

**T.R.
SAKARYA UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

**SYNTHESIS AND CHARACTERIZATION OF CARBON
NANOMATERIAL(S) BY HYDROTHERMAL CARBONIZATION
OF VARIOUS WASTES**

PhD THESIS

Monika SHARMA

Nanoscience and Nanoengineering Department

JULY 2025

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Thesis Advisor: Assoc. Prof. Dr. A. Suna ERSES YAY

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The thesis work titled “SYNTHESIS AND CHARACTERIZATION OF CARBON NANOMATERIAL(S) BY HYDROTHERMAL CARBONIZATION OF VARIOUS WASTES” prepared by Monika SHARMA was accepted by the following jury on 16/07/2025 by unanimously/majority of votes as a PhD THESIS in Sakarya University Graduate School of Natural and Applied Sciences, Nanoscience and Nanoengineering department.

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(16/07/2025)

Monika SHARMA





To my family and country.



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Monika SHARMA



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ABBREVIATIONS

BET	: Brunauer–Emmett–Teller
BM	: Ball Milling
CDs	: Carbon Dots
DPPH	: 1,1-diphenyl-2-picrylhydrazyl
DTA	: Differential Thermal Analysis
EDS	: Energy Dispersive X-ray Spectroscopy
FTIR	: Fourier Transform Infrared Spectroscopy
GWP	: Global Warming Potential
HCNs	: Hydrothermal Carbonaceous Nanospheres
HHV	: Higher Heating Value
HTC	: Hydrothermal Carbonization
IC₅₀	: Half-Maximal Inhibitory Concentration
LCA	: Life Cycle Assessment
LCI	: Life Cycle Inventory
LCIA	: Life Cycle Impact Assessment
SEM	: Scanning Electron Microscopy
TEM	: Transmission Electron Microscopy
TGA	: Thermogravimetric Analysis
UPV	: Ultrasonic Pulse Velocity
XRD	: X-ray Diffraction
ZOI	: Zone of Inhibition



SYMBOLS

%	: Percentage
wt %	: Weight Percent
°C	: Degree Celsius
g	: Gram
mg	: Milligram
mL	: Milliliter
μm	: Micrometer
m	: Mass [kilogram]
nm	: Nanometer
R²	: Coefficient of Determination
s	: Second
min	: Minute
h	: Hour
η	: Efficiency



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SYNTHESIS AND CHARACTERIZATION OF CARBON NANOMATERIAL(S) BY HYDROTHERMAL CARBONIZATION OF VARIOUS WASTES

SUMMARY

This research investigates a sustainable and resource-efficient approach to biomass waste management by synthesizing high-value carbon nanomaterials through hydrothermal carbonization (HTC). Three distinct biomass wastes: pomegranate peel waste (PPW), marigold flower waste (MFW), and cotton fabric waste (CFW), were subjected to HTC under varying conditions to explore their conversion into functional carbon-rich products. Among the tested feedstocks, PPW emerged as the most promising precursor for carbon nanomaterial production, yielding well-defined hydrothermal carbonaceous nanospheres (HCNs) with diameters ranging from 50 to 300 nm. In contrast, the carbon materials derived from MFW and CFW exhibited irregular and poorly defined morphologies. Additionally, carbon dots (CDs) displaying strong blue luminescence were successfully recovered from the liquid phase of the PPW-HTC process, demonstrating the feasibility of dual-phase valorization from a single waste stream.

To assess the environmental viability of the process, a prospective life cycle assessment (LCA) was conducted. The analysis identified electricity consumption for reactor heating (75–79%) and drying (20–22%) as the dominant contributors to environmental impact. Scenario modeling indicated that replacing the current electricity mix with renewable sources could reduce abiotic depletion and global warming potential by up to 120%. Sensitivity analysis of wastewater disposal routes revealed that while switching to treatment plants offers only minor improvements at laboratory scale (<1%), the benefits become more pronounced at industrial scales. The scenario involving CD recovery (HTCa) exhibited comparatively higher environmental burdens due to full energy allocation but avoided reliance on high-purity chemical precursors commonly used in conventional CD synthesis. This strategy highlights the environmental potential of integrating biomass-based inputs and waste valorization into emerging nanomaterial production pathways, aligning with circular economy principles. HCNs demonstrated significant potential as green antioxidants. Results from DPPH and phosphomolybdenum assays revealed strong radical-scavenging activity, comparable to ascorbic acid, a standard antioxidant. These findings support the use of HCNs as a sustainable alternative to fossil-derived nanomaterials and synthetic antioxidants, offering both environmental and human health benefits. Under the assay conditions employed in this study, HCNs exhibited minimal antibacterial activity. While these results indicate limited antibacterial effectiveness at the tested concentrations, they also suggest that HCNs may be less cytotoxic, potentially supporting their use in biocompatible or non-disruptive applications. Future studies should explore their performance under varying experimental conditions or investigate modifications to enhance antibacterial efficacy. In addition, the study evaluated the application of HCNs in cement composites.

Incorporating HCNs resulted in improved workability and enhanced flexural strength in certain samples, along with a reduction in density without significant compromise in compressive strength. The method of HCNs incorporation was found to significantly influence the final properties of the composites. Although the sustainability impact of low-dosage additions is limited, these findings show the potential of HCNs as a useful addition in cement-based systems, suggesting the need for further research and optimization—particularly when combined with other sustainability-enhancing materials.



FARKLI ATIK TÜRLERİNİN HİDROTERMAL KARBONİZASYON YÖNTEMİ İLE KARBON NANOMALZEMELERİNE SENTEZİ VE KARAKTERİZASYONU

ÖZET

Bu araştırma, hidrotermal karbonizasyon (HTK) yöntemini kullanarak biyokütle atıklarının sürdürülebilir şekilde yüksek katma değerli karbon nanomalzemelere dönüştürülmesine yönelik derinlemesine ve disiplinler arası bir inceleme sunmaktadır. Yeşil kimya, döngüsel ekonomi ve yaşam döngüsü düşüncesi ilkelerine dayanan bu çalışma, organik atık üretimiyle ilişkili önemli çevresel sorunlara bütüncül bir çözüm yaklaşımı geliştirmektedir. Araştırmanın temelini, genellikle göz ardı edilen ya da sorunlu olarak nitelendirilen bazı organik atık türlerinin, uygun ve sürdürülebilir işlem yöntemleri ile değerlendirilebilecek potansiyele sahip olması oluşturmaktadır. Yenilenebilir ve bol miktarda bulunabilen bu atıklar, çevresel iyileştirmeden inşaat ve biyomedikal uygulamalara kadar birçok alanda kullanılabilecek ileri düzey nanoyapılı malzemelere dönüştürülebilmektedir.

Bu vizyon doğrultusunda, HTK işlemine uygunluğu, bileşim özellikleri ve temin edilebilirlikleri dikkate alınarak üç farklı biyokütle atığı seçilmiştir: tarım ve gıda işleme endüstrisinin bir yan ürünü olan nar kabuğu atığı (NKA); törensel veya dekoratif kullanımlar sonrası sıklıkla atılan, süs bitkisi endüstrisinden türetilmiş otsu bir atık olan kadife çiçeği atığı (KÇA); ve endüstriyel tekstil atığı ile yaygın bir belediye katı atığı olan pamuklu kumaş atığı (PKA). Bu öncül malzemelerin her biri, karbonizasyonu teşvik etmeye yönelik aynı ve kontrol altında tutulan işlem koşulları altında HTK işlemine tabi tutulmuştur. Amaç, bu hammaddelerin içsel bileşim farklılıklarının nihai ürünlerin özelliklerini nasıl etkilediğini değerlendirmektir.

DeneySEL sonuçlar, seçilen hammaddelerin karbonizasyon davranışlarında belirgin farklılıklar olduğunu göstermiştir. Üç malzeme arasında, hidrotermal karbonik nanosferlerin (HKN) üretimi için en uygun öncül maddenin nar kabuğu atığı olduğu belirlenmiştir; bu nanosferler, 50 ila 300 nanometre arasında değişen boyutlara sahip belirgin küresel morfoloji sergilemiştir. Buna karşın, KÇA ve PKA kaynaklı ürünler, düzensiz ve zayıf tanımlanmış karbon yapıları vermiştir. Bu bulgular, HTK yönteminin nanomalzeme sentezindeki etkinliğinin, kullanılan biyokütlenin fizikokimyasal yapısına yüksek düzeyde bağlı olduğunu ve başarılı karbon nanomalzeme üretimi için uygun moleküler yapıya sahip hammaddelerin seçiminin kritik önem taşıdığını göstermektedir.

Katı fazlı karbon kürelerin ötesinde, bu çalışma aynı zamanda nar kabuğu atığının iki fazlı değerlendirilmesini mümkün kılarak dikkate değer bir gelişme sunmuştur. HTK işleminden elde edilen sıvı fazda, ultraviyole ışık altında parlak mavi floresan yayan, ultra küçük ve ışıldayan karbon noktalarının bulunduğu tespit edilmiştir. Bu karbon noktalarının optik özellikleri, UV-Vis spektroskopisi kullanılarak karakterize edilmiş ve oluşumlarının başarılı olduğuna işaret eden belirgin absorpsiyon pikleri saptanmıştır. Karbon noktaların floresans davranışı çeşitli konsantrasyonlarda değerlendirilmiş ve maksimum emisyonun 0.05 mg/mL konsantrasyonda

gerçekleştiği, daha yüksek konsantrasyonlarda ise tipik söndürme etkilerinden dolayı sinyal yoğunluğunda azalma olduğu gözlemlenmiştir. Ayrıca çözücü bağımlı floresans analizinde gliserolün floresans sinyalini belirgin şekilde artırdığı, toluen gibi apolar çözücülerin ise sinyali bastırdığı görülmüştür. Bu bulgular, PPW kaynaklı Karbon noktaların çok yönlü kullanıma açık olduğunu ve algılama, görüntüleme ve optoelektronik cihazlar gibi çeşitli uygulama alanlarında potansiyele sahip olduğunu göstermektedir.

Sentezlenen HKN'ler; yapısal, morfolojik ve fizikokimyasal özelliklerinin belirlenmesi amacıyla kapsamlı şekilde karakterize edilmiştir. Bu amaçla Taramalı Elektron Mikroskopu (SEM), Geçirimli Elektron Mikroskopu (TEM), X-Işını Difraksiyonu (XRD), Fourier Dönüşümlü Kızılötesi Spektroskopisi (FTIR), Raman Spektroskopisi, Brunauer–Emmett–Teller (BET) yüzey alanı analizi ve Termal Analiz (TGA-DTA) gibi ileri düzey analiz teknikleri kullanılmıştır. Sonuçlar, modifiye edilmemiş HKN'lerin termal stabiliteye sahip olduğunu ve hidrofobik özellik sergilediğini göstermiştir. Bu da onları kirletici adsorpsiyonu ve kompozit malzeme uygulamaları açısından uygun adaylar haline getirmektedir.

HKN'lerin fiziksel son işlemlere karşı dayanıklılığını ve performansını anlamak amacıyla, mekanik modifikasyon yöntemi olarak bilyalı öğütme uygulanmıştır. Bu işlem, TEM analizlerinde görülebileceği üzere, kümelenme ve yüzey sıkışması gibi belirgin morfolojik değişimlere neden olmuştur. Bu yapısal değişiklikler, yüzey alanı ve toplam gözenek hacminde önemli ölçüde azalmaya yol açmış, Raman spektroskopisi ise kusur yoğunluğunda artış olduğunu ortaya koymuştur. Bu sonuçlar, nanoyapı fonksiyonelliğini koruma ile belirli malzeme özelliklerini geliştirme arasındaki hassas dengeyi vurgulamaktadır.

Sentez sürecinin çevresel etkilerini daha geniş bir perspektiften değerlendirmek amacıyla ileriye dönük bir yaşam döngüsü değerlendirmesi (YDA) gerçekleştirilmiştir. YDA kapsamında, HTK işleminin tüm aşamaları—hammadde hazırlığından malzeme karakterizasyonuna kadar—ele alınmış; enerji tüketimi ve emisyonlar odak noktası olmuştur. Değerlendirme, çevresel yükün büyük kısmının reaktörün ısıtılması için kullanılan elektrikten (%75–79) ve malzemelerin kurutulmasından (%20–22) kaynaklandığını ortaya koymuştur. Senaryo modelleriyle, konvansiyonel elektrik kaynaklarından yenilenebilir enerjiye geçilmesi durumunda, abiyotik kaynak tüketimi ve küresel ısınma potansiyelinde %120'ye varan azalmalar sağlanabileceği gösterilmiştir. Karbon noktalarının geri kazanımını içeren HTKa senaryosu, tam enerji tahsisi gerektirdiği için daha yüksek enerji girdisi talep etmiş olsa da, geleneksel karbon noktaları sentez yollarında kullanılan sentetik ve yüksek saflıkta kimyasallara olan bağımlılığı azaltarak çevresel avantajlar sağlamıştır. Ayrıca, atık su bertaraf yöntemlerinin duyarlılık analizleri, laboratuvar ölçeğinde sınırlı etkiler görülse de, endüstriyel ölçeklemelerde daha belirgin çevresel iyileştirmelere yol açabileceğini ortaya koymuştur. Bu bulgu, HTK sürecinin ticari ölçekte çevresel açıdan kabul edilebilir biçimde uygulanabileceğine işaret etmektedir.

HKN'lerin potansiyel uygulamaları, bu malzemeler açısından görece az araştırılmış iki temel alanda değerlendirilmiştir: biyomedikal bilimler ve inşaat mühendisliği. Biyomedikal bağlamda, HKN'lerin antioksidan aktiviteleri DPPH ve fosfomolibden yöntemleri ile test edilmiştir. Elde edilen sonuçlar, HKN'lerin serbest radikalleri etkin şekilde uzaklaştırabildiğini ve yaygın bir standart olan askorbik asit ile benzer performans sergilediğini göstermiştir. Bu durum, HKN'leri sentetik antioksidanlara

potansiyel alternatifler olarak konumlandırmakta; düşük toksisite ve çevresel sürdürülebilirlik gibi iki temel avantaj sunmaktadır. Ayrıca, HKN'lerin potansiyel antibakteriyel etkileri, agar difüzyon tekniği ile belirli antibiyotiklere karşı test edilmiştir. *E. coli* ve *S. aureus*'a karşı elde edilen sonuçlar, antibakteriyel etkinin ihmal edilebilir düzeyde olduğunu göstermiştir. Bu sınırlı aktivite, antimikrobiyal etkilerin istenmediği biyoyumlu uygulamalarda avantaj sağlayabilir. Bununla birlikte, bu malzemelerin antibakteriyel etkinliğinin daha yüksek dozlar, farklı bakteri türleri veya yüzey modifikasyonları ile daha kapsamlı şekilde araştırılması gerekmektedir.

İnşaat alanında ise, HKN'lerin çimento esaslı kompozitlerdeki etkisi değerlendirilmiştir. %1'e kadar olan düşük dozajlar, ıslak ve kuru karıştırma teknikleriyle uygulanmış ve elde edilen kompozitler fiziksel ve mekanik özellikler açısından test edilmiştir. Sonuçlar, HKN ilavesinin çimento hamurlarının işlenebilirliğini artırdığını, seçilen örneklerde eğilme dayanımını geliştirdiğini ve genel yoğunluğu hafifçe azalttığını göstermiştir. Basınç dayanımı ise önemli ölçüde etkilenmemiştir. Ayrıca, HKN uygulama yönteminin nihai malzeme özelliklerini belirlemede kritik rol oynadığı vurgulanmış ve maksimum performans için karıştırma tekniğinin optimize edilmesi gerekliliği ortaya konmuştur. Eklenen HKN miktarı, çimento üretiminin sürdürülebilirlik profiline anlamlı bir katkı sağlamasa da, iyileştirilmiş mekanik özellikler, HKN'lerin çimento esaslı sistemlerde işlevsel katkı maddesi olarak kullanılabileceğini göstermektedir—özellikle yapı sektöründeki karbon ayak izini azaltmaya yönelik diğer yeşil malzemelerle birlikte değerlendirildiğinde.

Sonuç olarak, bu araştırma, nar kabuğu gibi bir biyokütle atığından çok işlevli karbon nanomalzemelerin çevresel açıdan sorumlu ve uygulanabilir bir yöntemle üretilebileceğini göstermektedir. Aynı biyokütle kaynağından hem hidrotermal karbonik nanosferlerin hem de karbon noktalarının başarıyla elde edilmesi, tek bir atık türünün çok sayıda katma değerli ürüne dönüştürüldüğü döngüsel ekonomi ilkesinin somut bir örneğini sunmaktadır. Elde edilen bulgular, HTK yönteminin nanomalzeme sentezi için çevre dostu ve ölçeklenebilir bir süreç olduğunu ortaya koymakta ve sürdürülebilir malzeme tasarımı, süreç optimizasyonu ve uygulama geliştirme alanlarında yeni araştırma perspektifleri açarak, atık değerlendirme, yeşil üretim ve daha sürdürülebilir bir geleceğe yönelik somut stratejiler önermektedir.



1. INTRODUCTION

1.1. Background

Over the last few decades, the exploitation of our planet has accelerated at an exponential rate, leading to environmental degradation beyond the realm of imagination. This relentless pressure on natural resources has given rise to numerous challenges, including acid rain; air, water, and soil pollution; energy shortages; fossil fuel depletion; ozone layer depletion; urban sprawl; and growing waste disposal concerns. Collectively, these issues contribute to the overarching crisis of climate change, which poses a profound threat to our very existence. The urgency of addressing climate change across all levels of society has been strongly emphasized by the Intergovernmental Panel on Climate Change (IPCC, 2023). Every step toward a carbon- neutral world—whether at the individual, community, national, or global level—is essential. This includes making informed choices, enacting effective public policies, and adopting cleaner energy sources and sustainable technologies. There is an urgent need to address these challenges to protect and preserve our planet for future generations, as underscored by leading global organizations such as the United Nations (n.d.), ensuring that progress in one domain does not come at the expense of another.

While the last centuries were marked by rapid industrial development, the 21st century is defined by the concept of sustainable development, which strikes a delicate balance between environmental preservation and economic progress. Technological advancements are crucial not only for driving economic progress but also for enhancing the overall quality of our lives.

Nanotechnology, once viewed as a speculative concept and a buzzword in the mid and late 20th century, has now emerged as a leading field of technology and innovation. Central to nanotechnology are nanomaterials, which play a pivotal role in its applications. Among these, carbon nanomaterials stand out due to their unique properties and broad range of applications. These materials are at the forefront of transforming various sectors, including electronics, energy, and healthcare, thus highlighting their role in development and improving living standards.

However, the production of these high-performance materials imposes significant environmental burdens and poses health risks. Conventional synthesis methods for carbon nanomaterials require extremely high temperatures, use hazardous and expensive chemicals, and often release substantial amounts of gaseous pollutants. Furthermore, the primary precursors for these materials typically derive from fossil fuels, such as graphite, carbon monoxide, methane, and other hydrocarbons, which further exacerbates environmental concerns. This reliance on fossil fuels introduces several critical challenges. Firstly, the over-exploitation of these non-renewable resources has pushed them to the brink of exhaustion, raising concerns about long-term material security. Secondly, fossil fuels are major contributors to global warming and are responsible for extensive ecological disturbances, including air and water pollution, habitat destruction, and climate instability. Lastly, carbon nanomaterials derived from fossil fuel-based precursors are often associated with toxicity, posing serious health risks to both humans and the environment.

As the demand for carbon nanomaterials grows, the conflict between advancing technology and maintaining sustainability becomes increasingly evident. According to Friends of the Earth (n.d.), a prominent environmental advocacy group, there is a growing demand to apply a precautionary approach to the regulation of nanotechnology, prioritizing the health of people and the environment over corporate profits. A major concern among environmentalists regarding nanomaterials is the fact that their infinitesimally small size makes them difficult to handle. Nanoscale powders, including carbon-based nanomaterials, have been found to exhibit significant respirable dustiness, which can penetrate deep into the lungs and pose toxic risks if inhaled (Evans et al., 2013). Furthermore, at the nanoscale, even familiar substances can exhibit completely unique and often unpredictable behaviors, meaning materials can have different impacts on the environment and human health, thereby presenting new toxicity risks. The decreasing size of carbon-based materials could increase their toxicity (Rezazadeh Azari & Mohammadian, 2020), further complicating their environmental and health implications. These concerns raised the need to think, develop, and adopt approaches that are safer and more sustainable. While the extraordinary properties offered by carbon nanomaterials are too attractive to ignore, the ecological, environmental, and health concerns related to their sources and

synthesis processes are equally pressing. Therefore, it is urgent to seek sustainable, green alternatives for both precursors and synthesis methods.

To address this need, we have adopted the principles of green chemistry and the circular economy in our approach to producing carbon nanomaterials. These fundamental pillars of sustainable development have guided our efforts to find effective and sustainable alternatives. Biomass waste, with its abundance, carbon richness, and low cost, emerges as a particularly promising option. It is gaining global attention as a versatile resource for producing advanced carbon materials, bioenergies, and biofuels. As a renewable resource, biomass waste holds significant potential for addressing environmental and energy challenges. It contributes to environmental sustainability by reducing reliance on fossil fuels and enhancing the circular economy through effective waste valorization. With thousands of different types of biomass waste on Earth, each requiring specific conversion methods, selecting the right process is crucial to maximizing the benefits. In this context, hydrothermal carbonization, a thermochemical process, aligns with the principles of green chemistry and the circular economy by reducing waste and promoting sustainable resource utilization (Ischia & Fiori 2021). Hydrothermal carbonization stands out as a sustainable method for transforming waste biomass into valuable carbon-rich products, supporting a greener and more efficient approach to energy and material production.

1.2. Research Motivation

The primary goal of this study is to develop carbon nanomaterials that are not only efficient but also sustainable and environmentally friendly throughout their lifecycle. This research focuses on producing these materials in a way that minimizes environmental impact, avoiding the use of harmful substances and ensuring that their end-of-life phase has minimal negative effects on the environment.

While completely phasing out fossil fuels for energy applications remains challenging due to existing infrastructure and energy demands, replacing fossil fuels as precursors for valuable carbon materials is a more achievable and impactful step. This shift reduces dependence on fossil resources and encourages the use of renewable biomass. By producing carbon materials from biomass, sustainable alternatives can be created for fields such as electronics, environmental remediation, and advanced materials. This

approach aligns with the circular economy, turning waste biomass into valuable products while contributing to resource recovery and sustainability.

Everything on Earth decomposes eventually, but the rate at which this happens varies greatly. Some materials break down in seconds, while others can persist for millions of years. The harmful effects of plastic pollution are well-known, and there is growing consensus on the need to address it. Collective conscious consumption, such as refusing single-use plastics, can help reduce waste. However, biomass waste presents a unique challenge. Contrary to popular belief, organic waste can also have significant environmental impacts if not managed properly. Improper disposal can slow decomposition and release greenhouse gases, highlighting the need for more effective biomass waste management strategies.

Biomass waste, comprising by-products from agriculture, forestry, animal waste, food waste, industrial by-products, and municipal solid waste (US NREL, n.d.). To align with the Sustainable Development Goals (SDGs) and the European Union's waste management hierarchy, which prioritizes material recovery, conventional methods like landfilling and incineration must be phased out. EU directives 2018/850 and 2018/851 set targets, aiming to reduce landfilling to 10% or less and increase recycling to a minimum of 65% by 2035 (European Parliament and Council, 2018a, 2018b).

As the population grows and living standards improve, biomass production will continue to rise. For instance, increasing food production to feed more people results in more food-related biomass. The best way to manage biomass waste and prevent it from becoming a larger problem is to utilize it efficiently—transforming "trash into treasure," which is the central theme of this research study.

1.3. Aims and Objectives

A major concern that often goes overlooked in the production of carbon materials from biomass via the hydrothermal carbonization (HTC) process is the wastage of feedstock. Traditionally, the HTC process yields carbon materials from either the solid phase or the liquid phase. In both cases, after filtration, the desired material is collected, and the remaining byproducts are discarded, leading to inefficient utilization of the feedstock. Given that this study focuses on the principles of green chemistry and supports the circular economy, we aim to maximize resource efficiency by producing valuable materials from both the solid and liquid fractions.

Aim: The primary aim of this research was to explore the feasibility of using the hydrothermal carbonization process to produce sustainable alternative carbon nanomaterials suitable for broader applications.

Objectives: To achieve this aim, the following specific objectives were pursued:

- a). Characterize the synthesized nanomaterials using advanced microscopic and spectroscopic techniques to determine their structural, chemical, and functional characteristics.
- b). Evaluate the environmental impact of the HTC process through a comprehensive life cycle assessment (LCA), focusing on energy consumption, emissions, and overall sustainability.
- c). Evaluate the environmental impact of the HTC process through a comprehensive life cycle assessment (LCA), focusing on energy consumption, emissions, and overall sustainability.
- d). Explore the multifunctional applications of the synthesized carbon nanomaterials in both the biomedical and construction industries. Investigate their potential applications, particularly their ability to enhance the properties of cement composites and their antioxidant and antibacterial activities for biomedical uses.

1.4. Research Questions

The central research question guiding this study is: How can waste biomass be effectively utilized to develop sustainable carbon nanomaterials through hydrothermal carbonization, and what are the potential environmental benefits and challenges associated with their application?

To address this central question, the study will explore the following sub-questions:

- a). Which types of biomass waste are most suitable for the synthesis of carbon nanomaterials using HTC?
- b). How does the composition of different biomass feedstocks influence the properties of the final hydrothermally carbonized products?
- c). What are the potential environmental impacts of the HTC process in the synthesis of carbon nanomaterials?

- d). What are the advantages and potential challenges of incorporating synthesized carbon nanomaterials into cement composites, and how do these materials impact the properties of the composites?
- e). What is the potential of synthesized carbon nanomaterials in biomedical applications, particularly in terms of their antioxidant and antibacterial properties?



2. LITERATURE REVIEW

2.1. Overview of Carbon Nanomaterials

Defining nanomaterials has always been challenging due to the complexity and uncertainty surrounding the specific size range and properties that qualify a material as a nanomaterial. The nanoscale refers to a range from 1 to 100 nanometers, where materials often exhibit different properties compared to their larger, bulk forms. However, various international standards and recommendations have provided differing definitions of nanomaterials, emphasizing different aspects of size, shape, and aggregation.

2.1.1. Evolution of nanomaterial definitions

2.1.1.1. ASTM E2456-06 (2006)

The American Society for Testing and Materials (ASTM) defines a nanoparticle as “*a subclass of ultrafine particles with lengths in two or three dimensions between 1 and 100 nanometers*”. A note clarifies that the definition focuses primarily on size rather than properties, which has been a subject of debate regarding the importance of size-related properties.

2.1.1.2. ISO/TS (2008)

The International Organization for Standardization (ISO), in their Technical Specification (TS) 27687, defines the nanoscale as “*approximately 1 nm to 100 nm, with the lower limit intended to exclude single atoms or small groups of atoms as nanomaterials*” (International Organization for Standardization [ISO], 2008). The definition acknowledges that unique properties often appear within this size range, though the size limits are considered approximate.

Key points to note are:

- Properties that differ from bulk materials are usually (but not always) observed within this size range.
- The lower limit is introduced to avoid including single atoms or molecules.

However, ISO later withdrew this specification. In their latest ISO/TS 80004, nanomaterials are defined as “*materials with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale,*” with the nanoscale defined as the “*length range approximately from 1 nm to 100 nm*” (International Organization for Standardization [ISO], 2023).

2.1.1.3. SCENIHR categories (2010)

The European Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) took a different approach by subdividing nanomaterials into three categories (Scientific Committee on Emerging and Newly Identified Health Risks [SCENIHR], 2010):

- Category 1: Materials with a size greater than 500 nm, where the distribution at the lower end is assumed to exceed 100 nm. For these materials, a classical risk assessment can be sufficient, considering the particulate nature of the material.
- Category 2: Materials with a size between 100 nm and 500 nm, which may require a detailed nano-specific risk assessment if more than 0.15% of particles are below 100 nm.
- Category 3: Materials sized between 1 nm and 100 nm, which are automatically considered nanomaterials and require a thorough nano-specific risk assessment.

2.1.1.4. OECD-WPMN (2012)

The Organisation for Economic Co-operation and Development’s Working Party on Manufactured Nanomaterials (OECD-WPMN) defines manufactured nanomaterials as “materials in the 1-100 nm size range that may include both novel materials and those developed from existing substances” (OECD, 2012). The focus here is on materials intentionally created for their nanoscale properties, without much emphasis on aggregates or agglomerates.

2.1.1.5. EU recommendation (2022)

In the most comprehensive definition, the European Union Recommendation (2022) defines “*a nanomaterial*” as “*a natural, incidental, or manufactured material*

consisting of solid particles that are present, either on their own or as identifiable constituent particles in aggregates or agglomerates, and where 50% or more of these particles in the number-based size distribution fulfill at least one of the following conditions: (a) one or more external dimensions of the particle are in the size range 1 nm to 100 nm; (b) the particle has an elongated shape, such as a rod, fiber, or tube, where two external dimensions are smaller than 1 nm and the other dimension is larger than 100 nm; (c) the particle has a plate-like shape, where one external dimension is smaller than 1 nm and the other dimensions are larger than 100 nm.”

Key points to note here are:

- ‘Particle’ means a minute piece of matter with defined physical boundaries; single molecules are not considered ‘particles’.
- ‘Aggregate’ means a particle comprising strongly bound or fused particles.
- ‘Agglomerate’ means a collection of weakly bound particles or aggregates where the resulting external surface area is similar to the sum of the surface areas of the individual components.

In this study, we adopt the EU 2022 Recommendation, as it provides a comprehensive framework for defining nanomaterials by considering particle shape, size distribution, and aggregation. Within this context, carbon nanomaterials are classified as a unique subset of nanomaterials predominantly composed of carbon. Carbon, the fourth most abundant element in the universe and the foundation of all known life on Earth, exhibits remarkable properties such as catenation and tetravalency, enabling the formation of diverse molecular structures known as carbon allotropes. Until the late twentieth century, diamond, graphite, and amorphous carbon were the only recognized carbon allotropes. However, the discovery of fullerenes in 1985 revolutionized the field, leading to the identification of many other allotropes and the emergence of a novel class of materials: carbon nanomaterials, which are characterized by their nanoscale dimensions and diverse morphologies, paving the way for innovative applications across various fields.

2.1.2. Types of carbon nanomaterials

In this section, a brief introduction of some of the important carbon nanomaterials is presented.

2.1.2.1. Fullerenes

The discovery of fullerenes represents a major scientific breakthrough in the field of nanomaterials. Fullerenes consist of carbon atoms connected by single and double bonds, forming a closed or partially closed mesh composed of hexagonal and pentagonal rings. These molecules can have various shapes and sizes, such as hollow spheres, ellipsoids, or tubular structures. Although fullerenes were conceptualized in the 1970s, they were only discovered serendipitously in 1985 by H.W. Kroto, R.F. Curl, and R.E. Smalley, who were later awarded the Nobel Prize in Chemistry in 1996 (Nobel Prize Organisation, 1996). In fullerenes, carbon atoms are usually in the sp^2 -hybridized form and linked by covalent bonds. C_{60} , the most common and well-known fullerene, has 12 pentagonal and 20 hexagonal rings with a diameter of about 0.7 nm. Since the shape of these fullerenes resembles geodesic domes, they were named Buckminsterfullerene after the renowned architect Buckminster Fuller, who designed these domes (Kroto et al. 1985).

2.1.2.2. Carbon nanotubes

Carbon nanotubes (CNTs), discovered in 1991 by Japanese researcher S. Iijima, are cylindrical structures formed by rolling graphene sheets into tubes, with bonds closing the ends (Iijima, 1991). Based on their structure, CNTs are classified into two main types: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). These nanotubes can vary significantly in size, with diameters ranging from a few ångströms to hundreds of nanometers and lengths extending from nanometers to meters (Zhang et al. 2014). They exist in various forms, such as powders, films, sponges, and solutions, and can be functionalized with a wide range of chemical species. Additionally, CNTs can be organized into diverse microscopic or macroscopic structures with varying strength and stiffness, resulting in materials that range from carbon fiber-like structures to nanoscopic colloids (Heller et al. 2020).

2.1.2.3. Graphene

Graphene is a two-dimensional allotropic form of carbon, consisting of single layers of carbon atoms arranged in a hexagonal honeycomb lattice. In graphene, carbon atoms exhibit sp^2 -hybridization and are connected by σ - and π -bonds in this two-dimensional crystal lattice. Like fullerenes, graphene was theoretically studied for a long time before its actual discovery. P.R. Wallace, a Canadian physicist, first

proposed the theory of graphene in 1947 (Wallace, 1947). It was not until more than 50 years later that Geim and Novoselov experimentally produced graphene from graphite in 2004 (Novoselov et al. 2004), and they were awarded the Nobel Prize in 2010 (Nobel Prize Organisation, 2010). Graphene possesses many unique physical properties, including being the thinnest substance ever made, as well as exhibiting extremely high mechanical rigidity and thermal stability. These attributes have made it one of the most talked-about materials of the early 2000s. Consequently, graphene became a focal point of scientific research, leading to the launch of the Graphene Flagship in 2013. This initiative is one of the largest research programs of the European Union, dedicated to exploring and harnessing the potential of this groundbreaking material (Graphene Flagship, 2024).

2.1.2.4. Carbon nanofoam

Carbon nanofoam is a three-dimensional material consisting of randomly interconnected, nano-sized carbon clusters arranged in a regular hexagonal pattern. This structure resembles that of aerogel and is often described as a mist-like arrangement of carbon tendrils (Ali, 2022). Discovered in 1997 by Andrei V. Rode and colleagues, carbon nanofoam is among the lightest solid materials known, with a density of approximately 2 mg/cm³. Unlike other carbon allotropes, which typically feature sp³ (e.g., diamond and graphite) or sp² hybridizations (e.g., fullerenes and CNTs), carbon nanofoam exhibits both sp² and sp³ hybridizations, contributing to its unique structure (Rode et al. 1999). It is known for its ability to withstand extremely high temperatures, high surface area, and excellent electrical insulation properties (Ali, 2022).

2.1.2.5. Carbon nanofibers

Carbon nanofibers (CNFs) are cylindrical nanostructures characterized by graphene layers arranged in stacked cones, cups, or plates. CNTs, which are also cylindrical in shape, fall under the category of CNFs, with graphene layers wrapped into seamless cylinders. Both CNFs and CNTs are classified as filamentous carbon materials (Morgan, 2005; Park & Kim, 2015).

2.1.2.6. Carbon nanodiamonds

Carbon nanodiamonds (CNDs) are carbon nanoparticles with a truncated octahedral structure, typically ranging from 2 to 8 nm in diameter. They combine the properties of diamonds, such as high hardness, strength, and chemical stability, with the attributes of nanomaterials, including a very small size, large surface area, and high adsorption capacity (Zhu et al. 2012). The discovery of nanodiamonds dates back to 1963 when Soviet scientists observed that nuclear explosions using carbon-based trigger explosives produced these nanoparticles (Danilenko et al. 2004). Figure 2.1 presents schematic representations of the aforementioned types of carbon nanomaterials, generated using AI-based tools based on structural descriptions available in the literature.

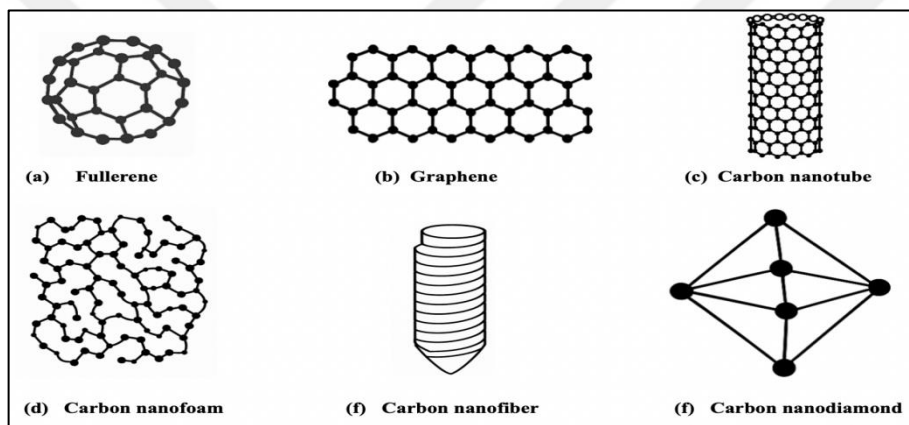


Figure 2.1. Schematic diagrams of various types of carbon nanomaterials.

This study primarily focuses on two specific types of carbon nanomaterials: carbon nanospheres and carbon dots, which are discussed next.

2.1.2.7. Carbon nanospheres

Spherical-shaped carbon materials, also known as carbon spheres, are unique nanostructures characterized by pairs of pentagonal and heptagonal carbon rings connected in a spherical arrangement. These materials are intriguing nanomaterials with potential applications as electrodes in supercapacitors, lithium-ion batteries, photocatalysis, and other fields (Nieto-Marquez et al., 2011; Gupta et al., 2019). Carbon spheres can range in size from a few millimeters to microns, or even down to a few nanometers (Nieto-Marquez et al., 2011). When most of these spheres fall within the nanoscale or sub-micron range, they are commonly referred to as carbon nanospheres (CNSs). CNSs can be classified in several ways:

i). According to their size (Serp et al., 2001):

- C_n family and graphitized onion-like structures: Typically have diameters ranging from 2 to 20 nm.
- Nanosized spheres: Less graphitized structures with diameters between 50 nm and 1 μ m.
- Carbon beads: Have diameters ranging from one micron to several microns.

ii). According to their nanometric texture (Inagaki et al., 1997):

- Concentric: Carbon layers arranged in concentric circles.
- Radial: Carbon layers arranged radially from the center.
- Random: Carbon layers arranged randomly.

iii). According to their Structure:

- Solid-dense nanospheres: Nanosphere characterized by a dense, non-hollow structure.
- Hollow nanospheres: Nanospheres with an empty core surrounded by a carbon shell.
- Core-shell nanospheres: Nanospheres consisting of an inner core encapsulated by an outer carbon shell.

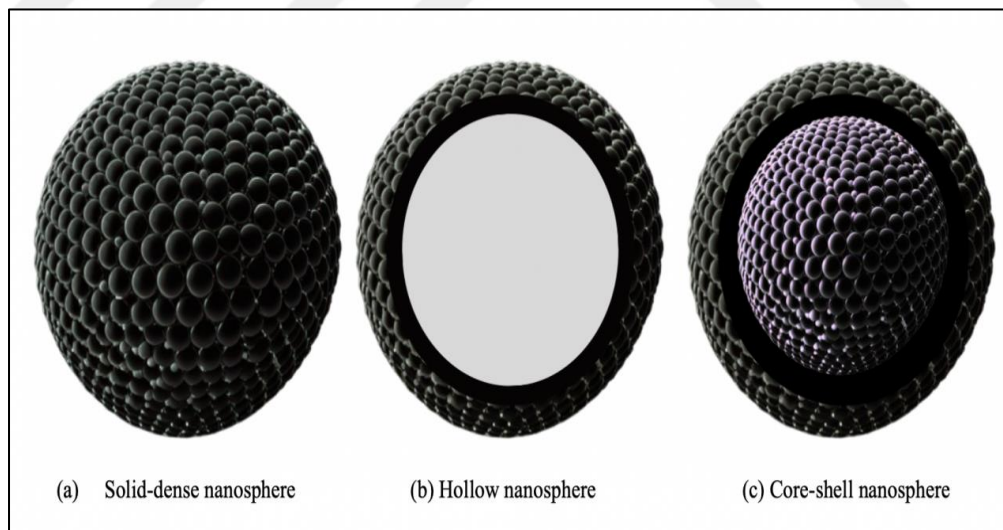


Figure 2.2. Structural classification of carbon nanospheres.

The synthesis of carbon nanospheres predominantly relies on fossil-fuel-derived precursors such as ethylene, polystyrene, phenolic resins, formaldehyde, and melamine-formaldehyde, with their production commonly achieved through methods like the template approach, spray-drying, the Stöber method, and chemical vapor

deposition (Yao et al., 2024). These synthetic routes often involve petrochemical-based materials sourced from fossil fuels. This heavy dependence on non-renewable feedstocks raises concerns regarding environmental sustainability and the ecological impact of carbon nanospheres production.

2.1.2.8. Carbon dots

Carbon dots (CDs) are zero-dimensional carbon-based nanomaterials with sizes typically ranging from 1 to 10 nanometers. They were first discovered serendipitously by Xu et al. (2004) during the purification of SWCNTs. Due to their similar optical properties and nanoscale dimensions, CDs are often compared to quantum dots (QDs), the semiconductor nanocrystals. However, unlike traditional QDs, which are composed of heavy metals such as cadmium selenide (CdSe), lead selenide (PbSe), or indium arsenide (InAs) and are often passivated with outer shells like zinc sulfide (ZnS) or cadmium sulfide (CdS) (Acharya et al., 2017), CDs are primarily made of carbon, making them more biocompatible and environmentally safer. They are also known by other names, including carbon nanodots and fluorescent carbon nanoparticles. When exposed to UV light, CDs absorb photons, exciting electrons to higher energy levels. As these electrons return to their ground state, they release energy as visible light, a phenomenon known as fluorescence. CDs are gaining significant attention due to their unique properties, including water solubility, high photoluminescence quantum yield, low cost, and biocompatibility.

Conventional quantum dots, although useful in fields like biosensing, solar cells, and medical imaging, are often limited by their toxicity due to heavy metals. CDs provide a safer and environmentally friendly alternative, offering tunable and comparable photoluminescent behavior. CDs exhibit unique photoluminescent properties, absorbing UV light typically in the 200–400 nm range and emitting visible light within the 400–750 nm spectrum. The wavelength of the emitted light is primarily influenced by particle size, surface chemistry, and the degree of graphitization (Figure 2.3). Smaller CDs, which are generally less graphitized, tend to emit light at shorter wavelengths, often appearing blue, whereas larger or more graphitized CDs exhibit red-shifted emissions (Ding et al. 2022). Additionally, surface states and functional groups present on the CDs modulate their electronic properties, influencing both the wavelength and intensity of the emitted light.

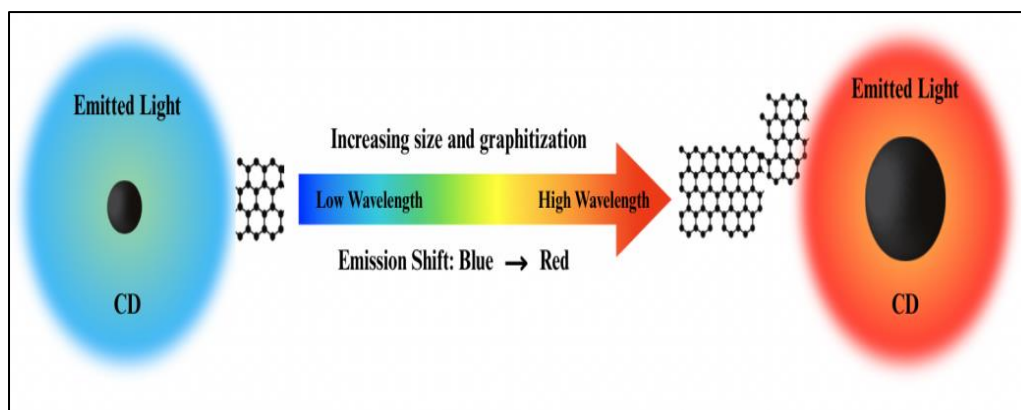


Figure 2.3. Emission color shift in carbon dots (from blue to red, indicating increasing photoluminescence wavelength with size and graphitization).

The optical properties of CDs are typically characterized using UV-Visible spectroscopy to analyze absorption properties and fluorescence spectroscopy to determine emission wavelengths and photoluminescence behavior. The UV region is commonly divided into three sub-regions: UV-A (315–400 nm), UV- B (280–315 nm), and UV-C (200–280 nm). For CDs, maximum absorption typically occurs below 380 nm within this UV range. Their unique ability to tune fluorescence through variations in particle size and surface chemistry significantly enhances their versatility for optical applications. This tunability, combined with their lower toxicity and improved biocompatibility, makes CDs a superior alternative to conventional quantum dots in terms of both safety and performance.

2.1.3. Applications and current market of carbon nanomaterials

Carbon nanomaterials possess exceptional properties such as high strength, large surface area, excellent conductivity, and photoluminescence. These attributes enable their widespread use in fields like healthcare, energy, electronics, and nanotechnology. Their biocompatibility makes them ideal for biosensors and drug delivery, while their conductivity supports energy storage devices and electronic components. With growing advancements in aerospace, defense, and renewable energy, carbon nanomaterials are becoming essential for next-generation technologies. Table 2.1 outlines their key applications based on these unique properties.

The global carbon nanomaterials market was valued at USD 3.6 billion in 2022 and is projected to reach approximately USD 40.71 billion by 2032, reflecting a significant CAGR of 27.5% from 2023 to 2032 (Precedence Research, 2023).

Key factors driving this growth include:

- Extended end-use applications, such as lithium-ion batteries for electronics and electric vehicles.
- The shift towards high-performance and sustainable vehicles in the automotive industry.
- Diverse economic activities, including manufacturing, mining, and semiconductors.
- Investment in new technologies and manufacturing plants.
- Advancements in research and development fueled by increasing industry interest.

Table 2.1. Applications of carbon nanomaterials based on their properties.

Properties	Applications	References
High mechanical strength, high specific surface area, high sensitivity to electrical field/high carrier mobility, strong adsorption, high affinity binding	Biosensors, drug delivery system, supercapacitors, stem cell based tissue engineering	Nasir et al. (2018); Hamzah et al. (2017)
High photoluminescence, high solubility, high stability, chemical inertness, functionalization, biocompatibility	Bioimaging, optoelectronics, sensors, photocatalysts	Wang and Hu et al. (2014)
High electron mobility, high thermal conductivity, high current density, transparent and conductive properties, metallic/semiconductors properties	Electronic applications (eg. transistors, transparent thin films, LSI wiring etc.)	Nasir et al. (2018)
High surface area, catalyst support, ion adsorption	Energy storage application (eg. capacitors, fuel cells, lithium ion batteries etc.)	Nasir et al. (2018)
Thin and strong, light weight, high thermal conductivity, high physical strength, high electronic conductivity, metallic/semiconductor-properties	Nanotechnology-based applications in the fields of aerospace, defense, automotive etc	Nasir et al. (2018)

2.1.4. Conventional methods of carbon nanomaterials synthesis

The synthesis of carbon nanomaterials traditionally involves two key components: the choice of raw materials and the technique employed for synthesis. Conventionally, these nanomaterials are produced from fossil-based precursors like polyacrylonitrile, ethylene gas, polyvinyl alcohol, and rayon. Although there are various methods for producing carbon nanomaterials, the primary techniques include arc discharge, laser ablation and chemical vapor deposition.

2.1.4.1. Arc discharge

S.Iijima first reported the discovery of MWCNTs, prepared using the arc discharge method (Iijima & Ichihashi, 1993). In this method, an AC plasma arc discharge is generated between two sets of graphite electrodes in an inert (argon) atmosphere. The discharge temperature is usually in the range of 2000-4000°C. At such a high temperature, sublimation of graphite takes place which is deposited at the cathode. This deposited soot contains MWCNTs. For producing SWCNTs, the same setup can be used, but suitable catalyst particles, such as Ni-Co, Co-Y, Ni-Y, or rare-earth metals, are added to the electrodes (Iijima & Ichihashi, 1993; Loiseau et al., 2006; Loos, 2014). The arc discharge method can be modified a little for the production of fullerene where an arc discharge is generated between two graphite electrodes placed facing each other in the airtight chamber under a partial pressure of helium or argon. The electrical discharge that results brings the temperature up to 6000°C which is hot enough for the carbon contained in the graphite to sublime resulting in ejection of carbon atoms from solid to form a plasma. Subsequently, these atoms travel to the colder end of the chamber to get nanomaterial deposit accumulated on the cathode (Loiseau et al. 2006).

2.1.4.2. Laser ablation

Laser ablation was the first method used for synthesis of fullerenes (Kroto et al. 1985). In the laser ablation method, a target graphite is vaporized by laser radiation at high temperatures (~1200°C) under constant flow of inert gasses. The laser vaporization produces various carbon species that accumulate in the collector cooled by water (Thess et al. 1996). Doping the graphite target with transition metals can result in the formation of SWCNTs with a uniform diameter (Loos, 2014).

2.1.4.3. Chemical vapor deposition

Chemical vapor deposition (CVD) is a deposition method in which a carbon-rich gas is decomposed into a substrate at relatively high temperature and vacuum in a chamber (Xie et al. 2000). During the process of CVD, the formation of CNTs takes place by nucleation and growth of carbon atoms releasing from the decomposition of the precursor. This process can take place with or without the help of a catalyst. The properties of the end product can be tuned in accordance to the different CVD parameters such as the types of carbon sources (gas), catalysts, substrates, and different temperatures; which makes the CVD a highly controllable process for the synthesis of nanomaterials (Loos, 2014).

2.2. Impact of Conventional Carbon Nanomaterials and Their Production Methods

Carbon nanomaterials (CNM) have found widespread applications across various industries as already discussed, but they also raise significant environmental concerns. The rapid growth of nano-based products raises the risk of toxic engineered carbon nanoparticle exposure through inhalation, ingestion, and skin penetration, leading to human health issues like cytotoxicity and DNA damage, and negatively impacting ecosystems through bioaccumulation and biomagnification (Patil & Lekhak, 2020). The growing body of research highlighting the toxicity of these materials, particularly carbon nanotubes, has led to increased scrutiny. In response, some groups have advocated for the restriction or outright ban of CNTs in the European Union, and a Swedish non-profit organization has added them to the Substitute It Now (SIN) list (Hansen & Lennquist, 2020).

Conventional methods for producing CNM, such as arc discharge, laser ablation, and CVD, may have substantial environmental impacts due to their high energy demands and associated emissions. For instance, CVD, widely used for CNT synthesis, generates harmful byproducts like methane, volatile organic compounds (VOCs), and polycyclic aromatic hydrocarbons, posing significant environmental risks. Additionally, the CVD process is particularly energy-intensive, often requiring temperatures above 1000°C, which significantly contributes to its environmental footprint. One of the earliest studies evaluating the environmental impact of SWCNTs production, comparing CVD, arc discharge, and HiPCo (high-pressure carbon

monoxide) methods, revealed that while emissions related to electricity usage were the biggest contributors, the CVD process produced the largest quantity of other emissions (excluding those from electricity), which were an order of magnitude higher than those of the arc discharge and HiPCo processes (Healy et al. 2008). Implementing green chemistry principles and using environmentally benign precursors are recommended to mitigate the environmental impacts of the CVD process and similar methods.

2.3. Inclusion of Sustainability in Carbon Nanomaterials Production

Due to the realization of the negative environmental and toxicological impacts of conventional nanomaterials, the paradigm of research has been slowly shifting towards incorporating sustainable practices. The principles of green chemistry and the circular economy serve as two fundamental pillars of sustainable development, guiding efforts toward creating more resource-efficient and environmentally friendly processes and products.

In 1998, Anastas and Warner introduced the twelve principles of green chemistry in their publication *Green Chemistry: Theory and Practice*. These principles, which remain foundational for improving materials, products, synthesis processes, and systems, emphasize the use of renewable feedstocks, safer chemicals, waste prevention, and energy efficiency—defining an efficient synthesis route as one that aligns with these guidelines (Anastas & Warner, 1998).

Complementing this, the concept of a circular economy offers a pathway to transition from the current open and linear economic model to a sustainable, closed-loop system, promoting overall sustainable development (Sillanpaa & Ncibi, 2019; Rodríguez-Antón et al. 2022). Initially centered on the ‘4 Rs’ of waste management: Reduce, Reuse, Recycle, and Recover, this framework has evolved into the more comprehensive ‘9 Rs’ approach (Refuse, Rethink, Reduce, Reuse, Repair, Refurbish, Remanufacture, Repurpose, Recycle, and Recover), as outlined in the EU Waste Framework Directive (Directive (EU) 2018/851 amending Directive 2008/98/EC; European Parliament & Council, 2008, 2018).

Together, green chemistry and circular economy frameworks emphasize the integration of eco-friendly practices and circularity as essential to sustainable development. Despite its potential, global circularity remains low, standing at just

7.2% in 2023, down from 9.1% in 2018 and 8.6% in 2020, according to the Circularity Gap Report (2023). The exclusive reliance on virgin materials is cited as the primary reason for this decline (Fraser et al., 2023). In this context, adopting sustainable approaches, such as utilizing waste biomass to produce valuable carbon-rich products, directly aligns with the principles of the circular economy.

2.4. Biomass as the Alternate

Biomass (waste) is one of the promising alternatives to conventional, resource-intensive virgin materials, aligning with the principles of green chemistry and the circular economy. Biomass broadly refers to any material derived from living or recently living organisms. While there is no universally accepted definition, most descriptions share similar elements.

The United Nations Framework Convention on Climate Change (UNFCCC) defines biomass as follows (UNFCCC, 2005):

(a). *Biomass means non-fossilized and biodegradable organic material originating from plants, animals, and microorganisms. This includes products, by-products, residues, and waste from agriculture, forestry, and related industries, as well as the non- fossilized and biodegradable organic fractions of industrial and municipal wastes. Biomass also includes gases and liquids recovered from the decomposition of non- fossilized and biodegradable organic material.*

(b). *Biomass residues mean biomass by-products, residues, and waste streams from agriculture, forestry, and related industries.*

According to the Directive 2009/28/EC from the European Parliament, biomass is defined as *the biodegradable fraction of products, wastes, and residues from biological origins such as agriculture (including vegetal and animal substances), forestry, and related industries, including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal wastes* (European Parliament, 2009).

The U.S. Energy Information Administration (EIA) defines biomass as *any renewable organic matter originating from plants and animals* (U.S. EIA, 2024).

2.4.1. Composition of biomass

Biomass is a complex mixture of variable components which include carbohydrates (such as cellulose, hemicellulose and starch), lignin, extractives, lipids, proteins, water, hydrocarbons, ash, and other compounds (Demirbaş, 2009).

- Cellulose: Cellulose is the most abundant natural polymer on earth. It is a polysaccharide of glucose monomers held together by β (1 $\rightarrow$ 4) glycosidic bonds. It consists of straight chains, which enables formation of strong intra- and inter-molecule hydrogen bonds and thus has a high degree of crystallinity which makes it resistant to hydrolysis.
- Hemicellulose: Hemicellulose, the second major component of biomass, is a heteropolymer consisting of several monosaccharides including xylose, mannose, and glucose, among others. It has an amorphous structure and hence it is more susceptible to hydrolysis than crystalline cellulose.
- Lignin: Lignin is an intricate array of aromatic alcohols held together by C–C or C–O–C bonds. Lignin, intertwined with cellulose and hemicellulose together to form biomass structure which provides rigidity to lignocellulosic materials, such as trees.
- Other: Starch is another biomass component, consisting of glucose units connected by β (1 $\rightarrow$ 4) and α (1 $\rightarrow$ 6) bonds. There are two types of starch: amylose, which has a linear structure, and amylopectin, which has a more branched structure. Biomass also contains small amounts of extractives, volatiles, and ash, which can still impact the conversion process. Ash consists of inorganic materials, either naturally present or introduced externally. Additionally, biomass, especially from animal and microbial sources, includes lipids and proteins (Williams et al. 2017).

It is the variation of these components which decides the nature of different types of biomass. Generally, cellulose is the most abundant natural polymer, accounting for 35–55% of lignocellulosic biomass. Hemicellulose is the second most abundant natural polymer, accounting for 20–35 wt. %, followed by lignin which represents 10–30 wt. % of lignocellulosic biomass. Usually, more than 90% of lignocellulosic and 80% of herbaceous biomass is made up of three main components i.e. cellulose, hemicellulose and lignin (Williams et al. 2017).

2.4.2. Waste management of biomass

Given the inevitable generation of biomass, the effective disposal and management of this waste have become critically important. A report by the World Bank projected that the global waste generation is expected to increase to 3.40 billion tonnes annually by 2050, if it continues to grow at the same pace without any immediate steps taken to tackle it (Kaza et al., 2018). The driving force behind this increment is found to be rapid urbanization along with high growth of population. The report points out that currently the world generates about 2.01 billion tonnes of municipal solid waste (MSW) annually out of which approximately 33 percent of that is not managed effectively and sustainably. Furthermore, the largest category of waste is found to be food and green waste which makes up 44 percent of global waste. It is also discussed in the report that open dumping and disposing of the solid waste in landfills without the gas capture system contributed towards the global emission of 1.6 billion tonnes of carbon dioxide (CO₂) equivalent greenhouse gas emissions (Kaza et al. 2018).

Hence, sustainable management of the waste becomes an issue of concern. Over the years, various methods have been implemented for managing biomass waste. Landfilling, incineration, composting, and anaerobic digestion are some common waste treatment and disposal methods. The choice of technique depends on factors such as the type and amount of biomass waste, geographical location, and available resources. None of these methods can be considered a foolproof solution, as each has its own advantages and disadvantages. For instance, landfilling is the oldest and most common method of waste disposal. While it is easy and economical, it produces toxins, leachate, and harmful greenhouse gases (such as CO₂ and methane), which contribute to global warming and cause water and soil pollution (EPA, n.d.; Siddiqua et al. 2022). Incineration, on the other hand, is popular for its ability to conserve landfill space, reduce waste volumes, and generate electricity. It can drastically reduce waste mass by 95-96% and reliably produce heat and power under various weather conditions (European Commission n.d.). However, incineration also has significant drawbacks. Constructing an incineration plant is expensive, and even modern facilities designed to capture most emissions still produce hazardous by-products, including dioxins and heavy metals (Pan et al. 2022). This suggests that incineration may merely shift pollution problems from one environmental medium to another (Seager, 2022). Similarly, composting and anaerobic digestion can produce odor nuisances that

significantly impact emotional well-being and pose health risks due to high levels of ammonia, hydrogen sulfide, and dimethyl disulfide in the ambient air (Han et al., 2020).

The complexities of evolving problems require innovative approaches. Instead of merely disposing of waste, we should aim to benefit from it. This approach aligns with the principles of the circular economy, which repurposes waste rather than discarding it. An effective way to manage biomass waste is by converting it into something useful, addressing both waste disposal and material production. A substantial volume of biomass is readily available for conversion into significant amounts of energy, chemicals, and other products through appropriate methods. Transforming waste into value-added products, or "trash-to-treasure," using biomass conversion techniques is a practical strategy for achieving these objectives.

2.4.3. Biomass conversion techniques

Biomass efficiently captures atmospheric CO₂ through photosynthesis, serving as a temporary carbon sink. However, this role is short-lived, as microbial decomposition eventually releases this stored CO₂ back into the atmosphere (Titirici et al., 2007). Unlike some other resources, such as fossil fuels, biomass is most beneficial when actively utilized, whether as fuel, feed, feedstock for valuable products, or converted into stable forms. This is because unused, decaying biomass releases carbon dioxide back into the atmosphere, contributing to carbon emissions. With thousands of biomass types on Earth, each requires specific treatment to unlock its potential. Dry agricultural waste and wood are ideal for direct combustion, while biomass with high moisture content needs conversion into other forms first. These conversion processes, essential for utilizing biomass in energy and value-added products, are broadly categorized into biochemical and thermochemical methods. Biochemical conversion includes processes such as anaerobic digestion, fermentation, or composting which involves the use of enzymes of bacteria or other microorganisms to break down biomass (Williams et al., 2015). Pyrolysis, torrefaction, gasification and hydrothermal carbonization come under thermochemical processes in which the conversion of biomass happens with the help of heat. A summary of these thermochemical methods, along with their favored operating conditions, is presented in Table 2.2.

Pyrolysis is the process in which the decomposition of biomass occurs at high temperatures in the absence of oxygen (Vuppaladadiyam et al. 2023). Torrefaction is similar to pyrolysis but takes place at relatively lower temperatures. Gasification involves converting solid biomass into various gases using heat and varying amounts of oxygen (Cortazar et al., 2023). However, these thermochemical processes require biomass with minimal moisture content, or else prior drying is needed, which demands significant energy and increases operational costs.

This moisture requirement limits the range of biomass types that can be explored and utilized, leaving many high-moisture biomasses untreated. Hydrothermal carbonization the core focus of this study and also known as wet pyrolysis, offers a promising solution for converting wet biomass. Conducted in the presence of sub-critical liquid water, HTC is particularly well-suited for processing biomass with high moisture content.

Table 2.2. Thermochemical conversion methods and their operating conditions.

Thermochemical Conversion Method	Favored Conditions	Operating	References
Slow Pyrolysis	Temperature: 300–700 °C Heating Rate: Slower (5–30 °C/min) Residence Time: >30 min		Vuppaladadiyam et al. (2022); Patra et al. (2021)
Intermediate Pyrolysis	Temperature: Up to 500 °C Heating Rate: Moderate (100– 500°C/min) Residence Time: 2–4 s Process Time: 30–1500 s		Jerzak et al. (2022); Vuppaladadiyam et al. (2022)
Fast Pyrolysis	Temperature: 450–800 °C Heating Rate: Higher (10– 1000 °C/s) Residence Time: <20 s		Vuppaladadiyam et al. (2022); Patra et al. (2021)
Flash Pyrolysis	Temperature: 800–1200 °C Heating Rate: >1000 °C/s Residence Time: <2 s		Vuppaladadiyam et al. (2022)
Gasification	Temperature: 700–1200 °C		Cortazar et al. (2023)
Torrefaction	Temperature: 200–300 °C		Chen et al. (2018)
Hydrothermal Carbonization	Temperature: 180-250 °C		Hejna et al. (2023)

2.5. Hydrothermal Carbonization

Hydrothermal carbonization (HTC) presents a promising pathway for converting biomass waste into valuable carbon-rich materials. The concept dates back over a

century to Friedrich Bergius's pioneering work in 1913 (Bergius, 1913). Since then, its development has evolved through significant milestones, from biomass experiments in the 1930s to renewed interest in the early 2000s, particularly marked by Antonietti and his team's synthesis of carbon spheres and mechanistic studies (Antonietti, 2011).

HTC is a thermochemical process that converts wet biomass into a carbon-rich solid (hydrochar), accompanied by liquid and gaseous by-products. This conversion occurs in a sealed autoclave under subcritical water conditions at moderate temperatures (typically 180–250°C) and elevated pressures over residence times ranging from minutes to several hours (Titirici et al., 2009; Libra et al., 2011).

The process mimics the natural formation of coal, with the key distinction that the slow geological timeframes are replaced by elevated temperatures that accelerate the kinetics of carbonization reactions. The conditions used in HTC—moderately high temperatures, higher pressures, exclusion of oxygen, and weakly acidic pH—closely resemble those found in natural coal-forming environments (Titirici et al., 2009).

In HTC, biomass is submerged in water, where it remains in its liquid phase under subcritical conditions, enabling a range of chemical reactions, including hydrolysis, dehydration, decarboxylation, and polymerization. If the temperature and pressure exceed the supercritical threshold of 374°C and 22.1 MPa, respectively, the process transitions to hydrothermal gasification, producing primarily gaseous products (Libra et al., 2011). Some studies have explored the use of alternative moisture sources, such as activated sludge and landfill leachate, in HTC (Li et al., 2014; Venna et al., 2020); however, it remains essential to maintain a hydrous environment for effective biomass conversion (Basso, 2016). A timeline of key developments in the HTC process is presented in Figure 2.4.

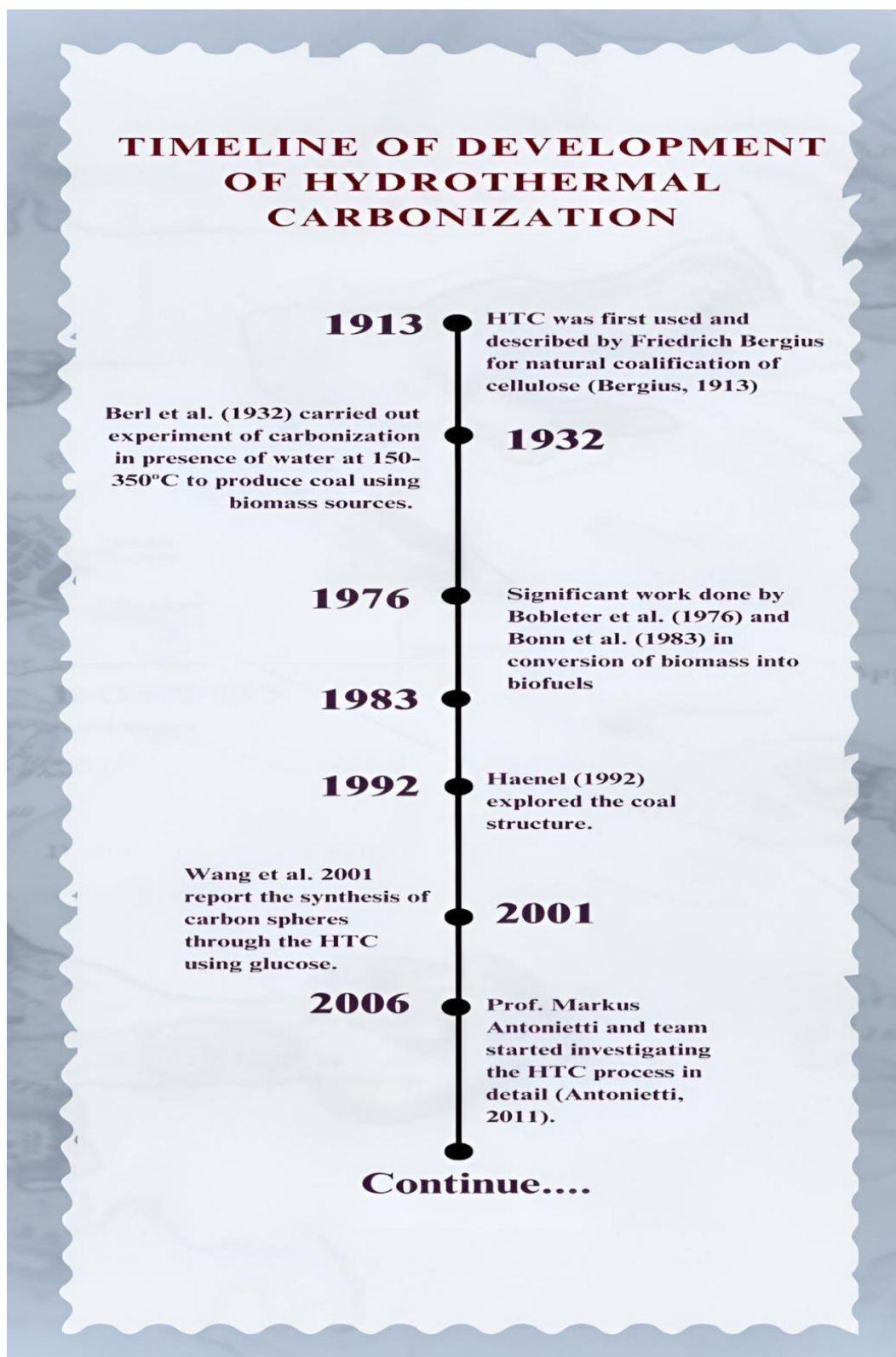


Figure 2.4. Timeline depicting the development of the HTC process

HTC yields three primary products: a solid carbon-rich material (hydrochar), a liquid phase containing a variety of organic compounds, and a minor fraction of gases. The

solid product, hydrochar, is composed mainly of fused aromatic structures, which enhance its thermal and structural stability (Berge et al., 2011).

The liquid phase is a complex mixture that includes organic acids (e.g., acetic acid), aldehydes, alkenes, and aromatic compounds such as furanic and phenolic derivatives. It also contains sugar-derived volatile organic compounds, including furfural (Funke & Ziegler, 2010; Lu et al., 2012; Berge et al., 2011; Xiao et al., 2012).

The gaseous by-products consist primarily of CO₂, along with trace levels of CO, CH₄, H₂, and light hydrocarbons such as ethane, propene, and butane. The generation of CO₂ is predominantly driven by decarboxylation reactions, with the gas composition varying depending on reaction severity (Lu et al., 2012).

2.5.1. Chemical reactions and mechanisms involved

The precise chemical mechanisms behind HTC remain complex due to the heterogeneity of biomass. However, the reactions are similar to those in pyrolysis, including hydrolysis, dehydration, decarboxylation, condensation polymerization, and aromatization (Libra et al., 2011).

- **Hydrolysis:** Cellulose begins hydrolysis around 200°C, hemicellulose between 180–200°C, and lignin between 180–220°C. Reaction pathways involve the breakdown of hemicellulose into sugars like D-xylose and their conversion into furfural or levulinic acid. Similarly, cellulose hydrolyzes into D-glucose, which transforms into 5-HMF and further into acids. Lignin decomposes into phenolic compounds.
- **Dehydration and Decarboxylation:** Dehydration removes hydroxyl groups, while decarboxylation eliminates carboxyl and carbonyl groups, producing CO₂ and CO, respectively. These processes lower the H/C and O/C ratios, increasing the carbon content of hydrochar.
- **Polymerization and Aromatization:** Soluble polymers form via polymerization of furan-like compounds, leading to the creation of aromatic clusters, the primary building blocks of hydrochar. Temperature, time, and pressure influence aromatic structure formation.

2.5.2. Operating parameters

2.5.2.1. Temperature

Temperature is the most critical parameter influencing HTC outcomes. Typical ranges (180–300°C) decompose:

- Hemicellulose (~200–240°C)
- Cellulose (~200–270°C)
- Lignin (~200–300°C.)

2.5.2.2. Residence time

Residence times range from several minutes to few days, with specific durations tailored to biomass type and desired outcomes.

2.5.2.3. pH

Mildly acidic conditions accelerate HTC reactions by mimicking natural coal formation processes. While pH effects vary among studies, acidity generally enhances reaction rates.

2.5.2.4. Pressure

HTC operates under autogenic pressures (~10–65 bar), ensuring water remains in its liquid state, crucial for effective hydrolysis.

2.5.2.5. Solid content

The biomass-to-water ratio significantly affects conversion efficiency. Solid loads between 20–90% are typical, balancing water's hydrolytic role with hydrochar yield.

2.5.3. Rationale for selecting HTC as the synthesis process

HTC was selected as the synthesis method due to its strong alignment with green chemistry principles, particularly in terms of energy efficiency and environmental sustainability. Initially employed primarily for biomass pre-treatment and dewatering (Robbiani, 2013; Boutaieb et al., 2021), HTC has since emerged as a promising technique for producing value-added carbon materials from biomass. It is recognized as a green, cost-effective alternative among thermochemical conversion processes, operating under relatively moderate conditions. A key advantage of HTC is its ability

to function at lower temperatures (180–250°C) compared to pyrolysis (>300°C) and gasification (>700°C). This significant reduction in operational temperature lowers energy demand and contributes to a smaller environmental footprint, in line with the green chemistry principle of minimizing energy use.

Another critical benefit is HTC's capacity to process biomass with high inherent moisture content (typically 75–90%) without the need for energy-intensive drying. This not only conserves energy but also reduces processing steps, further supporting efficient resource use.

HTC utilizes water as both the reaction medium and chemical participant. Operating at elevated pressures, water remains in the liquid phase, enabling its catalytic behavior and often eliminating the need for additional chemical additives. This contributes to reduced chemical inputs and waste, consistent with green chemistry goals.

The process is also highly versatile, accommodating a wide range of biomass feedstocks with differing moisture contents and compositions. This flexibility enhances the sustainable use of regionally available biomass resources. Moreover, HTC's ability to carbonize air-dried or wet feedstocks without pre-treatment minimizes raw material use, reduces reliance on synthetic chemicals, and promotes reuse—further aligning with green chemistry practices.

Understanding the influence of biomass composition on hydrochar quality is essential to avoid feedstock-resource mismatch and unnecessary waste. HTC's compatibility with wet biomass ensures a practical and sustainable conversion pathway.

Finally, HTC yields hydrochar with a significantly higher energy density than the original biomass, making it suitable for applications such as biofuel for heat and electricity generation (Sharma, Sarmah and Dubey, 2020). The properties of hydrochar are comparable to those of conventional fossil fuels, such as lignite coal (Böttger et al., 2023), offering a viable renewable energy alternative and a pathway to reduce fossil fuel dependence.

2.5.4. Potential environmental impacts of HTC compared to other methods

The HTC process offers significant improvements in energy efficiency and a reduction in carbon footprints compared to traditional biomass treatment methods. For instance, a study by Mannarino et al. (2022) evaluated the environmental performance of integrating HTC with a water resources recovery facility for sewage sludge treatment.

The results showed that HTC could achieve up to a 98% reduction in environmental impacts, particularly in the Climate Change category, compared to traditional composting. This reduction was attributed to the valorization of hydrochar as a lignite substitute and the use of process water in anaerobic digestion for biogas production. However, attempts to recover phosphorus from HTC process water revealed some negative environmental impacts, highlighting the complexity of the process and the importance of selecting more efficient alternatives for phosphorus recovery to minimize environmental impacts.

HTC can also be integrated with various other methods, such as incineration, gasification, and anaerobic digestion, to enhance conventional waste treatment systems. Stobernack et al. (2021) demonstrated that incorporating an HTC step for treating MSW significantly improved net exergy (usable energy efficiency) by up to 93%, while simultaneously reducing the global warming potential (GWP) by 30%. This dual benefit offers a clear advantage over conventional methods like anaerobic digestion and composting, showcasing the potential of HTC for optimizing waste management systems and reducing their environmental footprint.

2.5.5. HTC for the production of carbon nanomaterials

HTC has emerged as an efficient and environmentally friendly method for synthesizing carbon spheres and carbon dots from various organic compounds found in biomass. For instance, Sevilla and Fuertes (2009a) demonstrated the synthesis of uniform, spherical micrometer-sized particles with diameters ranging from 0.4 to 6 μm , using saccharides such as glucose, sucrose, and starch. These particles were produced at temperatures between 170 and 240 $^{\circ}\text{C}$, and the morphology of the materials could be modulated by adjusting the synthesis conditions, including the concentration of the aqueous saccharide solution, the temperature of the hydrothermal treatment, the reaction time, and the type of saccharide used. In a related study, Sevilla and Fuertes (2009b) prepared carbon spheres from cellulose at temperatures in the range of 220–250 $^{\circ}\text{C}$, resulting in agglomerates of carbonaceous microspheres with sizes approximately 2–5 μm .

Further research by Liu et al. (2015) explored the production of carbon spheres from agarose using HTC. This study revealed that both micro-sized and nano-sized carbon spheres could be synthesized, with the yield, size, and number of spheres being

controlled by the amount of agarose in the solution. They demonstrated that a higher concentration of agarose led to larger carbon spheres, although concentrations above 5.0% prevented sphere formation due to the limited solubility of agarose. Yan et al. (2015) succeeded in synthesizing carbon nanospheres of much smaller sizes from four different carbon sources: xylose, glucose, sucrose, and saccharides derived from the acid hydrolysis of pine wood. The nanospheres produced ranged in size depending on the precursor used, with xylose and glucose yielding particles of 80 nm and 100-150 nm, respectively, when heated at 180°C for 12 hours with continuous stirring. Sucrose produced larger nanospheres of 300-400 nm under the same conditions, while saccharides derived from pine wood produced nanospheres of 50-100 nm when heated at 210°C for 12 hours.

Simsir et al. (2017) contributed to this area by emphasizing the influence of feedstock composition on particle size and formation time. They demonstrated that the hydrothermal carbonization of glucose at 200°C for 48 hours resulted in the formation of carbon spheres with a narrow size distribution of approximately 560 nm. In contrast, the hydrothermal carbonization of chitosan at the same temperature produced densely aggregated carbon spheres with a uniform size of approximately 42 nm after 18 hours. Similarly, Gupta et al. (2019) studied the effect of initial solution concentration on the formation of carbon nanospheres using various saccharides under HTC conditions at 180°C. Their results showed that starting with a 0.005 M solution, sucrose, glucose, and xylose produced carbon nanospheres with diameters of approximately 160 nm, 40 nm, and 20 nm, respectively.

Papaioannou et al. (2018) prepared carbon dots from glucose at 200°C for 6 hours, resulting in particles with an average size of 5.15 ± 0.83 nm. Similarly, Crista et al. (2020) prepared carbon dots with an average size of 6.9 ± 2.0 nm using citric acid as the carbon source and urea as the nitrogen source under hydrothermal conditions at 200°C for 2 hours.

Though these pure sources are effective for small-scale production, they are unsuitable for large-scale applications. Their derivation requires additional processes such as separation and purification, making them unsustainable for broader use (Skoog et al., 2022). However, when applied to real biomass, the HTC process often generates irregularly shaped carbonaceous particles. This irregularity limits its suitability for

producing engineered carbon particles for specific applications, thereby confining its use primarily to energy generation (González-Arias et al., 2022).

This study aims to test the hypothesis that the unique morphology of carbon particles is influenced more by the relative proportions of biomass components than by inherent limitations of the HTC process itself. While theoretically, any biomass can undergo hydrothermal carbonization, selecting the right type of biomass is crucial for achieving desired properties in the resulting hydrochar.

2.5.6. Biomass feedstocks selection

Over time, the use of food materials, such as fruit juices and pulp, as feedstocks has gained popularity. While these renewable carbon sources can produce high-quality carbon material, they are not viable for large-scale production due to ethical concerns related to the "*food vs. feed vs. fuel*" debate (Muscat et al. 2020). The use of less abundant biomass feedstocks has also shown promise, but their limited availability poses challenges for future applications.

To effectively replace fossil fuels, it is essential to select biomass feedstocks that are competitive with fossil fuels in both economic and technological aspects. Abundant, easily available, non-food, waste biomass feedstocks with high carbon content have the potential to bring these methods to a commercial scale. Therefore, the following criteria were followed for selecting the type of biomass waste suitable for the present study:

- The raw materials should be non-food biomass waste to avoid competing with food resources.
- They should be relatively unexplored in previous research, offering new insights.
- The materials need to be readily available to ensure practical implementation.
- They should have a broad impact, making the findings applicable beyond specific regions.
- The selected materials must be diverse to allow for a comprehensive comparison of how different biomass compositions affect the final HTC products.
- There should be a substantial amount of waste generated from these materials to align with the study's focus on waste management.

For this purpose, the following three biomass waste materials were selected as primary feedstocks. These materials are frequently overlooked in conventional waste management programs and are often disposed of irresponsibly. However, they possess significant potential as valuable sources of carbon precursors, which is the focus of this study:

(a). Agricultural and food industry waste: Discarded pomegranate peel waste (PPW)

Pomegranate peel waste is significant globally, with millions of tons discarded each year. Pomegranate Market size was valued at USD 221.32 Million in 2023 and is projected to reach substantial growth of USD 375.68 Million by 2031, growing at a CAGR of 9.23% from 2024 to 2031 (Verified Market Research, 2025). Leading producers include India, China, Iran, Turkey, Afghanistan, the US, Iraq, Pakistan, Syria, and Spain. In India, pomegranate production reached approximately 3 million metric tons in 2021-22, while Turkey produced 647,676 tons in 2021 (KiliçariSlan Özkan, 2023). Notably, 35-55% of these pomegranates become waste annually, accounting for around 54% of the fruit post-juice extraction. In 2017, the world generated an estimated 1.9 million metric tons of pomegranate peel, which makes up around 50% of the pomegranate fruit (Singh et al., 2023). Improper disposal of this waste in landfills releases methane—a greenhouse gas more than 80 times more potent than CO₂ over a 20-year period—contributing significantly to environmental pollution (United Nations Environment Programme, 2021). Converting PPW into valuable products through HTC presents a promising approach to reduce these environmental impacts and efficiently utilize the waste.

(b). Herbaceous waste from the floral industry: Disposed marigold flower waste (MFW)

The floral industry generates substantial waste, particularly in countries like India and Sri Lanka, where up to 40% of production goes unsold and is discarded (Dutta & Kumar, 2021). A study estimates that India generates approximately 4.74 million tonnes of floral waste per day from various religious and social programs (Atal, 2022). Improper disposal of flower waste in landfills and water bodies leads to greenhouse gas emissions. The decomposition of this waste also releases odors and fosters the spread of pathogens (Choudhury & Deka, 2024). Marigold flowers, widely used in

cultural and religious ceremonies, contribute significantly to this waste. Given the environmental impact of floral waste and the cultural significance of marigolds, converting MFW through HTC presents an eco-friendly approach that not only reduce the problems of improper disposal and harmful emissions but also promotes the effective reuse of organic waste.

(c). Municipal solid waste: Cotton fabric waste (CFW)

The fashion industry is a major contributor to global pollution, responsible for approximately 10% of total greenhouse gas emissions and a significant portion of microplastics found in oceans (Beall, 2020). It also generates about 4% of global waste, with clothing production doubling over the past two decades due to the rise of fast fashion—a model centered on rapid production and low-cost, disposable garments (Igini, 2023). Reports indicate that nearly 92 million tons of garments are discarded in landfills annually, and by 2030, this number is projected to exceed 134 million tons (Beall, 2020; Igini, 2023). Despite various recycling initiatives, only about 12% of textiles are recycled globally, and a mere 1% is reused to make new clothing items (Beall, 2020; Charnley et al., 2024). Cotton, a primary material in textile production, presents both challenges and opportunities for sustainability. While it is a renewable and biodegradable natural fiber, its cultivation requires significant water and energy inputs, alongside the use of pesticides, which can have detrimental environmental effects. The choice of 100% cotton fabric waste for HTC aligns with efforts to address these environmental challenges by converting textile waste into valuable carbon products. This approach not only mitigates the environmental impact of textile waste but also explores the potential for utilizing other natural and synthetic textile wastes in future studies. Thus, HTC represents a promising technology to transform textile waste into valuable resources, contributing to sustainable practices in the fashion industry.

2.6. Life Cycle Assessment

The utilization of the HTC process for waste management and energy conversion, particularly through hydrochar production as fuel, is steadily gaining traction, with a few companies now actively operating HTC plants on a commercial scale. However, applying the HTC process for large-scale production of nanomaterials remains in its infancy and requires extensive research into all aspects before it can become

commercially viable. The HTC sector is currently a "blue ocean" market with minimal competition, which means it has significant opportunities for innovation in developing new applications and refining existing processes. Identifying and addressing current hotspots within the process will be crucial for realizing its full potential and advancing towards commercial viability.

The successful transition of any technology from the laboratory to the market depends on several factors, including scalability, economic feasibility, and environmental impact, among others. Research and development should place equal emphasis on both product efficiency and the efficiency of its production process. Often, an exceptional performance of a product can overshadow its environmental impact during manufacturing, with performance prioritized over production efficiency (Seager, 2022).

In the circular economy, the future success of any process or product or service depends on its sustainability and evaluating the environmental impact of the process is crucial. Here, the concepts of Life Cycle Thinking (LCT) and Life Cycle Assessment (LCA) become particularly relevant. LCT aims to identify improvements in goods and services that reduce environmental impacts and resource use across all life cycle stages, with the goal of avoiding burden shifting (European Commission, 2010). LCA, in turn, serves as a tool to implement the principles of LCT. As a crucial tool, LCA significantly contributes to the objectives of global climate agreements and broader sustainability goals by identifying environmental hotspots within a product, process, or service. By pinpointing these areas of concern, LCA enables decision-makers to explore the most sustainable pathways, whether through redirecting, diverting, replacing, reducing, or eliminating the identified hotspots. This systematic approach ensures that sustainability is integrated into every stage of the life cycle, ultimately leading to more environmentally responsible outcomes.

2.6.1. LCA principles and methodologies

LCA is a tool within environmental systems analysis (ESA) and forms part of the ISO 14000 series of environmental management standards. The ISO defines LCA as “the compilation and evaluation of the inputs, outputs, and the potential environmental impacts of a product system throughout its life cycle” (International Organization for Standardization, 2006a, 2006b). The term “life cycle” refers to the entire journey of a

product—from raw material acquisition to final disposal, as illustrated in Figure 2.5. The general categories of environmental impacts considered in LCA include resource use, human health, and ecological consequences.



Figure 2.5. A typical life-cycle of a product

2.6.2. LCA stages

The life cycle of most manufactured products involves five main stages.

- (i). Raw Material Acquisition: This stage involves the extraction and processing of raw materials from natural resources.
- (ii). Manufacturing: The raw materials are used to produce the product.
- (iii). Distribution: The manufactured product is distributed to consumers.
- (iv). Use: The product is used by consumers.
- (v). Disposal: The product reaches the end of its useful life, leading to disposal. This stage may include multiple steps such as remanufacturing, recycling, and final disposal through incineration or landfilling.

Each stage involves energy consumption, emissions, and waste generation, contributing to environmental impacts such as water discharges, gaseous emissions, energy consumption, depletion of nonrenewable resources, and solid waste generation (Tranquillo et al., 2022).

2.6.3. LCA phases

There are four phases included in LCA: goal and scope, life cycle inventory (LCI) analysis, life cycle impact assessment (LCIA) and interpretation as shown in Figure 2.6 (Hauschild, 2005).

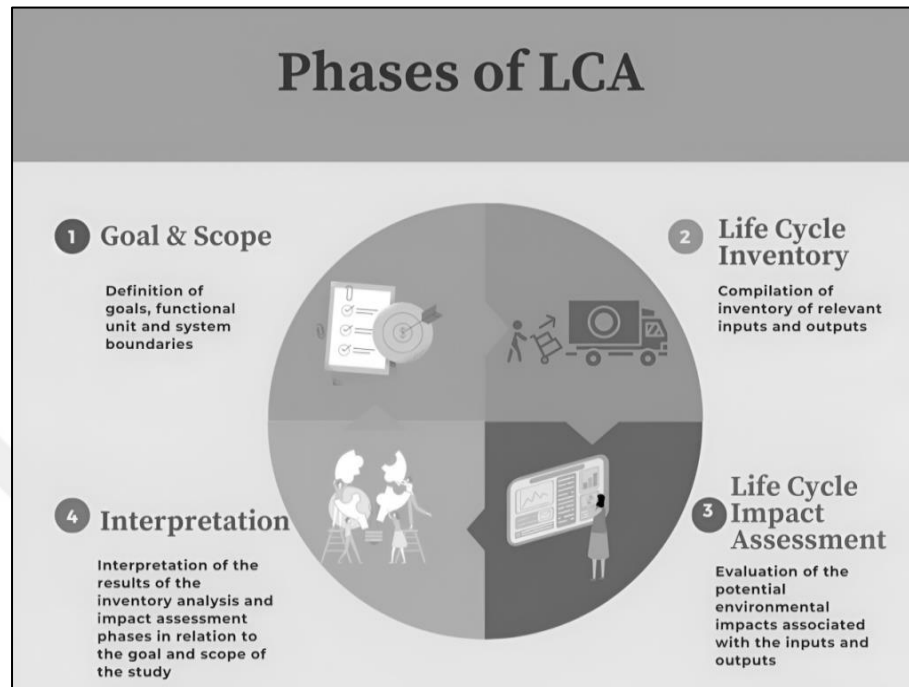


Figure 2.6. Phases of LCA based on ISO standards.

2.6.3.1. Goal and scope

In the goal and scope phase, the aims of the study are clearly defined. According to ISO (2006b), the goal should state: *“the intended application, the reasons for carrying out the study, the intended audience and whether the results are intended to be used in comparative assertions intended to be disclosed to the public”* (ISO 2006b, 7). The main steps involved in this phase are:

- the exact definition of the functional unit,
- the identification of the system boundaries,
- the identification of the allocation procedures,
- the studied impact categories and the LCIA models used, and
- the identification of data quality requirements.

2.6.3.2. Life cycle inventory

The life cycle inventory (LCI) phase involves data collection and calculation procedures for quantifying inputs and outputs of the studied system. This includes energy, water, and materials usage, as well as air emissions, solid waste disposal, and wastewater discharge. Data collected concern foreground processes and background processes. Foreground data describes the system technically, while background data describes the system environmentally with emission factors that can be obtained from databases (Deiso, n.d.). Data are validated and put in relationship to the process units and functional units.

2.6.3.3. Life cycle impact assessment

The life cycle impact assessment (LCIA) phase involves linking LCI results to environmental impact categories and indicators. This is achieved through LCIA methods, which first classify emissions into impact categories and then characterize them into common units for comparison. According to ISO (2006a), LCIA includes mandatory steps—Selection of Impact Categories, Classification, and Characterization—along with optional steps like Normalization, Grouping, and Weighting. The selection of impact categories should align with the purpose and scope of the study, carefully defining the impacts associated with the product or system. Classification assigns the inventoried material and energy inputs and outputs to relevant impact categories. During the classification stage, results that contribute to more than one category are appropriately categorized. Characterization quantifies the contributions of each classified input and output to their respective impact categories using characterization factors, which represent the impact intensity of a substance relative to a reference substance. Normalization involves comparing quantified impact category results against a reference value, expressed as dimensionless values. Grouping sorts LCIA results into groups based on indicator characteristics, geographical location, or priority level, as defined by the study's goals. Weighting assigns importance values to impact categories, multiplying normalized results by weighting factors to generate a single overall score. In the final stage, impact potentials are calculated for each category, and the accuracy of results is assessed based on the study's purpose and scope. The impact analysis results should include detailed

explanations of methods used, clearly stated system boundaries, and any assumptions or simplifications made (Hauschild, 2005; Cokaygil, 2016; Demirel et al., 2017).

2.6.3.4. Life cycle interpretation

Finally, in the life cycle interpretation phase, all the results from LCI and LCIA are evaluated in accordance with the defined goal and scope. This step includes conclusions, explanation of limitations and also provides the recommendations. Sensitivity, consistency checks, uncertainty analysis and accuracy of obtained results are also addressed in this step (Hauschild 2005).

2.6.4. Impact categories

The impact assessment phase evaluates a product, process, or service based on several categories, including global warming, acidification, eutrophication, ozone depletion, photochemical ozone formation, human toxicity, ecosystem toxicity, resource depletion, land use, water use, particulate matter formation, ionizing radiation, ecotoxicity, marine eutrophication, and terrestrial eutrophication. These categories collectively provide a comprehensive understanding of the environmental burdens associated with the life cycle of the studied system.

Impact categories in life cycle assessment can be divided into two main types: midpoint and endpoint categories.

2.6.4.1. Midpoint impact categories

Midpoint impact categories assess environmental impacts at an intermediate stage between the inventory analysis and the final damage or endpoint. These categories are typically expressed in terms of specific environmental issues or indicators. Examples include:

- **Global Warming Potential (GWP):** Measures the impact of greenhouse gases on climate change.
- **Acidification Potential:** Assesses the contribution of emissions to acid rain.
- **Eutrophication Potential:** Evaluates the impact of nutrient emissions on aquatic ecosystems.

2.6.4.2. Endpoint impact categories

Endpoint categories assess the environmental impacts at the final stage of the LCA, translating midpoint indicators into potential damages to human health, ecosystem quality, and resource availability. Examples include:

- **Human Health:** Evaluates the potential impacts on human health, such as risks of diseases or premature death.
- **Ecosystem Quality:** Assesses the damage to ecosystems, such as biodiversity loss or habitat degradation.
- **Resource Depletion:** Measures the potential impacts related to the depletion of natural resources.

2.6.5. Types of LCA

Ideally, LCA should encompass the entire life cycle of a product to provide a comprehensive evaluation. However, due to practical constraints, it is not always feasible to perform a full-scale LCA. As a result, various types of LCA have been developed to address specific purposes and stages of the life cycle.

2.6.5.1. Scope-based LCA categories

Cradle-to-Cradle LCA: Evaluates the product lifecycle from raw material extraction to the end-of-life, where the product is repurposed or recycled, completing a closed-loop system. In a circular economy, The "cradle back to cradle" approach should be the most desirable and widely aimed-for LCA method for achieving maximum sustainability (Bjørn and Hauschild, 2018).

- **Cradle-to-Grave LCA:** Assesses the entire lifecycle of a product from raw material extraction (cradle) to disposal (grave).
- **Cradle-to-Gate LCA:** Focuses on the lifecycle from raw material extraction to the point where the product leaves the production facility (gate).
- **Gate-to-Gate LCA:** Examines a specific portion of the production process, focusing on the environmental impacts between two defined points.
- **Well-to-Wheel LCA:** Specifically used for assessing the environmental impacts of fuel or energy sources, from extraction to the point of use in vehicles (Wulf and Kaltschmitt, 2016).

2.6.5.2. Approach-based LCA categories

- Full and Streamlined LCAs: A full LCA is a conventional approach, which is comprehensive, data-intensive, and time-consuming, whereas a streamlined LCA offers a simplified alternative. By concentrating on critical stages or specific aspects of the lifecycle, a streamlined LCA reduces complexity and data demands, making the analysis more efficient and facilitating the wider use of LCAs during early system planning and design (Wang, Levis et al. 2021).
- Attributional and Consequential LCAs: Attributional LCA examines the environmental impacts directly associated with a specific product or process, attributing these impacts to distinct life cycle stages. In contrast, Consequential LCA assesses the broader environmental impacts that result from changes within a system, making it especially useful for evaluating the effects of policy decisions or shifts in market demand (Ekvall, 2020).

2.6.5.3. Time perspective-based LCA categories (Seager, 2022)

- Prospective LCA: Focuses on assessing the environmental impacts of future technologies or scenarios, often used in the context of innovation and development.
- Ex-Ante LCA: Evaluates the potential environmental impacts of a product or process before it is fully developed or implemented, similar to prospective LCA but often with a specific focus on early-stage technologies or policies.
- Anticipatory LCA: Examines the potential long-term environmental impacts of emerging technologies or practices, considering a range of future scenarios to guide decision-making.

2.6.6. Life cycle assessment of nanomaterials

Despite the growing interest in nanotechnology and the increasing production of nanomaterials, there remains a significant gap in the comprehensive environmental assessment of these materials. Most evaluations have traditionally relied on Risk Assessment (RA), which primarily addresses the toxicological risks associated with chemical exposure of a substance (Miseljcic & Olsen, 2018). However, RA alone is insufficient to assess the overall impacts of nanomaterials. While concerns about the environmental impacts of nanomaterials are rising, the application of LCA to these

materials is still relatively underexplored. Nizam et al. (2021) performed a comprehensive review of LCA studies on nanomaterials and reported that over a span of 19 years (2001–2020), only 126 studies related to the LCA of nanomaterials were published in scientific indexed journals. In our literature survey, we found that most LCA studies on nanomaterials focused on metal nanoparticles (Pourzahedi & Eckelman 2015; Ettrup et al. 2017; Temizel-Sekeryan et al. 2020) and fossil-based carbon nanomaterials such as carbon nanotubes (Temizel-Sekeryan et al. 2021) and graphene (Arvidsson 2017; Munuera et al. 2021).

The development of nanomaterials represents a dynamic and rapidly evolving field, with new innovations emerging daily. However, this progress has not been matched by a corresponding emphasis on their LCA, resulting in a significant gap between the development of nanomaterials and the understanding of their environmental and health impacts. The disparity in research emphasis becomes evident when examining the volume of published literature. A search conducted on ScienceDirect (2024) using the keywords "nanomaterial" AND ("synthesis" OR "production" OR "application") yielded 201,673 results for English-language research articles published between 2006 and 2024. In stark contrast, a search using the keywords "Nanomaterial+lifecycle" returned only 410 results within the same period. This significant discrepancy underscores the limited focus on LCA in nanomaterial research compared to the expansive body of work dedicated to their synthesis, production, and application.

Addressing this disparity is critical, as integrating LCAs alongside the development of nanomaterials can identify potential shortcomings and enable improvements at an early stage. Recognizing this need, a pioneering report from a workshop held nearly two decades ago in 2006—jointly organized by the Woodrow Wilson Center Project on Emerging Nanotechnologies, the U.S. Environmental Protection Agency, and the European Commission—emphasized the importance of applying LCA to nanomaterials, even with imperfect data (Klöpper et al., 2007). The report recommended that researchers should not wait for near-perfect data before conducting LCAs. Instead, it urged them to address uncertainties transparently and focus on protecting human health and the environment during these early stages. This served as a key motivation for incorporating LCA into our study.

2.7. Applications of Synthesized Carbon Nanospheres

HTC-derived carbon materials have traditionally been explored for applications in energy storage (Hao et al., 2017), supercapacitors (Wang et al., 2019), batteries (Yu et al., 2019), adsorption (Ighalo et al., 2022), and soil enhancement (Islam et al., 2021). This study, however, expands their potential by assessing the antioxidant and antibacterial properties of hydrothermally carbonized nanospheres for biomedical and other applications, while also exploring their innovative use as a partial replacement for cement in the construction industry.

2.7.1. Antioxidant and antimicrobial potential

Conventional carbon nanomaterials, typically synthesized from fossil-based precursors, are known to induce oxidative stress (Jena et al. 2022), inflammation (Yuan et al. 2020), and cytotoxic effects (Jović et al. 2020; Kharlamova & Kramberger 2023; Xu et al. 2024). Carbon nanoparticles exhibit tissue-specific effects on various organisms at the molecular level, and consequently, their release into the environment should be carefully regulated due to their potential to exert toxic effects on living systems (Jena et al. 2022). In contrast, carbon nanomaterials derived from biomass through green synthesis techniques, such as hydrothermal carbonization, offer a promising alternative due to their lower toxicity potential. To assess the safety and suitability of materials for biological and environmental applications, evaluating their antioxidant activity is essential, as it provides insights into their ability to mitigate oxidative stress and potential impacts on living systems and ecosystems. High antioxidant activity reflects the ability to neutralize reactive oxygen species, reducing oxidative stress and improving the safety profile of these materials (Ayoka et al. 2022). By investigating these properties, safety concerns can be effectively addressed, paving the way for the development of carbon nanomaterials with enhanced biocompatibility and minimized health and environmental risks.

Despite their potential, research on the antioxidant activity of biomass-derived carbon nanomaterials remains limited. Here, the antioxidant potential of hydrothermally carbonized nanospheres from waste biomass (pomegranate peel) via hydrothermal carbonization, using two widely recognized spectrophotometric methods: radical scavenging activity via the DPPH assay and total antioxidant activity using the phosphomolybdenum method was evaluated.

The DPPH assay, or 2,2-diphenyl-1-picrylhydrazyl assay, evaluates the ability of antioxidants to scavenge free radicals, offering valuable insights into their potential health benefits and practical applications. Renowned for its simplicity and reliability, the DPPH assay is widely used to quantify antioxidant capacity across a range of substances. The procedure involves mixing a test sample with a DPPH solution, where a decrease in absorbance at 517 nm signifies antioxidant activity (Gulcin & Alwasel, 2023). The DPPH assay plays a pivotal role in evaluating materials for biomedical applications, particularly those aimed at addressing oxidative stress-related diseases. The DPPH assay can be effectively adapted for environmental applications, particularly for evaluating reducing species in particulate matter from various sources (Frezzini et al. 2019).

DPPH is a nitrogen-centered free radical characterized by its deep purple color, which exhibits strong absorbance at 517 nm in the visible spectrum. This purple color arises from the presence of unpaired electrons within the DPPH molecule. When an antioxidant donates an electron or a hydrogen atom to DPPH, the radical is neutralized, forming the reduced DPPH-H form. This process results in a distinct color change from deep purple to pale yellow, with a corresponding decrease in absorbance at 517 nm (depicted in Figure 2.7). The extent of this absorbance reduction is directly proportional to the antioxidant activity of the sample (Frezzini et al. 2019).

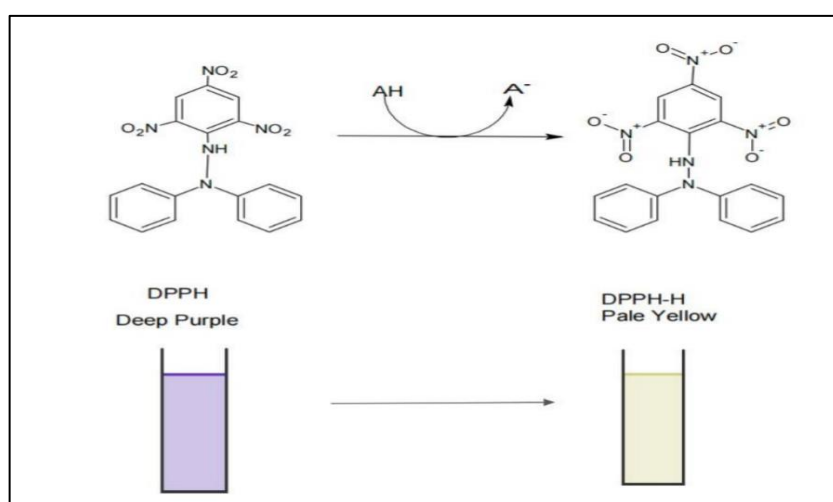


Figure 2.7. Principle behind DPPH assay.

The phosphomolybdenum method is a cost-effective approach developed by Prieto et al. (1999) based on the reduction of molybdenum from its +6-oxidation state (Mo (VI)) to its +5 state (Mo (V)) by antioxidant compounds, resulting in the formation of a

greenish blue-colored phosphomolybdenum (V) complex. The absorbance of this complex is measured spectrophotometrically at 695 nm, allowing for the quantification of total antioxidant capacity. The method provides quantitative results, expressing antioxidant capacity in terms of ascorbic acid equivalents.

The agar diffusion method for studying antimicrobial activity dates back to the late 19th century. In 1889, Martinus Beijerinck first described a technique using agar to observe bacterial growth inhibition, laying the foundation for modern antimicrobial susceptibility testing (Hossain, 2024). Over time, various modifications of this method have been developed. The agar well diffusion method, employed in this study, is a simple, cost-effective, and widely used technique for evaluating antibacterial activity by measuring the zone of inhibition around wells containing antimicrobial agents. In this method, bacterial cultures are evenly spread on agar plates—a gel-like medium derived from red algae—to provide a suitable growth environment. Wells are then created in the agar and filled with the test sample. Following incubation, the diameter of the clear zone surrounding each well is measured, indicating the extent of bacterial growth inhibition and reflecting the antimicrobial potential of the sample (Hossain, 2024).

2.7.2. Potential for partial replacement of cement

Some parts of this section are reproduced from the following published article:

Sharma, M., Öztürk, İ. Ş., Emiroğlu, M., & Erses Yay, A. S. (2025). Performance evaluation of biomass-derived hydrothermal carbonaceous material in cement-based composites. *Case Studies in Construction Materials*, 22, e04291. <https://doi.org/10.1016/j.cscm.2025.e04291>. Published under the Creative Commons CC BY-NC 4.0 license.

Over the years, the quest to improve the performance of cement concrete has led to numerous innovations and advancements in materials science. Among these innovations, the incorporation of carbon particles into cement mixtures has proven beneficial, enhancing the mechanical, physical, and chemical properties of cement composites, resulting in stronger, more durable materials that are resistant to various environmental factors.

Carbon materials, particularly CNTs, have been shown to enhance the mechanical properties of cement composites, as demonstrated in various studies over the years (Li

et al., 2005; Musso et al., 2009; Chaipanich et al., 2010; Cui et al., 2022, Zhang et al., 2023). In some of the earliest and most important studies, researchers established the positive effects of CNT interaction with cement-based materials, forming a foundation for ongoing research in the field. Yakovlev et al. (2006) reported that adding 0.05% CNTs by mass to non-autoclaved foam concrete made with Portland cement reduced thermal conductivity by 12–20% and increased compressive strength by up to 70%. Konsta-Gdoutos et al. (2010) demonstrated that MWCNTs significantly enhance the fracture resistance, stiffness, and durability of cement paste, while also reducing porosity and autogenous shrinkage. Chang et al. (2011) conducted experiments on CNT-reinforced cement mortar and found that the proper dispersion of MWCNTs significantly improved the flexural strength, compressive strength, and toughness of the composites. Similarly, Liu et al. (2012) investigated the use of MWCNTs in cement composites and found that their incorporation improved the 7-day compressive strength by 22% and enhanced the microstructure of the material.

The application of CNTs in cementitious composites has also been extended to their electrical and electromagnetic wave-absorbing properties (Wang et al., 2013; Xu et al., 2021). Varisha et al. (2021) studied the mechanical and durability performance of cement mortar incorporating CNTs and nanosilica as admixtures, demonstrating enhanced properties. In another study, Andrade Neto et al. (2021) examined the combined effects of CNTs and metakaolin on cementitious matrices, highlighting their potential for improving material performance.

Apart from CNTs, graphene-based materials have also demonstrated potential in enhancing cementitious composites. For example, Baomin and Shuang (2019) reported that incorporating well-dispersed graphene nanoplatelets (GNPs) into cement improved the hydration process, resulting in a denser internal structure and superior mechanical performance. Similarly, Liu et al. (2024) investigated the application of graphene oxide (GO) in cement mortars exposed to chloride ions, which typically deteriorate compressive strength. Their results showed that GO addition increased compressive strength from 38 ± 5.2 MPa to 44.5 ± 0.2 MPa, emphasizing the functional role of nanomaterials in mitigating performance loss under harsh conditions.

Nevertheless, the widespread adoption of CNTs and graphene remains limited due to their high production costs, making them less feasible for large-scale construction

applications. As a result, researchers are increasingly focused on identifying more sustainable and economically viable alternatives. This pursuit has become even more critical considering the environmental footprint of the construction sector, which accounts for over one-third of global energy use, greenhouse gas emissions, resource depletion, and waste generation (Gasparri et al., 2023). With annual global concrete consumption surpassing 30 billion tonnes and the cement industry contributing at least 8% of anthropogenic CO₂ emissions (York & Europe, 2021), reducing emissions is essential to achieving the target of carbon-neutral concrete by 2050.

The key challenge lies in discovering cost-effective and sustainable materials that can offer comparable performance to CNTs and graphene, but without their environmental or economic drawbacks. In this context, the use of industrial and agricultural waste—known as green or sustainable construction materials—has gained momentum. This approach not only helps minimize environmental impact but also enhances cement properties by incorporating recycled or waste-derived components.

One promising route involves the use of biochar, a carbon-rich material derived from biomass, which also offers carbon sequestration benefits. Biochar has been studied as a filler or reinforcement in cementitious systems, aiming to improve mechanical and durability characteristics. For example, Ferro et al. (2014) investigated the use of carbonized hemp hurds, reporting improvements in the performance of cement composites. Ahmad et al. (2015) and Ferro et al. (2015) reported similar enhancements using carbonized bamboo and coconut coir, respectively. Khushnood et al. (2015) demonstrated improvements in strength and fracture resistance by incorporating nano/micro carbonized bagasse fibers at up to 1 wt%. More recently, Restuccia and Ferro (2016) showed that hazelnut shell biochar, produced at 800°C, significantly enhanced the strength, ductility, and flexibility of cement composites, especially at an optimal loading of 0.8 wt%. These studies employed different techniques of pyrolysis, annealing, and CVD to produce biochar.

While various methods exist for producing carbon additives from biomass, HTC remains relatively underexplored in cement applications. Unlike pyrolysis, which generally requires high temperatures ranging from 300°C to 800°C (Legan et al., 2022), HTC operates at substantially lower temperatures (180°C–250°C), offering a more energy-efficient and environmentally benign alternative. One notable exception is the work of Santos et al. (2023), who utilized HTC to convert rice husk into a

functional additive for cement mortar. Despite this, research on the valorization of fruit peel waste through HTC for cementitious applications remains scarce.

This study addresses that gap by exploring the feasibility of synthesizing carbon-rich materials from fruit peel waste via HTC and evaluating their performance as sustainable additives in cement composites. This approach not only aligns with circular economy principles but also offers a novel pathway to reduce the environmental footprint of the construction sector without compromising material quality.



3. MATERIALS AND METHODS

3.1. Raw Materials and Preparation

As mentioned in the previous chapter, the following biomass waste materials were selected as feedstocks for this study: pomegranate (*Punica granatum*) peel waste (PPW), marigold (*Tagetes*) flower waste (MFW), and 100% cotton (*Gossypium*) fabric waste (CFW). In alignment with the principles of green chemistry, water is used as the sole solvent, with no additional chemicals or catalysts employed. The peels were separated, air-dried, and stored for subsequent use. Although pre-drying of feedstocks is not required in the HTC process, in this study, the feedstocks were air-dried for long-term storage and to maintain uniformity in the experiments.

3.2. Determination of Biomass Composition

The cellulose, hemicellulose, and lignin contents of the three biomass feedstocks were determined using a chemical analysis method primarily based on the protocol by Yang et al. (2006), chosen for its greater suitability in analyzing a wide range of lignocellulosic biomasses and its relevance to thermal conversion studies, as well as its compatibility with standard laboratory equipment.

The procedure was further supplemented with elements from other well-established methods, including those by Van Soest (1963), TAPPI (1994), and NREL (Sluiter et al., 2008), to ensure methodological robustness. The analysis was conducted by Lenience Biotech Lab, Bhopal, M.P., India. The experimental process involved four chemicals: (1) Acetone, (2) Sodium hydroxide (NaOH- 0.5 mol/L), (3) Sulfuric acid (98%), and (4) Barium chloride (BaCl₂) solution. The procedure followed by the lab is detailed below, and involves estimating the content per gram of the sample.

3.2.1. Extractives in biomass

1 g of the sample (A) was treated with 60 mL of acetone and heated at 90°C on a hot plate for 2 hours. After heating, the samples were dried in an oven at 105–110°C until a constant weight was achieved (B). The extractives content was calculated using the formula:

Amount of Extractives (g) = A - B.

3.2.2. Hemicellulose in biomass

The extractives-free sample (B), weighing 1 g, was treated with 150 mL of 0.5 mol NaOH solution and heated at 80°C for 3.5 hours on a hot plate. Afterward, the samples were thoroughly washed with distilled water until all Na⁺ ions were removed and then dried in an oven at 105–110°C until a constant weight was achieved (C). The hemicellulose content was calculated using the formula:

Amount of Hemicellulose (g) = B - C.

3.2.3. Lignin in biomass

To determine lignin content, 1 g of the extractives-free sample (B) was treated with 30 mL of 98% sulfuric acid. The sample was left at room temperature for 24 hours, then heated to 100°C on a hot plate for an hour. The mixture was filtered, and the solid residue was thoroughly washed with distilled water until sulfate ions were no longer detectable in a titration with 10% BaCl₂ solution. The residue was then dried in an oven at 105–110°C until a constant weight was achieved (D), which represents the lignin content.

3.2.4. Cellulose in biomass

The cellulose content (E) was determined by subtracting the weights of the other components (extractives, hemicellulose, and lignin) from the initial weight of the sample. The total cellulose content was calculated using the equation: (A - B) + (B - C) + D + E = 1 g, with E representing the cellulose content.

3.3. Hydrothermal Carbonization Process

The HTC experiments were carried out in a 250 mL stainless steel autoclave under self-generated pressure. The reactor consisted of a Teflon container containing the prepared sample, a magnetic stirrer, a manometer, and a PID-controlled heating device connected to a thermocouple (Figure 3.1). The temperature (T), reaction time (t), and biomass-to-water ratio (B:W) were optimized based on results from preliminary experiments. Accordingly, all samples were subjected to identical conditions: T = 180°C and 250°C, t = 2 h and 4 h, and B:W = 1:20. After the reaction, the reactor was allowed to cool naturally to room temperature, and the solid product was separated from the liquid phase using vacuum filtration with glass microfiber filters (GVS Filter

Technology). The collected solids were dried in an oven at 105°C. The liquid product was centrifuged at 13,500 rpm for 30 minutes to separate the solvent, followed by vacuum filtration and drying at 105°C for 2 hours to obtain carbon dots. The produced carbon nanospheres were modified using a Planetary Ball Mill PULVERISETTE 6, operated at 400 rpm for 30 minutes.

The biomass-to-water ratio of 1:20 was chosen to simulate an extreme-case scenario, ensuring sufficient aqueous medium for efficient reaction kinetics and uniform heat transfer during the HTC process. While the feedstocks were air-dried for experimental consistency and long-term storage, it is important to note that under practical HTC conditions, biomass typically retains high inherent moisture content—for example, 60–80% for pomegranate peel waste, with 73.6% reported by Al-Rawahi et al. (2013). To compensate for the lack of natural moisture and facilitate the hydrothermal reaction, an increased amount of water was added. Although this higher water content resulted in lower hydrochar yields and more wastewater, it will inform future optimization efforts toward more practical biomass-to-water ratios in the HTC process without mass transfer limitations.

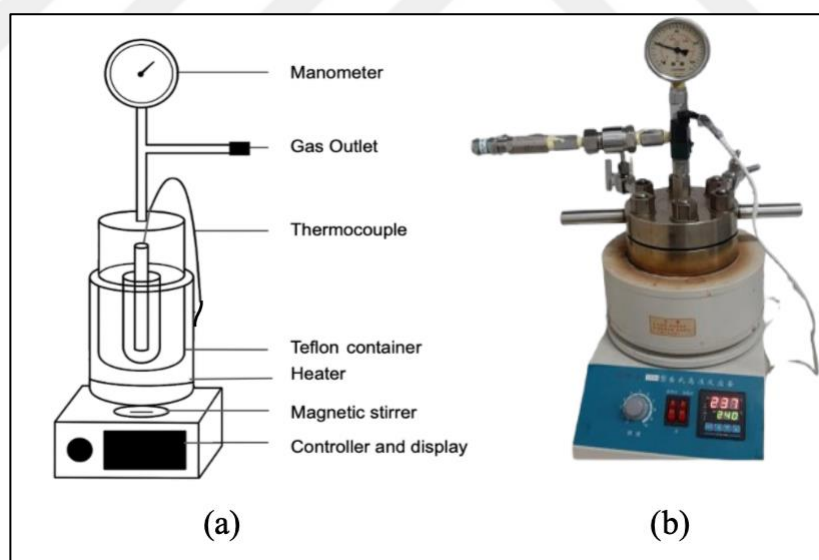


Figure 3.1. HTC reactor setup: (a) schematic and (b) actual photograph.

3.4. Characterization Techniques

The physicochemical properties, structural features, and energetic performance of the raw biomass and HTC products were systematically analyzed using a variety of

advanced characterization techniques in order to look into the materials' composition, structure, and energy content.

- **Physicochemical measurements**

The liquid conductivity and pH of the prepared raw materials solution and process liquids were measured using a Hach Multimeter HQ 40d probe meter. This allowed for the evaluation of ionic content and the acidity/basicity of the HTC medium, which are key factors influencing the overall carbonization process.

- **Morphological and structural analysis**

The surface morphology of the samples was examined using a field-emission scanning electron microscope (FE-SEM), specifically the QUANTA 400F Field Emission SEM, which offers a resolution of 1.2 nm. This technique provided high-resolution images to assess the structural transformation and surface changes induced by hydrothermal carbonization. Additionally, the internal structure of the materials was investigated through transmission electron microscopy (TEM) using a FEI/Tecnai G2 Spirit Biotwin 120 kV TEM (CTEM), which enabled visualization of the materials at the nanoscale.

- **Crystallographic analysis**

Structural phase analysis of the synthesized materials was performed via X-ray diffraction (XRD) using a Panalytical Empyrean Series 2 Diffractometer with Cu K α radiation ($\lambda = 0.154059$ nm). The XRD measurements were carried out over a 2θ range of 10–90° with a step interval of 0.02°, operating at 40 kV and 30 mA. This method provided insights into the crystalline structure and degree of order in the samples.

- **Elemental and energy analysis**

Elemental compositions (C, H, N, S) of the biomass and HTC products were determined using a FLASH 2000 CHNS elemental analyzer, which helped quantify the carbonization efficiency. The higher heating value, or calorific content, of the samples was measured using an IKA C 200 bomb calorimeter to assess the energy content of the raw biomass and HTC products.

- **Molecular and structural characterization**

Raman spectroscopy was performed using a RAMANRXN1 System from Kaiser Optical Systems, with a 785 nm excitation wavelength and a 60-second acquisition

time. This technique was used to analyze the carbon bonding structure in the materials, specifically focusing on the D and G bands, which are indicative of the degree of carbon ordering. The UV–visible absorption spectra of carbon dots (where applicable) were recorded using a Shimadzu UV-1900 spectrometer, providing additional structural and optical properties.

- **Porosity and surface area analysis**

The surface area of the biomass and HTC products was determined using the multipoint Brunauer–Emmett–Teller (BET) method. The Barrett–Joyner– Halenda (BJH) method was employed to assess the pore volume and pore size distribution from nitrogen adsorption–desorption isotherms. These measurements are critical for understanding the porous nature of the carbonized products and their potential applications.

- **Hydrophobicity assessment**

The hydrophobicity of the prepared sample was evaluated using a water droplet contact angle test conducted on the surface of the material. Photographs of the water droplet were captured using the digital camera of a mobile phone, and the contact angle was subsequently measured using ImageJ Software. This technique provides a direct and effective method for assessing the water- repellent properties of the material.

- **Integrated TGA and DTA analysis**

The thermal properties of the samples were analyzed simultaneously using a Shimadzu DTG-60H Thermogravimetric Analyzer (TGA) and Differential Thermal Analyzer (DTA) to understand their thermal stability and decomposition behavior. The analysis was conducted from room temperature up to 1000 °C under a nitrogen atmosphere, using a heating rate of 20 °C per minute and a nitrogen flow rate of 50 ml/min.

- **Energetic performance calculations**

Solid mass yield (SMY), energy densification ratio (EDR), and energy yield (EY) of the solid end- products were calculated using the following standard equations:

$$SMY \% = \left[\frac{\text{mass of solid HTC product(dry)}}{\text{mass of raw material (dry)}} \right] \times 100 \quad (3.1)$$

$$EDR = \left[\frac{\text{HHV of solid HTC product(dry)}}{\text{HHV of raw material (dry)}} \right] \quad (3.2)$$

$$EY\% = SMY\% \times EDR \quad (3.3)$$

3.5. Life Cycle Assessment Methodology

3.5.1. Goal and scope

The goal of this LCA study is to provide data about the environmental impact of the produced HCNs through HTC at a commercial scale to the researchers involved in the development of the technology. The study was conducted in accordance with the ISO 14040 and ISO 14044 standards for life cycle assessment. Laboratory-scale inventory data were upscaled to commercial scale using the methodology outlined by Piccinno et al. (2016) and analyzed with SimaPro 9.5.0.2 Software. The study identifies potential production weak links in advanced carbon materials through HTC, aiding researchers in understanding environmental implications at commercial scale. Additionally, contribution analysis identifies production hotspots, enabling early environmental impact mitigation during R&D.

3.5.1.1. Functional unit definition

The selected functional unit is 1 kg of HCNs produced from PPW. This unit provides a standardized basis for comparing different process scenarios and allows for benchmarking against other carbon-based materials. Although the average solid yield from laboratory experiments is approximately 27.60%, which would theoretically result in about 1.35 kg of HCNs per batch, the output is fixed at 1 kg. This adjustment accounts for real-world losses and operational inefficiencies expected during scale-up. It also aligns with ISO 14044 guidelines, which recommend defining the functional unit based on the delivered function of the product system.

3.5.1.2. System boundary

The system boundary is limited to a cradle-to-gate perspective, as illustrated in Figure 3.2. This scenario, referred to as the reference scenario (HTCr). Two alternative scenarios, the improved scenario (HTCi) and the alternate scenario (HTCa), are introduced later in section 3.5.5.

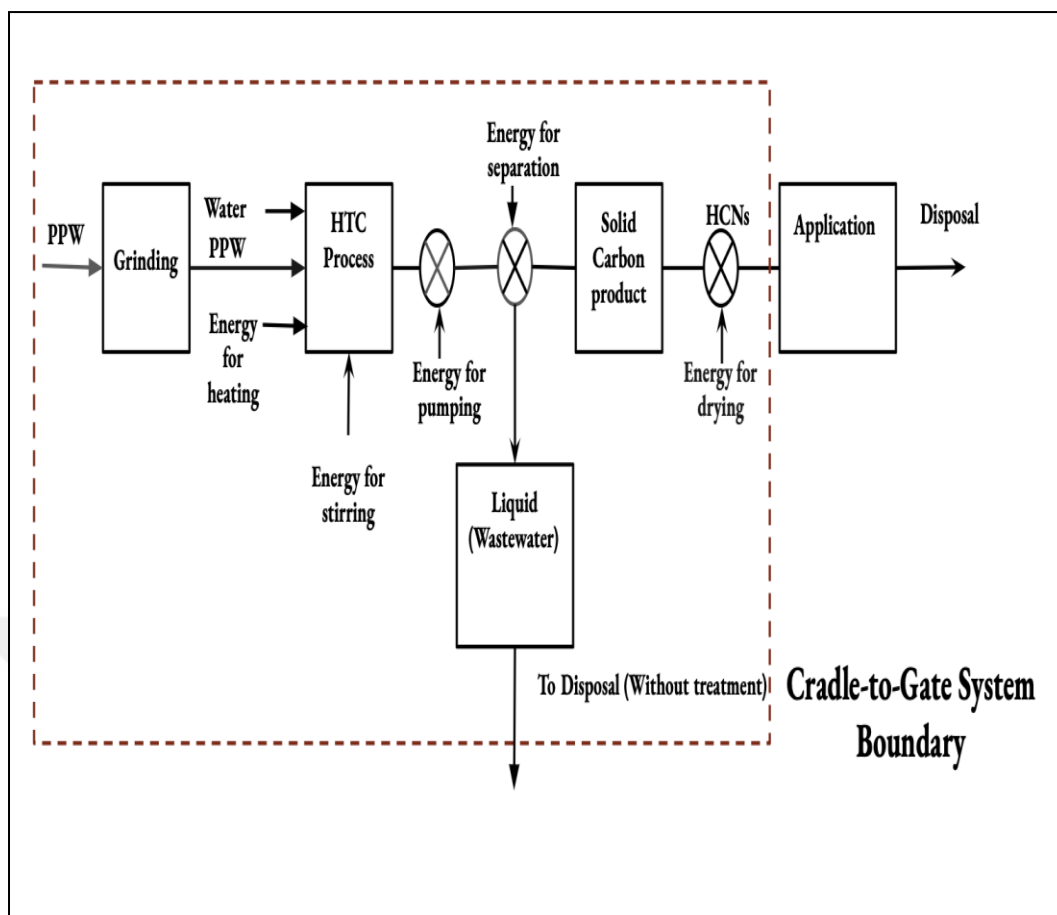


Figure 3.2. System boundary for the reference scenario (HTCr), where wastewater is directly discharge without treatment.

3.5.1.3. Co-product allocation

During the HTC process, a co-product, CDs, is also recovered from the wastewater stream in the alternate scenario (HTCa). As the production of CDs is not the primary objective, and they are recovered from a process waste stream without additional resource input, no environmental burden is allocated to them in any scenario.

In the reference (HTCr) and improved (HTCi) scenarios, wastewater is treated or disposed of directly, without valorization. In HTCa, however, the additional processing required to extract CDs is fully included in the environmental impacts attributed to 1 kg of hydrothermal carbon nanospheres, while the CDs are treated as a zero-burden co-product under the cut-off approach. This approach was adopted due to the exploratory nature of the study and the limited characterization of the CDs.

3.5.2. Life cycle inventory (LCI)

The details of all inputs, outputs, necessary calculations, and electricity consumption for each process step—namely grinding, heating, stirring, pumping, and drying—are summarized in Table 3.1. For modeling electricity consumption and production, the dataset “Electricity, medium voltage | market for | Cut-off, S” from the Ecoinvent database was utilized within the SimaPro software environment.

3.5.3. Impact assessment

CML-IA baseline V3.05/EU25 calculation method is used to assess environmental impact, covering impact groups such as abiotic depletion, abiotic depletion (fossil fuels), global warming, ozone layer depletion, human toxicity, freshwater ecotoxicity, marine ecotoxicity, terrestrial ecotoxicity, photochemical oxidation, acidification, and eutrophication.

3.5.4. Limitations

The present lifecycle study focused on the synthesis process of producing biomass-derived carbon nanomaterials through hydrothermal carbonization. However, due to the scarcity of relevant literature and the absence of standardized benchmarks for comparison, we were unable to perform a comparative analysis with other processes or products to avoid any unfair comparisons. Consequently, the study is limited to documenting the specifics of the process adopted in this research without benchmarking against existing synthesis processes or carbon nanomaterials.

Table 3.1. Summary of inputs, outputs, and calculations used for LCA.

LCA Input/Output	Description/Calculation	Variables used in calculation
HTC reactor inputs	-	PPW= 5kg Water = 95 l Reactor size= 500 l Reaction temperature, $T_r = 250^\circ\text{C} = 523.15\text{ K}$ Outside/starting temperature, $T_o = 25^\circ\text{C} = 298.15\text{ K}$ Specific heat capacity of water, $C_p(\text{Water}) = 4184\text{ J/kgK}$ Specific heat capacity of PPW, $C_p(\text{PPW}) = 1516\text{ J/kgK}$ (Kianmehr et al. 2012)
Energy for heating	$Q_{react} = \frac{Q_{heat} + Q_{loss}}{\eta_{heat}}$ $Q_{heat} = c_p \times m_{mix} \times (T_r - T_o)$ $Q_{loss} = A \times \frac{k_a}{s} \times (T_r - T_o)$	Density of water, $d(\text{water}) = 997\text{ kg/m}^3$ Density of PPW, $d(\text{PPW}) = 637\text{ kg/m}^3$ (Sharayei et al. 2019) Efficiency heat $\eta_{heat} = 74\%$ (Piccinno et al. 2016) Surface area of the reactor, $A = 3.716\text{ m}^2$ (Piccinno et al. 2016) Thickness of the insulator, $s = 0.075\text{ m}$ (Piccinno et al. 2016) Thermal conductivity of the insulation material, $k_a = 0.042\text{ W/mK}$ (Piccinno et al. 2016) Mass of mixture, $m_{mix} = 100\text{ kg}$ Time of the reaction, $t = 4\text{ hours} = 14400\text{ seconds}$

Table 3.1. (Continued): Summary of inputs, outputs, and calculations used for LCA.

Energy for stirring		$E_{stir} = \frac{N_p \times p_{mix} \times N^3 \times d^5 \times t}{\eta_{stir}}$	Power number of impeller, $N_p = 3.44$ (Piccinno et al. 2016) Rotational speed of agitator, $N = 1.785$ (Piccinno et al. 2016) Impeller diameter, $d = 0.296$ (Piccinno et al. 2016) Time of the reaction, $t = 14400$ sec Efficiency of stirrer, $\eta_{stir} = 0.9$ (Piccinno et al. 2016) Density of the reaction mixture, $p_{mix} = 972.289$ kg/m ³ Gravitational acceleration, $g = 9.8$ m/s ²
Energy for pumping		$E_{pump} = \frac{m \times g \Delta h}{\eta_{pump}}$	Height difference for the gravitational head, $\Delta h = 4.2$ (Piccinno et al. 2016) Efficiency of pump, $\eta_{pump} = 0.75$ (Piccinno et al. 2016) Mass transferred, $m = 82.5$ kg (Reference and Improved scenarios)
Energy for separation	----		1-10 kWh/ton dry material (Piccinno et al. 2016)
Energy for drying		$Q_{dry} = \frac{c_{p.liq} \times m_{liq} \times (T_{boil} - T_0) \Delta H_{vap} * m_{vap}}{\eta_{dry}}$	Boiling Temperature, $T_{boil} = 100^\circ\text{C} = 373.15$ K Outside/starting temperature, $T_0 = 25^\circ\text{C} = 298.15$ K Specific heat capacity of water, C_p (Water) = 4184 J/kgK Enthalpy of evaporation $\Delta H_{vap} = 2270$ kJ/kg. Efficiency of dryer, $\eta_{dryer} = 0.80$ (Piccinno et al. 2016) Mass of the solvent to be evaporated, $m = 6.5$ kg (Reference and Improved scenarios) Mass of the solvent to be evaporated, $m = 6.5$ kg + 128.7g (Alternate scenario)
Output			
Product/Yield		Upscale of lab yield (by simple multiplication)	
Emissions		Stoichiometric amounts (same as lab protocol)	

3.5.5. Sensitivity analyses

3.5.5.1. Scenario 1: Changing the disposal route

The most significant emission in the HTC process stems from the liquid waste. Therefore, a sensitivity analysis was conducted by changing the disposal scenario. Instead of directly releasing the liquid byproduct into the waste stream (referred to as the reference scenario, HTC_r), it was diverted to a wastewater treatment plant (referred to as the improved scenario, HTC_i) shown in Figure 3.3.

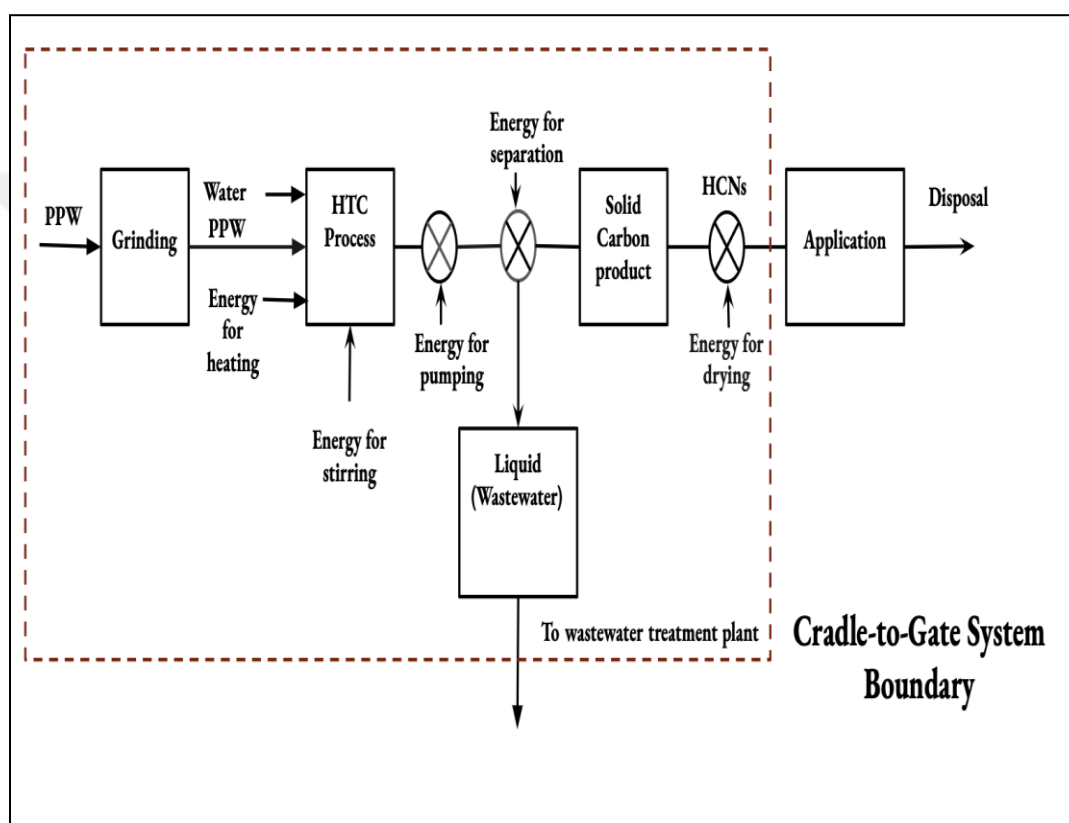


Figure 3.3. System boundary for the improved scenario (HTC_i), incorporating wastewater treatment after HTC processing.

Additionally, another scenario was explored in which an attempt was made to synthesize carbon dots from the wastewater before sending it to the treatment plant (referred to as the alternate scenario, HTC_a) shown in Figure 3.4.

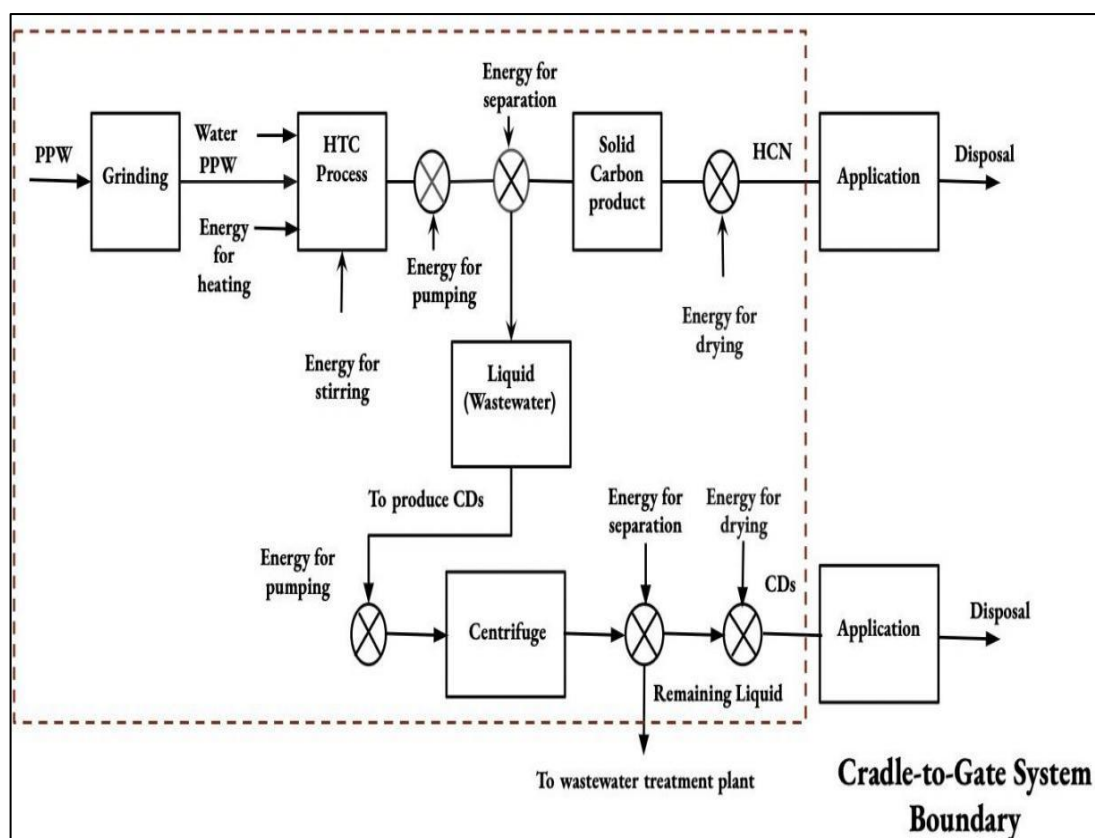


Figure 3.4. System boundary for the alternate scenario (HTCa), including carbon dots (CDs) recovery from wastewater prior to treatment.

The summary of input energy requirements and output details for the three LCA scale-up scenarios—the reference scenario (HTCr), the improved scenario (HTCi), and the alternate scenario (HTCa)—is provided in Table 3.2. Each scenario results in the production of 1 kg of HCNs, with the HTCa scenario additionally generating approximately 60 g of CDs as a co-product. The table details the energy inputs associated with each unit operation—grinding, heating, stirring, pumping, separation, drying, and centrifugation—highlighting the variations introduced through process modifications or added steps. It also notes differences in liquid waste output and its handling, either through disposal or treatment, thereby reflecting the potential sustainability improvements achieved in the improved and alternate scenarios.

Table 3.2. Input energies and output details for all three scale-up LCA scenarios.

Input Energy (kWh)	Reference Scenario HTCr	Improved Scenario HTCi	Alternate Scenario HTCa
Energy for grinding	0.08	0.08	0.08
Energy for heating, <i>Qheat</i>	36.7420	36.7420	36.7420
Energy for stirring, <i>Estir</i>	0.192107	0.192107	0.192107
Energy for pumping, <i>Epump</i>	0.00125895	0.00125895	0.00241875
Energy for separation	0.065	0.065	0.085
Energy for drying	10.355	10.355	18.637
Energy for centrifugation	-	-	0.1
Total	47.435	47.435	55.839
Outputs			
Solid	1 kg of HCNs	1 kg of HCNs	1 kg of HCNs +60.6 g (≅60 g) of CDs
Liquid	≅76 liters of wastewater (to disposal)	≅76 liters of wastewater (to wastewater treatment plant)	≅74 liters of wastewater (to wastewater treatment plant)

3.5.5.2. Scenario 2: Changing the electricity mix

A second sensitivity analysis was conducted for the improved HTC scenario (HTCi) by varying the electricity mix across three different geographic locations to evaluate how changes in energy sourcing influence the overall environmental impact. The selected locations represent distinct electricity grid compositions, incorporating varying shares of renewable, fossil-based, and nuclear energy. The electricity mix data used for this analysis is summarized in Table 3.3 (Ritchie and Rosado, 2020; Ember Climate, 2022). The selected locations include:

- **Türkiye:** where the present study is originally conducted, serving as the control for comparison with the other scenarios. The major source of electricity production for 2022 in Türkiye was coal, accounting for 34.06% of its overall production, followed by natural gas at 23.21% and hydropower at 20.57%.

- **Netherlands:** primarily dependent on natural gas, which contributes 39.70% to its total electricity generation, followed by wind and coal at 17.87% and 12.30%, respectively.
- **Switzerland:** Swiss electricity generation relies on more sustainable energy sources, with hydropower dominating at 48.96%, followed by nuclear power at 38.47%, and solar power at 6.22%.

Table 3.3. Data of the electricity mix of the three countries.

Source	Electricity Production (in Terawatt-hour, TWh)		
	Türkiye	Netherlands	Switzerland
Coal	111.08	14.80	0.00
Gas	75.70	47.75	0.50
Other fossil	2.44	5.16	1.22
Nuclear	0.00	4.16	23.95
Hydropower	67.09	0.05	30.48
Wind	35.14	21.49	0.17
Solar	15.84	17.08	3.87
Bioenergy	7.92	9.79	0.96
Other renewables	10.90	0.00	1.11
Total	326.11	120.28	62.26

This LCA study can be classified as an attributional, cradle-to-gate, and streamlined LCA, as it focuses specifically on the environmental impacts of producing hydrothermal carbon nanospheres at a commercial scale while simplifying the scope to critical lifecycle stages. Additionally, it falls under the categories of prospective and ex-ante LCA, as it evaluates the potential environmental implications of an emerging technology during its early development phase and scales lab-scale inventories to industrial levels to guide future applications. This combined approach ensures a focused yet forward-looking analysis to aid in early-stage decision-making and technology improvement.

3.6. Applications

3.6.1. Evaluation of antioxidant activity potential

All materials and instruments used in this section were procured from Indian suppliers, and the experiments were carried out at RB Science Lab, Bhopal (India).

- **Chemicals used:** The reagents and chemicals used for evaluating the antioxidant activity of the prepared HCNs were sourced from various suppliers. DPPH (C₁₈H₁₂N₅O₆) was obtained from Oxford Fine Chemicals. Ethanol was purchased from Merck, while sulfuric acid was procured from Qualigens. Ammonium molybdate, sodium phosphate, ascorbic acid, and dimethyl sulfoxide (DMSO) were supplied by CDH (Central Drug House). Additional DMSO was also obtained from Rankem.
- **Instrumentation:** The assays were conducted using a UV-Visible spectrophotometer (Labtronics, LT-2201), an electronic weighing scale (Wensar, PGB-220), and a sonicator (Labman, LMUC-3). A water bath from BioTechnics India (BTI) was also employed, and volumetric flasks were sourced from ASGI.

3.6.1.1. DPPH assay

- **Preparation of DPPH solution:** To prepare the DPPH solution, 8 mg of DPPH was accurately weighed and dissolved in a small volume of 99.5% ethanol. The final volume was adjusted to 100 mL using 99.5% ethanol to obtain the working DPPH solution (Chaurasia et al. 2023).
- **DPPH assay procedure:** For the assay, sample solutions ranging from 5 to 25 µg/mL were prepared in ethanol through sonication. To begin the reaction, 1.5 mL of each sample solution was mixed with 1.5 mL of the DPPH solution. The mixture was then incubated at room temperature for 30 minutes, kept in the dark to avoid interference from light. After the incubation, the absorbance of the solution was measured at 517 nm using a UV-Visible spectrophotometer, with the corresponding blank solution as a reference. The blank was prepared by mixing 3 mL of ethanol. The control sample, used for calculating the percentage inhibition, was prepared by using 3 mL of DPPH solution without any sample (Chaurasia et al. 2023). The percentage inhibition or Radical

Scavenging Activity of DPPH free radicals was determined based on the following formula:

$$\% \text{Inhibition} = \frac{A_{\text{control}} - A_{\text{sample}}}{A_{\text{control}}} \times 100 \quad (3.4)$$



Figure 3.5. DPPH stock solution (left) and sample test tubes (right).

The DPPH assay is visually represented in Figure 3.5 to illustrate the experimental setup and differentiate between the control and treated samples. The image on the left displays the prepared DPPH stock solution, characterized by its deep violet color, which signifies the presence of free radicals. The right panel shows test tubes containing the blank and samples with increasing concentrations. The progressive fading of color across the tubes indicates radical scavenging activity and reflects the antioxidant capacity of the tested samples.

3.6.1.2. Phosphomolybdenum assay

The Total Antioxidant Capacity (TAC) of the sample was evaluated using the phosphomolybdenum assay.

- **Preparation of phosphomolybdenum reagent**

The phosphomolybdenum reagent was prepared by dissolving 0.049 g of ammonium molybdate and 0.036 g of sodium phosphate in 0.588 mL of sulfuric acid. The final solution volume was adjusted to 10 mL using distilled water (Jafri et al. 2017).

- **Phosphomolybdenum assay procedure**

To prepare the sample, 10 mg of the dried sample was dissolved in 1 mL of DMSO via sonication. A 400 μ L aliquot of this solution was mixed with 4 mL of the

phosphomolybdenum reagent and incubated in a boiling water bath at 95°C for 90 minutes. After cooling to room temperature, the absorbance was measured at 695 nm. For the control, 1 mL of DMSO was used instead of the sample solution, while ascorbic acid (10 mg/mL in DMSO) served as the standard (Jafri et al. 2017). The TAC of the sample, expressed as a percentage, was calculated to represent its antioxidant potential relative to the standard antioxidant, ascorbic acid. The TAC was computed using the formula:

$$\text{TAC\%} = \frac{(A_{\text{sample}} - A_{\text{control}})}{(A_{\text{ascorbic acid}} - A_{\text{control}})} \times 100 \quad (3.5)$$

3.6.2. Evaluation of antibacterial activity potential: Agar well diffusion bioassay

All materials and instruments used in this section for the evaluation of antibacterial activity potential of the prepared material(s) were procured from Indian suppliers, and the experiments were carried out at RB Science Lab, Bhopal (India).

- **Chemicals used:** Nutrient broth and nutrient agar were supplied by Microgen, while acetonitrile was procured from Merck. Azithromycin, used as the standard drug, was obtained from Ind Swift Pharma. The bacterial strains, *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*), were sourced from IMT, Chandigarh (India). Distilled water was used throughout the experiment.
- **Instrumentation:** The instruments selected for the experiment ensured precision and adherence to sterile working conditions. A laminar air flow bench from Navyug Udyog was utilized for aseptic preparation. Accurate measurements were achieved using an electronic weighing scale (Wensar, PGB-220). The heating mantle and water bath, both from BioTechnics India, facilitated the preparation of solutions. Standard and sample dilutions were prepared using volumetric flasks from ASGI. The incubator from Labtronics maintained the required temperature for bacterial growth, and the antibiotic zone reader from Sentwin was used to measure the zones of inhibition.
- **Preparation of nutrient broth:** A total of 13 g of readymade nutrient broth powder was dissolved in 1000 mL of distilled water. Gentle heating was applied to ensure complete dissolution, followed by sterilization in an autoclave to maintain aseptic conditions.

- **Preparation of nutrient agar:** For the nutrient agar, 23 g of readymade agar powder was dissolved in 1000 mL of distilled water with gentle heating. The solution was subsequently sterilized in an autoclave.
- **Preparation of sample:** Carbon material samples were dissolved in acetonitrile with the aid of sonication. The resulting solution was diluted to achieve final concentrations of 50 µg/mL, 100 µg/mL, and 150 µg/mL for testing.
- **Preparation of standard:** Azithromycin, employed as a standard, was dissolved in distilled water to prepare a 100 µg/mL solution.
- **Assay procedure:** Sterile agar media was poured into plates and allowed to solidify. The solidified agar plates were inoculated with bacterial broth using a sterile spreader. Wells were made in the agar using a sterile cork borer and filled with the prepared sample solutions. The plates were incubated at 37°C for 24 hours to promote bacterial growth. Following incubation, the zones of inhibition (ZOI) were measured using an antibiotic zone reader.

As illustrated in Figure 3.6, part (a) shows the application of azithromycin as the standard reference for antibacterial activity, while part (b) depicts the sample being tested. The clear zones surrounding the wells indicate the extent of bacterial growth inhibition, which reflects the effectiveness of the compounds under evaluation.

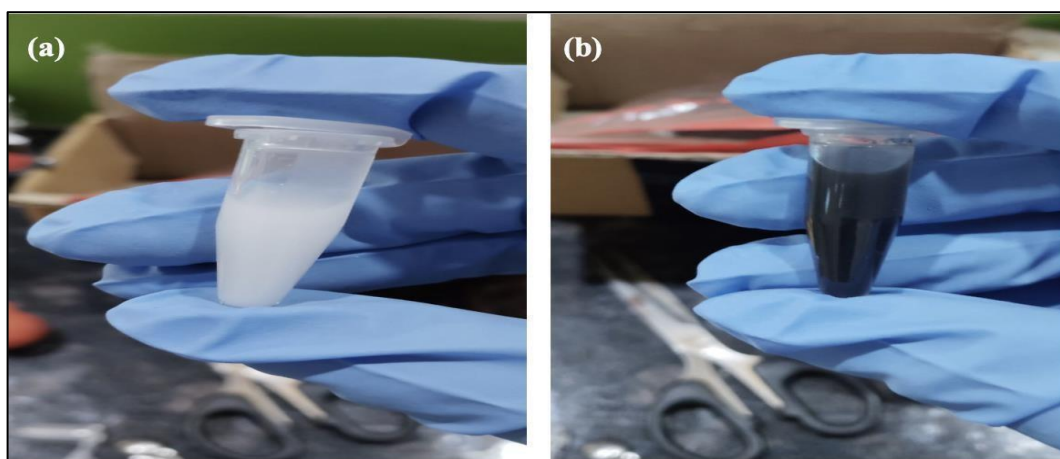


Figure 3.6. Antibacterial activity testing using (a). azithromycin as the standard, and (b). HCNs sample.

3.6.3. Evaluation of cement replacement potential

This methodology section has been adapted from the previously published article: Sharma, M., Öztürk, İ. Ş., Emiroğlu, M., & Erses Yay, A. S. (2025). Performance evaluation of biomass-derived hydrothermal carbonaceous material in cement-based

composites. *Case Studies in Construction Materials*, 22, e04291. <https://doi.org/10.1016/j.cscm.2025.e04291>. Published under the Creative Commons CC BY-NC 4.0 license. Additionally, a few images have been added for better clarity.

3.6.3.1. Preparation of cement composite

To prepare the cement composite, HCNs derived from pomegranate peel waste were incorporated into the mixture along with the other key materials, which are as follows:

- **Water:** Potable tap water was employed for both mixing and curing purposes in this study. The water had a pH of 7.76, contained 8.7 mg/L of chloride, 10.2 mg/L of sulfate, and had a total hardness of 11.5 mg/L.
- **Cement:** The cement used in the study was CEM I 42.5 R, which complies with the EN 197-1 standard. The physical and chemical characteristics of this cement are provided in Table 3.4.
- **Sand:** CEN standard sand, compliant with the EN 196-1 specification and possessing a density of 2.56 g/cm³, was utilized as the aggregate in the formulation of the mortar mixtures. The particle size distribution and chemical composition of the sand, as determined by XRF analysis, are presented in Table 3.5.

Table 3.4. Properties and chemical composition of cement used in the study.

Physical Properties		Chemical (%)	Composition
Density (g/cm ³)	3.15	Magnesium oxide (MgO)	1.39
Blaine fineness (cm ² /g)	3790	Calcium oxide (CaO)	63.15
Loss in ignition (%)	2.70	Sulfur trioxide (SO ₃)	3.61
Main compound (Bogue's equation)		Ferric oxide (Fe ₂ O ₃)	3.15
C ₃ S	>60	Aluminum oxide (Al ₂ O ₃)	4.27
C ₂ S	<15	Silicon dioxide (SiO ₂)	19.25
C ₃ A	<10	Sodium oxide (Na ₂ O)	0.44
C ₄ AF	>8	Chloride	0.041

Table 3.5. Granulometry and XRF analysis of the CEN standard sand.

Granulometry and XRF Analysis							
Granulometry							
Sieve size (mm)		2.00	1.60	1.00	0.50	0.16	0.08
Cumulative Retained (%)	0	7±2	33±2	67±2	87±2	99±1	
XRF Analysis							
Chemical Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	Loss on Ignition	
%	90.81	4.85	0.59	0.84	2.49	0.40	

3.6.3.2. Mix proportions and preparation method

To investigate how HCNs derived from pomegranate peel influence the physical, mechanical, and durability characteristics of cement mortar, the following preparation method was adopted to prepare various samples for the testing:

- Nine distinct mortar mixes were prepared: one reference mix without HCNs, four mixes incorporating HCNs via the dry mixing method, and four mixes using the wet mixing method.
- Mixes followed a constant weight ratio of cement (or cement + HCNs): sand: water = 1:3:0.5.
- The amount of water was calculated based on the sum of the cement + HCNs. HCNs replaced cement at 0.1%, 0.25%, 0.5%, and 1% by weight.
- Each batch used 450 g of cement (or cement + HCNs), 1350 g of sand, and 225 g of water (see Table 3.6).

- **Dry Mixing Method**

HCNs powder was dry-blended with cement in the specified dosages before water addition. Then it was stirred along with water using a mechanical mixer at 440 rpm for 5 minutes. Resulting samples were labeled: HCN0.1%D, HCN0.25%D, HCN0.5%D, HCN1%D.

- **Wet Mixing Method**

HCNs was pre-dispersed in mixing water using an ultrasonic mixer (Sonics Vibra-Cell VCX 500) for 15 minutes to prevent agglomeration. The suspension was then added

to the dry components and mixed under the same mechanical conditions. Resulting samples were labeled: HCN0.1%W, HCN0.25%W, HCN0.5%W, HCN1%W. Ultrasonic (for wet-mixed samples only) and mechanical mixing (for both types of samples) were employed to ensure uniform nanoparticle dispersion. Mixing continued until a homogeneous mix was visually confirmed.

- **Casting and Curing**

Fresh mortar was poured into 4×4×16 cm steel molds, with three samples cast per mix. After 24 hours, specimens were demolded, labeled, and cured in water until testing at 7 and 28 days. All the equipments and materials are visually summarized in Figure 3.7 and detailed proportions are listed in Table 3.6.

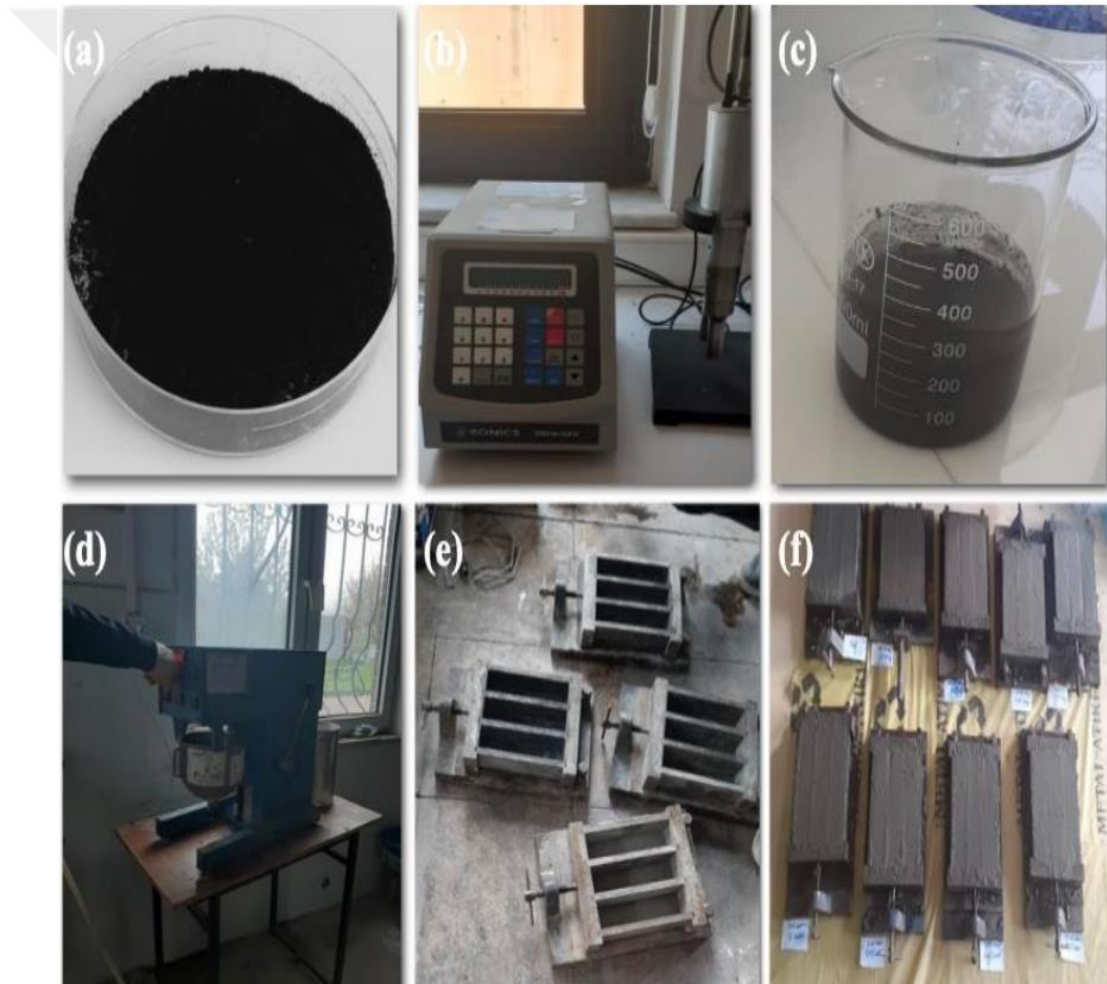


Figure 3.7. Preparation and mixing process of cement–carbon nanocomposites: (a) HCNs prepared for the study. (b) Ultrasonic mixer used for the wet-mixing process. (c) Wet-mixed solution containing water and HCNs. (d) Mechanical cement mixing process applied to all samples. (e) 4x4x16 cm steel molds for prismatic specimens. (f) Freshly prepared samples placed in the molds.

Table 3.6. Mix proportions for cement composites.

Code	Sample	Cement (g)	Sand (g)	w/(cement+HCNs) ratio	HCNs (%)
R	Reference Mortar	450	1350	0.5	-
HCN0.1%D	Mortar with 0.1% of HCNs dry mixed in cement first then with water	449.55	1350	0.5	0.1
HCN0.1%W	Mortar with 0.1% of HCNs mixed in water first then with cement	449.55	1350	0.5	0.1
HCN0.25%D	Mortar with 0.25% of HCNs dry mixed in cement first then with water	448.875	1350	0.5	0.25
HCN0.25%W	Mortar with 0.25% of HCNs mixed in water first then with cement	448.875	1350	0.5	0.25
HCN0.5%D	Mortar with 0.5% of HCNs dry mixed in cement first then with water	447.75	1350	0.5	0.5
HCN0.5%W	Mortar with 0.5% of HCNs mixed in water first then with cement	447.75	1350	0.5	0.5
HCN1%D	Mortar with 1% of HCNs dry mixed in cement first then with water	445.5	1350	0.5	1
HCN1%W	Mortar with 1% of HCNs mixed in water first then with cement	445.5	1350	0.5	1

3.6.3.3. Test methods and measured properties

SEM and EDS analyses were performed to confirm the successful incorporation of nanoscale HCNs into the cement matrix. A flow table test was conducted to assess the consistency of the mortars produced according to the specified mix ratios. Tests on hardened mortar specimens for each mix series included density, water absorption, porosity, capillary water absorption, ultrasonic pulse velocity, compressive strength, and flexural strength.

- **Flow table test**

Consistency of the mortar mixtures was evaluated using the flow table test, following the EN 1015-3 standard using the following procedure:

- Prepared cement mortar mixtures was placed into the flow table mold in two layers for each sample.

- Each layer was compacted with at least 10 short strokes using a compaction bar to eliminate air voids.
- Excess mortar was leveled off, and the surrounding disk surface was cleaned for accurate measurement.
- The mold was lifted vertically, and the table was jolted 15 times at a frequency of one jolt per second to allow the mortar to spread.
- The spreading diameter was measured in two perpendicular directions.
- The average of these two measurements was taken as the flow value, representing the workability of the mix.

- **Density, water absorption and porosity**

4x4x16 cm prismatic mortar specimens, exposed to curing for 7 and 28 days, were used to determine density, water absorption, and porosity, following ASTM C642 standards in the following manner:

(i). Specimen preparation:

- Oven Drying: Specimens were dried in an oven at $105 \pm 5^{\circ}\text{C}$ for 24 hours to remove moisture.
- Weight Measurement: Post-drying weights were measured with a precision balance ($\pm 0.01\text{g}$), recorded as dry weight (w_d).

(ii). Saturation process:

- Dried specimens were submerged in water until they reached constant mass.
- Excess surface water was wiped off, and the saturated weight (w_s) was recorded.

(iii). Immersion weight measurement:

- The immersed weight (w_w) of each specimen was measured using a specific gravity frame while suspended in water.

(iv). Calculation of properties:

- The following equations were used to calculate density (B), water absorption (WA), and porosity (P):

$$B = \frac{w_d}{(w_s - w_d)} \quad (3.6)$$

$$WA = \frac{(w_s - w_d)}{w_d} \times 100 \quad (3.7)$$

$$P = \frac{(w_s - w_d)}{(w_s - w_w)} \times 100 \quad (3.8)$$

Where, w_s is the dry surface saturated specimen weight, w_w is the saturated specimen weight in water, w_d is the oven dried specimen weight, B is the density, WA is the water absorption and P is the porosity.

The curing setup used throughout the process is illustrated in Figure 3.8.

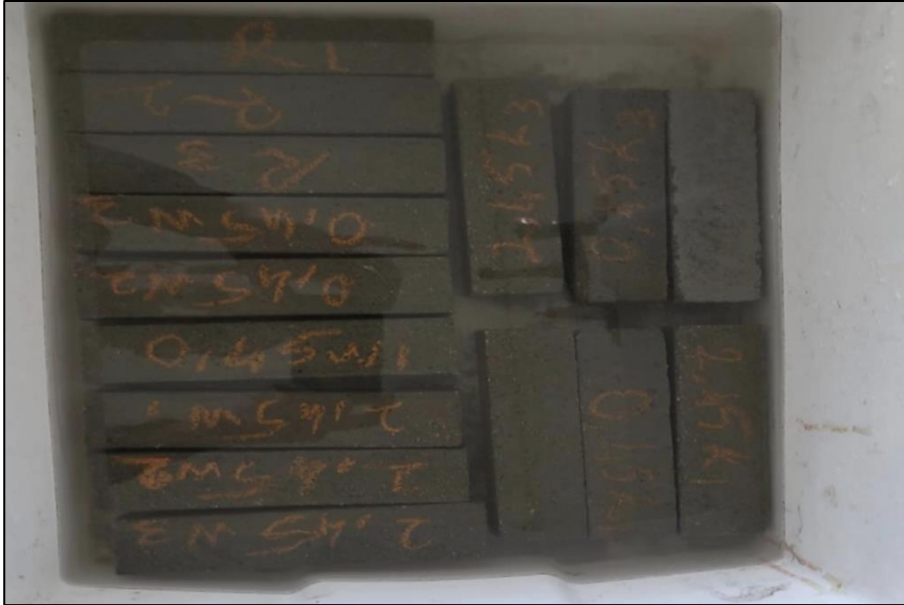


Figure 3.8. Samples submerged in water for the curing process.

- **Capillary water absorption test**

The capillary water absorption test was conducted on 28-day-old mortar specimens in accordance with ASTM C1585, incorporating minor modifications to the standard preconditioning procedure. The objective was to assess the rate and extent of water uptake over time. The experimental setup, illustrated in Figure 3.9, displays the controlled arrangement used to monitor the amount of water absorbed by the specimens under standardized conditions. The procedure for the capillary water absorption test is as follows:

(i). Specimen preparation:

- Three prismatic specimens (4×4×16 cm) were prepared for each mix series.
- Specimens were oven-dried at $105 \pm 5^\circ\text{C}$ until a constant mass was achieved, deviating from ASTM C1585 to allow for better drying control. After drying, specimens were cooled to ambient temperature before testing.
- All sides of the specimens, except the bottom, were sealed with a waterproofing material (white paint was used) to ensure unidirectional water flow and minimize surface evaporation during the testing procedure.

(ii) Initial weighing:

- Specimens were initially weighed using a precision balance (± 0.01 g) prior to immersion to obtain the initial dry weight (W_0).

(iii) Immersion:

- Specimens were placed vertically on support bars in a container, ensuring that the water level was maintained 4–5 mm above the specimen base to ensure consistent contact with water.
- The water level was monitored and maintained throughout the test to ensure consistency.

(iv) Monitoring water uptake:

- Specimen masses were recorded at specified intervals, as per ASTM C1585, to monitor the cumulative water uptake (absorption). The mass change (m_t) was recorded at regular intervals, and the corresponding water absorption was calculated.

v) Capillary water absorption calculation:

- Capillary water absorption was calculated using Equation 3.9:

$$I = \frac{m_t}{a \times d} \quad (3.9)$$

Where, I is the absorption (mm), m is the mass change at time t (g), a is the exposed area (mm^2), d is the water density (g/mm^3).

(vi) Regression analysis:

- A linear regression curve was fitted to the capillary water absorption data against the square root of time ($\sqrt{t}$) to assess sorptivity. Sorptivity is derived from the slope of the linear portion of the graph, indicating the rate of capillary water absorption.

(vii) Absorption classification:

- Initial Absorption: The slope of the curve from 0 to 6 hours.
- Secondary Absorption: The slope from 1 day to 8 days.



Figure 3.9. Experimental setup for capillary water absorption testing.

- **Ultrasonic Pulse Velocity**

- Ultrasonic pulse velocity (UPV) tests were performed to assess the internal integrity and homogeneity of the mortar specimens. UPV tests were conducted on 4×4×16 cm prismatic mortar specimens, prepared using the designated mixture proportions for each series and tested in accordance with the EN 12504 standard to ensure methodological consistency and result reliability.
- Cured specimens were oven-dried at 105°C until a constant mass was reached to eliminate moisture influence on wave propagation.
- The UPV device used in the experiment was equipped with transmitting and receiving probes to measure wave transit through the specimens.

- Ultrasonic waves emitted by the transmitting probe passed through the specimen and were captured by the receiving probe. The transit time was recorded in microseconds (μs) with high precision.
- Ultrasonic gel was applied to the contact surfaces between probes and specimens to ensure effective transmission and reception of ultrasonic waves.
- UPV measurements were taken along the length of each specimen to evaluate internal continuity.
- Measurements were performed after 7 and 28 days of curing to monitor changes in internal structure over time.
- Each mixture series was tested using three specimens, and the average UPV was calculated from individual readings.
- Velocity calculation: The ultrasonic pulse velocity (U , km/h) was determined using the equation:

$$U = \frac{L}{t} \quad (3.10)$$

Where L is the specimen length (mm) and t is the measured transit time (μs).

The UPV test setup is shown in Figure 3.10, providing a schematic representation of the equipment and specimen arrangement.



Figure 3.10. Ultrasonic pulse velocity (UPV) test setup.

- **Compressive Strength**

The following procedure was adopted to determine the compressive strength of the tested samples:

- The tests were performed on prism halves obtained from broken mortar specimens, as specified in the flexural strength section of the EN 196-1 standard.
- A compression testing machine with a 200 kN load cell was used, and the loading rate was maintained at 2400 N/s throughout the test.
- For each mix series, compressive strength was determined by averaging the values obtained from three cube specimens.
- The experimental setup used to perform the compressive strength tests is shown in Figure 3.11.



Figure 3.11. Compressive strength test setup for evaluating the load-bearing capacity of samples.

- **Flexural Strength**

- Flexural strength was evaluated on 4×4×16 cm prismatic mortar specimens in accordance with the EN 196-1 standard.

- A three-point bending test was conducted for each mix series using a displacement-controlled testing machine.
- The testing device was equipped with a 50 kN load cell, and the span length between the supports was fixed at 100 mm.
- Each prism was placed with one side face resting on the support cylinders, ensuring that its longitudinal axis was perpendicular to the supports.
- A vertical load was applied through the central loading roller to the top face of the prism at a constant rate of 50 N/s until failure.
- The flexural strength for each specimen was calculated using Equation 3.11, based on the maximum load applied during the test and the average of the three values was reported as the flexural strength of the corresponding mix series.

$$f_r = \frac{3PL}{2bxd^2} \quad (3.11)$$

Where , f_r is the flexural strength (N/mm²), P is the maximum applied load (N), L is the span length (mm), b is the specimen width (mm), and d is the specimen depth (mm). The experimental setup used for flexural testing is depicted in Figure 3.12.



Figure 3.12. Flexural strength test setup: before (intact) and after fracture (broken).



4. RESULTS AND DISCUSSION

4.1. Lignocellulosic Content in the Feedstocks

The results obtained from the chemical analysis of the biomass samples reveal their composition, including the amounts of hemicellulose, cellulose, and lignin present in each feedstock. The comparative amounts of these components in the different biomass samples are summarized visually in Figure 4.1. Out of the three samples the cellulosic content was observed to be highest in CFW, followed by MFW and then PPW. Also, among the three samples, the PPW sample was observed to have highest extractive biomass (12%) while the extractive biomass for MFW sample was 7% and CFW has lowest extractive biomass (4%).

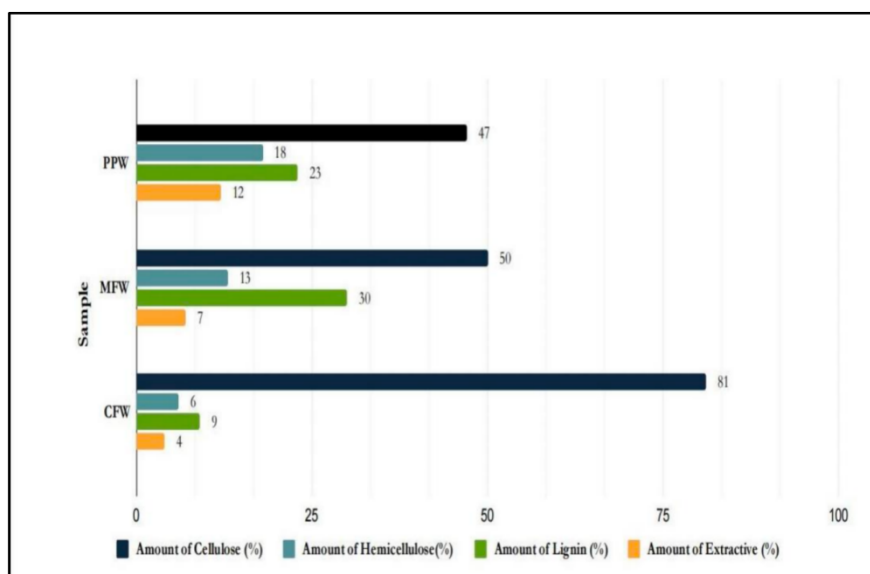


Figure 4.1. Lignocellulosic content in biomass samples.

4.2. Effect of Biomass Composition on Various Properties of HTC Products

Figure 4.2 shows typical outputs from the HTC experiments conducted in this study. As illustrated in the figure, processing at lower temperature (180°C) resulted in lighter-colored outputs and higher liquid yields, while higher temperature (250 °C) produced darker outputs and lower liquid yields with a higher degree of carbonization. The influence of temperature, residence time, and acidity on the physicochemical

properties of HTC products has been extensively reported in the literature over the years (Libra et al., 2011; Reza et al., 2014; Zhang et al., 2019). Therefore, this study focuses primarily on how the intrinsic composition of different biomass types affects the characteristics of the resulting solid carbonaceous materials.



Figure 4.2. Liquid and solid outputs of HTC at 180°C (left) and 250°C (right).

In the following sections, the influence of biomass composition on individual physicochemical parameters of the solid carbonaceous products is discussed in detail.

4.2.1. Effect on pH and electrical conductivity

The pH values of the three biomass samples were measured before and after HTC (Figure 4.3a). PPW and MFW samples exhibited minimal pH variation, remaining weak acids throughout the process. However, CFW samples, initially basic, significantly decreased to highly acidic post-HTC. This decrease in pH during the HTC process can be attributed to the formation of various acidic compounds, such as acetic, formic, and levulinic acids due to the hydrolysis of hemicellulose and cellulose components, as suggested by several authors previously (Hoekman et al., 2013; Basso 2016). Conversely, the formation of the weak acidic phenolic compounds due to the hydrolysis of lignin during the HTC of the biomass as investigated by Basso (2016) may have contributed to balancing out the overall acidity in the case of PPW and MFW samples. Thus, the decomposition of cellulose and hemicellulose contents play a crucial role in forming strong acids, while weak acidic phenols from lignin decomposition may counterbalance acidity.

The electrical conductivity (EC) is increased with varying percentages in all the samples post HTC (Figure 4.3b). All the samples after the HTC process show semiconductive properties, since EC is less than 10^4 S m^{-1} but higher than 10^{-8} S m^{-1} (Hoffmann et al., 2019). The raw samples with higher cellulose content (PPW and CFW) initially exhibit lower conductivity but show an increase after the HTC process. The MFW sample, which has higher lignin content, shows higher initial conductivity and a further increase after HTC though it is a marginal increase. On the other hand CFW, richest in cellulose among all the three samples, had the lowest initial conductivity but it increased to exceptional level after HTC. The findings reflect that cellulose content in the raw state tends to decrease electrical conductivity, while lignin content can enhance it, highlighting the influence of both components on conductivity. However, after decomposition, the feedstocks with higher initial cellulose content show more increase in the electrical conductivity.

Since full carbonization of all samples was only achieved at 250°C for 4 hours, out of the other tested operating conditions (180°C for 2 and 4 hours, and 250°C for 2 hours), subsequent characterization methods mainly focused on comparing the samples PPW-250/4, MFW-250/4, and CFW-250/4 with their respective raw samples. (In some sections, these samples are interchangeably referred to as PPW HTC, MFW HTC, and CFW HTC).

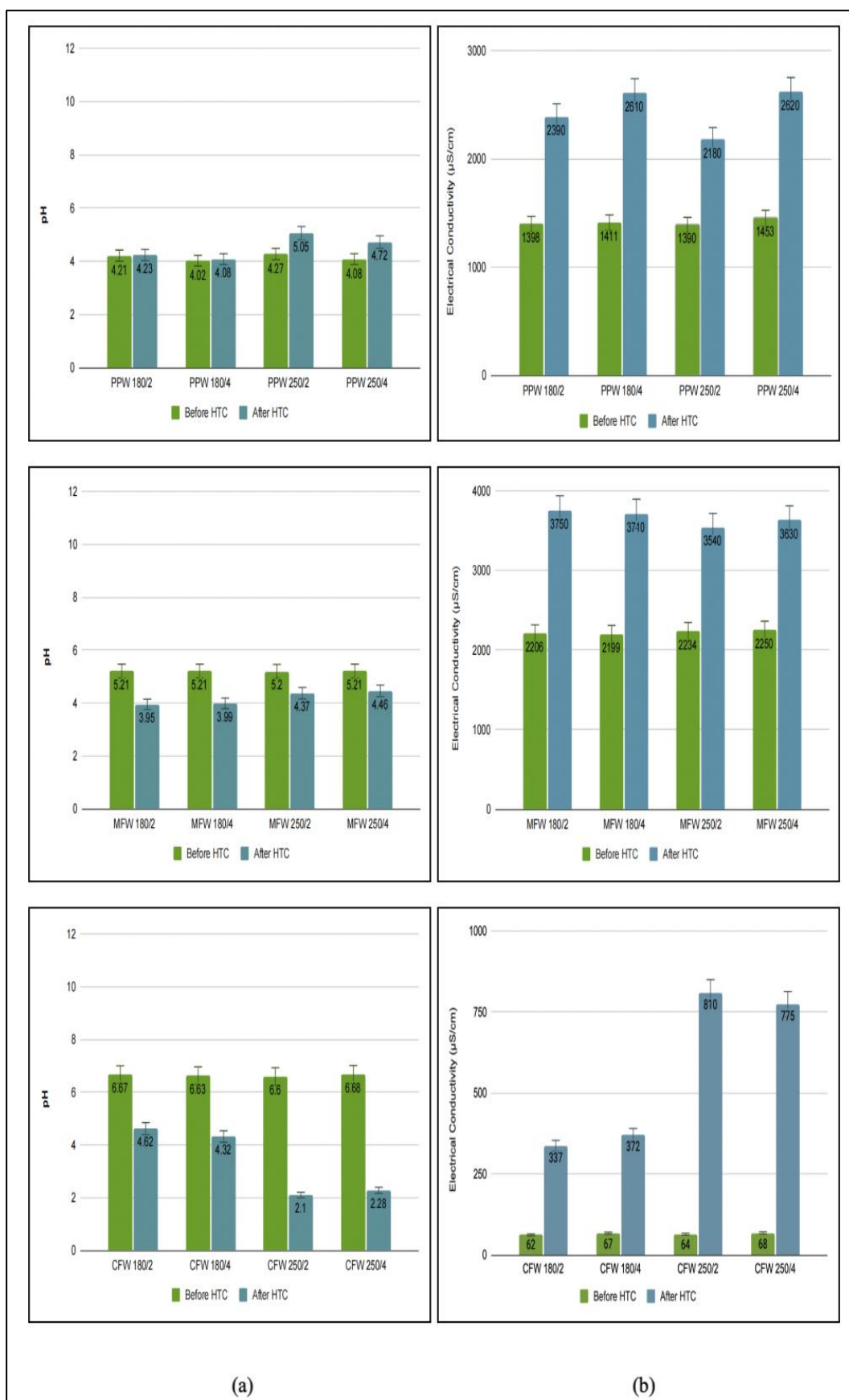


Figure 4.3. (a). pH and (b). conductivity of samples before and after HTC.

4.2.2. Effect on elemental composition

Table 4.1 presents the elemental analysis (CHNO) of the raw biomass samples and their corresponding HTC-treated products (250 °C, 4 h), detailing the carbon (C), hydrogen (H), nitrogen (N), and oxygen (O) contents. The results clearly illustrate the chemical transformations induced by the HTC process. All samples exhibit an increase in carbon and nitrogen content and a decrease in oxygen and hydrogen content, typical of carbonization. However, the extent of these changes depends on the composition of the raw material.

CFW, primarily composed of cellulose, breaks down more readily during HTC, resulting in the most pronounced transformation—with a 56.3% increase in carbon and a 76.87% decrease in oxygen due to the rapid decomposition of oxygenated groups. PPW shows a 42.3% increase in carbon and a 59.87% decrease in oxygen, indicating moderate carbonization influenced by its mixed cellulose–lignin composition. In contrast, MFW undergoes the least change in carbon (12.15%) and oxygen (33.60%), but the highest hydrogen loss (15.45%), aligning with the structural stability and decomposition resistance of lignin. These trends highlight that lignin-rich biomass resists transformation, while cellulose-rich feedstocks yield more carbon-rich, stable carbon materials.

Table 4.1. Elemental analysis of raw and HTC-treated samples.

Sample	C (%)	H (%)	N (%)	O (%)	H/C	O/C
PPW-Raw	54.411	5.442	0.728	39.419	0.100	0.724
PPW-250/4	77.476	4.761	1.946	15.817	0.061	0.204
MFW-Raw	67.574	7.250	1.812	23.364	0.107	0.346
MFW-250/4	75.782	6.132	2.576	15.510	0.081	0.205
CFW-Raw	54.247	6.291	0.762	38.700	0.116	0.713
CFW-250/4	84.782	5.381	0.887	8.950	0.063	0.106

Additionally, the CFW sample exhibited the most significant reductions in both O/C and H/C ratios, with decreases of 85.13% and 45.69%, respectively, after HTC. This can be attributed to its high cellulose and low hemicellulose and lignin content. Since cellulose decomposes readily under HTC, even at lower temperatures, this results in

substantial reduction and indicates the highest degree of carbonization among the samples.

In contrast, the MFW sample, with its highest lignin content, exhibited the least decrease in both O/C and H/C ratios—40.75% and 24.30%, respectively—confirming lignin's inherent resistance to decomposition. The PPW sample showed intermediate decreases in O/C (71.82%) and H/C (39%) ratios.

The O/C and H/C ratios for solid HTC products are key indicators of carbonization and carbon material quality. In general, all samples demonstrated a significant decrease in both ratios after HTC, a trend well supported by previous studies. The O/C ratios, which reflect chemical stability, were measured at 0.204, 0.205, and 0.106 for the PPW-HTC, MFW- HTC, and CFW-HTC samples, respectively. These values suggest high stability, as an O/C ratio near 0.20 is associated with an estimated half-life of up to 1000 years (Spokas, 2010).

4.2.3. Effect on energy content and solid mass yields

The higher heating values (HHV) and solid mass yields of the raw biomass samples and their corresponding carbonized products are presented in Table 4.2. In their raw states, PPW, MFW, and CFW samples had similar HHV values, with marginal difference within the range of ± 2.02 MJ/kg. After the HTC, the HHV values of these biomass samples increased appreciably however the differences between their HHV values remain relatively small (± 3.09 MJ/kg). These results align with previous studies, such as Qin et al., 2020, which concluded that the interactions of lignin, cellulose, and hemicellulose have a limited impact on the HHV of biochar. Similarly, Lu and Berge 2014 found that the energy content of the solid HTC products is not much sensitive to changes in feedstock chemical/structural characteristics. However, a minor difference between the HHV of MFW-250/4 and PPW- 250/4 samples was observed, despite not much variation in the values of their biomass composition. Studies have indicated that the presence of lignin in the feedstock can lead to a higher HHV of the resulting hydrochar, suggesting that lignin plays a crucial role in determining the energy density of the hydrochar (Güleç et al., 2021; Sun et al., 2023). This higher lignin content potentially explains the MFW-250/4 product's higher HHV compared to PPW-250/4.

Table 4.2. Energy content and solid mass yields of raw and HTC-treated samples.

Sample	HHV (MJ/kg)	EDR	EY %	SMY %
PPW-Raw	15.52			
PPW-250/4	24.69	1.59	43.90	27.60
MFW-Raw	16.65			
MFW-250/4	27.51	1.65	61.13	37.00
CFW-Raw	17.54			
CFW-250/4	27.78	1.58	52.89	33.40

This study confirms prior findings linking biomass composition to solid yield. High lignin content is typically associated with lower solid yield due to lignin gasification, during degradation, leading to increased gaseous product formation and a subsequent decrease in overall solid yield (Hoekman et al., 2013). Consistent with this understanding, the CFW sample, high in cellulose and low in lignin, yielded more solids than PPW sample. MFW showed a notable difference as compared to PPW, suggesting a potential influence of hemicellulose proportion on mass yield, as noted in prior studies (Reza et al., 2011). These results demonstrate that the synergistic effect of all the biomass components has a more pronounced impact on HHV and solid yield compared to considering each component individually, with higher initial carbon content yielding the highest outputs, as seen with MFW, aligning with the findings from Lu and Berge (2014).

4.2.4. Effect on other properties

4.2.4.1. Surface area results

The BET surface area and porosity characteristics of the raw and HTC-treated biomass samples, as presented in Table 4.3, reflect the critical influence of the biomass composition—particularly the proportions of cellulose, hemicellulose, and lignin—on structural transformation during hydrothermal carbonization. The surface area was determined using the multipoint Brunauer–Emmett–Teller (BET) method, while the pore volume and pore size were evaluated using the Barrett–Joyner–Halenda (BJH) method.

CFW, composed almost entirely of cellulose, exhibited the highest surface area both before (19.65 m²/g) and after HTC (29.68 m²/g), along with a corresponding increase in pore volume. This enhancement is attributed to cellulose’s inherent microfibrillar structure, which contains amorphous regions and inter-fibril voids that facilitate pore

development during HTC. Cellulose is widely recognized for its ability to yield highly porous materials through thermal and physical treatments, which explains the substantial porosity increase observed in CFW.

In contrast, PPW, with its mixed cellulose–hemicellulose–lignin matrix, showed a dramatic relative increase in surface area (from 1.26 to 19.97 m²/g) and pore volume, albeit from a much lower starting point. The BJH desorption analysis of PPW-250/4 revealed a cumulative pore volume of 0.149 cm³/g and a mode pore diameter of 2.16 nm, indicating the formation of well-developed mesopores. These results suggest effective degradation of the amorphous cellulose and hemicellulose fractions in PPW, while the presence of lignin may have constrained the ultimate porosity achievable.

MFW, which contains the highest lignin content among the three, displayed a slight decrease in surface area after HTC (from 9.09 to 8.33 m²/g), underscoring lignin’s resistance to structural decomposition at 250 °C. The highly aromatic and crosslinked nature of lignin inhibits micropore development and, at moderate HTC temperatures, may promote condensation or softening that restricts pore formation. Overall, these findings highlight that cellulose-rich biomass such as CFW is most favorable for producing high surface area and porous carbonaceous materials via HTC, whereas lignin-rich feedstocks may require higher thermal input or post-treatment activation to achieve similar structural enhancements

Table 4.3. BET surface area, pore size, and pore volume of raw and HTC-treated samples.

Sample	BET Surface Area (m ² /g)	Pore Size (nm)	Pore Volume (cm ³ /g)
PPW-Raw	1.26	2.691	0.007768
PPW-250/4	19.97	2.160	0.14900
MFW-Raw	9.09	1.919	0.02815
MFW-250/4	8.33	1.781	0.02320
CFW-Raw	19.65	2.164	0.03495
CFW-250/4	29.68	1.662	0.06587

A more detailed investigation was conducted on PPW, as it was the only biomass that underwent complete carbonization under all the selected HTC conditions. In addition to the raw and 250°C/4 h samples included in the main comparison, intermediate HTC conditions were also evaluated for PPW to better understand the progressive evolution of its porosity characteristics.

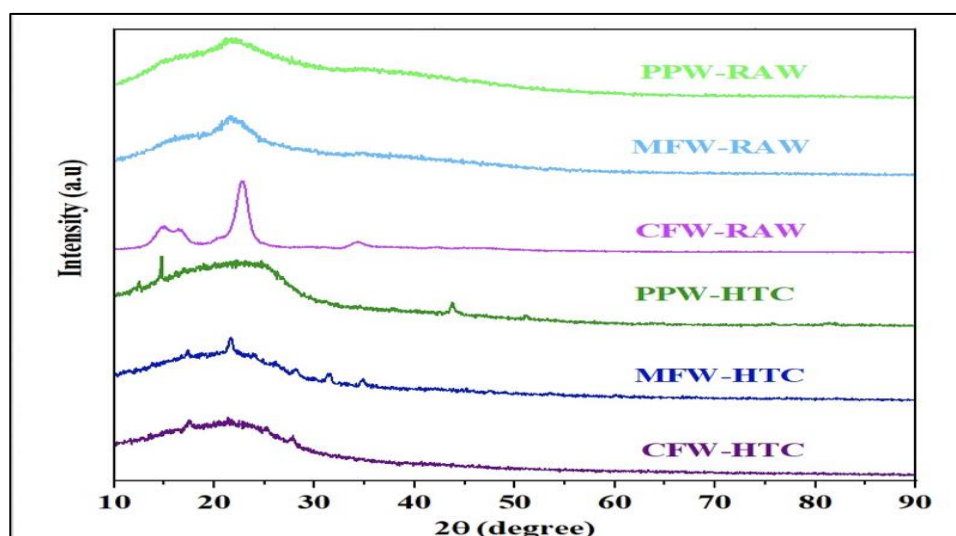
Table 4.4. BET surface area, pore size, and pore volume of other PPW samples.

Sample	BET Surface Area (m ² /g)	Pore Size (nm)	Pore Volume (cm ³ /g)
PPW-180/2	10.65	1.645	0.03092
PPW-180/4	11.08	1.878	0.05142
PPW-250/2	12.49	2.134	0.09497

As shown in Table 4.4, samples PPW-180/2, PPW-180/4, and PPW-250/2 exhibited increasing trends in both BET surface area and pore volume with temperature and residence time, supporting a gradual breakdown of structural barriers and development of accessible porosity prior to complete carbonization.

4.2.4.2. X-ray diffraction results

The XRD results shown in Figure 4.4, indicate that all the obtained solid HTC products are amorphous in nature, with the most prominent peak can be observed near 22° corresponding to the typical amorphous carbon (Wang et al., 2019; Yu et al., 2019). In the spectrum of PPW-HTC one more peak is observed near 44° associated with the interlayer reflection of the hexagonal carbon structure (Yu et al., 2019). The findings also align with existing literature, which state that cellulose, as a crystalline component, typically exhibits a sharp peak at around $2\theta=22^\circ$, while lignin and hemicelluloses are amorphous (Gbenebor et al., 2023). This characteristic is evident in the sharper peak of the raw sample of CFW, where cellulose is the dominant component. The broader amorphous peaks observed in the spectra of raw samples of PPW and MFW can be attributed to their higher lignin and hemicellulose contents.

**Figure 4.4.** XRD patterns of raw and HTC samples.

4.2.4.3. Raman spectroscopy results

Raman spectroscopy revealed distinct D and G bands in all samples, confirming the carbonaceous nature of the materials. The D band, typically observed around 1350 cm^{-1} , is associated with sp^3 -hybridized carbon atoms and indicates structural disorder and defects. In contrast, the G band, appearing near $1580\text{--}1600\text{ cm}^{-1}$, corresponds to the stretching vibrations of sp^2 -hybridized carbon atoms, signifying graphitic ordering, as illustrated in Figure 4.5. The specific positions and intensities of these bands were used to calculate the intensity ratio of the G-band to D-band (I_G/I_D) ratio, a widely accepted metric for evaluating the degree of graphitization and structural order in carbon-based materials. An I_G/I_D value greater than 1 indicates a higher level of graphitic order, whereas a value less than 1 suggests a more amorphous or structurally disordered carbon matrix.

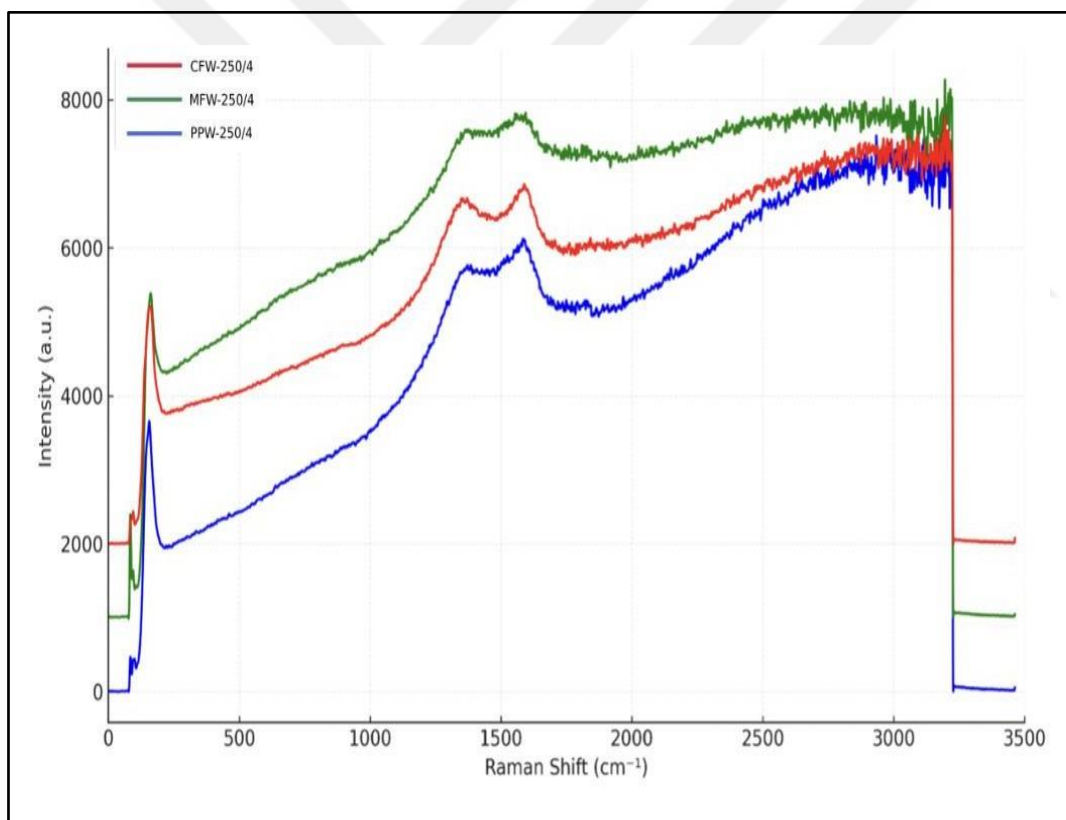


Figure 4.5. Raman spectra of HTC samples.

Among the samples, PPW exhibited a D band at 1359.72 cm^{-1} and a G band at 1584.10 cm^{-1} , yielding the highest I_G/I_D ratio (1.072). This indicates a relatively high degree of structural ordering and the formation of graphitic-like domains within the otherwise amorphous matrix. In comparison, CFW presented a slightly lower ratio (1.046), with

a D band at 1351.90 cm^{-1} and a G band at 1589.20 cm^{-1} , while MFW showed the lowest ratio (1.030), along with a D band at 1366.60 cm^{-1} and a G band at 1559.50 cm^{-1} .

4.2.4.4. Scanning and transmission electron microscopy results

The SEM images of the solid HTC samples derived from the three different biomass sources reveal distinct morphological differences (Figure 4.6).

Under the same operating conditions, PPW-250/4 sample exhibited a morphology characterized by definite cross-linked spherical structures in both nano and sub-micron ranges (Figure 4.6b), similar to the structure of carbon nanospheres observed in the study by Yu et al. (2019). In contrast, the carbonized material from the other two feedstocks displayed an indefinite structure (Figure 4.6d and 4.6f).

Wang et al. (2001) and Sevilla and Fuertes (2009b), whose studies continue to serve as key references in the development of HTC-derived carbon materials, reported the synthesis of carbon microspheres ranging from $0.25\text{ }\mu\text{m}$ to $5\text{ }\mu\text{m}$ from sucrose and $0.4\text{ }\mu\text{m}$ to $6\text{ }\mu\text{m}$ from various saccharides, respectively. In contrast, the carbon nanospheres synthesized in this study are markedly smaller, with sizes in the range of approximately $50\text{--}300\text{ nm}$, highlighting the influence of feedstock selection and process conditions.

While in the SEM image of the CFW-250/4 sample, observable indications suggest the potential formation of spherical morphology by the carbon particles, in the SEM image of the MFW-250/4 sample, there is an absolute absence of any definite shape formation resulting in the most irregular morphology. This irregular morphology is likely due to MFW's higher lignin content, known for resisting complete decomposition during HTC and leaving behind residual components that affect the ultimate morphology of the carbonaceous product (Gong et al. 2023)

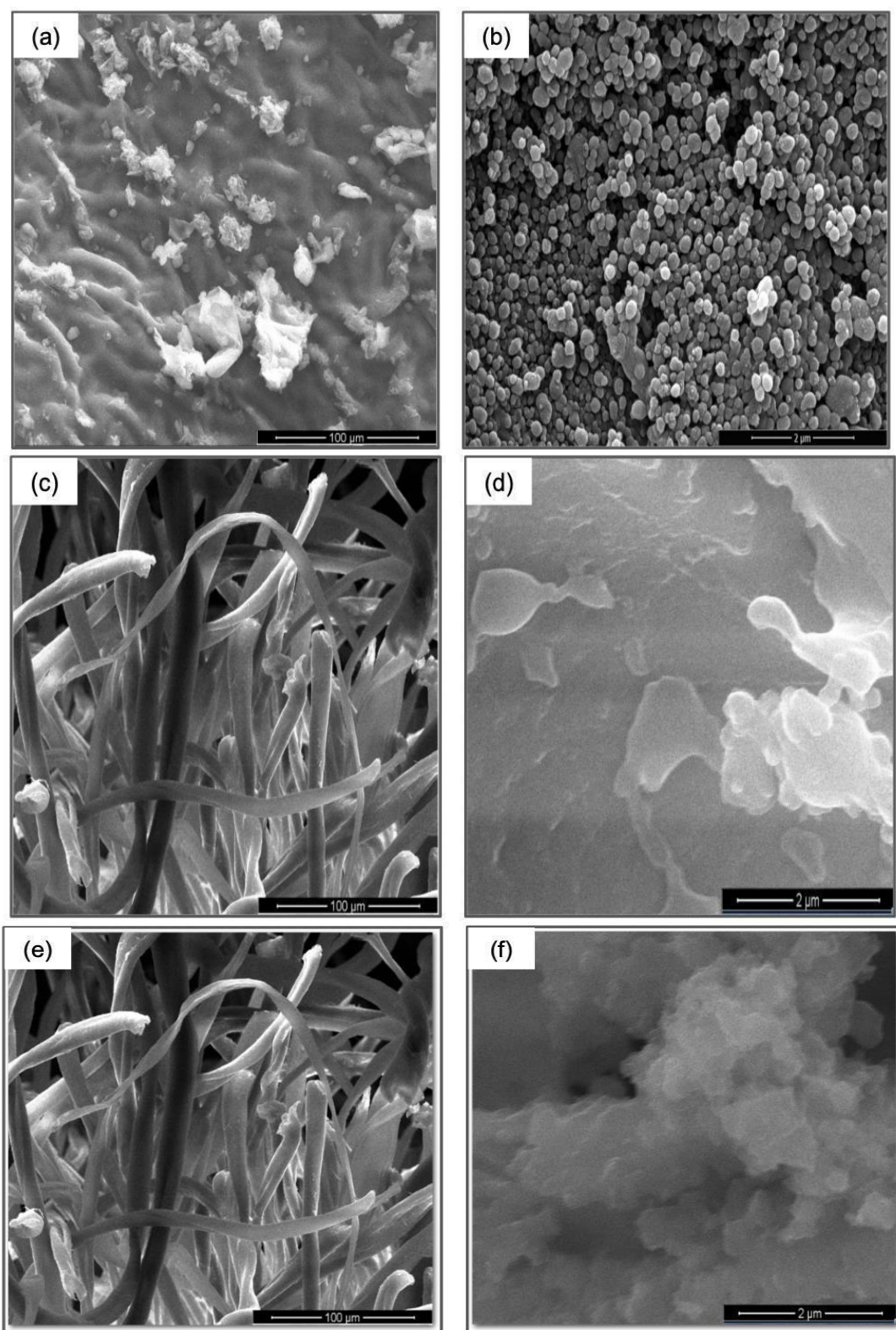


Figure 4.6. SEM images of raw and HTC samples: (a). PPW-Raw, (b). PPW-250/4, (c). MFW-Raw, (d) MFW-250/4, (e) CFW-Raw, and (f) CFW-250/4.

TEM analysis further confirms the presence of spheres in the nanosize range for the HTC PPW-250/4 sample (Figure 4.7). These nanospheres form hexagonal patterns and

agglomerate similarly to previous studies where carbon nanospheres were prepared from coconut fiber (Adewumi et al., 2018) and bamboo fiber (Lahsmin et al., 2019).

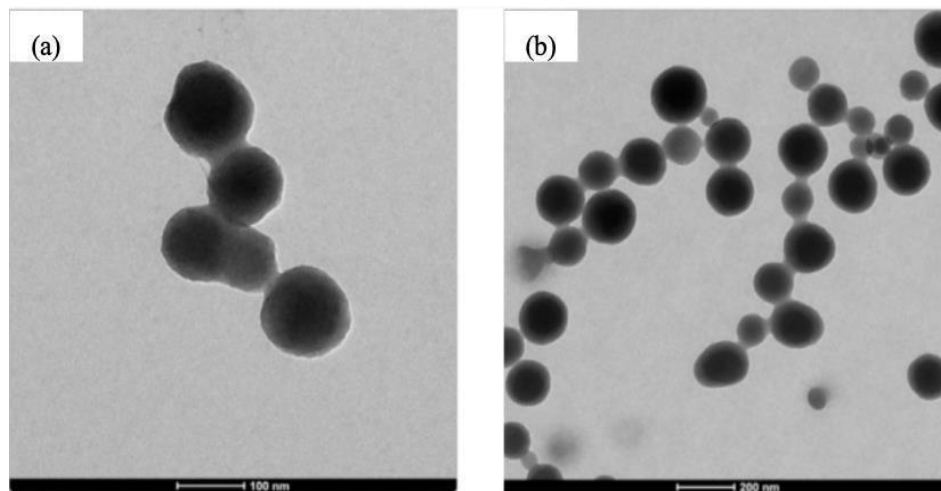


Figure 4.7. TEM images of PPW-derived carbon nanospheres: (a) at 50 nm and (b) at 100 nm scales.

Since fully carbonized particles in the nanometer range were obtained exclusively from the PPW-250/4 sample, it was selected for further investigation, including carbon dots recovery from its HTC-derived wastewater, surface modification, and application studies. Additional characterizations were performed to support its suitability for these applications. This sample exhibited the highest degree of carbonization among all tested conditions, as confirmed by its structural features. Given its distinct nanoscale morphology and hydrothermal synthesis route, the resulting material is hereafter referred to as hydrothermally carbonized nanospheres (HCNs)—a term appropriate for HTC-derived carbon nanostructures. The LCA was also focused on this sample to assess its environmental implications.

4.3. Other Properties of Hydrothermally Carbonized Nanospheres

Having established the suitability of the PPW-250/4 sample (as HCNs) for further investigation based on its carbonization properties, nanoscale morphology, and structural features, additional material properties were explored to assess its performance in various applications. The following sections outline evaluations of the HCNs' hydrophobicity, chemical structure via FTIR, and thermal stability through TGA and DTA, providing valuable insights into their functionality and performance. Some of these results are adapted from previously published paper:

Sharma, M., Öztürk, İ. Ş., Emiroğlu, M., & Erses Yay, A. S. (2025). Performance evaluation of biomass-derived hydrothermal carbonaceous material in cement-based composites. *Case Studies in Construction Materials*, 22, e04291. <https://doi.org/10.1016/j.cscm.2025.e04291>. Published under the Creative Commons CC BY-NC 4.0 license.

4.3.1. Hydrophobicity assessment

The hydrophobicity of the synthesized HCNss was assessed to understand their intrinsic surface properties, which are crucial in determining how the material behaves when incorporated into other matrices, such as cement composites. The contact angle of a water droplet placed on the HCNs surface was measured to be 140.50° (Figure 4.8), classifying the material as overhydrophobic ($120^\circ < CA < 150^\circ$), according to the classification by Zemajtis et al. (2023). This high contact angle suggests that the HCNs surface is dominated by non-polar functional groups, contributing to its resistance to water absorption. These findings are consistent with previous work by Heidari Joula and Farbod (2015), who reported a contact angle of approximately 153° for carbon nanospheres synthesized hydrothermally from sucrose and further annealed, indicating superhydrophobic behavior. The similarity in surface water-repellent behavior highlights the potential of HCNs for applications where water resistance is desirable.

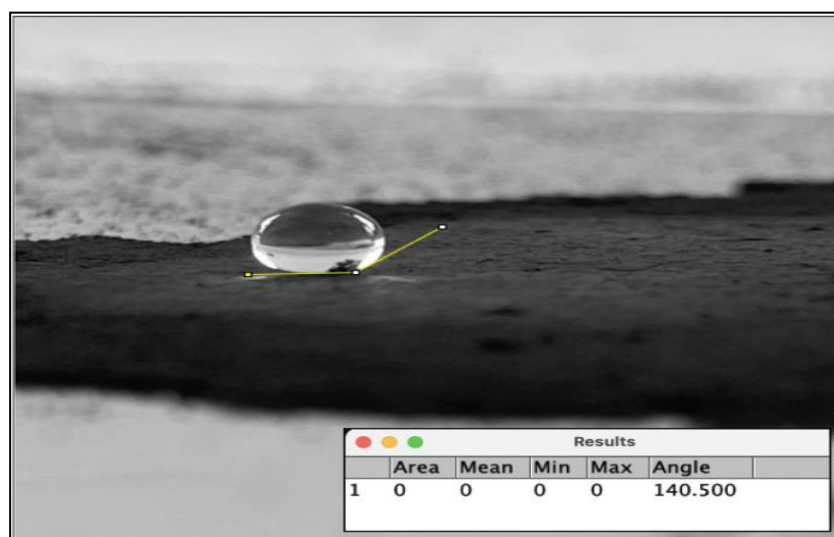


Figure 4.8. Hydrophobicity of PPW-HCNs via contact angle measurement.

4.3.2. Fourier transform infrared spectroscopy

The FTIR spectrum of the synthesized HCNs was recorded over the range of $500\text{--}4500\text{ cm}^{-1}$ to investigate their functional groups and structural characteristics, as shown

in Figure 4.9. Several distinct peaks were observed, each corresponding to specific surface functionalities. A broad absorption band at 3369 cm^{-1} is attributed to O–H stretching vibrations, indicating the presence of hydroxyl groups typically associated with alcohols or phenols (InstaNANO, 2024). The peak at 2929 cm^{-1} corresponds to C–H stretching vibrations of aliphatic $-\text{CH}_2$ and $-\text{CH}_3$ groups (InstaNANO, 2024). A sharp band at 1593 cm^{-1} is associated with C=C stretching in aromatic rings or conjugated structures, suggesting aromatic condensation and partial graphitization during hydrothermal carbonization. The adjacent peak at 1504 cm^{-1} may be related to aromatic skeletal vibrations, though contributions from N–O stretching of nitro compounds cannot be excluded (InstaNANO, 2024). A prominent peak at 1211 cm^{-1} is attributed to C–O stretching vibrations, characteristic of ether linkages, specifically alkyl aryl ethers, likely formed through lignin depolymerization during carbonization (InstaNANO, 2024). Additionally, a carbonyl stretch observed at 1687 cm^{-1} , characteristic of carboxylic acids, ketones, and esters, further supports the presence of these functional groups. Another C–O stretch at 1109 cm^{-1} is also noted. These findings are consistent with those reported by Wu et al. (2023), further validating the presence of these functional groups in HCNs.

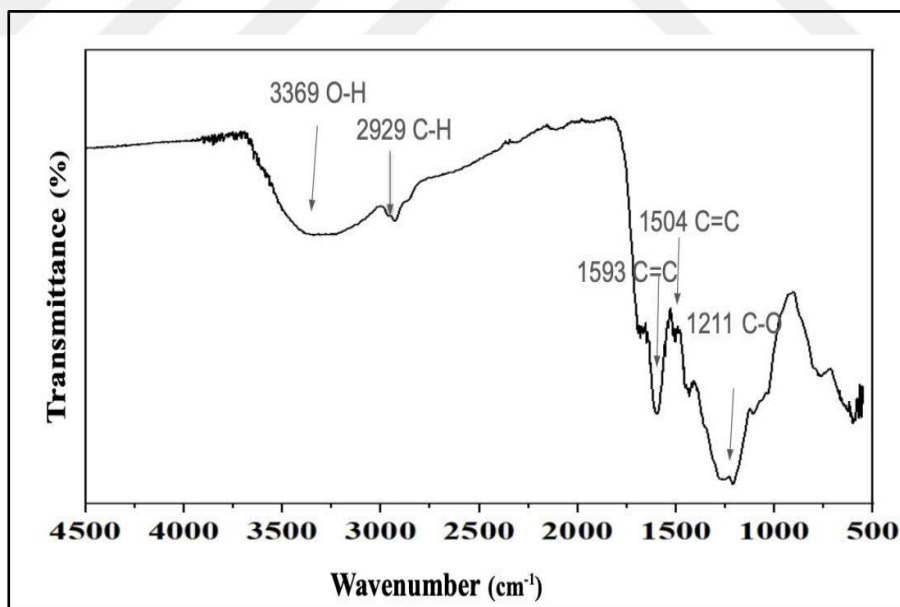


Figure 4.9. FTIR spectra of the HCNs.

4.3.3. Integrated TGA-DTA analysis

The thermal decomposition behavior of the HCNs was investigated using simultaneous TGA-DTA analysis under a nitrogen atmosphere, revealing a complex thermal profile characterized by multiple weight loss stages (Figure 4.10). The TGA

data indicate a multi-phase degradation pattern, resulting in a total weight loss of 97.95%, with only minimal residual mass remaining.

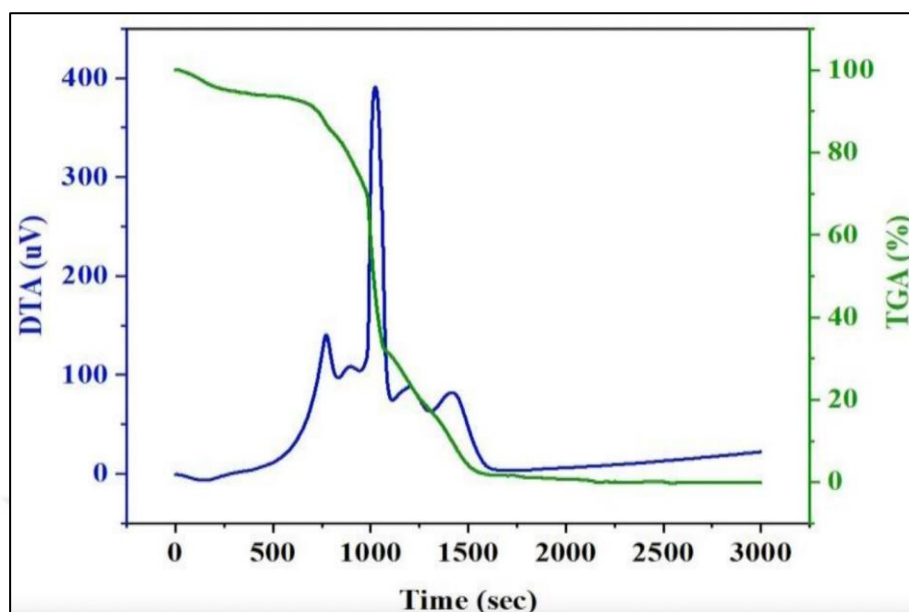


Figure 4.10. TGA and DTA graphs of the HCNs.

The initial weight loss of approximately 0.9% up to 100°C was attributed to the evaporation of adsorbed moisture and light volatile components, supported by a slight exothermic peak at 182.5°C in the DTA curve. A significant weight loss of 43.23% occurred between 260°C and 430°C, with a peak at 307°C corresponding to intense exothermic reactions and a heat release of 529.58 J/g. A secondary decomposition phase between 430°C and 510°C, accounting for an additional 12.68%–16.26% mass loss, reflected the breakdown of more stable carbonaceous structures formed during HTC, as evidenced by DTA peaks at 442°C and 510°C. Beyond 510°C, the material reached thermal stability, with minimal mass loss observed up to 700°C, marking the complete combustion of the HCNs and confirming the formation of a thermally resistant carbonaceous residue. The total weight loss of 97.95% indicated extensive thermal degradation, leaving behind a carbon-rich, thermally stable residue. These findings were further validated by the TGA-DTA curves, where sharp exothermic peaks and the gradual stabilization of the material after 1500 seconds signified the major decomposition and stabilization stages, respectively. These results for HCNs are consistent with previous reports on aquatic biomass-derived hydrochar (Poomsawat & Poomsawat, 2021). Overall, the findings highlight the potential of HCNs for

applications requiring high thermal stability and carbon content, demonstrating their suitability for such applications.

4.4. Properties of Carbon Dots

4.4.1. Raman spectroscopy of carbon dots

Raman spectroscopic analysis of PPW-250/4 CDs, recovered from the HTC process water, revealed distinct peaks at approximately 1365.2 cm^{-1} (D-band) and 1587.6 cm^{-1} (G-band), as shown in Figure 4.11. The I_G/I_D was approximately 1.075, signifying a slightly higher degree of graphitization and a more ordered structure compared to PPW-HCNs, which exhibited an I_G/I_D ratio of 1.072.

These findings align with previous studies on carbon dots synthesized from biomass, such as corn straw (Mu et al., 2024), and are consistent with earlier observations of the graphitic nature of carbon dots (Dager et al., 2019). This suggests that the prepared CDs exhibit a predominantly graphitic structure, enhancing their potential for applications requiring high conductivity and structural stability.

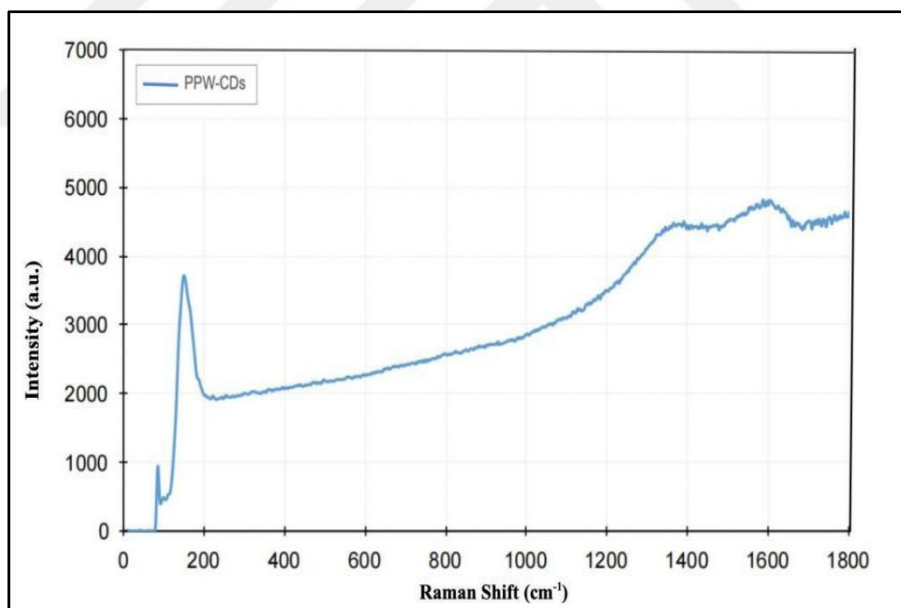


Figure 4.11. Raman spectrum of PPW-250/4 CDs.

4.4.2. Optical properties of carbon dots

When the aqueous solution of CDs derived from the liquid fraction of the PPW-250/4 sample after obtaining HCNs was exposed to UV light at a wavelength of 365 nm, a strong blue fluorescence was observed (Figure 4.12). The UV-vis spectroscopy curve revealed two characteristic absorption peaks at 254 nm and 320 nm, corresponding to

π - π^* and n- π^* electronic transitions, respectively. This pattern is consistent with previous studies on CDs, such as those by Liu et al. (2020) and Başıoğlu et al. (2020), confirming the successful synthesis of CDs from the liquid by-product of the HTC process applied to waste pomegranate peels.

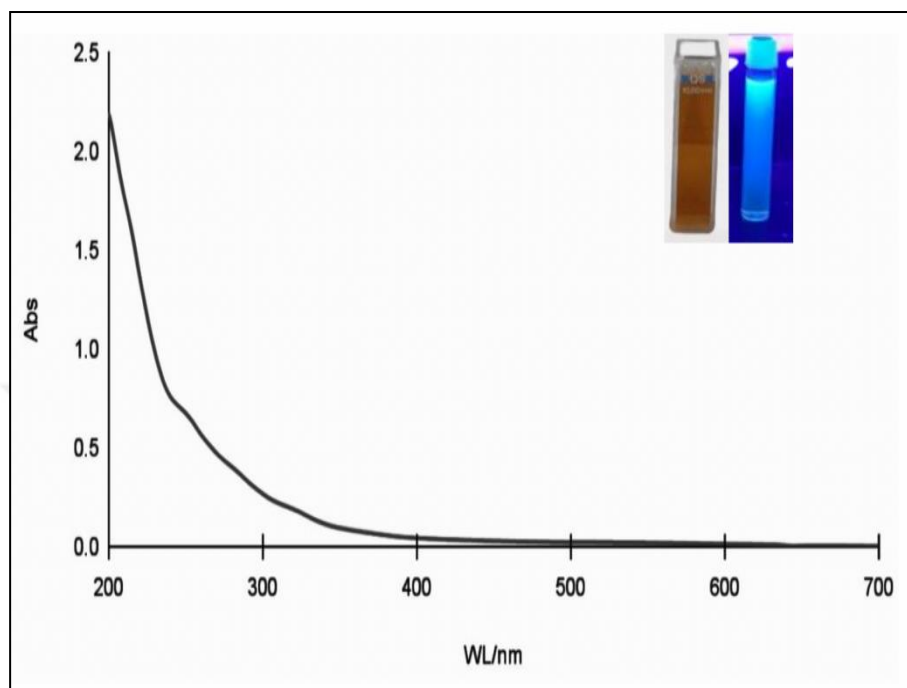


Figure 4.12. UV-Vis spectrum and luminescence of PPW-CDs. Inset: Aqueous solution of CDs exposed under natural day light (left) and UV light (right).

The fluorescence behavior of the synthesized CDs was evaluated under UV light (365 nm) across varying concentrations (0.01, 0.05, 0.5, and 1 mg/mL). As illustrated in Figure 4.13, the emission intensity initially increased with concentration, reaching a maximum at 0.05 mg/mL. This suggests that 0.05 mg/mL is the optimal concentration for achieving strong fluorescence without significant quenching. At higher concentrations, particularly at 0.5 and 1 mg/mL, a noticeable decline in fluorescence intensity was observed. This reduction is likely due to aggregation-induced quenching, a well-known phenomenon where carbon dots fluoresce strongly at low concentrations but show reduced emission at higher concentrations due to particle aggregation and reabsorption effects. As reported by Ru et al. (2022), beyond a certain concentration threshold, the photoluminescence of CDs diminishes as aggregation promotes non-radiative decay pathways and inner filter effects.

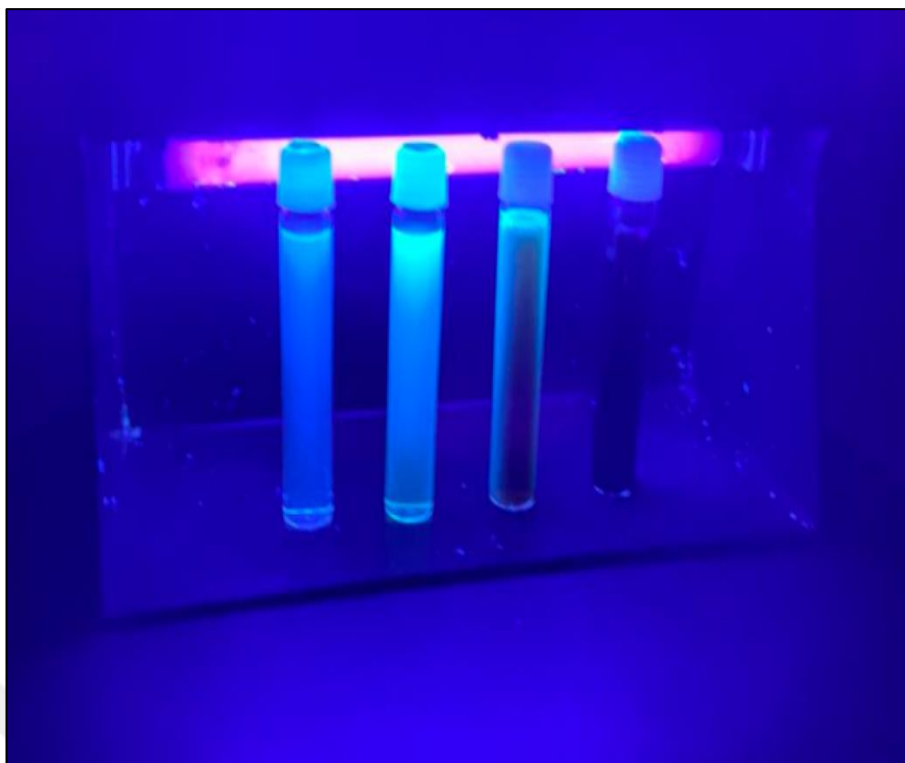


Figure 4.13. Fluorescence emission of PPW-CDs at varying concentrations (left to right: 0.01,0.05,0.5,1 mg/mL).

To further investigate their optical properties, the fluorescence behavior of the carbon dots was examined in various solvents, including dimethylsulfoxide (DMSO), acetone, glycerol, ethanol, and toluene under UV light. The fluorescence intensity varied significantly across the tested solvents, as shown in Figure 4.14. Notably, the highest fluorescence intensity was observed in glycerol, whereas toluene exhibited negligible fluorescence. These findings emphasize the versatile optical characteristics of the produced carbon dots, indicating their potential for diverse applications across different solvent environments.

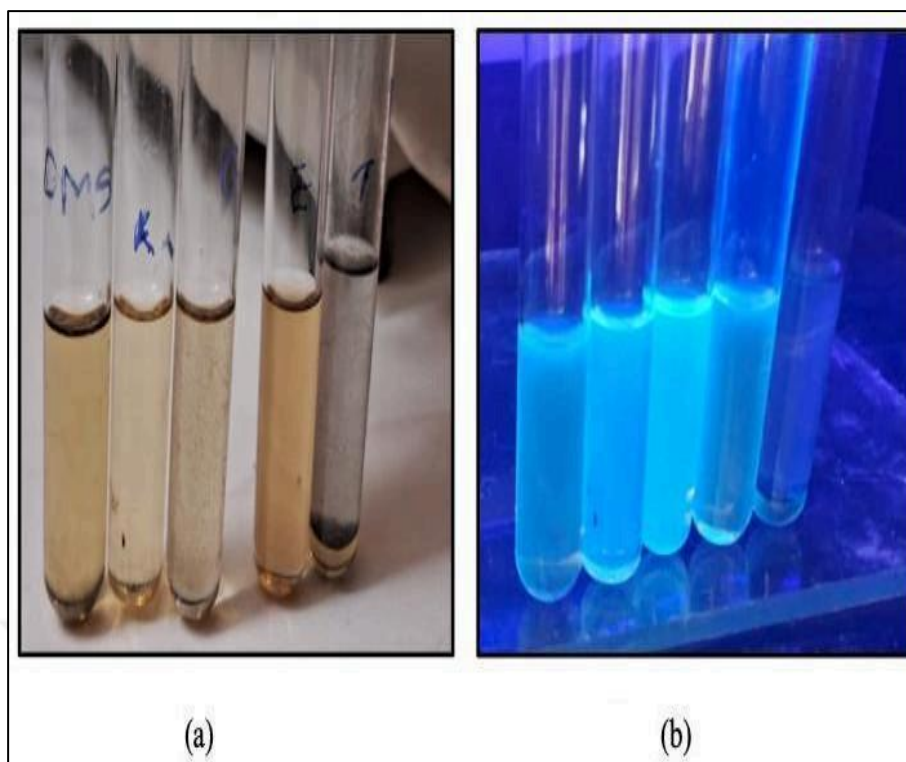


Figure 4.14. Dispersion of PPW-CDs under (a) daylight and (b) UV in different solvents (arranged from left to right as DMSO, acetone, glycerol, ethanol, and toluene).

4.5. Effect of Ball Milling on Hydrothermally Carbonized Nanospheres

The modification of carbon nanospheres derived from PPW through one-step HTC, followed by ball milling, led to notable structural and morphological transformations. Ball milling was incorporated as a post-treatment strategy to investigate its impact on the morphology, surface area, and structural order of hydrothermally carbonized nanospheres, with the aim of enhancing their material properties for broader potential applications. TEM spectroscopy revealed distinct morphological differences between the unmodified and modified samples. The unmodified sample (PPW-HCNs) exhibited well-defined, discrete spherical nanostructures with a uniform size distribution and minimal aggregation (Figure 4.15a). In contrast, the ball-milled sample (PPW-BM) showed significant agglomeration and morphological distortion, with fused and irregularly shaped particles (Figure 4.15b).

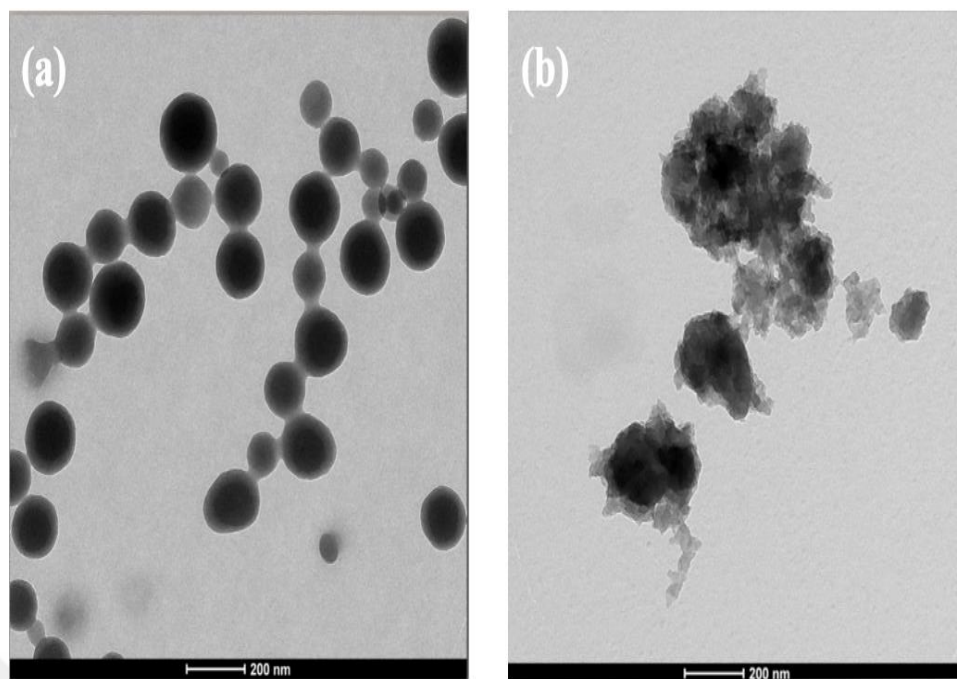


Figure 4.15. TEM images of HCNs: (a). before and (b). after ball milling.

The ball milling process appears to have promoted particle aggregation and structural compaction, as supported by BET surface area and porosity data. PPW-HCNs exhibited a BET surface area of $19.97 \text{ m}^2/\text{g}$, with a pore size of 2.16 nm and a pore volume of $0.149 \text{ cm}^3/\text{g}$ —characteristics indicative of a relatively porous and accessible nanostructure. Following ball milling, the PPW-BM sample showed a considerable decline in these parameters: the surface area decreased to $9.827 \text{ m}^2/\text{g}$, the pore size increased to 2.758 nm , and the pore volume dropped to $0.06974 \text{ cm}^3/\text{g}$. These changes suggest that ball milling induced partial collapse or fusion of the porous framework, thereby reducing accessible surface area and increasing aggregation.

The Raman spectroscopic analysis presented in Figure 4.16 further supported these structural changes. The PPW-BM sample exhibited a D band at 1353.81 cm^{-1} and a G band at 1591.05 cm^{-1} . Compared to PPW-HCNs, which had an I_G/I_D ratio of 1.072, the ball-milled PPW-BM sample showed a reduced ratio of 1.043. This decrease reflects a higher degree of structural defects and disorder, consistent with the morphological degradation observed in the TEM images.

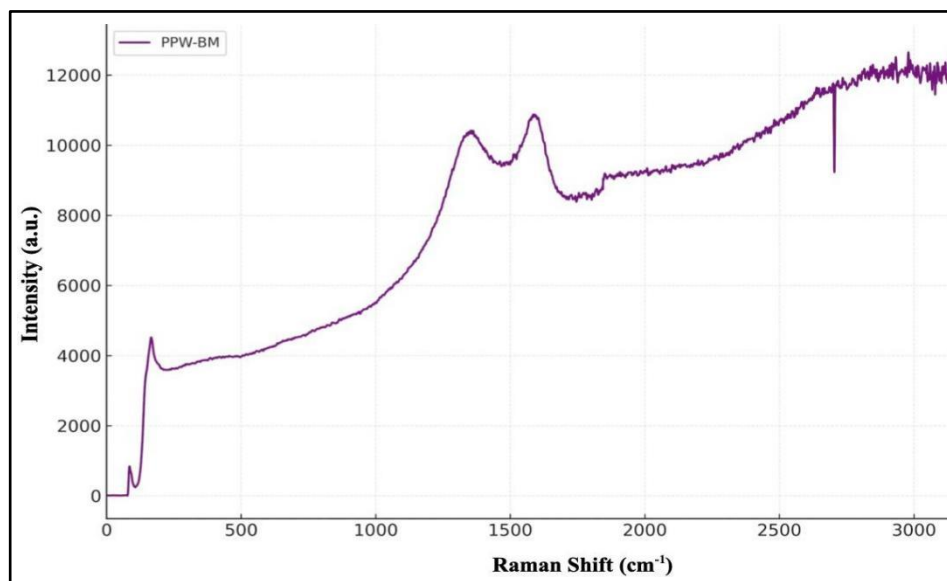


Figure 4.16. Raman spectrum of ball-milled PPW sample.

Overall, these findings demonstrate that while ball milling can effectively alter the morphology and surface characteristics of HTC-derived carbon nanospheres, it also introduces substantial structural disorder and enhances aggregation—factors that may limit their functionality in applications requiring high surface area and well-preserved nanostructures.

4.6. LCA Results

The results of the LC characterization analysis of the HTC_r process on all the aforementioned impact categories is provided in table 4.5 whereas Figure 4.17 shows the impact on the five environmental categories: abiotic depletion (fossil fuels), global warming, human toxicity, acidification, and eutrophication based on above results. It is observed that the process exerts a significant impact on fossil fuel-based abiotic depletion (238.26 MJ) and global warming potential (20.09 kg CO₂ eq). The large amounts of electricity (approximately 36.74 kWh) consumed during the HTC_r process is the primary contributor to this negative impact. Utilizing fossil fuels such as hard coal, natural gas, and lignite for electricity generation is considered to have the most significant adverse effect on fossil fuel-based abiotic depletion.

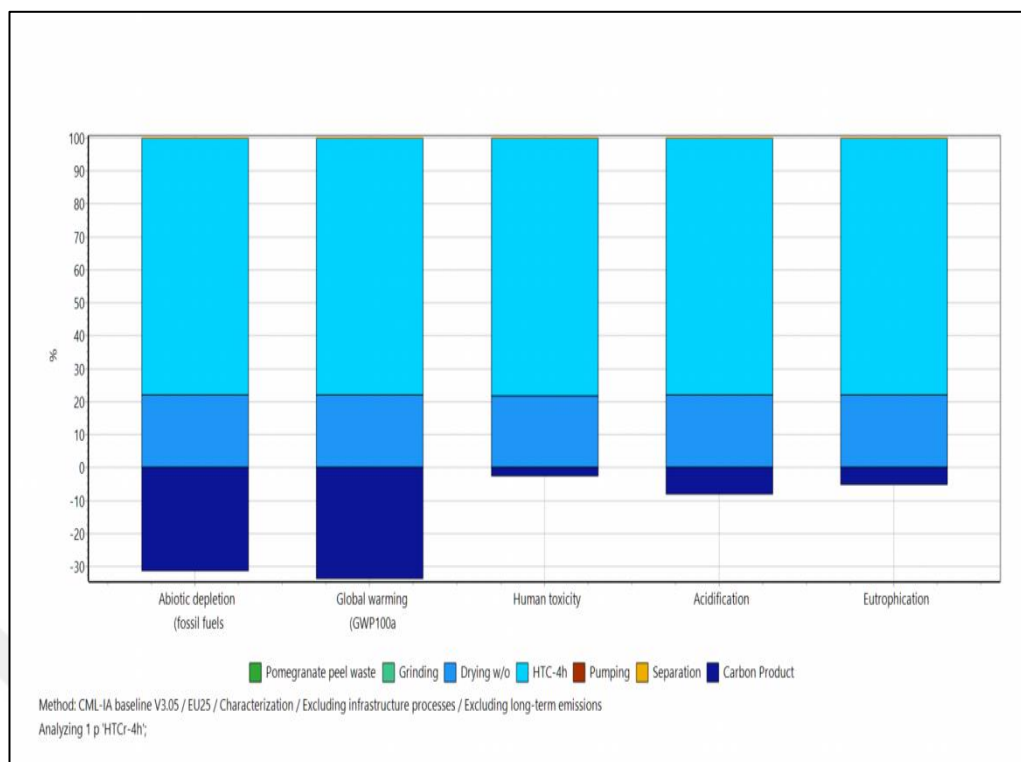


Figure 4.17. Impact of HTC process on various environmental categories.

The generation of CO₂ during the use of electricity from fossil-based fuels is the major contributor to global warming, while eutrophication and acidification result from the extraction and processing methods of lignite and hard coal used in energy production, contributing to overall burdens. However, product recovery at the end of the whole HTC process in the form of HCNs from the waste biomass of discarded pomegranate peels has a profound positive effect across all the environmental impact categories. It helps to bring the overall emission reduction in the category of fossil fuel based abiotic depletion and global warming potential up to about 45.36% and 50.60% respectively. Additionally, no significant toxicity was found at the HTC boundary system, aside from minor effects from electricity use. Utilizing eco-friendly carbon sources like pomegranate peel waste further minimizes toxicity risks.

The LC characterization for global warming potential (GWP 100) across various process steps in the HTC process, as shown in Figure 4.18, reveals the carbon footprint associated with each stage. The main HTC process itself represents the most substantial source of emissions, contributing 23.6 kg CO₂ eq. This emphasizes the critical role of the HTC stage in determining the overall environmental footprint of carbon product production. Similarly, drying is identified as another major significant contributor to emissions, accounting for 6.61 kg CO₂ eq.

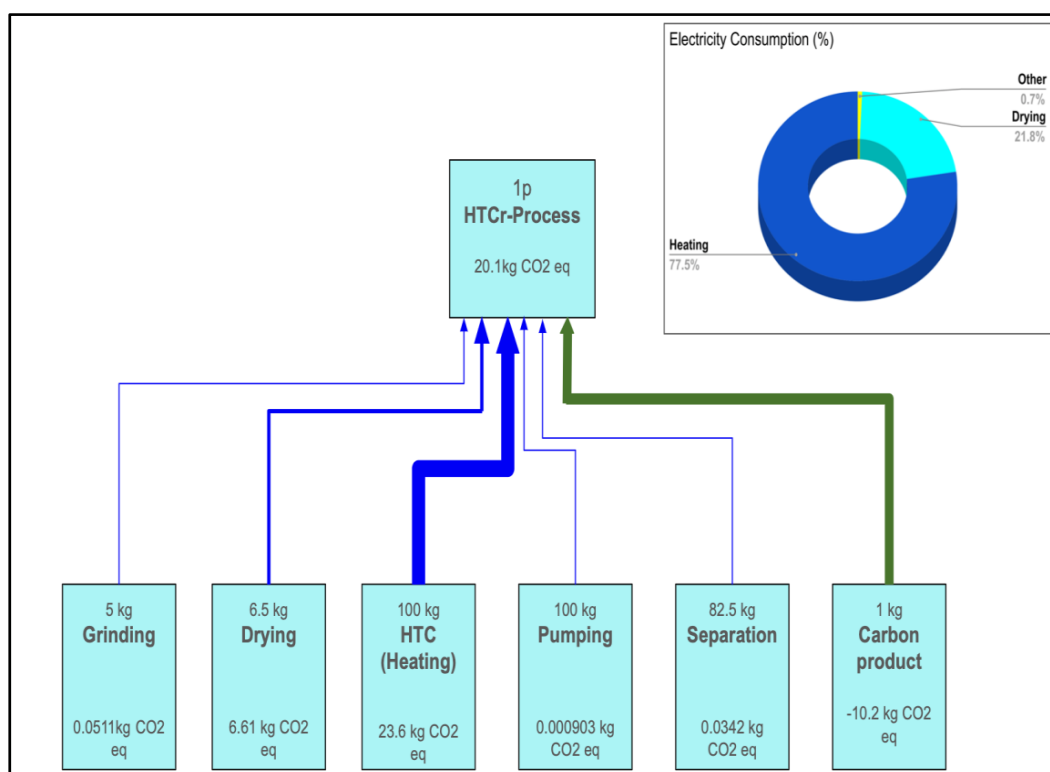


Figure 4.18. Global warming impact and electricity consumption in HTC.

This highlights the energy-intensive nature of the drying process and emphasizes the potential for optimization or alternative drying methods to reduce emissions. While grinding, pumping, and separation activities contribute relatively minor amounts of emissions individually (0.0511 kg CO₂ eq, 0.000903 kg CO₂ eq, and 0.0342 kg CO₂ eq, respectively), they collectively play a role in the overall carbon footprint. Improving their efficiency, optimizing their operating parameters, or using their more sustainable alternative can improve the environmental impact of the overall HTC process. Interestingly, the carbon product stage, which is the stage of recovery of the end-carbon product, i.e., HCNs, demonstrates a negative emission value of -10.2 kg CO₂ eq, causing the total emissions from all process steps to be reduced to about 20.09 kg CO₂ eq.

4.6.1. Sensitivity analyses results

4.6.1.1. Impact of disposal scenario

The first sensitivity analysis assessed the environmental impact of modifying the wastewater disposal route. The results for the selected impact categories—abiotic depletion (fossil fuels), global warming potential (GWP100), human toxicity, acidification, and eutrophication—are illustrated in Figure 4.19, with detailed data

provided in Table 4.5. The improved scenario (HTCi) yields a consistent but minimal reduction (<1%) across all impact categories compared to the reference scenario (HTCr), indicating only marginal environmental improvements. Although this may appear insignificant at the lab scale (based on ~76 liters of wastewater), even small differences in disposal practices can translate into substantial impacts at industrial scales, where wastewater volumes are much higher.

Among the three scenarios, the alternate scenario (HTCa) shows the highest environmental impacts, with increases ranging from 17% to 35% across categories. However, this result should be understood in the context of turning waste into valuable materials. In HTCa, CDs are recovered from the wastewater stream without the use of additional raw materials, unlike conventional CDs synthesis, which depends heavily on high-purity precursors and dedicated processes. HTCa thus represents a waste-to-value approach, converting process waste into functional nanomaterials. Importantly, no environmental credits were assigned for displacing conventional CDs production. Instead, the full energy and emissions associated with CDs recovery were attributed to the production of 1 kg of hydrothermal carbonaceous nanospheres. The CDs were treated as a zero-burden co-product under the cut-off approach, which contributes to the higher apparent impact of HTCa. This strategy was chosen for both practical and methodological reasons. First, the study aimed to explore a simple, low-cost wastewater valorization route without relying on speculative crediting. Second, the functional equivalence of the CDs to commercial products was not yet established due to limited characterization. Without such validation, applying system expansion or assuming displacement of conventional products would be premature.

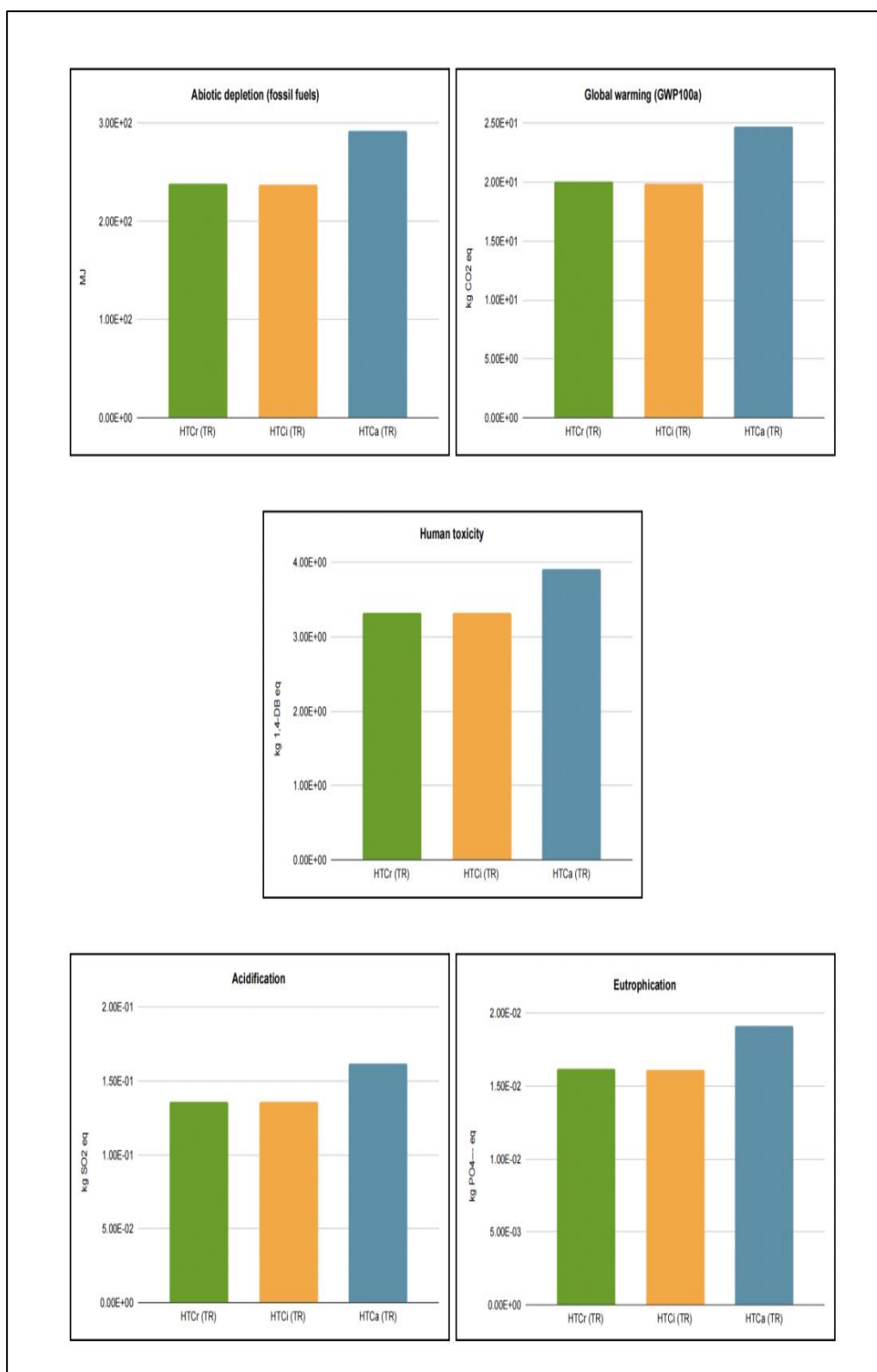


Figure 4.19. Impact of disposal scenarios on environmental categories.

As HTC remains a relatively new thermochemical method, ongoing research continues to optimize its processes and applications. Consequently, comprehensive environmental assessments are still limited, and direct comparisons across studies are

often complicated by differences in functional units, system boundaries, and process conditions. Nevertheless, available literature consistently shows that as CDs production scales from laboratory to industrial levels, the relative contribution of electricity declines, while the environmental burden associated with precursor materials becomes increasingly dominant. For example, Crista et al. (2020) evaluated hydrothermal synthesis of CDs using citric acid (50 kg) and urea (16 kg) in 330 kg of deionized water, resulting in a low synthesis yield of approximately 2%. Citric acid contributed the most to environmental impacts across categories, with urea as the second-highest contributor. Similarly, Sendão et al. (2020) found that in a 1,000 L hydrothermal batch using 327 kWh, electricity contributed only 5.9%–11.7% of total environmental impacts, while citric acid and urea were the dominant contributors. These findings are reinforced by Fernandes et al. (2021), who assessed CDs production at multiple scales. At the lab scale, electricity was the primary impact driver—contributing up to 90% of human health impacts for glucose-based CDs. At industrial scale (1,000 kg), the role of electricity declined significantly to 31.4%. Similarly, electricity consumption ranged from 274.5 kWh (citric acid-based CDs) to 774.2 kWh (glucose-based CDs) at the 100 kg scale, yet the largest contributors were precursors like para-phenylenediamine, which drove the majority of resource depletion and toxicity. At the 1,000 kg scale, electricity accounted for less than 2% of total impacts, while para-phenylenediamine alone contributed 53.8% of resource use impacts.

To evaluate the effect of biomass-based inputs, Johny et al. (2024) assessed CDs production from citric acid and eucalyptus leaf biomass. Their results showed that adding eucalyptus leaves reduced the overall environmental burden by 31% on average, including 54% less land use, 57% less ozone depletion, and 17% less ionizing radiation. Citric acid alone accounted for up to 85% of land use and 76.2% of ozone depletion, while ethylenediamine, another common reagent, significantly contributed to marine eutrophication (56.9%), ionizing radiation (40%), and fossil resource scarcity (39.4%). These findings highlight the environmental benefit of replacing high-impact precursors with biomass-based alternatives, as demonstrated in the HTC_a scenario. By using discarded pomegranate peel waste and recovering CDs from process wastewater, this approach reduces reliance on virgin materials and avoids the environmental burdens associated with chemical-intensive synthesis.

Table 4.5. Result of LCA characterization and sensitivity analysis of different disposal scenarios on various environmental categories.

Impact category	Unit	HTCr (TR)	HTCi (TR)	HTCa (TR)
Abiotic depletion	kg Sb eq	3.31E-08	3.12E-08	4.44E-08
Abiotic depletion (fossil fuels)	MJ	2.38E+02	2.37E+02	2.92E+02
Global warming (GWP100a)	kg CO ₂ eq	2.01E+01	1.99E+01	2.47E+01
Ozone layer depletion	kg CFC-11 eq	7.23E-07	7.22E-07	8.76E-07
Human toxicity	kg 1,4-DB eq	3.32E+00	3.32E+00	3.91E+00
Freshwater aquatic ecotoxicity	kg 1,4-DB eq	3.56E-01	3.56E-01	4.19E-01
Marine aquatic ecotoxicity	kg 1,4-DB eq	1.52E+04	1.52E+04	1.80E+04
Terrestrial ecotoxicity	kg 1,4-DB eq	2.23E-02	2.23E-02	2.63E-02
Photochemical oxidation	kg C ₂ H ₄ eq	4.80E-03	4.79E-03	5.73E-03
Acidification	kg SO ₂ eq	1.36E-01	1.36E-01	1.62E-01
Eutrophication	kg PO ₄ --- eq	1.62E-02	1.61E-02	1.91E-02

4.6.1.2. Impact of electricity mix scenario

Since electricity consumption was identified as the primary contributor to environmental impacts in this study, conducting a sensitivity analysis by varying the electricity mix was essential. The results for the selected impact categories—abiotic depletion (fossil fuels), global warming potential (GWP100), human toxicity, acidification, and eutrophication— are illustrated in Figure 4.20, with detailed data provided in Table 4.6.

In this comparative analysis, abiotic depletion (fossil fuels) shows a marginal increase of 1.89% under the Netherlands electricity mix, whereas a substantial reduction of 119.05% is observed under the Swiss electricity mix, relative to the Turkish baseline. Similarly, GWP100 decreases by approximately 11.5% for the Netherlands and by 120% for Switzerland, highlighting the strong influence of the electricity mix on climate change impacts. Human toxicity potential also exhibits notable reductions of 72.29% and 87.35% under the Netherlands and Swiss mixes, respectively.

Furthermore, acidification and eutrophication potentials consistently decrease under both alternative electricity scenarios.

These trends align with previous studies, such as Owsianiak et al. (2016), who demonstrated the critical role of electricity grid composition in HTC systems when comparing Spain and Germany, and Potrč Obrecht et al. (2021) and Shafique and Luo (2022), who reported that renewable energy sources like wind and solar substantially lower greenhouse gas emissions compared to fossil-based grids. This study not only supports these findings but also extends them to the context of hydrothermally carbonized nanomaterial production from biomass.

While the general trend of lower environmental impacts under cleaner electricity mixes was expected, this study provides system-specific quantifications for hydrothermally carbonized nanospheres at commercial scale. By analyzing sensitivity across multiple impact categories, it offers a clearer understanding of how electricity sourcing affects the environmental footprint of HTC-derived carbon materials. These insights are critical for informing early-stage process design and supporting sustainable scale-up.

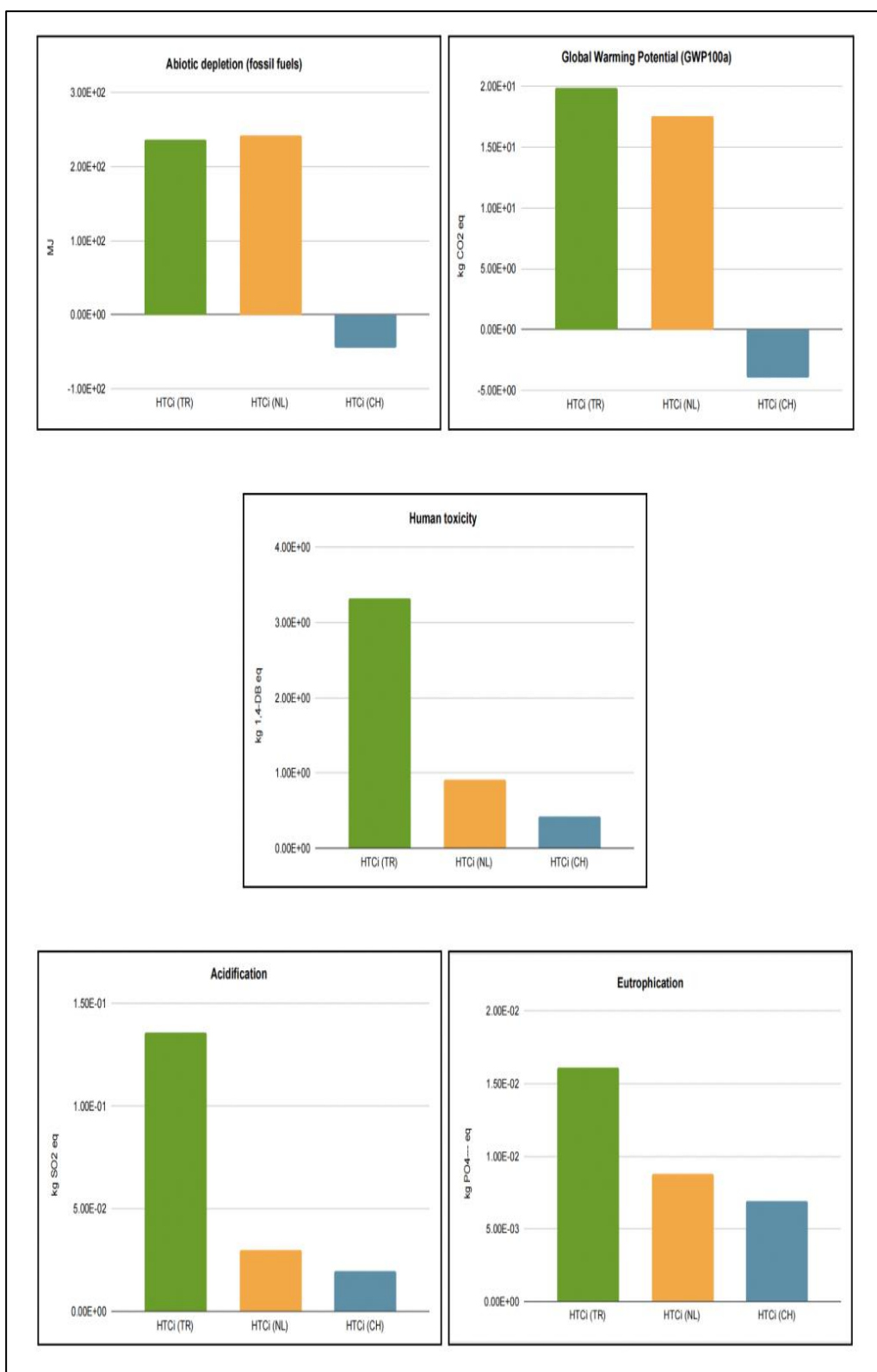


Figure 4.20. Impact of electricity mix scenarios on environmental categories.

Table 4.6. Result of sensitivity analysis of electricity mix scenarios of three countries on various environmental categories.

Impact category	Unit	HTCi (TR)	HTCi (NL)	HTCi (CH)
Abiotic depletion	kg Sb eq	3.12E-08	3.80E-07	1.19E-06
Abiotic depletion (fossil fuels)	MJ	2.37E+02	2.42E+02	-4.53E+01
Global warming (GWP100a)	kg CO ₂ eq	1.99E+01	1.76E+01	-4.01E+00
Ozone layer depletion	kg CFC-11 eq	7.22E-07	1.22E-06	2.19E-06
Human toxicity	kg 1,4-DB eq	3.32E+00	9.17E-01	4.22E-01
Freshwater aquatic ecotoxicity	kg 1,4-DB eq	3.56E-01	4.05E-02	3.65E-02
Marine aquatic ecotoxicity	kg 1,4-DB eq	1.52E+04	8.11E+03	2.14E+03
Terrestrial ecotoxicity	kg 1,4-DB eq	2.23E-02	1.15E-02	3.61E-03
Photochemical oxidation	kg C ₂ H ₄ eq	4.79E-03	1.08E-03	-1.81E-04
Acidification	kg SO ₂ eq	1.36E-01	2.98E-02	1.94E-02
Eutrophication	kg PO ₄ --- eq	1.61E-02	8.77E-03	6.92E-03

4.7. Applications Results

4.7.1. Results of antioxidant activity evaluation

4.7.1.1. Radical-scavenging ability

The DPPH assay results demonstrated the radical-scavenging ability of the prepared carbon nanomaterial (HCNs) in comparison to ascorbic acid, a well-established antioxidant. At the tested concentration, ascorbic acid exhibited 84.46% inhibition of DPPH radicals, which served as a benchmark for high antioxidant activity. The various concentrations of the HCNs sample solution show the percentage of inhibition of DPPH, with concentrations of 5 µg/mL showing an absorbance of 0.537 and 38.63% inhibition, 10 µg/mL showing an absorbance of 0.468 and 46.51% inhibition, 15 µg/mL showing an absorbance of 0.365 and 58.29% inhibition, 20 µg/mL showing an absorbance of 0.244 and 72.11% inhibition, and 25 µg/mL showing an absorbance of 0.15 and 82.86% inhibition. The results displayed a dose-dependent increase in percentage inhibition, ranging from 38.63% at 5 µg/mL to 82.86% at 25 µg/mL. This trend suggests that the HCNs exhibits a dose-dependent antioxidant effect, with higher concentrations showing greater radical-scavenging activity. At the highest

concentration (25 $\mu\text{g/mL}$), the HCNs's antioxidant activity (82.86%) was almost identical to that of ascorbic acid (84.46%). This strong antioxidant potential of the sample is noteworthy, as it demonstrates that the HCNs can neutralize free radicals with a potency comparable to that of a widely recognized antioxidant. In comparison, carbon dots (CDs) synthesized using a one-pot sand bath method from the leaves of the medicinal plant *Azadirachta indica* exhibited $64.01 \pm 2.60\%$ inhibition at 25 $\mu\text{g/mL}$ (Gedda et al., 2023) while the honey-mediated carbon nanoparticles combined with silver nanoparticles-based nanocomposite exhibited remarkable antioxidant activity when assessed using the DPPH assay, with inhibition values of 62.48%, 75.24%, 82.69%, 88.47%, and 89.76% observed at concentrations of 10, 20, 30, 40, and 50 $\mu\text{g/mL}$, respectively (Manigandan et al., 2024). Similarly, CDs derived from tomato juice showed an inhibition range from 54.7% at 4 ppm to 63.8% at 20 ppm (Rodríguez-Varillas et al., 2022), while CDs derived from glutathione exhibited a lower inhibition range, from 21.0% at 4 ppm to 60.0% at 20 ppm (Murru et al., 2020).

These findings reinforce the significant antioxidant activity of HCNs), highlighting their potential as effective natural antioxidants and offering a sustainable alternative to synthetic antioxidants.

4.7.1.2. Dose-response relationship

To further explore the relationship between the sample concentration (x) and its radical- scavenging ability i.e % inhibition (y), the DPPH assay experimental data were fitted to a quadratic model. The equation:

$$y = 29.4 + 1.61x + 0.222x^2 \quad (4.1)$$

The model demonstrated an excellent fit to the experimental data, as indicated by a high coefficient of determination ($R^2 = 0.996$). This suggests that the equation effectively captures the dose-dependent response of the sample's antioxidant activity. This behavior aligns with the expected dose-dependent antioxidant activity, wherein higher sample concentrations result in enhanced radical scavenging. The high R^2 value confirms the accuracy of the quadratic model, validating its application for predicting inhibition values and determining the critical IC_{50} value, as visually represented in Figure 4.21.

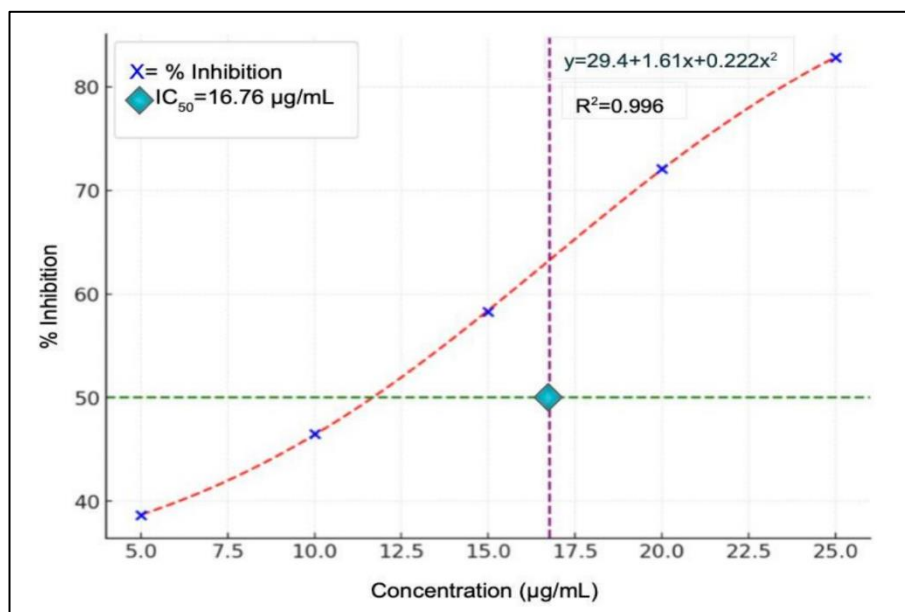


Figure 4.21. DPPH assay dose-response of synthesized HCNs.

4.7.1.3. IC₅₀ determination

The IC₅₀ (Half-Maximal Inhibitory Concentration) value is a commonly used parameter to quantify the potency of an antioxidant, representing the concentration required to achieve 50% inhibition of free radicals, such as DPPH radicals. A lower IC₅₀ value indicates a higher ability to remove DPPH radicals. Often, EC₅₀ (Effective Concentration 50), which refers to the concentration of a substance that produces 50% of the maximum possible effect, is used interchangeably with IC₅₀.

In this study, the IC₅₀ value was estimated to be between 10 µg/mL (46.51%) and 15 µg/mL (58.29%) based on the experimental data. However, applying a mathematical model to the dose-response relationship yielded a more precise IC₅₀ value of approximately 16.76 µg/mL. This value aligns well with the dose-response curve, which visually demonstrates the increasing % inhibition with sample concentration (Figure 4.21). This result is comparable to the CDs prepared from the leaves of the medicinal plant *Azadirachta indica*, which exhibited free radical scavenging activity with an EC₅₀ value of 13.87 µg/mL (Gedda et al., 2023). However, it is much higher than the EC₅₀ value for CDs prepared from red cabbage, which was calculated to be approximately 224 µg/mL (Sharma, Das & Yun, 2020).

4.7.1.4. Total antioxidant capacity

The total antioxidant capacity (TAC) of the sample was assessed using the phosphomolybdenum assay by measuring absorbance at 695 nm for the sample (HCNs), ascorbic acid (standard), and a control (Table 4.7). TAC, expressed as a percentage, quantifies the antioxidant potential of the sample relative to ascorbic acid. The TAC of the prepared HCNs was found to be 85.43%, with an Ascorbic Acid Equivalent (AAE) of 8.543 mg/mL (or 8543 µg/mL). This indicates that the antioxidant capacity of the HCNs is equivalent to that of 8.543 mg/mL of ascorbic acid. These results highlight the sample's strong antioxidant properties, closely aligning with the activity of ascorbic acid, a benchmark antioxidant.

When compared to other biomass-derived carbon nanomaterials, HCNs demonstrated a significantly higher TAC. In comparison, the TAC of carbon nanoparticles obtained from *Carica papaya* leaves was found to be 23.00 µg/mL (Gudimella et al., 2021), while the TAC of carbon dots derived from *Azadirachta indica* leaves ranged from 108.59% to 148% across increasing concentrations (5–50 µg/mL) (Gedda et al., 2023).

Table 4.7. Results of phosphomolybdenum assay.

Solution	Absorbance at 695 nm
Standard (Ascorbic Acid)	0.743
Control	0.146
Sample (HCNs)	0.656

4.7.1.5. Correlation between antioxidant activity and functional groups present

Antioxidants neutralize free radicals through two primary mechanisms: donating a hydrogen atom or donating an electron (Al-Mamary & Moussa, 2021). The antioxidant activity of the synthesized HCNs is strongly associated with its radical-scavenging ability, which can be attributed to the functional groups identified via FTIR spectroscopy (Figure 4.8). The FTIR analysis revealed key functional groups in HCNs that likely contribute to its antioxidant properties, potentially stabilizing free radicals through hydrogen or electron transfer, thus enhancing its effectiveness as an eco-friendly antioxidant. The broad peak at 3369 cm⁻¹ corresponds to O-H groups (hydroxyl groups in alcohols, phenols, or carboxylic acids), which play a significant

role in antioxidant activity due to their ability to donate hydrogen atoms to neutralize free radicals (Al-Mamary & Moussa, 2021; Chen et al., 2020; Charlton et al., 2023; Wang, Kong et al., 2019). Additionally, the carbonyl stretch (carboxylic acids, ketones, and esters) at 1687 cm^{-1} suggests that HCNs may donate electrons to stabilize free radicals (Al Mamary & Moussa, 2021; Charlton et al., 2023). The aromatic C=C stretch at 1593 cm^{-1} indicates the presence of conjugated systems, which could stabilize radicals via resonance, further enhancing the antioxidant capacity (Charlton et al., 2023; Parcheta et al., 2021). Other functional groups, such as C-O stretches at 1211 cm^{-1} and 1109 cm^{-1} , may also contribute to the redox activity of HCNs by enabling electron donation. These functional groups work synergistically to improve the ability of HCNs to neutralize free radicals. The presence of aromatic C-H bending at 796 cm^{-1} and 601 cm^{-1} further supports the antioxidant potential, as these groups might interact with reactive species. These findings reinforce the significant antioxidant activity of the HCNs prepared in this study from the waste pomegranate peels, highlighting their potential as effective natural antioxidants and offering a sustainable alternative to synthetic antioxidants.

4.7.2. Results of antibacterial activity evaluation

The ZOI was used as an indicator of antibacterial activity, with larger zones reflecting greater effectiveness. For the standard drug Azithromycin ($100\text{ }\mu\text{g/ml}$), the ZOI measured 20 mm , demonstrating strong antibacterial activity. In contrast, the test samples at all three concentrations ($50\text{ }\mu\text{g/ml}$, $100\text{ }\mu\text{g/ml}$, and $150\text{ }\mu\text{g/ml}$) exhibited a minimal ZOI of 1 mm . This negligible inhibition zone indicates that the test samples did not significantly inhibit the growth of *E. coli* or *S. aureus* under the assay conditions (Figure 4.22). These results suggest that the HCNs exhibits almost negligible antibacterial activity under the tested concentrations and conditions. Several factors may contribute to this outcome, as highlighted in the literature on carbon-based nanomaterials (Maleki Dizaj et al., 2015). One possible explanation could be the low concentrations used in the assay. It has been observed that antibacterial activity increases with higher concentrations of carbon nanoparticles (Lopez-Diaz et al., 2023). For instance, Ma et al. (2020) found that carbon nanoparticles derived from osmanthus leaves exhibited the strongest antibacterial effect at a concentration of $1000\text{ }\mu\text{g/mL}$, while carbon nanoparticles derived from milk vetch showed the least antibacterial activity, with a significant percentage of bacterial survival at the same concentration.

Ma et al. also emphasized that carbon-based nanomaterials derived from different plant sources show varying antibacterial effectiveness, which they attributed to the distinct natural substances present in each plant source.

The surface charge on the material may also contribute to the minimal antibacterial activity observed in our study. As noted by Maleki Dizaj et al. (2015), positively charged fullerene compounds were the most effective against *E. coli*, while negatively charged compounds showed little to no effect. This is likely because negatively charged bacterial cell walls interact more strongly with positively charged materials, thereby enhancing antibacterial efficacy. Typically, HTC products have negatively charged surfaces (Danso-Boateng et al., 2022). Further investigations are necessary to explore the material's potential activity at higher concentrations or under alternative experimental setups, including variations in bacterial strains, pH levels, or exposure durations.

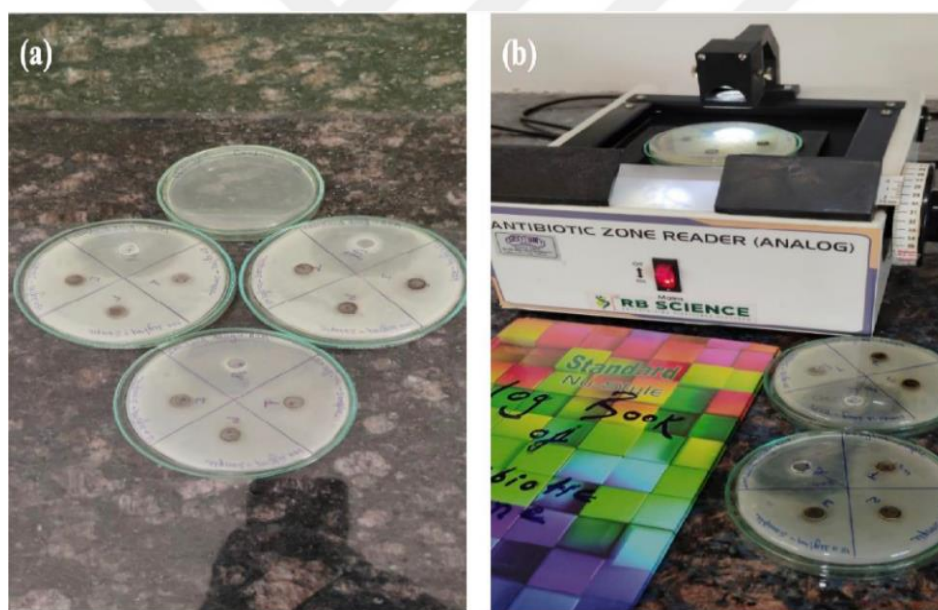


Figure 4.22. (a). Agar well diffusion setup (showing a Petri dish with wells loaded with the standard antibiotic Azithromycin and sample solutions at different concentrations); (b). Measurement of the zone of inhibition (using a ZOI reader).

The minimal ZOI observed may also indicate that the material is less disruptive to bacterial growth under the tested conditions, which could be advantageous for applications where non-toxic or biocompatible materials are desired. Similar findings have been reported in earlier studies involving carbon-based nanomaterials synthesized through hydrothermal carbonization. For example, Lin et al. (2018)

demonstrated that carbon nanoparticles derived from *Lactobacillus plantarum* biomass (CDs-LP) did not inhibit *E. coli* growth but were effective in preventing biofilm formation, highlighting that not all carbon nanomaterials function via bactericidal pathways. Notably, these carbon nanoparticles also exhibited low cytotoxicity and high biocompatibility. Nevertheless, if enhanced antibacterial performance is required, further surface modifications or compositional adjustments to the material may be necessary.

4.7.3. Result of application in cement composites

This result section has been reproduced from the previously published article:

Sharma, M., Öztürk, İ. Ş., Emiroğlu, M., & Erses Yay, A. S. (2025). Performance evaluation of biomass-derived hydrothermal carbonaceous material in cement-based composites. *Case Studies in Construction Materials*, 22, e04291. <https://doi.org/10.1016/j.cscm.2025.e04291>. Published under the Creative Commons CC BY-NC 4.0 license.

4.7.3.1. SEM and EDS analysis of carbon-cement composite

The SEM analysis was conducted to evaluate the incorporation of HCNs into the cement matrix, considering their nanoscale size. The primary objective was to determine whether the HCNs were successfully integrated into the matrix or if they were lost during the mixing process, potentially due to poor dispersion or as airborne dust. SEM images of the cement-carbon composite (Figure 4.23) clearly demonstrate that the HCNs were successfully embedded within the matrix, as evidenced by the presence of the carbon particles, which are marked by red circles. These particles appear primarily in aggregated or clustered forms, which aligns with the expected behavior of HCNs.

Further confirmation was obtained through EDS analysis, which was conducted to verify the presence of carbon within the composite. The EDS spectra clearly demonstrate the presence of carbon, providing quantitative evidence that the HCNs have been successfully incorporated into the cement matrix. These results complement the SEM observations, reinforcing the conclusion that the carbon particles are effectively integrated into the cement matrix.

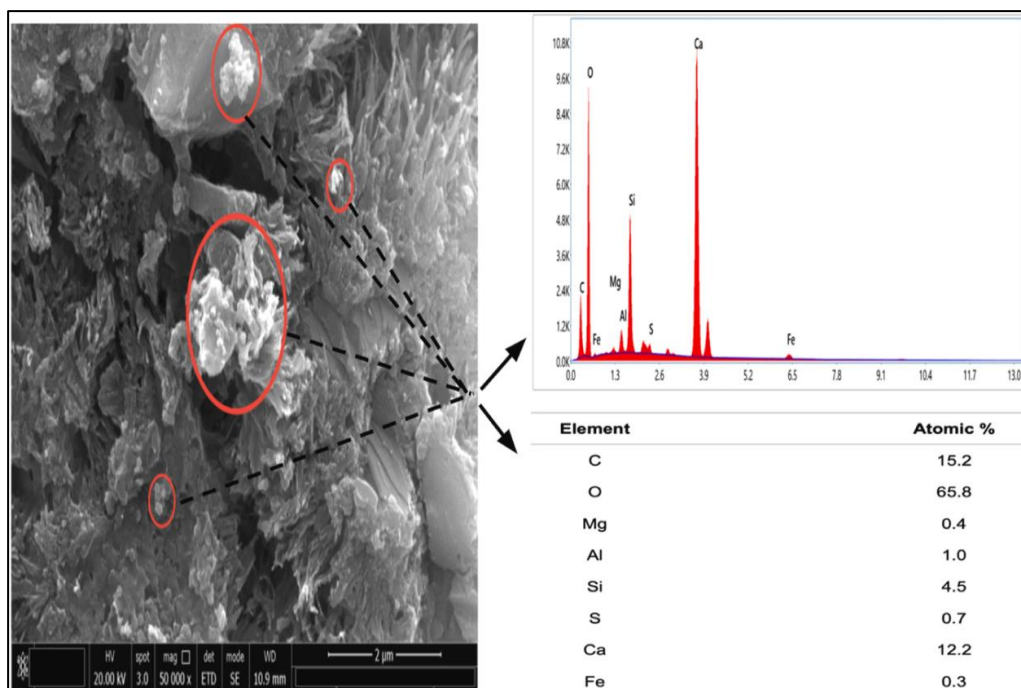


Figure 4.23. SEM and EDS of cement–carbon composite

4.7.3.2. Workability

The workability of fresh cement composites, evaluated using the flow table test, was significantly affected by the addition of hydrothermal carbonaceous nanospheres (HCNs) as a partial cement replacement (Figure 4.24). In dry-mixed samples, the increase in workability was noticeable but inconsistent, possibly due to uneven dispersion of HCNs within the cement matrix, which may have disrupted the uniformity of the mix. In contrast, wet-mixed samples exhibited a more consistent and gradual improvement in flowability across increasing HCNs dosages.

This behavior contrasts with previous findings. Yang and Wang (2021) reported that adding biochar to cement composites generally reduces workability due to its water absorption capacity and porous structure. Sirico et al. (2022) also found that increased biochar dosages tend to hinder flowability, often requiring the use of superplasticizers to compensate for the loss. Similarly, Sacdalan et al. (2023) observed that biochar incorporation typically results in reduced workability, attributing this to its hydrophilic and porous nature, which interferes with water availability in the mix.

In the present study, however, the wet-mixed samples showed an improved and dose-dependent enhancement in workability, reaching up to 12.0% at 1% HCNs dosage.

This improvement may be attributed to the overhydrophobic nature of HCNs, which likely affects the water-particle interaction differently than traditional biochar, resulting in better dispersion and reduced friction within the mix. While the dry-mixed samples exhibited more variation, they still showed enhanced workability at lower HCNs concentrations. Overall, these results indicate that the mixing method and the specific dosage of HCNs significantly influence the workability performance of the resulting cement composites.

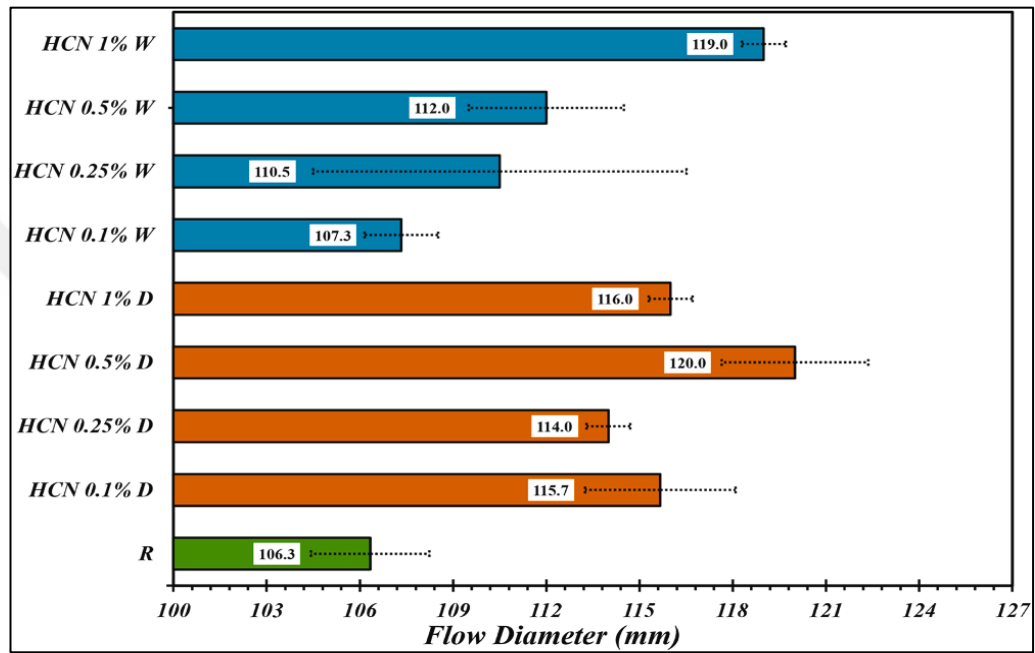


Figure 4.24. Results of flow table test.

4.7.3.3. Permeability characteristics

To assess the permeability properties of the carbon-cement composites, tests for water absorption, porosity, and capillary water absorption were conducted. These tests helped evaluate the material's resistance to water ingress and its potential effects, providing a detailed understanding of the composite's ability to withstand water penetration and its long-term performance.

(i) Water absorption and porosity behaviour

The influence of HCNs on the water absorption behavior of cementitious composites displayed a clear dependency on both dosage and mixing strategy over time. After 7 days of curing, a progressive increase in water absorption was observed in dry-mixed samples with increasing HCN content: rising by 0.36%, 1.74%, 1.86%, and 2.07% for 0.1%, 0.25%, 0.5%, and 1% dosages, respectively (Figure 4.25). This trend aligns with

early findings on biochar-induced permeability in cement matrices, where poorly dispersed particles tend to act as pore formers (Gray et al., 2014).

In contrast, wet-mixed samples demonstrated a non-linear trend. At lower dosages (0.1% and 0.25%), water absorption was relatively higher (1.85% and 2.36%, respectively), but declined significantly at higher dosages, reaching 2.03% for 0.5% and 1.47% for 1% HCNs. This reversal suggests that ultrasonic-assisted wet mixing improves dispersion at higher concentrations, reducing inter-particle agglomeration and blocking capillary pathways: a mechanism also hinted at in the recent study by Praneeth et al. (2021). By the 28-day mark, both dry- and wet-mixed composites with 0.1% and 0.25% HCNs demonstrated water absorption levels similar to the control. However, specimens containing 0.5% and 1% HCNs, especially those dry-mixed, displayed significantly higher absorption. This increase is attributable to the inherent porous nature of pomegranate-derived HCNs, which facilitates additional moisture ingress (Gray et al., 2014).

Porosity measurements further supported these observations (Figure 4.25). At 7 days, both dry- and wet-mixed samples at 0.1% and 0.25% exhibited comparable porosity. However, at 0.5% and 1%, dry-mixed samples showed markedly higher porosity than their wet-mixed counterparts, indicating inefficient particle distribution and poor interfacial bonding in the dry-mixing method. By 28 days, the porosity increase became more pronounced in dry-mixed samples with higher HCN content (0.25%, 0.5%, and 1%), while wet-mixed specimens maintained relatively stable porosity at equivalent dosages. This supports the idea that wet dispersion helps mitigate porosity development at elevated HCN levels.

Earlier work has consistently linked higher dosages of carbonaceous materials to increased porosity in cement systems due to their internal pore structure and surface morphology (Praneeth et al., 2021; Zhao et al., 2024). However, the current findings extend this understanding by revealing that even low concentrations of HCNs can significantly affect porosity. After 7 days, porosity values ranged from 1.01% to 4.92%, and from 0.64% to 4.15% after 28 days. This result is supported by Rashid et al. (2024), who noted that the internal porosity and fine particle size of biochar materials play a pivotal role in determining their influence on the overall void structure of cement composites.

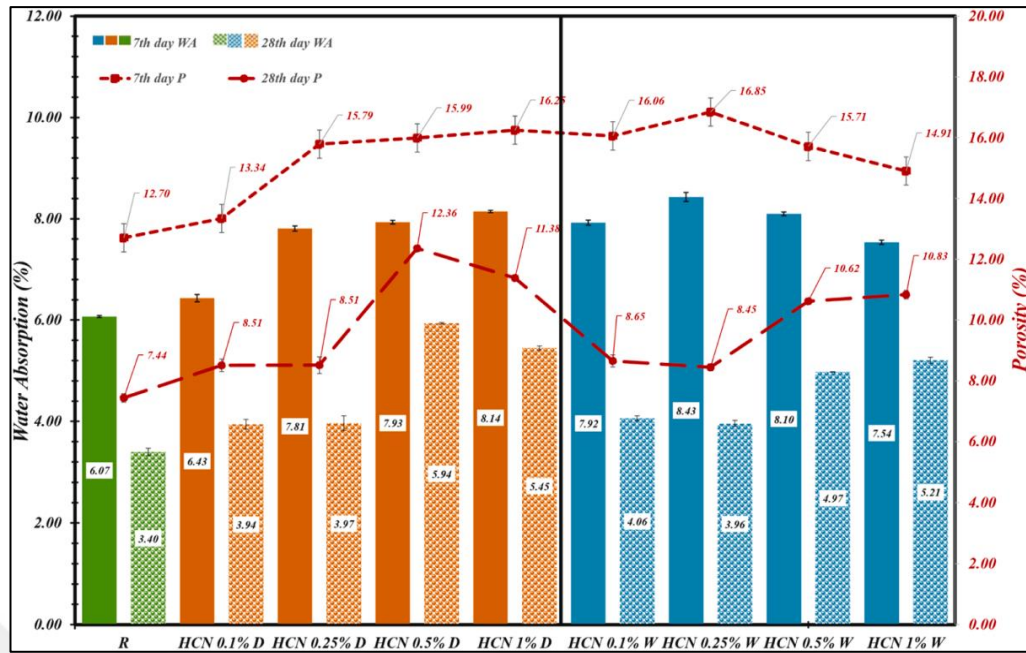


Figure 4.25. Results of water absorption and porosity.

Specifically, the HCNs used in this study possessed a high surface area ($19.97 \text{ m}^2/\text{g}$), mesoporous structure (average pore diameter of 2.16 nm), and considerable pore volume ($0.149 \text{ cm}^3/\text{g}$). These features contribute to increased air and moisture entrapment within the matrix. Moreover, particle agglomeration, especially in dry mixing, likely resulted in localized voids that intensified the porosity even at lower dosages—consistent with the conclusion of Zhao et al. (2024) on the relationship between biochar dispersion and void formation.

Hence, the study highlights how the porous architecture and surface characteristics of HCNs can significantly influence both water absorption and porosity in cement composites. However, the extent of these effects is strongly governed by mixing method and dosage, with wet-mixing at moderate concentrations offering a more controlled approach to enhance performance while limiting unwanted porosity development.

(ii) Capillary water absorption

Capillary water absorption is a critical indicator of the durability of cementitious composites, reflecting their pore structure, permeability, and resistance to moisture ingress. This process typically unfolds in two distinct phases: the initial phase, characterized by rapid uptake through finer capillaries and micropores within the first

24 hours, and the secondary phase, defined by slower, diffusion-driven absorption into the matrix beyond that period.

To assess the influence of HCNs on capillary behavior, both the primary and secondary absorption coefficients, along with total water absorption, were measured and are presented in Table 4.8.

Table 4.8. Capillarity coefficients of cement-composite samples.

Sample	Initial capillary absorption (mm / $\sqrt{s}$) $\pm$ Standard Deviation	Secondary capillary absorption (mm / $\sqrt{s}$) $\pm$ Standard Deviation	Total water absorption (mm) $\pm$ Standard Deviation
R	0.0048 $\pm$ 0.0015	0.0011 $\pm$ 0.00020	1.354 $\pm$ 0.28
HCN0.1%D	0.0113 $\pm$ 0.0010	0.0011 $\pm$ 0.00031	2.667 $\pm$ 0.10
HCN0.25%D	0.0092 $\pm$ 0.0005	0.0003 $\pm$ 0.00015	2.104 $\pm$ 0.07
HCN0.5%D	0.0115 $\pm$ 0.0015	0.0049 $\pm$ 0.00088	3.958 $\pm$ 0.56
HCN1%D	0.0079 $\pm$ 0.0011	0.0033 $\pm$ 0.00020	2.854 $\pm$ 0.11
HCN0.1%W	0.0078 $\pm$ 0.0011	0.0003 $\pm$ 0.00028	1.771 $\pm$ 0.24
HCN0.25%W	0.0064 $\pm$ 0.0014	0.0004 $\pm$ 0.00018	1.438 $\pm$ 0.31
HCN0.5%W	0.0086 $\pm$ 0.0017	0.0019 $\pm$ 0.00019	2.583 $\pm$ 0.24
HCN1%W	0.0099 $\pm$ 0.0008	0.0028 $\pm$ 0.00021	2.937 $\pm$ 0.05

Graphical representations of the results are shown in Figures 4.26 and 4.27, illustrating the effects of HCN dosage and incorporation method on the water transport properties of the samples. Figure 4.26 compares the cumulative water uptake (g/cm²) for both control and HCN-modified samples. This graph demonstrates how varying HCN content (ranging from 0.1% to 1% by weight of cement) and different mixing methods (wet vs. dry) influence the total absorption capacity of the cement composites. Figure 4.27 presents the time-dependent capillary water absorption, where cumulative water absorption is plotted against the square root of time ($\sqrt{t}$) to assess sorptivity. The graph includes the linear regression equations ($y = kx + c$) and R^2 values, which describe the fit and absorption kinetics of the capillary action. Sorptivity values, calculated from the slope of the linear portion of the curves, reflect the permeability and capillary transport properties of each sample's pore structure.

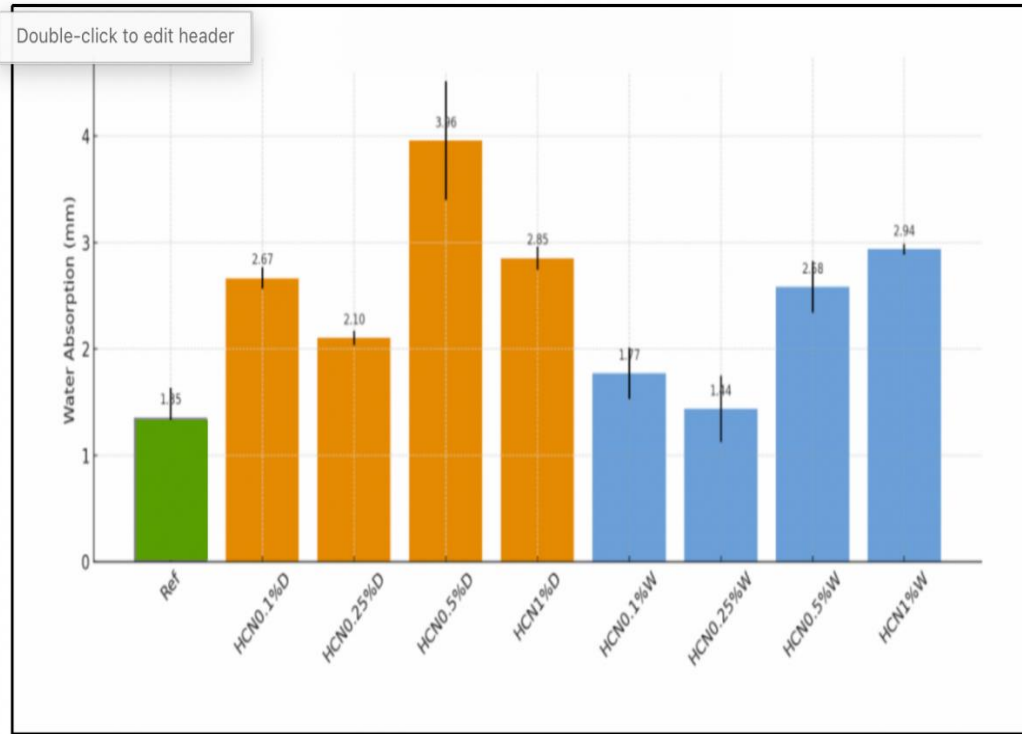


Figure 4.26. Total capillary water absorption of all samples after the experiment.

Among the dry-mixed specimens, the HCN0.5%D mix exhibited the highest total water absorption (3.958 mm), accompanied by elevated primary and secondary absorption coefficients. These outcomes correlate with its observed high workability, lower density, and reduced compressive strength, suggesting that excessive dry-blended nanocarbon can lead to agglomeration and microvoids formation, which in turn facilitate capillary water flow. In contrast, HCN0.25%D demonstrated a significantly lower total absorption (2.104 mm), indicating that this dosage may represent an optimal threshold for pore refinement, where HCNs enhance the microstructure without causing clustering.

Wet-mixed specimens consistently outperformed their dry-mixed counterparts in terms of reduced capillary absorption. This improvement is primarily attributed to the ultrasonic dispersion process used in wet mixing, which enhances the uniform distribution of HCNs, mitigates particle agglomeration, and helps seal capillary pathways. Notably, the HCN0.25%W sample showed the lowest total absorption (1.438 mm) as well as the lowest initial and secondary absorption coefficients, reflecting improved densification and a less connected pore network. Other wet-mixed samples, such as HCN0.1%W and HCN0.5%W, also exhibited lower absorption

values than their corresponding dry-mixed specimens, further underscoring the benefits of wet dispersion.

Interestingly, while a general trend of increased water absorption with higher HCN content was observed in the wet-mixed group, the HCN0.25%W sample deviated from this pattern by displaying a marked decrease in both initial and secondary absorption. This suggests that a moderate concentration of 0.25% under wet mixing conditions yields the most favorable balance between particle dispersion and matrix densification.

Overall, these findings indicate that while the naturally porous structure of HCNs has the potential to increase moisture uptake, this effect can be effectively mitigated through controlled dosage and dispersion techniques. The performance differences observed between dry- and wet-mixed samples emphasize the role of processing methods in determining the final permeability characteristics of cement-based composites. When properly incorporated, particularly through optimized wet mixing, HCNs can act not as pore formers but as pore blockers, contributing positively to durability.

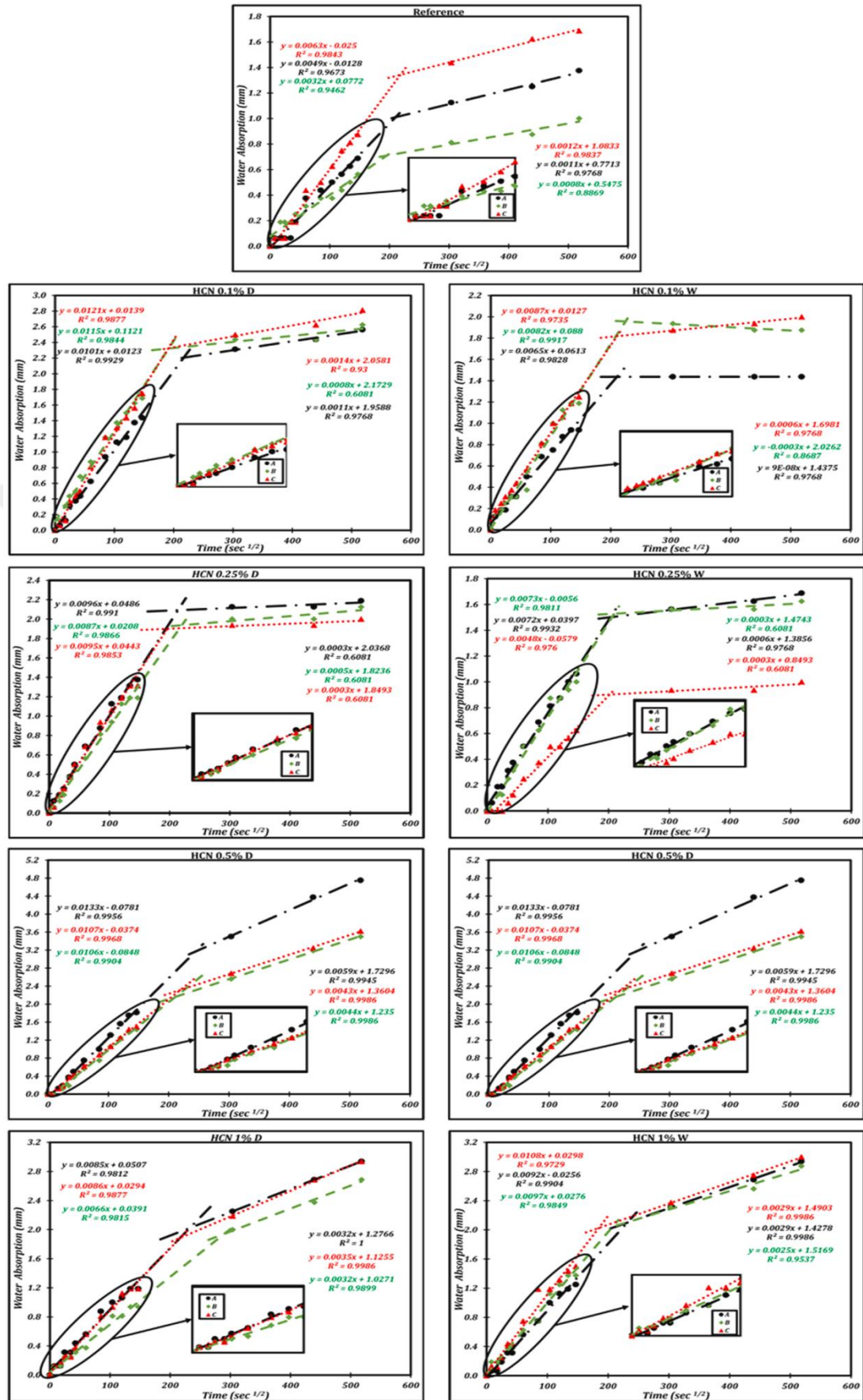


Figure 4.27. Time-dependent water absorption in cement composites.

4.7.3.4. Density

The incorporation of HCNs resulted in a consistent reduction in the density of all mortar samples compared to the reference, as observed at both 7 and 28 days (Figure 4.28). At 28 days, wet-mixed specimens displayed a near-linear decline in density with increasing HCNs dosage, while dry-mixed samples exhibited relatively stable values between the 0.5% and 1% dosages. At the highest concentration tested, the effect of mixing method became less pronounced, with HCNs 1%D and HCNs 1%W producing comparable density values.

Although the density decrease at the 1% dosage was approximately 5% relative to the control, this reduction is significant when considering earlier studies using higher substitution levels. For instance, Cuthbertson et al. (2019) reported a notable shift toward lightweight concrete with the inclusion of 15% biochar, and Sirico et al. (2022) observed a comparable density reduction with 10% biochar replacement. More recently, Santos et al. (2023) attributed density reductions to the partial substitution of cement with lower-density materials, such as hydrochar derived from rice husk. In contrast to these studies, the comparatively small dosages used in the present work suggest that the density reduction may not be solely due to material replacement but rather to the intrinsic properties of HCNs, especially their porous morphology and low specific gravity, which contribute to lowering the overall composite density.

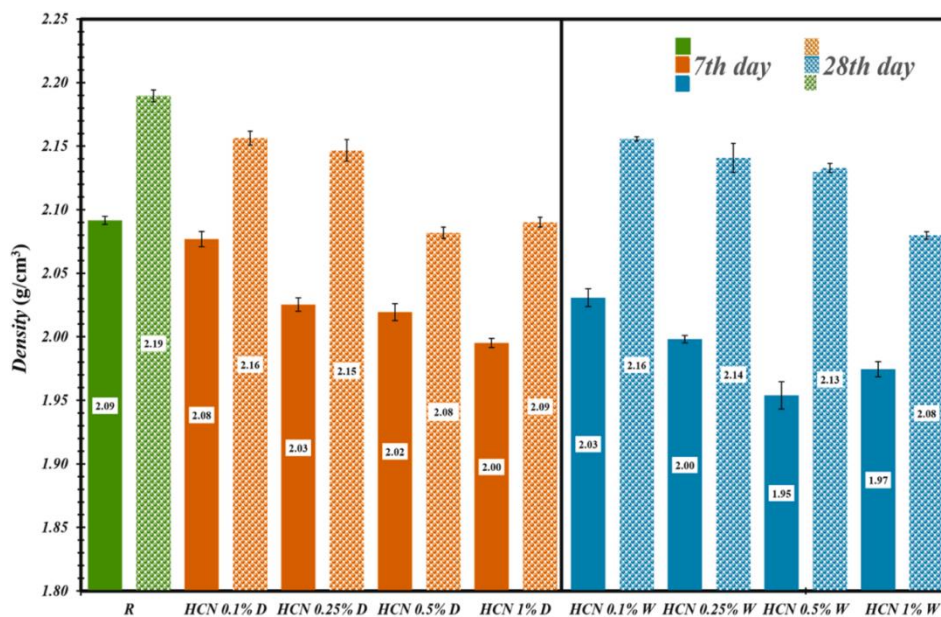


Figure 4.28. Results of density measurement test.

4.7.3.5. Ultrasonic pulse velocity analysis

Figure 4.29 illustrates the UPV test results, a nondestructive evaluation technique used to assess the internal quality and homogeneity of cementitious materials. After 7 days of curing, most HCNs-containing samples exhibited decreased UPV values compared to the reference, with reductions ranging from 4.25% to 10.75%, except for the HCNs 0.1% D specimen, which showed a modest 1.75% increase. By the 28th day, the reductions became less pronounced, ranging from 1.39% to 7.84%. In the wet-mixed series, a clear dose-dependent decline in UPV was observed at 28 days, whereas no consistent trend was evident in the dry-mixed specimens. At higher dosages (0.5% and 1%), statistically significant reductions ($p < 0.05$) were recorded for both mixing approaches.

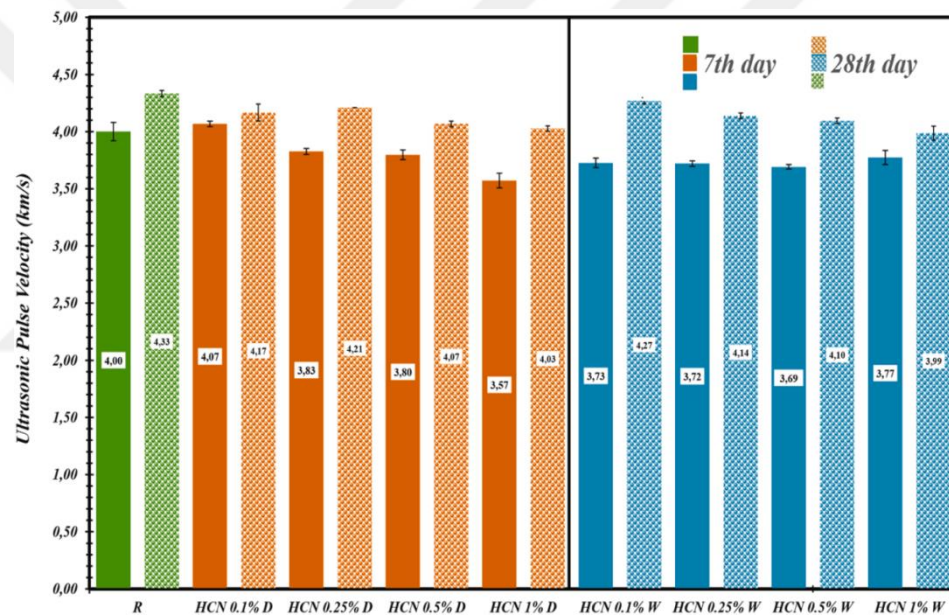


Figure 4.29. Results of UPV test.

The sensitivity of UPV to material density and elastic modulus is well documented in the literature. Benaicha et al. (2015) demonstrated that UPV is highly sensitive to a material's density and elastic modulus. Ersoy et al. (2019) further emphasized that UPV primarily reflects material homogeneity rather than geometric or measurement-related variables. The incorporation of biochar, as reported by Yang and Wang (2021), tends to lower UPV due to the porous nature of biochar, which decreases the overall composite density and compromises material uniformity. Similarly, in this study, although UPV values were reduced, the majority of the specimens retained a UPV value above 4 km/s after 28 days of curing, except for the HCNs 1% W sample. This

threshold of 4 km/s is generally considered indicative of good concrete quality, suggesting that incorporating small amounts of HCNs does not severely compromise the structural integrity of the cement. Overall, while the inclusion of HCNs led to a reduction in UPV, especially at higher concentrations, the results confirm that small dosages of HCNs, particularly those up to 0.5%, do not significantly degrade the cementitious properties. This finding supports the potential use of HCNs in cement composites without significantly affecting the overall material quality.

4.7.3.6. Mechanical performance of cement composites

The integration of HCNs had a noticeable effect on the mechanical properties of cement composites, particularly influencing both compressive and flexural strengths. These effects varied with dosage and mixing method, reflecting the complex interaction between HCNs's porous structure and the cement matrix.

(i) Compressive strength

After 7 days of curing, cement composites incorporating HCNs showed a decline in compressive strength relative to the control, with the most notable reduction occurring at the 0.5% dosage in both wet- and dry-mixed samples (Figure 4.30). This early-age strength loss is likely attributed to the elevated water absorption and capillary uptake previously observed in HCN-containing mixes.

The porous architecture of HCNs can retain excessive moisture, thereby disrupting the initial hydration reactions essential for strength development. This observation aligns with findings by Yang and Wang (2021), who reported that biochar-based additives with internal porosity may delay the formation of early hydration products, negatively impacting early compressive strength. However, a significant improvement in performance was observed between days 7 and 28. During this period, HCN-modified samples exhibited accelerated strength development, ultimately surpassing the reference mix. Most notably, the 0.5% wet-mixed sample achieved a 70.93% increase in compressive strength, compared to just 23.52% in the control. This enhancement is attributed to the delayed, sustained release of water retained within the porous structure of HCNs, which prolongs hydration and supports continued formation of calcium silicate hydrate. This internal curing effect supports the "reservoir" mechanism described by Yang and Wang (2021), wherein porous nanomaterials act as moisture reservoirs that facilitate long-term strength gain.

To assess the influence of mixing method, independent t-tests were conducted on compressive strength data at both 7 and 28 days. The analyses revealed no statistically significant difference between wet- and dry-mixed samples ($p = 0.876$ and $p = 0.445$, respectively), implying that the compressive strength is largely unaffected by whether HCNs are wet- or dry-mixed.

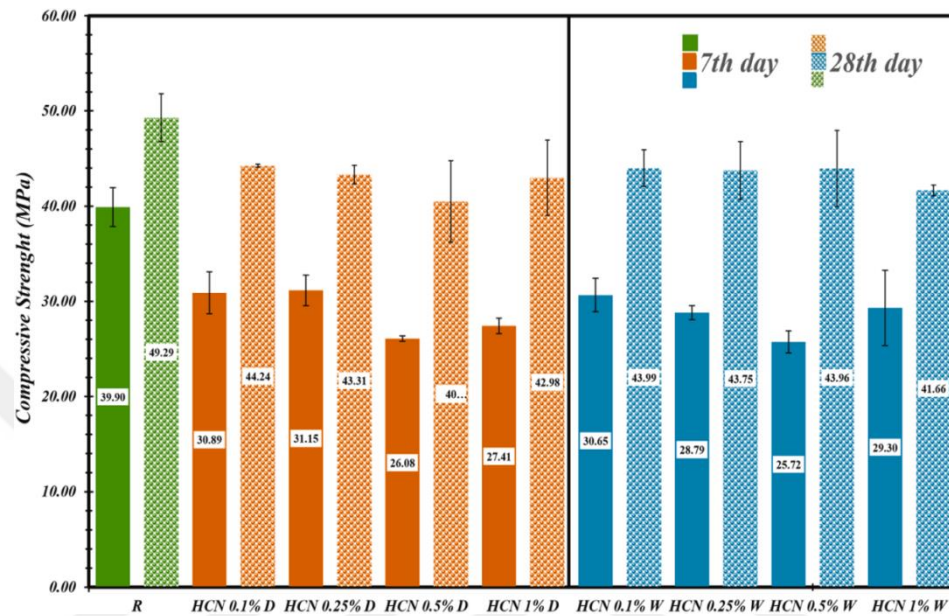


Figure 4.30. Results of compressive strength test.

Although the inclusion of HCNs initially impairs early compressive strength, its significant contribution to long-term strength gains suggests considerable potential for enhancing the durability of cementitious materials. Future research extending the curing period beyond 28 days may provide further insights into the role of HCNs in hydration kinetics and their long-term mechanical performance.

(ii) Flexural strength

Flexural strength exhibited distinct trends at 7 and 28 days (Figure 4.31). After 7 days of curing, dry-mixed samples initially showed reduced strength at the 0.1% HCNs dosage but improved with increasing HCNs content, reaching a maximum 25% gain at 1% HCNs compared to the reference. In contrast, wet-mixed samples outperformed dry-mixed ones in early strength, with the 0.25% HCNs wet mix achieving the highest flexural strength—37% above the reference. Statistical analysis confirmed that, at lower HCNs contents (0.1% and 0.25%), wet-mixed samples exhibited significantly higher flexural strength than their dry-mixed counterparts ($p < 0.05$). However, at higher dosages (0.5% and 1%), wet-mixed samples showed slight reductions in

strength but still surpassed the control. At 28 days, both mixing methods exhibited a gradual decline in flexural strength with increasing HCNs dosage. This decline is attributed to the pore characteristics of the material: while low HCNs content (0.1%–0.25%) enhances matrix density and cohesion, higher dosages (0.5%–1%) introduce excessive porosity due to the high pore volume and small pore size of HCNs, thereby compromising structural integrity. This explanation is supported by capillary water absorption and porosity tests, which revealed higher porosity and water uptake at higher HCNs dosages. At 28 days, dry-mixed samples generally outperformed wet-mixed ones, with the HCNs 0.1% D sample achieving the highest flexural strength of 8.98 MPa—just 0.33% below the reference. The performance gap between the two mixing methods narrowed over time at all dosage levels ($p = 0.4197$).

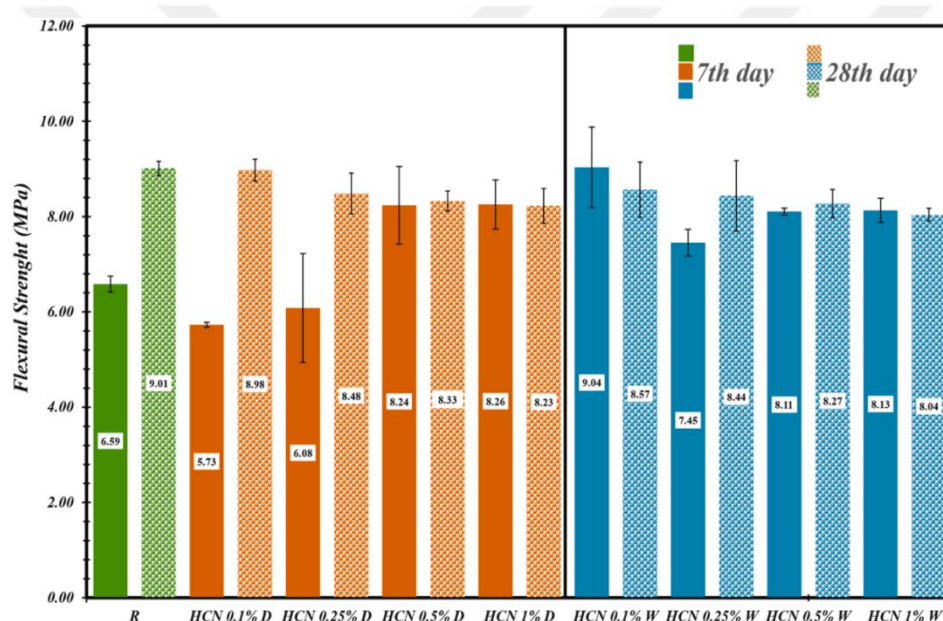


Figure 4.31. Results of flexural strength test.

These findings suggest that incorporating HCNs improves long-term compressive strength by facilitating ongoing hydration; however, the increase in porosity at higher dosages may hinder flexural strength. To achieve a balanced enhancement in both compressive and flexural properties, careful adjustment of HCNs dosage and dispersion is essential.

The current study revealed a consistent enhancement in the workability and flowability of cement composites incorporating hydrothermal carbon nanospheres (HCNs). This outcome stands in contrast to earlier findings by Andrade Neto et al. (2021), who reported that the inclusion of carbon nanotubes (CNTs) and metakaolin in cementitious

systems led to higher yield stress and plastic viscosity, ultimately diminishing the fluidity of the mix. More recently, Ahmad and Zhou (2023) observed a substantial decrease in the flowability of concrete when CNTs were added, particularly at elevated dosages, attributing this to particle agglomeration. In contrast, the HCNs synthesized from pomegranate peel waste in this study demonstrated the capacity to improve mix fluidity, presenting a compelling alternative to traditional nanomaterials. These results suggest that, when properly dispersed, HCNs can mitigate common issues associated with CNTs and potentially offer a more cost-effective and application-friendly solution in cement technologies.

The mechanical performance results further highlight the effectiveness of incorporating HCNs into cement composites. After 7 days of curing, dry- and wet-mixed samples with higher HCNs dosages exhibited notable flexural strength improvements of approximately 23–25%.

Remarkably, the most significant enhancement was observed in the wet-mixed sample containing just 0.1% HCNs, which demonstrated a 37.18% increase compared to the control.

These findings suggest that even minimal additions of HCNs can substantially boost mechanical performance. In addition to strength gains, the inclusion of HCNs led to a reduction in composite density by up to 6.67%, pointing to their potential in the development of lightweight cementitious materials. Collectively, these outcomes highlight the dual functionality of HCNs, enhancing both workability in the fresh state and mechanical integrity in the hardened state, thus offering a promising strategy for designing more sustainable and high-performance cement composites.



5. CONCLUSION AND RECOMMENDATIONS

This study demonstrates the feasibility and environmental significance of synthesizing valuable carbon nanomaterials from biomass waste using hydrothermal carbonization (HTC). Among the three biomass sources investigated—pomegranate peel waste (PPW), marigold flower waste, and cotton fabric waste—PPW emerged as the most promising precursor, yielding well-defined hydrothermal carbonaceous nanospheres (HCNs) under optimized HTC conditions of 250°C for 4 hours, without requiring additional chemicals. The resulting nanospheres exhibited comparable quality to those produced using pure compounds or harmful chemical additives, emphasizing the eco-friendly potential of this process. Furthermore, the HTC liquid fraction of PPW yielded carbon dots with strong blue luminescence, offering additional value-added products.

The environmental analysis, conducted through LCA, highlights the dual impact of the HTC process: while it efficiently utilizes biomass waste, electricity consumption for reactor heating and drying remains the primary contributor to environmental burdens. Transitioning to cleaner energy sources could significantly reduce the GWP100 and ADP by over 100%. Additionally, utilizing HTC liquid waste for carbon dot production further enhances resource efficiency, aligning with circular economy principles.

HCNs derived from PPW was incorporated into cement composites at low dosages (ranging from 0.1% to 1%), leading to improved workability and significant increases in flexural strength, alongside a reduction in density. This reduction contributes to producing lighter concrete without notably compromising compressive strength. However, the sustainability impact of these low dosages remains limited, highlighting the need to explore higher concentrations or combine HCNs with other sustainable materials to fully unlock its potential.

It is noteworthy that even small quantities of HCNs can significantly influence cement composite properties, emphasizing the importance of optimizing these additions for enhanced performance. Nevertheless, while low dosages of HCNs bring improvements to specific properties, their overall sustainability contribution is modest, and their

production process may introduce additional environmental challenges. To fully capitalize on the advantages of hydrothermal carbonaceous materials in cement, further research is required to optimize their use and investigate potential combinations with other additives. Previous studies have shown that incorporating biochar or other biomass-derived carbon materials can substantially improve the sustainability of cement concrete, especially through CO₂ absorption. However, these benefits often come with trade-offs in workability, density, and strength. Therefore, combining HCNs with other sustainability-boosting materials could offer a promising approach to balance performance enhancements with environmental benefits. This also underscores the potential of hydrothermal carbonization as a sustainable method for producing carbon materials from a variety of organic and biowaste feedstocks for use in cement composites.

Additionally, the antioxidant activity of the synthesized HCNs was evaluated using DPPH and phosphomolybdenum assays, showcasing performance comparable to that of ascorbic acid. Functional group analysis via FTIR identified hydroxyl, carbonyl, and aromatic groups, suggesting their role in the strong radical-scavenging potential of HCNs. This highlights the dual applicability of HCNs in both construction and biomedical fields, offering a sustainable alternative to fossil-derived materials and synthetic antioxidants.

In conclusion, this study aligns with the growing trend of utilizing waste materials to produce sustainable carbon nanomaterials while addressing the often-overlooked challenge of managing organic waste compared to plastic and other non-biodegradable waste. By innovatively valorizing waste biomass, this research advances circular economy principles and sets the foundation for more sustainable practices. The successful production of multifunctional hydrothermal carbonaceous nanospheres from waste biomass marks significant progress in resource-efficient technologies. These findings emphasize the potential of hydrothermal carbonization as a sustainable approach for converting biomass waste into high-value materials with promising environmental and industrial applications. Further optimization and scale-up efforts are essential to fully realize the environmental and functional benefits of these innovative materials.

5.1. Future Recommendations

Future research should expand the LCA system boundary to include the application and disposal phases of carbonaceous nanoproducts, ensuring a more comprehensive understanding of their overall environmental impact. Given the significant influence of electricity sources, optimizing the energy mix toward cleaner alternatives should be a priority. If centralized renewable energy is unavailable, on-site rooftop solar panels could provide a more environmentally friendly and efficient solution, representing a smart and cost-effective investment for long-term sustainability. Conducting a feasibility study on solar panel installation could help assess potential benefits and inform energy optimization strategies. In the future, the performance of the recovered CDs can be benchmarked against commercial standards to establish their functional equivalence. If this is achieved, applying a system expansion approach could be justified. This would allow us to account for the avoided burdens of conventional CDs production, potentially reducing the overall environmental impacts associated with the HTC_a scenario and providing a more complete understanding of the benefits of waste valorization.

While the absence of antimicrobial activity may benefit soil ecosystems, it could also leave soils vulnerable to pathogens, potentially increasing the risk of plant diseases. For applications requiring antimicrobial properties, modifications to the material should be explored. Techniques such as surface functionalization, incorporation of antimicrobial agents, increasing the tested sample quantity, or doping with metal ions could enhance the antibacterial properties of HCNs. Studies have demonstrated that integrating nanoparticles such as silver or zinc oxide into biomass-derived materials significantly improves their antimicrobial efficacy against a wide range of pathogens. Future research could focus on such modifications to expand the functional versatility of HCNs and maximize its applicability across various fields.

This study highlights the potential of HCNs as a supplementary material in cement composites as a partial replacement for cement. However, its effects are currently limited. The use of surfactants or other dispersion-enhancing agents could improve the uniform distribution of HCNs within the cement matrix, potentially leading to enhanced performance in future applications.



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