STRUCTURAL BEHAVIOR OF RICE HUSK BIOCHAR CONCRETE

Thesis Submitted For the Award of the Degree of

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Declaration

I, hereby declared that the presented work in the thesis entitled "STRUCTURAL BEHAVIOR OF RICE HUSK BIOCHAR CONCRETE" in fulfilment of degree of **Doctor of Philosophy (Ph. D.)** is outcome of research work carried out by me under the supervision of Dr. R.L. Sharma, working as a professor, in the school of civil engineering of Lovely Professional University, Punjab, India and Dr. Harpal Singh, working as a professor, in the department of civil engineering of Guru Nanak Dev Engineering College, Ludhiana, Punjab, India. In keeping with general practice of reporting scientific observations, due acknowledgements have been made whenever work described here has been based on findings of other investigator. This work has not been submitted in part or full to any other University or Institute for the award of any degree.

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Certificate

This is to certify that the work reported in the Ph. D. thesis entitled "STRUCTURAL BEHAVIOR OF RICE HUSK BIOCHAR CONCRETE" submitted in fulfillment of the requirement for the reward of degree of **Doctor of Philosophy (Ph.D.)** in the School of Civil Engineering of Lovely Professional University, Punjab, India, is a research work carried out by Research Scholar, Akash Aneja (Registration No. 41800100), is bonafide record of his original work carried out under my supervision and that no part of thesis has been submitted for any other degree, diploma or equivalent course.

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Abstract

Cement production is currently the major source of greenhouse gas (GHG) emissions liable for nearly 5% of the world-wide emissions. Greenhouse gas emissions during cement production arise from the processing of clinker where a large amount of fossil fuel is burnt for energy generation, and the remaining part comes from the energy it takes to get to the necessary high temperatures. Partial replacement of cement by residuals from agricultural industries is one of the key strategies to mitigate CO_2 emissions. Therefore, agro-waste materials are gaining importance in the construction industry. The objective of this research is to investigate biochar as an alternate supplementary cementitious material (SCM). Elements analysis, scanning electron microscopy, thermogravimetric analysis, and energy-dispersive X-ray spectroscopy were used to describe the physical and chemical characteristics of biochar. Chapelle test was conducted to determine the pozzolanic activity of the biochar. The analysis shows that rice husk biochar can be accepted as pozzolanic material. The experimental study outlines the durability and mechanical properties of the cement mortar. For this purpose, 2%, 4%, 6%, 8%, and 10% biochar prepared from rice husk at 550^{o} C, has been introduced in the cement mortar to replace cement. The cement mortar properties such as flowability, flexural strength, compressive strength, water absorption, etc. were studied. Microscopic properties have also been studied with the help of non-destructing techniques such as scanning electron microscopy and X-ray powder diffraction techniques. The mechanical strength properties of cement mortar significantly improved with a 2% replacement of cement by biochar. As compared to the control specimens, the increase in compressive and flexural strengths was found as 9.55% and 12%, respectively. The compressive strength loss due to sulphate attack is minimized when 2% and 4% biochar replaces the cement in the composite. Hence, the durability of the composite is increased. Mechanical and durability properties of concrete incorporating binary blended cement with varying amounts of biochar i.e. 0%, 2%, 4%, 6%, and 8% were studied. The mechanical performance was evaluated using compressive and flexural strength tests, and durability using water loss, permeability, and resistance to sulfate attack. The results indicate that concrete containing 4% biochar

has significantly improved strength and durability because the finer biochar particles have a packing effect resulting in the formation of a dense matrix.

The environmental impact of biochar concrete is quantified with the Cradle-to-gate lifecycle assessment (LCA) approach using the IMPACT World+ framework. The sustainability of the concrete prepared by replacing cement with 4% biochar is improved substantially without affecting the mechanical performance of the concrete. The study provides a valuable insight for the inclusion of biochar in concrete providing an effective and economic way of solid agricultural waste management.

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Phagwara

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Terminology

%	Percentage
2θ	Angle between the incident beam and a scattered beam of X-Ray
ASTM	American Society for Testing and Materials
BIS	Bureau of Indian Standards
BRHA	Black Rice Husk Ash
C	Carbon
CA	Coarse Aggregates
Ca	Calcium
CaO	Calcium Oxide
$Ca(OH)_2$	Calcium Hydroxide
CLSM	Controlled Low Strength Material
CM	Control Mix
CO_2	Carbon dioxide
CS	Compressive Strength
C-S-H	Calcium Silicate Hydrate
CTM	Compression Testing Machine
D_{avg}	Average base diameter
D_o	Original base diameter
DES	Directorate of Economics and Statistics
EDS	Energy Dispersive Spectroscopy
FA	Fine Aggregates
FAC	Fly Ash Modified Concrete
f_c	Compressive strength of concrete
f_{ck}	Characteristic Strength of Concrete
f_{target}	Target Strength
FM	Fineness Modulus
GBC	Ground Biochar
GHG	Green House Gases

GGBS	Granulated Ground Blast Furnace Slag
gm	Gram
IEA	International Energy Agency
K	Potassium
Kg	Kilogram
LCA	Life Cycle Assessment
LCIA	Life Cycle Impact Assessment
Mg	Magnesium
$MgSO_4$	Magnesium Sulfate
MK	Metakaolin
MPa	Mega Pascal
ml	Milli Litre
Mt	Metric ton
MM	Milli Meter
m^3	metre cube
m_s	Mass of Saturated Sample
m_d	Mass of Dried Sample
Na_2SO_4	Sodium Sulfate
NBC	Normal Biochar
O	Oxygen
OPC	Ordinary Portland Cement
PFA	Pulverized Fly Ash
POFA	Palm Oil Fuel Ash
PPCB	Punjab Pollution Control Board
PSDC	Particle Size Distribution Curve
RH	Rice Husk
RHA	Rice Husk Ash
RHB	Rice Husk Biochar
RMC	Ready Mix Concrete

S	Standard Deviation
SCM	Supplementary Cementitious Materials
SEM	Scanning electron Microscope
Si	Silica
SiO_2	Silicon Dioxide
SO_4	Sulfate
SF	Silica Fumes
TEP	Toxic Equivalency Potential
TGA	Thermogravimetric Analysis
TWA	Tobacco Waste Ash
WBA	Wood Based Biomass Ash
WBSCD	World Business Council for Sustainable Development
XRD	X-ray Diffraction
μm	Micro meter
σ_f	Flexural Strength

Abstract

Cement production is currently the major source of greenhouse gas (GHG) emissions liable for nearly 5% of the world-wide emissions. Greenhouse gas emissions during cement production arise from the processing of clinker where a large amount of fossil fuel is burnt for energy generation, and the remaining part comes from the energy it takes to get to the necessary high temperatures. Partial replacement of cement by residuals from agricultural industries is one of the key strategies to mitigate CO_2 emissions. Therefore, agro-waste materials are gaining importance in the construction industry. The objective of this research is to investigate biochar as an alternate supplementary cementitious material (SCM). Elements analysis, scanning electron microscopy, thermogravimetric analysis, and energy-dispersive X-ray spectroscopy were used to describe the physical and chemical characteristics of biochar. Chapelle test was conducted to determine the pozzolanic activity of the biochar. The analysis shows that rice husk biochar can be accepted as pozzolanic material. The experimental study outlines the durability and mechanical properties of the cement mortar. For this purpose, 2%, 4%, 6%, 8%, and 10% biochar prepared from rice husk at 550^o C, has been introduced in the cement mortar to replace cement. The cement mortar properties such as flowability, flexural strength, compressive strength, water absorption, etc. were studied. Microscopic properties have also been studied with the help of non-destructing techniques such as scanning electron microscopy and X-ray powder diffraction techniques. The mechanical strength properties of cement mortar significantly improved with a 2% replacement of cement by biochar. As compared to the control specimens, the increase in compressive and flexural strengths was found as 9.55% and 12%, respectively. The compressive strength loss due to sulphate attack is minimized when 2% and 4% biochar replaces the cement in the composite. Hence, the durability of the composite is increased. Mechanical and durability properties of concrete incorporating binary blended cement with varying amounts of biochar i.e. 0%, 2%, 4%, 6%, and 8% were studied. The mechanical performance was evaluated using compressive and flexural strength tests, and durability using water loss, permeability, and resistance to sulfate attack. The results indicate that concrete containing 4% biochar

has significantly improved strength and durability because the finer biochar particles have a packing effect resulting in the formation of a dense matrix.

The environmental impact of biochar concrete is quantified with the Cradle-to-gate lifecycle assessment (LCA) approach using the IMPACT World+ framework. The sustainability of the concrete prepared by replacing cement with 4% biochar is improved substantially without affecting the mechanical performance of the concrete. The study provides a valuable insight for the inclusion of biochar in concrete providing an effective and economic way of solid agricultural waste management.

Chapter-1

1.1 Introduction

The security of the environment is among the major challenges of society and sustainability is the primary concern of all world economies. Accelerated economic growth, characterized by large-scale construction activity has led to widespread use of concrete and the environmental damage caused by the excessive use of concrete is now evident and a lot of research is underway to decarbonize this wonder material. Today, China is the biggest producer and user of concrete. Its rapid economic expansion has been fuelled by large-scale construction activity and the use of concrete, making it one of the world's fastest-growing economies. After China, India is the second-largest manufacturer and consumer of concrete [1]. By the year 2050, the production of concrete is projected to increase by 6.3 times the current production. It will be around 20% - 30% of global production as per IEA and W.B.C.S.D [2].

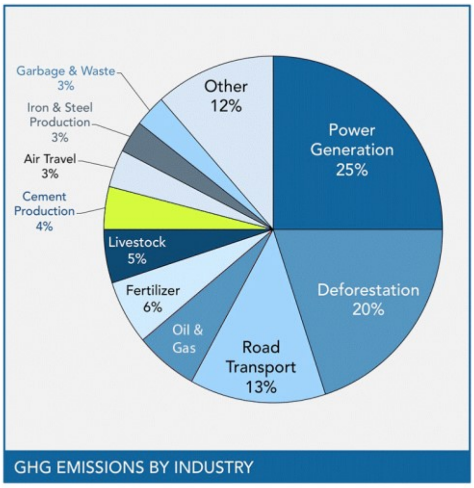

Figure 1.1: 2022 GHG emissions by industry (Source: GreenSpec)

Significant emissions of greenhouse gases involved in mining, processing, transportation, and the extraction of raw materials have serious impacts on the environment. The manufacturing process of cement being highly energy-intensive, carbon dioxide emission is a serious concern worldwide. Despite the fact that cement makes only a small percentage of the concrete mix (about 12% by volume), research indicates that it is responsible for the bulk of greenhouse gas (GHG) emissions. Cement production accounts for 4% to 5% of global GHG emissions (Figure 1.1) when all phases of the manufacturing process are included [3]. The calcination stage, where limestone is converted into calcium oxide (CaO), accounts for half of the emissions (quicklime) and the remaining half comes from energy it takes to get to the necessary high temperatures [4].

The concrete, however, has extremely high embodied energy because of extraction, manufacture and transportation of its constituent materials namely cement, stone, sand and water. CO_2 is produced by energy consumption, which adds to GHG emissions and global warming. The total environmental influence of the built environment and projects may be greatly reduced by lowering embodied energy. Understanding how much energy or carbon is integrated into a building's components is critical for developing more environmentally friendly materials and products.

Various studies indicate the usage of industrial and agricultural waste as a cement supplement in the concrete as an effective alternative to reduce CO_2 emissions [5]. Several reports incorporating agrowaste in concrete have been documented in multiple studies and the properties of concrete containing agrowaste from rice husk, bagasse, tobacco, oyster shell, cork, groundnut, oyster shell, sawdust, etc. have been compared [6]. The agrowaste concrete containing ash from rice husk, tobacco, cork, and groundnut shell showed better workability as compared to the concrete comprising ash from sawdust, bagasse, and oyster shell. The inclusion of the waste products namely residuals from industries such as pulverized fly ash (PFA), granulated ground blast furnace slag (GGBS), metakaolin (MK), silica fumes (SF), etc. have been reported in the numerous studies [7]. These supplementary cementitious materials (SCM), though not cementitious in themselves, but contain enough silica in a reactive form which in the presence of water at normal temperature reacts with lime to generate stable insoluble compounds having cementing characteristics. However, the recent trend is towards the use of agricultural solid waste which is available in abundance in many developing countries. The inclusion of agricultural waste by-products in the concrete mix has increased significantly in the past decades [8].

India has 17.7% of the total population of the world and is one of the largest agriculture-based economy generating a huge amount of unwanted agricultural waste [9], along with residuals of food grains. As per the records of DES (Directorate of

Economics and Statistics), the generation of sugarcane, wheat, and rice in India is estimated to be 560 Mt in the year (2012-23) [10]. Rice husk is an agro-waste that accounts for nearly 20% of the world's yearly rice production [11]. Punjab Pollution Control Board (PPCB) statistics indicate that paddy stubble burning is practiced over 12.9 lakh hectares of agricultural land, accounting for almost 43 percent of the state's rice lands. Therefore, the treatment of agricultural waste causes serious environmental problems because the siliceous components in it are difficult to decompose and are regarded as waste [12]. Also, stubble burning being practiced by the farmers to clear the land has become a major cause of air pollution in Northern parts of India.

Numerous studies have been reported on agriculture waste based concrete using rice husk ash as a successful substitute for binder in the concrete [13-16]. However, in many cases, the environmental impact of outdoor incinerators is largely ignored. Pyrolysis or the controlled burning of RH at temperatures over 550°C under controlled conditions of temperature, heating rate, and little to no oxygen supply yields pozzolanic reactive rice husk ash (RHA) known as biochar. The quality, however, depends upon the kind of feedstock, combustion rate, burning temperature, and oxygen supply all affect its characteristics [17]. It's being studied as a carbon sequestration approach and combating climate change. According to research conducted by the UK Biochar Research Centre, biochar can store 1 gigaton of carbon each year on a conservative basis [18]. The advantage of increased marketing and adoption of biochar might be the storage of 5–9 gigatons of carbon per year in biochar soils. This research thesis focused on utilizing biochar as supplementary material in concrete to produce value-added sustainable material with reduced embodied carbon, better mechanical and durable properties.

1.2 Scope and Methodology

India is the world's second-largest rice cultivator. Massive amounts of agricultural waste in the form of rice husk are produced in India. This waste can be reutilized by converting it into a Biochar through effective sustainable techniques [9] and under controlled conditions through the process of pyrolysis [19]. Currently, biochar is being investigated as a bio-asphalt binder in the construction industry [20,21]. Biochar is also being used as an additive in wood/polypropylene composites [22,23]. Its applications are gaining importance due to its easy availability and enhancement of the physio-chemical properties of concrete. The rice husk processed through pyrolysis not only solves the problem of environmental pollution but also improves the characteristics of the concrete. Despite the fact, existing literature suggests that biochar has a significant potential to replace cement in concrete [61, 84], it is very challenging to develop a universal mixing design strategy as the characteristics of rice husk biochar are dependent on the kind of feedstock, combustion rate, burning temperature, oxygen supply and production conditions [17].

To study and enhance the mechanical stability and durability of concrete, the characterization of biochar is done to physically and chemically examine the properties of the biochar that can impact the strength and durability properties for the better execution of the biochar in the concrete. Therefore, the proposed research work is intended to investigate the mix design approach in which biochar can be utilized to partially replace the cement in cement mortar and concrete to produce value-added sustainable material with reduced embodied carbon, better mechanical and durable properties with the following key points :

- Inclusion of biochar in the cement mortar to reduce the amount of cement used and to enhance the properties of the material.

- Minimizing the cement concentration with the addition of biochar to increase the performance, mechanical qualities, and durability of a concrete mix blended with RHB.

- Lifecycle analysis of concrete. To ensure the development of optimum design, to partially replace the cement without impacting concrete's strength and durability.

1.3 Objectives

The principal objective is to determine the feasibility of inclusion of rice husk biochar to proportionally replace the binder in the cement mortar and concrete. Therefore, the list of objectives is as follows:-

a) To investigate the mechanical and durability properties of cement mortar incorporating agrowaste.

b) To study the mechanical properties of agro-waste based concrete.

c) To study the Micro-structural and durability properties of agro-waste based concrete.

d) A Comparative Lifecycle Assessment of Ordinary and Agrowaste Based Concrete.

1.4 Thesis organization

Chapter 1 highlights the problem statement, research significance and the objectives of the present research followed by comprehensive literature review detailed in Chapter 2 which summarizes the properties of biochar to be used as an ingredient in concrete. Chapter 3 provide the characteristics of the materials used in the production of cement mortar and concrete, and the details of test methods used in the study. Chapter 4 includes the mix proportions, evaluation of fresh and mechanical characteristics of cement mortar and concrete, respectively and the comparative lifecycle assessment approach. Chapter 5 concludes the findings of the research work with recommendations. Chapter 6 elaborates the recommendations for the future work.

Concluding Remarks

This chapter justifies the need of the study as we see the growth in the construction industry and rising demand of cement and concrete, we must focus on the sustainable production or the green concrete. Cement production is projected to increase between 3.6 and 6.3 fold between 2010 and 2050. By 2050, India's cement production is expected to be around 20% to 30% of Global Production.

Chapter-2

2.1 Literature Review

Extensive study has been carried out to analyze many by-products of waste as a possible alternatives for cement, natural sand, and coarse aggregates. The replacement of these raw materials with the waste by-products from agriculture industries is an eco-friendly key to the issues regarding the scarcity of non-renewable natural raw materials and an alternate way of waste disposal. Several agricultural waste residues are already employed in concrete as cement substitutes. A detailed study on the researches carried out is given below:

2.1.1 Agrowaste as a partial substitute of binder in cement mortar

Several reports incorporating agrowaste in concrete have been documented in multiple studies and concrete's properties incorporating agrowaste from rice husk, black rice hush ash, bagasse, tobacco, oyster shell, cork, groundnut, oyster shell, sawdust, etc. have been compared. In comparison to OPC mortar, the application of a ternary blend of ordinary Portland cement (OPC), powdered rice husk ash (RHA), and categorized fine fly ash, at a later age results in mortar with better strengths at minimal RHA and FA replacement levels. With minimal replacement levels of up to 20% cementitious materials, the porosity of pozzolan-containing mortar declines, but increases with 40% replacement level. The usage of single pozzolan and the ternary mixture of OPC, RHA, and FA greatly improves the chloride induced protection against corrosion of mortar significantly. Ternary mix mortar has higher corrosion resistance than single pozzolan mortar [24].

"B. Chatveera et al. [25] investigated durability of cement mortar by replacing cement partially with rice husk bark ash at the levels of 0%, 10%, 30%, and 50%. At the replacement levels of 30% and 50% of Black rice husk ash (BRHA), the expansion of the mortars was less than those mixed with sulfate-resistant cement. The high level of ground BRHA replacement has the beneficial impact of increasing resistance in Na_2SO_4 solution. However, in $MgSO_4$ solution, addition of BRHA had a negative effect on sulphate resistance, resulting in increased strength loss."

According to research by Lura et al. [26], a novel kind of light weight aggregate (LWA) made from biomass-derived waste performs very well with an internal curing in high-performance mix due to its adequate coarse porous morphology, water desorption and absorption behaviour. Analyses of the autogenous deformation, internal relative humidity, and neutron tomography serve to determine the effect of internal curing in bio-LWA mortars. The particle morphology and mechanical characteristics of cement paste infill with various RHA concentrations (0 - 6%) (RCPB) are investigated considering three types of pores considered: micropores (0.1 m), secondary pores (0.1-100 m), and major pores (>100 m). Secondary pores account for the greatest fraction of overall volume, followed by micropores and major pores. The volume percentage of major pores and micro pores reduces as curing time increases, while UCS raises and the fraction of secondary pores decreases. The UCS raises up to 6% with RHA dose. It has a linear exponential link with RHA ratio [27].

Choi et al. [28] conducted experiments to examine the properties of Biochar and found that replacing cement with Biochar to the extent of 5% enhances the concrete 28 days compressive strength by 10%. "Gupta et al. [29] used the biochar coating to boost the mechanical bonding of polypropylene (PP) fibres and cement paste. The goal of the study was to lessen one of the main problems with PP fibres, which is the introduction of tiny air pockets that leads to a rise in capillary pores and air spaces. The experimental results showed that biochar coating increased the mechanical strength and decreased the permeability of mortar samples due to the densification of mortar paste surrounding the fibres (as biochar tends to absorb some of the mixing water and release it to promote hydration at a later age), as well as due to enhancing mechanical bonding of fibres and mortar by roughening the surface of PP and encouraging friction."

S. Gupta et al. [30] used biochar processed through mixed wood sawdust as an inclusion in the cement mortar to replace cement. The results reveal that the biochar inclusion of 2% weight by cement was found to be effective in improving permeability, durability and mechanical strength properties. Although flexural strength was not greatly impacted, the experimental findings revealed that adding biochar can give mortar ductility under flexure. However, the inclusion of biochar modifies the behaviour of mortar when it cracks under flexure. The load-displacement results concludes that with the inclusion of biochar in the cement mortar, cement mortar show ductile failure whereas the control specimen gave brittle failure. It is determined that biochar behaves as a micro-reinforcer in mortar mixture, assisting in the deflection of fracture paths and the generation of numerous cracks, culminating in ductile failure.

The research conducted by S. Gupta et al. [31] evaluates the use of biochar prepared from wood waste to be deployed as a cement additive in cement mortar. Reduced water permeability of produced mortar samples containing a small biochar concentration (1-2%) was related to biochar's strong water retention capabilities, which resulted in loss of mixing water and consequent densification of mortar. Samples with a greater biochar concentration (5-8%), on the other hand, revealed the contradictory results, showing that the increased porosity was driven by a greater proportion of porous biochar particles in the cement. According to the results of the investigation, 1-2 weight percent addition of biochar could be suggested to increase cement mortar's strength and decrease its permeability.

Another study by S. Gupta et al. [32] shows that "adding biochar as an internal curing additive at 2% (based on %wt. of cement) improved the actual strength of the concrete in both dry and pre-soaked circumstances. The investigation also verified a significant increase in the mortar's strength after air drying. The addition of pre-soaked biochar reduced water accessible porosity by 18-20%, resulting in a 55-60% reduction in sorptivity and depth of water penetration. All of this encourages the potential technique of utilizing biochar as an internal curing agent."

"S. Gupta et al. [33] investigated the viability of employing mixed wood sawdust (MWBC), mixed food waste (FWBC), and rice waste (RWBC) biochar as a carbon-sequestering component in mortar is examined. While FWBC is made from a combination of rice, meat, and vegetables in a set proportion, RWBC is made from plain, boiled rice. Results demonstrate that adding 1-2 weight percent of FWBC and RWBC to mortar yields mechanical strength comparable to control mix. The reduction in water penetration and sorptivity caused by 1 wt% of FWBC was 40% and 35%, respectively, demonstrating greater mortar impermeability. In terms of mechanical and permeability qualities, biochar made from mixed wood sawdust performed better. Compressive and tensile strength increases of up to 20% were observed, although sorptivity and depth of water penetration decreased by roughly 60% and 38%, respectively, in comparison to control. Date palm ash, a waste product, has been used as a reliable binder to improve the characteristics of mortar and concrete. Comparative to standard OPC concrete, 10% date palm ash replacement has enhanced compressive strength up to 360 days. By offering intermediate penetrability compared to high in OPC, 10% PA replacement improves the penetrability of chloride ions, which will protect reinforcing bars from corrosion more effectively than other combinations. Lowest rate of water absorption ensuring decreased permeability is achieved with 10% PA substitution [34]."

When 2.5% biochar generated by biomass gasification of wood waste is introduced to cement mortar in various amounts, up to 2.5 percent by weight of binder, the compressive strength drops somewhat for all cement mortar specimen, with a comparable pattern at 7- and 28-day curing. In the case of mortar, however, an ideal proportion of 1 percent by weight of binder may be achieved, resulting in a minor gain in flexural strength and fracture energy [35]. Alice Sirico et al. [36] explored the application of biochar generated via a standardised technique of gasification of wood waste at 700^{o}C as micro-nano particles in cement mortars which act as a filler and a partial substitute for cement. Mechanical experiments show that adding 2.5% biochar increases flexural strength and fracture energy while retaining compressive strength and workability.

Ivana Carevic et al. [37] correlated the physical and chemical properties of wood biomass ash (WBA) to be used as an inclusion in the cement composite. It was found that increase in water demand in mixes containing WBA are related to the WBA's shape, high porosity, large specific area of the particles, high amount of free calcium oxide, and other chemical characteristics. High alkali concentration also results in increased water requirements because more alkali ions speed up hydrolysis of aluminate by reducing the discharge of Ca^{2+} ions from the gypsum, which reduces the effectiveness of gypsum action during aluminate hydration. The delay in setting is caused by a higher alkali and magnesium oxide concentration in the binder, as well as a low pozzolanic oxide level, especially in pastes with a higher WBA content. The delay in the initial setting might be caused by an increase in the level of heavy metals. As a result, the transition of metal hydroxides into new metal hydroxyl complexes causes the delay. This results in a large demand of calcium and hydroxide ions and consequently causes a delay in the production of portlandite and C-S-H gel. Amphoteric metals including tin, zinc and led are commonly employed as setting retardants. Additionally, larger amounts of loss on ignition (LOI) may result in delayed setting.

Kanghao Tan et al. [38] investigated “the fresh, hardened properties and thermal conductivity characteristics of four types of mortar samples, each having a percentage of cement substituted by powdered BC pyrolyzed at 400°C, 500°C, 600°C, and 700°C. The cement weight replacement ratio of BC was chosen at 0%, 1%, 3%, 5%, and 10%, respectively. The results indicated that 1-3% BC addition (regardless of pyrolysis temperature) was the ideal amount to improve mortar strength without affecting the other mechanical parameters. 1% inclusion of biochar pyrolyzed at 400°C reduced water absorption and fluidity by 9.0% and 39.0%, respectively. Furthermore, as the BC concentration is increased, the albedo and thermal conductivity of mortars containing BC pyrolyzed at various temperatures drops linearly.”

“S. Gupta et al. [39] investigated the influence of biochar particle size and surface morphology on rheology, strength development and permeability of cement mortar, under moist and dry curing condition. Experimental results show that the flowability and viscosity of cement paste is more affected by macro-porous coarser (or ‘normal’) biochar particles of size 2–100 μm (NBC) compared to fine (or ‘ground’ biochar), which is in the size range of 0.10–2 μm (GBC). Addition of both GBC and NBC accelerated hydration kinetics and improved early (1-day) and 28-day strength by 20–25% compared to the control. Water permeability, measured by capillary absorption was reduced by about 50% compared to control mortar, due to the addition of 0.50–1% NBC and GBC respectively. GBC is found to be more effective in minimizing loss in strength and water tightness under dry curing condition.”

“S. Muthukrishnan et al. [40] thermally processed rice husk into different forms of rice husk ash (RHA) and rice husk biochar (RHB). RHA from uncontrolled burning improves ductility under compressive loading, thus indicating its potential to be a controlled low strength material (CLSM). Addition of RHB as partial replacement of industrial grade rice husk ash significantly improves strength due to internal curing effect. Combination of RHA and RHB eliminates autogenous shrinkage over the 42-day period of study. 20% replacement of cement with RHA and RHB improved durability and strength."

Self-sensing cement mortar has been created using char and foundry sand as a carbon-based filler. The findings show that pyrolyzed char is the optimum carbon filler for lowering mortars' electrical resistivity (by about 42%) and water absorption (by about 17%) while maintaining their compressive strength. Additionally, the addition of char as filler and fibres has a synergistic impact on lowering the electrical resistivity of mortars, despite their being a modest drop in strength properties and a rise in water suction [41]. The impact of high temperatures on the compressive strength performance of biochar introduced mortar in a study shows that 5% inclusion of biochar as a cement substitution in the mix exhibited higher performance than other samples at elevated temperatures being subjected to 200°C, 450°C, and 700°C, retaining approximately 88%, 76%, and 38% of compressive strength, respectively [42]. The impact of 0.5 - 4 wt% partial cement substitution with biochar generated from olive stone, rice husk, and wood chips indicates that the addition of olive stone and rice husk biochar marginally enhances the compressive strength of the specimen. This enhancement was caused by the filler effect, the hardness of olive stone biochar particles, and their uneven morphology. In addition to the filler effect, the pozzolanic reaction was attributed for the development of RHB mechanical characteristics. Up to 4% cement substitution with biochar resulted in equivalent capillary water absorption while without imposing significant capillary porosity on the matrix material. As a consequence, the inclusion of biochar was able to minimise the amount of cement while maintaining the material's durability [43].

"L. Restuccia et al. [44] experimented nano particles of biochar derived from wood waste in different cement composites aiming at determining the optimal percentage of addition aiming in improvement of mechanical properties. Based on the experimental results, it was observed that the addition of biochar as 2 wt% and 2.5 wt% for cement pastes and mortars, respectively can increase the flexural strength and fracture energy of cementitious composites."

2.1.2 Agrowaste as a partial substitute of binder in concrete

W. Tangchirapat et al. [45] investigated palm oil fuel ash (POFA) as a pozzolan in concrete. Based on their particle size, the experimental results demonstrates that the Portland cement Type I can be replaced by 10% of POFA (particle size 15.91 μm) and 20% of POFA (particle size 7.4 μm) as the compressive strength outcomes of concrete containing 10% and 20% of POFA at 90 days were higher than those of Portland cement Type I, whereas normal POFA (original particle size) is not acceptable for use as a pozzolanic ingredient in concrete. The previous researches show that the use of RHA as a pozzolan has increased significantly in the past. 30% RHA from boiler burnt husk waste could be usefully combined with cement without impacting the properties of concrete [46].

For durability, replacement of cement by 20% Black rice husk ash (BRHA) increases the resistance of concrete against acid and sulphate attacks (B. Chatveera et al. 2011) [47]. Analysis of the structural parameters of RHA concrete reveals that while 10% substitution of cement by RHA improves compressive strength, there is no substantial improvement in tensile strength owing to the inclusion of RHA. Flexural strength studies show a marginal improvement with 10 to 25% RHA replacement levels. Flexural strength tests demonstrate a modest improvement with RHA replacement levels ranging from 10% to 25%. Rice Husk Ash concrete, on the other hand, has a number of advantageous characteristics that make it a long-lasting and good structural concrete for both short- and long-term concerns [48].

RHA is high in amorphous reactive silica. The chemical composition of RHA changes depending on the degree of control over the combustion process. A thoroughly regulated burning of rice husk at 700°C is appropriate for producing RHA comprising over 80% amorphous silica. In terms of pozzolanic reactivity with cementitious materials, RHA's fineness and specific surface area are also critical. As a result, a suitable amount of time should be spent grinding. To provide a better filler effect, the suggested minimum mechanical grinding duration is roughly 30 minutes; however, the grinding time might vary based on the origin of RHA. 30% cement substitution by rice husk ash particles with an average diameter of 20 micrometres or smaller is proposed [49]. The studies also reported the optimum water and binder proportions for replacing cement with rice husk ash (RHA). Maximum compressive strength has been reported with 15% RHA and 0.5 water-cement ratios (K. Ganesan et al.), 10% RHA and 0.55 water-cement ratio (N.K. Krishna et al. 2016), and 15% RHA and 0.4 water-cement ratio (S.A. Zareei et al. 2017) [45, 50, 51]. Because of the presence of nano silica, the inclusion of 3% RHA in the concrete mix containing 20% fly ash exhibits greater strength than the Fly ash optimised concrete (FAC). The nano silica in RHA improves the polymerized layered lattice and rough surface texture, which improves the bonding among cement paste and aggregates and hence strength characteristics and durability of concrete [52]. According to A.A. Raheem et al., "rice husk ash-blended Palm Kernel Shell Concrete (RHA-blended PKSC) with 40% PKS and 15% RHA in a 1:1.5:3 mix ratio met the compressive strength and thermal conductivity parameters suggested for lightweight aggregate concrete for structural and insulation applications. Concrete's thermal conductivity dropped as the amount of PKS and fixed RHA in the mix surged, and it rose as curing time increased. Concrete's thermal resistivity improved as the amount of PKS and fixed RHA in the mix grew, while it reduced as curing time increased [53]."

The impact of rice husk ash (RHA) inclusion on the physical and microstructural specifications of high-performance concrete (HPC) samples revealed that concrete specimen with 10% RHA show exhibits greater compressive, splitting tensile, and flexural strengths with the maximum compressive strength recorded throughout all curing ages. Because of the refining of the microstructure by the RHA integrated, the microstructure of the samples with RHA becomes denser than the control as the curing ages increase. The higher the RHA content in HPC, the greater the porosity of HPC samples. The RHAC-10 mixture has the lowest porosity [54]. Adding fine (rather than coarse) RHA particles improves flexural, compressive, and tensile strength values while limiting chloride ion penetration over time. 14% RHA inclusion as a replacement for conventional Portland cement in concrete with a water-cement ratio of 0.3 performed better in terms of both durability and strength. Increasing water-cement ratio found to have a detrimental influence on mix porosity [55].

Z.A. Zeidabadi et al. [56] studied "the influence of two agricultural wastes, rice husk and bagasse, which were pyrolyzed at 700°C to form biochar, on the mechanical qualities of concrete samples having varying concentrations of cement replacements with biochar from 0 to 10%. Concrete samples containing 5% biochar exhibits greater compressive strength than the controlled samples whereas 5% treated bagasse biochar shown 78% more tensile strength when compared with the concrete containing was compared to concrete without any biochar."

P. Moreno et al. 2018 [57] studied "the influence of replacement of cement with tobacco waste ash (TWA). According to the study, replacement of cement with 10% tobacco waste ash having water-binder ratio as 0.5, increases the compressive strength by 51% as compared to the control mixture after 28 days. Anjaneya Dixit et al. [58] found that biochar has the potential to be included in the concrete as a cement replacement material when 5% of cement was replaced by mixed wood sawdust biochar. The design mix containing 5% biochar showed comparable strength to the conventional concrete mix."

Ali Akhtar et al. [59] investigated "the use of 100% recycled coarse aggregate and wash mixed sand in concrete using waste derived silicon rich char as a cement replacement at levels ranging from 0.1 to 0.75% of total volume of concrete. Rice husk and improved poultry litter char both boosted compressive and splitting tensile strength at 0.1% of total volume. Rice husk char at 0.1% increased compressive and splitting tensile strength by 17% and 3%, respectively. However, improved poultry litter and rice husk at 0.75% replacement generated the highest flexural strength of all char mixtures. Char was also discovered to minimize water absorption by up to 0.5% of total volume and to eliminate permeable spaces in recycled aggregate concrete by forming a thick structure. The 15% inclusion of biochar produced from dried distillers grains in the concrete resulted in linear decrease in concrete density and was marked as 1454 kg/m^3. Because it generated pore networks inside the concrete, the addition of biochar also significantly boosted the sound absorption coefficient of concrete over the frequency range of 200-2000 Hz. With 2 wt% of biochar, the thermal conductivity of the concrete decreased the most, falling to 0.192 W/(mK) [60]."

S. Gupta et al. [61] investigated the biochar pyrolyzed from woody biomass to partially replace the cement in the concrete. Investigation reveals that 0.5 and 2% biochar inclusion improve compressive strength by 16% and 9%. The inclusion prevents disruption of the microstructure of concrete during thermal treatment, resulting in 22–25% lower permeability when compared to conventional concrete specimens.

D. Suarez-Riera et al. [62] conducted the study to evaluate the effect of wood chips biochar as a cement replacement in cement mortar samples. The study suggests that biochar act as a micro-reinforcement in the cement paste. The findings show that the 2% biochar has improved the fracture energy of the cement mortar and enhanced the flexural strength by 15%.

Y. Qin et al. [63] utilized the biochar prepared from Eucalyptus plywood waste as a cement replacement additive in pervious concrete in the range from 0-13.5% cement replacement by weight. The presence of biochar has minimal to no effect on porosity and water permeability. Biochar pervious concrete samples absorb roughly 0.8% more than the conventional pervious concrete mixes. The results reveal that the pervious concrete mixes exhibiting biochar inclusion up to 6.5% possesses stronger compressive and split tensile strength when compared with conventional mixes. "K. Tan et al. [64] present a modified method for adding biochar (BC) particles into pervious concrete as a hygroscopic filler in order to extend its evaporative cooling effect. The pervious concrete was prepared by replacing the cement in weight, by 5.0% of BC particles. The albedo, emissivity, porosity, microstructure morphology, water absorption, and evaporation of pervious concrete were investigated. The biochar inclusion had minimal effect on the emissivity and porosity of pervious concrete while considerably lowering the albedo. They would considerably improve the water absorption and retention capabilities of pervious concrete by contributing to the numerous micro-pores and greater specific surface area of carbonaceous particles." The admixture of 5.0% crushed BC enhanced the total water absorption of pervious concrete from 100 ± 2 kg/m^3 to 117 ± 8 kg/m^3. When compared to typical pervious concrete, the excess water absorption could significantly lower the surface temperature by up to 3-6°C throughout the evaporation process, with an additional cooling period of 6h. The effect of 15% rice husk ash on strength qualities on M30 concrete with w/c ratio 0.45 revealed that the rice husk ash inclusion had high compressive, split tensile, and flexural strength values. Tests on reinforced beams revealed that rice husk ash beams had greater ultimate load values than standard M30 concrete beams [65].

According to W. Zhenhong et al. [66], there is a presence of higher amount of oxides of aluminium, silica and iron in the products prepared through gasification of sludge and garbage as compared to the concentration in cement. Therefore, the reaction of all such oxides with the products of secondary hydration of cement, $Ca(OH)_2$, contributes more calcium-silicate-hydrate. Replacement of cement by this biochar at 20% and 8% improved the mechanical properties of the concrete and if adopted globally for the concrete production will promisingly process all worldwide municipal sludge, reduce cement production by 1.148×10^9 tonnes, save 9×10^8 tonnes coal, and store 1.98 Gt CO_2, causing 5.5% of global CO_2 emissions. “Biochar derived from agricultural waste of date palm in Saudi Arabia was used as an 0.75–1.5 wt% inclusion in the concrete resulting in 28–29% increase in compressive strength. The flexural strength of biochar-concrete containing 0.75 wt% biochar was 16% greater than the control specimen. The high ultrasonic pulse velocity values and low electrical resistivity of biochar-based concrete demonstrate that the inclusion of biochar produced a better concrete free of internal faults and cracks, as well as improved structural integrity. According to the strengths, weaknesses, opportunities, and threats (SWOT) analysis, biochar-based concrete outperformed standard concrete, is appropriate for harsh settings, and has chances for circular economy and applications in diverse construction designs [67].”

2.1.3 Sustainable concrete production

Due to widespread environmental damage prompted by the use and the processing of concrete, a lot of research is underway to decarbonize this wonder material. Various studies indicate that concrete with partial cement substitution can significantly lessen its negative environmental effect. The inclusion of waste materials such as pulverized fly ash (PFA), granulated ground blast furnace slag (GGBS), metakaolin (MK), silica fumes (SF), and other residuals from industries has been described in several study outcomes [7]. Tait et al. conducted a comparative LCA of concrete mix (100% plain cement, 35% FA, and 70% GGBS) using the “cradle to gate” approach to characterize the environmental impact and embodied carbon. The results show that using 70 percent

GGBS in a concrete mix reduces CO_2 emissions without compromising the concrete's performance [68]. Kim et al. also carried out the environmental impact analysis of concrete mixes of different compressive strengths. The results show that the global warming potential and photochemical oxidant creation are increased because of the higher strength of the concrete whereas acidification potential and eutrophication potential are reduced [69]. However, the recent trend is to use plant or agriculture-based solid waste which is also available in abundance, particularly in many developing countries. Invariably, the agricultural waste is not properly managed and is either left to accumulate or burnt in the open resulting in the generation of waste in a significant amount. As per World Bank records, by 2025, the worldwide generation of waste from agriculture is expected to be 2.2 billion tonnes per year [70].

Several researchers have discussed the feasibility of using agricultural waste such as rice husk bark ash, waste ash from palm oil and black rice husk ash, etc. as a cement supplement in the concrete. Agro-waste materials such as oyster shells, bagasse ash, and sawdust ash are already being used as alternatives for partial replacement of cement in concrete [6]. Ground shell ash, sugarcane bagasse ash, and coconut shells are also used as a replacement in green concrete [71]. Although replacing cement with SCMs are widely known ways to make highly durable and environmentally friendly concrete, a cost-competitive supply of these materials might outweigh the environmental benefits of concretes made with such by-products. J. Fort et al. studied the environmental impact by partially substituting cement with biomass fly ash in concrete. The analysis revealed that by replacing 20% of cement with biomass fly ash, significant reductions in energy consumption (approximately 25%) and CO_2 emissions can be achieved without affecting the strength properties of concrete [72].

Although replacing cement with SCMs is one of the most well-known strategies for producing more durable and sustainable concrete while reducing environmental impacts, the cost-competitive supply of such materials can counterbalance the environmental advantage of concretes made with such by-products. To evaluate the performance of waste by-products from agriculture industries in terms of their quality, costs, and their social and environmental aspects, R. Teixeira et al. (2015) replaced cement with different percentages of biomass and coal fly ash in concrete. The study shows that the concrete with 60% cement replacement by biomass fly ash is the best alternative to produce more durable and sustainable concrete with reduced CO_2 emissions [73].

Dandautiya et al. (2019) [74] analyzed the environmental impact of concrete containing fly ash and copper tailings as cement replacement material by using the midpoint assessment method. The reductions observed in the mid-point level indicators were 38% in climate change, 34.3% in water depletion, 31.9% in agriculture land occupation, 34.8% in fossil depletion, 35.4% in particulate matter, 32.6% in human toxicity, 25.2% in metal depletion, and 33.6% in ozone depletion. Pavlikova et al. 2019 [75] investigated the reduction of CO_2 emissions and energy consumption by using wood-based biomass ash (WBA) as a partial lime hydrate substitution in mortar composition. The environmental study revealed that increasing the WBA percentage in mortar dry mix reduced both carbon dioxide generation and energy usage.

2.1.4 Properties of biochar

Existing literature suggests that biochar has a significant potential to replace cement in concrete. Biochar is a waste by-product derived from the thermochemical conversion of agrowaste under a controlled supply of oxygen. It is an eco-friendly waste treatment procedure known as pyrolysis. It is a carbon-rich and fine-grained product in which the carbon content varies depending upon the processing temperature which is varied from 300° to 800° C. Exceeding the temperature beyond 800° C decreases the yield of biochar without increasing its carbon content [45]. The combined effect of an elevated heat treating temperature (500°C and above) and a extended residence time (60 min) maximises the hardness and modulus values. Both the pyrolysis temperature and the residence time have a considerable effect on the hardness and modulus of a biochar, with temperature being the most influential. When the carbon molecules in a biochar are more organised, the biochar gains higher mechanical abilities [76]. The high molar ratio of Oxygen and Carbon (O/C) confirms the formation of the network of interconnected chains and long-term stability in the rice husk biochar [77].

Particles ranging in size from nano to micro scale can have a significant impact on the mechanical characteristics of concrete; the initial benefits would result from the influence of biochar's small particle size. The introduction of carbon-based nanoparticles have been observed to counter the brittle behaviour of cement that has resulted in increased strength by enhancing composite ductility [44]. As a result, finer biochar particles may be used to tune the brittle behaviour of concrete without affecting mechanical strength [78].

Biochar is a carbon-rich component and cement carbonation begins with the dissolving of the absorbed carbon dioxide gas molecules, which leads to the development of carbonic acid. Carbonic acid then combines with calcium hydroxide (primarily) and C-S-H (at a slower rate) to produce calcium carbonate. Additionally, it is important to consider that the carbonation will be significantly less effective if the pores of the concrete matrix are filled with water molecules (which would reduce the dispersal of carbon dioxide) or if in dry conditions (not enough moisture to dissolute CO_2 that will lead to the formation of carbonic acid) [79]. Despite the fact that carbon dioxide in the air causes the process of carbonation to occur naturally, it is intentionally induced in the concrete to take advantage of the improved mechanical qualities of calcium carbonate. Concrete carbonation can be accelerated in one of two ways: externally by keeping concrete samples in the exposure to a CO_2-filled environment, or internally by the inclusion of CO_2-filled components into the design mix. “S. Gupta et al. subjected biochar to treatment in a sealed container with high CO_2 concentration and under normal pressure and temperature, and then introduced this “saturated” biochar (1.67 mmol of CO_2 per g of biochar) into a mortar mix in the amount of 2% by weight of cement. The internal carbonation was ensured by performing thermogravimetry and XRD analyses of the ground mortar samples when the amounts of calcium hydroxide and calcium carbonate (%) were estimated and compared between mortar samples. The study showed that for the given biochar dosage, a mix with CO_2-treated biochar ended up with the highest (5.80%) amount of calcium carbonate. Interestingly, a mix with untreated biochar also resulted in increased calcium carbonate formation (3.08%) when compared with a reference plain mortar (2.15%). This reassures the earlier emphasized hydration enhancing properties of biochar. However, the mortar samples with CO_2-treated biochar added showed the lowest compressive and tensile strength characteristics when compared with the controlled mortar and the mix with untreated biochar. This was attributed to a possible microcracking and debonding due to volume expansion as a result of carbonation chemical reactions [30].” Ironically, Wang et al. [80], introduced the idea of external carbonation of biochar-added mortar samples, which were treated in the controlled CO_2 environment under 16 psi pressure for 24 hours. TGA analysis of CO_2-treated mortar block showed a 21% reduction in CH content (transferred to C-S-H and CC), which has resulted in the rise of compressive strength by 68%.

The study conducted by Ryan Mrad indicates that biochar obtained from rice husk is a porous material that enables water to penetrate easily into it [81]. The porosity increases the water retention capacity of the biochar and also serves as an internal curing agent that improves the hydration rate of the cement. Internal curing is different from regular curing where water is added to the external surfaces. The moisture lost due to external drying or consumed during hydration reaction is restored by drawing water from the pores of the biochar [26]. It increases the rate of hydration of the cement by supplying the water from its pores filled with water within the concrete [81].

During the investigation, it has been found that the finer biochar particles mix with lime to provide a stable lime-pozzolana compound with definite cementitious properties [82]. The free lime present in the mix is hydrolyzed. Due to the presence of carbon, biochar has the filler effect [83] that enables the particles to outspread in the blended cement paste resulting in an improved hydration reaction. It is a well-known fact that pozzolanic activity has a significant impact on the durability and strength gain of concrete, the amount of $Ca(OH)_2$ fixation during the titration can be used to determine an agrowaste's pozzolanic activity. For example, J.J Nair et al. [84] conducted a study on untreated and treated coconut shell biochar samples. The untreated biochar produces 208.7 mg of $Ca(OH)_2$, but the pre-treated biochar produces nearly twice as much. Pavlikova et al. [75] conducted the pozzolanic activity test also known as Chapelle test, and found 1294 mg Ca(OH)2/g of wood-based biomass ash (WBA) fixation, demonstrating its reactivity in lime-based blends.

2.2 Research Gap

1. From the literature review, it can be seen that agro-waste has been used for developing concrete but a lot many limitations have also been reported along-with. This is primarily because of the stage at which an agro-waste could be used.
2. In most of the studies that are reported, suggests that agro-waste has not been processed before its utilization in concrete. This has led to poor results and insignificant usage in construction.
3. No study provides an adequate investigation into effect of rice husk biochar on the fresh and hardened properties of cement mortar and concrete.
4. Furthermore, no study have been performed comparing the lifecycle assessment of the ordinary and Biochar concrete that can form the basis for optimization of the concrete mix design

Concluding Remarks

According to the literature assessment, it is seen that biochar has been introduced in the cement mortar and concrete as a cement replacement material in the recent years but agricultural waste has been used for this purpose for many years. As biochar has the potential to be used as a component in concrete, extensive study has been initiated on its usage.

Chapter-3

3.1 Materials and Test Methods

The experimental frame work shown in Figure 3.1 is followed to examine the effect of inclusion of biochar as a partial replacement of cement in cement mortar and concrete. The research work includes characterization of materials, tests for fresh and hardened properties of cement mortar and concrete, non-destructive tests and lifecycle analysis. The following flowchart is adopted for the present research work:

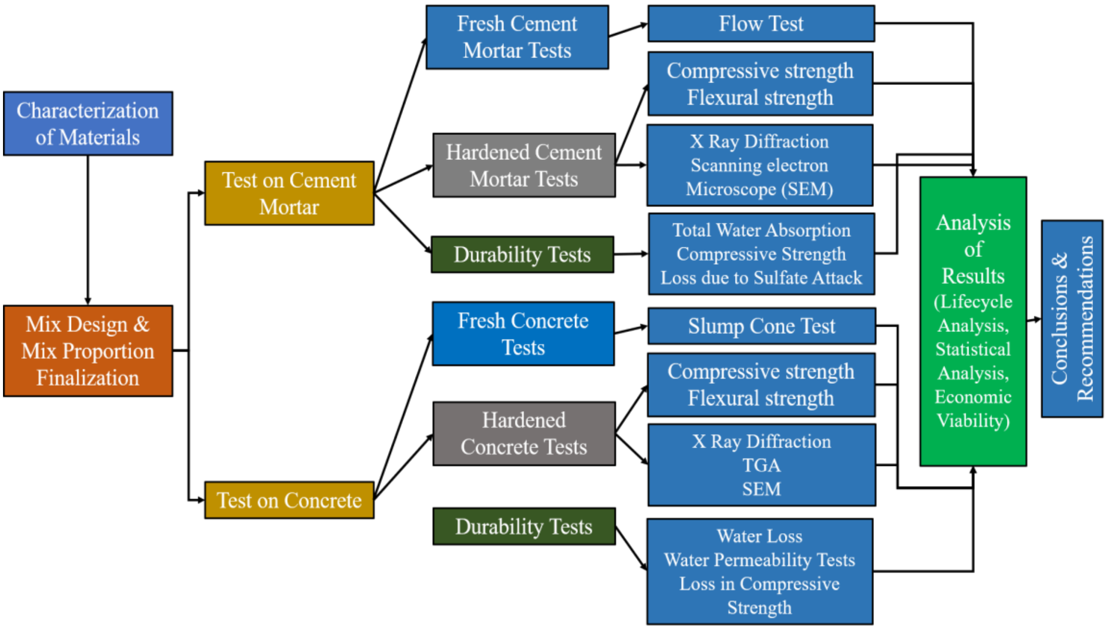

Figure 3.1: Flowchart showing experimental frame work.

The research methodology employed to accomplish the objectives of the present research work is explained in Table 3.1. The experimental work performed in the laboratories and the techniques employed to study the properties of cement mortar and concrete are tabulated as follows:-

Table-3.1: Methodology

Objective	**Analysis to be under taken**	**Instruments/ processes/ software to be used**
To investigate the mechanical and	Flow test Compressive strength	Flow Table

durability properties of cement mortar incorporating agrowaste.	Split Tensile Strength Flexural strength Compressive strength loss due to Sulfate attack Water Absorption X Ray Diffraction Scanning electron Microscope (SEM)	Compression Testing Machine X Ray Diffraction Scanning electron Microscope (SEM)
To study the mechanical properties of agro-waste based concrete.	Sand Gradation Curve Workability Compressive strength Flexural strength Correlation Analysis Regression Analysis	Sieve Analysis Slump Cone Test Compression Testing Machine
To study the Micro-structural and durability properties of agro-waste based concrete.	X Ray Diffraction Scanning electron Microscope (SEM) Thermogravimetric Analysis Water Loss Compressive strength loss due to Sulfate attack Permeability Test	X Ray Diffraction Scanning electron Microscope (SEM) Thermogravimetric Analysis Compression Testing Machine Concrete Permeability Test Apparatus
A Comparative Lifecycle Assessment of Ordinary and Agrowaste Based Concrete	To evaluate and quantify the impacts of the product over the whole life using the cradle-to-gate approach.	The Impact assessment of production of $1m^3$ concrete as developed in OpenLCA software

3.1.1 Cement

Ordinary Portland cement (OPC) of grade 43 shown in Figure 3.2 was used as a main binder constituent to prepare the specimens of cement mortar and concrete. In the experimental study the OPC grade 43 conforming to BIS: 8112-1989 [85] is used. Its physical properties such as specific gravity, fineness following procedures in BIS: 4031 (Part-1) [86], standard consistency following procedures in BIS: 4031 (Part-4) [87], soundness following procedures in BIS: 4031 (Part-3) [88], initial and final setting time following the procedures in BIS: 4031 (Part-5) [89] have been determined and shown in Table 3.2. The chemical composition of OPC is shown in Table 3.3.

Figure 3.2: OPC Grade 43 Cement

Table 3.2:- Physical Properties of Cement (Grade 43)

Material	Specific gravity	Fineness (%)	Standard Consistency (%)	Soundness Of cement	Initial Setting time	Final setting time
Cement (43 grade)	3.2	97.54	32	1mm	97 Min.	348 Min.

Table-3.3: Chemical Compositions of Ordinary Portland Cement

Materials	Chemical Composition (%)					
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O
OPC Grade 43	21	5.5	3.5	67	2.3	2.5

3.1.2 Aggregates

The locally available natural sand conforming to Zone-II (BIS: 383-1970) [90] shown in Figure 3.3 (a) is used as a fine aggregate. The particle size distribution curve of the sand determined by following the procedures in BIS: 2386, Part-1 [91] with the maximum size of 4 mm and the fineness modulus of 2.53 is shown in Figure 3.4. The specific gravity of the fine aggregates and water absorption found using BIS: 2386, Part-3 [92] is 2.5 and 1% respectively. Coarse aggregates shown in Figure 3.3 (b) with a maximum size of 20 mm with a specific gravity of 2.63 and a fineness modulus of 6.8 is used in the present research work.

(a) **(b)**

Figure 3.3 (a) Dry Sand **(b)** Coarse Aggregate

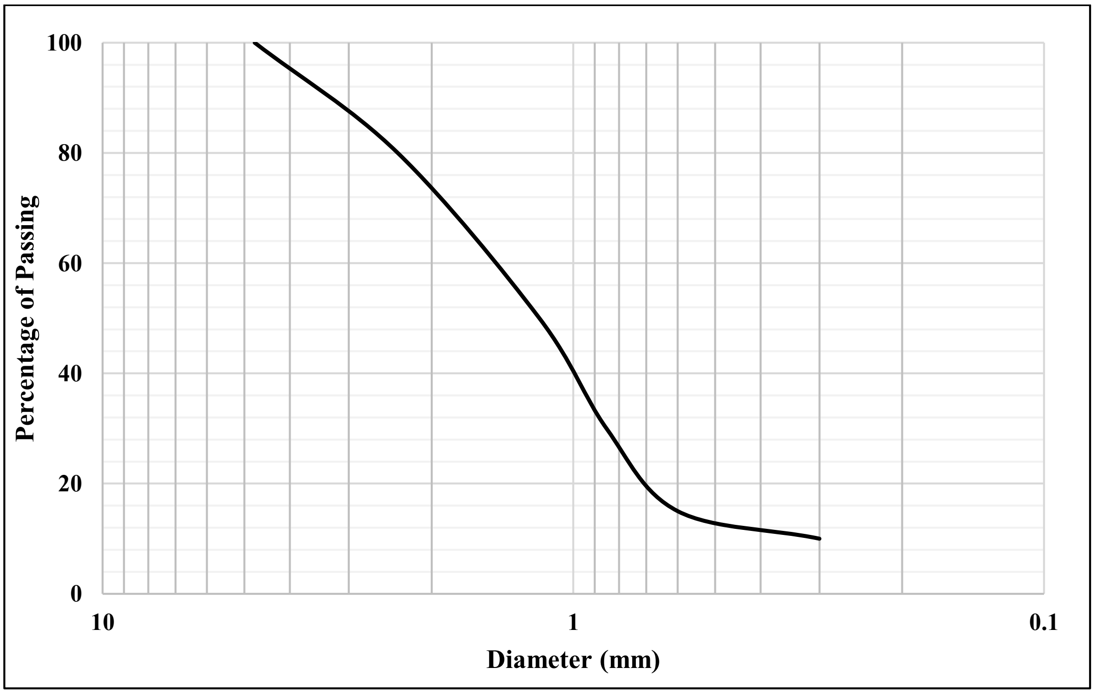

Figure 3.4 - Particle size distribution curve of sand

3.1.3 Rice husk Biochar (RHB) characterization

3.1.3.1 Biochar Preparation

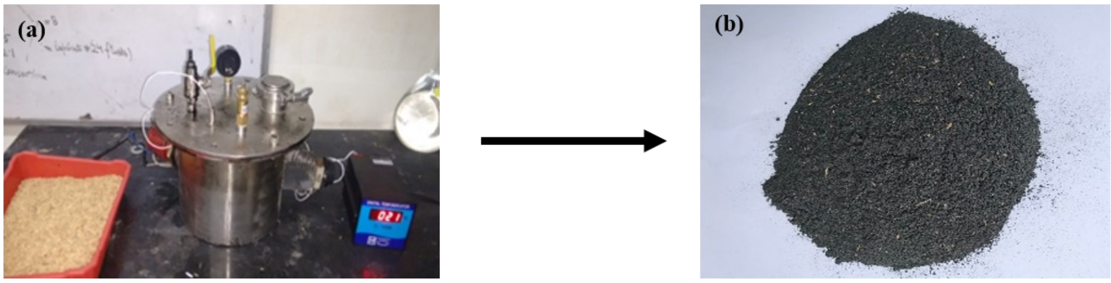

Figure 3.5: (a) Kiln used to prepare Biochar (b) Biochar

The key component of the current study is biochar (Figure 3.5), which is made in the labs of the Punjab Agricultural University in Ludhiana from rice husk agricultural leftover gathered from paddy fields in Punjab (India). The biochar is produced under controlled conditions through pyrolysis at a maximum operating temperature of 550°C to avoid thermal cracking and secondary pyrolysis, which results in significant solids yield of 40% as shown in Table 3.4. The biochar is dried at a temperature of 60–65 °C before the process of pyrolysis. The porosity of the produced biochar is between 60% and 70%. Fragmentation and vapour yields may rise with a wider temperature range.

Table 3.4: Properties of Biochar

Biochar	**Bulk density (g/cm^3)**	**Ash content (%)**	**Porosity (%)**	**pH**	**EC (mS/cm)**	**CEC (Cmol Kg^{-1})**	**Yield (%)**
550^0C (Rice Husk)	0.086±0.004	79.0±8.9	61.27±7.2	8.11±0.7	2.87±0.34	6.76±0.7	38.4±1.8

3.1.3.2 Energy-Dispersive X-ray Spectroscopy (EDS) analysis

The basic elemental biochar composition from the EDS analysis in Figure 3.6 shows that it is a carbon-rich material also containing other elements such as Carbon (C) 50.2%, Oxygen (O) 34.4% and Silica (Si) 13.5%, in addition to traces of Potassium (K), Calcium (Ca) and magnesium (Mg).

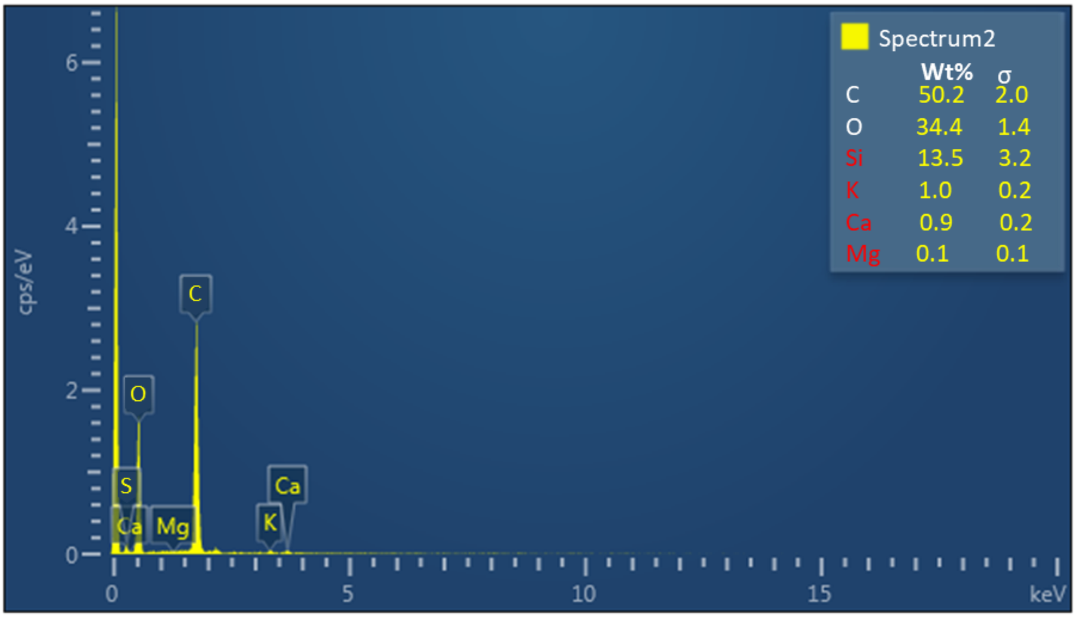

Figure 3.6: Energy-Dispersive X-ray Spectroscopy (EDS) analysis of Biochar samples.

Rice-husk biochar contains a sufficient amount of silica (13.5%). The silicon dioxide in biochar combines with extra calcium hydroxide ($Ca(OH)_2$) in the final stage of the subsequent pozzolanic reaction to generate C-S-H gel, which increases the strength of the pozzolanic composite, or biochar concrete.

$$(3CaO.SiO_2) + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O\ (gel) + 3Ca(OH)_2 \tag{3.1}$$

$$2(2CaO.SiO_2) + 4H_2O \rightarrow 3CaO.2SiO_2.3H_2O(gel) + Ca(OH)_2 \tag{3.2}$$

The pozzolanic reaction between SiO_2 and $Ca(OH)_2$ is as follows:

$$2SiO_2 + 4Ca(OH)_2 \rightarrow 3CaO.2SiO_2.3H_2O(gel) + Ca(OH)_2 \tag{3.3}$$

The biochar produced is cooled, powdered mechanically and packed in sealed containers.

3.1.3.3 Pozzolanic Activity Measurement

To evaluate the pozzolanic activity of the biochar using Chapelle test [75], sample is prepared by mixing 1gm biochar and 2gm of calcium oxide powder in a 25 ml of deionized water. After stirring the solution for 16 hours at 90°C, it is cooled down. Then 250 ml of 0.7M sucrose is mixed and stirred for 15 minutes, filtered and a small amount of 0.1% phenolphthalein is mixed. The final solution is then treated with 0.1 N HCl. The amount of Ca $(OH)_2$ consumed per gram is evaluated using the following equation:

$$Ca(OH)_2 = 2 * \frac{V_b - V_s}{V_b} * \frac{74}{56} * 1000 \quad (3.4)$$

where V_b denotes the volume of 0.1 N HCl used in the blank test (without biochar), V_s denotes the volume of 0.1 N HCl used to treat the solution containing biochar sample. The pozzolanic activity of biochar was found as 960 mg of $Ca(OH)_2$/g which satisfies the minimum required value of 650 mg of $Ca(OH)_2$ [75].

3.1.3.4 Particle Size Distribution Curve

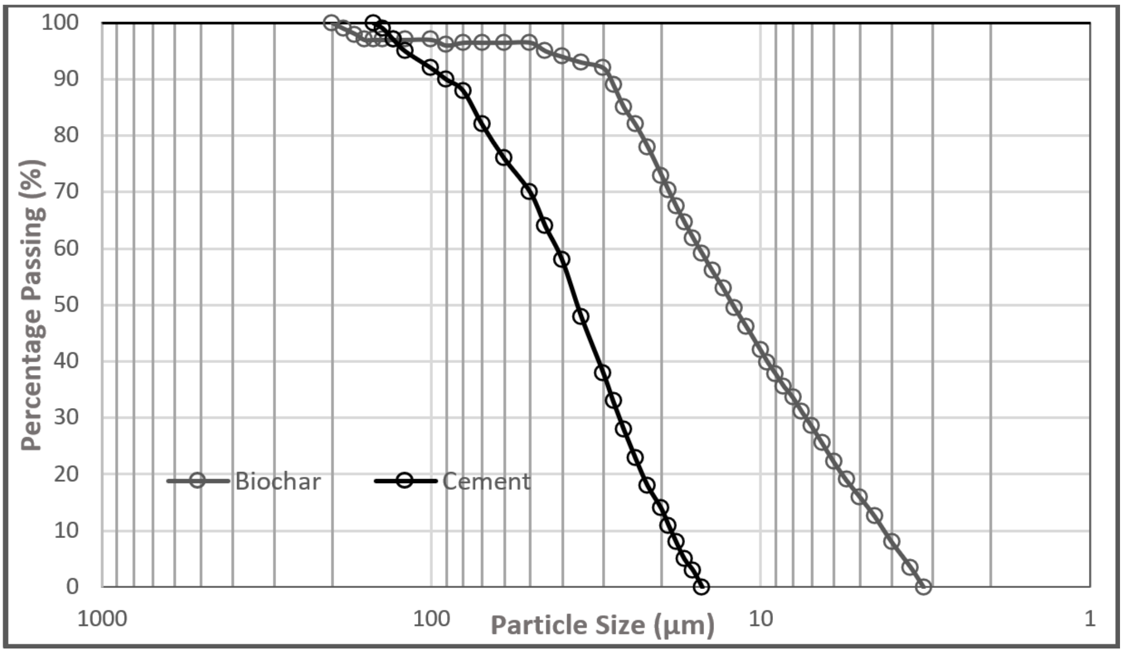

Figure 3.7: Particle Size Distribution of Biochar & Cement Particles

Malvern Zetasizer Nano ZS90 analyzer is used to measure the size of biochar and cement particles. Figure 3.7 depicts the particle size distribution curve, which demonstrates that around 40% of the biochar particles are finer than 10 µm. This indicates that biochar particles with a finer surface area and pozzolanic reactivity have a larger surface area and pozzolanic reactivity than cement particles.

3.1.3.5 Thermogravimetric Analysis (TGA)

Thermal analysis of the biochar samples was carried out in Perkin Elmer TGA 4000 instrument using Nitrogen gas at 20 ml/min. The weight of the biochar sample was taken as 7.579 mg. The temperature in the instrument was raised from 30°C to 800°C at 20°C/min and then kept at 800°C for 1.0 minute.

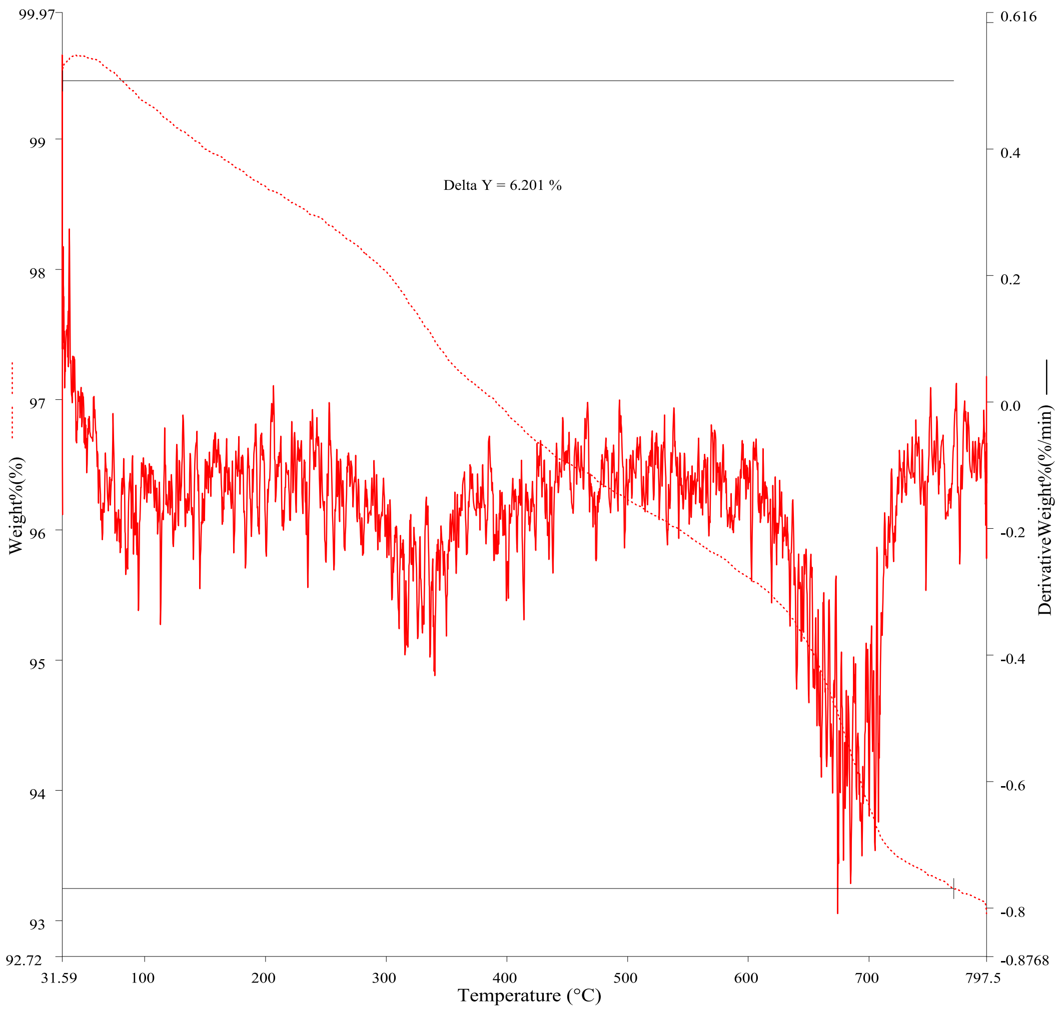

Figure 3.8: TGA curve for rice husk biochar (RHB)

To create graphs, the weight loss of the biochar sample corresponding to the temperature increase was noted. Less than 6.201% of the weight loss of rice husk biochar is recorded up to 800°C due to the presence of silica in the biochar. The thermal profile shown by the TGA curve in Figure 3.8 represents the thermostability of the biochar [35].

3.1.3.6 X-ray Diffraction

The sample was coarsely powdered and subjected to X-ray diffraction analysis using the "Bruker D8 Advance" instrument to determine the biochar's crystalline phase. The analysis is done over a 2θ range of 10° - 50° at a scanning rate of 0.15°θ/s. The red colour peaks obtained at 24 degrees indicates the significant proportion of silica in RHB as observed in Figure 3.9. The pattern was determined by diffraction peaks, which were matched with the diffraction pattern of SiO_2 to obtain the required crystals. The phase identifies an amorphous pattern with crystalline edges in Figure 3.9 demonstrating the stability and durability of the biochar [82]. Thus, biochar influences the hydration reaction and strength properties.

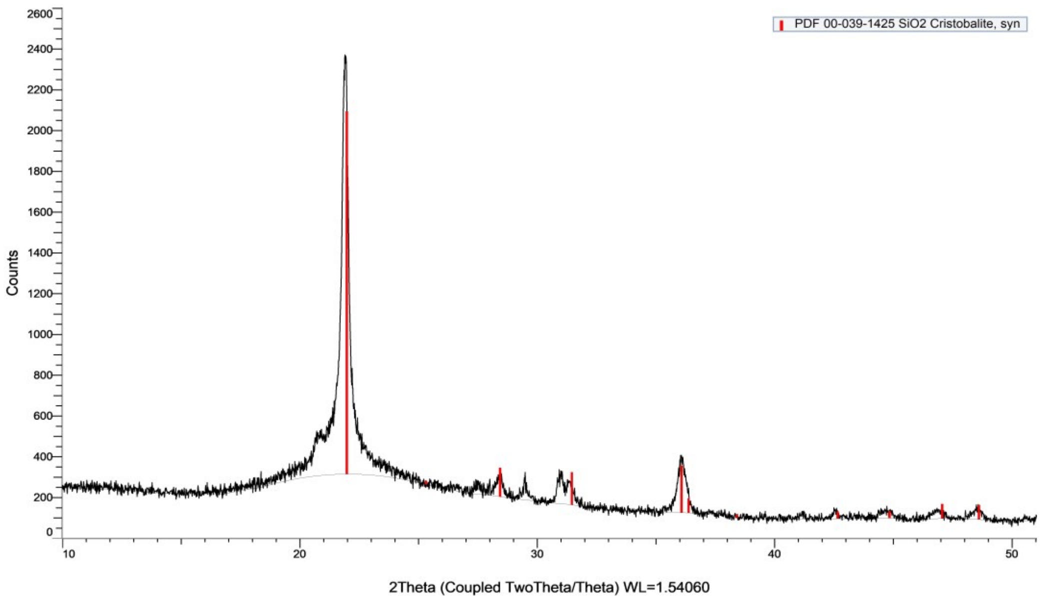

Figure 3.9: Phase identification of biochar

3.1.3.7 Scanning Electron Microscopy Analysis

JEOL FESEM scanning electron microscope was used to determine the morphology of biochar samples. A few nanometres thick Gold-coating was done on biochar samples to get high-resolution images. The pores created during the pyrolysis can be observed in Figure 3.10(c). The size range of (1-10) microns is shown in SEM images at 1,100 and 15,000 magnifications (Figure 3.10(a, c). The extensively cross-linked fibers can be observed through magnified images as shown in Figure 3.10(b). The cellular and microporous structure of the particles with interconnected fibers indicates their higher water absorption and retention capacity, which act as an internal curing agent [81,84] in the concrete and increase the degree of hydration when needed. The particles thus serve as a water storage reservoir in the concrete mix. Figures 3.10(d, e, f) show the elemental maps of Silica, Oxygen, and Potassium in the biochar samples as reported in Figure 3.6.

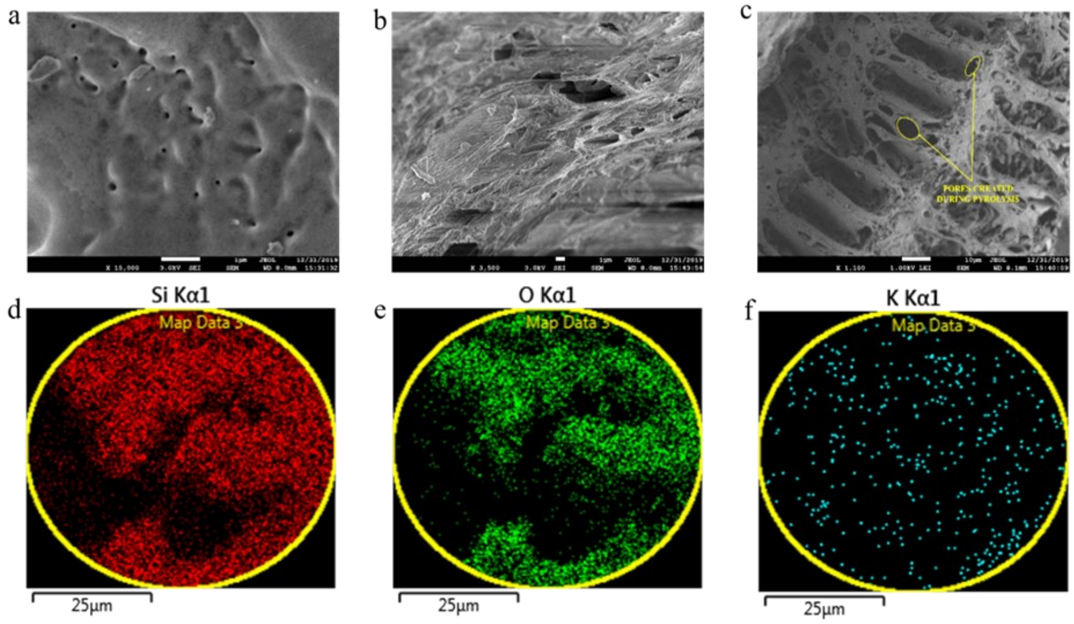

Figure 3.10: Scanning electron microscope images and color-coded EDS maps of biochar particles

3.2 Mortar Mix Proportion

To study the mechanical and durability properties of cement mortar incorporating agrowaste is a first objective of this research. Therefore, to examine the influence of biochar in cement mortar paste, six mixes, including the control mix, were prepared by replacing cement with biochar from 0 to 10%. The different mix proportions and the amounts of cement, biochar, sand and water are given in Table 3.5. According to earlier studies, the amount of biochar in cement mortar ranges from 0 to 15% replacement of cement [31, 38, 42]. The experimental research conducted in the lab of Lovely Professional University in India reveals that the effective water-cement ratio is reduced when more than 10% of the binder is replaced with biochar. This is due to biochar's greater ability to retain water (1gm of RHB retains 1.5 gm of water). With the foregoing information, 70.6 mm cubes of cement mortar were cast with a water-binder (biochar is also considered as binder) ratio of 0.5 using Portland cement and sand in the proportion of 1:3 (1 part cement, 3 parts sand). All of the mixes' flowability was evaluated during the mixing process; the findings are displayed in Figure 4.1. Volume of mortar is assumed to be 1m^3. Dry volume is calculated as 1.33m^3. Thus, amount of cement and fine aggregate calculated are shown in Table 3.4.

Table 3.5: Mix Proportions of Cement Mortar

Cement Mortar Type	Cement Replacement	Cement (Kg/m^3)	Biochar (Kg/m^3)	Sand (Kg/m^3)	Water (Kg/m^3)
CM (Control Mix)	0	478.8	0	1655.85	240
CR2 (Mix with 2% cement replacement)	2%	469.2	9.576	1655.85	240
CR4 (Mix with 4% cement replacement)	4%	459.65	19.15	1655.85	240
CR6 (Mix with 6% cement replacement)	6%	450.0	28.72	1655.85	240
CR8 (Mix with 8% cement replacement)	8%	440.5	38.3	1655.85	240
CR10 (Mix with 10% cement replacement)	10%	430.92	47.88	1655.85	240

3.3 Concrete Mix Design

It is a procedure of evaluating the appropriate mix proportions of binder, fine aggregates, coarse aggregates and water based on their physical and chemical properties such that the composite thus fabricated must achieve the required fresh, hardened and durability properties.

Design Procedure

Concrete mix for M25 concrete conforming to IS 10262 (2009) [93] was designed as per the following procedure:

Step-1. Target strength is determined using 28 day characteristic compressive strength (f_{ck}) by the following relation:

$$f_{target} = f_{ck} + 1.65S \quad (3.5)$$

Where, f_{target} is the target strength, f_{ck} is the characteristic compressive strength and S = $4 N/mm^2$ is the standard deviation adopted for M25 grade of concrete from table 2 of IS 10262-2019 [93].

Thus for M25 grade of concrete, target strength calculated is 31.6 MPa.

Step-2. For table 5 of IS 456 [94], water cement ratio (0.5) for moderate exposure condition is adopted to achieve the desired workability.

Step-3. The mix proportion of one metric cube of concrete is to be evaluated. The maximum size of aggregates are taken as 20mm and the coarse aggregates are angular in shape. Maximum water content of 186 Kg from Table 2 of IS 10262- 2009 [93] is adopted. Therefore, estimated water content is calculated as $186 + (3/100)186 = 191.6\, Kg/m^3$.

Step-4. Minimum cement content for moderate exposure and M25 grade of concrete from table 5 of IS 456 [60] is 300 Kg. Therefore, the desired cement content is 383.2 Kg.

Step-5. As per IS 10262- 2009, Volume of coarse aggregate per unit volume of total aggregate = 0.62 (for w/c ratio – 0.5 and fine aggregate (maximum size = 20mm) conforming to Zone-II) = $0.62\, x\, 95\% = 0.589 m^3$ (For pumpable concrete, coarse aggregate proportion may be reduced up to 5%). Thus, volume of fine aggregate is $1 - 0.589 = 0.411$.

Step-6. Volume of cement is calculated as
$(Mass\ of cement/specific gravity\ of\ cement)\ x\ ^1/_{1000} = (383.2/3.2) x\ ^1/_{1000} = 0.11975\ m^3$.
Volume of water - $(Mass\ of\ water/specific gravity\ of\ water)\ x\ ^1/_{1000} = (191.6/1) x\ ^1/_{1000} = 0.1916\ m^3$.
Volume of total aggregates - $a - (b + c) = 1 - (0.11975 + 0.1916) = 0.68865\ m^3$

Thus, Mass of coarse aggregates – $0.68865\ x\ 0.589\ x\ 2.63\ x\ 1000 = 1066.76\ Kg$

Mass of fine aggregates - $0.68865\ x\ 0.441\ x\ 2.5\ x\ 1000 = 707.58\ Kg$

3.3.1 Concrete Mix Proportions

To evaluate the mechanical performance of biochar concrete, five mix designs including a control mix were developed by replacing cement with biochar in concrete in varying amounts (0-8%) as illustrated in Table 3.6. The water-binder ratio was taken as 0.5. The proportion of biochar was based on the previous studies, past investigations performed in the lab, and the loss of free water in the mix. The replacement of binder with biochar beyond 8% results in a loss of free water in the mix. The slump used for the workability tests varies between 90 to 63 mm. A substantial amount of superplasticizer is demanded for maintaining workability of the concrete mix having biochar of more than 8%, which significantly affects the overall strength characteristics of the concrete [95]. The concrete's performance was evaluated using tests for water loss, compressive strength, flexural strength, and permeability.

Table 3.6: Mix Proportions of Concrete

Mix	Bio char (%)	Cement (kg/m^3)	Biochar (kg/m^3)	Fine Aggregates (kg/m^3)	Coarse Aggregate (kg/m^3)	Water (Kg/m^3)
CM (Control Mix)	0	383.20	0.00	707.60	1066.75	191.60
B2(Mix with 2% cement replacement)	2	375.50	7.65	707.60	1066.75	191.60
B4 (Mix with 4% cement replacement)	4	367.85	15.30	707.60	1066.75	191.60
B6 (Mix with 6% cement replacement)	6	360.20	23.00	707.60	1066.75	191.60
B8 (Mix with 8% cement replacement)	8	352.55	30.65	707.60	1066.75	191.60

3.4 Experimental Test Procedure

The experimental test procedure includes various destructive, non-destructive test performed in the laboratory for evaluating fresh, hardened and durability properties of cement mortar and concrete. Lifecycle analysis has also been carried out to evaluate and quantify the impacts of concrete over the whole life using the cradle-to-gate approach.

3.4.1 Fresh properties of cement mortar and concrete

3.4.1.1 Flowability

Flowability of cement mortar samples of different mixes is conducted using a flow table test conforming to IS: 5512 :1983 [96] to determine the water content for cement mortar specimens (Figure 3.11). The flow of cement mortar is measured by calculating the average base diameter by the following relation:

$$Flow = \left[\left(D_{avg} - D_o\right)/D_o\right]x100 \quad (3.6)$$

Where, D_{avg} = Average base diameter, D_o = Original base diameter

Figure 3.11: Flow Table Test Setup

3.4.1.2 Workability

Slump cone tests conforming to IS: 7320-1974 [97] were conducted to measure the workability of different concrete mixes. Concrete was poured in four layers over the cleaned mould (as shown in Figure 3.12). The layers of concrete were compressed with a tamping rod (16 mm diameter, rounded end) over the course of 25 strokes to ensure that the concrete was evenly distributed throughout the mould. The surplus concrete mass was removed using a trowel after the top surface had been tamped. By lifting the mould vertically, the concrete was then instantly removed through the mould. The slump is determined by subtracting the height of the conical mould from the peak of the settled concrete.

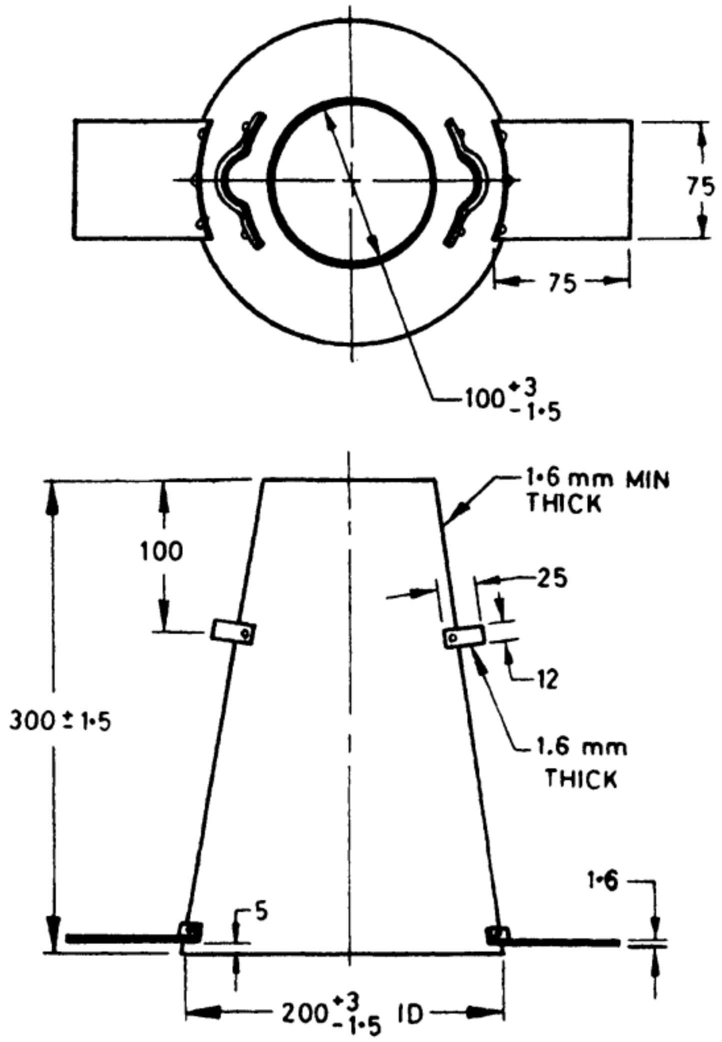

Figure 3.12: Slump Cone Test Setup

3.4.2 Hardened properties of cement mortar and concrete

3.4.2.1 Compressive Strength

To compare the compressive strength of different specimens of cement mortar, 70.6 mm size cube moulds conforming to IS: 4031(Part 7): 1988 [98] were used. After 24 hours, cubes were taken out of the moulds and immersed in clean water. Three specimens were tested for compressive strength for each period of curing according to IS: 4031 (Part-7). The compressive strength after 7, 14 and 28 days of curing were tested and compared.

Based on different mix proportions with the variation of biochar content, concrete cubes of 150mm x 150mm x 150 mm conforming to IS: 10086-1982 [99] standards, were prepared and cured for 7, 14, 28, 90 and 545 days. The cubes were taken out of the water after a predetermined curing period, and any remaining surface water and grit were wiped off. The cubic specimen is then put into the 3 MN-capable equipment (Figure 3.13) in such a way that the load is applied from top and bottom side of the specimen. Compressive strength of samples is calculated as follows:

$$Compressive\ Strength\ (MPa) = \frac{F_c}{A_c} \tag{3.7}$$

where F_c represents the maximum load and A is the are of the specimen in contact with the auxiliary plates.

Figure 3.13: Compression Test Setup

3.4.2.2 Flexural Strength

Tests for flexural strength of cement mortar beam specimen, measuring 160mm x 40mm x 40mm (Figure 3.14) were carried out for each period of curing and tested following the requirements of ASTM 348–02 [100].

The flexural strength test of concrete beams is carried out on a three-point arrangement conforming to ASTM C78/C78M (2016) [101] procedure. The tests were carried out on prismatic samples of 100mm x 100mm x 500mm after 28 days of curing in water for various concrete mixes. The experimental test is conducted on a compression testing machine where the sample is placed on two supporting pins a fixed distance apart. Flexural strength for cement mortar beam is calculated using equation (3.8).

$$\sigma_f = {}^{3FL}\!/_{2bd^2} \quad (3.8)$$

where, σ_f is flexural strength, L, b, and d are length, breadth, and depth respectively of cement mortar sample and F is the maximum load applied.

Figure 3.14: Flexural Strength Test Setup

3.4.3 Durability properties

3.4.3.1 Total Water Absorption

To determine the amount of water absorbed by cement mortar specimens, the cured specimens were dried for 48 hours in an oven at a temperature of 100 + 10º C, and then the temperature was gradually reduced to room temperature. The mass of dried samples was recorded and samples were again immersed in water to saturate for 24 hours. Before measuring the mass of wet specimens, excess water was removed using a cloth. TWA (Total Water Absorption) was calculated using equation (3.9) [102].

$$TWA = (m_s - m_d)x \, {}^{100}/_{m_d} \quad (3.9)$$

where m_s and m_d are the masses of saturated and dried samples respectively.

3.4.3.2 Water Loss

Water loss determines the water retention capacity of the concrete mixes for internal curing of the concrete. High water retention and internal curing improves the mechanical properties of the concrete by increasing the effective hydration of cement in the composite [28].

3.4.3.3 Water Permeability Tests

Concrete has pores through which water, air or other substances can enter and exit. Permeability is a major of the amount of these substances entering the concrete matrix. This parameter is a determinant of the long-term durability of concrete. Thus, to increase chemical resistance and to prevent the steel from rusting, concrete must not allow any substance to enter. Water permeability test of concrete is done conforming to IS:3085-1965 [103] as shown in Figure 3.15. The coefficient of permeability shall be calculated as follows:

$$K = \frac{Q}{AT\frac{H}{L}} \quad (3.10)$$

where

K = coefficient of permeability in cm/sec;

Q = quantity of water in millilitres percolating over the entire period of test after the steady state has been reached;

A = area of the specimen face in cm*;

T = time in seconds over which Q is measured; and

$\frac{H}{L}$ = ratio of the pressure head to thickness of specimen, both L expressed in the same units.

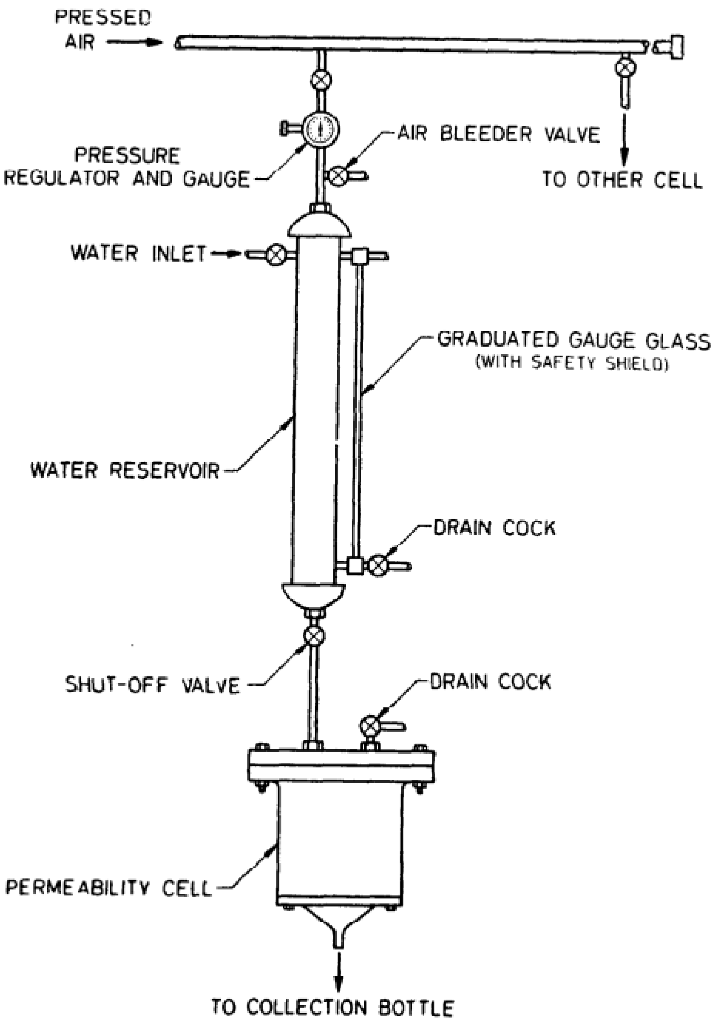

Figure 3.15: Permeability Test Setup

3.4.3.4 Compressive Strength Loss Due to Sulphate Attack

Sulfate attacks on concrete can be caused by sodium sulfate solution or other salts containing SO_4^{2-} ions. SO_4 present in the solution interacts with Ca^{2+} ions in the concrete and produces gypsum which causes micro-cracks and lowers the mechanical strength of C-S-H gel.

After the cement mortar samples were cured for 28 days, the samples were divided into two sets; one set of cement mortar specimens were immersed in the 5% Na_2SO_4 solution and the second set of cubes were immersed in water for testing after 7, 28, 56, and 90 days [104]. The percentage of loss of compressive strength was determined by comparing the compressive strength of samples immersed in Na_2SO_4 solution and water.

Likewise, the compressive strength of the concrete specimens immersed for 90 days in 5% Na_2SO_4 solution was compared with the concrete specimens cured in water for comparing strength loss.

3.4.4 Non-destructive tests

3.4.4.1 Thermogravimetric analysis (TGA)

TGA is a technique of material characterization using a method of thermal analysis in which weight loss of concrete specimens in the finely powdered form corresponding to the rise in temperature in the inert atmosphere is recorded to obtain plots [30,42]. The temperature is gradually raised from 30°C to 600°C at 20°C/min. Thermal analysis of the samples are carried out in thermogravimetric analyser namely Perkin Elmer TGA 4000 instrument using Nitrogen as inert gas.

3.4.4.2 X-ray Diffraction

The strength and durability of composites of cement mortar and concrete are directly affected by the crystalline size, texture, and mineralogical composition. The specimens of cement mortar and concrete were finely ground and analysed using X-ray diffraction (XRD) [56].

3.4.4.3 Scanning Electron Microscopy (SEM)

The morphology of cement mortar and concrete samples is studied using JEOL FESEM. A few nanometres thick Gold-coating was done on samples to get high-resolution images. The mortar and concrete samples were finely ground and were examined under scanning electron microscopy (SEM). The magnified images of cement mortar paste, sand, and biochar particles show the surface texture, roundness, and smoothness of the respective particles [33].

3.4.5 Lifecycle Analysis of Biochar Concrete

A Life Cycle Assessment (LCA) is a useful technique for monitoring the environmental implications of a product or process in its whole life cycle [105]. It takes to account all the aspects that could harm or benefit the environment. The assessment follows the steps stipulated in [106, 107]. It is a systematic approach that consists of four phases as shown in Figure 3.16.

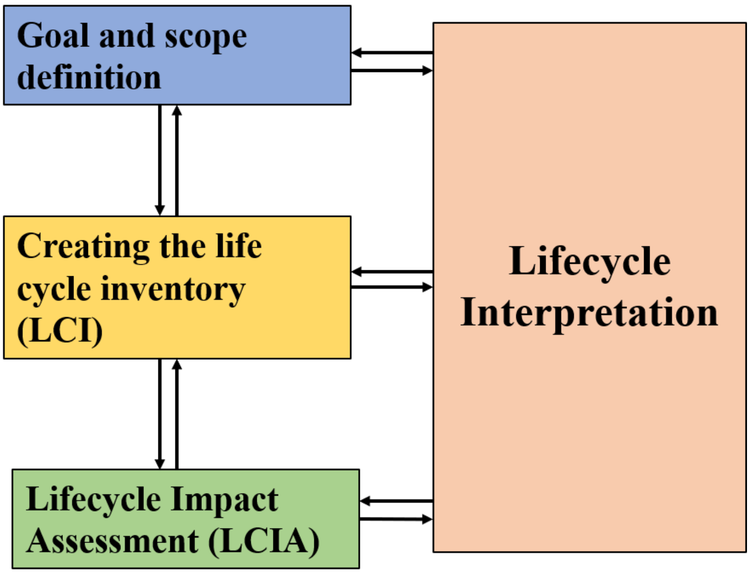

Figure 3.16: LCA Phases

3.4.5.1 Goal and Scope Definition

In this study, the purpose of LCA is to critically examine the environmental impact of ordinary and biochar concrete. One metric volume of concrete is considered as a functional unit. Figure 3.17 depicts the system boundary. The system boundary for analysis is shown in Figure 3.17. The process involves the mining of raw materials (cement, water, and aggregates), transportation, and the manufacturing of concrete. The Cradle represents the mining or the extraction of the material from the Earth and the Gate – the fresh concrete moving out of the RMC plant. Figure 3.18 represents the model graph for the production of 1m^3 concrete as developed in OpenLCA software based on the system boundary.

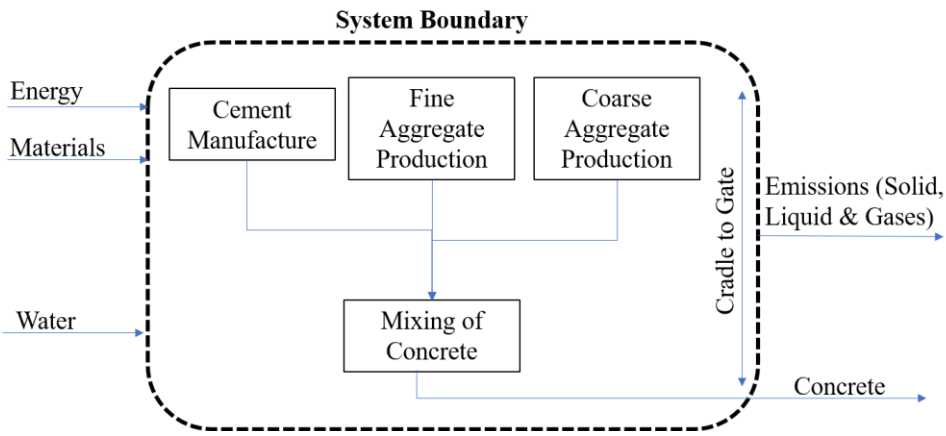

Figure 3.17: LCA Framework for Concrete production

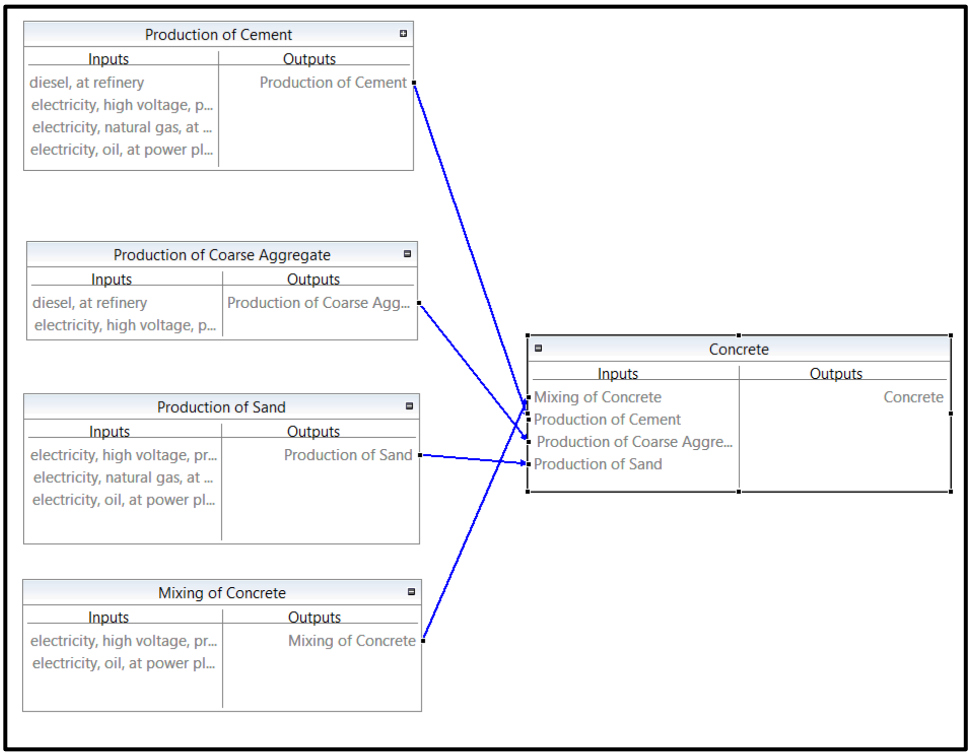

Figure 3.18: Model graph for the production of 1m3 concrete (Source: OpenLCA)

3.4.5.2 The Life Cycle Inventory (LCI)

The second phase in LCA is the life cycle inventory, which entails gathering data and methods for quantifying the proper inputs and outputs of a product system. Inputs refer to the resources used for the production whereas outputs include emissions to air, water, soil, etc. In this research, inventory results involve the collection of data on cement. The process map for a typical cement plant is shown in Figure 3.19.

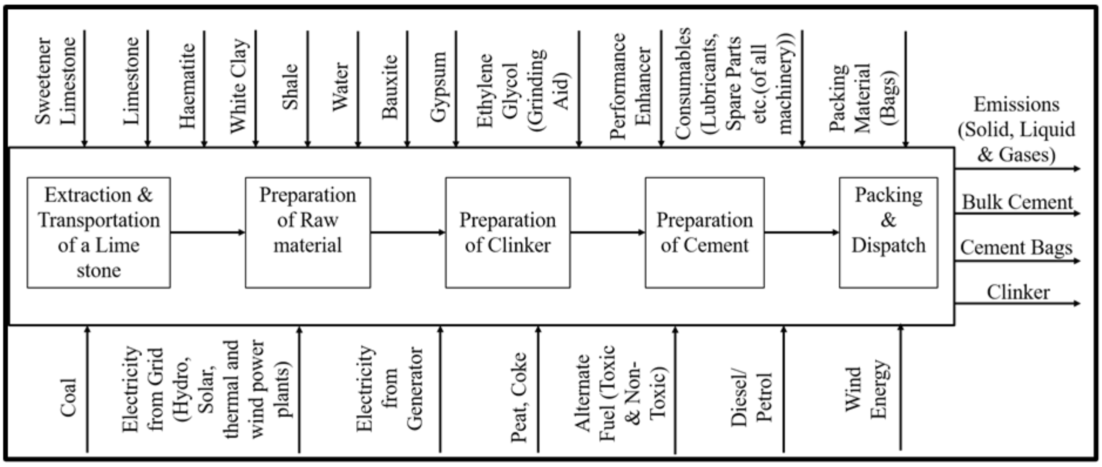

Figure 3.19: LCA Framework for cement production

Table 3.7 shows the supplies and transportation inventory list taken in to consideration in each concrete formulation. The life cycle analysis software "OpenLCA" was preferred to quantify the impact categories and to determine the potential influence on the environment. In the analysis, utilization of energy, fuels, raw materials and the discharge or pollutants emitted into the air, water, and soil during the processing of cement, sand, aggregate, and mixing of the concrete is considered. The inventory data for a production of one cubic meter of concrete is shown in Table 3.7. The inventory analysis has been done considering mix proportions shown in Table 3.6 and are based on "Life Cycle Assessment of Concrete", Environmental and Energy Systems Studies [108]. Depending on the lifecycle assessment range, system boundary, inputs, and outputs for the production of ordinary concrete and Biochar concrete, inventory of the materials are shown in Table 3.7 and 3.8, respectively. Since Biochar is a residual and landfilled, therefore, any emissions allocated to the materials are not considered significant for the production of the concrete and are not included within the system boundary. Environmental costs have not been considered with the processing of material due to its ready-to-use qualities.

Table 3.7: Inventory of materials for the production of $1m^3$ concrete

INPUTS								
Flow	Category	Sub-Category	Unit	Ordinary Concrete	Biochar Concrete (2%)	Biochar Concrete (4%)	Biochar Concrete (6%)	Biochar Concrete (8%)

Electricity, high voltage (at grid)	Electricity	Production mix	MJ	78926.5	77025.4	77021.6	77017.8	77014.0
Electricity, natural gas, (power plant)	Natural gas	Power plants	MJ	0.01650	0.01600	0.01602	0.01602	0.01601
Diesel (refinery)	Oil	Fuels	kg	1.148	1.112	1.105	1.098	1.091
Electricity, oil (power plant)	Oil	Power plants	MJ	0.8030	0.7830	0.7829	0.7826	0.7824
Peat (ground)	Resource	Biotic	kg	0.00053	0.00051	0.00050	0.00051	0.00051
Renewable fuels	Resource	Biotic	kg	0.0052	0.0051	0.0050	0.0051	0.0051
Energy, from coal	Resource	In ground	MJ	738.23	706.00	691.66	677.26	662.86
Hard coal	Resource	In ground	MJ	198.68	190.	186.14	182.20	178.39
Energy, potential (hydropower reservoir)	Resource	In water	MJ	0.82	0.80	0.79	0.80	0.80

Table 3.8: Outputs (Emissions released in the production of 1m^3 concrete)

Flow	Category	Unit	Ordinary Concrete	Biochar Concrete (2%)	Biochar Concrete (4%)	Biochar Concrete (6%)	Biochar Concrete (8%)
Ammonia	Emission to air	kg	0.0213	0.0207	0.0206	0.0205	0.0204
Carbon dioxide	Emission to air	kg	898.85	871.76	866.27	860.80	855.30
Carbon monoxide	Emission to air	kg	1.420	1.386	1.380	1.386	1.386
Hydrocarbons, aliphatic, alkanes, unspecified	Emission to air	kg	0.230	0.224	0.224	0.224	0.224
Methane	Emission to air	kg	4.88	4.74	4.72	4.70	4.68
Nitrogen oxides	Emission to air	kg	1.75	1.69	1.68	1.67	1.66

Particulates, < 10 um	Emission to air	kg	0.222	0.216	0.215	0.215	0.214
Phenol	Emission to air	kg	3.71E-05	3.55E-05	3.48E-05	3.40E-05	3.33E-05
Sulfur trioxide	Emission to air	kg	1.060	1.035	1.034	1.033	1.032

3.4.5.3 Life Cycle Impact Assessment (LCIA)

IMPACT World+ is a mid-point-based framework in which LCIA can be expressed in four viewpoints as shown in Figure (mid-point level viewpoint, damage level viewpoint, AoP viewpoint, and AoC viewpoint). An AoP viewpoint is categorized by grouping damages to human health, environmental quality, resource availability and ecosystem services as shown in Figure 3.20. An AoC viewpoint is expressed in terms of water-related damages, carbon-related damages, and other harms to human health and the environment [109].

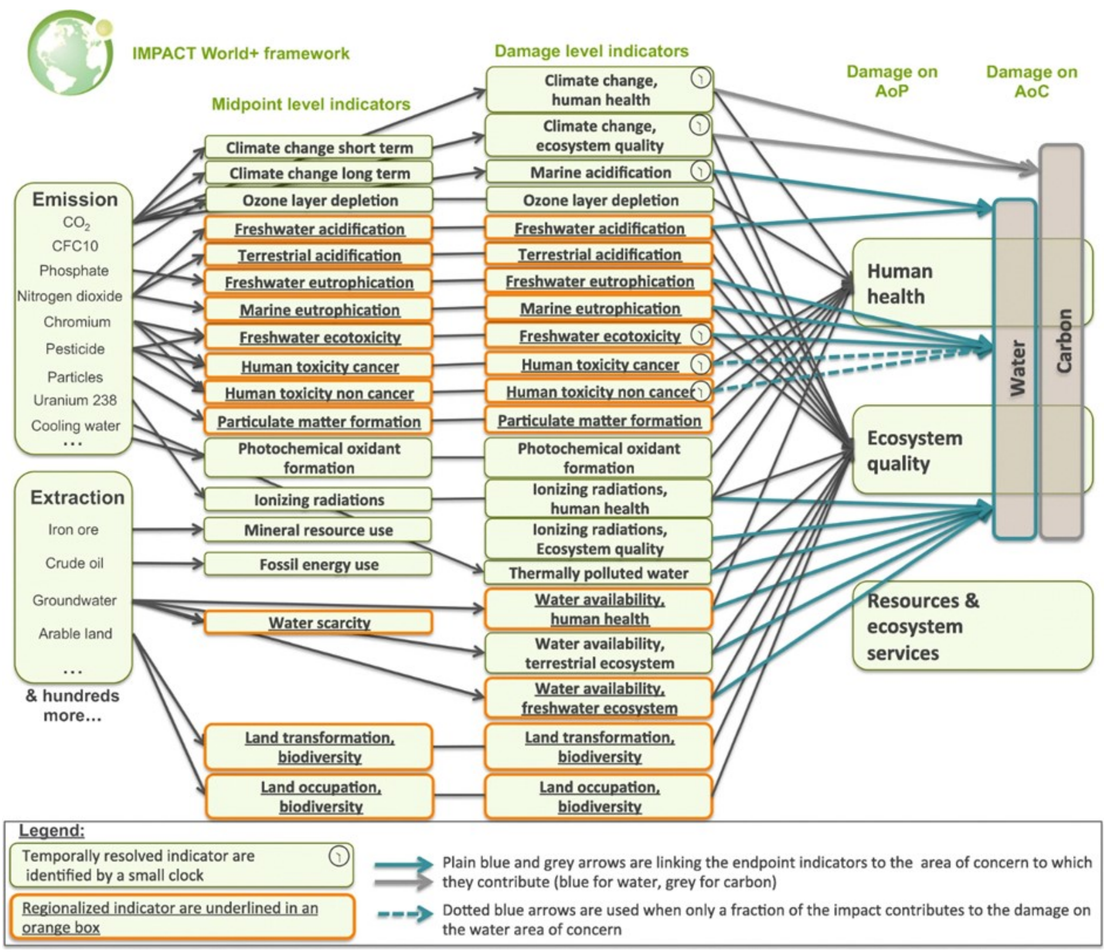

Figure 3.20: IMPACT World+ LCIA framework (Source: http://www.impactworldplus.org)

3.4.5.3 Lifecycle Interpretation

It is the fourth phase in LCA in which concrete mix designs are compared based on the following main issues: recognizing serious-environment issues, greenhouse gases emission evaluation for establishing the results to determine their reliability, framing conclusions, and recommendations. Thus, the most sustainable mix design of concrete is established.

Concluding Remarks

The characterization shows that the materials used in the study has the potential to be utilized for the production of cement mortar and concrete. The methodology used in the study focuses on mechanical strength properties, microstructural and durability analysis. The environmental analysis using life cycle assessment method for the comparative analysis of conventional and agrowaste based concrete will be showcasing the impact of inclusion of biochar as a cement replacement material on the different environmental indicators.

Chapter-4

4. Results & Discussions

4.1 Influence of biochar inclusion on the properties of cement mortar

4.1.1 Flowability

Flowability of all the samples of different mixes (Figure 4.1) was conducted to determine the water content for cement mortar specimens. Biochar absorbs and retains a substantial amount of mixing water, resulting in a stiffer mix. The physically absorbed water in biochar is eventually released during mortar hardening and can aid in internal curing. It was found that percentage of biochar content in the mix increases, the flow diameter decreases due to the more porosity and water-retaining capacity of biochar, hence reducing the flow and workability of the fresh cement mortar. Therefore, the samples with high biochar content give a lower flow diameter than the samples with low biochar content which effects compactness of cement mortar, that can lead to increase voids in the hardened paste.

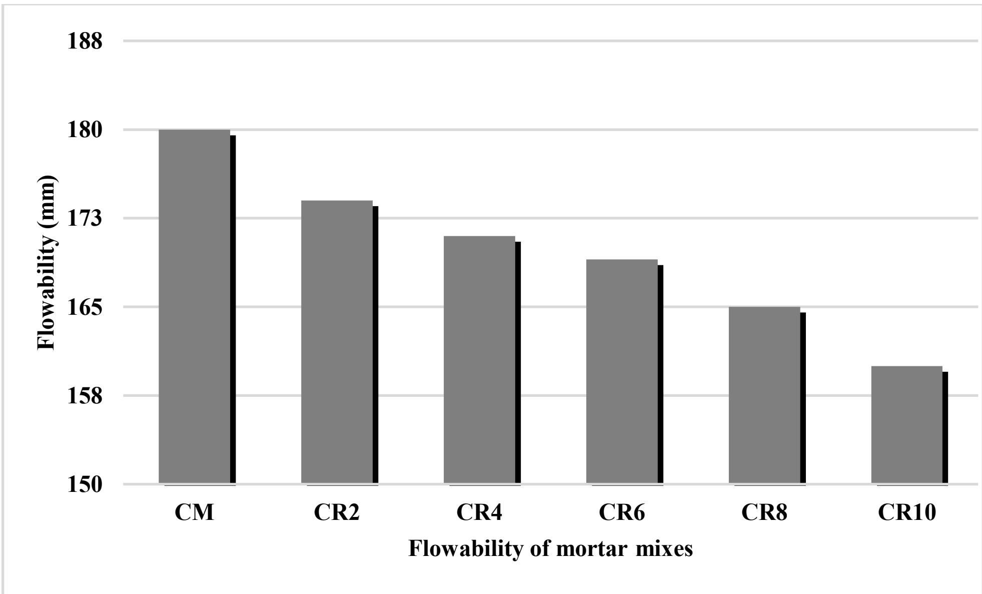

Figure 4.1: Flowability of Cement Mortar Mixes

4.1.2 X-ray Diffraction

The strength and durability of cement mortar composite are directly affected by the crystalline size, texture, and mineralogical composition. The specimens were finely ground and analyzed using X-ray diffraction (XRD). The assessment of the particles in the cement mortar mix CR2 is done by diffraction peaks in Figure 4.2 indicating the pattern and are matched to obtain the required crystals. The analysis shows silica (Si), calcium hydroxide $Ca(OH)_2$ with dicalcium, tricalcium silicate (C2S/C3S) phases, and calcium silicate hydrate (CSH). Peaks for CR2 are obtained at 2θ positions as shown in Figure 4.2.

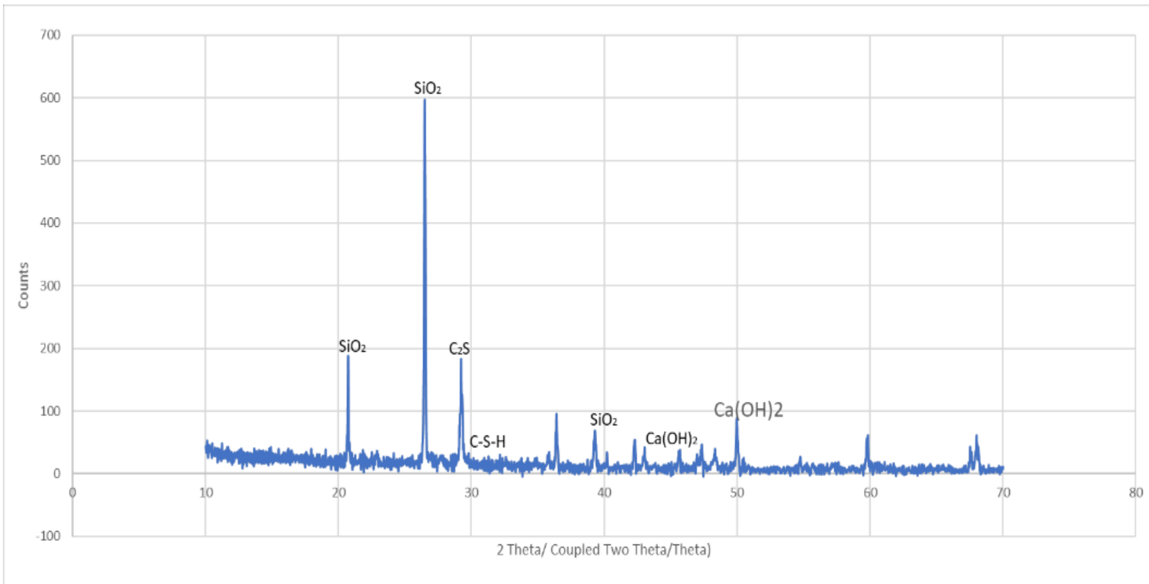

Figure 4.2: X-ray Diffraction Profile of Cement Mortar Mix With 4% Cement Replacement With Biochar

4.1.3 Scanning Electron Microscopy (SEM)

The mortar samples were finely ground and were examined under scanning electron microscopy (SEM). The magnified images of cement mortar paste, sand, and biochar particles show the surface texture, roundness, and smoothness of the respective particles. The magnified image in Figure 4.3(c) shows the hydrated phases of the cement mortar, sand appears as a grey colour whereas the voids in black shows porosity. Figure 4.3(d) shows dense gel formation at the interface of mortar and aggregate paste after 28 days of hydration. The microstructural properties of cement mortar are shown in Figure 4.3(d). The higher number of macro-pores of CR2 sample shows an improved interface zone in comparison to the plain cement mortar that can be easily distinguished due to the presence of pores and voids in the mortar paste. The result indicates the formation of CSH (Calcium silicate hydrate) due to the increased rate of hydration where the biochar particles act as micro fillers which densifies the cement mortar paste.

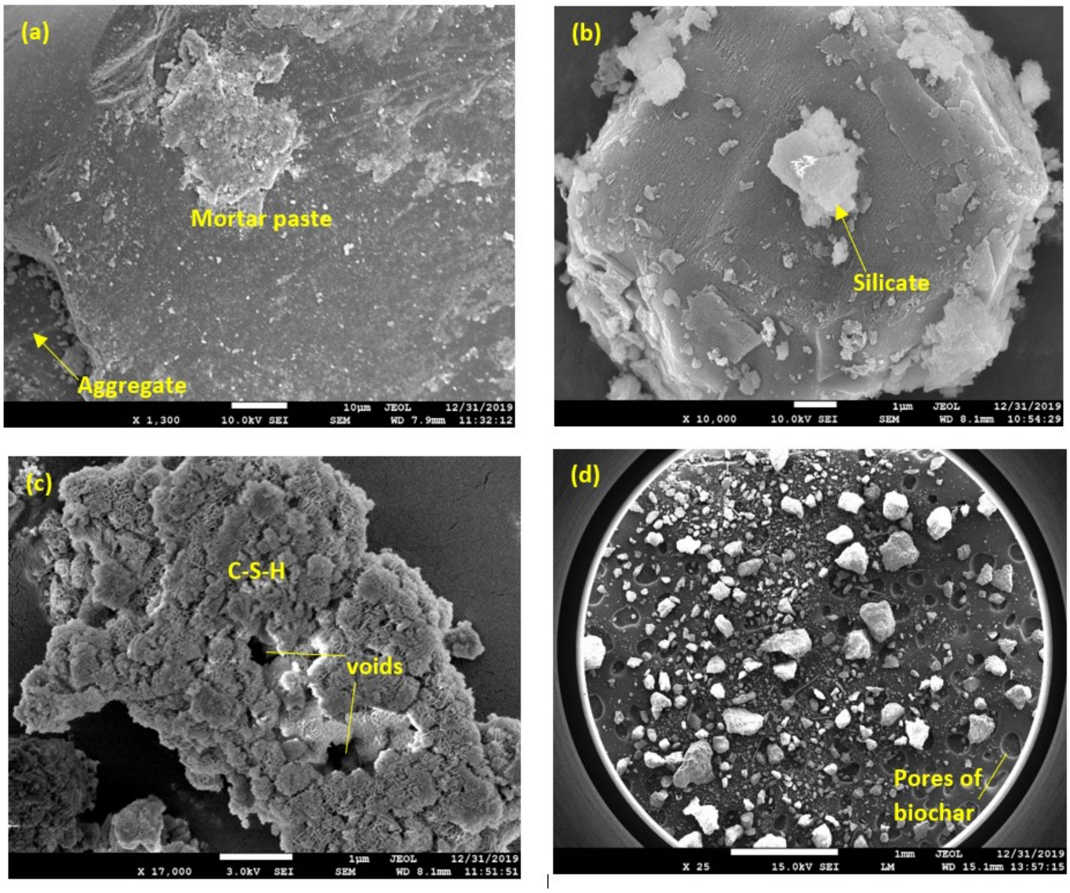

Figure 4.3 (a): Magnified Image Showing Mortar Mix and Aggregates, **(b)** Magnified Images Showing Silica, **(c)** Magnified Image of CR2 Sample Showing Voids and C-S-H Paste **(d)** Magnified Image Showing Pores of Biochar

4.1.4 Total water absorption (TWA)

TWA for the cement mortar mixes cured from (3 to 28) days is presented in Figure 4.4. Results suggest that the total water absorption (TWA) decreases with the age. It is observed that with the increase in biochar inclusion, CR2 shows a 0.5% increment as compared to the control specimen. Water absorption of the samples continuously increases due to the porosity and the water retention capacity of the biochar. Water absorption properties are also associated with the amount of porous carbon and microstructural properties (packing) of the cement mortar mixes as shown in Figure 4.3 (SEM images of the different mixes).

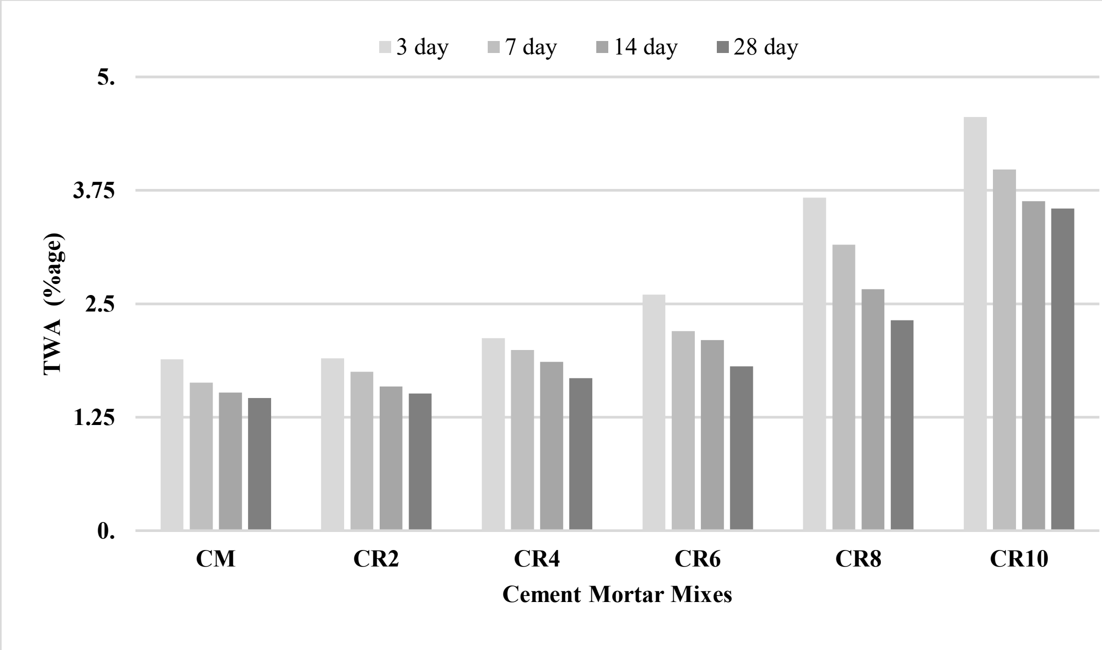

Figure 4.4: Total Water Absorption of the Mortar Mixes

4.1.5 Compressive Strength

The results presented in Figure 4.6 shows the effect of cement replacement with biochar in cement mortar cubes. After 7, 14, and 28 days of curing, compressive strength of cement mortar cubes were tested as shown in Figure 4.5. It has been discovered that mortars with varying biochar concentrations increase compressive strength in different ways. For example, inclusion of biochar at 2% and 4% resulted in increase in 28th day compressive strength by 8% and 2% respectively. In contrast, the inclusion of biochar at 6%, 8% and 10% results in a drop of strength by 28%, 34% and 43% respectively.

From the experimental analysis (Figure 4.6), it is clear that the maximum compressive strength (CS) of CR2 is obtained when 2% of cement in the mortar mix is replaced by Biochar. This is most likely owing to biochar's micro-filler action, which speeds hydration and resulting in a more compact matrix. Improved particle packing results in a more compact matrix that effectively transmits stress via composite action. The decline in compressive strength (CS) is noticed with the inclusion of biochar beyond 2%. The reduction in strength caused by the addition of a large amount of biochar can be attributed to the mortar's low density and larger porosity.

Figure 4.5: Compressive strength Test of Cement Mortar Cube of Size 70.6 x 70.6 x 70.6 mm^3

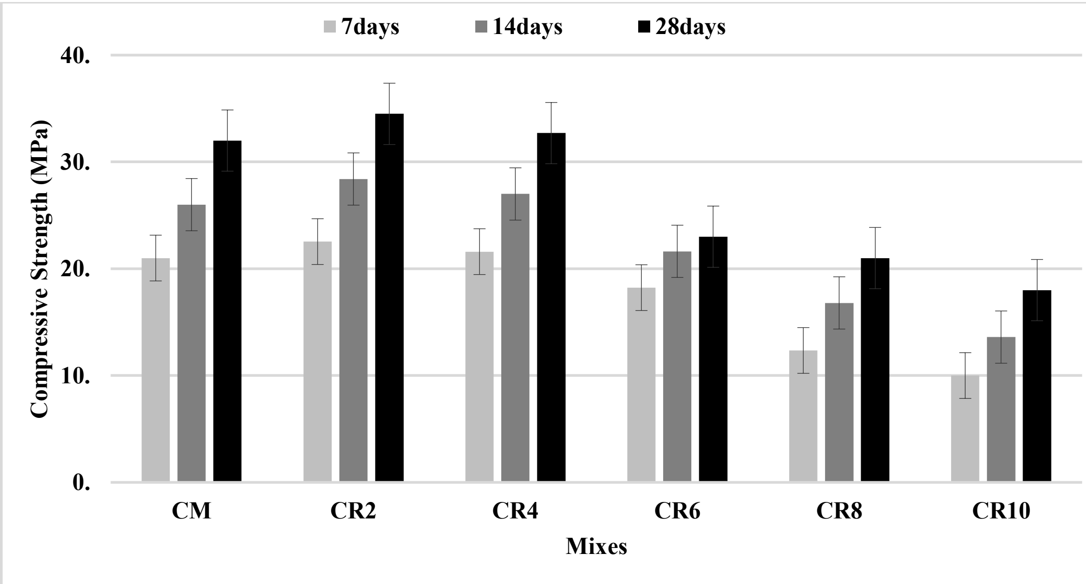

Figure 4.6: Compressive Strength (CS) of Cement Mortar Mixes at 7, 14, and 28 Days

4.1.6 Flexural Strength

The flexural strength results in Figure (4.8) depicts the influence of cement replacement with biochar in cement mortar. The flexural strength of cement mortar beams is tested after curing for 7, 14, and 28 days under a 3-point bending test as shown in Figure 4.7.

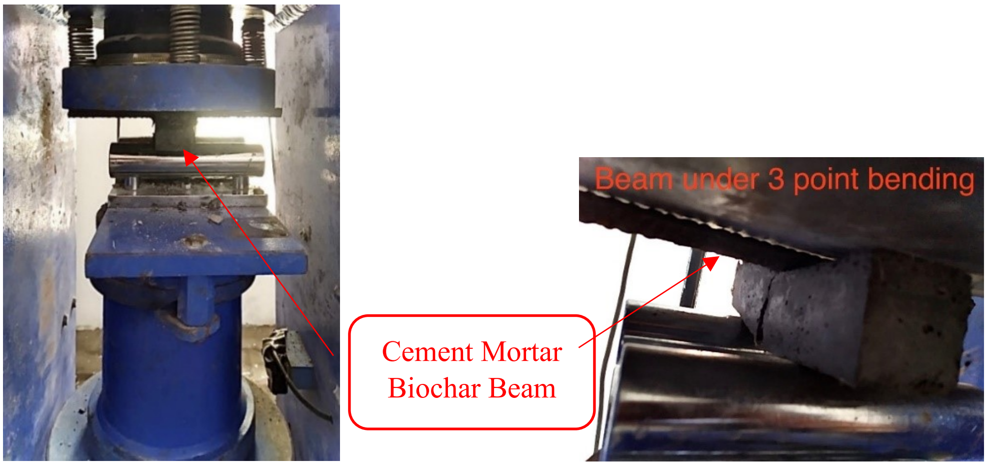

Figure 4.7: Flexural Strength Test of Cement Mortar Beam of Dimension (160 x 40 x 40) m^3

It is seen that 28^{th} day flexural strength is enhanced when cement is replaced by 2% and 4% biochar in cement mortar mix by 12% and 3.5% respectively when compared to the ordinary mix. The flexural strength of cement mortar with the inclusion of biochar at 6%, 8% and 10% results in 75%, 67.5% and 60% respectively of the control cement mortar. This finding is consistent with the findings of consistent with K. Tan et al. [38] that addition of 1% biochar results in 13% improvement in 28 days flexural strength as compared to control cement mortar samples and the flexural strength diminishes with increase in biochar inclusion. The addition of 3%, 5%, and 10% biochar results in flexural strength that is 105%, 98%, and 80% of that of the plain cement mortar, respectively.

According to the study [31], a high biochar dose causes inhomogeneity in the hardened mortar, which affects flexural strength. Moreover, flexural strength loss may be caused by the creation of air spaces in the tensile plane as a result of the inclusion of too much biochar. High dosages of biochar trap air that produced gaps in cured mortar due to its tiny particle size and porous nature.

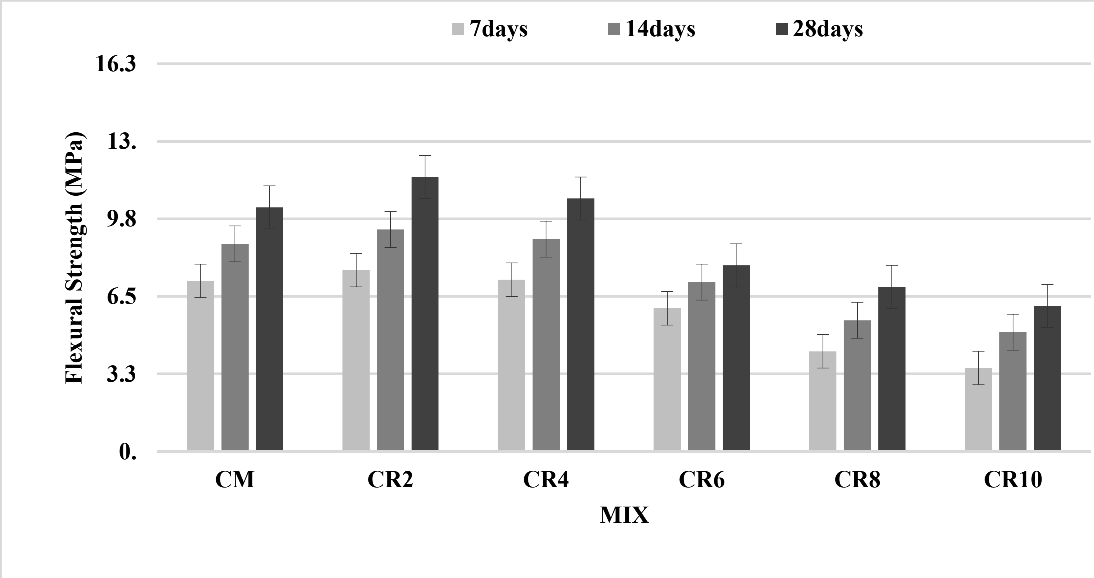

Figure 4.8: Flexural Strength of Different Mixes of Cement Mortar at 7, 14, and 28 Days

4.1.7 Compressive Strength loss due to Sulphate attack

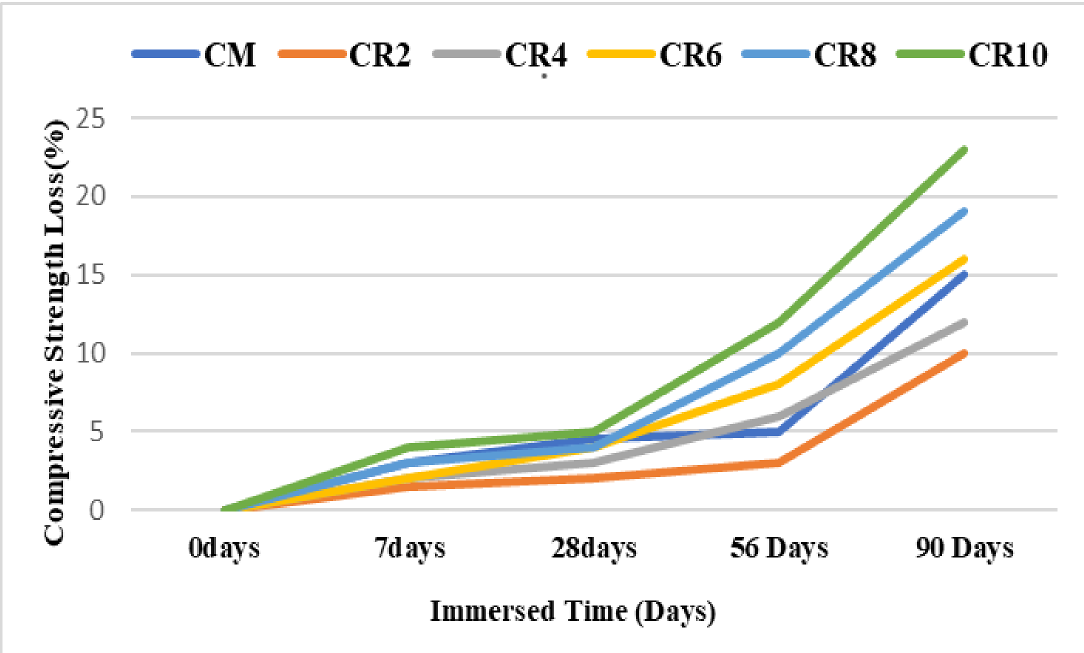

Figure 4.9: Compressive Strength Loss (%) of Different Mixes of Cement Mortar at 7, 28, 56, and 90 Days

It is cleared from Figure 4.9, that a higher loss in compressive strength of the control mix is seen when compared with the loss in compressive strength of CR2 and CR4 specimens. The result indicates the rise in pozzolanic activity between biochar and calcium hydroxide $Ca(OH)_2$ yielding the additional calcium silicate hydrate. More compressive strength loss is seen with the increase in biochar inclusion in cement mortar. This is due to the microporous structure of biochar that allows Sulphate ions to react with $Ca(OH)_2$ resulting in compressive strength loss.

4.2 Influence of biochar inclusion on the properties of concrete

4.2.1 Workability

Slump cone tests have been conducted to determine the workability of different concrete mixes. The results shown in Figure 4.10 illustrates that workability is significantly decreased with the increase in cement replacement with Biochar. It was found that the samples with high biochar content gave lower slump values than the samples with low biochar content. The workability of the control mix with 0% Biochar is 96 mm but with the inclusion of biochar up to 8%, it is reduced to 63 mm. The decrease in workability is due to the greater porosity and water retention capacity of biochar.

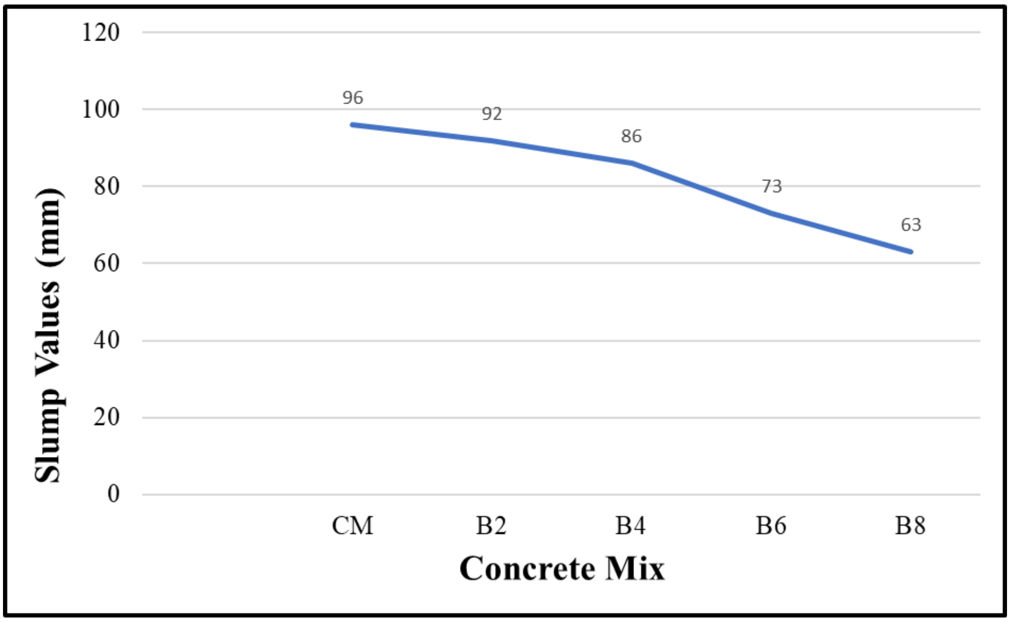

Figure 4.10: Workability of concrete

4.2.2 Water Loss

Water loss determines the water retention capacity of the concrete mixes for the internal curing of the concrete. Figure 4.11 depicts the increase in weight loss up to 28 days due to water evaporation. It can be noticed that biochar concrete mixes show a substantial reduction in water loss as compared to conventional concrete. This indicates the better water retention capacity of the biochar particles that act as internal curing agents for the concrete. Microporous cellular structure and interconnected fibers of the biochar particles result in a less porous structure which improves the durability of the concrete.

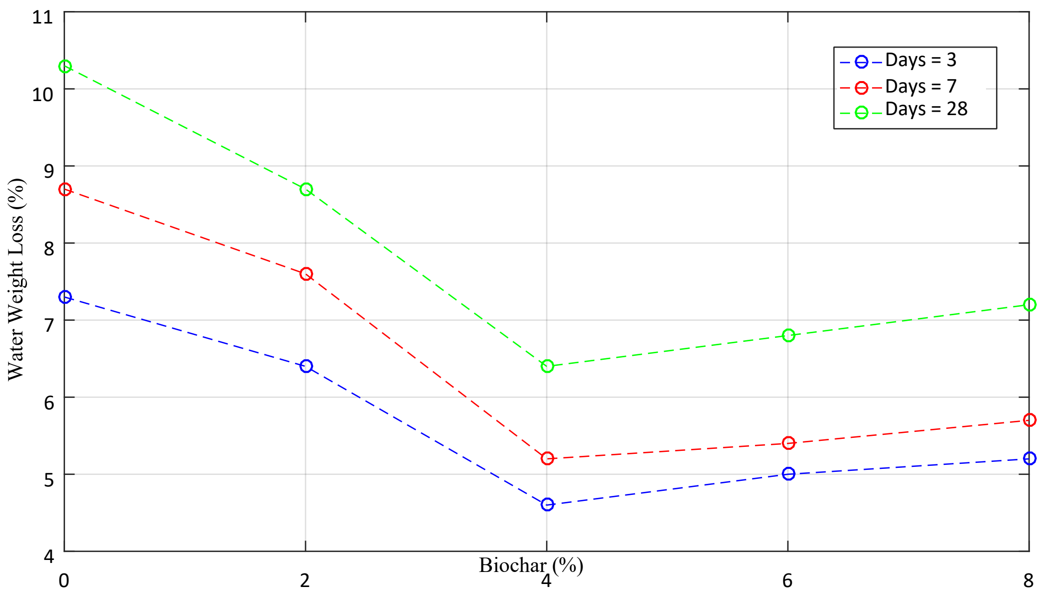

Figure 4.11: Weight loss of concrete

4.2.3 Compressive Strength

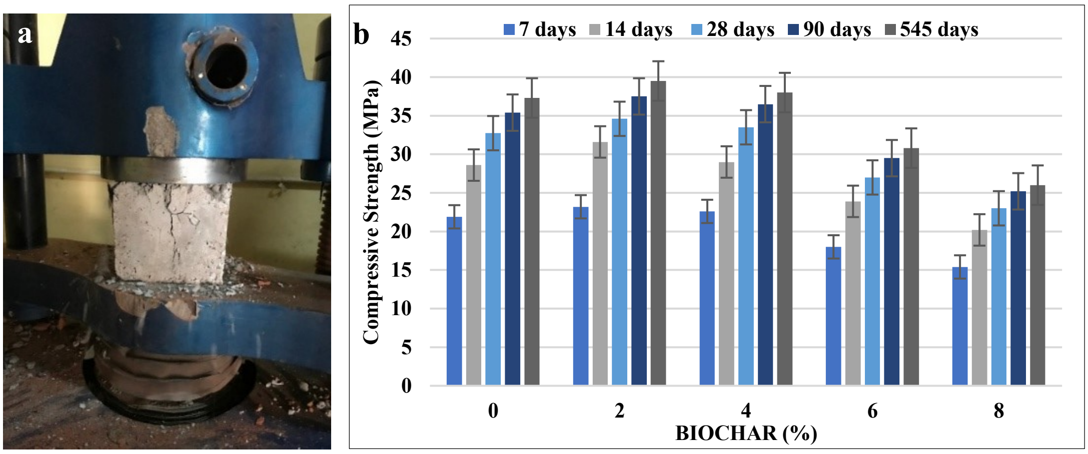

Figure 4.12: (a)Compressive strength test of 150 mm concrete cube; (b)Average compressive strength.

The experimental outcomes of compressive strength of concrete mixes with the variation of biochar content following 7, 14, 28, 90 and 545 days of water curing are shown in Figure 4.12 (b). In comparison to the other concrete combinations, the concrete mix containing 2% Biochar as a cement substitute had the maximum compressive strength for all the curing ages. This may be because biochar has the water retention property which helps to maintain moisture during curing. The finer biochar particles combine with lime to form a stable lime-pozzolana complex with concrete-like characteristics. As a result, any free lime in the mix is hydrolyzed. The controlled specimen and the concrete mix with 4% replacement of cement with biochar show similar results whereas the concrete mix beyond 4% replacement of cement gives lower compressive strength.

4.2.4 Flexural Strength

The flexural strength test is carried out on a three-point arrangement as shown in Figure 4.13(a). The tests were carried out on prismatic samples of 100x100x500 mm after 28 days of curing in water for various concrete mixes. The experimental results of the concrete specimen with a variation of biochar content are presented in Figure 4.13(b). The concrete mix with 2% and 4% biochar content shows better flexural strength results than other concrete mixes. This is in contrast with the compressive strength of similar concrete mixes. The controlled specimen and the mix with 6% biochar gave comparable flexural strength. From the experimental findings, it is evident that with the inclusion of biochar in the concrete mixes, the flexural strength of the concrete is improved. In composite materials, the bond between biochar and cement particles prevents early cracks in the specimen by diverting the fracture. Therefore, additional energy is required to break the bond strength.

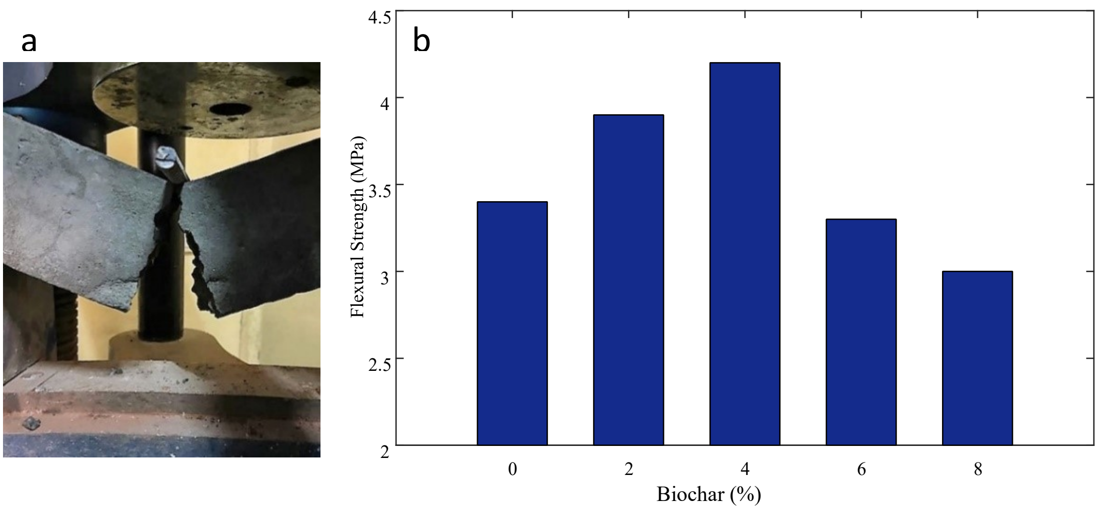

Figure 4.13: (a) Flexural strength test of 100x100x500 mm concrete beam; (b) Flexural strength of concrete mixes after 28 days of curing.

4.2.5 Thermogravimetric Analysis (TGA)

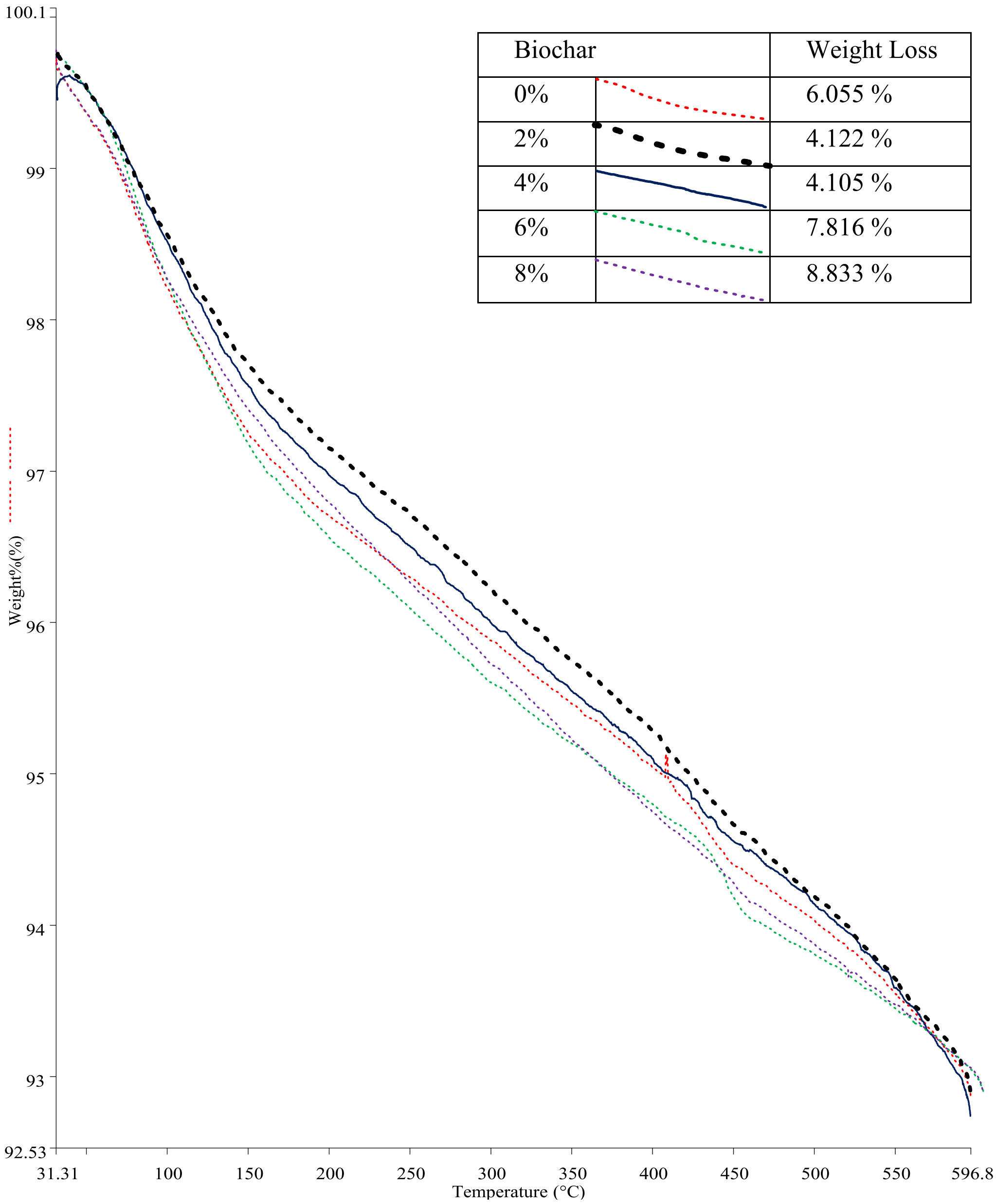

Figure 4.14: Weight loss (%) of control and biochar composites.

Thermal analysis of the powdered concrete samples was carried out in Perkin Elmer TGA 4000 instrument using Nitrogen gas at 20 ml/min. The temperature in the instrument was raised from 30°C to 600°C at 20°C/min and then kept at 600°C for 1.0 minute. The weight loss of all the concrete composites corresponding to the rise in temperature was recorded to obtain plots are illustrated in Figure 4.14. It can be seen that concrete mixes incorporating biochar (2% and 4%) exhibit higher thermal stability due to the lower weight loss results as compared to the other mixes. Moisture loss from the concrete to the surrounding environment, breakdown of calcium silicate hydrate (C-S-H), and other hydration phases cause weight loss up to 300°C.Also, in the temperature range (0°C to 400°C), the relative mass change found is more in B2 and B4. The 2% and 4% biochar concrete mix specimen shown a considerable upward shift. The larger quantity of dehydration of chemically bonded water from the CSH gel and other hydration products is related to these changes, implying improved hydration in biochar samples.

4.2.6 X-Ray Diffraction (XRD)

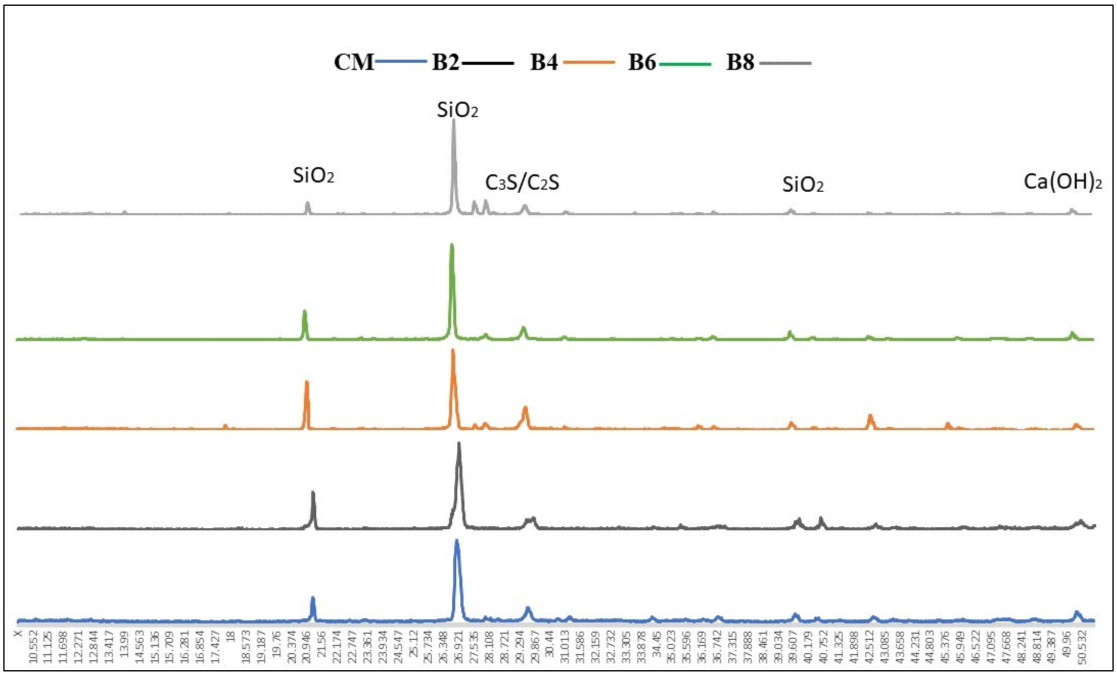

Figure 4.15: Phase identification of biochar concrete.

The primary phases generated by the inclusion of Biochar in concrete mixtures were identified using X-ray diffraction. XRD examination revealed that all spectra contained silica and calcium hydroxide, as well as dicalcium and tricalcium silicate phases (C2S/C3S) and calcium silicate hydrate (CSH) (Figure 4.15). Peaks produced for the Control mix, B2, B4, B6, and B8 appeared at the 2θ positions, although with varied intensities. For example, highest peak for C3S/C2S was obtained at 29.29° by B4 which corresponded to greater splitting tensile strength. Likewise, the calcium hydroxide spike at 50.5° was largest in B6 samples while B4 showed the lowest hydrated calcium. These findings lead us to the conclusion that B6 limits the formation of calcium hydroxide more than other biochar concrete specimens, lowering the CSH and hence the strength performance. TGA exhibits a similar pattern, therefore it is possible that 2% and 4% additions of biochar increase hydration in concrete specimens.

4.2.7 Scanning Electron Microscopy (SEM)

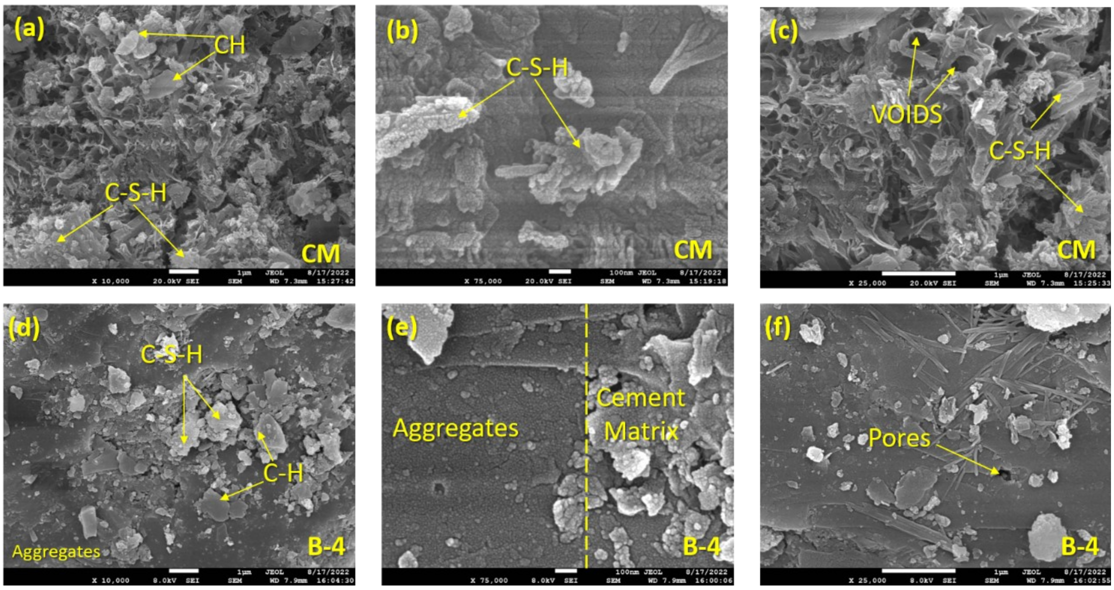

Figure 4.16: SEM images of controlled mix and B4 concrete mix at different magnifications.

Inclusion of biochar influences the microstructure of concrete. Figure 4.16(a, b & c) and Figures 4.16(d. e & f) shows the SEM images of controlled specimen and concrete mix with 4% biochar respectively. The concrete samples were finely ground and were examined under scanning electron microscopy (SEM). Concrete samples with 4% rice husk biochar and a control specimen were SEM examined at 10,000, 75000, and 25000 magnifications. Concrete mix with 4% biochar inclusion exhibits dense microstructure as shown in the Figure 4.16. This reveals that the pozzolanic interaction between the biochar and calcium hydroxide was produced by the hydration of Portland cement. Biochar's amorphous silica combines with excess calcium hydroxide ($Ca(OH)_2$) to generate C-S-H gel, which increases the strength of biochar concrete. Because of the higher rate of hydration, the result shows the development of C-S-H (Calcium silicate hydrate).

4.2.6 Water Permeability Tests

Figure 4.17: Permeability test of concrete cubes

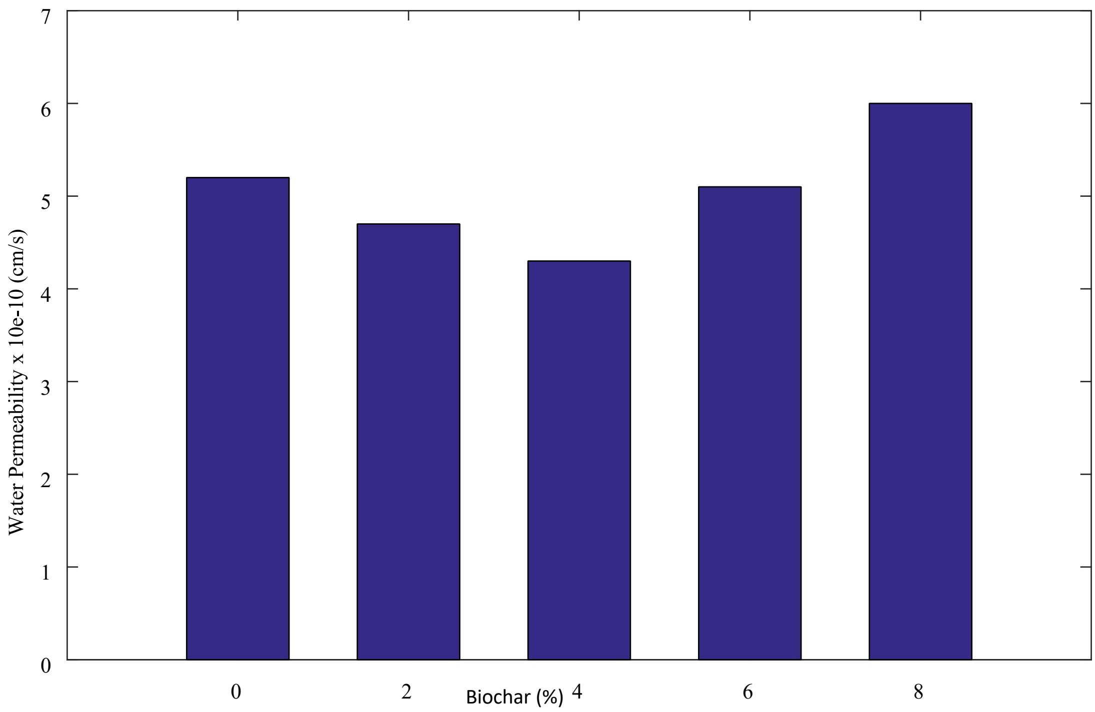

Figure 4.18: Water Permeability of different concrete mixes

Concrete has pores through which water, air or other substances can enter and exit. Permeability is a measure of the amount of these substances entering the concrete matrix. This parameter is a determinant of the long-term durability of concrete. Thus, to increase chemical resistance and to prevent the steel from rusting, concrete must not allow any substance to enter. Figure 4.18 shows that the inclusion of 2% and 4% biochar resulted in a reduction in permeability by 9.6% and 17.3% respectively when compared with control concrete. This signifies that the cement paste is more compact as the finer biochar particles act as a filler that enhances hydration reaction and fills the voids with fine particles. Thus, reducing the pore size and impeding fluid penetration paths thereby improving the durability of the concrete.

4.2.9 Loss in Compressive Strength

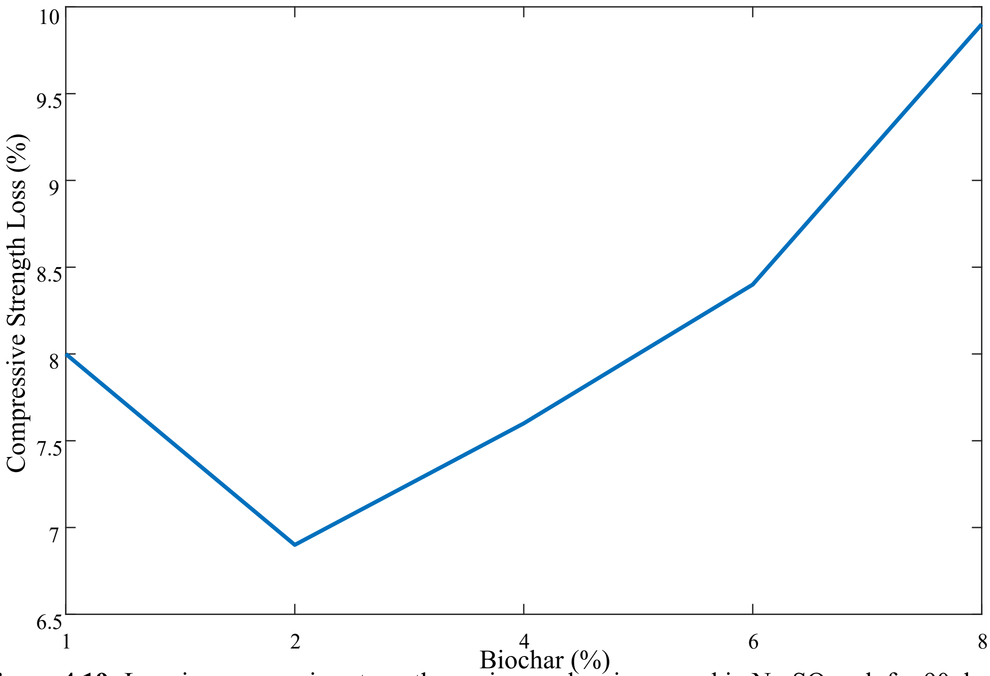

Figure 4.19: Loss in compressive strength specimen when immersed in Na_2SO_4 sol. for 90 days.

Sulfate attacks on concrete can be caused by sodium sulfate solution or other salts containing SO_4^{2-} ions. SO_4 present in the solution interacts with Ca^{2+} ions in the concrete and produces gypsum which causes micro-cracks and lowers the mechanical strength of C-S-H gel. The compressive strength of the concrete specimens immersed for 90 days in 5% Na_2SO_4 solution was compared with the concrete specimens cured in water. Figure 4.19 shows that when the control mix is immersed in a sulfate solution, it loses 8% of its compressive strength, whereas the B2 and B4 concrete mixes lose 6.9% and 7.4% of their compressive strength, respectively. This explains the packing effect of biochar particles and lower permeability that results in blocking sulphate ions. Increased biochar inclusion reduces the formation of C-S-H compounds, resulting in reduced compressive strength and an increased sulphate attack in B6 and B8 concrete mixes, respectively.

4.3 Lifecycle Assessment Results

4.3.1 Impact Assessment (Damage Level Viewpoint)

The life cycle assessment results are accessed in open LCA software with two commonly used methods: impact world+ midpoint level indicator and impact world+ damage level indicators. Both of the methods reveal a positive impact of the replacement of cement with Biochar. The results presented in Figure 4.20 are the damage level indicators formed by considering the midpoint level indicators. The results from the damage level indicators reveal the contribution of global emissions and extractions by the concrete mixes that impact human health and the ecosystem. A similar trend can be seen in every impact level indicator. The conventional concrete with no cement replacement has the highest impact. The mix designs with 2% replacement of cement with Biochar show the lower impact and as we increase the percentage of biochar inclusion up to 4%, 6%, and 8%, there is a consistent decrease in the environmental load percentage.

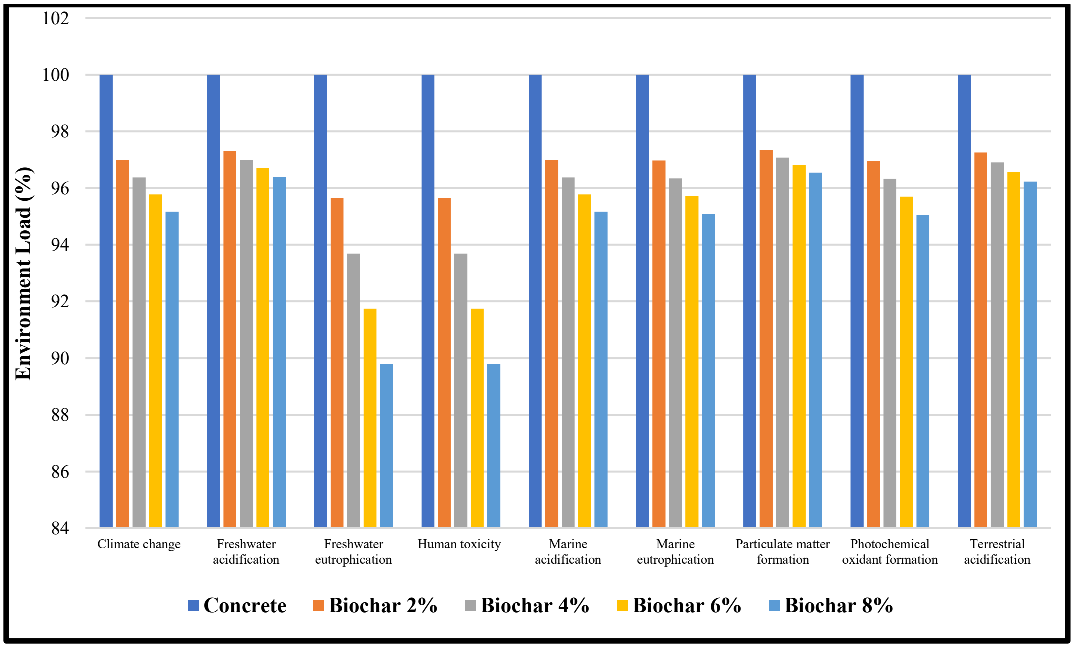

Figure 4.20: Impact World+ Assessment: Characterization

4.3.2 Normalization

In LCA, normalization is done to avoid the scale effects to compare the environmental impact of each category and interpretation of the results. Figure 4.21 illustrates the relative significance of the 10 impact level indicators. Climate change shows the highest normalized value for all the concrete mixes, followed by marine acidification and terrestrial acidification.

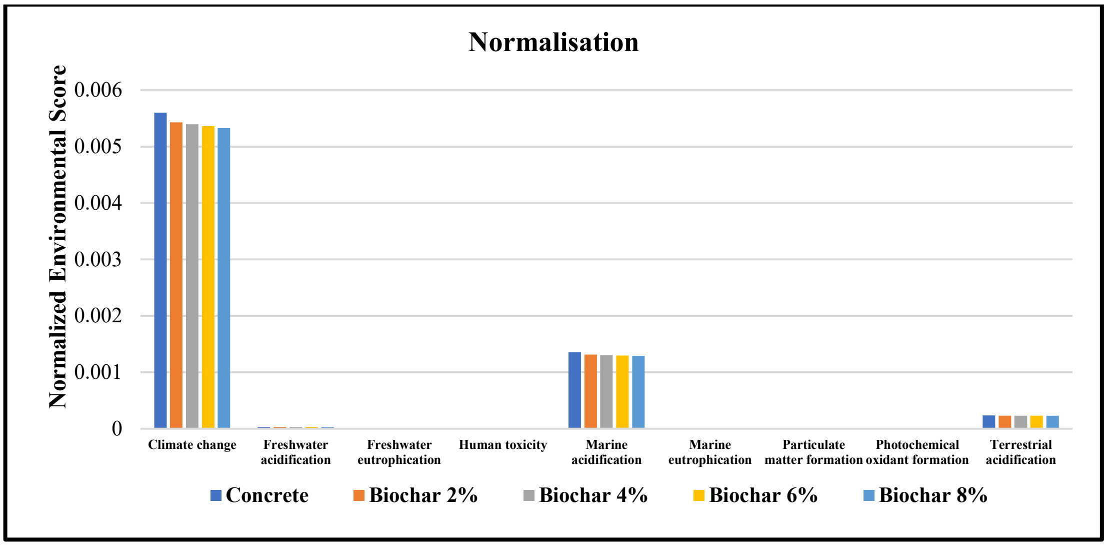

Figure 4.21: Impact World+ Assessment: Normalisation

4.3.3 Relative Importance

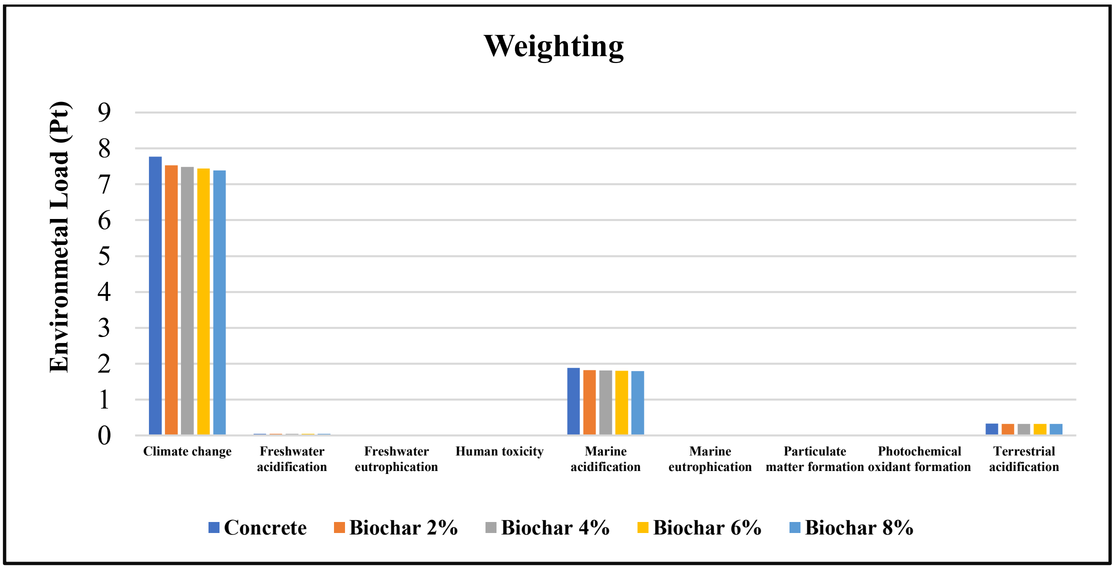

Figure 4.22: Impact World+ Assessment: Weighting

The relative importance of each environmental impact indicator is expressed by weighting average which is found by calculating the average of the multiple of the weighting factor of each impact level indicator and the normalization values. Figure 4.22 illustrates the weighting of each impact level indicator. Climate change shows the highest importance of all the impact level indicators, followed by marine acidification and terrestrial acidification.

4.3.4 Single Score: Environmental Load

For easy understanding of the environmental impact of different concrete mixes, the total single scores formed from the results of weighting are shown in Figure 4.23. These single scores are assigned to each mix and are compared. The total single score represents the environmental impact of the product in terms of percentage which has no dimensions. Among all the concrete mixes, conventional concrete mix shows the maximum single score. As demonstrated in Figure 4.23, the score decreases as the proportion of biochar in cement increases. The concrete mix with 8% replacement of cement has the lowest score.

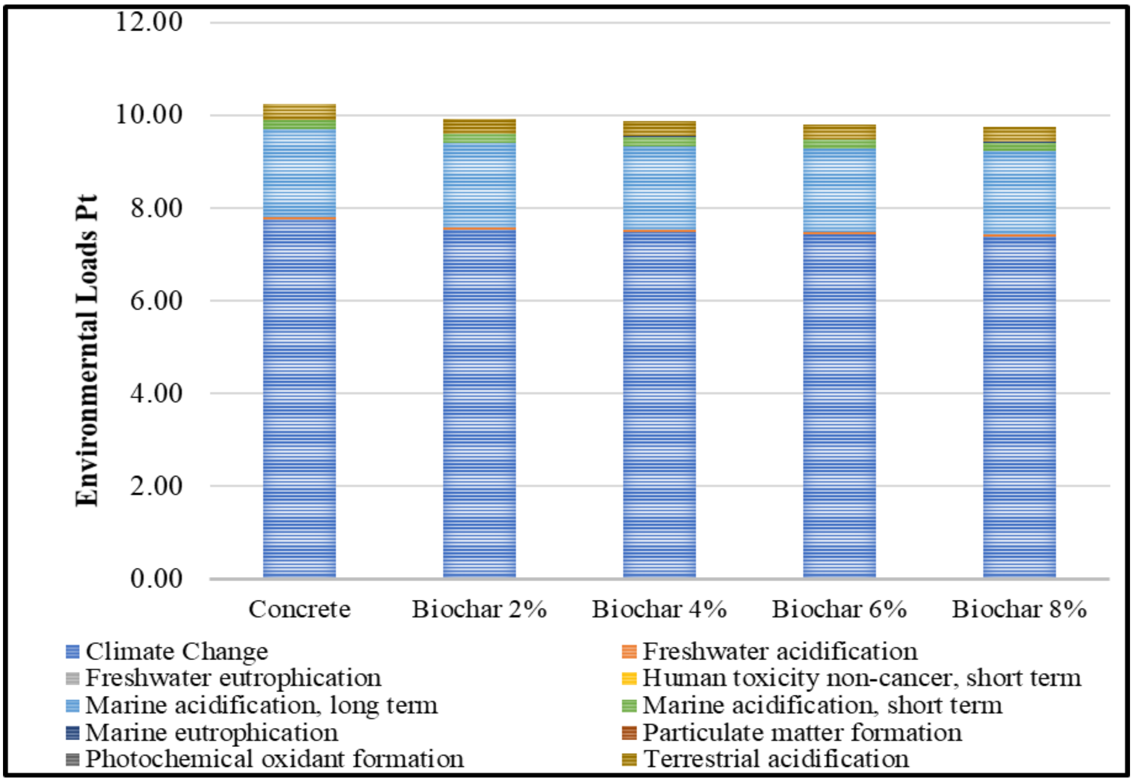

Figure 4.23: Impact World+ Assessment: Single Score

4.3.5 Impact Assessment (Midpoint Level View Point)

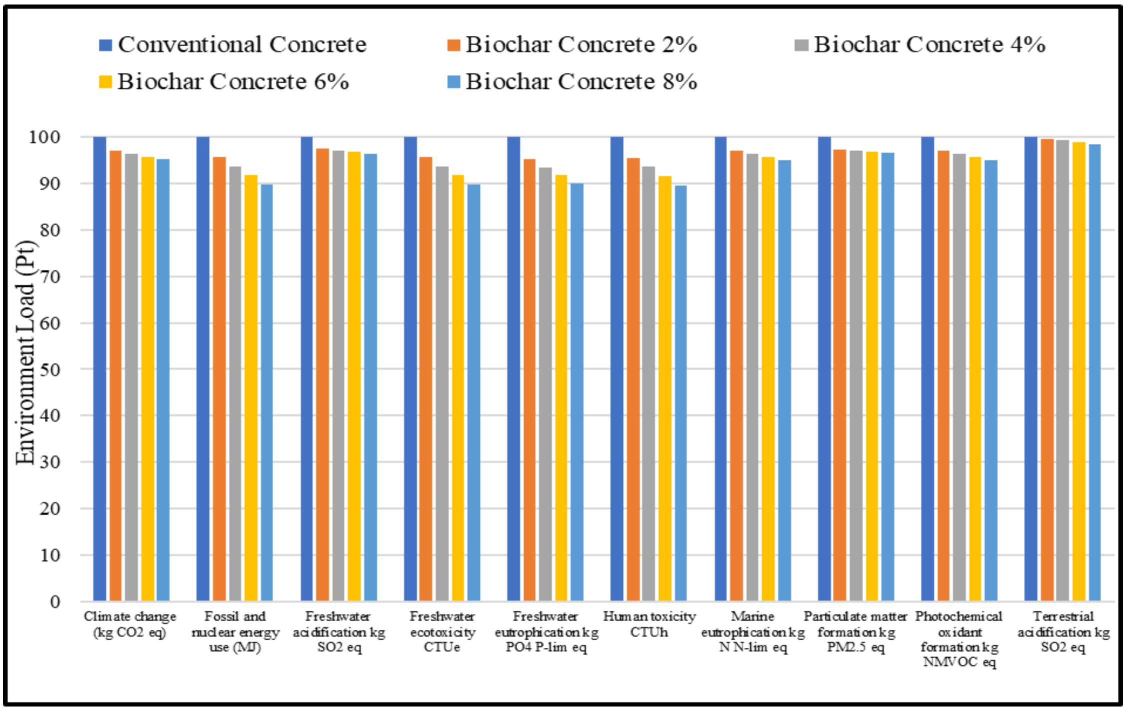

Figure 4.24: Impact World+ Midpoint Assessment: Characterization

The Impact World+ midpoint method measures the climate change as the amount of heat greenhouse gases capture in the atmosphere in terms of $kgCO_2$ eq. as shown in Figure 4.24 and Table 4.1. The higher replacement of cement with biochar results in a lower amount of carbon dioxide emissions. The impact of freshwater acidification is calculated using the same conclusion model as climate change, with H+ concentrations impacting 50% of the species. Figure 4.24 shows the maximum environmental impact from the conventional concrete and a decline in trend is observed with the inclusion of biochar. Impact assessment of the terrestrial acidification is based on the atmospheric deposition of sulfuric acids, nitric acids, and ammonium relationships with water and soil ecosystems sensitivity. Up to 10% reduction in freshwater ecotoxicity can be observed in Figure 4.24 when cement is replaced up to 8% respectively. The freshwater eutrophication results show a similar trend with freshwater ecotoxicity. Human toxicity refers to the quantitative toxic equivalency potential (TEP) which represents the potential damage of a unit of chemical discharged into the environment, is referred to as human toxicity. Ecotoxicity and human toxicity impact is based on the USEtox version specified according to global parameters. The results show an 11% decline in human toxicity when cement is replaced up to 8% in the concrete mix. Overall, it is obvious that using Biochar as a cement substitute in concrete results in a significant reduction in the impact categories' values.

Table 4.1: Impact Assessment Table: Characterization

Impact category	Reference unit	Conventional Concrete	Biochar Concrete 2%	Biochar Concrete 4%	Biochar Concrete 6%	Biochar Concrete 8%
Climate change	$KgCO_2$ eq (long)	901.00	874.00	868.50	863.00	857.50
Fossil and nuclear energy use	MJ deprived	738.25	706.00	691.60	677.26	662.86
Freshwater acidification	$kgSO_2$ eq	1.23E-11	1.198 E-11	1.194 E-11	1.19 E-11	1.186E-11
Freshwater ecotoxicity	CTUe	0.00083	0.00080	0.00079	0.00077	0.00076
Freshwater eutrophication	$kgPO_4$ P-lim eq	1.7 E-08	1.6 E-08	1.59E-08	1.5E-08	1.52 E-08
Human toxicity non cancer	CTUh	3.25 E-12	3.1E-12	3E-12	2.98 E-12	2.9 E-12
Marine eutrophication	KgN N-lim eq	0.026	0.025	0.025	0.025	0.026
Particulate matter formation	KgPM2.5 eq	0.250	0.242	0.240	0.239	0.239
Photochemical oxidant formation	KgNMVOC eq	1.75	1.69	1.68	1.67	1.66
Terrestrial acidification	$KgSO_2$ eq	8 .00 E-06	7.76 E-06	7.74 E-06	7.71 E-06	7.68 E-06

4.3.6 Carbon Dioxide Emissions

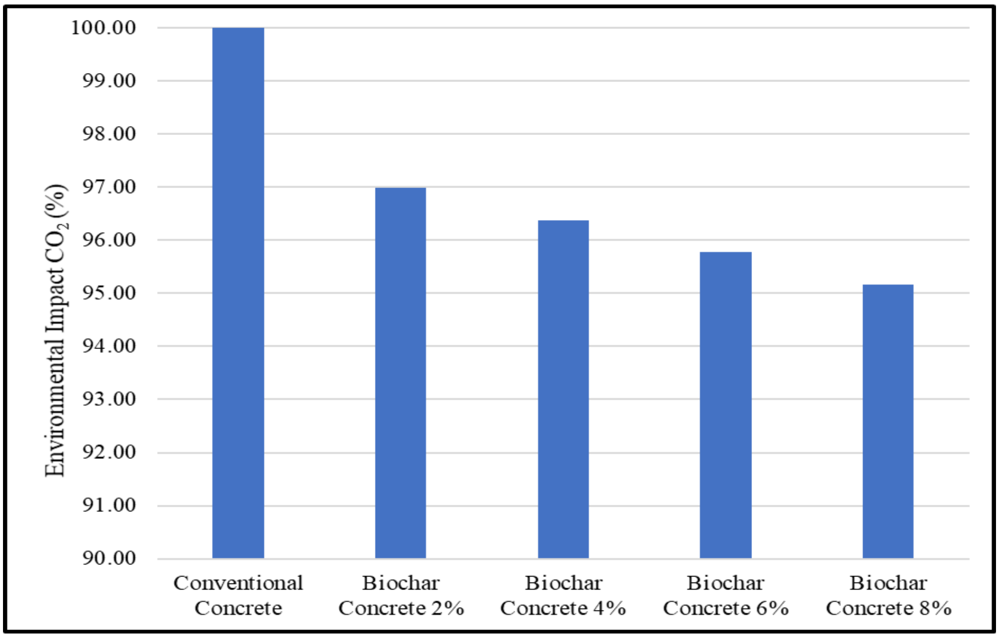

Figure 4.25: CO_2 emissions from concrete mixes

The environmental implications arising from the manufacturing of one kilogramme of concrete using cement binder with varied proportion of biochar are outlined in Table 4.1. It has been discovered that concrete using simply plane cement as a binder has the greatest environmental effect values. It can be observed from Table 4.1 that the amount of carbon dioxide emitted during the production of one kg of concrete using only plane cement as binder is 901 kg CO_2 eq whereas the emission decreases to 857.50 kg with the replacement of cement by biochar to the extent of 8%. These results are also illustrated graphically in Figure 4.25. It is estimated in the year 2013, India produced 100-million-tonnes of concrete [110] that accounts for the release of 3.604e10 $kgCO_2$. Thus, the present study indicates that the production of concrete using cement binder with 4% replacement by biochar can reduce the carbon dioxide emissions up to 1.3e9 $kgCO_2$.

Concluding Remarks

The results demonstrates the positive impact of inclusion of biochar up to a certain limit of replacement of cement with biochar on the mechanical properties of cement mortar and concrete. The microstructural and durability properties of cement mortar and concrete are improved as well. The comparative environmental analysis shows that using biochar as a cement substitute in concrete results in a significant reduction in the impact categories' values.

Chapter-5

Statistical Analysis

Methods of Analysis

Correlation and regression are statistical techniques used to assess the mechanical and durability characteristics of biochar concrete, and the findings are analysed statistically in relation to this research on rice husk biochar concrete.

5.1 Correlation Analysis

The correlation is a statistical tool for determining the degree and direction between two variables. This approach was used to determine the relationship between compressive and flexural strength achieved after 28 days of curing of all the concrete mix with varying biochar content (0 to 8%).

The proven correlation approaches employed for this investigation are Pearson correlation coefficient and Spearman's Rank-Order Correlation. Pearson correlation coefficient is calculated as in 5.1

$$r = \frac{n(\sum xy) - (\sum x \sum y)}{\sqrt{[n\sum x^2 - (\sum x)^2][n\sum y^2 - (\sum y)^2]}} \tag{5.1}$$

Where, "r" is Pearson correlation coefficient,

"x" is the first variable

"y" is the second variable

Spearman's "Rank order correlation coefficient" is mathematically expressed as in 5.2

$$r_S = 1 - \frac{6\sum D^2}{n(n^2-1)} \tag{5.2}$$

Where, "r_s" is Spearman 's rank order correlation coefficient,

"D" is the difference between the ranks

"n" is the no. of observations

Both the correlation values of Pearson correlation coefficient and Spearman's Rank-Order Correlation lies between +1 and −1 and can be interpreted by calculating the average value and making a comparison with the following interpretation table of Spearman Rank-Order Correlation Coefficients and Karl Pearson's correlation technique as shown below:

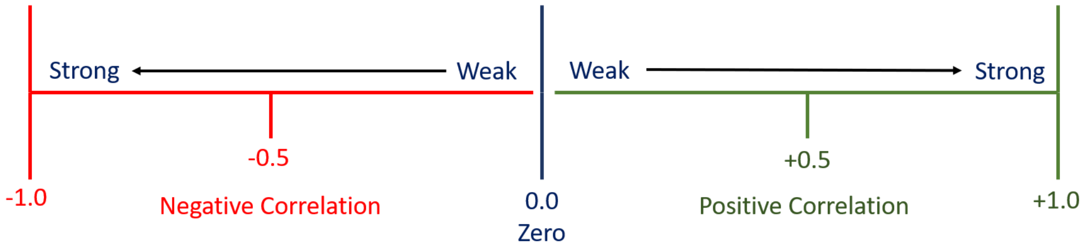

Figure 5.1: Degree of relationship - Karl Pearson's correlation method

Table 5.1: Interpretation table of Spearman Rank-Order Correlation Coefficients (Adapted From Dancey and Reidy, 2004 [110])

Spearman (r_s)	Correlation
≥0.70	Very strong relationship
0.40-0.69	Strong relationship
0.30-0.39	Moderate relationship
0.20-0.29	Weak relationship
0.01-0.19	No or negligible relationship

5.1.1 Correlation between Compressive Strength and Flexural Strength

Let "x" be the compressive strength after 28 days of curing and "y" be the flexural strength after 28 days of curing for all mix proportions with varying biochar content (0-8%). The details of the of Karl Pearson's correlation coefficient are given in Table 5.2.

Table 5.2: calculation of parameters

Sr. No.	Mix	x	y	x^2	y^2	xy
1	CM	32.74	3.3	1071.9076	10.89	108.042
2	B2	34.6	3.5	1197.16	12.25	121.1
3	B4	33.5	3.8	1122.25	14.44	127.3
4	B6	27	3.1	729	9.61	83.7
5	B8	23	2.6	529	6.76	59.8
Sum		150.84	16.3	4649.3176	53.95	499.942

"r" (Pearson correlation coefficient) is calculated from the equation 5.1

$$r = \frac{5(499.942) - (150.84)(16.3)}{\sqrt{[(493.8824)][(4.06)]}} = 0.916$$

Spearman's Rank-Order Correlation

Spearman's Rank-Order Correlation coefficient is calculated and tabulated as shown in Table 5.3

Table 5.3: calculation of parameters

Sr. No.	Mix	X	y	Rank for Compressive Strength	Rank for Flexural Strength	Difference in ranks (D)	D^2
1	CM	32.74	3.3	3	3	0	0
2	B2	34.6	3.5	1	2	-1	1
3	B4	33.5	3.8	2	1	1	1
4	B6	27	3.1	4	4	0	0
5	B8	23	2.6	5	5	0	0
SUM ($\sum D^2$)							2

"r_s" (Spearman's Rank-Order Correlation coefficient) is calculated from the equation 5.2

$$r_S = 1 - \frac{6(2)}{5(5^2 - 1)} = 0.9$$

The average of both the correlation coefficients is calculated as

$$\frac{0.916 + 0.9}{2} = 0.908$$

From Figure 5.1 and Table 5.1: Interpretation table of Spearman Rank-Order Correlation Coefficients (Adapted from Dancey and Reidy, 2004 [111]), it is interpreted that there is a very strong correlation relationship between compressive and flexural strength with a value of 0.908.

5.2 Regression Analysis

"Regression analysis is the study of the nature and extent of association between two or more variables on the basis of the assumed relationship between them with a view to predict the dependence of one variable on the other [112]."

The linear relationship has been assumed between the compressive strength and weight loss (%). The parameters of the equation are determined as follows:

For linear relationship, $y = a + bx \pm e$ (5.3)

Where,

"y" = dependent variable,

"x" = independent variable

a = regression line intercept

b = slope

e = error

Because a straight line has no turning point, therefore "e" has zero value.

The correlation coefficient, "r" is calculated from the equation (5.1). Then the slope "b" is calculated from the relation (5.4)

$$b = r\frac{S_y}{S_x} \tag{5.4}$$

The intercept "a" is calculated as

$$a = \bar{y} - b\bar{x} \tag{5.5}$$

The regression model of compressive strength vs weight loss (%)of all the concrete mixtures with varying biochar content (0-8%) is developed during thermal analysis to predict a linear relationship between the results.

The result of compressive strength and weight loss (%) of concrete made with partial replacement of cement with biochar in the ratio (0%, 2%, 4%, 6% and 8%) are represented as y and x, respectively as shown in Table 5.4 to find the regression of y on x.

Table 5.4: calculation of parameters

Sr. no.	x	y	x^2	y^2	xy	x- x̄	y - ȳ	$(x-\bar{x})^2$	$(y-\bar{y})^2$
1	6.055	32.74	36.663	1071.907	198.240	-0.131	2.572	0.017	6.615
2	4.122	34.6	16.990	1197.160	142.621	-2.064	4.432	4.260	19.642
3	4.105	33.5	16.851	1122.250	137.517	-2.081	3.332	4.331	11.102
4	7.816	27	61.089	729.000	211.032	1.629	-3.168	2.656	10.036
5	8.833	23	78.021	529.000	203.159	2.646	-7.168	7.005	51.380
SUM	30.931	150.84	892.57	209.616	892.570	0	0	18.271	98.776
	x̄ = 6.182	ȳ = 30.168							
	S_x = 0.854	S_y = 1.987							

$$r = \frac{5(892.57) - (30.931)(150.84)}{\sqrt{[(91.356)][(493.884)]}} = -0.954$$

$$b = -0.954\frac{1.987}{0.854} = -2.22$$

$$a = 30.168 - (-2.219)(6.182) = 43.90$$

Hence, the linear relationship developed between the two variables is

$$y = 43.90 - 2.22x \qquad (5.6)$$

The linear relation thus developed between compressive strength and weight loss (%) is represented through equation (5.6). The plot using the above equation is drawn as shown in Figure 5.2 The R^2 value of approximately 91% indicates a substantial association between compressive strength and weight loss (%). This means that during thermal analysis, low weight loss (%) corresponds to rise in compressive strength. The linear relationship found between the compressive strength of biochar concrete with varying biochar content (0-8%) and its weight loss (%) has a great significance in developing the sustainable biochar concrete.

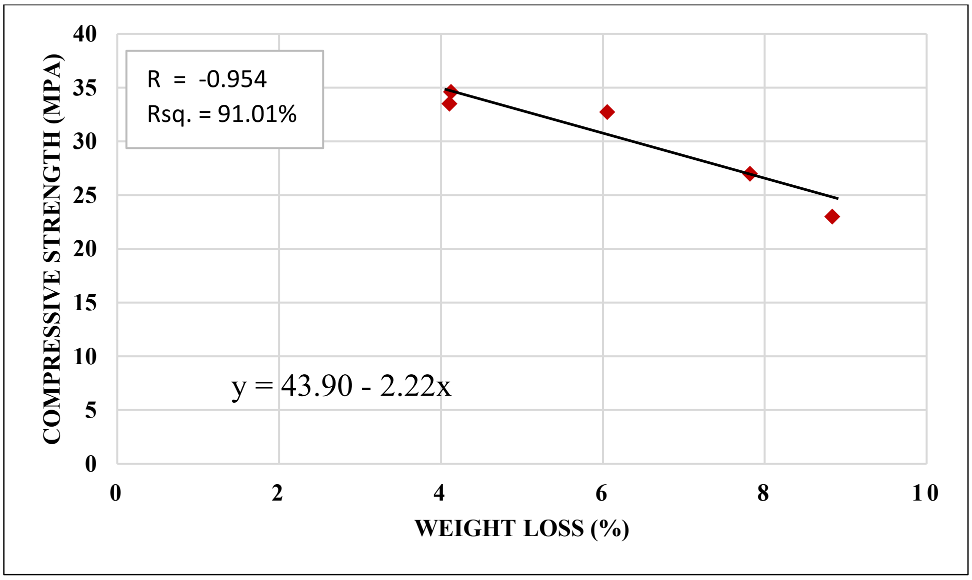

Figure 5.2: Regression analysis of compressive strength vs weight loss (%)

Concluding Remarks

The regression analysis shows low weight loss (%) corresponds to rise in compressive strength and the R^2 value of approximately 91% indicates a substantial association between compressive strength and weight loss (%). Whereas, through correlation analysis, it is proved that there is a very strong correlation relationship between compressive and flexural strength with a value of 0.908.

Chapter-6

6.0 Economic Viability

With an inclusion of Biochar in varying proportion as a cement replacement in concrete, the economic viability assessment is requisite as the replacement will only be possible if the resulting concrete mix has a lower or equal expenditure. Cost analysis was performed to compare the cost of materials required per cubic meter of concrete for all mix proportions is shown in table 6.1. The cost in INR per kg of all the ingredients are calculated from the material purchased from retailer and the cost was tallied. The cost of production of biochar varies with the cost of availability of rice husk in the market. As cost of rice husk changes, the production cost of rice husk biochar also changes. The market price per kilogram of biochar is procured from Shraddha Agrozone, Pune, Maharashtra. At that time market rate of rice husk was Rs. 4.5/- Kg and biochar was Rs.7.5/- per Kg which makes it Rs. 0.5/- cheaper than the OPC-43 grade cement. The cost of materials per cubic meter for control mix calculated is Rs. 4066, as shown in Table 6.1, and it decreases with an inclusion of biochar.

Table 6.1: Cost Analysis of Biochar concrete with varying Biochar content

Material	**Rate (INR) at source**	**Rate per Kg**	**Mix Proportions**									
			Biochar (0%)	**Cost**	**Biochar (2%)**	**Cost**	**Biochar (4%)**	**Cost**	**Biochar (6%)**	**Cost**	**Biochar (8%)**	**Cost**
OPC-43 Grade	Rs. 400/- per 50 kg bag	8	383.2	3065.60	375.5	3004.00	367.85	2942.80	360.2	2881.60	352.55	2820.40
Biochar	Rs. 200/- per Kg	7.5	0	0	7.65	57.40	15.3	114.75	23	172.50	30.65	229.88
Fine Aggregate	Rs. 500/- per cu ft	0.66	707.6	467.00	707.6	467.00	707.6	467.00	707.6	467.00	707.6	467.00
Cost Aggregate	Rs. 375/- per cu ft	0.5	1066.75	533.40	1066.75	533.40	1066.75	533.40	1066.75	533.40	1066.75	533.40
Cost of materials required per cubic meter of concrete				**4066.00**		**4061.80**		**4057.95**		**4054.50**		**4050.68**

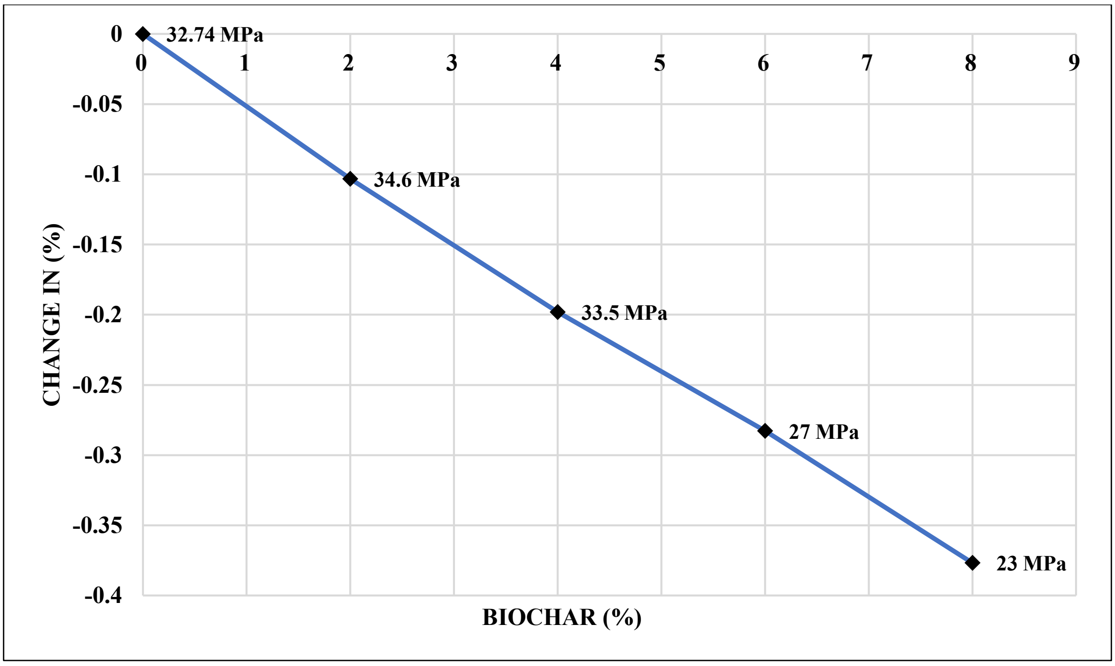

Figure 6.1: Percentage change in cost with the variation of biochar in concrete

Figure 6.1 depicts the change in %age of cost with an increase in inclusion of Biochar in the concrete. The x-axis represents the increase in biochar content, y-axis represents the decrease in %age of cost, the line in the graph represents the decrease in the %age of cost with an increase in the biochar content whereas the label of the points on the line displays compressive strength (MPa). When compared to controlled concrete, the percentage change in cost has decreased, but the compressive strength of the biochar concrete mixtures has increased in 2% and 4% biochar mix and then decline in strength has been observed with an inclusion of the biochar beyond 4%.

Concluding Remarks

The cost of the mix containing 2% and 4% biochar is reduced by 0.1% and 0.2% respectively when compared to the control concrete, and there is a considerable improvement in compressive strength of 5.68% and 2.32% respectively, which is quite large.

Chapter-7

7.0 Conclusions

Production of sustainable concrete using binary cement is a global practice to reduce GHG emissions and mitigate its environmental impacts. This research work is carried out to develop sustainable and green concrete by the partial replacement of cement with Biochar. The analysis performed investigates both the strength parameters as well as the overall environmental impact of the product. Performance investigation of cement mortar and concrete containing different fractions of RHB leads to the following conclusions as shown in Table 7.1.

Table 7.1: Objectives with their respective conclusions in the present research

Sr. No.	Objectives	Conclusions
a)	To investigate the mechanical and durability properties of cement mortar incorporating agrowaste.	➢ The porous structure and the water retention capacity of the biochar significantly affects the fresh properties of cement mortar. The flowability is decreased and the water absorption capacity of cement mortar increases with the inclusion of biochar.
		➢ The effective distribution of the particles due to the filler effect induced by the presence of carbon in the biochar leads to enhanced hydration reaction in the cement paste which improves the early strength of the mix. The water retention capacity of the biochar makes it an internal curing agent that ultimately results in increasing the overall strength of the composite. The compressive and flexural strength is increased by 7.8% and 12%, respectively with the inclusion of 2% biochar in the composite.
		➢ The compressive strength loss due to sulphate attack is minimized when 2% and 4% biochar replaces the cement in the composite. Hence, the durability of the composite is increased.
(b)	To study the mechanical properties of agro-waste based concrete.	➢ The workability of the concrete is reduced with the inclusion of biochar. The decrease in workability is due to the water retention capacity of biochar.
		➢ The pozzolanic activity induced by the 4% inclusion of RHB in the concrete improves its flexural strength, and compressive strength as compared to the control mix.
		➢ The linear relation developed in regression analysis between compressive strength and weight loss (%) indicates 91% substantial association between compressive strength and weight loss (%). This shows low weight loss (%) corresponds to rise in compressive strength.
c)	To study the Micro-structural and durability properties of agro-waste based concrete.	➢ Biochar concrete with 4% inclusion of biochar show substantial reduction in water loss(%) which attributes to the better water retention capacity of the biochar particles that act as internal curing agents for the concrete.
		➢ Higher thermal stability and relative mass change in the temperature range (0°C to 400°C) reflects more dehydration of chemically bound water from the CSH gel , implying greater hydration in biochar specimen.

		➢ The increased hydration has a substantial impact on the durability of the concrete, because the finer biochar particles function as a filler, densifying the concrete matrix. The inclusion of 2% and 4% biochar resulted in a reduction in permeability by 9.6% and 17.3% respectively thereby improving the durability of the concrete.
		➢ Microporous cellular structure and interconnected fibers of the biochar particles leads to a less porous structure which results lowering permeability, thus reducing compressive strength loss in sulphate attack in concrete mixes with 2% and 4% biochar inclusion.
d)	A Comparative Lifecycle Assessment of Ordinary and Agrowaste Based Concrete	➢ The sustainability of the concrete prepared by replacing cement with 4% biochar is improved substantially without affecting the mechanical performance of the concrete. The performed lifecycle assessment carried out reveals the positive impact of the replacement of cement with Biochar. The CO_2 emissions are considerably lowered by the inclusion of Biochar in the concrete mix. The analysis shows that in India alone, the reduction in carbon dioxide emissions up to 1.3e9 $kgCO_2$ can be achieved with the replacement of cement with 4% biochar in the production of concrete. ➢ The cost of the mix containing 2% and 4% biochar is reduced by 0.1% and 0.2% respectively when compared to the control concrete, , and there is a considerable improvement in compressive strength of 5.68% and 2.32% respectively, which is quite large.

Chapter-8

Future Scope

1. General

This dissertation is a detailed investigation of the inclusion of the rice husk biochar as a partial replacement of cement in the cement mortar and concrete to produce value-added sustainable material with reduced embodied carbon, better mechanical and durable properties. The research work includes the detailed characterization of RHB, experimental work and environmental analyses which explains the impact of inclusion of RHB on the properties of concrete and the environment.

2. Recommendations for future studies

1. Biochar obtained from other agricultural waste materials can be prepared and studied.
2. Comparison between different biochar samples and analysis of their characteristics that might enhance the properties of the cement mortar and concrete can be performed to achieve optimum results.
3. Water/binder ratio is fixed for this current experimental work, however, for variable water/binder ratio, such analysis can be performed to understand the physical and chemical properties of the concrete mixture.
4. Furthermore, no study regarding the use of Alccofine and glass fibres in conjunction with agro waste has been reported. On the other hand, both Alccofine as well as glass fibre can been used to modify the concrete properties constructively.

References

[1] A.K. Hatfield, Mineral Commodity Summaries. Reston, Virginia: U.S. Geological Survey, pp 42-43, 2021.

[2] I.E.A & W.B.C.S.D, Technology Roadmap: Low Carbon Technology for the Indian Cement Industry. International Energy Agency and WBCSD, 2020.

[3] Greenspec, "The Environmental Impacts of Concrete", https://www.greenspec.co.uk/building-design/environmental-impacts-of-concrete/, 2022.

[4] A. Bosoga, O. Masek and J.E Oakey, "CO_2 Capture Technologies for Cement Industry", Energy Procedia, pp. 133-140, 2009.

[5] H.S. Arel and E. Aydin, "Use of Industrial and Agricultural Wastes in Construction Concrete", ACI Materials Journal, 115, 2018.

[6] J.K. Prusty, S. K. Patro and S. S. Basarkar, "Concrete using agro-waste as fine aggregate for the sustainable built environment – A review," International Journal of Sustainable Built Environment, 5, pp. 312-333, 2016.

[7] A.A. Elsayed, "Influence of Silica Fume, Fly Ash, Super Pozz and High Slag Cement on Water Permeability and Strength of Concrete", Jordan Journal of Civil Engineering, Vol. 5, No. 2, 2011.

[8] J. He, S. Kawasaki and V. Achal, "The utilization of agricultural waste as agro-cement in concrete: A review", Sustainability, 12, 6971, 2020.

[9] S. Bhuvaneshwari, H. Hettiarachchi and J. N. Meegoda, "Crop Residue Burning in India: Policy Challenges and Potential Solutions," International Journal of Environmental Research and Public Health, 16, 832, 2019.

[10] "National Policy for Management of Crop Residues (NPMCR)", Ministry of Agriculture, India, 2014.

[11] E. Rafiee, S. Shahebrahimi, M. Feyzi1 and M. Shaterzadeh, "Optimization of synthesis and characterization of nano silica produced from rice husk (a common waste material)",, International Nano Letters, Springer, 2, 29, 2012.

[12] H. Elbasiouny, B.A. Elbanna, E.A. Najoli, A. Alsherief et al., "Agricultural Waste Management for Climate Change Mitigation: Some Implications to Egypt", Waste Management in MENA Regions, Springer Water, Chapter-8, 2012.

[13] A. Gautam, R. Batra and Nishant Singh, “A study on use of rice husk ash in concrete”, Engineering Heritage Journal (GWK), 01-04, 2019.
[14] V. Vishwakarma, D. Ramachandran, N. Anbarasan and A.M. Rabel, “Studies of rice husk ash nanoparticles on the mechanical and microstructural properties of the concrete”, Recent Advances In Nano Science And Technology (Materials Today: Proceedings), 3, pp. 1999–2007, 2016.
[15] M. Amin and B.A. Abdelsalam, “Efficiency of rice husk ash and fly ash as reactivity materials in sustainable concrete”, Sustainable Environment Research, 29:30, 2019.
[16] S.A. Zareei, F. Ameri, F. Dorostkar and M. Ahmadi, “Rice husk ash as a partial replacement of cement in high strength concrete containing micro silica: Evaluating durability and mechanical properties”, Case Studies in Construction Materials, 7, 73–81, 2017.
[17] M. Tripathi, J.N. Sahu and P. Ganesan, “Effect of process parameters on production of biochar from biomass waste through pyrolysis: A review”, Renewable and Sustainable Energy Reviews, 55, 467–481, 2016.
[18] S. Shackley, S. Sohi, R.I., J. Hammond et al., “Biochar, Tool for Climate Change Mitigation and Soil Management”, UK Biochar Research Centre (UKBRC), School of GeoSciences, Science and Engineering at The University of Edinburgh, Edinburgh, Scotland EH8 9YL, Chapter-6, 2013.
[19] J. Lehmann, J. Gaunt and M. Rondon, "Biochar Sequestration in Terrestrial Ecosystems- A Review”, Mitigation and Adaptation Strategies for Global Change, pp. 403-427, 2006.
[20] Z.Y. Mahssin, N.A. Hassan et al., “Converting Biomass into Bio-Asphalt – A Review”, IOP Conf. Series: Earth and Environmental Science, 682, 2021.
[21] F. Piccolo, F. Andreola , L. Barbieri and I. Lancellotti, “Synthesis and Characterization of Biochar-Based Geopolymer Materials”, Applied Sciences, 11, 10945, 2021.
[22] O. Das, A.K. Sarmah and D. Bhattacharyya, “A novel approach in organic waste utilization through biochar addition in wood/polypropylene composites”, Waste Management, 2015.

[23] O. Das, D. Bhattacharyya and A.K. Sarmah, “Sustainable eco–composites obtained from waste derived biochar: a consideration in performance properties, production costs, and environmental impact”, Journal of Cleaner Production, 2016.
[24] P. Chindaprasirt and S. Rukzon, “Strength, porosity and corrosion resistance of ternary blend Portland cement, rice husk ash and fly ash mortar”, Construction and Building Materials, 22, pp. 1601–1606, 2008.
[25] B. Chatveera and P. Lertwattanaruk, "Evaluation of sulfate resistance of cement mortars containing black rice husk ash”, Journal of Environmental Management, pp. 1435-1441, 2009.
[26] P. Lura, M. Wyrzykowski, C.Tang and E. Lehmann, “Internal curing with lightweight aggregate produced from biomass-derived waste”, Cement and Concrete Research, 59, pp. 24–33, 2014.
[27] J. Wang, J. Fu, W. Song and Y. Zhang, “Effect of rice husk ash (RHA) dosage on pore structural and mechanical properties of cemented paste backfill”, Journal of materials research and technology, 17, pp. 840 – 851, 2022.
[28] W. C. Choi, H. D. Yun and J. Y. Lee, "Mechanical Properties of Mortar Containing Bio-Char From Pyrolysis”, Korean Institute of Structural Maintenance and Inspection, 2010.
[29] S. Gupta, H.W. Kua and S.Y.T. Cynthia, “Use of biochar-coated polypropylene fibers for carbon sequestration and physical improvement of mortar”, Cement and Concrete Composites, 2017.
[30] S. Gupta, H.W. Kua and C.Y. Low, “Use of biochar as carbon sequestering additive in cement mortar”, Cement and Concrete Composites, 2018.
[31] S. Gupta, H.W. Kua and S.D. Pang, “Biochar-mortar composite: Manufacturing, evaluation of physical properties and economic viability”, Construction and Building Materials, 167, pp. 874–889, 2018.
[32] S. Gupta and H.W. Kua, “Effect of water entrainment by pre-soaked biochar particles on strength and permeability of cement mortar”, Construction and Building Materials, 159, pp. 107–125, 2018.
[33] S. Gupta, H.W. Kua and H.J.Koh, “Application of biochar from food and wood waste as green admixture for cement mortar”, Science of the Total Environment, 619–620, pp. 419–435, 2018.

[34] W.A. Kutti, A.B.M.S. Islam and M. Nasir, “Potential use of date palm ash in cement-based materials”, Journal of King Saud University – Engineering Sciences, 31, pp. 26–31, 2019.
[35] A. Sirico, P. Bernardi, B. Belletti et al., “Mechanical characterization of cement-based materials containing biochar from gasification”, Construction and Building Materials, 246, 118490, 2020.
[36] A. Sirico, P. Bernardi, B. Belletti and A. Malcevschi, “Biochar-based cement pastes and mortars with enhanced mechanical properties”, Frattura ed Integrita Strutturale, 54, pp. 297-316, 2020.
[37] I. Carevic, A.B. evic, N. Stirmer and J.S. Bajto, “Correlation between physical and chemical properties of wood biomass ash and cement composites performances”, Construction and Building Materials, 256, 119450, 2020.
[38] K. Tan, X. Pang, Y. Qin, J. Wang, “Properties of cement mortar containing pulverized biochar pyrolyzed at different temperatures”, Construction and Building Materials, 263, 120616, 2020.
[39] S. Gupta and H.W. Kua, “Carbonaceous micro-filler for cement: Effect of particle size and dosage of biochar on fresh and hardened properties of cement mortar”, Science of the Total Environment, 662, 952–962, 2019 .
[40] S. Muthukrishnan, S. Gupta and H. Kua, “Application of rice husk biochar and thermally treated low silica rice husk ash to improve physical properties of cement mortar”, , Theoretical and Applied Fracture Mechanics, Elsevier, 2019.
[41] A. Mobili, C. Giosue, T. Bellezze, G.M. Revel and F. Tittarelli, “Gasification Char and Used Foundry Sand as Alternative Fillers to Graphene Nanoplatelets for Electrically Conductive Mortars with and without Virgin/Recycled Carbon Fibres”, Appl. Sci., 11, 50, 2021.
[42] S. Navaratnama, H. Wijayab,, P. Rajeev, P. Mendis and K. Nguyen, “Residual stress-strain relationship for the biochar-based mortar after exposure to elevated temperature”, Case Studies in Construction Materials, 14, 00540, 2021.
[43] H. Maljaee, H. Paiva, R. Madadi, L.A.C. Tarelho, M. Morais and V.M. Ferreira, “Effect of cement partial substitution by waste-based biochar in mortars properties”, Construction and Building Materials, 301, 124074, 2021.

[44] L. Restuccia, G.A. Ferroa, D.S. Riera et al., “Mechanical characterization of different biochar-based cement composites”, Procedia Structural Integrity, 25, 226–233, 2020.
[45] W. Tangchirapat, T. Saeting, C. Jaturapitakkul et al., " Use of waste ash from palm oil industry in concrete," Waste Management, 27, 81 – 88, 2007.
[46] K. Ganesan, K. Rajagopal and K. Thangavel, “Rice husk ash blended cement: Assessment of optimal level of replacement for strength and permeability properties of concrete”, Construction and Building Materials 22, 1675–1683, 2008.
[47] B. Chatveera and P. Lertwattanaruk, "Durability of conventional concretes containing black rice husk ash," Journal of Environmental Management, pp. 59-66, 2011.
[48] G.A. Akeke, M.E. Ephraim, Akobo, I.Z.S and J.O. Ukpata, “Structural properties of rice husk ash concrete”, International Journal of Engineering and Applied Sciences, 2013.
[49] A. Siddika, M.A. Mamun, R. Alyousef and H.M. Hosseini, “State-of-the-art-review on rice husk ash: A supplementary cementitious material in concrete”, Journal of King Saud University – Engineering Sciences, 33, pp. 294–307, 2021.
[50] N. K. Krishna, S. Sandeep and K. M. Mini, "Study on concrete with partial replacement of cement by rice husk ash”, Materials Science and Engineering, 149, 012109, 2016.
[51] S. A. Zareei, F. Ameri, F. Dorostkar and M. Ahmadi, "Rice husk ash as a partial replacement of cement in high strength concrete containing micro silica: Evaluating durability and mechanical properties," Case Studies in Construction Materials, 2017.
[52] V. Vishwakarma, D. Ramachandran, N. Anbarasan and A.M. Rabel, “Studies of rice husk ash nanoparticles on the mechanical and microstructural properties of the concrete”, Materials Today: Proceedings 3, 1999–2007, 2016.
[53] A.A. Raheem, K.O. Oriola, M.A. Kareem and R. Abdulwahab, “Investigation on thermal properties of rice husk ash-blended palm kernel shell concrete, Environmental Challenges, 5, 100284, 2021.
[54] D.O. Nduka, B.J. Olawuyi,, E.O. Fagbenle, B.G. Fonteboa, “Mechanical and microstructural properties of high-performance concrete made with rice husk ash internally cured with superabsorbent polymers”, Heliyon 8, 10502, 2022.

[55] A.A.K. Al-Alwan, M. Al-Bazoon and F.I. Mussa, “The impact of using rice husk ash as a replacement material in concrete: An experimental study”, Journal of King Saud University – Engineering Sciences, 2022.
[56] Z.A. Zeidabadi, S.Bakhtiari, H. Abbaslou and A.R. Ghanizadeh, “Synthesis, characterization and evaluation of biochar from agricultural waste biomass for use in building materials”, Construction and Building Materials, 181, 301–308, 2018.
[57] P. Moreno, R. Fragozo, S. Vesga, M. Gonzalez, L. Hernandez, I.D. Gamboa and J. Delgado, “Tobacco waste ash: a promising supplementary cementitious material”, International Journal of Energy and Environmental Engineering, 9, 499–504, 2018.
[58] A. Dixit, S. Gupta, S.D. Pang and H.W. Kua, “Waste Valorisation using biochar for cement replacement and internal curing in ultra-high performance concrete”, Journal of Cleaner Production, 238, 117876, 2019.
[59] A. Akhtar and A.K. Sarmah, “Strength improvement of recycled aggregate concrete through silicon rich char derived from organic waste”, Journal of Cleaner Production, 2018.
[60] D. Cuthbertson, U. Berardi, C. Briens and F. Berruti, “Biochar from residual biomass as a concrete filler for improved thermal and acoustic properties”, Biomass and Bioenergy, 120, pp. 77 – 83, 2019.
[61] S. Gupta, K.H. Wei and P.S. Dai, “Effect of biochar on mechanical and permeability properties of concrete exposed to elevated temperature”, Construction and Building Materials, 234, 117338, 2020.
[62] D.S. Riera, L. Restuccia and G.A. Ferro, “The use of Biochar to reduce the carbon footprint of cement-based materials”, Procedia Structural Integrity, 26, 199–210, 2020.
[63] Y.Qin, X. Pang, K. Tan and T. Bao, “Evaluation of pervious concrete performance with pulverized biochar as cement replacement”, Cement and Concrete Composites, 119, 104022, 2021.
[64] K. Tan, Y. Qin, T.Du, L. Li et al., “Biochar from waste biomass as hygroscopic filler for pervious concrete to improve evaporative cooling performance, Construction and Building Materials, 287, 123078, 2021.
[65] RA.B. Depaa, V. Priyadarshini, A. Hemamalinie, J Francis Xavier and K Surendrababu, “Assessment of strength properties of concrete made with rice husk ash”, Materials Today: Proceedings, 45, pp. 6724–6727, 2021.

[66] W. Zhenhong , M. Chen, H. Fang, J. Peng et al., “Replacement of biochar from waste for cement:
mechanisms and eco-benefits”, Research Square, 2022.
[67] K. Khan, M.A. Aziz, M. Zubair and M.N. Amin, “Biochar Produced from Saudi Agriculture Waste as a Cement Additive for Improved Mechanical and Durability Properties—SWOT Analysis and Techno-Economic Assessment”, Materials, 15, 5345. 2022.
[68] M.W. Tait and W.M. Cheung, “A comparative cradle-to-gate life cycle assessment of three concrete mix designs”, Int J Life Cycle Assess, Vol 21, pp 847–860, 2016.
[69] T. Kim, S. Tae and C.U. Chae, “Analysis of environmental impact for concrete using LCA by varying the recycling components, the compressive strength and the admixture material mixing”, Sustainability, Vol 8, pp 389, 2016.
[70] D. Hoornweg and P.B. Tata, “What a Waste: A Global Review of Solid Waste Management”, Washington: Urban development series, pp 15, 2012.
[71] D. Singh and J. Singh, “Use of agro-waste in concrete construction”, International Journal of Environment, Ecology, Family and Urban Studies”, Vol 6, pp 119-130, 2016.
[72] J. Fort, J. Sal, J. Zak and R. Cerny, “Assessment of Wood-Based Fly Ash as Alternative Cement Replacement”, Sustainability, Vol 12, 2020.
[73] E.R. Teixeira, R. Mateus, A.F. Camoes and L. Bragança, “Comparative environmental life-cycle analysis of concretes using biomass and coal fly ashes as partial cement replacement material”, Journal of Cleaner Production, pp 1-10, 2015.
[74] R. Dandautiya and A.P. Singh, “Utilization potential of fly ash and copper tailings in concrete as partial replacement of cement along with life cycle assessment”, Waste Management, 99, 90–101, 2019.
[75] M. Pavlíková, L. Zemanová, J. Pokornýet al., “Influence of Wood-Based Biomass Ash Admixing on the Structural, Mechanical, Hygric, and Thermal Properties of Air Lime Mortars”, Materials, 12, 2227, 2019.
[76] O. Das, A.K. Sarmah, and D. Bhattacharyya, “Structure–mechanics property relationship of waste derived biochars”, Science of the Total Environment, 538, pp. 611–620, 2015.

[77] A. Tomczyk, Z. Sokołowska and P Boguta, “Biochar physicochemical properties: pyrolysis temperature and feedstock kind effects”, Rev Environ Sci Biotechno, Vol 19, pp 191–215, 2020.
[78] K.J. Shin, S.C. Lee and Y.Y. Kim, “Role of fine aggregates on mechanical properties of mortar”, Materials Research Innovations, Vol. 19, 2015.
[79] B. Johannesson and P. Utgenannt, “Microstructural changes caused by carbonation of cement mortar”, Cement and concrete research, 31, pp. 925-931, 2001.
[80] L. Wang, L. Chen, D.C.W. Tsang et al., “Biochar as green additives in cement-based composites with carbon dioxide curing”, Journal of Cleaner Production, 2020.
[81] R. Mrad and G. Chehab, “Mechanical and Microstructure Properties of Biochar-Based Mortar: An Internal Curing Agent for PCC”, Sustainability, 11, 2491, 2019.
[82] L.F. Morales, K. Herrera, J.E. Lopez and J.F. Saldarriaga, “Use of biochar from rice husk pyrolysis: assessment of reactivity in lime pastes”, Heliyon, 7, e08423, 2021.
[83] P. Moreno, R. Fragozo, S. Vesga, M. Gonzalez, L. Hernandez, I.D. Gamboa and J. Delgado, “Tobacco waste ash: a promising supplementary cementitious material”, International Journal of Energy and Environmental Engineering, 9, 499–504, 2018.
[84] J.J. Nair, S. Shika and V. Sreedharan, “Biochar Amended Concrete for Carbon Sequestration”, IOP Conf. Series: Materials Science and Engineering, 936, 012007, 2020.
[85] Ordinary Portland Cement 43 Grade – Specification, IS 8112, Second revision, New Delhi, India.: BIS (Bureau of Indian Standards), 2013.
[86] Methods of Physical Tests for Hydraulic Cement, Determination of fineness by dry sieving, IS: 4031, New Delhi, India.: BIS (Bureau of Indian Standards) (Part-1), 1996.
[87] Methods of Physical Tests for Hydraulic Cement, Determination of standard consistency of standard cement paste, IS: 4031, New Delhi, India.: BIS (Bureau of Indian Standards) (Part-4), 1988.
[88] Methods of Physical Tests for Hydraulic Cement, Determination of soundness, IS: 4031, New Delhi, India.: BIS (Bureau of Indian Standards) (Part-3), 1988.
[89] Methods of Physical Tests for Hydraulic Cement, Determination of initial and final setting times, IS: 4031, New Delhi, India.: BIS (Bureau of Indian Standards) (Part-5), 1988.

[90] Specification for coarse and fine aggregates from natural resources for concrete, IS: 383, New Delhi, India.: BIS (Bureau of Indian Standards), 1970.
[91] Methods of test for aggregates for concrete, IS: 2386, New Delhi, India.: BIS (Bureau of Indian Standards), Part-1, 1963.
[92] Methods of test for aggregates for concrete, IS: 2386, New Delhi, India.: BIS (Bureau of Indian Standards), Part-3, 1963.
[93] Concrete mix proportioning- guidelines, IS: 10262, New Delhi, India.: BIS (Bureau of Indian Standards), 2009.
[94] Plain and reinforced concrete – code of practice, IS: 456, New Delhi, India.: BIS (Bureau of Indian Standards), 2000.
[95] H.A. Alaka, L.O. Oyedele and O.L.T Coker, "Effect of excess dosages of superplasticizer on the properties of highly sustainable high-volume fly ash concrete", International Journal of Sustainable Building Technology and Urban Development, Taylor & Francis, 2016.
[96] Specification for flow table for use in tests of hydraulic cements and pozzolanic materials, IS: 5512, New Delhi, India.: BIS (Bureau of Indian Standards), 1983.
[97] Specification for concrete slump test apparatus, IS: 7320, New Delhi, India.: BIS (Bureau of Indian Standards), 1974.
[98] Methods of physical tests for hydraulic cement, Determination of compressive strength of masonry cement, IS: 4031, New Delhi, India.: BIS (Bureau of Indian Standards), Part-7, 1988.
[99] Specifications for moulds for use in tests of cement and concrete, IS: 10086, New Delhi, India.: BIS (Bureau of Indian Standards), 1982.
[100] Standard Test Method for Flexural Strength of Hydraulic Cement Mortar, ASTM 348-02:, Web Reference - http://www.astm.org/cgi-bin/resolver.cgi?C348.
[101] Standard Test Method for Flexural Strength of Concrete (Using Simple Beam with Third-Point Loading), ASTM C78/C78M-15a:, Web Reference - https://www.astm.org/c0078_c0078m-15a.html.
[102] A. Hamood, J. M. Khatib and C. Williams, "The effectiveness of using Raw Sewage Sludge (RSS) as a water replacement in cement mortar mixes containing Unprocessed Fly Ash (u-FA)", Construction and Building Materials, 147, 27-34, 2017.

[103] Method of test for permeability of cement mortar and concrete, IS:3085, New Delhi, India.: BIS (Bureau of Indian Standards), 1965.

[104] E. Sancak and F. Özkan, "Sodium Sulphate Effect on Cement Produced with Building Stone Waste," Journal of Materials, 2015.

[105] M.M. Khasreen, P.F.G Banfill and G.F. Menzies, "Life-Cycle Assessment and the Environmental Impact of Buildings: A Review", Sustainability, 1, 674-701, 2009.

[106] Environmental Management- Lifecycle assessment- Principles and framework, BIS: 14040, Bureau of Indian Standards, New Delhi, India, 2006.

[107] Environmental Management- Lifecycle assessment- Requirements and guidelines, BIS: 14044, Bureau of Indian Standards, New Delhi, India, 2006.

[108] J. Sjunnesson, "Life Cycle Assessment of Concrete. Environmental and Energy Systems Studies", Lund University, Department of Technology and Society, Master Thesis, 2005.

[109] C.Bulle, M. Margni, L. Patouillard et al., "IMPACT World+: a globally regionalized life cycle impact assessment method", The International Journal of Life Cycle Assessment, 24:1653–1674, 2019.

[110] BMTPC, "Criteria for Production Control of Ready Mix Concrete for RMC Capability Certification", Building Materials & Technology Promotion Council, Ministry of Housing & Urban Poverty Alleviation, Government of India, New Delhi, 2013.

[111] C.P. Dancey and J. Reidy, "Statistics without maths for psychology: using SPSS for windows", London, England: Prentice-Hall, 2004.

[112] S.A. Adeosun, "STS202: Statistics for physical sciences and engineering", www.crescent-university.edu.ng. 2019.

List of Publications

1. "To Investigate the Mechanical and Durability Properties of Cement Mortar Incorporating Agrowaste", Journal of Green Engineering (JGE), Volume-11, Issue-1, January 2021, Pages 54-71.
2. "Mechanical and Durability Properties of Biochar Concrete", International Conference on Material Science and Sustainable Manufacturing Technology 2022, Materials Today: Proceedings (Article: MATPR33421, Accepted for Publication: 23 June 2022).

List of Conferences

1. "A Comparative Lifecycle Assessment of Ordinary and Agrowaste Based Concrete", International Conference on Smart Environment Management and Solutions, April 2022.
2. "Mechanical and Durability Properties of Biochar Concrete", International Conference on Material Science and Sustainable Manufacturing Technology 2022.

APPENDIX – 1 : Paper Published

Journal of Green Engineering (JGE)

Volume-11, Issue-1, January 2021

To Investigate the Mechanical and Durability Properties of Cement Mortar Incorporating Agrowaste

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Abstract

This work is performed to develop a cement mortar by incorporating biochar agrowaste. The experimental study outlines the durability and mechanical properties of the mortar. For this purpose, 2%, 4%, 6%, 8%, and 10% biochar prepared from rice husk at 550° C, has been introduced in the cement mortar to replace cement. The cement mortar properties such as flowability, flexural strength, compressive strength, water absorption, etc. were studied. Microscopic properties have also been studied with the help of non-destructing techniques such as scanning electron microscopy and X-ray powder diffraction techniques. The strength properties of cement mortar significantly improved with a 2% replacement of cement by biochar. As compared to the control specimens, the increase in compressive and flexural strengths was found as 9.55% and 12% respectively. However, the fresh properties such as flowability are reduced with the addition of the biochar. For durability, sulphate resistance test is carried out with a 5% Na_2SO_4 solution. The compressive strength loss is found to decrease when biochar is replaced up to 4%, whereas the loss increases with further increase in the inclusion of biochar beyond 4%. The study of the findings reveals that the addition of Biochar greatly affects the properties of the cement mortar.

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Mechanical and durability properties of biochar concrete

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ABSTRACT

Cement production, which now accounts for over 7% of global CO_2 emissions, could be a major roadblock to the Paris Agreement's goal of net-zero emissions by 2050. Greenhouse gas emissions during cement production arise from the processing of clinker where a large amount of fossil fuel is burnt for energy generation, and the remaining part comes from the energy it takes to get to the necessary high temperatures. Partial replacement of cement by residuals from agricultural industries is one of the key strategies to mitigate CO_2 emissions and help promote sustainability. The objective of the present research work is to investigate biochar, prepared by pyrolyzing rice husk (RH) at 550 °C, as an alternate supplementary cementitious material (SCM). The physical and chemical properties of biochar were characterized using elemental analysis, scanning electron microscopy, thermogravimetric, and energy-dispersive X-ray spectroscopy. Compressive strength, flexural strength, water loss, permeability, and resistance to sulfate attack tests were used to investigate the mechanical and durability features of concrete containing varied concentrations of biochar. Chapelle test was conducted to determine the pozzolanic activity of the biochar. The results indicate that concrete containing 4% biochar improved compressive strength by 2.32%, flexural strength by 23.52%, and durability by 17.3% because the finer biochar particles have a packing effect resulting in the formation of a dense matrix.

1. Introduction

Today, sustainability is the primary concern of all world economies. Cement manufacturing contributes between 4 and 8% of global CO_2 emissions, making the building industry a critical contributor to long-term sustainable growth. [1]. The environmental damage caused by the widespread use of concrete is now evident and a lot of research is underway to decarbonize this wonder material. Several studies show that using waste from industry and agriculture as a cement supplement in concrete is an efficient way to minimize CO_2 emissions [2]. The inclusion of agricultural waste by-products in the concrete mix has increased significantly in the past decades [3]. Rice husk is an agricultural byproduct that accounts for almost 20% of global rice output each year [4]. According to data from India's Punjab Pollution Control Board (PPCB), paddy stubble burning is performed on over 12.9 lakh hectares of agricultural land, accounting for nearly 43 percent of the state's rice lands. As a result, because the siliceous components in agricultural waste are difficult to degrade and are classed as waste, their management causes major environmental difficulties. [5]. Also, stubble burning being practiced by the farmers to clear their land has become a major cause of air pollution in Northern parts of India. Numerous studies have been reported on agro-waste-based concrete blended with rice husk ash as a successful partial replacement of cement in the concrete [6–9]. But, in many cases, the environmental impact of outdoor incinerators is largely ignored. Pyrolysis, or the controlled burning of RH at temperatures above 550 °C with little to no oxygen supply, produces pozzolanic reactive rice husk ash (RHA), also known as biochar. The quality, however, is determined by the type of feedstock, combustion rate, burning temperature, and oxygen supply, all of which have an impact on the product's quality [10].

Currently, biochar is being investigated as a bio-asphalt binder in the construction industry [11,12]. Biochar can be obtained from agricultural waste and wood tailings under controlled conditions for sustainable applications in concrete. Its applications are gaining importance due to its easy availability and enhancement of the physio-chemical properties of concrete [13–15]. For example,

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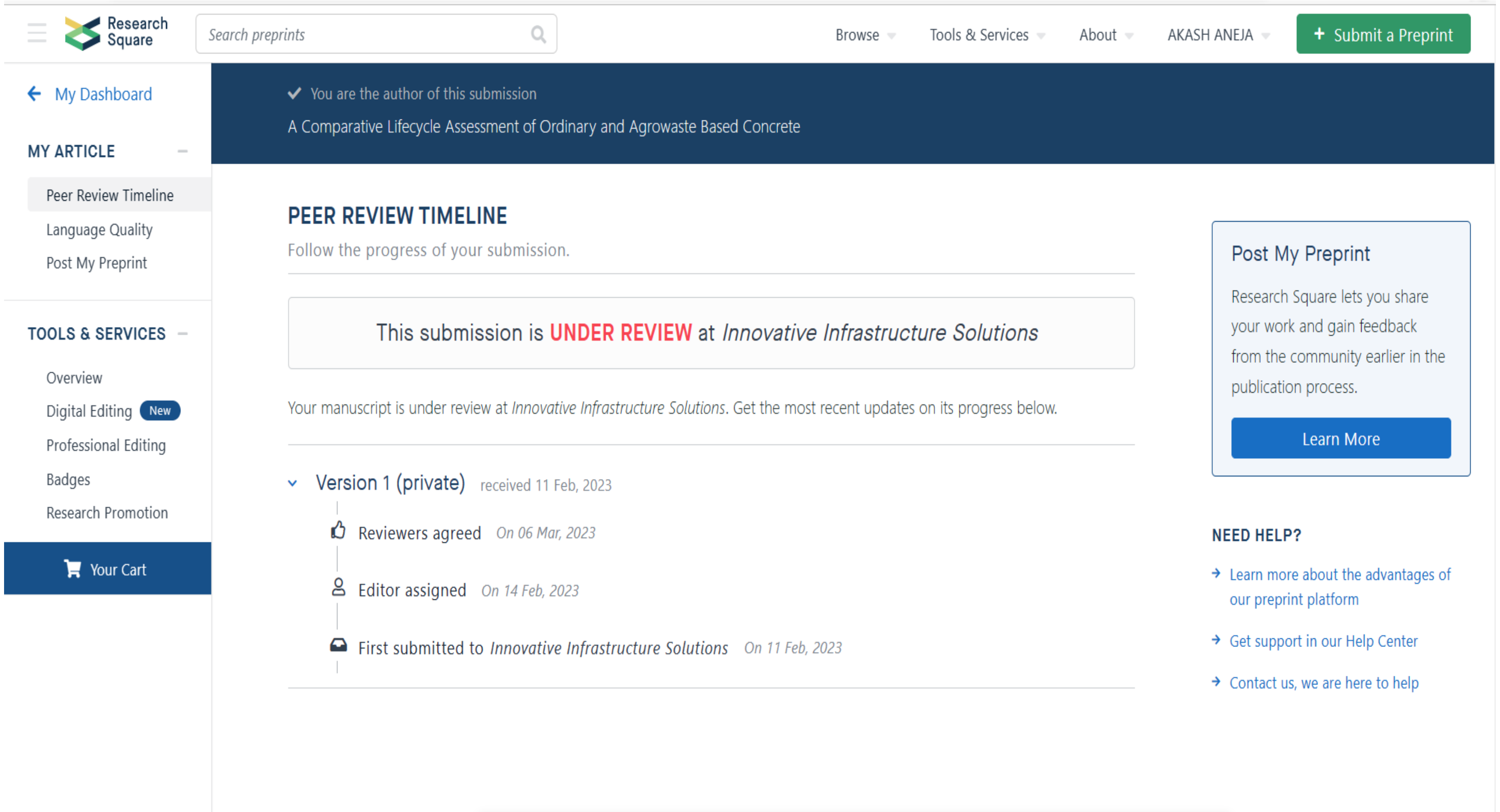
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APPENDIX – 2: Paper presented in International Conferences

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