ARTICLE

Preliminary Study of Agricultural Waste as Biochar Incorporated into Cementitious Materials

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ABSTRACT

Incorporating small amounts of biochar into cementitious materials has partial effects on the environment. In this present study, rice husk was collected as agricultural biomass from a local area of Roorkee Uttarakhand, which contains siliceous material to a significant extent. Biochar was prepared from agricultural waste in a muffle furnace at a temperature of 500 °C for 90 min and ground to a fineness of less than 10 µm. Prior to incorporation into building envelopes such as mortar and concrete, a basic study on cement pastes is essentially required. For this purpose, different dosages of biochar such as 0, 3%, 5% and 10% wt. were replaced with cement in cementitious materials. Physical properties such as water absorption, density and porosity were investigated. Furthermore, mechanical and thermal properties such as compressive strength and thermal conductivity were studied. Advanced tools like field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and thermogravimetric analyzer (TGA) were used to identify the hydration products. As the dosages increased in the cement matrix, the physical properties of sample were increased and porosity decreased. The compressive strength of biochar incorporated cement paste improved according to 0, 3%, 5% and 10% wt. It further reveals that as the dosage increased, the thermal conductivity of the samples decreased significantly. Moreover, the sustainable assessment showed that biochar could reduce embodied carbon, embodied energy and strength efficiency substantially over the control sample. A satisfactory result was obtained at 5% wt. and 10% wt. of biochar. The overall result revealed that biochar up to 10% wt. can be incorporated into mortar and concrete due to better results than the control mix.

Keywords: Rice husk; Silicious material; Biochar; Cement; Hydration
1. Introduction

Increased CO$_2$ emissions from cement industries are one of the most critical hazards to the atmosphere in recent times. The rise of industrial development radically increased CO$_2$ discharges day by day [1,2]. Human activity has contributed significantly to this increase in energy production for manufacturing industries. Construction-related industries, among other production activities, have contributed significantly to global CO$_2$ emissions [3]. Only 7% of the world’s CO$_2$ emissions come from the production, processing, and manufacturing processes used in cement production [4]. Research has been carried out all around the world to provide effective solutions to reduce CO$_2$ emissions from the cement production industries [5]. The impact of alternative bio-based components and life cycle assessment (LCA) and the impact of alternative bio-based components in cement manufacturing were also investigated [6]. The addition of bio-based materials and cellulosic materials degrade the cement properties and delay the hydration process respectively [7,8]. Converting these biobased materials to biochar is a successful technique because of its superior thermal and mechanical properties, sustainability, and capacity to lower CO$_2$ emissions [9]. The thermal and mechanical qualities of cement-based products are influenced by the quantity of biochar used, its origin, preparation method, and particle size [10]. In comparison to other incineration techniques, pyrolysis produces biochar, a stable carbon-rich material that releases less CO$_2$ into the environment. The circumstances under which biochar is produced have a significant impact on its quality. The yield of pyrolysis products as well as their physicochemical and microstructural characteristics are influenced by variables such as pyrolysis temperature range, pressure, heating rate, and residence duration [11]. The variety of biomass feedstock chosen determines the physicochemical optimal-bonding variation of biochar, including surface area, pore size, cation exchange capacity and water retention capacity [12]. Formation of hydrogen bonds between water molecules and having OH groups on biochar surfaces, biochar contains highly porous substance with a significant surface area [13]. Biochar is prepared by fast and slow pyrolysis methods. The combustion process in the absence of oxygen leads to the degradation of biomass in various phases depending on the chemistry and composition of the raw feedstock. Biomass consists mostly of cellulose, hemicellulose, and lignin. The proportion of hemicellulose, lignin and cellulose in the biomass determines how much fixed carbon the biochar contains. Biochar with a pore width of less than 30 mm was the most effective at holding water, and biochar with micropore sizes between 5 and 30 mm was found to be the most active particle in absorbing and holding moisture. High propensity for water absorption in biochar with pores of 5-6 µm diameter [14,15]. Nowadays, biochar is used as soil remediation, carbon sequestration, filler in polymeric materials, conversion purposes and energy storage purposes, etc. [16]. The addition of higher dosage of biochar to cement matrix led to fluidity, demand of superplasticizer and reduction of free water [17]. Ahmad et al. [18] reported that less bamboo biochar was required to improve the compressive strength of the cement composite. Gupta and Kua [19] evaluated the yield stress and plastic viscosity of biochar-cement composites, finding that coarse biochar had a bigger impact on the flowability and viscosity of cement paste than fine biochar. Additionally, it was revealed that micro biochar particles excelled macroporous biochar in terms of early strength (1- day and 7-day) and water tightness. Recent studies have found that the best filler percentage for biochar derived from food and wood waste was 2% since it increased compressive strength the most [20]. Akhtar and Sarmah [21] studied three different forms of biochar such as rice husk, paper and pulp sludge, and chicken litter. No matter which type of biochar was utilised, the study showed that adding biochar to concrete reduced its compressive strength. However, the type of biochar used determines how much the compressive strength of concrete is reduced [22]. They found that adding biochar reduced the compressive strength of cement-based materials, yet cement samples made with biochar effectively reached to
12.5 MPa minimum compressive strength needed to prepare mortar for structural usage after 28 days. The higher reduction in cement content caused by higher biochar dosages, mechanical strength is lowered. This results in a significantly reduced production of the hydration product. However, cementitious composites’ mechanical strength may be increased by adding biochar at lower replacement amounts [23]. According to Ahmad et al. [18], adding 0.08 wt% of inert bamboo charcoal particles to mortar might increase its flexural strengths and toughness by 66% and 103%, respectively. Using five different ratios (0, 1, 3, 5, and 10% wt.), the biochar added to the cement before being combined with water and sand. The mortar’s thermal conductivity was decreased by the addition of biochar. For instance, the addition of 1% wt., 3% wt., 5% wt., and 10 wt% of biochar decreased by 16%, 22%, 30%, and 39%, respectively, in comparison to the reference mortar [24]. The thermal performance of cement pastes containing sugarcane bagasse biochar has been reported to have decreased significantly. The heat conductivity dropped by 30% and 45%, respectively, in the 6% biochar-cement composites after 90 and 28 days of curing respectively [25]. The samples with 1 and 2% biochar by weight showed the highest decrease in thermal conductivity, reporting 0.208 to 0.230 W/(m.K), and specifically, 0.192-0.197 W/(m.K) for cementitious materials [26]. The porosity of the matrix and Inter Transitional Zone (ITZ) are improved by biochar, which typically has D90 and D50 between 9 µm and 5 µm and was very efficient in reducing the capillary water absorption rate [27]. Tasdemir [28] demonstrated, when compared to the control mix, the initial sorptivity of commercial wood, Singapore wood biochar and 5% wt. coconut were reduced by 38%, 29% and 28% respectively. Most of the research found that adding fine fillers to cementitious composites refines the matrix’s pores and increases ITZ [28]. According to certain research, the amount of biochar incorporated, the w/b ratio, the pyrolytic temperature, and the size of the biochar all have an impact on the reduction in water absorption. A considerable quantity of capillary holes is introduced into the matrix by an increase in the percentage of biochar and the w/b ratio, which causes the open porosity and moisture transportation of cementitious material to increase [29]. The addition of biochar at low concentrations (0.1-0.5 wt%) has been described to reduce water absorption of recycled aggregate, which was due to high porosity. This was attributed to the biochar’s ascendant filler effect, which creates compact matrix with fewer voids for water absorption [30]. The primary features provided to the mortar to prevent moisture evaporation and shrinkage are the water absorption and retention capabilities of biochar. The moisture transfer qualities of cement mortar are greatly influenced by the water retention capacity of the biochar. Although less polar functional groups in the biochar produced at high temperatures cause it to lose its hydrophilicity, the consequence of increased porosity at elevated temperatures controls the retaining water capacity. The biochar’s ability to retain water is influenced by several elements, including morphology, porosity, pore size, and pore connectivity [31,32].

In this study, rice husk was converted into biochar at a temperature of 500 °C without the presence of oxygen. In order to assess the biochar and biochar in the cement matrix, sophisticated tools are used. With dosages of 0%, 3%, 5%, and 10%, the produced biochar is substituted for cement. Investigations were made into the physical, mechanical, and thermal characteristics of biochar used in cement paste. In-depth research was done on the morphology of incorporated biochar cement paste.

2. Materials and methods

2.1 Materials used in the experiment

Rice husk was purchased from a local source in Roorkee. The binder (OPC, Ultra-tech) was acquired from local market of Roorkee, Uttarakhand. The materials such as cement and biochar composition were presented in Table 1.
Table 1. Chemical composition of biochar and ordinary portland cement.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Biochar (%)</th>
<th>Ordinary portland cement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>1.9</td>
<td>61.05</td>
</tr>
<tr>
<td>SiO₂</td>
<td>89.17</td>
<td>22.23</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.98</td>
<td>6.01</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.12</td>
<td>2.19</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.89</td>
<td>2.15</td>
</tr>
<tr>
<td>MgO</td>
<td>---</td>
<td>3.09</td>
</tr>
<tr>
<td>Na₂O</td>
<td>---</td>
<td>0.51</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.2</td>
<td>0.12</td>
</tr>
<tr>
<td>MnO</td>
<td>0.11</td>
<td>0.16</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>1.2</td>
<td>0.045</td>
</tr>
<tr>
<td>LOI</td>
<td>---</td>
<td>0.081</td>
</tr>
</tbody>
</table>

2.2 Preparation biochar from rice husk biomass

350 g of rice husk is combusted in a muffle furnace at a temperature of 500 °C for 90 min at a ramp rate of 5 °C/min. A ball mill was used to compress the biochar for fine particles. A particle size analyzer (PSA) was used to measure the size of the biochar particles. The average particle distribution of biochar was 6.4 µm (Figure 1 and Table 3). It was used as a substitute for cement in the experiment. Elemental composition was measured using the method of ultimate analysis and their values are given in Table 2.

Table 2. Ultimate analysis of biochar.

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>61.05</td>
</tr>
<tr>
<td>H</td>
<td>0.53</td>
</tr>
<tr>
<td>N</td>
<td>2.47</td>
</tr>
<tr>
<td>S</td>
<td>0.13</td>
</tr>
<tr>
<td>O</td>
<td>35.82</td>
</tr>
</tbody>
</table>

2.3 Cement samples with rice husk biochar

At a water-to-binder (w/c) ratio of 0.5, cement was mixed with different concentrations of biochar (0%, 3%, 5% and 10%). The combination ratio of cement and biochar were presented in Table 4. These combinations were poured into a 25 mm × 25 mm × 25 mm mold. After a day, the samples were immersed in plain water. Water absorption, density, porosity, compressive strength, thermal conductivity, and characterization were made after 28 days.

Table 4. Mix proposition of cement paste.

<table>
<thead>
<tr>
<th>w/c : 0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement (%)</td>
</tr>
<tr>
<td>100</td>
</tr>
<tr>
<td>97</td>
</tr>
<tr>
<td>95</td>
</tr>
<tr>
<td>90</td>
</tr>
</tbody>
</table>

3. Physical properties of cement cubes with rice husk biochar

3.1 Water absorption

After 28 days, the cement with biochar samples was dried in an electric oven and adjusted to 100 °C for 24 hours. The samples were removed from the electrical oven after 24 hours, allowed to cool to room temperature, and their dry weights were calculated (Wₐ). The dried samples were immersed in normal water for 24 hours. Each sample was cleaned with a dry cloth to remove the remaining surface...
moisture before weighing while wet ($W_w$). The following method was used to calculate the percentage of water absorption of cement paste.

\[
\text{Water absorption (\%) } = \frac{W_w - W_d}{W_d} \times 100
\]

where, $W_d$ is oven dried sample weight (g), $W_w$ is wet samples weight.

### 3.2 Porosity and density

The density of biochar-incorporated cement paste samples was determined according to the mass and volume of the samples. The dimensions of the samples were measured with the help of a digital caliper accurate to 0.01 mm for four samples and the results were averaged for each dimension \[33\]. The cement with biochar samples was dried at 100 °C for 24 hours and subsequently for 28 days. The weight of dried samples ($W_d$) was calculated after 24 hours. The samples were dried, then soaked for 24 hours and then boiled for 5 hours. After cooling for 5 hours at room temperature, the cement with biochar samples was cleaned with a dry cloth to eradicate any external moisture from the boiled samples. After boiling, the weights of the samples were calculated ($W_b$). After cooling the cement with biochar samples were halted in water and the suspended weight of the samples was calculated ($W_s$).

\[
\text{Porosity (\%) } = \frac{W_b - W_d}{W_b - W_s} \times 100
\]

where $W_b$ is the sample weight after boiling, and $W_s$ is the sample suspended weight \[34\].

### 3.3 Compressive strength of biochar-incorporated cement paste

Specimens of cement cubes were prepared according to Section 2.3. Testometric UTM 50kN was used to evaluate the compressive strength of cement paste samples with biochar after 28 days.

### 4. Characterization of biochar-incorporated cement paste

#### 4.1 Field emission scanning electron microscopy (FESEM)

With the help of field emission scanning electron microscopy (Make: TESCAN, Model: MIRA 3), the morphology of the biochar-incorporated materials was examined in vacuo. Samples were mounted on carbon tape adhered to a stub after being coated with gold using an Electron Microscope Sciences gold sputter coater (model: K550X). The stub was inserted into the FESEM apparatus to examine the material microstructure.

The morphology of rice husk biochar was presented in Figure 2. The biochar appears intermittent shape and non-uniform surfaces with various

![Figure 2. Morphology of (a) Rice husk (b) Bio Char.](image)
heterogeneous porous arrangements. The porous arrangements depend on the method of combustion, biomass, heating rate and volatile content.

4.2 X-ray diffraction

The materials were pulverised, and then spread onto a glass slide. The sample on a glass slide was introduced into an X-ray diffraction equipment (Make: Rigagu, Model: D5110) and operated between the 2:5-80 range at a speed of 3 theta/min.

The XRD of rice husk biochar was presented in Figure 3. At elevated temperature, cellulose crystalline was changed due to the emergence of atoms in the carbon substance. The deficiency of crystalline intensity peaks informed that; the rice husk biochar is a semi-amorphous in nature (Figure 3) [35].

4.3 Thermogravimetric analysis

Under nitrogen atmosphere, flow rate 3.6 sccm/ min, and continuous heating temperature 5 °C/min, the weight loss of raw rice husk was determined using STA PT 1600 model. After 28 days, the hydration products were determined between ambient to 1000 °C. When calcium hydroxide dissociates during cement hydration, water is released. This water loss between 380 and 520 °C can be translated to portlandite and is estimated using the equations below.

\[
\%CH_{dx} = 4.11 \times dx_{(400-500 \, ^\circ \text{C})} \quad (3)
\]

where \( CH_{dx} \) and \( dx \) (400-500 °C) is the content of calcium hydroxide and the weight loss in the decarboxylation zone, respectively.

The chemically bound water \( (W_b) \) in the sample is determined using the following equation:

\[
W_b = W_{dh} + W_{dx} + 0.41(W_{dc}) \quad (4)
\]

where, \( W_{dh} \) (105-400 °C) is the percentage weight loss of dehydration, \( W_{dx} \) (400-500 °C) is percentage weight loss of dihydroxylation, \( W_{dc} \) (500-900 °C) is the percentage weight loss of decarbonation. The empirical factor 0.41 was employed to change in percentage weight loss of decarbonation of water. The percentage degree of hydration is determined using Equation (5) [36]:

\[
\alpha(\%) = \frac{W_b}{0.24} \times 100 \quad (5)
\]

The TGA of rice husk biochar was presented in Figure 4. There are two stages of mass loss observed at different temperatures. Mass loss is observed between 100 and 125 °C due to moisture content. Another one is 200 to 410 °C due to combustible and non-combustible gases. The moisture content in rice husk is about 6.84%. The second stage of weight loss is about 62.3%.

4.4 Thermal conductivity

A hot disk TPS 1500 instrument (ISO 22007-2) [37] was used to analyze the thermal performance of the samples under ambient conditions. After 28 days, the surface of the samples was flattened for effective contact with the temperature sensors. A temperature sensor was placed between the flat specimens. Working conditions were provided by inbuilt software to determine the thermal conductivity of the specimens.
5. Results and discussions

5.1 Initial and final setting of samples

The initial and final setting time of cement and cement containing biochar are shown in Figure 5. The initial and final setting time for cement is found to be 35 min and 560 min respectively. The replacement of different dosages of biochar led to a decrease in the initial and final setting times (30 min and 527 for 3%, 26 min and 480 min for 5% and 28 min and 520 min for 10%). The obtained results revealed that as the dosage of biochar accelerates initial and final setting time and cement hydration.

5.2 Compressive strength of samples

Mechanical strengths of the different dosages of rice husk biochar-incorporated samples were shown in Figure 6. The results revealed that the compressive strength of various dosages of biochar incorporated samples was first increased by 3% wt. and 5% wt. and then decreased by 10% of biochar than 5% of biochar but increased than the control. Compressive strength of samples enhanced by 13.6%, 19.2%, and 16.06% as compared to the control mix corresponding to 3%, 5% and 10% respectively. The improvement of a maximum proportion of C-S-H in the samples up to 5% wt. of biochar is attributed to the cement samples. This is turned out due to the density difference between raw materials such as cement and biochar. The compressive strength of the sample at 10% wt. of biochar is higher than 3% wt. of biochar. On the other hand, finer particles of biochar are placed between cement particles, which densified the cement paste [27,38,39].

Figure 4. TGA of rice husk (500 °C, 90 min and 5 °C/min).

Figure 5. Compressive strength of biochar incorporated cement paste.
5.3 Porosity and density

The porosity and density of samples were determined according to ASTM C 642 [35]. The obtained results were shown in Figure 7 and Figure 8. The porosity of the samples is decreased than the control mix as amount of rice husk biochar increases. The porosity of control mix is observed at 11.42%. The maximum reduction of porosity is examined at 5% wt. of biochar. 10.9%, 8.3% and 10.24% of porosity reduced than the control mixes subsequent to 3%, 5% and 10% (Figure 7). From Figure 7, it has been investigated that, the porosity of 10% wt. of samples was further reduced than the 3% wt. of sample. It means that rice husk biochar enhances the packaging density of cement matrix. Density is the physical property of cementitious materials. Densities of samples are increased as the amount of biochar increases (Figure 8). The density of the sample is 1.98 g/cm³. The maximum density of the sample is examined at 5% wt. of biochar. 2.04 g/cm³, 2.18 g/cm³ and 2.1 g/cm³ enhanced than the control mixes subsequent to 3%, 5% and 10% respectively (Figure 8). It means that as porosity is reduced, density of samples is increased (Figure 7 and Figure 8).

5.4 Water absorption

The water absorption of various dosages of biochar-incorporated samples was investigated according to ASTM C 642 [35]. The water absorption of the samples is decreased as compared to the control mix as amount of rice husk biochar increases. The water absorption of control mix is examined at 22.5%. The maximum reduction of water absorption is examined at 5% wt. of biochar. Following 3%,
5%, and 10%, there was a 17.2%, 14.2%, and 16.6% decrease in water absorption compared to the control mixes (Figure 9). In Figures 7 and 8, where porosity is decreased and density is raised, there is a reduction in water absorption due to these changes.

5.5 Morphology of samples

The morphology of various dosages of biochar-incorporated samples were shown in Figure 10. The hydration products in various dosages of biochar-incorporated samples increased as biochar content increased. The more compacted hydration products such as C-S-H, Ca(OH)$_2$ and ettringite are observed at 5% of biochar (Figure 10C). It means that the replacement of biochar with cement promoted hydration. The porous structure of the biochar also facilitated in the formation of hydration products and heterogeneous precipitation. Because of the filler effect and dense particle packing in the paste matrix, the compressive strength of the sample was increased by up to 10 wt.% [40]. The C-S-H concentration of cement paste is lower when 3% biochar is added than when 10% biochar is introduced. In addition, van der Waals’ gravity-assisted biochar particle aggregation in cement mixtures containing biochar (as a cement replacement) with 5% of biochar leads to lower hydration production in the mixtures, larger pores and cracks near the ITZ macroscopic mechanical properties [20].
5.6 XRD analysis of samples

The hydration products of crystalline phases such as Calcium silicate (CS1 and CS2), C-S-H, Calcium hydroxide (CH) and Calcite (C), are observed in Figure 11 corresponding to different peaks. The results showed that adding biochar increased the number of hydration products. In cement pastes containing 3%, 5% and 10% biochar, the CH peak at $2\Theta = 17.9^\circ$ is greater than that in normal paste sample. However, as the biochar dosage increased from 3% to 10%, it was found that the amount of CH decreased. Compared to the control sample, the intensity of C-S-H peak ($2\Theta = 31.9^\circ$) was increased by biochar from 3% to 10%. The C-S-H peak, however, is a lesser amount developed than with 3% of biochar. As seen in Figure 11, the C-S-H concentration is decreased in the cement sample.

Figure 10. Morphology (FESEM) of biochar incorporated cement paste (A) 0% (B) 3% (C) 5% (D) 10%.
Figure 11. Mineralogical (XRD) of biochar incorporated cement paste (A) 0% (B) 3% (C) 5% (D) 10%.

The weight loss of various dosages of biochar incorporated samples were shown in Figure 12. The effect of the first mass loss peak on the breakdown of C-A-H and C-S-H gels is observed in TGA curves from Figure 12. Endothermic peaks below 200 °C are brought about by the dehydration of CSH and ettringite phases. In thermographs, calcium silicate hydrate is identified by the loss of water in the range of 120-150 °C. The hydration products such as Calcium aluminate hydrates (C-A-H), calcium silicate hydrates (C-S-H) gel (105-400 °C), calcium hydroxide (C-H) (400-500 °C), and calcium carbonate (CC) (500-900 °C) are found at various temperature ranges. The addition of biochar (BC) resulted in an increased peak at 105-540 °C, demonstrating that the addition of biochar increased the generation of hydration products. The hydration products and degree of hydration were calculated using Equations (3), (4), and (5) [42,43]. The values for each are shown in Table 5. The CH concentration reduced as the biochar dose increased, but the C-S-H content increased from 0 to 10% of the biochar [44]. The degree of hydration is determined using Bhatty’s Equation (5). The degree of hydration is increased as biochar content is increased (Figure 13) from 49.4% to 55.5%. The maximum degree of hydration of sample is examined at 5% wt. The more hydration products in biochar with cement sample is due to the increment of the degree of hydration [45].

Table 5. Investigation of hydration products using TGA analysis.

<table>
<thead>
<tr>
<th>Dosage of Biochar</th>
<th>105-400°C</th>
<th>400-500°C</th>
<th>500-900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>6.9</td>
<td>2.1</td>
<td>7.0</td>
</tr>
<tr>
<td>3%</td>
<td>6.9</td>
<td>2.1</td>
<td>7.0</td>
</tr>
<tr>
<td>5%</td>
<td>6.9</td>
<td>2.1</td>
<td>7.0</td>
</tr>
<tr>
<td>10%</td>
<td>6.9</td>
<td>2.1</td>
<td>7.0</td>
</tr>
</tbody>
</table>
when compared to 5% biochar. Most calcite (C) peaks were evident at angles of 28.3° and 37.2°. The peaks in the XRD spectra of calcium carbonate are more prominent than those of calcium hydroxide. As a result, cement pastes are expected to contain more calcite. Biochar addition significantly increased C intensity at 2ϴ = 28.3° and 37.2°. Promoted calcite is one of the essential elements for the hardness of cement composite [41].

5.7 TGA analysis of samples

The weight loss of various dosages of biochar incorporated samples were shown in Figure 12. The effect of the first mass loss peak on the breakdown of C-A-H and C-S-H gels is observed in TGA curves from Figure 12. Endothermic peaks below 200 °C are brought about by the dehydration of CSH and ettringite phases. In thermographs, calcium silicate hydrate is identified by the loss of water in the range of 120-150 °C. The hydration products such as Calcium aluminate hydrates (C-A-H), calcium silicate hydrates (C-S-H) gel (105-400 °C), calcium hydroxide (C-H) (400-500 °C), and calcium carbonate (CC) (500-900 °C) are found at various temperature ranges. The addition of biochar (BC) resulted in an increased peak at 105-540 °C, demonstrating that the addition of biochar increased the generation of hydration products. The hydration products and degree of hydration were calculated using Equations (3), (4), and (5) [42,43]. The values for each are shown in Table 5. The CH concentration reduced as the biochar dose increased, but the C-S-H content increased from 0 to 10% of the biochar [44]. The degree of hydration is determined using Bhatty’s Equation (5). The degree of hydration is increased as biochar content is increased (Figure 13) from 49.4% to 55.5%. The maximum degree of hydration of sample is examined at 5% wt. The more hydration products in biochar with cement sample is due to the increment of the degree of hydration [45].

5.8 Thermal conductivity of samples

The Thermal conductivity of various dosages of biochar-incorporated samples was investigated according to (ISO 22007-2) [37]. The Thermal conductivity of the samples is decreased as compared to the control mix as amount of rice husk biochar increases. The thermal conductivity of the control mix is examined at 1.17 W/m.K. The maximum reduction of the thermal conductivity is examined at 5% wt. of biochar. Following 3%, 5%, and 10%, there was a 1.05 W/m.K, 0.86 W/m.K, and 0.93 W/m.K decrease in thermal conductivity compared to the control mixes (Figure 14). It is also necessary to look at dynamic heat transmission in building materials with added biochar. A study on dynamic heat transfer found that biochar has low heat reactivity [46]. This is because cement containing biochar has lower thermal conductivity than cement without. In addition, it was found that the main reason for the reduced thermal conductivity was the increased porosity of the biochar by releasing volatiles.

The obtained data are compared with the existing literature review and their observations were given in Table 6 for a better understanding of the experimental results.

<table>
<thead>
<tr>
<th>Dosage of Biochar</th>
<th>105-400 °C ($W_{ah}$)</th>
<th>400-500 °C ($W_{ah}$)</th>
<th>500-900 °C ($W_{ah}$)</th>
<th>$W_b$</th>
<th>α (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>6.9</td>
<td>2.1</td>
<td>7.0</td>
<td>11.9</td>
<td>49.4</td>
</tr>
<tr>
<td>3%</td>
<td>7.16</td>
<td>1.7</td>
<td>7.8</td>
<td>12.1</td>
<td>50.4</td>
</tr>
<tr>
<td>5%</td>
<td>8.3</td>
<td>1.8</td>
<td>10.5</td>
<td>14.4</td>
<td>60</td>
</tr>
<tr>
<td>10%</td>
<td>7.8</td>
<td>2.6</td>
<td>7.5</td>
<td>13.4</td>
<td>55.8</td>
</tr>
</tbody>
</table>
Figure 12. TGA analysis of biochar incorporated cement paste (A) 0% (B) 3% (C) 5% (D) 10%.
Figure 12. TGA analysis of biochar incorporated cement paste (A) 0%, (B) 3%, (C) 5%, (D) 10%.

Figure 13. Degree of hydration of biochar incorporated cement paste.

Table 6. Comparison of biochar incorporated cement based materials with present work.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Pyrolysis conditions</th>
<th>Biochar used as</th>
<th>Dosage</th>
<th>Main consequences</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td>Mixture of woodchips of local forest</td>
<td>900 °C</td>
<td>Filler</td>
<td>1%, 2.5%</td>
<td>Reduction of compressive strength with increasing biochar</td>
<td>[23]</td>
</tr>
<tr>
<td>Hardwood</td>
<td>500 °C</td>
<td>Cement replacement</td>
<td>5-20%</td>
<td>Comparable compressive strength with 5% of biochar as replacement</td>
<td>[47]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>450 °C</td>
<td>Silica fume replacement</td>
<td>0.1-0.75%</td>
<td>Water absorption reduction 17%, enhancement of mechanical strength increased optimum dosage of biochar</td>
<td>[30]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>500 °C</td>
<td>Cement replacement</td>
<td>40%</td>
<td>Acceleration of cement hydration, 15-20% higher compressive strength retention by mortar exposed to 450 °C</td>
<td>[48]</td>
</tr>
<tr>
<td>Wheat Straw</td>
<td>650 °C</td>
<td>MgO + ADP replacement</td>
<td>0.5, 1, 1.5%</td>
<td>Mechanical properties enhanced with biochar.</td>
<td>[49]</td>
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<tr>
<td>Wood saw dust</td>
<td>300-500 °C</td>
<td>Filler</td>
<td>1, 2, 5, 8%</td>
<td>Development of early age e strength</td>
<td>[20]</td>
</tr>
<tr>
<td>Wood saw dust</td>
<td>300-500 °C</td>
<td>Filler</td>
<td>2%</td>
<td>Higher degree of hydration by pre-soaked biochar, Improvement of strength and water tightness</td>
<td>[50]</td>
</tr>
<tr>
<td>Wood saw dust</td>
<td>500 °C</td>
<td>Cement replacement</td>
<td>2, 5, 8%</td>
<td>Increase of hydration degree</td>
<td>[27]</td>
</tr>
<tr>
<td>Peanut shells</td>
<td>850 °C, 750-850 °C</td>
<td>Filler</td>
<td>0.025, 0.05, 0.08, 0.2, 0.5, 1%</td>
<td>Increase in electromagnetic radiation shielding</td>
<td>[51]</td>
</tr>
<tr>
<td>Standardized biochar, Pyrolyzed polyethylene beads (CNBs) and coconuts shells</td>
<td>750-850 °C</td>
<td>Nano/Micro-filler</td>
<td>0.5, 1%</td>
<td>Flexural strength and fracture energy</td>
<td>[52]</td>
</tr>
<tr>
<td>Rice husk biochar</td>
<td>500 °C</td>
<td>Replacement with cement</td>
<td>0, 3, 5 and 10%</td>
<td>Significant results obtained upto 10% replacement</td>
<td>Present study</td>
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</tbody>
</table>
6. Life cycle assessment of Biochar incorporated cement paste samples

6.1 Estimation of CO₂ emission

The raw materials of CO₂ emission of OPC and water were adopted from the available literature. Carbon emission of rice husk biochar (RHBC) is determined based on specific assumptions such as transportation, processing of RHBC and 1 m³ of cement paste for each sample. The collection of Rice husk has mentioned in materials and methods section. The RHBC farm is located roughly 5 km from the lab where the casting and testing were done. The RHBC is transported using a heavy vehicle (HV) with a 1000 kg load capacity. Also, it is predicted that the ball milling of 1000 kg of RHBC will use approximately 169.7 kWh of power. According to the CO₂ benchmark database for the Indian power sector and the factors for road transport emissions specific to India, the CO₂ emission factor per kWh of electricity used in January 2023 is 0.79 kgCO₂/kWh and 0.148 kgCO₂/km for CUVs [53]. The amount of carbon in 1 kg of each type of cement paste RHBC is 0.135 kg. For each type of cement paste, embodied GHG ECO₂e and embodied energy EE are calculated based on the manufacture of 1 kg using the control and RHBC methods, as shown in the equation below.

\[ ECO₂e = \sum CO₂i \times m_i \]  
\[ EE = \sum E_i \times m_i \]  

CO₂i is the coefficient of embodied carbon, Ei is the coefficient of embodied energy coefficient per unit mass of component i, and m is resembles to the mass of cement paste component i per kg of cement paste [54,55]. The raw materials used to produce EE are derived from various sources as shown in Table 8. Moreover, the production of RHBC is involved in transport and ball milling. As shown in Tables 7 and 9, the estimated carbon footprint based on these aspects was 0.135 kgCO₂/kg. As a result of introducing RHBC into the cement paste, the embedment rate was significantly reduced. The inclusion of RHBC in cement as a replacement, the difference in ECO₂e for the different replacements. Figure 15 shows that the use of RHBC in cement paste significantly reduces the carbon content of the mixture. A mixed cement paste contains 3%, 5%, and 10% carbon, which is 6%, 15%, and 17%, respectively [56,57].

| Table 7. CO₂ emission factors for raw materials used in cement paste [56,57]. |
|---------------------------------|------------------|------------------|
| Cement                          | 0.82             | Water            | 0.0013 |
| Biochar                         | 0.135            |

| Table 8. Embodied energy for raw materials used in cement paste. |
|---------------------------------|------------------|------------------|
| Cement                          | 5.5              | Water            | 0.0017 |
| Biochar                         | 1.82             |

6.2 Embodied energy

Figure 16 illustrates the various embodied energy and RHBC percentages. It can be seen that the control solution produced significantly less EE than the other mixes. With RHBC values of 0, 3, and 5, as well as 10%, the amounts of EE are 6.71, 6.58, 6.49, and 6.26 MJ/kg, respectively. EE has decreased
by 1.93%, 3.27%, and 6.7% in comparison to the control sample. These findings show that partial RH replacement with cement lowers EE.

6.3 Estimation of eco-strength efficiency

Total CO₂ emissions vary depending on the RHBC combinations. Therefore, it is essential to concentrate on both material reduction and its impact on compressive strength in addition to the decrease of carbon content. Equation (8) is used to create environmental strength indicators [56].

\[
\text{Eco – strength efficiency} = \frac{\text{compressive strength of samples after 28 days}}{\text{Total embodied carbon of samples}} \tag{8}
\]

As shown in Figure 17, the 0% RHBC control sample has an efficiency of 0.0376 MPa/kg CO₂-equ. kg within 28 days. Figure 17 can show that the environmental strength performance of the RH replaced cement is increased at all levels compared to the control mortar. It may be due to the increase in strength of all mixed RHBC cement past sample after 28 days. By replacing OPC with 3%, 5%, and 10%, the efficiency of ecological intensity increased by 18.18%, 29.7%, and 28.26% respectively. As mentioned earlier, the RHBC replaced cement paste sample can be used for high compressive strength. However, it is important to focus on reducing the content of components by replacing the level of OPC and embodied carbon, as well as reducing the efficiency of environmental durability [60]. Although the RHBC contributes little to the reduction of CO₂ emissions, it ensures the protection of natural resources and can be used to develop environmentally friendly and energy-efficient mortars for the cement industry to promote sustainable development.
6.4 Cost assessment of rice husk biochar

The RHBC used in this study is untreated community waste sourced directly from industry. The resulting ash is disposed of on land, and RHBC’s processing costs are relatively lower than those of cement. Therefore, the cost of grinding, and CNSA shipments will be taken into account in this study. From Table 9, the total power consumption for grinding RHBC for and 1000 kg ball mill is 169.7 kWh. The cost of 169.7 units consumed to grind and ball mill 1000 kg of RHBC is Rs. 1201.00*/1000 kg. If 1000 kg of RHBC is transported over a distance of 5 km, the shipping cost of CNSA is 408.19*/1000 kg. Therefore, the total cost of CNSA is Rs. 1609*/kg. Calculating the amount of cement per m³ of cement with a mixing. Table 9 shows the total cost of mixing 1 m³ of cement.

7. Conclusions

This study substituted high doses of biochar in cementitious materials to reduce the use of cement in construction materials. For further incorporation into building envelopes, the mechanical, thermal and physical, performance of biochar with cement paste was investigated. The hydration products in the cement matrix were investigated using state-of-the-art equipment.

The biochar was successfully prepared under pressurised condition in muffle furnace. The particle size of biochar is observed at 6.4 µm after grinding in a ball mill. Further, 0, 3%, 5%, and 10% of biochar were replaced with cement. The initial and final setting time of cement with biochar is decreased as the replacement of biochar increased and it meets IS : 4031 (part-5)-1988.

The compressive strength of biochar with cement paste is increased as biochar dosage increased. The maximum compressive strength (44.85 Mpa) of the specimen was observed at 5% wt. of biochar. At 10% wt. of biochar, the superior strength (43.64 Mpa) was observed than control mix (37.6 Mpa). The porosity of specimen is decreased as biochar dosage increased. The maximum reduction of porosity of the specimen was observed at 5% wt. of biochar. At 10% wt. of biochar, the significant porosity of

<table>
<thead>
<tr>
<th>Energy requirements for 1000 kg of Rice husk</th>
<th>Transportation of 1000 kg of Rice husk</th>
<th>Total emission (kg CO₂/kg CNSA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total electrical Consumption (kg/CO₂/kWh)</td>
<td>Emission Factor</td>
<td>Distance (km)</td>
</tr>
<tr>
<td>169.7</td>
<td>0.79</td>
<td>5</td>
</tr>
</tbody>
</table>

Figure 17. Eco strength efficiency with biochar.

Table 9. CO₂ emission factor for rice husk.
the specimen was reduced strength than the control mix. The density of specimen is increased as biochar dosage increased. The maximum density of biochar with cement was observed at 5% wt. of biochar. At 10% wt. of biochar, the density of specimen was increased than the control mix. As the dosage of biochar increased in the cement matrix, the water absorption decreased due to change in porosity of specimen.

After 28 days, the morphology of specimen was observed with the help of FESEM. The results revealed that biochar enhances the cement hydration products up to 5% wt. There is no significant reduction of hydration observed at 10% wt. The formation of more calcium hydroxide and calcium carbonate because of using biochar particles in replacement of cement was confirmed by XRD and TGA results. The improvement in C-S-H was observed after the addition of 3%, 5%, and 10% wt. biochar to cement pastes that already contained biochar was initially attributed to the filler effect of biochar, which creates a nucleation site for cement hydration products. The obtained results also demonstrated that rice husk biochar encouraged the hydration products in cement matrix. Agricultural-based biochar is a sustainable substitute for lowering the cement requirement in building envelope cement-based materials. For all replacement levels of biochar, the sustainability assessment reveals a significant decrease in the embodied carbon, energy, and overall carbon footprint. For all of the mixes, the biochar blended cement sample’s eco-strength efficiency was significantly lower than that of the control mortar. Also, the cost analysis of the cement sample mixes showed that using biochar as an accelerator may be done affordably.

**Conflict of Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**References**


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