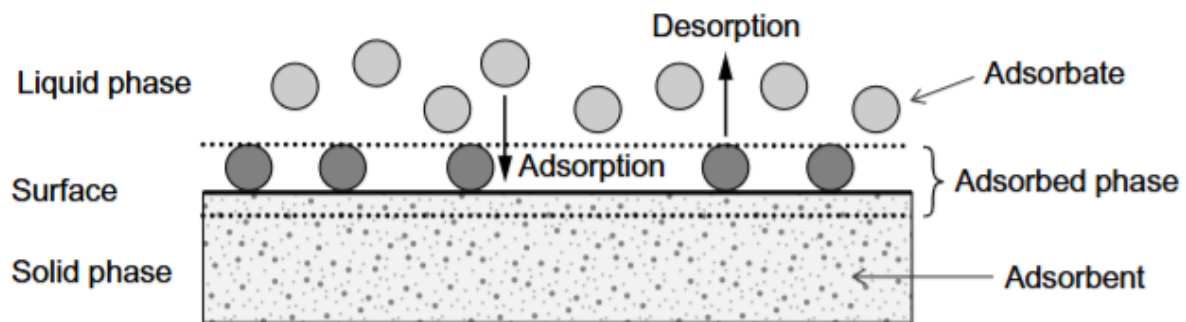


Fig. 7. Schematic illustration of the adsorption process (Worch, 2012)

Unlike absorption, where a substance penetrates into the bulk of another material, adsorption is confined to the surface, with porous adsorbents offering extensive internal surface areas that significantly enhance removal efficiency (Pourhakkak et al., 2021). Engineered adsorbents such as activated carbon or synthetic resins typically have surface areas ranging from 100 to 1000 m<sup>2</sup>/g due to their porous structures, which allow for the adsorption of various contaminants, including organic molecules and ions, especially in water and wastewater treatment applications (Worch, 2012; Faust & Aly, 1987).

Furthermore, adsorption is often reversible: under specific conditions (e.g., changes in pH, temperature, or concentration), the adsorbed species may be released back into the fluid phase through a process known as desorption (Worch, 2012). The energetically heterogeneous nature of most adsorbent surfaces means that different adsorption sites exhibit varying affinities for solutes, influencing both the capacity and selectivity of the process (Worch, 2012). This makes adsorption a highly adaptable and widely used technique in environmental remediation,

especially for the removal of pollutants from aqueous systems (Worch, 2012; Pourhakkak et al., 2021).

### **3.2 Mechanisms of Adsorption**

Adsorption is a surface phenomenon involving the accumulation of molecules or ions from a fluid phase onto the surface of a solid (Pourhakkak et al., 2021). The mechanisms of adsorption depend on the type of adsorbate, adsorbent, and environmental conditions. A fundamental mechanism in adsorption involves the interaction between the adsorbate and the surface sites of the adsorbent. In the case of CO<sub>2</sub> adsorption, studies suggest that atomic-level interactions, such as van der Waals forces and hydrogen bonding, play a key role in the attachment of CO<sub>2</sub> molecules to porous adsorbents (Pereira et al., 2023). For zeolite-based adsorbents, the mechanisms include both physical adsorption and chemisorption, where the porous structure of zeolites allows for high adsorption capacity due to the molecular sieving effect (Pérez-Botella et al., 2022). The formation of stable bonds between the adsorbate and the adsorbent is a critical aspect in determining the efficiency of the process, especially when complex molecules like hydrocarbons are involved (H. Li et al., 2023).

The surface chemistry of the adsorbent plays a critical role in determining the adsorption mechanism. In particular, density functional theory has been used to model and predict the interactions between CO<sub>2</sub> molecules and various adsorbents, providing a deeper understanding of how these molecular interactions occur at the atomic level (Y. Li et al., 2024). Similarly, the adsorption of pharmaceuticals onto adsorbents is governed by various mechanisms, including van der Waals forces and ionic bonding, which depend on the functional groups present on both the adsorbent and the adsorbate (Natarajan et al., 2022).

### **3.3 Factors Influencing Adsorption**

The efficiency of adsorption is influenced by a variety of factors, which can significantly alter the capacity and rate of adsorption. These include pH, temperature, concentration of the adsorbate, adsorbent characteristics, and contact time. Each of these factors impacts the adsorption process in different ways, and a summary of their roles is provided in Table 4 (Natarajan et al., 2022; H. Li et al., 2023). One of the most critical factors is the pH of the solution, as it affects the charge and ionization of both the adsorbent surface and the adsorbate. For example, in the case of heavy metal removal, the adsorption capacity of various adsorbents such as activated carbon and zeolites is highly pH-dependent (Pérez-Botella et al., 2022). Similarly, temperature plays an important role in adsorption efficiency. An increase in



temperature often increases the kinetic energy of the molecules, enhancing adsorption up to a certain point (Pourhakkak et al., 2021). However, too high of a temperature can lead to desorption or decreased adsorption efficiency.

Concentration of the adsorbate also affects the adsorption process. The initial concentration of pollutants in wastewater has been found to directly influence the rate of adsorption, with higher concentrations typically leading to greater adsorption capacities (Natarajan et al., 2022). Additionally, adsorbent characteristics, such as surface area, porosity, and the presence of functional groups, are essential factors determining the adsorption performance. Adsorbents with larger surface areas, such as activated carbon, exhibit higher adsorption capacity due to the availability of more active sites for interaction (H. Li et al., 2023).

The nature of the adsorbate is another important factor. For instance, the adsorption of pharmaceuticals is influenced by the polarity and size of the molecules, where hydrophobic compounds tend to have higher adsorption on non-polar adsorbents (Y. Li et al., 2024). The contact time between the adsorbent and adsorbate is also a critical factor, as adsorption tends to reach equilibrium over time. Optimizing contact time is essential for achieving maximum adsorption efficiency (Pereira et al., 2023).

Table 4. Summary of Key Factors Influencing Adsorption Efficiency and Their General Effects (Natarajan et al., 2022; H. Li et al., 2023)

<b>Factor</b>	<b>Description</b>	<b>Typical Effect on Adsorption</b>
<b>pH</b>	Affects surface charge of adsorbent and ionization of adsorbate	Influences electrostatic interactions; optimal pH varies by system
<b>Temperature</b>	Alters kinetic energy and solubility of solutes	Higher temperature can enhance or reduce adsorption depending on mechanism (endo/exothermic)
<b>Contact Time</b>	Duration of interaction between adsorbent and adsorbate	Longer times allow equilibrium to be reached, improving adsorption
<b>Adsorbent Dosage</b>	Mass of adsorbent used per volume of solution	Higher dosage generally increases total removal but may reduce capacity per gram due to site saturation

Table 4 (continued)

<b>Factor</b>	<b>Description</b>	<b>Typical Effect on Adsorption</b>
<b>Initial Concentration</b>	Concentration of solute at the start of the process	Affects driving force for mass transfer; higher concentrations often increase uptake but may saturate sites
<b>Surface Area &amp; Porosity</b>	Physical structure and internal area of the adsorbent	Greater surface area and porosity enhance adsorption performance
<b>Ionic Strength</b>	Presence of competing ions in solution	May inhibit or promote adsorption depending on competition for sites
<b>Agitation Speed</b>	Mixing intensity during adsorption	Enhances mass transfer but excessive speed may disrupt adsorbent structure
<b>Particle Size</b>	Size of adsorbent granules	Smaller particles increase surface area but may cause filtration issues

### 3.4 Applications of Adsorption in Leachate Treatment

Adsorption is widely applied in landfill leachate treatment due to its simplicity, cost-effectiveness, and ability to remove a broad spectrum of pollutants, including COD, ammonia, heavy metals, and dyes. The process has gained traction as a viable method for both preliminary and advanced stages of treatment.

Activated carbon, especially from agricultural residues like sugarcane bagasse, has been shown to be highly effective. Azmi et al. (2015) reported removal efficiencies reaching 126.58 mg/g for COD and 14.62 mg/g for ammonia nitrogen, highlighting its suitability for stabilized leachate.

Other materials such as biochar derived from pyrolyzed leachate sludge have demonstrated strong performance in metal adsorption, including cadmium and lead (Zhang et al., 2023). Modified bentonite clays, enhanced with surfactants, have also proven efficient in reducing COD and turbidity (Hajjizadeh et al., 2022).

Advanced materials like nano zero-valent iron offer high surface reactivity, achieving up to 75% COD removal under optimal conditions (Göçer et al., 2024). Additionally, hybrid

systems—such as those integrating adsorption with Fenton oxidation or membrane processes—can further enhance pollutant removal and system robustness (Pourhakkak et al., 2021; Yi et al., 2018; Aftab et al., 2024).

## 4. Activated carbon

### 4.1 Definition

Activated carbon (AC) is a porous carbonaceous material known for its exceptional adsorption capacity, particularly for organic compounds. Historically derived from carbonized materials such as wood or bone char, its use dates back to ancient Egypt (Dąbrowski, 2001). Modern ACs are produced from a variety of raw materials -including wood, coal, coconut shells, and synthetic polymers- through either chemical or physical activation processes (Worch, 2012). These methods generate a highly developed internal surface area, typically ranging from 800 to over 1,000 m<sup>2</sup>/g, and a complex pore structure dominated by micropores (Worch, 2012). The strong adsorptive properties of AC stem from Van der Waals forces,  $\pi$ - $\pi$  interactions, and hydrophobic effects, making it a widely used adsorbent in water and wastewater treatment, air purification, and industrial applications (Faust & Aly, 1998). The specific preparation method, pore size distribution, and surface chemistry determine its suitability for different uses (Worch, 2012).

### 4.2 Preparation of activated carbon

The preparation of AC involves three primary methods: chemical activation, physical activation, and the combination of both, each offering distinct advantages and suited for different applications (Table 5).

- **Chemical Activation** is a process where raw materials, such as coconut shells, wood, or other biomass, are treated with dehydrating chemicals like phosphoric acid or zinc chloride. This chemical treatment is followed by heating the material at temperatures ranging from 250°C to 600°C. The chemical agent acts as a dehydrating agent, facilitating the breakdown of cellulose structures and forming a carbon skeleton with a high surface area (Venegas-Gomez et al., 2017). This method is known for producing AC with higher surface areas but may result in residual chemicals, which can be a concern in certain applications such as water treatment (Mansurov et al., 2022).
- **Physical (Thermal) Activation**, on the other hand, involves two steps: carbonization and activation. During carbonization, the raw material is heated in an inert atmosphere at temperatures between 600°C and 900°C. This step removes volatile components, leaving behind a char. In the activation phase, the char is exposed to gases such as steam or carbon dioxide at higher temperatures (800°C to 1200°C), which further develop its

porous structure. The result is AC with a well-developed micropore network, suitable for various adsorption applications (Mirzaei et al., 2022). This method is preferred for its simplicity and the production of granular AC (GAC) that can be reused after regeneration.

- **Combined Chemical and Physical Activation:** To optimize the properties of AC, some processes combine both chemical and physical activation methods. For instance, a study by Mansurov et al. (2022) explored the production of activated and graphene-like carbon materials from rice husk. The process involved chemical activation using phosphoric acid, followed by physical activation with steam. This combination resulted in AC with enhanced surface area and porosity, making it suitable for various applications, including water treatment and energy storage.

Table 5. Comparison of Activated Carbon Preparation Methods (Adapted from Venegas-Gomez et al. 2017; Mirzaei et al. 2022; Mansurov et al. 2022).

Parameter	Chemical Activation	Physical Activation	Combined Activation
Raw materials	Biomass such as wood, coconut shells	Biomass or coal-based precursors	Biomass or pre-carbonized materials
Activation agent	Acids or salts (e.g. $H_3PO_4$ , $ZnCl_2$ )	Steam, $CO_2$ , or air	Chemicals followed by steam or $CO_2$
Temperature range	400–700 °C	800–1000 °C	Varies, typically high-temperature final step
Porosity development	Primarily micropores	Micropores and mesopores	Enhanced development of both micro and mesopores
Product form	Powdered or granular	Powdered or granular	Powdered or granular
Environmental considerations	Risk of chemical leaching if not washed	High energy consumption	More complex, but potentially more efficient

Table 5 (continued)

Parameter	Chemical Activation	Physical Activation	Combined Activation
Typical applications	Suitable for both gas and liquid treatment; microporous structure often preferred for gas adsorption	Suitable for both gas and liquid treatment; mesoporous structure often preferred for liquid-phase applications	Versatile for both phases; optimized for high-efficiency adsorption

### 4.3 Properties of activated carbon

The effectiveness of AC in environmental applications is closely linked to its physicochemical properties, which are determined by both the precursor material and the activation process. Among the most important characteristics are pore structure, specific surface area, surface functional groups, and adsorption behavior (Yahya et al., 2015).

- **Porosity and Surface Area**

The pore structure of AC is a critical determinant of its adsorption capacity. It typically exhibits a hierarchical pore network comprising micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm), with micropores playing a dominant role in the adsorption of small molecules (Ioannidou & Zabaniotou, 2007). Chemical activation techniques, such as the use of phosphoric acid ( $\text{H}_3\text{PO}_4$ ), have been shown to enhance porosity and create highly developed pore networks (Girgis et al., 2002). Depending on the activation parameters and precursor material, the Brunauer–Emmett–Teller (BET) surface area of AC may vary between 500 and 3000  $\text{m}^2/\text{g}$  (Moreno-Castilla et al., 2003).

- **Surface Chemistry and Functional Groups**

The surface chemistry of AC, particularly the presence of oxygenated functional groups (e.g., hydroxyl, carbonyl, carboxyl), significantly influences its hydrophilicity, surface acidity, and affinity for polar or charged molecules (Figueiredo et al., 1999). These functional groups can be introduced or enhanced through various chemical or thermal treatments. For example,

oxidation processes are known to increase surface acidity and improve adsorption of polar contaminants (Yahya et al., 2015).

- **Adsorption Performance**

The adsorption behavior of AC results from the interplay between its textural properties and chemical surface characteristics. AC prepared from date pits using  $H_3PO_4$  activation demonstrated elevated phenol adsorption capacity, attributed to its mesoporous structure and surface acidity (Girgis & El-Hendawy, 2002). Similarly, wood-based AC has shown high efficiency in the removal of organic pollutants, mainly due to its extensive microporosity and surface area (Moreno-Castilla et al., 2003).

#### **4.4 Comparison of Activated Carbon with Other Adsorbents for Leachate Treatment**

AC remains the benchmark material for leachate treatment due to its high surface area, microporosity, and tunable surface chemistry. While other materials -such as zeolites, biochar, clays, and industrial by-products- have been explored, AC consistently outperforms them in adsorption efficiency and reliability across diverse contaminants (Foo & Hameed, 2009).

AC's microporous structure enables the effective capture of both organic and inorganic pollutants. Its modifiable surface allows tailored interactions with a wide range of molecules (Bhatnagar & Sillanpää, 2010). In contrast, natural zeolites are selective for specific ions (e.g., ammonium) and less versatile for complex leachate compositions (Babel & Kurniawan, 2003).

Waste-derived adsorbents like fly ash or red mud are low-cost but often require pre-treatment and pose risks of secondary pollution. Even after modification, their adsorption capacity is lower than that of AC (Al-Qodah, 2000). Biochar offers some promise but suffers from inconsistent performance depending on feedstock and production method (Bhatnagar & Sillanpää, 2010).

A major advantage of AC is its stability and reusability via regeneration, which is less effective or feasible with many alternative adsorbents. While low-cost options are useful in specific cases, AC remains the most effective and broadly applicable material for leachate treatment.

A summary of the main differences between activated carbon and selected alternative adsorbents is presented in Table 6.

Table 6. Comparison of Activated Carbon with Selected Alternative Adsorbents for Leachate Treatment (Adapted from Bhatnagar and Sillanpää (2010) and Foo and Hameed (2009))

<b>Adsorbent type</b>	<b>Main target pollutants</b>	<b>Cost</b>	<b>Regenerability</b>	<b>Overall adsorption performance</b>
<b>Activated carbon</b>	Organics, heavy metals, dyes	Medium–High	High	High (broad-spectrum)
<b>Zeolite</b>	Ammonium, cations	Low	Moderate	Moderate (selective)
<b>Biochar</b>	Organics, metals	Low	Low–Moderate	Variable
<b>Fly ash</b>	Dyes, heavy metals	Very Low	Low	Low–Moderate



## 5. Biological treatment

### 5.1 Principles of Biological Treatment

Biological treatment refers to the use of microbial activity to break down organic pollutants in wastewater. It is widely adopted due to its environmental friendliness, operational cost-effectiveness, and high efficiency in removing biodegradable matter (Kamal et al., 2022; Kjeldsen et al., 2002). Microorganisms metabolize organic substances into simpler end-products such as water, carbon dioxide, methane, and biomass (Kjeldsen et al., 2002).

Two primary categories of biological treatment are **aerobic** and **anaerobic** processes (Table 7).

- **Aerobic systems:** they require oxygen and are effective at rapidly degrading organic matter and converting ammonia into nitrate through nitrification. They are commonly used in municipal and industrial wastewater treatment, especially when the waste is rich in readily biodegradable compounds (Kamal et al., 2022).
- **Anaerobic systems:** they operate in the absence of oxygen and rely on sequential microbial steps -hydrolysis, acidogenesis, acetogenesis, and methanogenesis- to convert organic compounds into methane and carbon dioxide. These systems are typically more suitable for high-strength wastewaters and have the added benefit of biogas production (Remmas et al., 2023).

The effectiveness of biological treatment depends on several factors, including microbial population dynamics, pollutant load, temperature, pH, and oxygen availability. Selecting between aerobic and anaerobic methods depends on the type and concentration of pollutants, treatment objectives, and operational constraints. In many cases, combining both processes - either in sequence or parallel- can improve performance and resilience.

Table 7. Comparison of Aerobic and Anaerobic Biological Treatment Processes (Adapted from Kamal et al., 2022; Kjeldsen et al., 2002; Remmas et al., 2023)

Parameter	Aerobic Treatment	Anaerobic Treatment
Oxygen Requirement	Requires oxygen (aeration)	Operates without oxygen
Degradation Rate	Fast	Slower

Table 7 (continued)

<b>Parameter</b>	<b>Aerobic Treatment</b>	<b>Anaerobic Treatment</b>
<b>Main End-Products</b>	CO <sub>2</sub> , H <sub>2</sub> O, biomass	CH <sub>4</sub> , CO <sub>2</sub> , small amount of biomass
<b>Energy Demand</b>	High (due to aeration)	Low
<b>Sludge Production</b>	High	Low
<b>Nutrient Removal</b>	Effective (e.g., nitrification)	Inefficient (often requires post-treatment)
<b>Tolerance to Toxins</b>	Generally lower	Generally higher
<b>Biogas Production</b>	No	Yes (methane recovery)
<b>Typical Applications</b>	Domestic/industrial wastewater, young leachate	High-strength wastewater, mature leachate

## 5.2 Biological Treatment of Leachate

Biological treatment plays a crucial role in landfill leachate management due to its economic viability and capacity to reduce high loads of biodegradable pollutants, particularly organic matter and nitrogen compounds. Leachate is known for its complex and variable composition, often containing a mixture of readily degradable organics alongside refractory substances such as humic and fulvic acids, phenols, and surfactants, as well as heavy metals and high ammonia concentrations (Renou et al., 2008; Naveen et al., 2017). In such contexts, the success of biological treatment depends on careful adaptation of the treatment process to the leachate's characteristics and age.

In young landfills, leachate is rich in volatile fatty acids and other readily biodegradable organic matter, making aerobic biological treatment particularly effective. Conventional systems such as activated sludge processes (ASP), illustrated in Fig. 8, can reduce COD by 30–70% under favorable conditions (Renou et al., 2008). However, as leachate matures, its organic fraction becomes more refractory and less biodegradable, leading to lower treatment efficiency. High ammonia concentrations, often exceeding 1000 mg/L, can inhibit microbial activity and necessitate process modifications such as extended aeration, pH control, temperature

regulation, or biomass acclimatization (Kim et al., 2023; Naveen et al., 2017). Moreover, microbial community composition shifts significantly with leachate age and nitrogen load, often requiring specialized consortia, including ammonia-oxidizing bacteria and denitrifiers, to maintain performance (Ahmed & Lan, 2012).

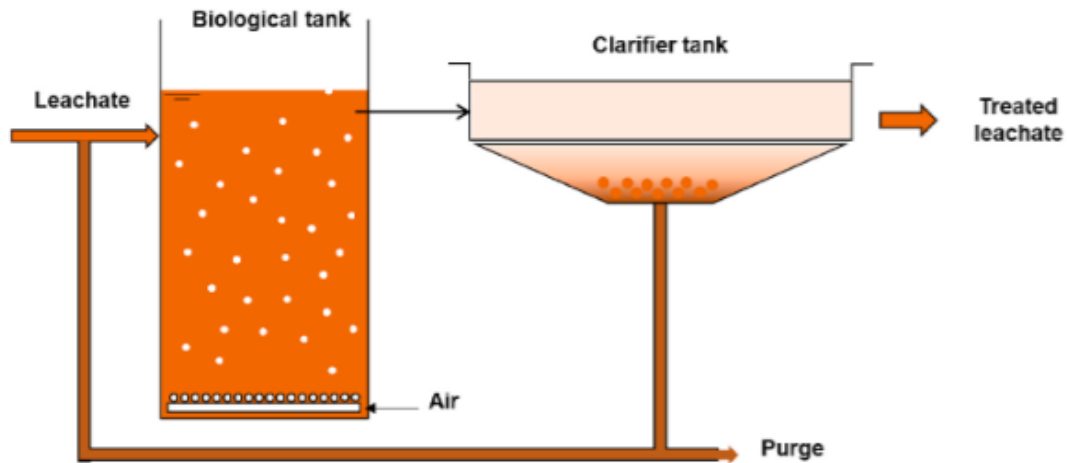


Fig. 8. Schematic representation of an activated sludge system applied to leachate treatment (Lebron et al., 2021).

To address these challenges, more flexible biological systems have been developed. Sequencing batch reactors (SBRs) offer operational versatility and facilitate simultaneous nitrification and denitrification within controlled time cycles, making them particularly effective for nitrogen-rich leachates. Studies have shown COD removal efficiencies exceeding 90% in landfill leachate using SBRs under optimized conditions (Askari et al., 2024; Kim et al., 2023). Membrane bioreactors (MBRs), which combine biological degradation with membrane separation, provide high-quality effluent and can handle complex leachate matrices with improved biomass retention. As shown in Fig. 9, MBR systems offer a compact and efficient solution for leachate treatment by integrating filtration and biological processing in a single unit. When treating stabilized leachates, MBRs have achieved over 95% COD and 90% total nitrogen removal (Ahmed & Lan, 2012). However, their application remains limited by operational costs and membrane fouling, especially with leachates containing suspended solids and refractory organics.

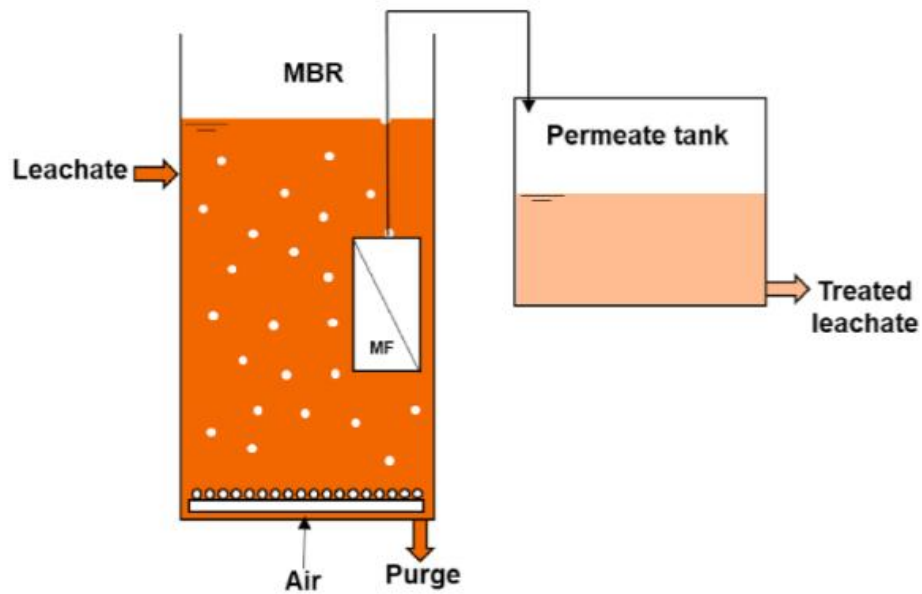


Fig. 9. Schematic representation of a membrane bioreactor applied to leachate treatment (Lebron et al., 2021)

Overall, biological treatment methods remain foundational in leachate management. Their ability to reduce organic loads and ammonia makes them well-suited for stabilized leachates, especially when process conditions are optimized or microbial communities are acclimated. However, the persistence of certain refractory compounds often necessitates further polishing. As a result, integrating biological processes with advanced physico-chemical or oxidation-based technologies is increasingly explored to enhance overall treatment efficiency and regulatory compliance.

## **6. Hybrid Treatment**

### **6.1 Concept of Hybrid Treatment**

Hybrid treatment refers to the integration of two or more complementary treatment methods - biological, physical, or chemical- to improve overall performance and address the shortcomings of single-process systems. In wastewater treatment, this strategy aims to enhance the removal of both biodegradable and resistant contaminants. The strength of hybridization lies in how one process can condition the effluent to improve the efficiency of the next (Dia et al., 2018; Jamrah et al., 2024).

Common combinations include adsorption-biological systems, electrocoagulation-biofiltration, and membrane-based sequences. For example, electrocoagulation can eliminate colloidal particles and reduce toxicity, improving the performance of biological degradation (Dia et al., 2018). Similarly, using activated carbon or similar materials for preliminary adsorption can enhance biodegradability and reduce microbial inhibition in subsequent biological stages (Genethliou et al., 2023). These combinations reflect a growing shift toward integrated, staged treatments rather than reliance on any single approach.

### **6.2 Hybrid Applications in Leachate Treatment**

Due to the complex and often recalcitrant nature of landfill leachate, hybrid systems are increasingly recognized as practical solutions for achieving treatment objectives. These configurations combine mechanisms that individually target different pollutant fractions, offering more complete and adaptable treatment pathways (Amaral et al., 2015; Spiniello et al., 2023).

Pilot-scale and full-scale studies have explored various configurations. For instance, Genethliou et al. (2023) demonstrated a hybrid process coupling activated carbon adsorption, electrocoagulation, and biological treatment, leading to significant improvements in effluent quality. Other systems have paired membrane filtration with chemical precipitation or advanced oxidation with natural wetland functions, depending on treatment goals and effluent characteristics (Spiniello et al., 2023; Amaral et al., 2015).

Among the various hybrid options, the combination of adsorption and biological treatment has shown particular promise in managing stabilized leachate. Together, these processes can effectively reduce a wide range of contaminants, including both biodegradable and persistent compounds. Their complementary mechanisms offer enhanced pollutant removal and

operational flexibility, making them a strong candidate for advanced leachate treatment strategies (Genethliou et al., 2023).

# Methods

# 1. Study Area and Sample Collection

## 1.1 Study Area

The study was conducted in Batna, the capital of the Aurès region, located in northeastern Algeria, approximately 425 km south of Algiers and 113 km southwest of Constantine (Fig. 10). The city spans 12,038.76 km<sup>2</sup> and is characterized by a semi-arid climate, with dry summers and relatively wet winters (Sefouhi et al., 2010b). It hosts a controlled municipal landfill that receives solid waste from Batna and neighboring communes, from which the leachate samples used in this study were collected.

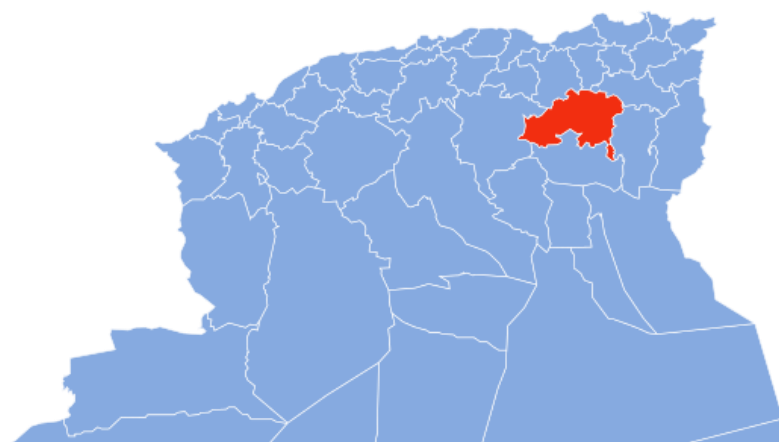


Fig. 10. Geographical location of Batna (Mouh2ijel, 2020).

In recent years, Batna has experienced continuous urban and economic growth, leading to a significant increase in municipal solid waste generation. Waste management in the city follows a linear system that includes collection, transportation, and final disposal in a landfill. While this model provides basic waste control, it also presents environmental challenges. The production of methane gas and leachate at the landfill contributes to air pollution and the contamination of soil and water resources (Sefouhi et al., 2010b).

## 1.2 Description of the Landfill

The controlled landfill of Batna, located in Chaâba, spans 25 hectares and receives approximately 400 tons of waste per day, including household and hospital waste—the latter incinerated on-site (Haddad & Aouachria, 2020; Sefouhi et al., 2010a). It is the only facility in the country accepting hospital waste. The site includes a weighbridge with radioactive monitoring, a sorting center, and a unit for industrial waste disposal (Haddad & Aouachria, 2020). Fig. 11 shows the main components of the site.





Fig. 11. Boundaries of the Batna landfill: 1- Administrative block, 2- Sorting block, 3- Leachate ponds, 4- Waste lockers, 5- Expansion area (Haddad & Aouachria, 2020).

Only two of the eight planned cells have been constructed so far, each with a capacity of 220,000 m<sup>3</sup> and a six-year service life (Sefouhi et al., 2010a). Waste is compacted but often left uncovered due to a lack of daily cover material, leading to odors, wind-blown litter, pests, and pollution (Sefouhi et al., 2010a).

Leachate is collected in ponds and partly reinjected into the cells, but some infiltrates the soil, posing a risk to groundwater. Biogas, mainly methane, is only partially captured and remains untreated (Sefouhi et al., 2010a). Fig. 12 illustrates the leachate ponds.



Fig. 12. Leachate storage ponds at the Batna landfill (Hamiouda & Karaali, 2024).

### 1.3 Sampling Procedure

Leachate samples were collected in 2024 by the Environmental Analysis Laboratory team of the Biotechnology Research Center, following standard procedures. Two types of containers were used: pre-rinsed 5-liter plastic bottles for physicochemical analyses (rinsed once with distilled water and three times with leachate), and sterilized 50 mL tubes for microbiological analysis (Fig. 13). Samples were transported to the laboratory in a cooler maintained at 4 °C and stored until the experimental work began in February 2025.



Fig. 13. Leachate sample containers: 5 L bottles for physicochemical analysis (left) and 50 mL tubes for microbiological analysis (right) (Hamiouda & Karaali, 2024).

## 2. Leachate Characterization

To manage the environmental risks related to leachate, it is essential to analyze its physico-chemical and microbiological composition. The characterization of these parameters helps to understand the nature of the leachate and to quantify the proportions of its constituents. In this study, the characterization was performed in 2024 by the same team from the Environmental Analysis Laboratory of the Biotechnology Research Center.

### 2.1 Physico-chemical Parameters

The measured parameters and their corresponding values are presented in Table 8:

Table 8. Physico-chemical Parameters Measured and Their Corresponding Values for Leachate Characterization

Parameter	Result
pH	8.26
Temperature (°C)	22
Electrical conductivity (ms/cm)	38.3
Salinity (ppm)	21.7
Total dissolved solids (g/L)	25.6
Dissolved oxygen (%)	0.1
Total nitrogen (mg/L)	1266.504
Ammoniacal nitrogen (mg/L)	1098.384
Nitrites (g/L)	0.49
Nitrates (g/L)	1.25
BOD (mgO <sub>2</sub> /L)	1050
COD (mgO <sub>2</sub> /L)	69700

## 2.2 Microbiological identification

Microbiological analyses aim to identify native bacterial populations present in the leachate, which can be exploited for biological treatment processes. Six bacterial strains were isolated from the leachate (GenBank accession numbers in parentheses). They are listed below:

- *Staphylococcus sp. Strain BMSOHbjKn 2024* (PP758812)
- *Cytobacillus sp. strain MSONbj 2024* (PP758813)
- *Rummeliibacillus sp. strain AAAB 2024* (PP758814)
- *Denitrificimonas sp. strain BMSOnj 2024* (PP758815)
- *Staphylococcus sp. strain MSONb 2024* (PP758816)
- *Bacillus sp. (in: firmicutes) strain MSObn 2024* (PP758817)

The isolated bacteria were stored in Petri dishes at 4 °C. When the experimental work began, they were revived for further use.

### **3. Preparation of Activated Carbon**

#### **3.1 Pre-treatment of Biomass Precursors**

##### **3.1.1 Biomass Collection**

Two types of green waste, orange peel and vegetable scraps (mainly onion residues), were collected from the street market (Souk) of Al-Athmania to serve as precursors for activated carbon production. The collected biomass is shown in Fig. 14.



Fig. 14. Collected biomass for carbon production.

##### **3.1.2 Washing**

The collected biomass was thoroughly washed with tap water, followed by distilled water. A second washing with hexane was performed under a chemical hood (Equiplabo). The biomass was then rinsed again with tap water and distilled water.

##### **3.1.3 Drying**

After washing, the biomass was placed in a sieve and left to drain. It was then air-dried for a short period before being spread out on wire racks and dried in an incubator (Memmert) at 105 °C for 24 hours. After drying, it was placed in a desiccator for one hour.



### 3.1.4 Grinding

The dried biomass was ground in two steps to obtain uniform 2 mm particles. First, it was reduced in size using a laboratory blender (Waring Commercial), then further milled with an ultra-centrifugal mill (Retsch ZM 200) equipped with a 2 mm sieve. The resulting biomass is shown in Fig. 15.

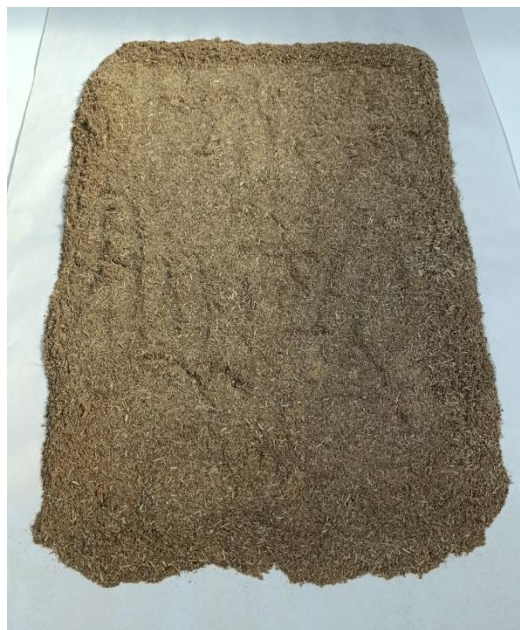


Fig. 15. Final pre-treated biomass

## 3.2 Characterization of the Biomass

To assess the physicochemical properties of the biomass used in the preparation of activated carbon, several standard analyses were performed. These characterizations aimed to determine the material's suitability for carbonization and its potential performance as an adsorbent. Parameters such as electrical conductivity, pH, organic matter content, elemental composition, and surface functional groups were evaluated using established ISO methods and analytical protocols.

### 3.2.1 Electrical Conductivity

The electrical conductivity (EC) of the biomass was measured according to ISO 11265:1994. A mixture of 10 g of biomass and 50 mL of distilled water was prepared, maintaining a 1:5 (m/V) biomass-to-water ratio. The mixture was agitated on an orbital plate shaker (Edmund Bühler GmbH) for one hour, then filtered. The EC of the filtrate was measured using a conductivity meter (Consort C6030).

### 3.2.2 pH

The pH of the biomass was measured following ISO 10390:2021, using the same 1:5 (m/V) biomass-to-distilled water mixture as for EC. However, after agitation, the mixture was left to settle for two hours before the pH was measured with a pH meter (SevenExcellence S400).

### 3.2.3 Determination of Organic Matter and Carbon Content

The organic matter content was measured using a modified loss on ignition (LOI) method at 550 °C, based on ASTM D7348-11. 5 g of the sample (biomass) were placed in a porcelain crucible and incinerated in a muffle furnace (Nabertherm) at 550°C for six hours, following a heating rate of 400°C per 15 minutes. After incineration, the remaining mass was measured, and the OM content of the biomass was determined using the following formula:

$$\%OM = \frac{\text{pre-ignition weight (g)} - \text{post ignition weight (g)}}{\text{pre-ignition weight (g)}} \times 100$$

To estimate the carbon content, the following relationship was applied:

$$\% \text{ Carbon content} = \%OM \times 0.5$$

This approximation follows the IPCC's default carbon fraction for biomass organic matter (0.5).

### 3.2.4 Determination of Nitrogen Content

Nitrogen content was determined using the Kjeldahl method in accordance with ISO 11261:1995. Three digestion flasks were prepared: two containing 0.2 g of the sample (biomass), and one blank without biomass. To each flask, 0.2 g of copper (II) sulfate pentahydrate (as catalyst) and 10 mL of 96% sulfuric acid were added. Digestion was then carried out at 400 °C for six hours using a Buchi Digest Automat, until the solutions became clear.

After cooling, 50 mL of 35% sodium hydroxide and 50 mL of distilled water were added, and distillation was conducted using a Buchi distillation unit. The released ammonia was collected in a 25 mL solution of 4% boric acid with Tashiro indicator. The ammonia content was determined via titration with 0.05N sulfuric acid until a color change occurred. The volume of

sulfuric acid used was determined, and the nitrogen content was then calculated using the following formula:

$$\%N = \frac{[V(\text{acid}) - V(\text{blank})] \times N(\text{acid}) \times 14.007}{\text{Sample weight}} \times 100$$

Where:

**%N** = Percentage of nitrogen in the sample

**V(acid)** = Volume of sulfuric acid used to titrate the sample (mL)

**V(blank)** = Volume of sulfuric acid used for the blank (mL)

**N(acid)** = Normality of the sulfuric acid solution

**14.007** = Atomic mass of nitrogen (g/mol)

**Sample weight** = Mass of the sample analyzed (mg)

### 3.2.5 Fourier Transform Infrared Spectroscopy

The biomass was characterized using Fourier-transform infrared spectroscopy (FTIR) in attenuated total reflectance mode (ATR-FTIR), performed with an Agilent Cary 660 spectrometer, following a modified version of the protocol described by Sunkar et al. (2023). Finely ground biomass was placed directly onto the ATR crystal and pressed with moderate force to ensure optimal contact. Spectra were recorded over the range of 4000–400  $\text{cm}^{-1}$ , with a resolution of 4  $\text{cm}^{-1}$  and averaged over 32 scans to improve the signal-to-noise ratio. A background scan was acquired before each measurement to correct for atmospheric and crystal interferences. Each sample was analyzed in triplicate to ensure reproducibility.

### 3.3 Activation procedure

The activation process applied in this study consisted of two sequential steps: chemical activation followed by physical activation. Together, these steps constituted the full activation procedure used to convert the pretreated biomass into activated carbon. The protocol was adapted from the method described by Sunkar et al. (2023).

#### 3.3.1 Chemical Activation

To activate the precursor material (biomass), it was fully immersed in boiling 30% phosphoric acid with continuous agitation for two hours. The mixture was then left to soak for an additional

24 hours without heating. After soaking, the material was washed with distilled water until its pH returned to its initial value, monitored using pH test paper. The washed material was then drained, dried in an incubator at 70°C until fully dry, and ground using a laboratory blender.

### **3.3.2 Physical Activation (carbonization)**

The dried and ground carbon precursor was placed in lidded porcelain crucibles, and nitrogen gas was introduced into both the crucibles and the muffle furnace to maintain an inert atmosphere. Carbonization was performed in two stages: first at 400 °C for 20 minutes (with a heating period of 15 minutes), then at 800 °C for 10 minutes (with a heating period of 10 minutes). After carbonization, the samples were allowed to cool gradually at room temperature. The resulting carbonized material was then manually ground using a mortar and pestle and sieved to obtain particles with a size of 400 µm.

## **3.4 Characterization of the Activated Carbon**

### **3.4.1 pH at the Point of Zero Charge**

The pH at the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of the activated carbon was determined using a salt-addition method, following the same protocol described by Bakatula et al. (2018). Eight crystallizing dishes were prepared, each containing 0.1 g of activated carbon in 10 mL of NaCl solution, followed by agitation. The initial pH was measured and found to be 7.09. Using sulfuric acid ( $\text{H}_3\text{PO}_4$ ) and potassium hydroxide (KOH), the pH was adjusted to eight different values ranging from 2.86 to 12.53. The samples were agitated for 24 hours. Afterward, the final pH was measured, and the  $\text{pH}_{\text{pzc}}$  was determined by plotting the final pH ( $\text{pH}_{\text{final}}$ ) against the initial pH ( $\text{pH}_{\text{initial}}$ ). The  $\text{pH}_{\text{pzc}}$  corresponds to the intersection point between the experimental curve and the bisector line ( $\text{pH}_{\text{final}} = \text{pH}_{\text{initial}}$ )

### **3.4.2 Fourier Transform Infrared Spectroscopy**

After activation, the material was characterized by ATR-FTIR using the same protocol and instrument previously described for the precursor biomass. Triplicate analyses were again performed to ensure reproducibility.

### **3.4.3 Raman Analysis**

Structural characterization of the activated carbon was carried out by Raman spectroscopy using a Thermo Scientific DXR Raman microscope, following a modified version of the protocol described by Cheng et al. (2017). The powdered activated carbon was carefully spread into a



uniform layer on a clean microscope slide and placed on the instrument's motorized stage. Focusing was performed using a 50× microscope objective to ensure precise alignment on the sample surface. Prior to each measurement, the spectrometer was calibrated with a silicon standard, ensuring the reference peak appeared at  $520.7\text{ cm}^{-1}$ . Spectra were acquired using a green laser at 532 nm with a fixed laser power of 10 mW and an exposure time of 2 seconds per spectrum. To improve the signal-to-noise ratio and minimize local heterogeneity effects, five consecutive spectra were collected from the same area and averaged to obtain a representative spectrum.

### **3.5 Encapsulation of Activated Carbon**

To facilitate the application of the activated carbon in physicochemical and hybrid leachate treatment, two types of alginate-based beads were prepared: one containing only powdered activated carbon (AC), and the other combining AC with a bacterial consortium isolated from the leachate. In both cases, the components were encapsulated within alginate beads formed by ionic gelation, resulting in small, uniform spheres

#### **3.5.1 Encapsulation of Activated Carbon Only**

For the preparation of physicochemically functional beads, 100 mL of a 3% (w/v) sodium alginate solution containing 1 g of powdered activated carbon was prepared. Simultaneously, 200 mL of a 2% (w/v) calcium chloride ( $\text{CaCl}_2$ ) solution was prepared to serve as the crosslinking bath. The alginate-AC mixture was introduced into the  $\text{CaCl}_2$  solution using a peristaltic pump (Ecoline), with a flow rate of 1.1. The  $\text{CaCl}_2$  solution was kept under continuous stirring using a magnetic stirrer to ensure homogeneous bead formation. Droplets were released from a height of 20 cm, allowing for the formation of spherical AC-alginate capsules upon contact with the  $\text{CaCl}_2$  solution.

Once the entire alginate-AC mixture was dispensed, the beads were left to harden in the  $\text{CaCl}_2$  bath under agitation for 1 hour. After crosslinking, they were rinsed with bidistilled water, immersed in it for 10 minutes, and rinsed again. The beads were then transferred to Kraft paper and left to air-dry at room temperature until completely dehydrated. A noticeable reduction in bead size was observed following drying. The setup used for this procedure is shown in Fig. 16.

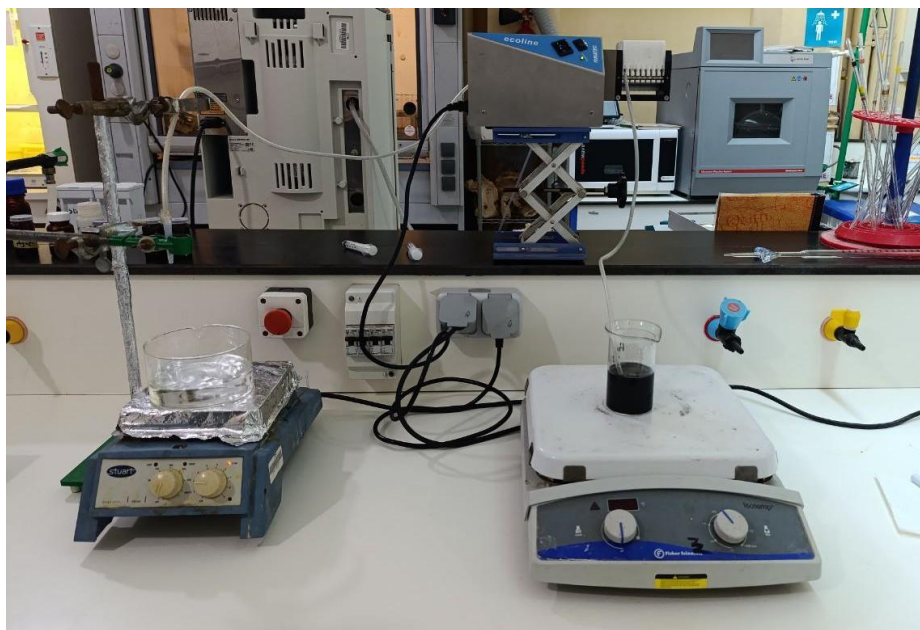


Fig. 16. Setup used for the encapsulation of activated carbon in alginate beads.

### 3.5.2 Encapsulation of Activated Carbon with Bacterial Consortium

#### 3.5.2.1 Revival of Bacterial Strains

To revive the six stored strains originally isolated from the leachate, each was inoculated on nutrient agar and in nutrient broth, followed by incubation at 30 °C for 24 hours. This duration ensures the presence of young, metabolically active cells suitable for application in leachate treatment. The turbidity observed in the broth confirmed the successful reactivation of the strains.

#### 3.5.2.2 Preparation of the Bacterial Consortium

The bacterial consortium used for the leachate treatment was prepared by pooling equal volumes of each of the six reactivated strains, taken directly from their respective nutrient broth cultures, into a sterile conical tube. The mixture was then centrifuged at 5500 rpm for 10 minutes at 4 °C using a Thermo Scientific Heraeus Biofuge Stratos Centrifuge. A portion of the supernatant was discarded, while enough volume was retained for the subsequent steps. The resulting bacterial pellet was resuspended by vortexing. An aliquot of the suspension was used to measure the optical density (OD) at 600 nm using a Thermo Scientific Helios Epsilon spectrophotometer, yielding a value of 1.2, indicative of a sufficient microbial load for treatment. The remaining suspension was used for the encapsulation of the activated carbon–bacteria mixture.

### 3.5.2.3 Encapsulation

The encapsulation followed the same procedure, with the addition of the bacterial consortium to the alginate-AC mixture. To preserve sterility, all materials and equipment used were sterilized, and the entire encapsulation process was conducted under a laminar flow hood (ALS VBH 72 C2).

The alginate-AC-bacteria mixture was dripped into the  $\text{CaCl}_2$  solution under sterile conditions using the same parameters as the first encapsulation: 1.1 flow rate, 20 cm drop height, and continuous magnetic agitation. After the encapsulation was complete, the beads were left in the  $\text{CaCl}_2$  solution for 1 hour, then rinsed with sterile bidistilled water, immersed for 10 minutes, and rinsed again. The final beads were placed in Petri dishes lined with Kraft paper and left to dry under the hood until completely dehydrated, resulting in significant shrinkage similar to the first formulation. The setup used for this procedure is shown in Fig. 17.

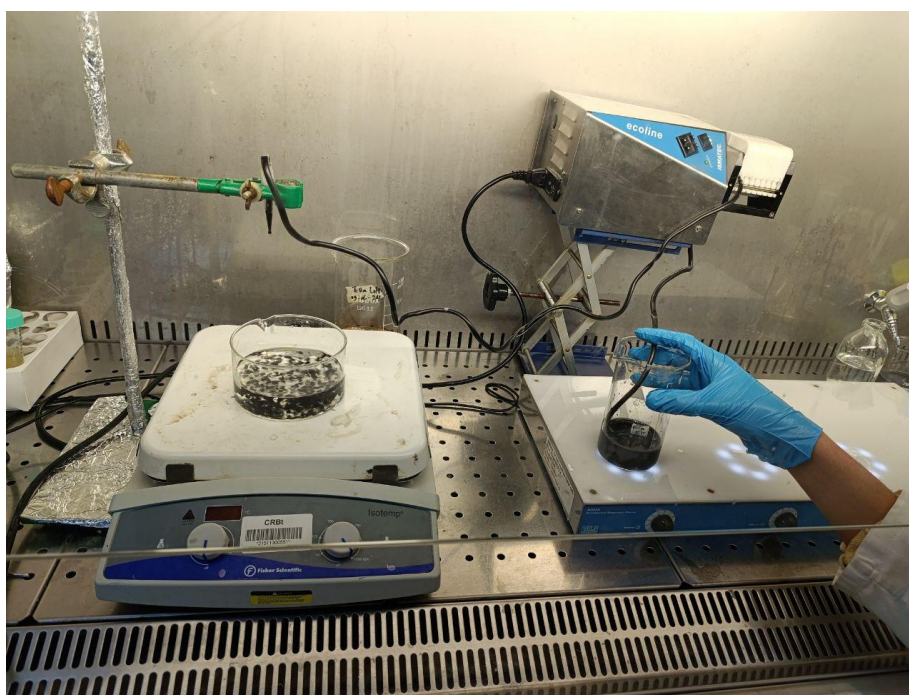


Fig. 17. Sterile encapsulation setup for activated carbon with bacterial consortium, conducted under a laminar flow hood.

## 4. Leachate Treatment

Leachate treatment was conducted using three approaches: physicochemical adsorption with AC beads, biological degradation using the isolated bacterial consortium, and a hybrid treatment combining both processes through encapsulated AC with bacteria. In all three cases, the leachate was first diluted at a 1:20 ratio, and a 0-minute time point was included as the

untreated reference. At each selected time point, samples were collected and subjected to physicochemical analyses to evaluate treatment progress.

#### **4.1 Physicochemical Treatment (Adsorption)**

In the physicochemical treatment, 1 g of AC beads was added to 50 mL of the diluted leachate. The mixture was placed in Erlenmeyer flasks and kept under continuous agitation on an orbital shaker. Six flasks were prepared, corresponding to the following contact times: 10, 15, and 20 minutes, as well as 1, 5, and 12 hours. At the end of each period, the activated carbon was removed using a sieve, and the remaining liquid was collected for analysis.

#### **4.2 Biological Treatment**

This treatment used only the bacterial consortium described earlier. Erlenmeyer flasks containing 50 mL of the diluted leachate and 700  $\mu$ L of the consortium were incubated at 30 °C with agitation on an orbital shaker. The selected time points were: 10, 15, and 20 minutes; 1, 5, and 12 hours; and 1, 3, 5, 8, 13, and 21 days. At each time point, a sample was transferred to a sterile Falcon tube and centrifuged at 6000 rpm for 10 minutes. The supernatant was then transferred to a second sterile tube, leaving the bacterial pellet behind to prevent further degradation. Analyses were then performed on the supernatant. Additionally, optical density was recorded throughout the treatment to monitor changes in microbial load. Petri dish cultures were prepared at both the beginning and end of the treatment to verify bacterial viability.

#### **4.3 Hybrid Treatment**

In the hybrid approach, 1 g of alginate beads containing both AC and the bacterial consortium was added to 50 mL of diluted leachate. The flasks were incubated at 30 °C under constant agitation. Alongside the time points used in the physicochemical treatment (10, 15, and 20 minutes; 1, 5, and 12 hours), additional longer intervals were included: 24 and 72 hours, as well as 5 and 21 days. At each interval, the capsules were removed under sterile conditions using a sterile sieve in a laminar flow hood. The leachate was then centrifuged at 6000 rpm for 10 minutes, and the supernatant was carefully transferred to a new sterile Falcon tube, separating it from any residual microbial content. Analyses were then carried out on the resulting liquid. To confirm bacterial survival within the capsules, Petri dishes were also inoculated at the start and at the conclusion of the treatment.

## **4.4 Characterization of Leachate After Treatment**

Following the three treatment approaches, several analyses were carried out to monitor changes in the leachate over time. All samples analyzed were collected at the corresponding time points defined in the previous section.

### **4.4.1 UV-Visible Spectrophotometry**

The spectral analysis of the treated leachate was conducted in accordance with the Beer–Lambert law, which describes a linear relationship between the absorbance of a solution and the concentration of the absorbing species. The procedure followed the spectrophotometric protocol described by Trabelsi (2014). At each sampling point, the leachate was collected and centrifuged to remove suspended particles. An aliquot of the clarified supernatant was then transferred into a clean, dry quartz cuvette suitable for measurements in the ultraviolet and visible ranges.

Spectral analysis was performed using a computer-controlled scanning spectrophotometer (Agilent Technologies Cary 60 UV-Vis). The spectrum was recorded over a wavelength range of 200 to 800 nm, covering both UV and visible regions. Absorbance was measured against a blank consisting of the initial leachate diluted at a 1:20 ratio, to correct for background interference. The resulting spectra were processed using OriginPro 2018 software. For each sample set, a specific wavelength corresponding to a characteristic absorbance peak of the target pollutant was selected. Absorbance values at this wavelength were extracted at various treatment times and plotted to generate a kinetic curve representative of the pollutant's evolution over time.

### **4.4.2 Total Organic Carbon**

For the measurement of TOC in the treated leachate, the procedure followed the protocol described by Rodier et al. (2009). The process began with the preparation of calibration solutions. Ultrapure water was used both as a blank and as the solvent for dilutions, while potassium hydrogen phthalate (KHP), serving as a primary reference standard, was used to construct an accurate calibration curve. A stock solution was prepared by dissolving 2.125 g of KHP in one liter of ultrapure water, followed by serial dilutions to obtain intermediate standards suitable for the measurement range.

Before analysis, each leachate sample was acidified by adding a few drops of phosphoric acid to release inorganic carbon in the form of carbon dioxide (CO<sub>2</sub>), which was then eliminated by

sparging with an inert gas. The sample was then introduced into the combustion furnace of the TOC analyzer (TELEDYNE TEKMAR), where organic carbon was oxidized to CO<sub>2</sub> at high temperature (680 to 1200 °C) in the presence of a catalyst. The resulting CO<sub>2</sub> was quantified using a non-dispersive infrared detector. The signal was compared against that of the standards to determine the TOC concentration, expressed in mg C/L.

#### 4.4.3 Chemical Oxygen Demand

The COD, which assesses the level of organic pollution in wastewater or natural waters, was measured according to the AFNOR T90-101 standard. In COD test tubes, 3 mL of acidic solution (sulfuric acid containing silver sulfate at 6.6 g/L), 0.1 g of mercury sulfate (HgSO<sub>4</sub>), 2 mL of the leachate diluted to a factor of 1:500, and 1 mL of potassium dichromate solution (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>: 2.4518 g/L) were mixed. Distilled water was used as the blank. The tubes were then hermetically sealed and placed in a heating block (WTW CR 2200) at 148 °C for 2 hours. Afterward, they were allowed to cool to room temperature.

The COD value was determined using a calibration curve by comparing the absorbance of the blank with that of the sample, indicating the amount of oxidant consumed. The COD concentration (in mg/L) was calculated using the following formula:

$$COD (mg/L) = [K_2Cr_2O_7](initial) - [K_2Cr_2O_7](residual)$$

#### 4.4.4 pH Measurement

The pH of the leachate was measured using a pH meter at the beginning and end of the treatment. Measurements were performed directly on the samples at each of these two time points.

# Results and Discussion

This section presents and interprets the results obtained throughout the study, which is built on two main components. The first focuses on the valorization of agricultural vegetable waste through the production and characterization of activated carbon. The second examines the treatment of landfill leachate collected from the Landfill of Batna, using three different systems: physicochemical (activated carbon), biological (indigenous bacteria isolated from the leachate), and hybrid (activated carbon encapsulated with bacteria). To evaluate the performance of these systems, a series of physicochemical and spectroscopic analyses were carried out. The results are structured accordingly: beginning with the characterization of the precursor biomass and the activated carbon produced from it, followed by a detailed evaluation of each treatment system in terms of pollutant removal efficiency and microbial activity, with an emphasis on comparative performance and observable transformations within the leachate.

## 1. Characterization of the Biomass

The suitability of a biomass for conversion into activated carbon depends on a range of physicochemical properties that influence its behavior during activation and its performance as an adsorbent. In this study, green waste composed of onion and orange residues was characterized through key parameters including electrical conductivity, pH, organic matter and carbon content, and nitrogen content. These indicators provide insight into the mineral composition, acidity, organic richness, and nitrogenous compounds present in the biomass, each of which plays a critical role in determining pore development, surface chemistry, and overall adsorptive capacity of the resulting activated carbon.

The measured parameters and their corresponding values are presented in Table 9:

Table 9. Physicochemical Properties of the Biomass

Parameter	Value
Electrical Conductivity ( $\mu\text{S}/\text{cm}$ )	1,764.5
pH	4.271
Organic Matter Content (%)	93.276
Carbon Content (%)	46.638
Total Nitrogen Content (%)	1.296



## 1.1 Electrical Conductivity

EC reflects the concentration of soluble ions released from biomass into water and is a key indicator of mineral content, which can significantly influence both thermal activation behavior and the adsorption performance of the resulting activated carbon (Foo & Hameed, 2009). In this study, the biomass filtrate exhibited an EC of **1,764.5  $\mu\text{S}/\text{cm}$** .

This relatively high EC value suggests that the precursor biomass is rich in soluble minerals—such as calcium, magnesium, potassium, and sodium—which can facilitate pore formation during carbonization by acting as natural activating agents. For instance, Adinaveen et al. (2016) found EC values of cellulose-derived carbonized materials reaching several thousands of  $\mu\text{S}/\text{cm}$ , with increased EC correlating to enhanced porosity and conductivity. Additionally, Baby and Girish (2010) observed a clear linear relationship between the electrical conductivity of spice extracts and their ash content, reinforcing EC as a viable proxy for mineral loading. Finally, Bedia et al. (2018) emphasized in their comprehensive review that mineral matter in lignocellulosic feedstocks plays a decisive role in both thermal decomposition patterns and pore structure development during pyrolysis.

Although chemical activation was performed using phosphoric acid, the high mineral content indicated by the elevated EC suggests that some degree of inherent activation may have occurred during carbonization (Adinaveen et al., 2016; Bedia et al., 2018). This opens up the possibility of optimizing future procedures by adjusting the acid concentration, potentially reducing chemical usage and associated costs (Foo & Hameed, 2009). Moreover, since rinsing was carried out post-activation, the risk of residual soluble ions releasing into treated water may be minimized; however, the initial EC value still highlights the importance of ensuring thorough washing and considering additional stabilization steps (Baby & Girish, 2010). Overall, the EC parameter provides a useful baseline for comparing biomass feedstocks and for refining activation protocols to tailor surface and structural characteristics of the final adsorbent (Ioannidou & Zabaniotou, 2007; Yahya et al., 2015).

## 1.2 pH

The pH of a biomass-water extract reflects the balance between acidic and basic functional groups present in the material, often influenced by organic acids, phenolic compounds, and ash content. It serves as a useful indicator of the chemical environment that may affect both the activation process and the adsorption behavior of the resulting carbon (Ioannidou &

Zabaniotou, 2007; Yahya et al., 2015). In this study, the biomass extract exhibited a pH of **4.271**, indicating moderately acidic characteristics.

This acidity is consistent with the nature of the precursor material-green waste derived from onion and orange residues- which are known to be rich in organic acids such as citric and malic acid (Siles López et al., 2010). A similar acidic pH range (around 4–5) was reported for fruit and vegetable waste biomass in studies assessing feedstock suitability for carbonization (Yahya et al., 2015).

The acidic pH can play a dual role during activation. On one hand, it may enhance chemical activation with phosphoric acid by facilitating bond cleavage and promoting dehydration, leading to better pore development (Foo & Hameed, 2009). On the other hand, residual acidic components could impact adsorbent surface chemistry, potentially favoring the removal of basic pollutants but hindering interaction with acidic species (Bedia et al., 2018). Moreover, a low initial pH can also inform the need for post-treatment neutralization or washing, especially when the final carbon is intended for water purification.

Taken together, these observations confirm the chemical signature of the green waste biomass and serve as a useful indicator of its compatibility with activation protocols and the likely surface behavior of the final adsorbent product.

### **1.3 Organic Matter and Carbon Content**

The organic matter (OM) content of a biomass is a fundamental parameter for evaluating its suitability as a precursor for activated carbon production, as it reflects the proportion of volatile, combustible material capable of contributing to char formation (Ioannidou & Zabaniotou, 2007; Yahya et al., 2015). In this study, the green waste biomass exhibited a high OM content of **93.276%**, resulting in an estimated carbon content of **46.638%** using the IPCC standard carbon fraction (0.5). These values indicate a highly organic and carbon-rich material, which is favorable for producing porous carbonaceous structures upon thermal treatment.

Comparable OM values have been reported in related studies. Yahya et al. (2015) highlighted OM levels exceeding 85% in vegetable-based residues, while Siles López et al. (2010) emphasized the particularly high organic content of orange peel biomass, underscoring its viability for carbonization. The combination of high OM and carbon content in this biomass suggests strong potential for achieving good yields and effective porosity development in activated carbon production.

The elevated OM level is advantageous, as it ensures a greater mass of volatile matter available for decomposition during thermal treatment, thereby aiding pore formation (Ioannidou & Zabaniotou, 2007). In addition, the relatively high carbon fraction provides a favorable foundation for generating high surface area materials suitable for adsorption applications.

Taken together, these results confirm that the selected green waste biomass offers excellent potential as a precursor for activated carbon, both in terms of carbon yield and structure-forming capacity during pyrolysis or chemical activation.

#### **1.4 Nitrogen Content**

The nitrogen content of biomass reflects its level of protein-rich and nitrogenous organic compounds, which can influence the surface chemistry of activated carbon and its adsorption properties (Ioannidou & Zabaniotou, 2007; Bedia et al., 2018). In this study, the Kjeldahl method determined a nitrogen content of **1.296%** for the green waste biomass. Comparable nitrogen contents have been reported in similar studies. Siles López et al. (2010) observed nitrogen levels around 1–2% in fruit and vegetable residues, while Ioannidou and Zabaniotou (2007) reported similar values for agricultural biomasses intended for carbonization.

Moderate nitrogen levels offer potential benefits: nitrogen functional groups may enhance the basicity and adsorption affinity of carbon surfaces, improving interactions with acidic pollutants (Bedia et al., 2018; Ioannidou & Zabaniotou, 2007). Moreover, research on onion-derived activated carbon demonstrates that nitrogen can be naturally retained during thermal treatment, introducing active functional groups even without deliberate doping (Musyoka et al., 2019). However, excessively high nitrogen in the precursor can produce unwanted volatile nitrogenous gases during activation (e.g., NO<sub>x</sub>), which may reduce carbon yield or complicate process control (Yahya et al., 2015).

On balance, the 1.296% nitrogen content observed here appears advantageous, providing sufficient opportunities for nitrogen-doped surface chemistry while avoiding significant yield losses or safety issues associated with higher nitrogen levels. This nitrogen profile contributes positively to the material's suitability for adsorption applications, especially those benefiting from nitrogen-functionalized surfaces.

## **2. Characterization of the Activated Carbon**

Following the activation process, the physicochemical properties of the resulting carbon material were analyzed to evaluate its suitability for leachate treatment. Key characterization

techniques, including point of zero charge ( $\text{pH}_{\text{pzc}}$ ), Fourier Transform Infrared Spectroscopy (FTIR), and Raman spectroscopy, were employed to assess surface chemistry, functional groups, and structural order. These analyses provide critical insights into the adsorptive behavior and reactivity of the activated carbon, helping to determine its effectiveness in removing pollutants from complex effluents.

## 2.1 pH at the Point of Zero Charge

The  $\text{pH}_{\text{pzc}}$  is the pH at which the surface of an adsorbent has no net electrical charge. Below this point, the surface is positively charged, favoring anion adsorption; above it, the surface becomes negatively charged, which promotes the adsorption of cations (Mestre et al., 2009).

In this study, the  $\text{pH}_{\text{pzc}}$  of the activated carbon produced from onion and orange residues was found to be **7.2**, as determined by the salt addition method (Fig. 18). The value corresponds to the intersection of the  $\text{pH}_{\text{final}}$  vs.  $\text{pH}_{\text{initial}}$  curve with the bisector line.

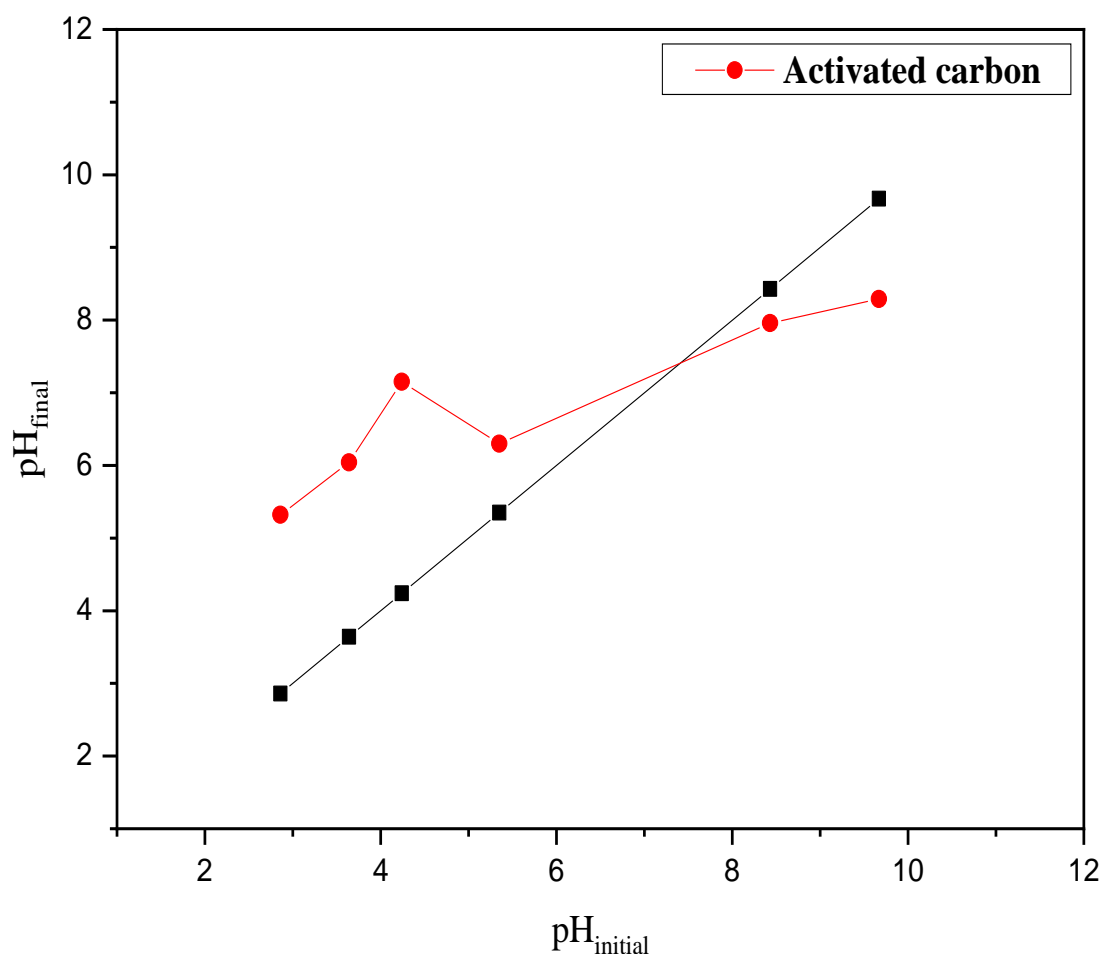


Fig. 18. Determination of the pH at the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of the activated carbon using the salt addition method. The intersection with the bisector line indicates  $\text{pH}_{\text{pzc}} = 7.2$ . (Graph plotted using OriginPro 2018).

This result is consistent with values reported for activated carbons derived from similar lignocellulosic biomasses. For instance, citrus peel-based activated carbon exhibited a  $\text{pH}_{\text{pzc}}$  around 6.9 (Foo & Hameed, 2009), which is comparable to the near-neutral value observed in this study. Such values are typical of green waste-derived carbons and reflect a surface chemistry rich in oxygen-containing functional groups, such as carboxylic and phenolic groups, characteristic of lignocellulosic precursors.

Since the leachate targeted for treatment has a pH of 8.26, the surface of the activated carbon will be negatively charged under operating conditions. This enhances its affinity for cationic pollutants, including metal ions and ammonium, which are commonly found in landfill leachates (Kurniawan et al., 2006). On the other hand, the removal of anionic species may be less efficient under these pH conditions, a limitation that was addressed in this study through the implementation of biological and hybrid treatment systems.

## **2.2 Fourier Transform Infrared Spectroscopy**

FTIR analysis was conducted on both the precursor biomass and the activated carbon to assess the chemical transformations induced by the two-step activation process. This process involved impregnation with phosphoric acid followed by thermal carbonization, both of which contribute significantly to surface functionalization (Mohammed et al., 2015). The corresponding spectra are shown in Fig. 19.

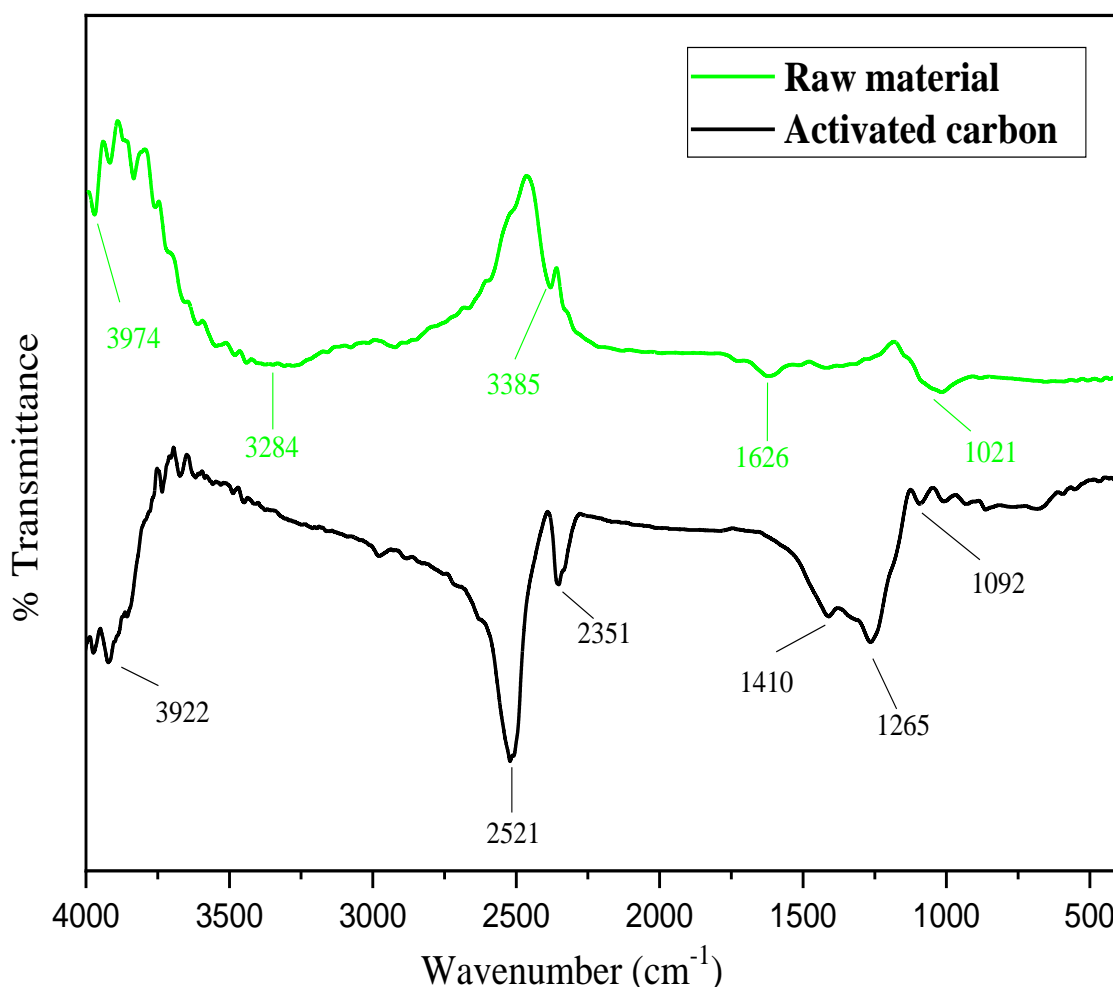


Fig. 19. FTIR spectra of the precursor biomass (green) and the activated carbon (black). Key transformations in surface functional groups are observed following activation. (Graph plotted using OriginPro 2018).

A small band near  $3922\text{ cm}^{-1}$ , likely corresponding to O–H stretching overtones or combination bands, was observed in both spectra. The slight reduction in its intensity after activation reflects the loss of free hydroxyl groups and the structural reorganization of the biomass matrix into a more condensed aromatic carbon framework (Maneerung et al., 2015).

In the raw biomass spectrum (green), a broad absorption band in the  $3284\text{--}3385\text{ cm}^{-1}$  region is attributed to O–H stretching vibrations of hydroxyl groups, typically found in cellulose, hemicellulose, and lignin (Maneerung et al., 2015). These peaks are significantly reduced in the activated carbon (black), indicating dehydration and the thermal decomposition of hydroxyl-containing structures during activation.

The distinct peak at  $1626\text{ cm}^{-1}$  in the raw biomass, assigned to C=O stretching of carbonyl or carboxylic acid groups, shifts and weakens after activation, appearing as a broader band near  $1410\text{ cm}^{-1}$ . This shift suggests the conversion of unstable carboxylic groups into more stable

aromatic carbon frameworks, a change commonly observed in phosphoric acid-assisted pyrolysis (Dechapanya & Khamwichit, 2023).

The disappearance of the band at  $1021\text{ cm}^{-1}$ , attributed to C–O stretching in polysaccharides, further confirms the decomposition of hemicellulose and cellulose during thermal treatment. Meanwhile, the emergence of new bands at  $1265$  and  $1092\text{ cm}^{-1}$  indicates the formation of ether and phenolic C–O bonds, likely introduced or stabilized by the presence of phosphoric acid, which is known to facilitate crosslinking and enhance the formation of stable phosphate esters (Ioannidou & Zabaniotou, 2007).

A weak peak at  $2521\text{ cm}^{-1}$ , observed only in the activated carbon spectrum, may correspond to C–S or P–H vibrations, possibly originating from sulfur-rich compounds in onion residues or phosphorus retained from the chemical activation step. These groups are known to enhance the affinity of activated carbon for heavy metals via complexation and organic leachate contaminants through hydrogen bonding (Phiri et al., 2024).

These spectral modifications are consistent with findings from similar biomass studies. Maneerung et al. (2015) and Liu et al. (2014) observed comparable reductions in O–H and C=O bands after activating lignocellulosic materials, along with the emergence of new oxygenated functionalities favorable for adsorption. Phosphoric acid activation, in particular, has been reported to generate surface groups that enhance adsorption capacity for both organic micropollutants and inorganic ions commonly found in landfill leachate (Dechapanya & Khamwichit, 2023).

Overall, the transformation of functional groups during activation improves the chemical affinity of the carbon surface for polar compounds and heavy metals. The emergence of acidic oxygen-containing groups and possibly sulfur functionalities provides reactive sites for adsorption of dyes, phenols, and toxic metal ions, making the material highly suitable for treating complex effluents such as landfill leachate.

### **2.3 Raman Spectroscopy Analysis**

Raman spectroscopy is widely used to assess the degree of structural order in carbonaceous materials. It provides insights into the graphitic or disordered nature of carbon, which strongly influences its adsorption behavior, particularly toward organic pollutants in complex effluents such as landfill leachate (Ferrari & Robertson, 2000; Characterization of carbon materials with Raman spectroscopy, 2023).

The Raman spectrum of the activated carbon (Fig. 20) exhibited two prominent peaks: the D band at  $1350\text{ cm}^{-1}$ , and the G band at  $1598\text{ cm}^{-1}$ . The D band is associated with disordered carbon structures and lattice defects, typically arising from edges, functional groups, or vacancies. In contrast, the G band corresponds to the  $E_{2g}$  vibrational mode of  $sp^2$ -bonded carbon atoms in graphitic domains, indicating the presence of ordered graphitic structures (Ferrari & Robertson, 2000; Characterization of carbon materials with Raman spectroscopy, 2023).

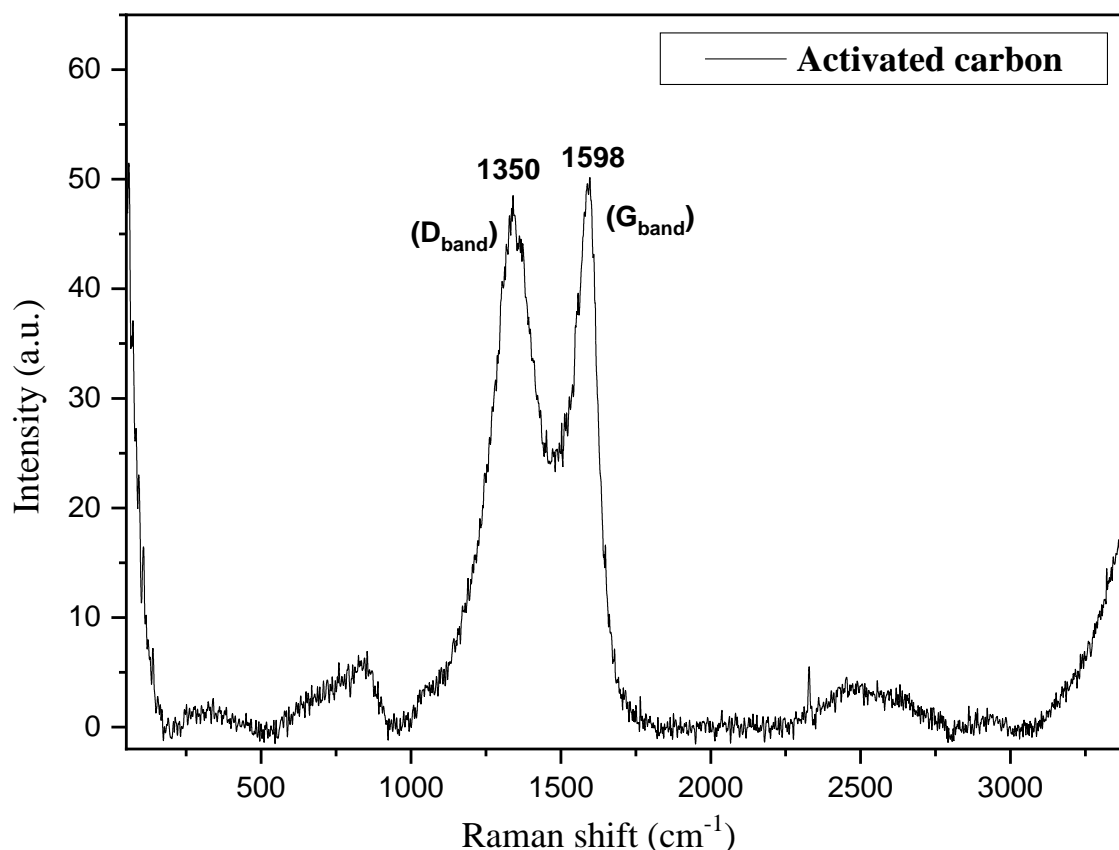


Fig. 20. Raman spectrum of the activated carbon showing D and G bands, indicating partial structural disorder. (Graph plotted using OriginPro 2018).

The observed D and G bands are characteristic of partially graphitized activated carbon. The slight upshift of the G band to  $1598\text{ cm}^{-1}$  (relative to the ideal graphite position near  $1580\text{ cm}^{-1}$ ) suggests a moderate level of disorder introduced during chemical activation with  $H_3PO_4$  and thermal treatment. The intensity of the D band indicates structural defects, which are commonly linked to the formation of functional groups and porous structures that enhance adsorption of pollutants (Yerdauletov et al., 2023).



### **ID/IG Ratio**

The ID/IG ratio serves as a key indicator of the degree of structural disorder in carbon materials: higher values indicate increased defect density, while lower values are associated with more ordered, graphitic structures (Ferrari & Robertson, 2000). Based on the measured Raman intensities, the ratio was calculated as follows:

Peak intensity values:

$$ID = 45.09$$

$$IG = 49.57$$

Calculated ratio:

$$ID/IG = \frac{45.09}{49.57} = 0.91$$

This value reflects a moderately disordered carbon structure, with partial graphitic ordering retained. Such a hybrid structure is considered ideal for adsorption applications, offering both surface reactivity and material stability. A similar ID/IG value of 0.86 has been reported by Yerdauletov et al. (2023) for activated carbon derived from lignocellulosic biomass (rice husk), supporting the relevance of the activation approach used in this work for treating leachate.

### **3. Leachate Treatment Systems**

To evaluate the performance of the prepared activated carbon and the encapsulated bacterial consortium, the leachate underwent three sequential treatments: physicochemical adsorption, biological treatment, and a hybrid approach combining both. Each process was assessed using key indicators like Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) to determine the extent of organic pollutant removal. The following subsections present and discuss the results of each treatment pathway, highlighting their individual efficiencies as well as the synergistic potential of the combined system in addressing the complex composition of landfill leachate.

### **3.1 Physicochemical Treatment (Adsorption)**

#### **3.1.1 Total organic carbon**

TOC provides a reliable measure of the organic pollutant load in leachate, particularly for assessing the effectiveness of adsorption-based treatment processes. High TOC values typically reflect the presence of diverse organic contaminants, including humic substances, volatile fatty acids, and other leachable carbon-based compounds originating from decomposing waste (Renou et al., 2008).

As shown in Fig. 21, a substantial decline in TOC concentration occurred over time during the physicochemical treatment process using activated carbon. The initial value, 634.064 ppm, dropped rapidly during the first stage of contact and gradually stabilized around 130 ppm after 300 minutes. This kinetic profile reflects a fast initial adsorption phase, likely driven by the high availability of active surface sites, followed by a slower diffusion-limited phase once surface saturation began. Similar two-phase adsorption kinetics have been observed in leachate studies using both granular activated carbon and biochar (Kulikowska et al., 2016). The observed plateau suggests the system approached adsorption equilibrium, with the remaining TOC attributed to recalcitrant organic compounds or limited access to internal pores.

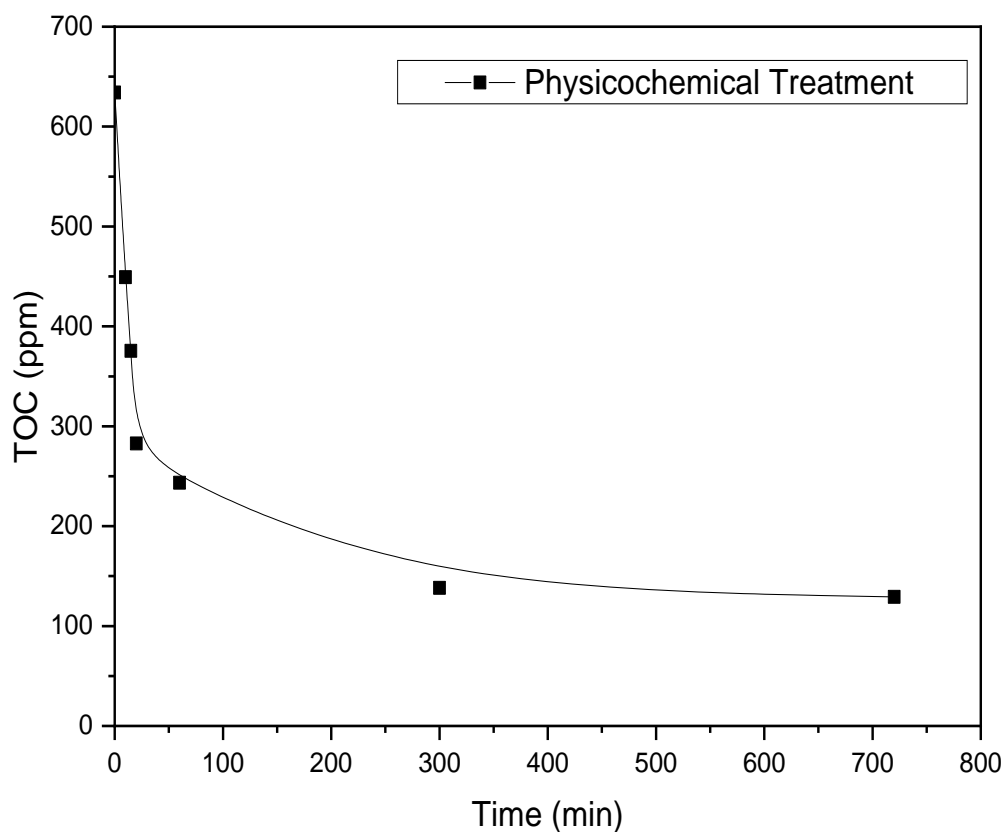


Fig. 21. Evolution of TOC concentration during physicochemical treatment of 1:20 diluted leachate. (Graph plotted using OriginPro 2018).

The effectiveness of the treatment is further supported by Fig. 22, which clearly shows a sharp difference in TOC levels before and after treatment. The final TOC value confirms the strong removal of dissolved organics, indicating efficient surface interactions between the leachate constituents and the activated carbon. These findings are consistent with prior work demonstrating the removal of UV-absorbing organics and TOC using activated carbon in real landfill leachate (Foo & Hameed, 2009).

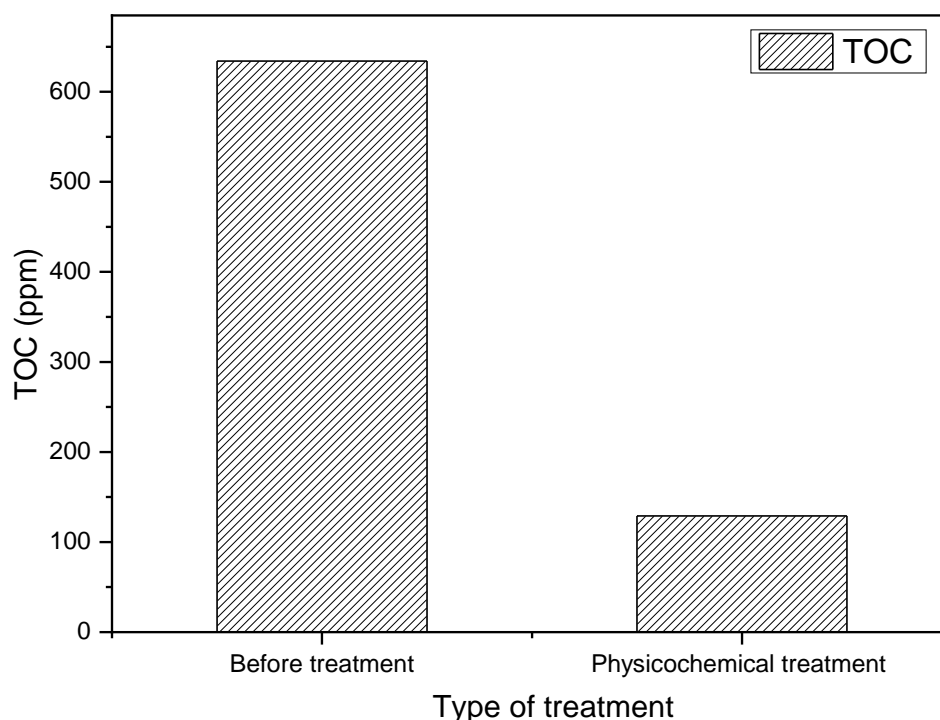


Fig. 22. Comparison of TOC concentration in 1:20 diluted leachate before and after physicochemical treatment. (Graph plotted using OriginPro 2018).

The rapid decline in TOC also reflects the suitability of the prepared carbon for fast adsorption, which is advantageous in practical applications where shorter contact times are preferred. Given the nature of the biomass precursor (green waste), it is likely that both micro- and mesoporous structures contributed to the observed removal, enabling the capture of a wide range of organic molecules, as similarly observed in biochar systems (Inyang et al., 2016).

### 3.1.2 Chemical Oxygen Demand

COD reflects the overall concentration of organic compounds in wastewater and is commonly used to assess the effectiveness of treatment methods (Kjeldsen et al., 2002). In adsorption processes, a decrease in COD indicates the retention of organic molecules on the surface or within the pores of the adsorbent.

In this study, the COD of the diluted raw leachate was initially 99792.44 mg O<sub>2</sub>/L, a value characteristic of highly loaded landfill effluents. After treatment with the prepared activated carbon, COD dropped significantly to 21166.63 mg O<sub>2</sub>/L (Fig. 23), achieving a removal efficiency of 78.78%.

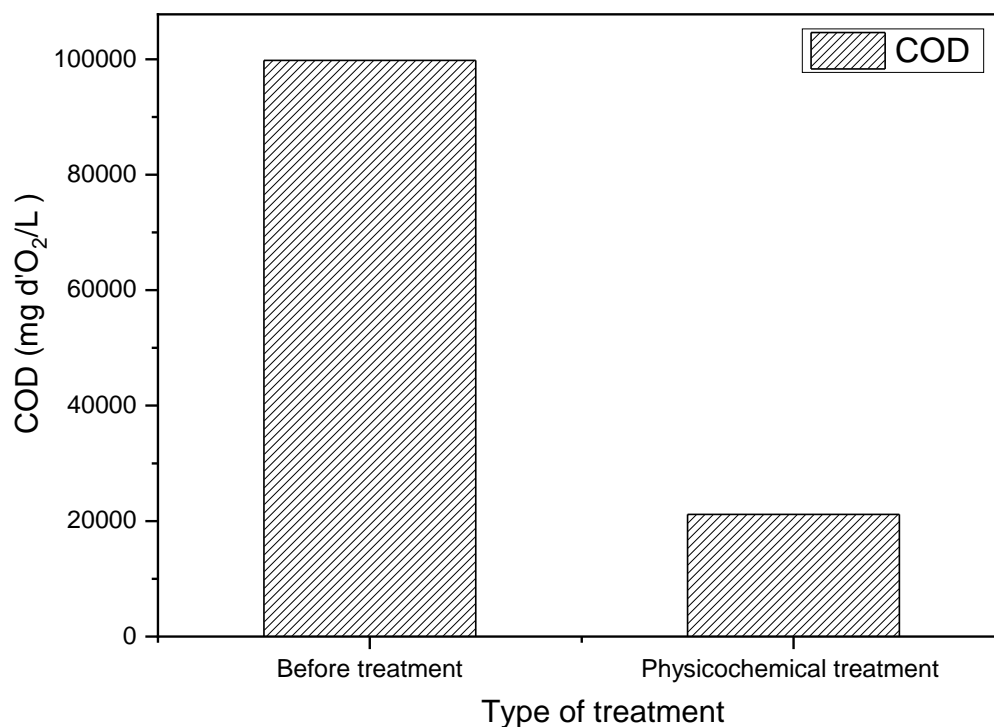


Fig. 23. Evolution of COD concentration before and after physicochemical treatment of leachate (diluted 1:20). (Graph plotted using OriginPro 2018).

This strong performance confirms the adsorption capacity of the carbon produced from green waste, particularly due to its porosity and the presence of surface functional groups developed during phosphoric acid activation. Similar COD reductions have been reported using other bio-based adsorbents; Kalderis et al. (2008) obtained over 70% removal using activated carbon made from rice husk, supporting the effectiveness of low-cost, biomass-based materials in treating high-strength effluents.

Despite the substantial decrease, the remaining COD suggests the persistence of refractory organics—such as humic substances or small polar compounds—that are less easily adsorbed (Renou et al., 2008). This highlights both the efficiency and the limitations of adsorption as a standalone treatment, particularly when dealing with complex leachate matrices. Nonetheless, the results demonstrate that activated carbon derived from green waste is an effective and sustainable option for significantly reducing the organic load of landfill leachate.

## 3.2 Biological Treatment

### 3.2.1 Total Organic Carbon

The evolution of TOC during biological treatment provides a direct insight into the microbial degradation of organic matter present in the leachate. In this case, a bacterial consortium previously isolated from the same leachate was used to treat the effluent. The progression of TOC over time (Fig. 24) followed a pattern typical of microbial growth (Fig. 25), where no significant removal was observed during the initial 12 hours. This lag phase is expected, as the bacteria undergo adaptation to the complex leachate matrix and begin metabolic activation.

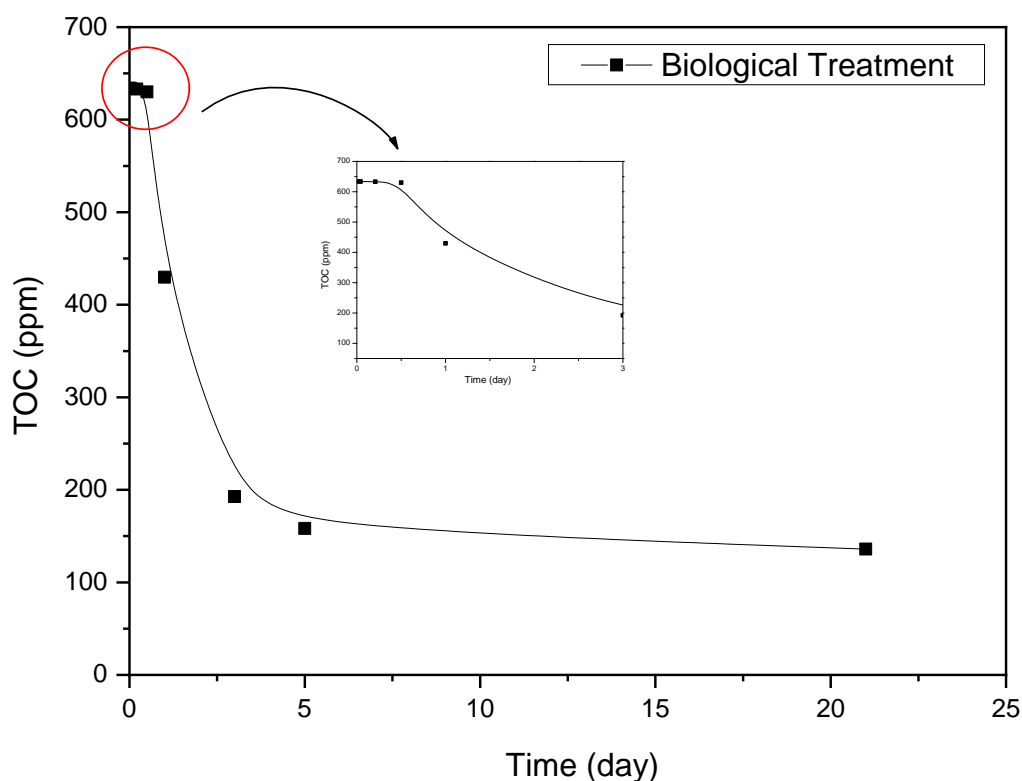


Fig. 24. Kinetics of TOC removal during biological treatment of leachate (diluted 1:20). (Graph plotted using OriginPro 2018).

A marked decline in TOC was observed between 12 hours and day 3, reflecting the exponential phase of microbial growth and the consortium's heightened metabolic activity. During this phase, easily degradable organic compounds were rapidly consumed, leading to a marked decline in carbon content. After day 3, the decline in TOC slowed, marking the onset of the stationary phase. By day 5, the majority of biodegradable compounds were consumed, and TOC levels plateaued, reaching a steady value of 135.92 ppm by day 21. This pattern confirms that

the microbial population successfully utilized the available organic matter, but that a residual fraction of more recalcitrant compounds remained, limiting further degradation.

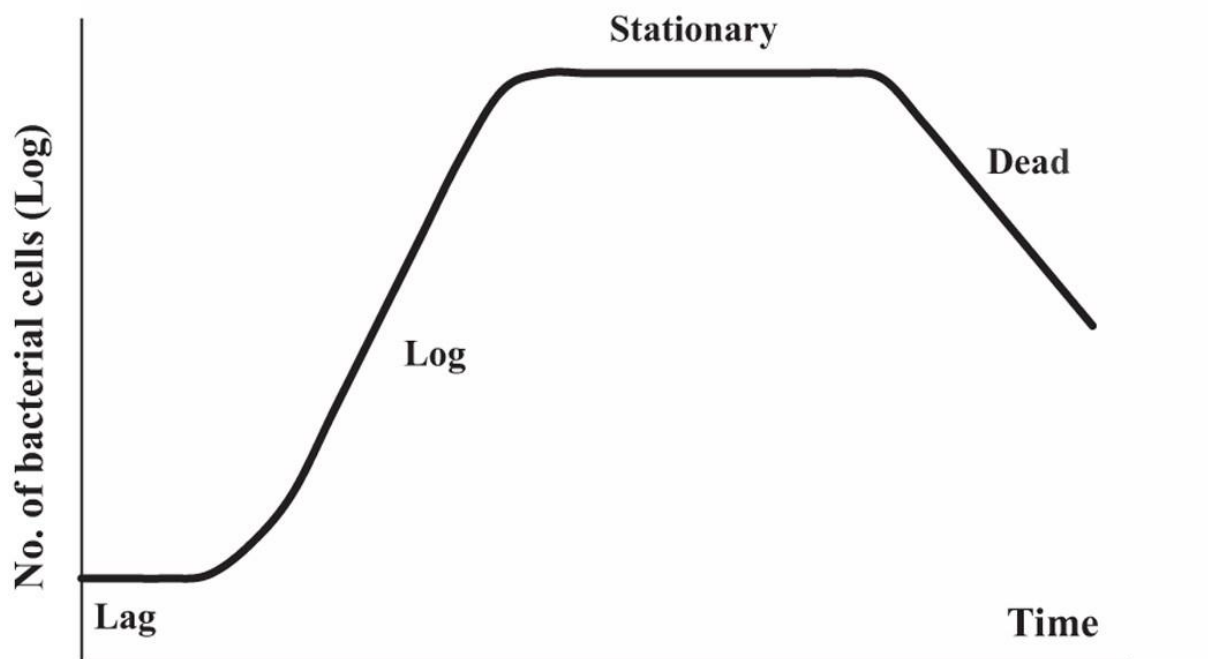


Fig. 25. Graphic representation of typical bacterial growth curve in culture medium (Wang et al., 2015).

The overall efficiency of the treatment is clearly demonstrated in Fig. 26, where TOC dropped from 634.064 ppm to 135.92 ppm, corresponding to a removal efficiency of 78.57%. This performance aligns with values commonly reported for biological treatment of landfill leachate. Dhamsaniya et al. (2023), for example, noted that adapted microbial systems can achieve 70–90% removal of organic contaminants, depending on operational conditions and microbial acclimation. Such results reinforce the effectiveness of employing indigenous bacterial consortia for the remediation of high-strength effluents like landfill leachate.

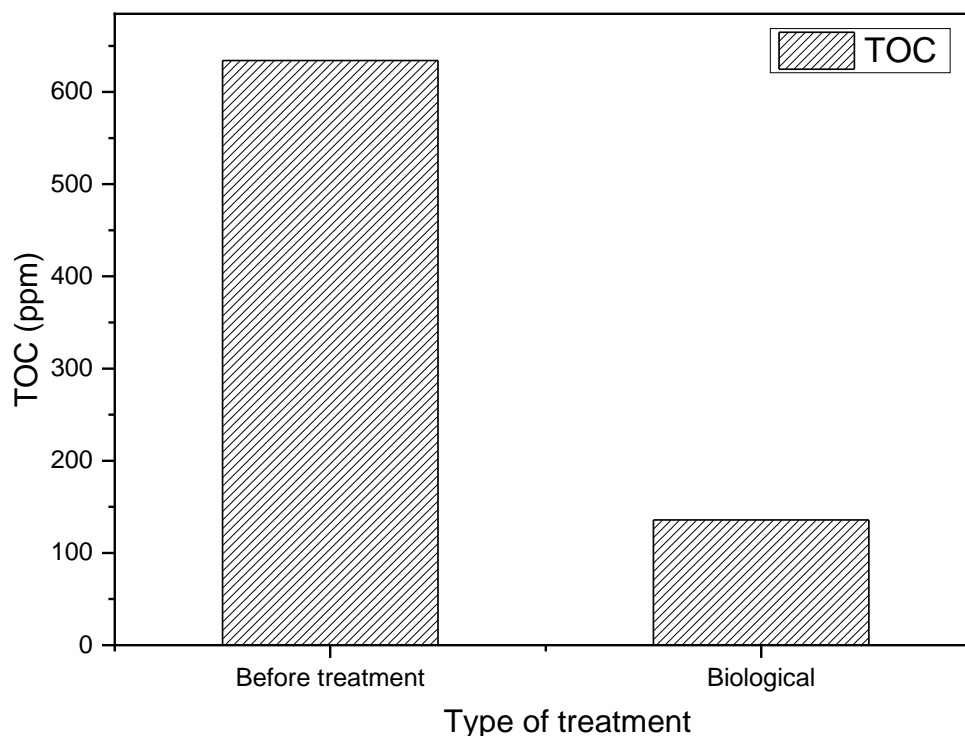


Fig. 26. Comparison of TOC concentration before and after 21 days of biological treatment of leachate (diluted 1:20). (Graph plotted using OriginPro 2018).

The kinetic behavior observed here reinforces the importance of residence time in biological systems. Although some refractory organics persist beyond treatment, the sharp decrease during the exponential phase underscores the high biodegradative capacity of the adapted bacterial community (Kurniawan et al., 2006). This confirms the relevance of biologically-based approaches as a key component of sustainable leachate management.

### 3.2.2 Chemical Oxygen Demand

COD reflects the total concentration of organic compounds that can be chemically oxidized, including both biodegradable and non-biodegradable fractions. In biological treatment processes, a reduction in COD is used to evaluate the metabolic activity of microorganisms and their ability to degrade organic pollutants (Kjeldsen et al., 2002).

In this study, a native bacterial consortium previously isolated from the same leachate was employed to treat the effluent. As illustrated in Fig. 27, the initial COD concentration was 99,792.44 mg O<sub>2</sub>/L, which decreased to 30,644.41 mg O<sub>2</sub>/L after treatment, corresponding to a removal efficiency of 69.29%. This decrease shows that the consortium can break down much of the organic matter, especially when its metabolic activity is highest. The results match those



found in previous research on biological treatment of leachate. According to Cecen and Aktas (2001), COD removal efficiencies between 60% and 90% are typical when using acclimated microbial populations under optimized aerobic or anaerobic conditions. Similarly, Klimiuk and Kulikowska (2005) reported COD reductions exceeding 70% in leachates treated with enriched bacterial cultures under batch conditions.

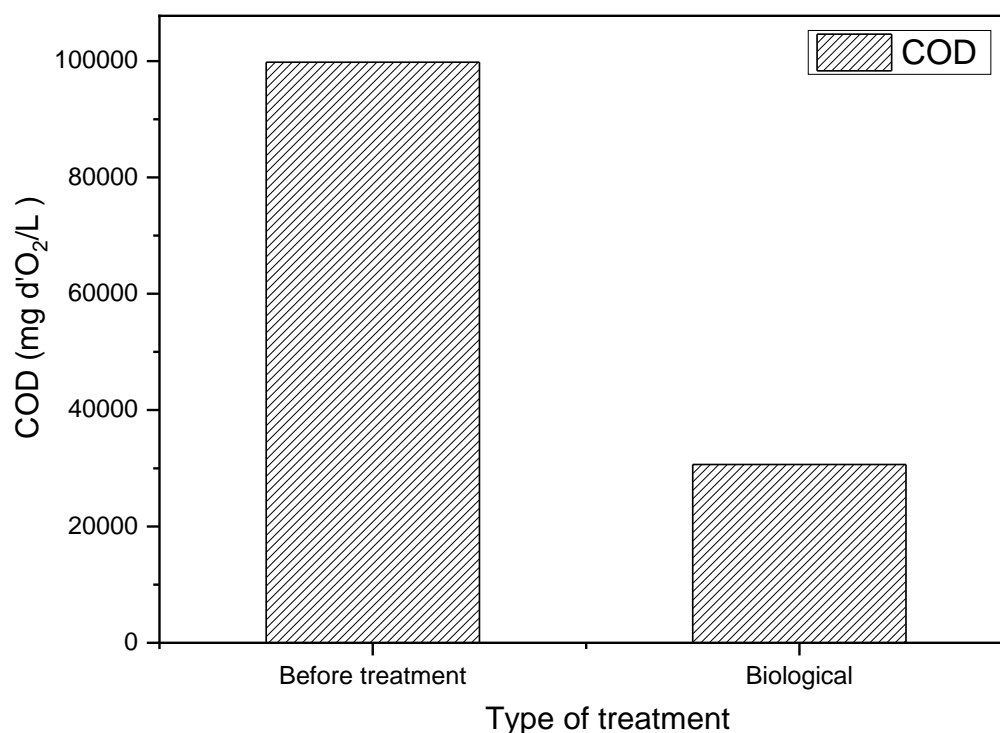


Fig. 27. Comparison of COD concentration before and after biological treatment of leachate (diluted 1:20). (Graph plotted using OriginPro 2018).

The remaining COD likely corresponds to persistent, recalcitrant organics that resist microbial degradation, such as humic substances, aromatic compounds, and other high-molecular-weight fractions (Kurniawan et al., 2006). These compounds are poorly metabolized by conventional microbial communities and may require complementary treatments, such as adsorption, for complete removal. Nonetheless, the results highlight the effectiveness of using an adapted indigenous consortium to reduce the biodegradable fraction of leachate and improve its treatability in a cost-effective and environmentally sustainable manner.

### 3.3 Hybrid Treatment

#### 3.3.1 Total organic carbon

The performance of the hybrid system, using activated carbon encapsulated with a native bacterial consortium, was evaluated through the evolution of TOC over 21 days. As shown in Fig. 28, the initial TOC concentration of 634.064 ppm decreased sharply within the first 12 hours, reaching 115.98 ppm. This rapid drop is attributed to the immediate adsorption of organic compounds onto the available surface area and within the porous structure of the activated carbon. At this stage, the system behaves predominantly like a physical adsorbent, with the carbon capturing readily accessible and low-molecular-weight organics from the leachate (Foo & Hameed, 2010).

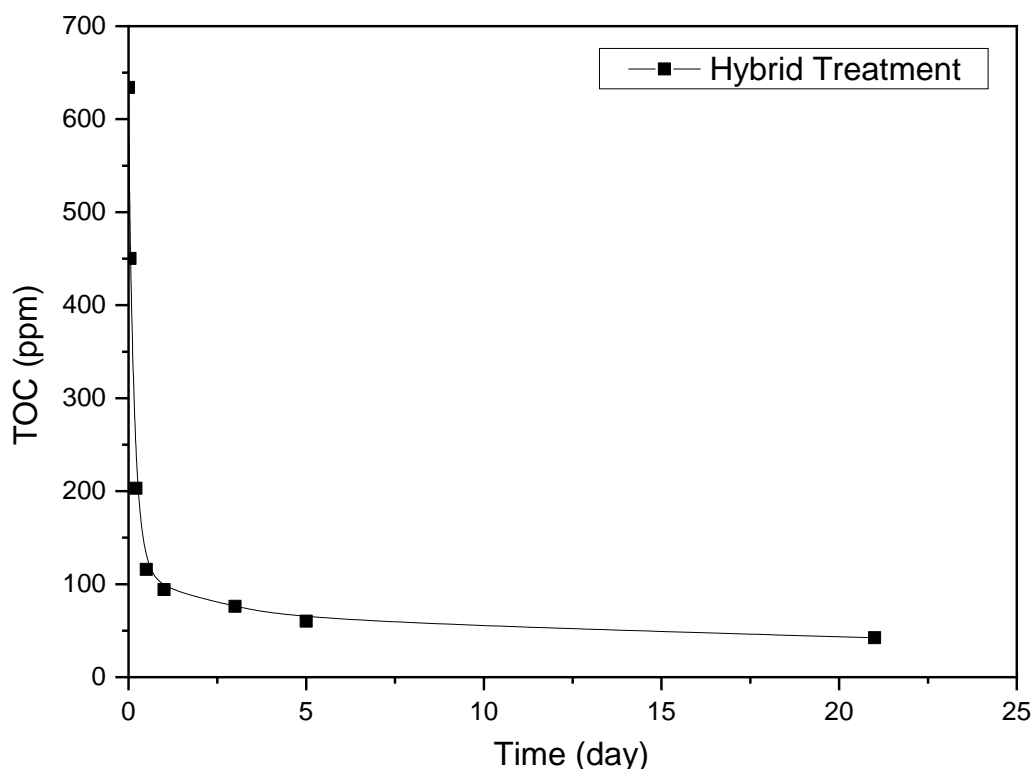


Fig. 28. Kinetics of TOC removal during hybrid treatment of leachate (diluted 1:20). (Graph plotted using OriginPro 2018).

Between 12 hours and day 5, the TOC continued to decline more gradually, reaching 60.19 ppm. This phase likely reflects the onset of biological activity, during which the immobilized bacteria adapt to the leachate environment and begin degrading adsorbed or residual dissolved organics. By day 21, the TOC approached a plateau at 42.4 ppm, indicating a stabilization phase.

where only slowly biodegradable or recalcitrant compounds remained. The progressive removal trend suggests that microbial degradation not only complements adsorption but may also regenerate some adsorption capacity by breaking down previously retained substances and reopening pore spaces (Gao et al., 2010). The final result is further illustrated in Fig. 29, which shows a total TOC reduction from 634.064 ppm to 42.4 ppm, corresponding to an overall removal efficiency of 93.31%. This performance significantly exceeds that of adsorption or biological treatment alone, highlighting the synergistic effect achieved by combining both processes. Similar findings were reported by Rivera Utrilla et al. (2013), who demonstrated improved TOC removal when activated carbon was coupled with microbial communities, attributing the effect to immediate adsorption followed by sustained biodegradation.

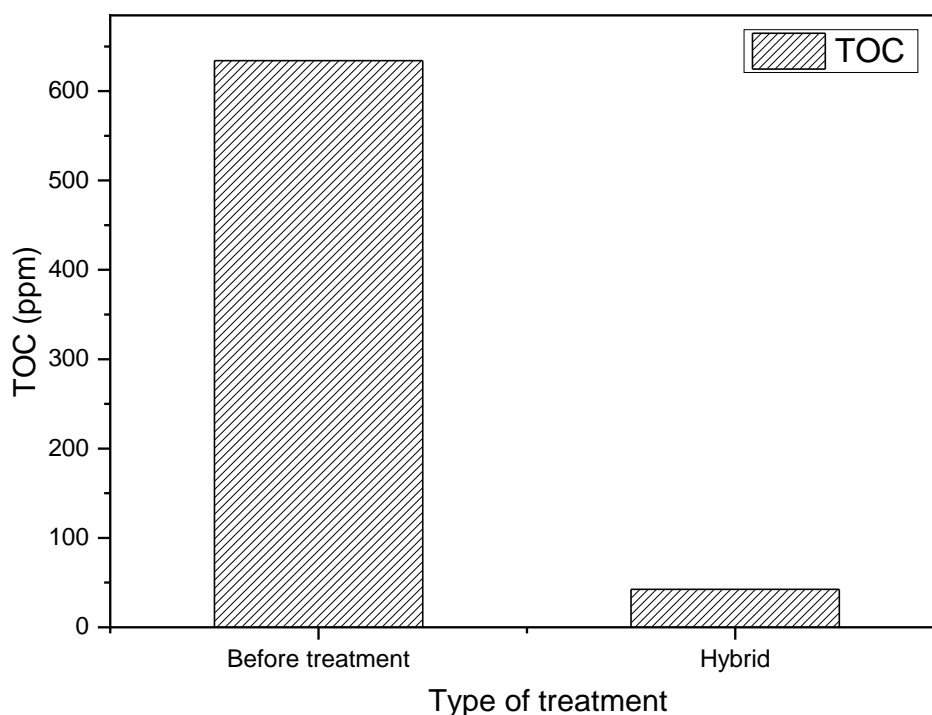


Fig. 29. Comparison of TOC concentration before (620 ppm) and after (40 ppm) 21 days of hybrid treatment. (Graph plotted using OriginPro 2018).

This dual-mechanism behavior confirms the potential of hybrid systems for treating high-strength leachates, especially those with both easily adsorbable and biodegradable organic fractions. The initial rapid adsorption phase ensures early reduction in pollutant concentration, while the longer-term biological phase extends the system's overall effectiveness by addressing residual organics that are otherwise poorly removed by either process alone.

### 3.3.2 Chemical Oxygen Demand

COD is a key indicator of the total organic load present in wastewater, including both biodegradable and non-biodegradable compounds. The hybrid treatment system achieved a substantial COD reduction, as shown in Fig. 30. The initial COD concentration of 99792.44 mg O<sub>2</sub>/L was reduced to 9408.55 mg O<sub>2</sub>/L after 21 days of treatment, corresponding to a removal efficiency of 90.57%.

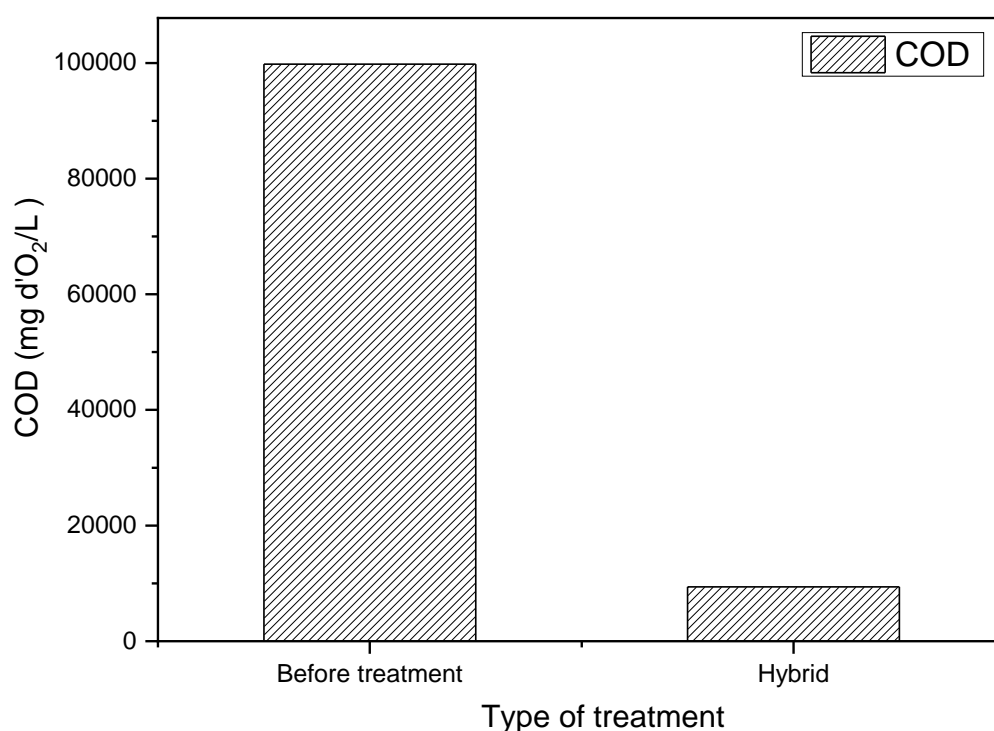


Fig. 30. COD concentration before and after hybrid treatment of leachate (diluted 1:20).  
(Graph plotted using OriginPro 2018).

This significant removal reflects the dual action of the hybrid system. In the early stages, activated carbon rapidly adsorbs readily available organic pollutants, reducing COD levels by physically trapping them in its porous matrix (Foo & Hameed, 2010). Over time, the immobilized bacterial consortium becomes metabolically active, degrading both dissolved and adsorbed organic matter. This biological degradation not only contributes directly to COD reduction but can also free up blocked adsorption sites by breaking down previously retained compounds, thereby enhancing the overall treatment efficiency (Rivera-Utrilla et al., 2013).

Similar results have been reported in the literature. For example, Serrano et al. (2010) and Alvarino et al. (2016) achieved COD removal efficiencies of up to 95% and 98%, respectively,

when treating synthetic wastewater with characteristics comparable to landfill leachate using hybrid systems that combined activated carbon with membrane bioreactor (MBR) technology, a biological treatment process that integrates suspended microbial activity with membrane filtration.

These findings support the effectiveness of hybrid systems in treating leachate with high COD concentrations. The combination of rapid initial adsorption and sustained microbial degradation enables both fast and prolonged pollutant removal, making this approach highly suitable for treating high-strength, heterogeneous effluents.

### **3.3.3 UV-Visible Spectrophotometry**

Unlike TOC and COD, which were employed to evaluate and compare the performance of all three treatment systems, UV-Visible spectroscopy was conducted exclusively for the hybrid system. This decision was based on the results of the previous parameters, which clearly identified the hybrid configuration as the most effective. Therefore, UV analysis was used as a complementary tool to assess the extent of organic matter removal and estimate the color reduction through calculation of the Color Number Index.

As shown in Fig. 31, a significant reduction in absorbance intensity was observed across the entire spectral range (200–800 nm) over the 21-day treatment period. The initial spectrum exhibited high absorbance values, particularly in the UV region (200–400 nm), which corresponds to the presence of aromatic and unsaturated organic compounds, such as humic and fulvic substances commonly found in landfill leachate (Kjeldsen et al., 2002). The visible region (400–700 nm), associated with color-causing chromophores, also showed a notable decline in absorbance, indicating a reduction in visual and chemical pollution.

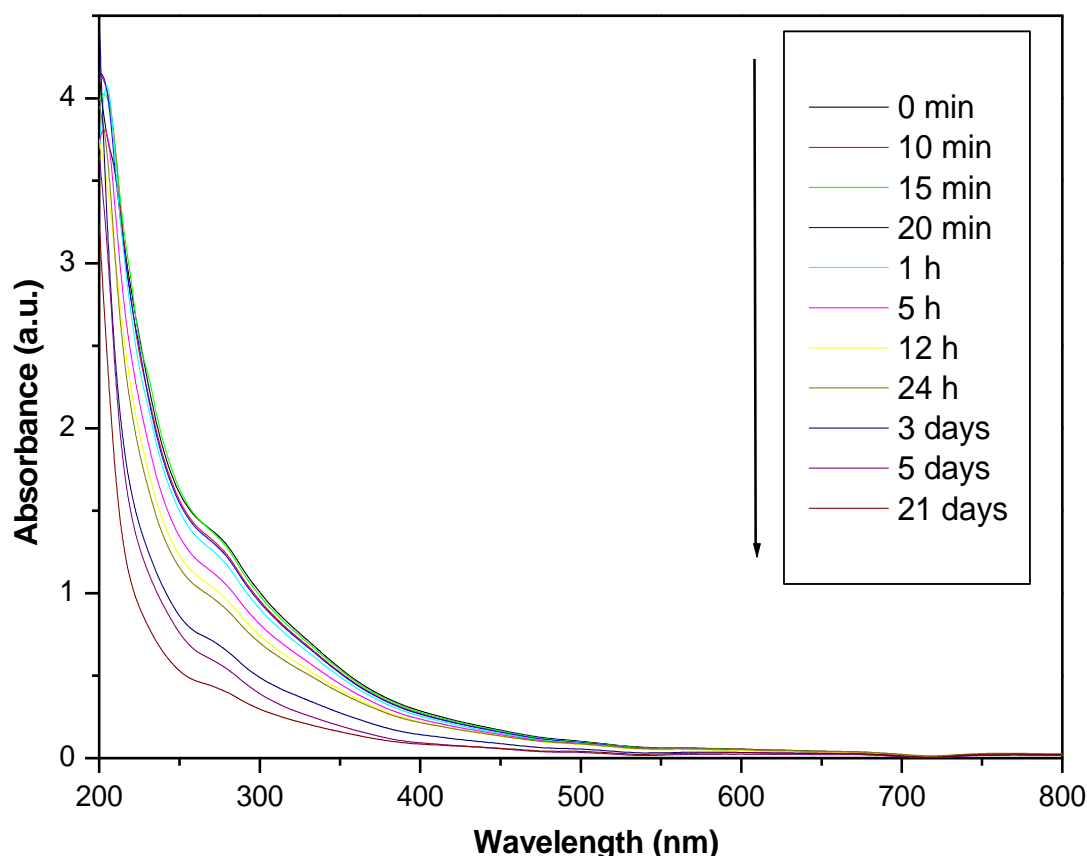


Fig. 31. Evolution of UV-Vis absorbance spectra during hybrid treatment of 1:20 diluted leachate. (Graph plotted using OriginPro 2018).

The marked decrease in absorbance across time points reflects the effective performance of the hybrid system. In the early phase of treatment, rapid adsorption of soluble organics onto the activated carbon surface likely contributed to the immediate drop in spectral intensity. As treatment progressed, microbial activity played an increasing role by degrading both free and adsorbed organic matter. This sequential mechanism is supported by previous studies showing that hybrid systems combining activated carbon and biological treatment result in deeper and more sustained removal of complex organics compared to either process alone (Rivera-Utrilla et al., 2013).

These spectral changes not only indicate a loss of aromaticity and molecular complexity in the leachate matrix, but also confirm the synergistic interaction between physical adsorption and microbial biodegradation in targeting a broad spectrum of UV-absorbing pollutants.

### 3.3.4 Color Number Index

The Color Number Index (CNI) is a quantitative measure derived from UV-Vis spectra to estimate the intensity of visible color in wastewater, primarily due to the presence of chromophoric compounds such as dyes, humic substances, and other colored organics. It serves as an indirect indicator of visual pollution and the degree of aromatic structure degradation during treatment.

The color number values were calculated using the formula (Krull & Döpkins, 2004):

$$CN = \frac{(Abs_{436})^2 + (Abs_{524})^2 + (Abs_{600})^2}{Abs_{436} + Abs_{524} + Abs_{600}}$$

Where  $Abs_{436}$ ,  $Abs_{525}$ ,  $Abs_{620}$  are the absorbance measurements corresponding to the wavelengths 436, 525, and 620 nm, respectively.

As illustrated in Fig. 32, the CNI decreased continuously throughout the treatment period. The black line (0–300 min) indicates a rapid initial drop, likely driven by the adsorption of color-causing substances onto the activated carbon surface. The red line (12 h to 21 days) shows a slower but steady decline, corresponding to microbial degradation of adsorbed chromophores and residual dissolved organics.

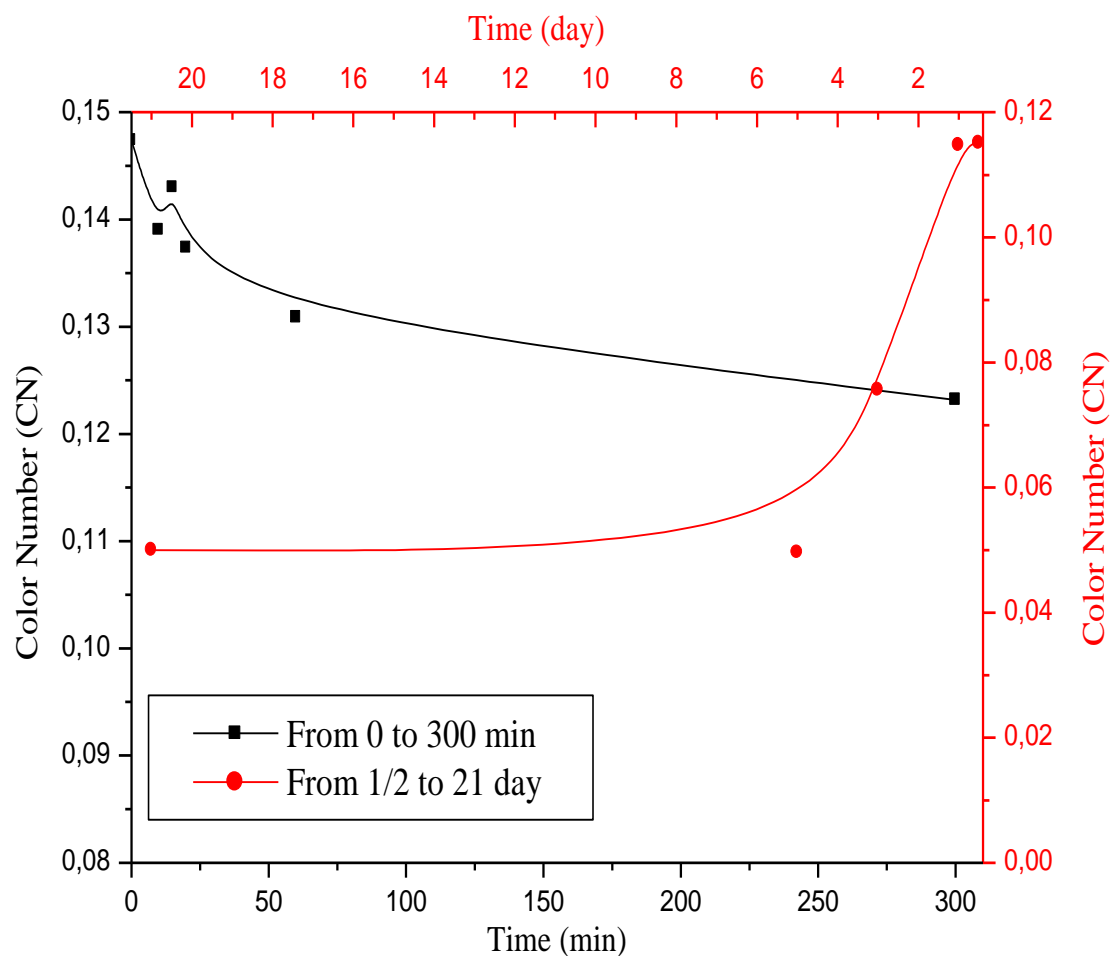


Fig. 32. Color Number Index derived from UV-Vis spectra, showing temporal decrease during hybrid treatment. (Graph plotted using OriginPro 2018).

This two-phase trend confirms the cooperative action of the hybrid system. Adsorption accounts for the early removal of high-molecular-weight and hydrophobic colorants, while biodegradation contributes to the gradual breakdown of structurally complex or smaller chromophores over time.

### 3.4 Comparative Performance of Treatment Systems

The comparative evaluation of the physicochemical, biological, and hybrid treatment systems was primarily based on the reduction of TOC and COD, which were measured consistently across all experiments. Fig. 33 illustrates the elimination rates (%) for both parameters across the three systems, offering a clear view of their relative efficiency. UV-Visible spectral analysis, which was performed only for the hybrid system, served to further characterize the removal of residual chromophores and confirm the advanced treatment performance observed through TOC and COD results.



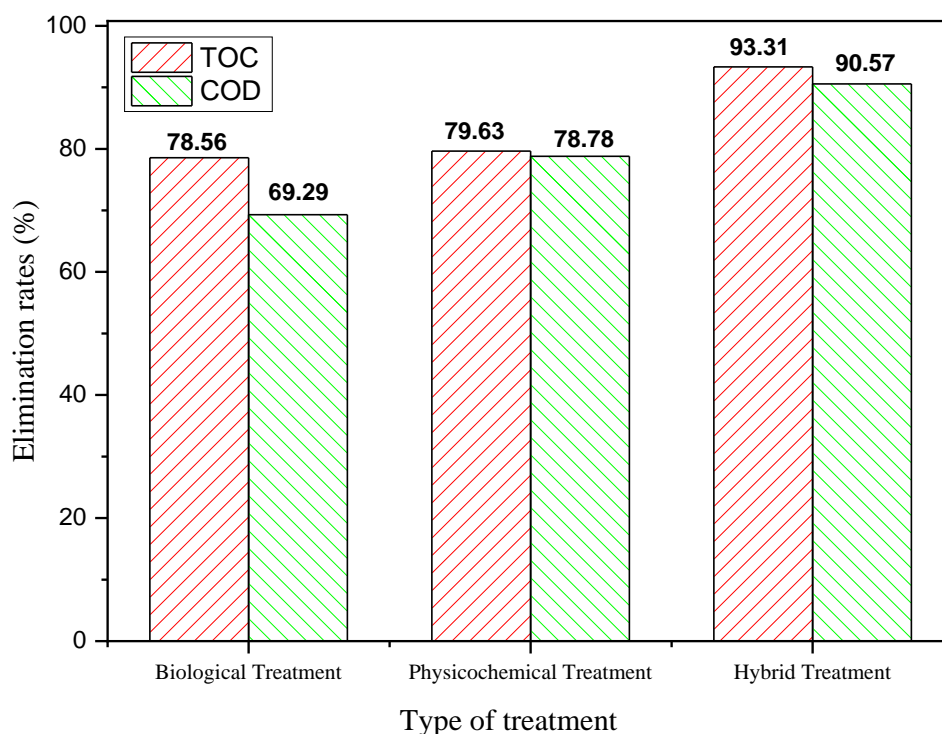


Fig. 33. Elimination rates of TOC and COD for physicochemical, biological, and hybrid treatment systems. All treatments were applied to leachate diluted at a 1:20 ratio. (Graph plotted using OriginPro 2018).

Fig. 33 clearly illustrates that both the physicochemical and biological treatment systems achieved commendable and relatively comparable removal efficiencies. The physicochemical process, employing activated carbon, resulted in TOC and COD removal efficiencies of 79.63% and 78.78%, respectively. Similarly, the biological system, utilizing indigenous bacterial strains isolated from the leachate, achieved 78.56% TOC and 69.29% COD removal. Despite the satisfactory performance of each individual process, the hybrid system outperformed both, achieving 93.31% TOC and 90.57% COD removal. These results underscore the synergistic advantage of integrating physicochemical and biological treatments for enhanced leachate remediation.

This performance disparity can be better understood by analyzing the removal kinetics presented in Fig. 34, which shows the evolution of TOC concentration over time for all three systems. The physicochemical system demonstrated a rapid initial decline in TOC, a hallmark of effective adsorption. However, this was followed by a plateau phase, likely due to pore saturation on the carbon surface, after which no significant further removal occurred—a common limitation in single-step adsorption processes (Mohan et al., 2014). In contrast, the

biological system displayed a clear lag phase, consistent with the need for bacterial adaptation to the complex matrix of the leachate. After this acclimation period, however, the system gradually achieved TOC levels similar to the physicochemical one, but at a slower rate.

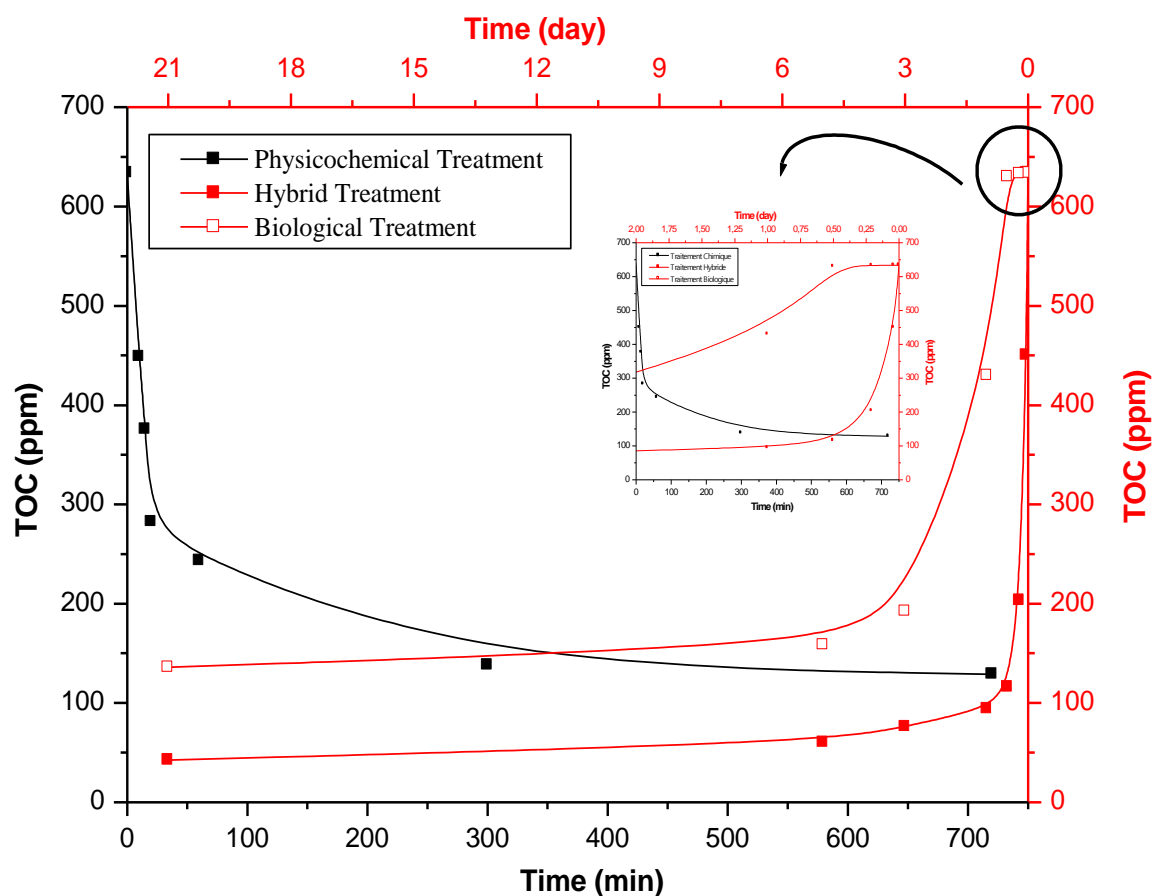


Fig. 34. Kinetics of TOC removal for the three treatment systems. (Graph plotted using OriginPro 2018).

The hybrid system, combining activated carbon with encapsulated bacteria, capitalized on the strengths of both mechanisms. Its kinetic profile in Fig. 34 shows a rapid initial drop (like the physicochemical system) but with continued TOC reduction even after the point at which the physicochemical system stabilized. This indicates that while adsorption provided immediate removal, the bacterial degradation sustained and extended the treatment process. Moreover, the interaction between adsorption and biodegradation likely freed blocked pores, allowing reactivation of carbon sites and extended contact with otherwise inaccessible organic compounds.

In addition, some organic molecules resist either adsorption or biodegradation individually. For example, high-molecular-weight humic substances or polar, low-aromatic compounds may exhibit poor affinity for carbon surfaces, while recalcitrant xenobiotics may escape enzymatic breakdown (Bashir et al., 2010). The hybrid system's dual mechanism enhances the likelihood of removing a broader spectrum of such pollutants by complementary pathways.

Overall, the hybrid system's superior performance is attributable to the synergy between fast physical adsorption and progressive biological degradation, allowing both immediate and sustained pollutant removal. These findings reinforce the hybrid model's suitability for treating complex effluents like leachate, where no single process is sufficient to address the wide range of contaminants present.

### **3.5 Microbial Activity Evolution During Treatment**

Monitoring microbial activity during both biological and hybrid treatment systems offers critical insights into the dynamics of biodegradation. In biological systems, the presence and proliferation of active microorganisms are essential for the breakdown of organic matter. In hybrid systems, microbial behavior can also reveal the nature of interactions between encapsulated bacteria and the supporting adsorbent, (activated carbon). Optical density measurements at 600 nm ( $OD_{600}$ ) provide an indirect means of assessing bacterial growth by quantifying the turbidity of the medium, which correlates with microbial concentration. In this study,  $OD_{600}$  was monitored over a 21-day period for both biological and hybrid systems. The temporal evolution of absorbance values is illustrated in Fig. 35, which compares bacterial growth kinetics across the two configurations

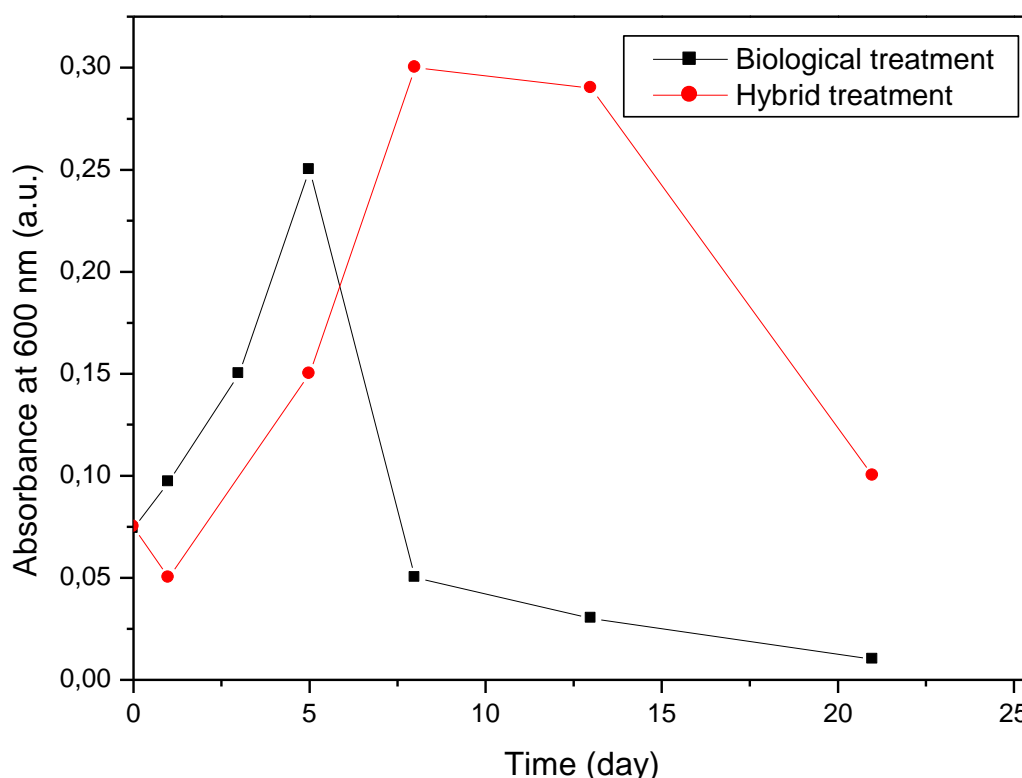


Fig. 35. Optical density at 600 nm over time during biological and hybrid treatments. (Graph plotted using OriginPro 2018).

### 3.5.1 Biological Treatment System

As illustrated in Fig. 35,  $OD_{600}$  values in the biological system increased steadily from the start of the experiment until day 5, peaking at 0.25 a.u., before declining to 0.01 by day 21. This pattern is characteristic of a typical microbial growth curve. The initial rise corresponds to the exponential phase, during which bacteria successfully adapted to the leachate environment and utilized available nutrients for rapid proliferation. The subsequent decline reflects the stationary and decline phases, associated with nutrient depletion and the accumulation of inhibitory metabolic byproducts in the medium (Wang et al., 2015). This pattern suggests that while the biological system supported microbial activity for a time, the sustainability of that activity was limited by environmental constraints within the medium, which ultimately reduced the degradation potential toward the end of the treatment period.

### 3.5.2 Hybrid Treatment System

In contrast, the hybrid system exhibited a distinct pattern. The OD<sub>600</sub> value was initially lower than that of the biological system, likely due to the encapsulation of bacteria within alginate-activated carbon beads, which limited their direct diffusion into the surrounding medium. Over time, however, a steady increase in absorbance was observed, reaching 0.3 a.u. by day 8, and then stabilizing at 0.1 a.u. by day 21.

This gradual rise can be attributed to the progressive release of bacteria from the interior of the beads into the leachate, as the activated carbon became increasingly saturated with pollutants. Saturation likely caused pore blockage and partial weakening of the bead structure, enabling microbial migration into the bulk solution. The resulting increase in OD<sub>600</sub> reflects a controlled enrichment of bacterial population, which contributed to the biological degradation of organic matter alongside the initial adsorptive process.

This trend highlights the hybrid system's functional advantage: it initiates treatment through rapid adsorption while simultaneously establishing a sustained biodegradation phase through the delayed release of active bacteria. Such a dual-phase mechanism supports continued organic matter removal, even after the carbon surface reaches saturation.

### 3.6 pH Variation Before and After Treatment

pH is a key indicator of chemical balance and microbial activity in wastewater treatment processes. It can influence adsorption efficiency, enzymatic stability, and pollutant solubility, making it an important parameter to monitor when evaluating treatment performance. In the context of landfill leachate, pH is typically elevated due to the presence of dissolved ammonia and bicarbonate ions, especially in mature leachates from methanogenic phases (Renou et al., 2008).

In this study, the initial pH of the leachate was measured at 8.26, confirming its alkaline character. After treatment, the final pH values across the three systems-physicochemical, biological, and hybrid-were observed to converge around neutrality, ranging between 7.1 and 7.23. This convergence toward neutral pH reflects a balanced interaction of physicochemical and biological processes throughout treatment.

In the physicochemical system, the drop in pH may be attributed to the adsorption of alkaline compounds such as ammonia, as well as the partial removal of buffering species. The biological system likely contributed organic acids through microbial metabolism (e.g., volatile fatty

acids), causing the pH to decrease. However, the intrinsic buffering capacity of the leachate may have prevented a more pronounced acidification. In the hybrid system, both mechanisms coexisted: the carbon adsorbed basic compounds while the bacteria generated weak acids during degradation, resulting in an overall pH stabilization near neutrality.

This moderate pH adjustment is advantageous, as it supports microbial viability, enhances the adsorption performance of activated carbon (especially near its point of zero charge), and facilitates potential downstream treatments or discharge requirements (Kjeldsen et al., 2002). The result also indicates that none of the systems caused excessive acidification or alkalinization, preserving the ecological compatibility of the treated effluent.

### 3.7 Visible Color Change of Treated Leachate

In addition to quantitative measurements of organic matter reduction, visual observations of treated leachate can offer a clear, practical indication of treatment effectiveness, especially for complex effluents like landfill leachate, which are often heavily pigmented due to humic substances, dyes, and aromatic degradation products. Fig. 36 presents a comparative image of the leachate samples before and after treatment with the three systems: physicochemical, biological, and hybrid.

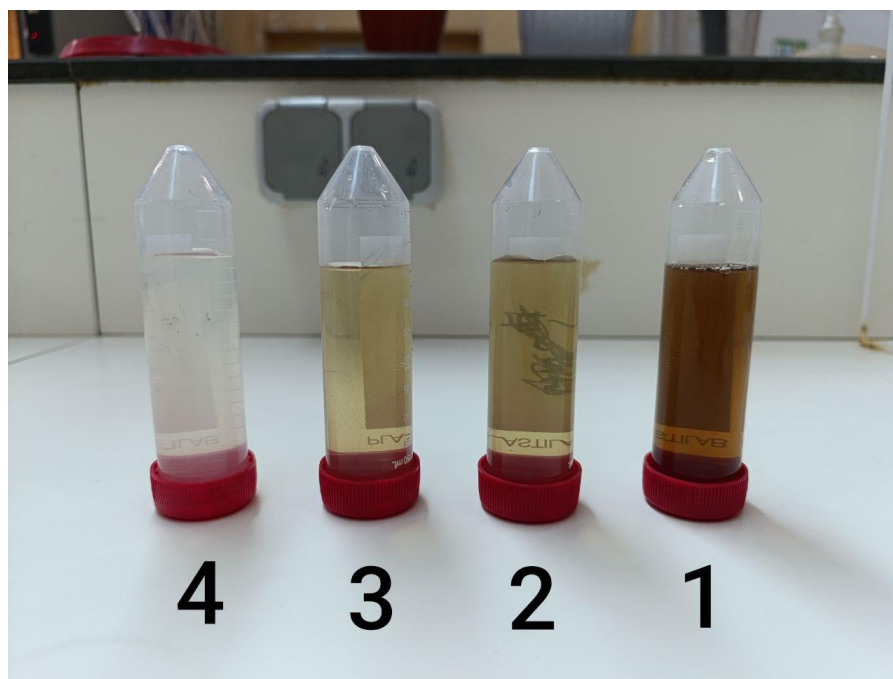


Fig. 36. Photographic comparison of landfill leachate: (1) before treatment, (2) after biological treatment, (3) after physicochemical treatment, and (4) after hybrid treatment.

The untreated leachate exhibits a dark brown coloration, characteristic of its high organic load and abundant chromophoric compounds. Following physicochemical treatment, a noticeable

improvement in clarity is observed, reflecting the effective removal of suspended solids and colored organics through adsorption onto activated carbon. The biological treatment also results in moderate clarification, likely attributable to microbial degradation of soluble organic matter and partial decolorization mediated by enzymatic activity.

However, the most significant visual improvement is seen in the hybrid-treated leachate, which appears markedly lighter, approaching full transparency. This near-complete removal of visible color aligns closely with the measured TOC and COD removal efficiencies (93.31% and 90.57%, respectively), and is further supported by UV-Vis spectral analysis and CNI results, which confirmed substantial degradation of chromophoric structures. The hybrid system's performance, therefore, extends beyond invisible pollutant metrics to clearly perceptible visual outcomes, reinforcing its effectiveness in both technical and practical terms.

The pronounced visual difference also suggests a broader spectrum of contaminant removal in the hybrid configuration, combining rapid physical adsorption with deeper molecular degradation. This final photographic comparison serves as both a qualitative validation of analytical results and a strong, tangible indicator of advanced treatment success.

# Conclusion



Landfills are one of the most common methods for municipal solid waste disposal, but they generate leachate, a highly polluted liquid containing organic matter, heavy metals, and other toxic substances. Effective treatment is essential to minimize the environmental risks of leachate, and current strategies often include physical, chemical, biological, or combined (hybrid) approaches.

This study demonstrated the feasibility of using green agricultural residues to produce low-cost, effective activated carbon, highlighting a sustainable approach to adsorbent preparation. The carbon was successfully characterized and showed favorable surface properties. FTIR analysis confirmed the presence of oxygen-containing and possibly sulfur-based functional groups, which enhance adsorption of dyes, phenols, and heavy metals. Raman spectroscopy revealed a moderately disordered structure with partial graphitization, features that contribute to both surface reactivity and structural stability. The  $\text{pH}_{\text{pzc}}$  value indicated that the surface remains negatively charged at the leachate's pH (8.26), favoring the removal of cationic species such as ammonium and metal ions.

The second part of the study focused on evaluating the treatment potential of the prepared activated carbon, bacterial strains isolated from the leachate, and a hybrid system combining both through encapsulation. Both the chemical and biological systems showed good pollutant removal performance, particularly in reducing the organic load of the leachate. However, the hybrid system showed the best performance, achieving 90.57% COD removal and 93.31% TOC removal. It also led to a marked reduction in UV-Vis absorbance across the entire spectral range and a continuous decline in the Color Number Index (CNI), indicating effective removal of both general organic load and colored compounds. These findings highlight the synergy between adsorption and biodegradation in treating complex landfill leachate.

The evolution of microbial load differed notably between the biological and hybrid systems. In the biological treatment, bacterial growth followed a typical curve with gradual increases in OD600. In contrast, the hybrid system showed a delayed but sustained rise, linked to the progressive release of bacteria from the alginate-carbon beads as adsorption sites became saturated. This transition enabled continued biodegradation even after adsorption declined, highlighting the hybrid system's dual-phase advantage: rapid initial adsorption followed by sustained biological activity.

The initial pH of the leachate was 8.26. After treatment, all three systems brought the pH closer to neutral, with final values ranging between 7.1 and 7.23. This adjustment supports microbial

activity, enhances adsorption near the point of zero charge, and improves the overall compatibility of the treated leachate with environmental discharge standards.

The hybrid system produced the most noticeable improvement in leachate clarity, with a shift from dark brown to near transparency. This visible change supports the analytical results and reflects the combined action of adsorption and biodegradation in removing chromophoric compounds.

Future research may explore the potential of scaling up the hybrid system to test its performance under real operating conditions and larger volumes. Evaluating the regeneration and reuse potential of the activated carbon can provide insight into the economic and environmental sustainability of the approach. Additional work can also focus on optimizing treatment conditions to improve efficiency and adaptability under varied conditions.

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## **Abstract**

This study evaluated a hybrid treatment system for landfill leachate from the Batna Landfill Center, Algeria, combining adsorption using activated carbon from green agricultural waste and biological degradation by indigenous bacteria. Characterization of the carbon showed favorable surface properties enhancing pollutant removal. Three treatment configurations were tested: physicochemical (adsorption only), biological, and hybrid (bacteria encapsulated in alginate-carbon beads). The hybrid system achieved the highest removal efficiencies, 93.31% total organic carbon (TOC) and 90.57% chemical oxygen demand (COD), along with effective color reduction and pH stabilization. Optical density monitoring revealed sustained microbial activity due to gradual bacterial release from the beads. Results demonstrate the hybrid system's synergistic advantages, offering a cost-effective and sustainable solution for landfill leachate management.

**Keywords:** Landfill, Leachate, Adsorption, Activated carbon, Biological treatment, Hybrid system.

## Résumé

Cette étude a évalué un système de traitement hybride pour le lixiviat du Centre d'enfouissement technique de Batna, en Algérie, combinant l'adsorption sur charbon actif issu de déchets agricoles et la biodégradation par des bactéries autochtones. La caractérisation du charbon a révélé des propriétés de surface favorables à l'élimination des polluants. Trois configurations de traitement ont été testées: physicochimique (adsorption seule), biologique et hybride (bactéries encapsulées dans des billes d'alginatecharbon). Le système hybride a atteint les meilleures efficacités d'élimination, 93,31 % de carbone organique total (COT) et 90,57 % de demande chimique en oxygène (DCO), ainsi qu'une réduction efficace de la couleur et une stabilisation du pH. Le suivi de la densité optique a révélé une activité microbienne soutenue, attribuée à la libération progressive des bactéries à partir des billes. Les résultats démontrent les avantages synergiques du système hybride, offrant une solution durable et économique pour la gestion des lixiviats de décharge

**Mots-clés :** Centre d'enfouissement technique, Lixiviat, Adsorption, Charbon actif, Traitement biologique, Système hybride.

## ملخص

قامت هذه الدراسة بتقييم نظام معالجة هجين لعصارة النفايات من مركز الدفن التقني بباتنة، الجزائر، يجمع بين الامتزاز باستخدام الكربون المنشط المستخرج من النفايات الزراعية والتحلل البيولوجي بواسطة بكتيريا محلية. أظهرت خصائص الكربون المُحضّر سطحًا ملائمًا لتعزيز إزالة الملوثات. تم اختبار ثلاث طرق للمعالجة: فيزيوكيميائية (امتزاز فقط)، بيولوجية، وهجينة (بكتيريا مغلفة في كريات من الألجينات والكربون). حقق النظام الهجين أعلى كفاءات الإزالة، بنسبة 93.31% للكربون العضوي الكلي (TOC) و 90.57% لمطلوبية الأكسجين الكيميائية (COD)، إلى جانب تقليل فعّال للون واستقرار في درجة الحموضة (pH). أظهر قياس الكثافة البصرية استمرار النشاط الميكروبي، نتيجة الإطلاق التدريجي للبكتيريا من الكريات. تُظهر النتائج الفوائد التكميلية للنظام الهجين، مما يجعله حلاً فعّالاً من حيث التكلفة ومستداماً لإدارة عصارة النفايات.

**الكلمات المفتاحية:** مركز الدفن التقني، العصارة، الامتزاز، الفحم المنشط، المعالجة البيولوجية، النظام الهجين.



<b>Academic year:</b> 2024-2025	<b>Presented by:</b> BENISSAAD Seif Eddine
<b>Application of a Hybrid Adsorption–Biodegradation System for Treating Algerian Landfill Leachate</b>	
<b>Thesis submitted in partial fulfillment of the requirements for the Master’s degree in Applied Microbiology</b>	
<p>This study evaluated a hybrid treatment system for landfill leachate from the Batna Landfill Center, Algeria, combining adsorption using activated carbon from green agricultural waste and biological degradation by indigenous bacteria. Characterization of the carbon showed favorable surface properties enhancing pollutant removal. Three treatment configurations were tested: chemical (adsorption only), biological, and hybrid (bacteria encapsulated in alginate–carbon beads). The hybrid system achieved the highest removal efficiencies, 93.31% total organic carbon (TOC) and 90.57% chemical oxygen demand (COD), along with effective color reduction and pH stabilization. Optical density monitoring revealed sustained microbial activity due to gradual bacterial release from the beads. Results demonstrate the hybrid system’s synergistic advantages, offering a cost-effective and sustainable solution for landfill leachate management</p>	
<b>Keywords:</b> Landfill, Leachate, Adsorption, Activated carbon, Biological treatment, Hybrid system.	
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