

Optimization of biochar and fly ash to improve mechanical properties and CO₂ sequestration in cement mortar

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ABSTRACT

The novelty of this study is to find out the optimum amount of biochar and high calcium fly ash to improve mechanical performance and promote CO₂ uptake in cement mortar. The potential of biochar-fly ash mixes was optimized using response surface methodology (RSM) considering the influence of different amounts of fly ash (FA), biochar (B), and their interactions to achieve the optimal mix design with improved performance and carbonate mineralization. Additionally, the effect on the mineralization of different polymorphs of calcium carbonate was also investigated. The experimental results indicate that the accelerated carbonation of high calcium fly ash mortar enriched with biochar enables the effective utilization of biochar up to 5% for enhancing both the mechanical properties and CO₂ sequestration. However, under normal curing conditions, it was observed that the optimal amount of biochar that can be used is <1%. This is a promising approach in terms of utilizing waste material and reducing cement content in the mix design together with the additional benefit of storing 50% of ambient CO₂ permanently in the cementitious matrix. Carbonation of biochar-fly ash cement composite substantially improves fracture strength, and modulus of elasticity compared to uncarbonated cement mortar at 7 and 28 days. The present study demonstrates the advantages of synergistically combining biochar and fly ash in the development of low-carbon, sustainable cementitious building materials that have the potential to transform building structures into carbon sinks in the future.

1. Introduction

Increased greenhouse gas emissions in the atmosphere have necessitated the implementation of measures to mitigate future CO₂ emissions. The construction industry heavily relies on concrete due to its low cost and mechanical benefits, with an annual consumption of over 30 billion tons. Due to the large quantities involved, the cement industry accounts for 7–8% of the global CO₂ emission [1]. These levels have triggered concern, prompting the development of more environmentally friendly alternatives. One approach to reducing net CO₂ emissions from the cement industry is to immobilize stable carbon in the cement matrix without compromising its other properties. Biochar, a sustainable carbon resource, has received increasing attention as a promising source of adsorbents for various applications, including water treatment, gas adsorption, and sequestration. Recently, studies have explored the use of biochar as an eco-friendly natural adsorbent material in concrete to capture atmospheric CO₂ [2,3]. Using biochar as an alternative material to replace cement can mitigate the CO₂ emissions from cement

industries, and eventually, carbon can be permanently stored in building structures [4,5]. According to the study, the addition of 1% of biochar to the concrete could absorb around 0.5 Gt of CO₂ annually, which is equivalent to nearly 20% of the total annual CO₂ emissions produced by the cement industry [6]. Others reported that the small carbon-rich biochar particles exhibited an internal curing and filling effect to improve the mechanical and durability properties of the cement-based material through pore closure and densification [7]. The study suggested that the addition of 1–2 wt% of biochar particles, depending on the chemical composition and processing conditions, can improve the compressive strength of cement composites by 10–20% compared to the control [8]. CO₂ curing of cement blocks prepared using biochar was effective to accelerate the mechanical performance [9]. In fact, the ability of biochar to combine 2–3 times more CO₂ than its own weight makes it a carbon-negative material [4]. This is of great importance to transform next generation buildings into carbon sinks and mitigate the net CO₂ emissions responsible from cement manufacturing and processing. The amount of biochar is still debatable to achieve the optimum

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properties of concrete. A recent study by [10] has found that 4 wt% addition of biochar to concrete can store 0.124 kg of CO₂. These promising results imply that biochar might be a possible material to substitute silica fume, clay, and fly ash in pozzolans, thereby lowering the carbon footprint of cement and concrete. Pozzolans are generally introduced to react with Ca(OH)₂ and form secondary C-S-H enhancing mechanical as well as durability properties. Among other supplementary materials, fly ash (FA) is one of the most common types of pozzolans, which is a by-product of the coal combustion process and is regarded as waste material. FA is classified as low calcium FA (L-FA) and high calcium FA (H-FA) based on its calcium content. The application of H-FA is still limited in the construction industry due to the presence of free CaO compared with L-FA. The presence of free CaO in a material can potentially hinder its long-term performance due to its dense structure and gradual hydration rate, which leads to volumetric expansion over time. Nevertheless, the abundance of free CaO in a substance renders it an ideal candidate for carbonate mineralization. Cementitious composites can undergo spontaneous carbonation when exposed to ambient CO₂ over extended periods during weathering processes [11]. Therefore, to access the CO₂ adsorption capability of material, the accelerated mineral carbonation method has been implemented in several investigations [12–14]. This method enables the rapid conversion of CO₂ into thermodynamically stable carbonates upon reaction with calcium ions, facilitating the efficient sequestration of CO₂. By conducting carbonation tests in an accelerated environment for extended periods, it is possible to identify the material's suitability for CO₂ uptake and develop carbon-negative concrete for future applications.

To date, the majority of the prior research on carbon curing has focused on employing either biochar or alternative pozzolans, none of the studies has optimized how much of both should be used in combination. The influence of the right combination of pozzolans and biochar on the effectiveness of CO₂ sequestration and other mechanical characteristics has not been thoroughly studied. In the present study, a statistical tool called RSM is used to optimize the amount of biochar and H-FA for improving compressive and flexural strength, young's modulus. Moreover, the optimized mix design was investigated for realizing their CO₂ sequestration and carbonate mineralization capability. This methodology is chosen to elucidate the synergic interaction of biochar and H-FA under CO₂ and water (normal) curing in order to develop carbon-zero (or negative) concrete. In addition, the formation of different polymorphs of calcium carbonate in presence of biochar and fly ash together was also investigated.

2. Experimental program

2.1. Materials

Cement mortar samples were prepared using Type I grade OPC 42.5 R (specific gravity 3.15) in accordance with ASTM C150-07 and standard sand that met ASTM C 778-17. The pozzolanic mineral additive H-FA with a bulk density of 2.40 was used confirming with ASTM C 618. The chemical composition of cement and H-FA (Class C) is provided in Table 1. Biochar (B) was received from Proton Power Inc. The chemical

Table 1
Chemical composition of OPC and class C Fly ash.

Oxides	Mass (%)	
	Cement	Class C Fly ash
CaO	66.9	24.3
SiO ₂	19.5	39.9
Al ₂ O ₃	3.52	16.7
Fe ₂ O ₃	3.37	5.8
SO ₃	3.97	3.3
Na ₂ O + K ₂ O	1.53	1.30
MgO	0.68	4.60

composition of biochar depends on the kind of feedstock and the pyrolysis conditions (temperature, heating rate, duration, etc). It mostly consists of carbon (>90%) with a bulk density of 0.55 g/cm³, other characterization of biochar can be found elsewhere [15]. SEM was used to characterize the size and shape of the biochar particles, which show angular and irregular particles with variable sizes ranging from 20 and 250 μm (shown in Fig. 1). The porous honeycomb-like microstructure of the biochar was shown by its morphology.

2.2. Methodology

2.2.1. Response surface methodology (RSM)

RSM is a statistical tool combined with mathematical regression used for optimizing the experimental process [16]. The selection of input variables and their levels (low to high) is important in RSM analysis because the influence of each variable and their interaction will affect the output responses. Generally, RSM can be used for linear or non-linear behavior of input variables and output responses, but mostly the data point results in the curvature which indicates the non-linear relationship. For the non-linear data, the polynomial model with a second-order function is suitable to fit the full quadratic model [16–18]. In our previous study, we have observed the combination of biochar and class C fly ash has a significant effect on mechanical and fracture properties, CO₂ uptake, and mineralization. Therefore, in this study, RSM was applied to obtain an optimum mix design with improved performance through conducting experimentation in the specified range of materials used. In this study, two factors and three-levels based center composite design was adopted, where the experimental points are located at the corners, the center of each edge, and the center point. To improve the regression analysis, the center point experiment space is replicated, as shown in Fig. 2. The amount of biochar (ranging from 1% to 5%) and fly ash (ranging from 10% to 40%) are considered as independent factors and divided into three levels (−1, 0, +1) based on the specified range. A total 10 number of experiments were conducted to calculate the responses such as compressive and flexural strength, modulus of elasticity of uncarbonated and carbonated mortar samples using the second-order polynomial equation (1) [19].

$$y = f + ax_1 + bx_2 + cx_1x_2 + dx_1^2 + ex_2^2 \quad (1)$$

where y is the predicted response, a and b are linear coefficients, x₁ and x₂ are the independent factors (variables), c is the interaction coefficient, d and e are the quadratic coefficients, and f is the intercept.

2.2.2. Sample preparation

In the present study, a total of 10 different combinations were

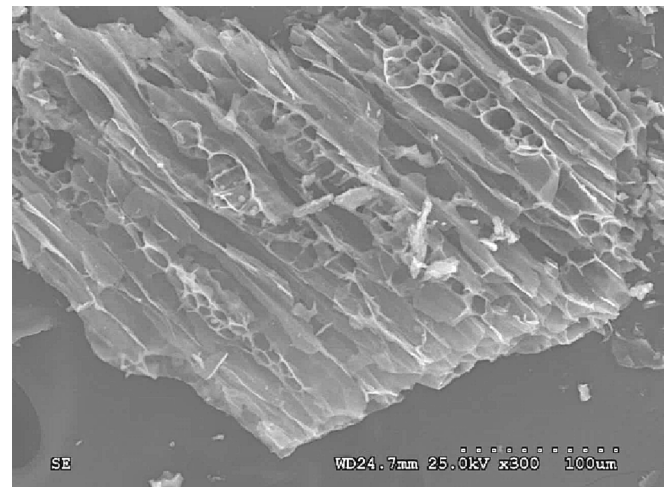


Fig. 1. SEM micrograph of biochar.

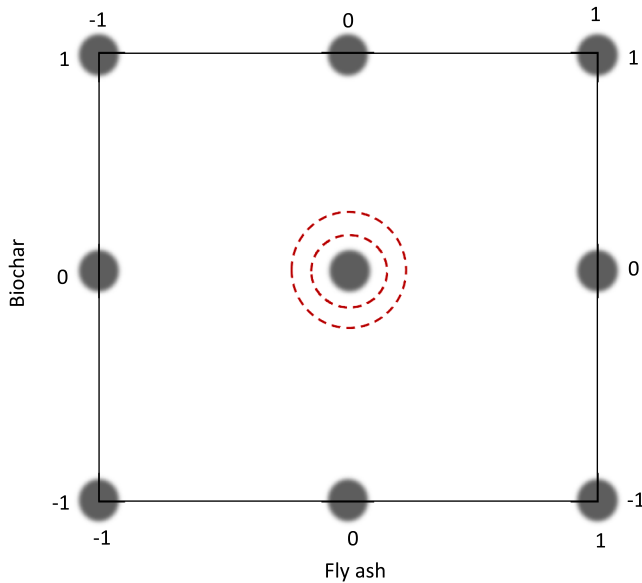


Fig. 2. Center Composite design (CCD) with two factors (FA and B) and three levels (-1,0,1).

designed and investigated based on the Design of experiments (DOE) approach. Detail of the mix proportions is provided in Table 2. The w/b and s/b ratios were fixed at 0.5 and 2.75, respectively. A reference sample of plain OPC mortar (without FA and biochar) was prepared separately for comparison. All mortar mixes were prepared at room temperature using a standard Hobart mixer equipped with a bowl mounted with stainless steel mixing blades following ASTM C305-12 guidelines. After the completion of the procedure, the mixture was cast in 40 mm × 40 mm × 160 mm molds and covered with polythene sheets to avoid evaporation. After 24 h, all the specimens were cured in a moist curing chamber at controlled temperature and humidity of 23 °C and 95%, respectively till the time of testing.

For the carbonation study, half of the specimens were transferred after 3 days of moist curing to a carbonation curing chamber maintained at 23 ± 5 °C, 65 ± 3% relative humidity, and 12% CO₂ concentration with all the surfaces exposed. This humidity value was selected based on literature as it corresponds to the ideal humidity for carbonation at 23 ± 5 °C [20,21]. The concentration of CO₂ was controlled at 12%, which is the typical amount of CO₂ emission from thermal power plants.

2.2.3. Testing methods

Flexural strength and Young's modulus of non-carbonated and carbonated mortars were performed using three-point bending tests following the Linear Elastic Fracture Mechanics (L.E.F.M.) [22,23]. Notched 40 mm × 40 mm × 160 mm specimens were prepared and tested in three-point bending at the age of 7 and 28 days. The prismatic specimens were cut using a water-cooled band saw featuring a 13.3 mm notch. The length of the notch was determined as per the RILEM

standard, which mandates a notch-to-depth ratio of 1:3 [24]. In accordance with ASTM C349-20 and ASTM C109/109 M-20, halves of the three-point bending tested prisms were used for evaluating compressive strength and Young's modulus. A closed-loop, 500 kN MTS servo-hydraulic system with displacement control was used for the tests. The speed remained steady at 0.3 mm/s.

Thermogravimetric analysis was used to calculate the amount of portlandite (CH) and different polymorphs of calcium carbonate (CaCO₃) such as vaterite, aragonite, and calcite, using Equations 2–4. In addition, based on the formation of calcium carbonate, the CO₂ uptake of the mixes was calculated (Equation 5).

$$CH, \% = \frac{M_{CH}}{M_{H_2O}} \cdot (M_{i1} - M_{i2}) \quad (2)$$

$$vaterite + aragonite, \% = \frac{M_{CaCO_3}}{M_{CO_2}} \cdot (M_{i2} - M_{i3}) \quad (3)$$

$$Calcite, \% = \frac{M_{CaCO_3}}{M_{CO_2}} \cdot (M_{i3} - M_{i4}) \quad (4)$$

$$CO_2 \text{ uptake}, \% = M_{i2} - M_{i4} \quad (5)$$

where M_{i1} is the mass percentages at the corresponding temperatures. M_{CH} , M_{H_2O} , M_{CO_2} and M_{CaCO_3} are respectively the molar mass of CH (74 g/mol), CaCO₃ (100 g/mol), H₂O (18 g/mol), and CO₂ (44 g/mol). On carbonation, depending on the reaction condition and extent of carbonation different polymorphs of CaCO₃ are formed in hydrated cement. Calcium carbonates can be found in different polymorphs such as vaterite, aragonite, and amorphous calcium carbonate (ACC) which are known as poorly crystalline forms, and their decomposition temperature range varies from 500 to 650 °C. On the other hand, the well-crystallized and thermodynamically stable form known as calcite, which decomposes at a temperature exceeding 650 °C. Several publications provide detailed information on the decomposition behavior of the different polymorphs of CaCO₃ [25–28]. The TGA curve in Fig. 3 is showing the temperature ranges considered for quantifying the amorphous and crystallized CaCO₃ in this study.

3. Results and discussions

3.1. Effect of biochar-enriched FA cement mortar on mechanical characteristics

3.1.1. Compressive strength of carbonated and non-carbonated mortars

Compressive strength is one of the preliminary studies to assess whether the combination of biochar and fly ash is suitable to be used in cementitious systems. Fig. 4, presents the contour plot of compressive strength obtained from specimens cured under a carbonation chamber (12% CO₂) at the testing ages of 7 and 28 days. The developed model is statistically significant, determined using p-value i.e. < 0.02, at a confidence interval of 95%. For carbonated plain OPC mortar (without FA and biochar), compressive strength testing was performed separately and observed 26.4 MPa, and 29.52 MPa strength at 7 and 28 days, respectively, provided in Table 3. The results observed from Fig. 4 suggest that after 7 days of carbonation, most of the mixes have lower compressive strength compared to plain OPC mortar excluding the combination of FA10B5 and FA40B0, which showed > 26 MPa. The reduction in strength could be due to the lower amount of cement with slow-reacting fly ash and inert biochar. Compared to their counterpart non-carbonated mixes, the compressive strength of batches FA10B0, FA25B0, and FA40B0 added with FA is comparable to that of the OPC mortar, while the addition of biochar decreases the improvement in strength after 7 days, as shown in Fig. 5. The great ability of biochar to absorb water due to the micropores present on its surface could be the cause of this reduction in strength. Incorporation of biochar into a cementitious system may result in a reduction in compressive strength

Table 2

Array of experiment design by RSM.

Exp.	Named as	Cement (%)	Fly ash (%)	Biochar (%)
1	FA10B0	90	10	0
2	FA10B2.5	87.5	10	2.5
3	FA10B5	85	10	5
4	FA25B0	75	25	0
5	FA25B2.5	72.5	25	2.5
6	FA25B5	70	25	5
7	FA40B0	60	40	0
8	FA40B2.5	57.5	40	2.5
9	FA40B5	55	40	5

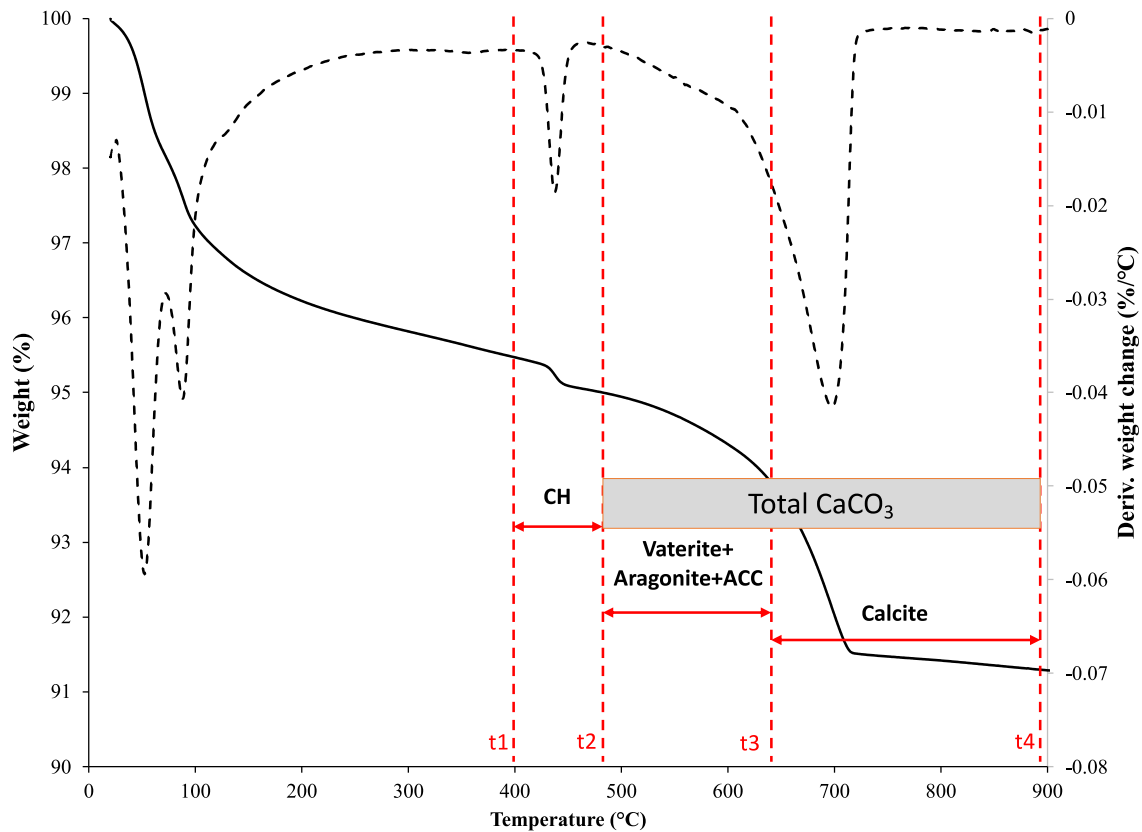


Fig. 3. TGA curve showing temperature ranges of hydration products.

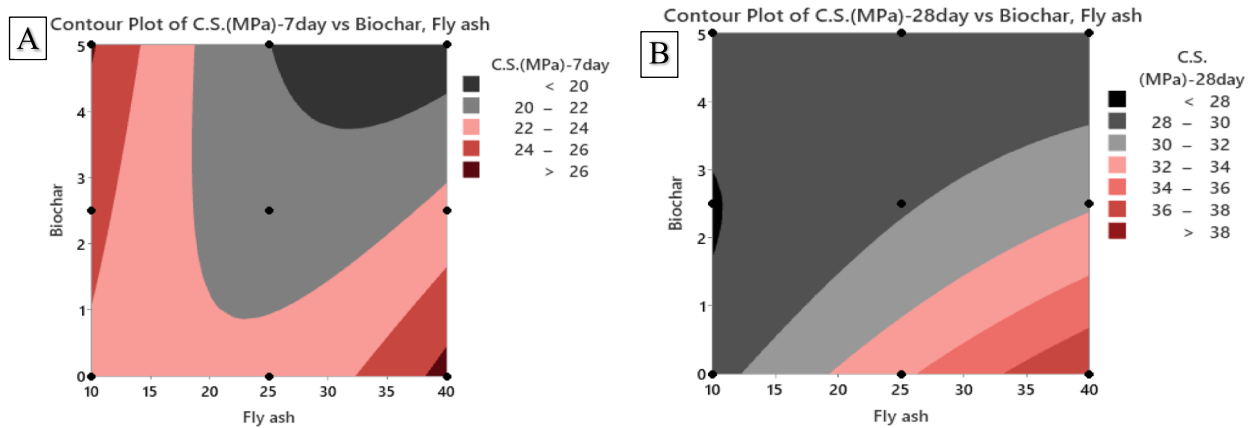


Fig. 4. Contour plot for compressive strength of carbonated fly ash and biochar mixes at 7-day (A), and 28-day (B).

Table 3

Mechanical testing results of carbonated plain OPC mortar (without biochar and FA).

	Carbonated cement mortar	
	7-day	28-day
Compressive strength (MPa)	26.47	29.52
Flexural Strength (MPa)	4.1	5.67
Young's modulus (GPa)	10.97	19.6

due to an increase in the content of carbonaceous particles that hinder secondary hydration. These particles tend to absorb the water intended for the progress of cement hydration, limiting the performance of the

cement [29]. Additionally, the inclusion of biochar in higher amounts may introduce more porosity to the cement matrix, thus reducing compressive strength.

However, with the progress of hydration time and carbonation till 28 days, It can be clearly noticed that the strength of all the designed mixes eventually increased with the increasing amount of fly ash and biochar except FA10B2.5 compared to plain OPC mortar. This is attributed to the synergy of fly ash and biochar, in which calcium from the H- FA reacts with CO₂ bound by the biochar to precipitate CaCO₃. This precipitation of CaCO₃ is deposited in the voids (pores) and increases the stiffness of the cement matrix. This is consistent with previous findings suggesting that the improved stiffness improves strength by reducing lateral deformation under compressive loading [30]. For the non-carbonated mixes (Fig. 5), FA-OPC significantly improved

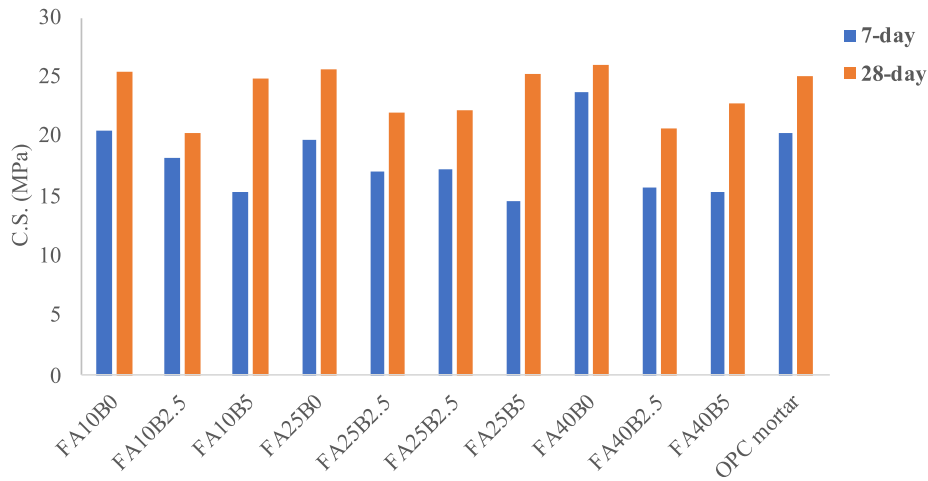


Fig. 5. Compressive strength of normal cured (non-carbonated) specimens [Experimental].

compressive strength compared to plain OPC mortar, while the addition of biochar showed no improvement in strength at 28 days compared to FA-OPC (without biochar). For the fly ash added composites, it is generally found that the improved mechanical properties at later ages are correlated with the development of secondary C-S-H as a result of the pozzolanic reaction that consumes calcium hydroxide. Biochar, on the other hand, is non-hydraulic in nature and does not participate in the chemical reaction. Therefore, due to its filling effect, it showed a modest improvement in strength only at higher dosages. For example: in the mixture FA10B5 and FA25B5.

3.1.2. Flexural strength of carbonated and non-carbonated mortars

Fig. 6 shows the flexural strength of all designed combinations of H-FA and biochar determined using 3-point bending tests. Similar to the compressive strength, it can be observed that the flexural strength of all mixtures increases as the hydration time progresses after 28 days, but the effect is more pronounced with the addition of biochar. According to Fig. 6(A), the contour plot of the carbonated mixes after 7 days, the flexural strength is comparable or marginally improved for all the mixes containing FA and biochar together, which can be attributed to the rapid ion dissolution and mineralization during accelerated carbon curing. However, a reduction in flexural strength was observed in some of the mixes, including FA10B2.5, FA25B2.5, and FA25B5, likely due to the development of heterogeneous air voids in the tensile plane through biochar, which could be responsible for the decrease in flexural strength. Akhtar et al [31], have also discovered that a high amount of biochar traps air, causing voids in hardened concrete and affecting flexural

strength.

Furthermore, prolonged exposure (28 days) of biochar-enriched FA mixes to CO₂ increased the reactivity of H-FA and formed carbonated hydration products. These products interlock within biochar and densify the micro-porous region of the biochar particles. As a result, the matrix structure becomes noticeably more tortuous and can withstand more bending energy without deformation. Therefore, the undesirable effects of biochar may be mitigated by mixing higher doses of biochar with H-FA fly ash. Biochar is also considered an alternative, environmentally-friendly microfiber reinforcement in the polymer composites [32] due to its superior advantageous properties over natural fibers. From the results presented in Fig. 7, which show the flexural strength of the non-carbonated mixes, it can be concluded that the addition of biochar to FA-cement mortar has a positive effect on flexural strength. This is evident from the fact that the mortar modified with biochar exhibits higher flexural strength after 28 days than the control OPC mortar. The increase in flexural strength is attributed to the improved interface between the biochar microparticles and the mortar matrix. The biochar particles act as barriers in the crack propagation pathway when embedded in hydration products, which contribute to the overall improvement in flexural strength.

3.1.3. Modulus of elasticity of carbonated and non-carbonated mortars

Fig. 8 presents a contour plot showcasing the elastic modulus of carbonated mixes of biochar-enriched FA-OPC mortar. The results demonstrate that the addition of biochar to the fly ash-cement mortar mixture leads to a significant improvement in the modulus of elasticity

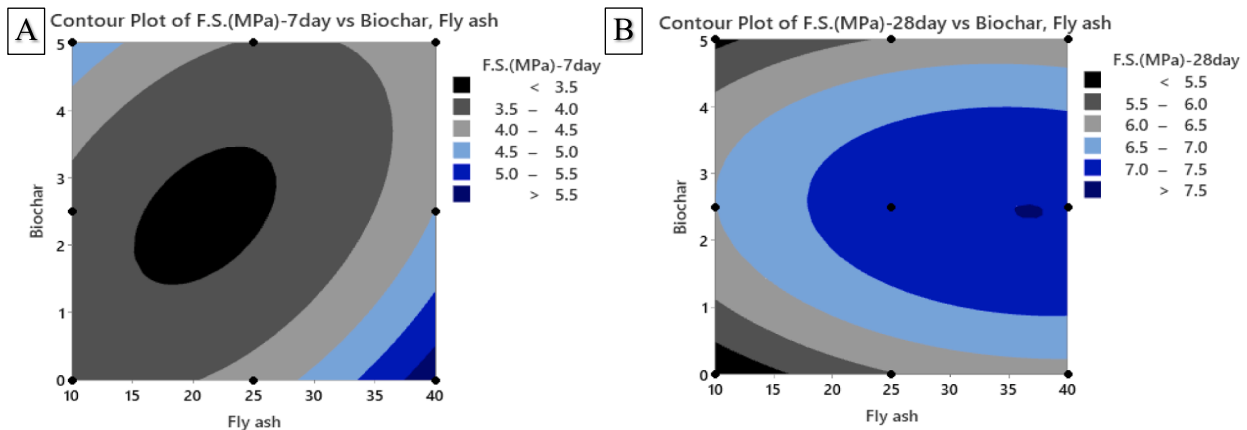


Fig. 6. Contour plot of flexural strength of carbonated mixes of fly ash and biochar at (A) 7-day, and (B) 28 day.

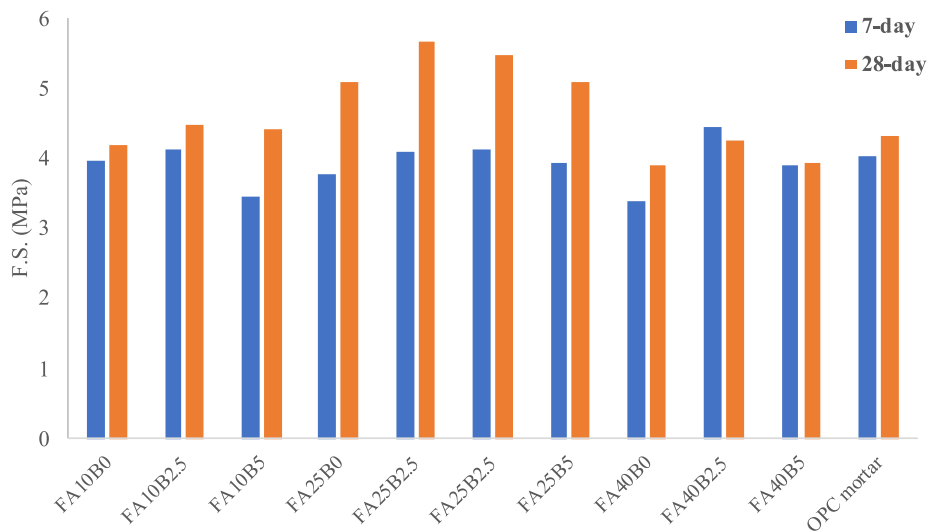


Fig. 7. Flexural strength of normal cured (non-carbonated) specimens [Experimental].

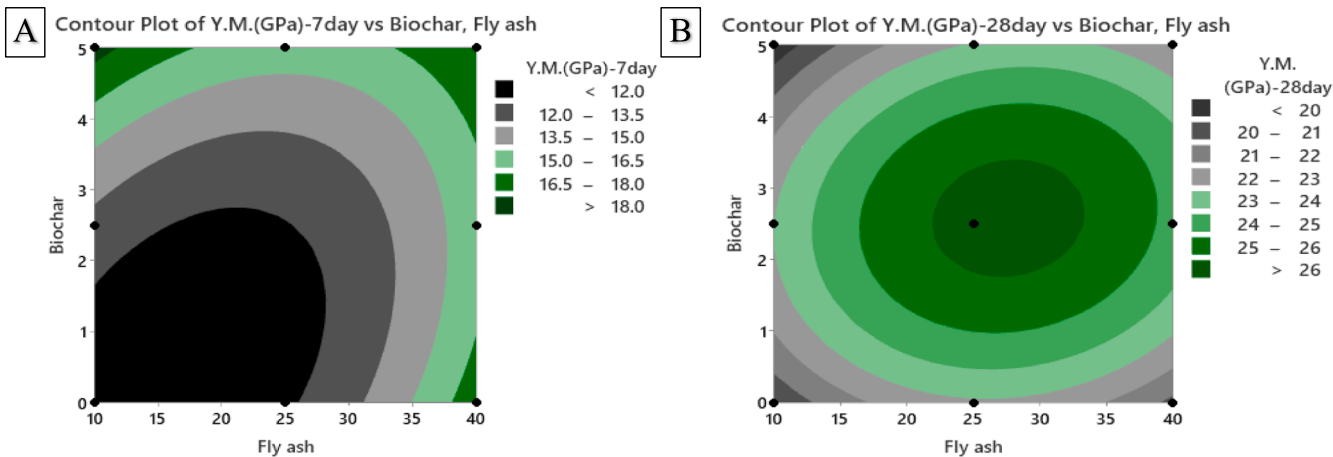


Fig. 8. Contour plot of Youngs' modulus of carbonated mixes of fly ash and biochar at (A) 7-day and (B) 28 days.

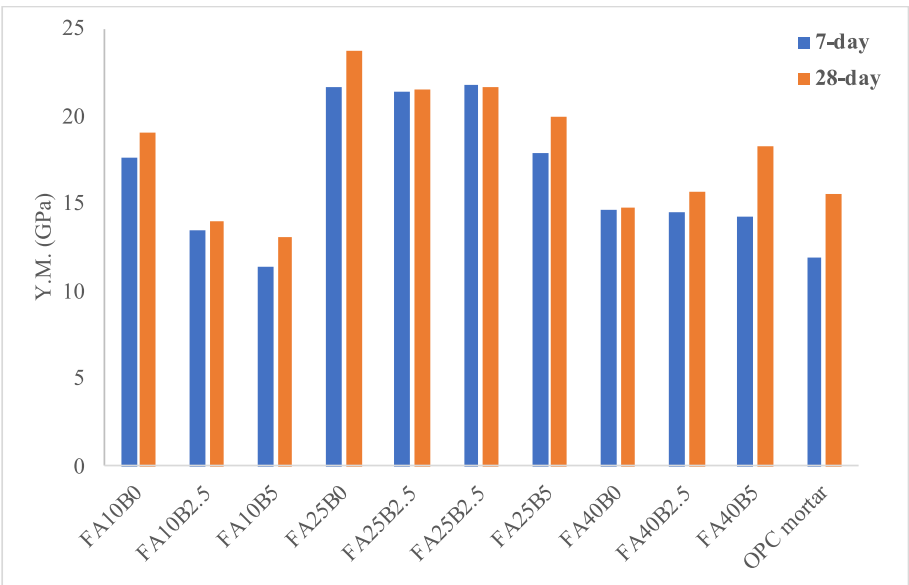


Fig. 9. Young's modulus of normal cured (non-carbonated) specimens [Experimental].

compared to carbonated OPC mortar. After 7 days of CO₂ curing, the modulus of carbonated OPC mortar was found to be 10.9 GPa, while in Fig. 8(A), all the combinations of biochar and FA exhibited higher values than OPC mortar. Similarly, Fig. 8(B) shows a remarkable increase in the modulus of elasticity after 28 days (Fig. 9).

In non-carbonated mixes, it was observed that the modulus of elasticity was higher than that of plain cement mortar for all combinations of biochar and FA. This improvement in elastic modulus is attributed to the increased stiffness of the cement matrix due to the presence of biochar. Prior research [33] has also reported similar findings, ascribing the increased strength to the biochar particles that absorb free water when embedded in the cement paste, leading to increased compactness of cementitious material by reducing the effective water-to-cement ratio. The high carbon content in pyrolyzed biochar microparticles further promotes the toughening mechanism of the cementitious matrix [34].

3.1.4. RSM modeling analysis

The present study employed center composite design (CCD) to investigate the optimum combination of biochar and H-FA to improve compressive and flexural strength and elastic modulus under accelerated carbon curing and normal curing conditions. A total of 10 combinations of H-FA and biochar were evaluated as listed in Table 2 and the responses such as compressive strength, flexural strength and elastic modulus after 7 and 28 days were recorded. To assess the accuracy of the values predicted from the experimental results, the 28-day data were compared. Subsequently, statistical analysis was performed to derive equations (1–3) and (4–6) for predicting the responses of the carbonated and non-carbonated specimens, respectively.

For carbonated;

$$C.S.(MPa) = 26.52 + 0.279FA - 0.599B + 0.00021FA^2 + 0.266B^2 - 0.0642FA*B \quad (1)$$

$$F.S.(MPa) = 4.024 + 0.1140FA + 1.143B - 0.001432FA^2 - 0.2075B^2 - 0.00367FA*B \quad (2)$$

$$Y.M.(GPa) = 15.54 + 0.565FA + 2.345B - 0.01087FA^2 - 0.529B^2 + 0.0139FA*B \quad (3)$$

For non-carbonated;

$$C.S.(MPa) = 22.68 + 0.2699FA - 2.991B - 0.00483FA^2 + 0.6255B^2 - 0.01680FA*B \quad (4)$$

$$F.S.(MPa) = 2.330 + 0.2304FA + 0.3300B - 0.004768FA^2 - 0.0557B^2 - 0.00127FA*B \quad (5)$$

$$Y.M.(GPa) = 10.04 + 1.176FA - 2.937B - 0.02612FA^2 + 0.1862B^2 + 0.0633FA*B \quad (6)$$

Analysis of variance (ANOVA) was performed to know the correlation between independent variables and responses to a collection of statistical models and it is arrayed in Table 4. From Table 4, it is evident that the p-value of the models is <0.025 which indicates that models are statistically significant for 95% confidence intervals. In general, p-value < 0.05 is typically considered to be statistically significant. Moreover, the R² value of compressive strength, flexural strength, and young's modulus are 92.5%, 93%, and 92.6% in carbonated mixes, which implies that there is a good correlation between experimental and predicted values. Fig. 10 (a, b, and c) show the correlation of experimental results with predicted data, where all the experimental values align well with predicted values. Hence, it is evident that the model arrived to predict the mechanical properties of biochar-enriched FA-cement

Table 4

Analysis of Variance (ANOVA) for compressive strength, flexural strength, and Young's modulus of carbonated mixes.

Source	DF	Compressive strength		Flexural Strength		Young's modulus	
		F-Value	p-value	F-Value	p-value	F-Value	p-value
Model	5	9.88	0.023	10.71	0.02	10.11	0.022
Linear	2	15.6	0.013	6.47	0.056	2.05	0.244
FA	1	13.73	0.021	12.89	0.023	4.02	0.115
B	1	17.47	0.014	0.06	0.822	0.08	0.793
Square	2	2.04	0.245	19.98	0.008	22.71	0.007
FA ²	1	0	0.958	2.09	0.221	13.47	0.021
B ²	1	3.93	0.119	33.95	0.004	24.61	0.008
2-way Interaction	1	14.12	0.02	0.65	0.464	1.04	0.365
FA*B	1	14.12	0.02	0.65	0.464	1.04	0.365
R ²		92.51%		93.05%		92.67%	

mortar is statistically significant and acceptable.

Similarly, for non-carbonated mixes, analysis of variance is derived to observe the effect of biochar and FA combination on mechanical properties. From Table 5, it confirms that the model is highly statistically significant as the p-value is < 0.01 at a 95% confidence interval. Furthermore, the high R² of the model demonstrates a desired and reasonable agreement between the experimental and predicted results dataset, shown in Fig. 11 (a), (b) and (c).

3.2. Optimal mix selection

The results discussed in section 3.1 suggest that accelerated carbon curing is a promising approach for enhancing the mechanical properties of biochar-enriched cement mortar and addressing the negative impact of biochar during normal curing in a moist environment. The study demonstrated that carbon curing can lead to compressive strength comparable to that of plain OPC mortar and allows for a higher percentage of biochar replacement, up to 5%. Additionally, the inclusion of H-FA facilitates both the hydration and carbonate mineralization processes due to its elevated calcium content. In contrast, when curing under humid conditions, only a replacement of up to 1% biochar is recommended, as higher percentages result in lower compressive strength, especially after 7 days. The addition of FA to biochar-enriched mortar was not found to be effective in improving mechanical properties due to the slow cementitious reactivity of FA in the early phase compared to Portland cement. In addition, the reduction in cement content resulted in a dilution effect that led to the formation of fewer hydration products. Previous studies have reported that the addition of up to 2% biochar can enhance the mechanical performance of cement-based materials, although this is dependent on the chemical composition and type of feedstock used to prepare the biochar. Fly ash is a commonly used mineral additive in the concrete industry but has already reached its maximum global availability. It is expected that the long-term availability of fly ash will decrease with the technological advances in the energy sector [35]. The use of other SCMs and fillers remains a challenge due to their variable chemical composition and reactivity, which may affect the performance of concrete. Several studies are currently underway to develop high-performance and sustainable construction materials [36,37].

In this study, we aimed to optimize the mixture of biochar and H-FA to achieve two desirable goals: (i) maximizing the use of biochar while using less fly ash, and (ii) obtaining higher or equivalent mechanical properties compared to plain OPC mortar after both 7 and 28 days of hydration. However, the results showed that under CO₂ curing, all combinations of biochar (1–5%) and H-FA (10–40%) resulted in a reduction in compressive and flexural strength after 7 days, which can be attributed to the dilution effect due to the reduction of cement. Finally, as carbonation progressed, the strength of the mixes eventually

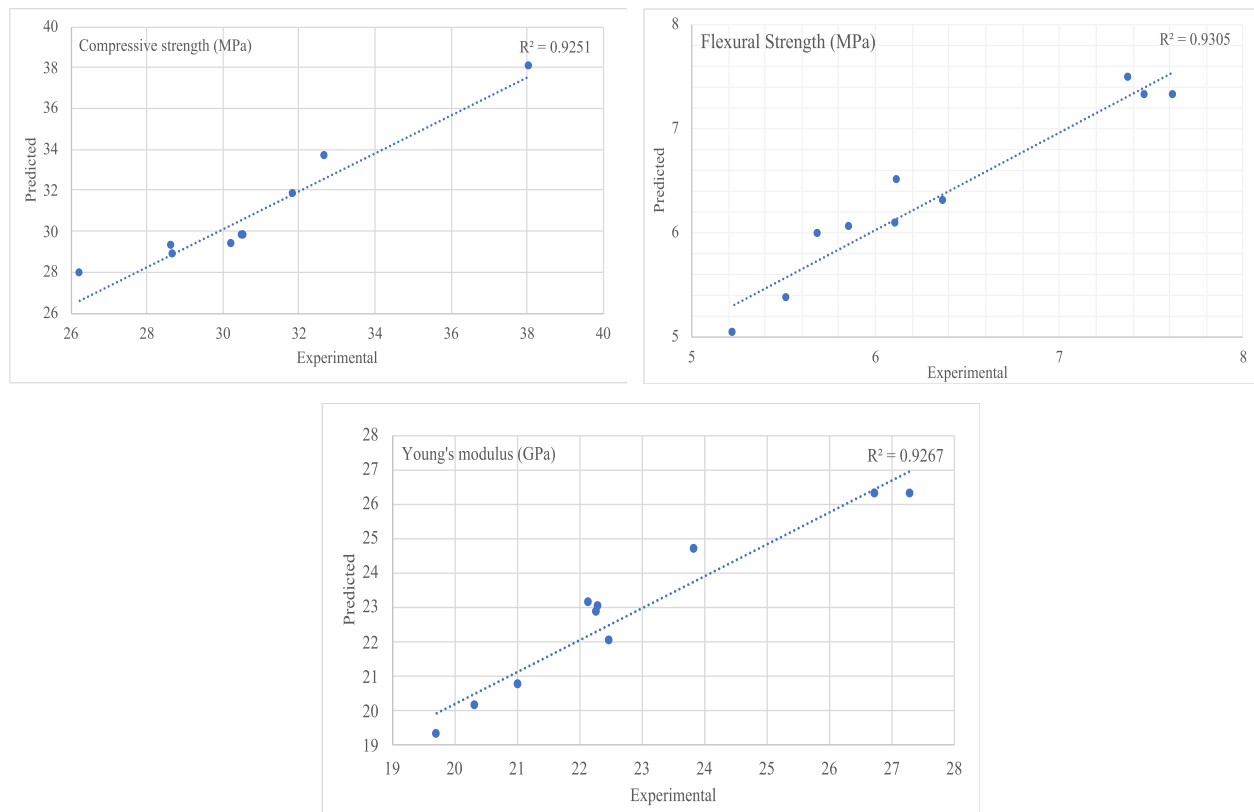


Fig. 10. Correlation between experimental vs predicted results for (a) compressive strength (b) flexural strength and (c) Young's modulus of carbonated specimens.

Table 5

Analysis of Variance (ANOVA) for compressive strength, flexural strength and Young's modulus of non-carbonated mixes.

Source	DF	Compressive strength		Flexural Strength		Young's modulus	
		F-Value	p-value	F-Value	p-value	F-Value	p-value
Model	5	19.49	0.007	45.62	0.001	30.04	0.003
Linear	2	3.87	0.116	5.95	0.063	5.33	0.074
FA	1	0.57	0.492	10.94	0.03	1.51	0.286
B	1	7.17	0.055	0.97	0.382	9.15	0.039
Square	2	42.97	0.002	107.81	0	54.55	0.001
FA ²	1	6.55	0.063	172.79	0	108.99	0
B ²	1	84.87	0.001	18.17	0.013	4.27	0.108
2-way	1	3.78	0.124	0.58	0.489	30.46	0.005
Interaction							
FA*B	1	3.78	0.124	0.58	0.489	30.46	0.005
R ²		96.06%		98.28%		97.41%	

improved after 28 days, which is attributed to the synergy between dissolution and carbonation. The increased reactivity of H-FA after 28 days of carbonation results in more calcium ions reacting with CO₂, assisted by the porous biochar, leading to significantly greater carbonation products. It is worth noting that this increase is more consistent with the mix FA10B5, which exhibited marginally higher compressive and flexural strength, as well as Young's modulus compared to plain OPC mortar at both hydration times of 7 and 28 days. In other mixes, at least one of the three mechanical properties did not meet the preferred criteria. For non-carbonic acid mixes, the addition of biochar to FA-OPC mortars did not significantly contribute to the increase in compressive strength, especially at early ages, however, it eventually attained the comparable strength after 28 days with the higher dosages such as FA10B5, FA25B5. In addition, with the increase in the percentage of substitute (FA40B5), a decrease in compressive strength was observed

due to the lower cementitious component. As explained earlier, the addition of biochar improved the flexural strength and modulus of elasticity after 28 days in almost all combinations. For evaluating the CO₂ capture and carbonate mineralization potential of biochar, the mixture of 10% FA and 5% biochar was considered optimal, as it performed efficiently under carbon curing conditions and met the desired criteria, shown in Table 6.

3.3. Thermogravimetric analysis

TGA curve of biochar is presented in Fig. 12, which shows approximately 30% of weight loss on heating at a temperature of 25 °C to 900 °C. The weight loss in the temperature between 40 °C and 130 °C corresponds to moisture absorbed inside the biochar particles and 650 °C to 750 °C corresponds to the decomposition of calcite. Fig. 13 (a and b), illustrate the TGA curves of the carbonated mix FA10B5 at 7 and 28 days and compared them with plain OPC and FA10 cement mortar. The weight loss observed at the respective temperature ranges owing to the dehydration or decomposition of hydration or carbonated products on heating at the temperature range of 25 °C –900 °C, as described in Fig. 3.

For the calculation of CH and CaCO₃, weight loss in the biochar-enriched carbonated mix was corrected to eliminate the influence of impurities present in the pristine biochar [38]. Figs. 14 and 15 show the net amount of CaCO₃ polymorphs (vaterite, aragonite, and calcite), as a percentage of cement mass after 7 and 28 days of carbonation. This value is calculated by subtracting the amount of carbonate formed during normal curing of respective specimens. The amount of CaCO₃ measured in non-carbonated mixes is supposed to be contributed by the decomposition of limestone mixed within OPC cement and a trace of calcite present in biochar. The range of different polymorphs was determined from DTG curves, showing prominent peak decomposition in the range of 400–475 °C, 475–675 °C and 675–900 °C corresponding to CH, vaterite + aragonite, and calcite, respectively.

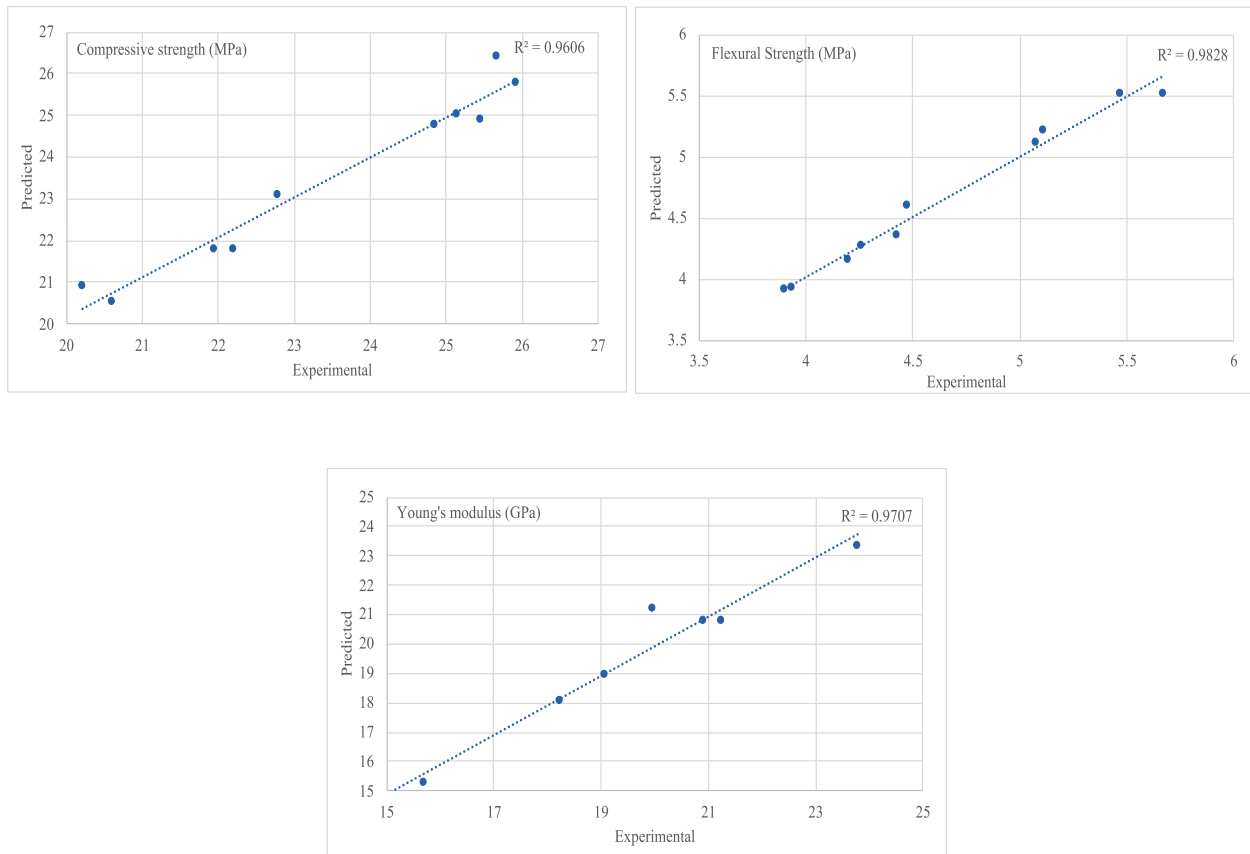


Fig. 11. Correlation between experimental vs predicted results for (a) compressive strength (b) flexural strength and (c) Young's modulus of non-carbonated specimens.

Table 6
Optimized mix for carbon sequestration study.

Carbonated specimens	7 day			28 day		
	C.S. (MPa)	F.S. (MPa)	MOE (GPa)	C.S. (MPa)	F.S. (MPa)	MOE (GPa)
OPC	26.47	4.05	10.97	29.52	5.15	19.6
FA10B5	26.59	5.01	16.98	30.51	5.52	19.72

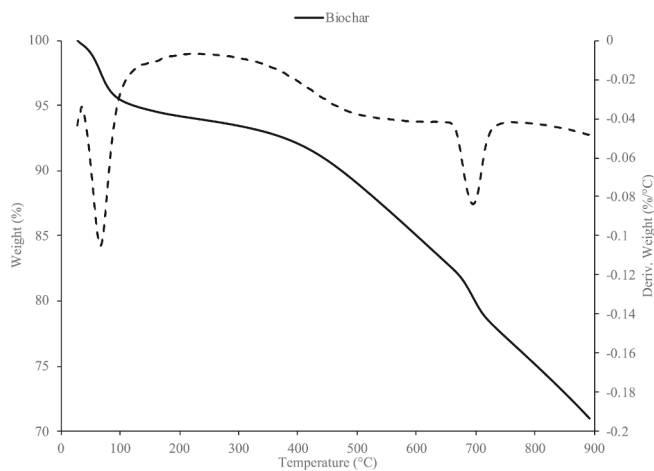


Fig. 12. TGA curve of biochar.

After 7 days of CO_2 curing, OPC mortar, FA10B0, and FA10B5 exhibited calcium carbonate contents of 4.4%, 5.1%, and 10.9%, respectively, in the temperature range of 475–675 °C. This indicates that the addition of fly ash and biochar has increased the mineralization of vaterite + aragonite or poorly crystalline carbonates. Compared to plain OPC, diffusion and dissolution of CO_2 occur more quickly in biochar and FA admixed mixes because of the reduction of cement content (and increase in w/c ratio). At the early age of carbonation, CO_2 dissolves in the pore solution to form carbonic acid (HCO_3^-), which consequently reacts with available calcium ions (Ca^{2+}) and precipitates as calcium carbonates. However, it has been shown in earlier studies that carbonation at a young age can result in higher amounts of poorly crystalline calcium carbonates. These carbonates are assumed to come from the C-S-H and are relatively unstable in comparison to calcite, which is formed from the carbonation of calcium hydroxide and is thermodynamically stable [39,40]. Vaterite and aragonite are the metastable phases that eventually get converted to calcite via dissolution and reprecipitation and lead to volume reduction because of this conversion. As volume reduction happens, porosity increases, causing more ingress of CO_2 and increasing the rate of the carbonation reaction at 7 days. After 28 days of carbonation, a similar trend has been seen with FA10B0 and FA10B5 showing 5.5% and 7.4% carbonate mineralization, respectively as compared to 4.8% in plain OPC mix.

The range from 675 to 900 °C corresponds to the decomposition of calcite, wherein FA10B0 and FA10B5 exhibited 3.9% and 5.2%, respectively, compared to 2.6% in OPC mix after 7 days of carbonation. This trend continued after extending the CO_2 curing to 28 days, and calculated 10.4%, 12.8%, and 15% calcite for OPC, FA10B0, and FA10B5, respectively. This indicates that the higher carbonate mineralization in biochar-enriched FA-OPC mix is promoted through the transformation of poorly crystalline calcium carbonates. After 7 and 28

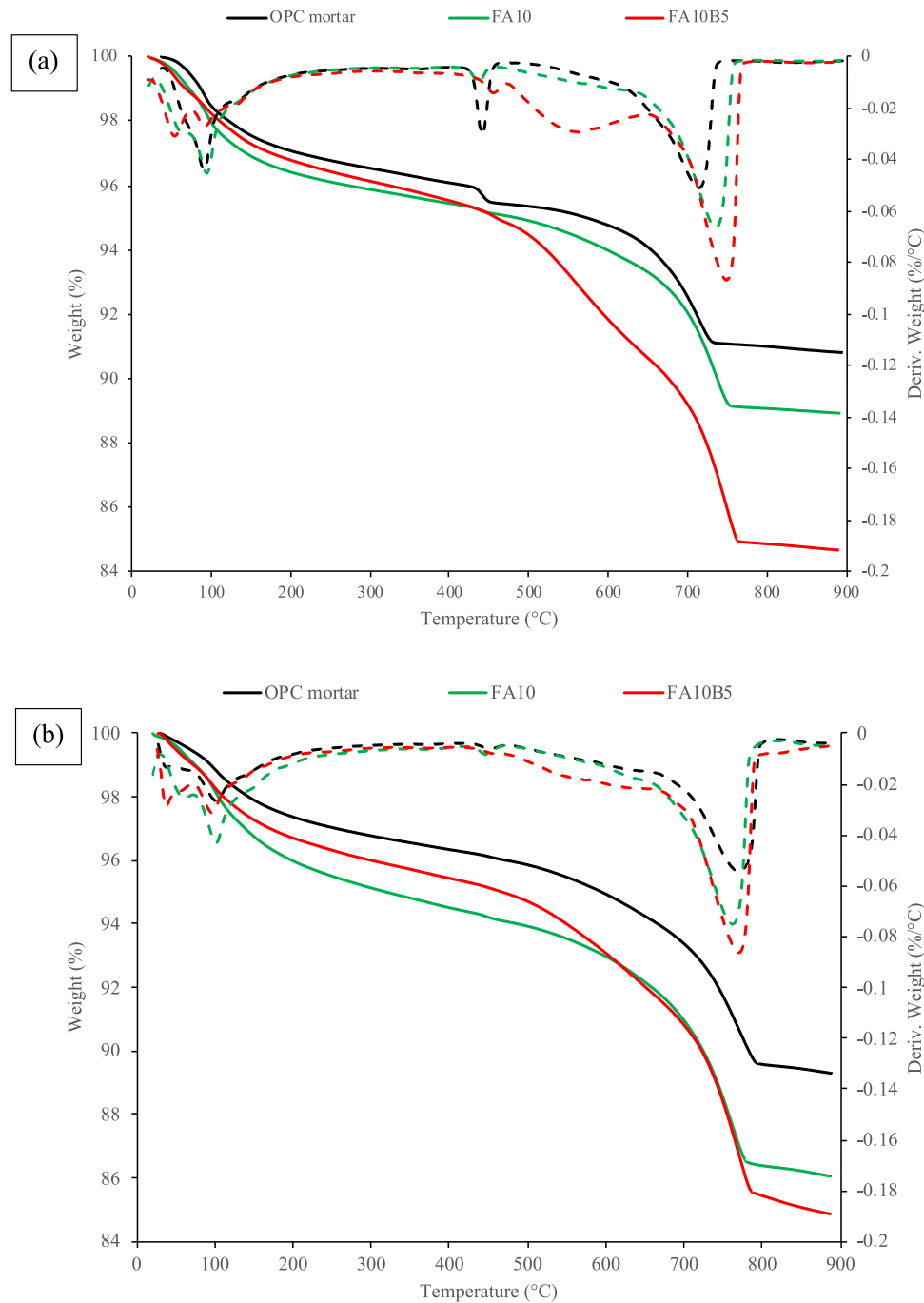


Fig. 13. TGA curves of carbonated mixes at 7-day (a) and 28-day (b).

days, respectively, FA10B5 estimated 16.2% and 22.9% of net CaCO_3 . FA10B0 and OPC, on the other hand, showed net calcium carbonate contents of 9.1% and 7% after 7 days, and 18.3% and 15.2% at 28 days, respectively. Based on the net calcium carbonate content, it was observed that the CO_2 uptake potential of biochar-enriched FA cement mix (FA10B5) increased by 50.5% and 25.8% compared to plain OPC and FA10B0 mixes, respectively, shown in Fig. 16. These results revealed that the addition of biochar to H-FA has higher potential for carbonate mineralization and sequestration compared to plain OPC and FA. This is attributed to the synergy of H-FA and biochar, where high calcium content provides a sufficient amount of Ca^{2+} ion and the mesoporous structure of biochar particles facilitates the diffusion of CO_2 to react with available calcium and formed calcium carbonates [15].

Fig. 17 displays the reduction in calcium hydroxide after 7 days and

28 days of carbonation compared to normal curing. The results indicated that the reduction of CH in OPC and FA10B0 is comparable at 7 days, while in FA10B5, the reduction of CH is substantially lower. This is attributed to the fact that the addition of biochar further reduced the amount of cement and produced less amount of calcium hydroxide. Alongside, CH converted to CaCO_3 upon early exposure to carbon-dioxide, which could be linked to the increase in compressive strength at an early age of carbonation of FA10B5 mix, as discussed earlier. It is interesting to note that after 28 days of CO_2 curing, plain OPC demonstrated a significantly higher reduction in CH compared to FA10B0 and FA10B5, indicating that in plain OPC the rate of carbonation increased at a later age due to the simultaneous progress of hydration and carbonation. In FA10B0 and FA10B5, the reduction is relatively smaller, confirming that a smaller amount of CH is carbonated at later ages. This

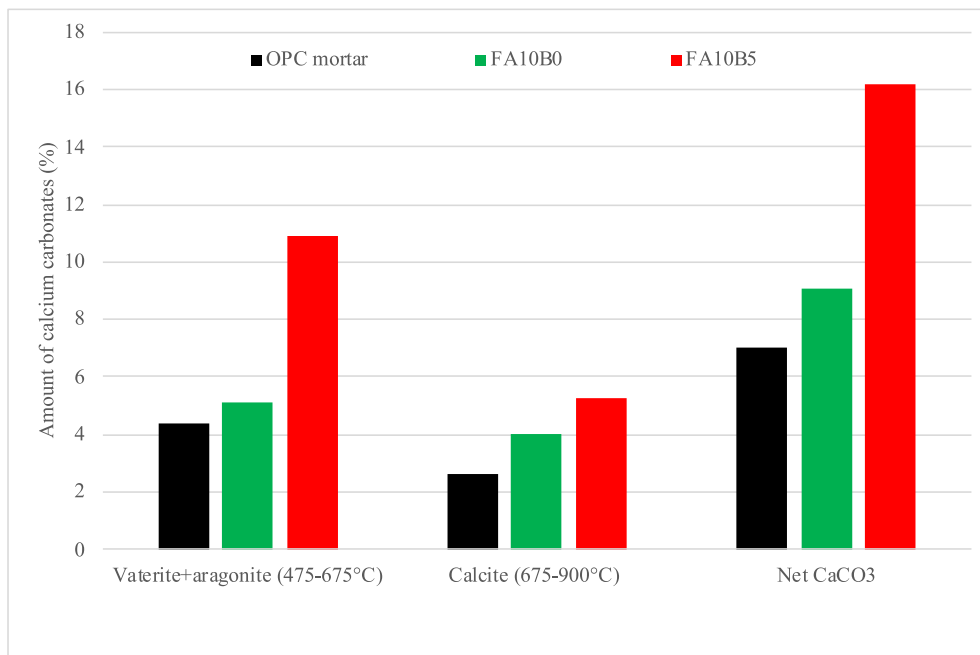


Fig. 14. Quantification of calcium carbonate from TG analysis after 7-day of CO₂ curing.

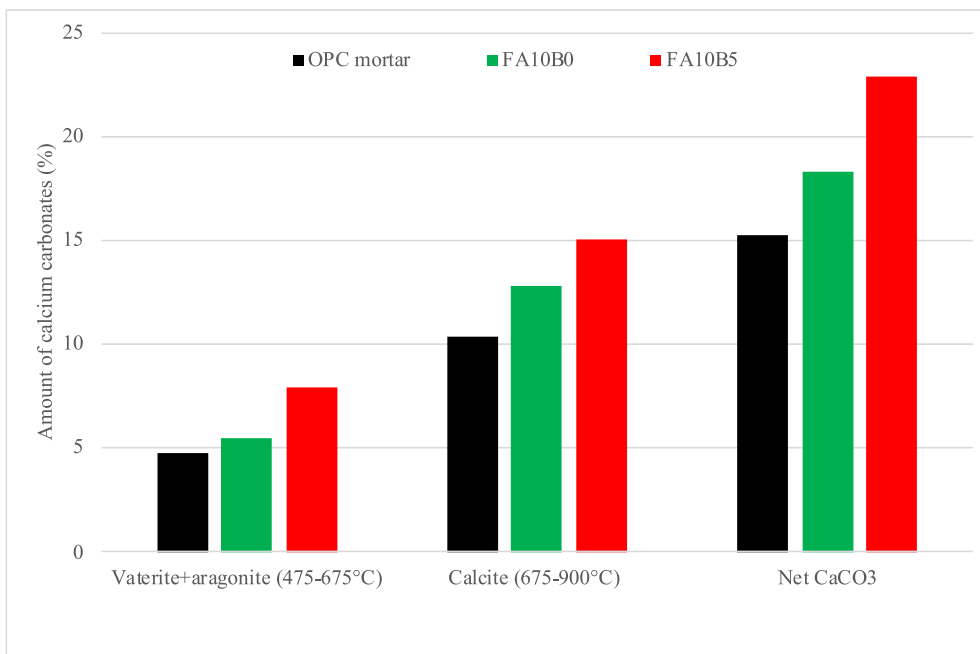


Fig. 15. Quantification of calcium carbonate from TG analysis after 28-day of CO₂ curing.

implies that in the cases of FA10B0 and FA10B5, the majority of the net carbonate is produced by converting a poorly crystalline polymorph to a thermodynamically stable calcite. The plausible explanation for the mechanism is that the presence of the porous and large surface area of the biochar accelerated the carbonation kinetics by facilitating CO₂ diffusion and carbonate mineralization in presence of calcium-rich fly ash.

4. Conclusions

In this study, the optimization of the combination of biochar and fly ash to enhance mechanical properties under two distinct curing regimes:

CO₂ and normal was investigated. For this purpose, the Center Composite Design approach of RSM was employed and the following conclusions were observed:

1. On carbonation, the interaction of biochar and calcium-rich fly ash as a partial cement replacement has a significant positive effect on compressive strength, while under normal curing conditions the incorporation of biochar reduces compressive strength due to its porous nature, leading to an increase in the overall porosity of the matrix.
2. Flexural strength and elastic modulus improve significantly with the addition of biochar due to its fibrillar structure, and the precipitation

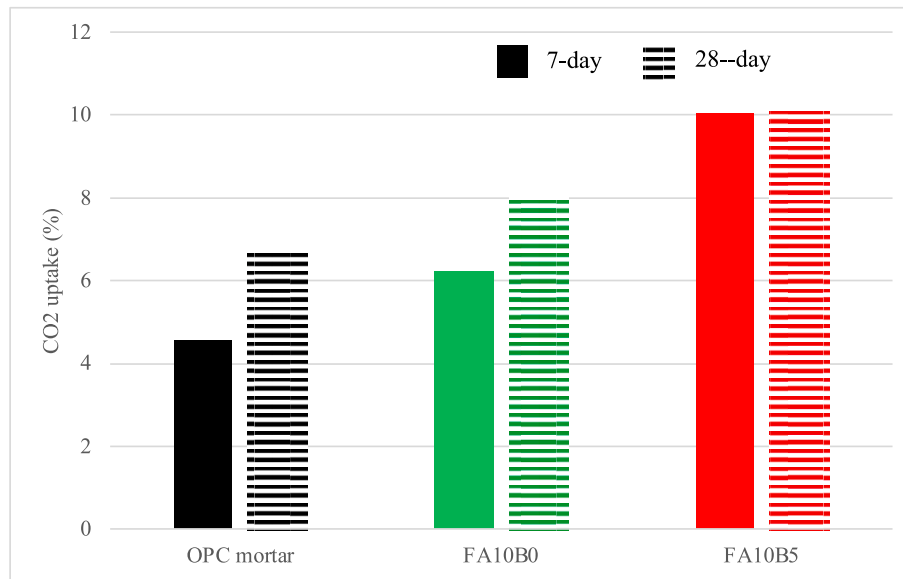


Fig. 16. Quantification of calcium carbonate from TG analysis after 28-day of CO₂ curing.

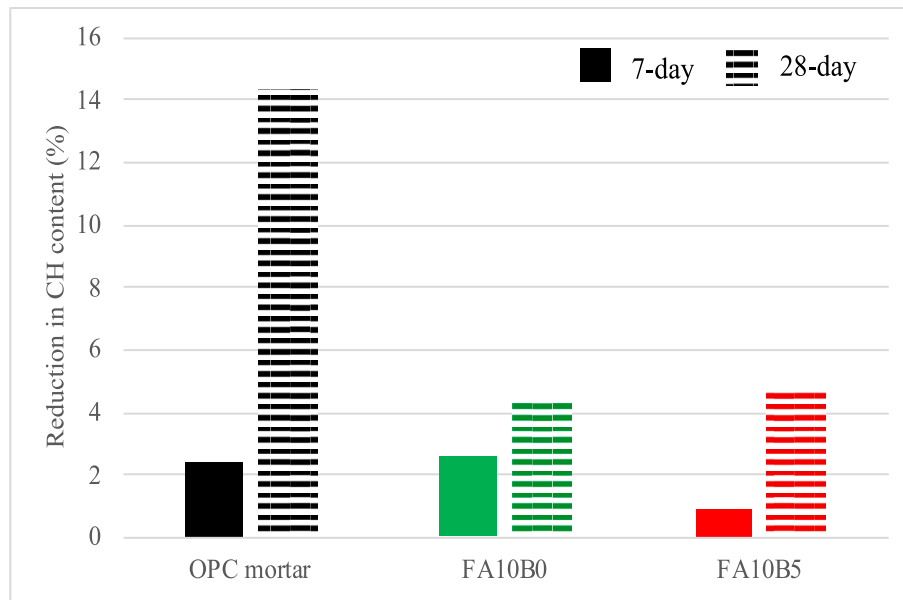


Fig. 17. Reduction in CH content after 7 and 28 days of CO₂ curing compared to normal curing.

- of hydration products inside the biochar particles increases stiffness and deflects crack propagation.
- ANOVA results show that the regression models for compressive strength, flexural strength, and young's modulus are statistically significant. The regression analysis of the models is of high precision as the p-value of the models was ≤ 0.023 for carbonated mixes and ≤ 0.007 .
 - Accelerated carbon curing opens an avenue for using higher amounts of biochar without compromising the mechanical properties. The combination of 10% fly ash and 5% biochar was optimized as it exhibited comparable or higher mechanical properties throughout the hydration time.
 - In the FA10B5 mixture, the reduction in CH content is lower compared to the control, which is due to the fact that the biochar promotes CO₂ adsorption without reducing alkalinity.
 - CO₂ uptake improved significantly by 119% and 50% in the FA10 + B5 mixture after 7 and 28 days, respectively. This is due to the

presence of a continuous porous network for CO₂ diffusion and sufficient calcium for carbonate mineralization.

- This study provides insight into the synergy between different combinations of biochar and fly ash, which could be helpful in developing a low-carbon sustainable concrete based on the required applications.

CRediT authorship contribution statement

Geetika Mishra: Conceptualization, Formal analysis, Investigation, Writing – original draft, Methodology, Validation, Writing – review & editing. **Panagiotis Danoglidis:** . **Surendra P. Shah:** Data curation, Resources, Supervision, Validation, Writing – review & editing. **Maria Konsta-Gdoutos:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Validation, Writing – review & editing.

Declaration of Competing 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.

Data availability

Data will be made available on request.

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