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Bamboo-derived Biochar as Partial Cement Replacement in Concrete for Carbon Dioxide Capturing and Sequestration

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Global urbanization has contributed to heightened carbon dioxide (CO_2) emissions due to extensive cement production for construction purposes. This research explores the viability of biochar as a means of sequestering CO_2. Biochar, a solid material derived from the thermochemical conversion of biomass in a low-oxygen environment, exhibits promising carbon capture capabilities. The primary objective of this study is to develop a concrete mixture design incorporating chemically-activated bamboo biochar as a partial replacement for cement and to assess its capability in capturing and sequestering CO_2. Bamboo biochar was produced at 300 °C and activated using sodium hydroxide. Cement replacement levels of 2 %, 5 %, and 8 % by weight were employed. Cylindrical concrete samples were subjected to compressive testing at 7 and 28 days, while the ability of biochar concrete to adsorb CO_2 was evaluated using an MQ135 gas sensor test. The carbonation depth was determined after subjecting the specimens to a one-month exposure to CO_2. The compressive strength test results confirmed that the 7-day strength of biochar-incorporated concrete was minimally below the standard strength while the 28-day strength was significantly higher. Meanwhile, the gas sensor test affirmed the effectiveness of biochar concrete in adsorbing CO_2, as evidenced by the increase in carbonation depth. These results indicate the potential of bamboo biochar as partial cement replacement in concrete to sequester CO_2 without majorly affecting its compressive strength.

1. Introduction

In recent decades, human-induced emissions of greenhouse gases (GHGs), notably CO_2, have exerted a detrimental impact on the environment (Hanifa et al., 2023). The proliferation of population and expansion of urban areas at a global scale have resulted in an escalated combustion of fossil fuels and increased rates of cement production, which serve as primary contributors to CO_2 emissions. This intensified release of CO_2, the principal GHG responsible for global warming (Amer et al., 2022), poses a substantial threat to the ecological system, manifesting in profound consequences such as prolonged droughts, disrupted precipitation patterns, heightened occurrences of heatwaves, and elevated sea levels. In the Philippines, approximately 128 million metric tons of CO_2 has been emitted in 2017, accounting for 0.33 % of the world's total emissions. Despite this relatively low share of global emissions, the Philippines has experienced a disproportionate impact in terms of both human fatalities and economic losses caused by climate-related hazards over a span of 20 years (1998-2019), as indicated by the Global Climate Risk Index ((Global Climate Risk Index ... 16 th Edition (2021), 2021)). To address this pressing issue, the integration of carbon sequestration technologies into cementitious systems emerges as a viable solution, aiming to mitigate the carbon footprint associated with cement production (Choi et al., 2012). There is a need for a suitable alternative material to replace cement while considering its distinct characteristics (Nair et al., 2020). A prominent approach in carbon capturing and sequestration involves the use of materials possessing high adsorption capacity (D’Alessandro et al., 2010).
In recent research, biochar has emerged as an innovative and promising material for carbon capture, primarily attributed to its porous structure. It is one of the potential candidates for the development of cost-effective CO_2 adsorbent suitable for large-scale implementation (Amer et al., 2022). Biochar, a recalcitrant carbonaceous

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material, is obtained through the pyrolysis process of biomass. It can be derived from various biomass sources, including agricultural residues and wood, offering versatility in its production (Pang, 2019). Notably, biochar exhibits a distinct cost advantage over other CO_2 adsorbents due to the abundant availability of biomass, while its utilization enables sustainable waste management practices. The adsorption capacity of raw biochar is relatively limited due to its underdeveloped pore structure and deficient surface chemistry. Chemical activation techniques are crucial to enhance its adsorption performance (Amer et al., 2022).

Biochar has commonly been activated using alkaline metal hydroxides, particularly potassium hydroxide (KOH) (Sajjadi et al., 2019). In comparison with KOH activation, sodium hydroxide (NaOH) chemical activation is less expensive, less corrosive, and more environmentally friendly. It also requires less dosage or weight measurement. Using the proper ratio of NaOH to biochar during activation directly influences the micropore volume and subsequent adsorption capability. A study showed that 32 % NaOH solution is the optimal percentage in developing exceptional CO_2 adsorption capacity in concrete (Tan et al., 2014).

The utilization of biochar in cementitious systems, such as concrete and mortar, has been a particular research hotspot in recent years. Carbonation in concrete served as an indicator of its CO_2 sequestration. It is the result of combining the adsorbed CO_2 and calcium hydroxide in concrete to form calcium carbonate. The study conducted by Flórez et al. (2019) revealed that as the quantity of pre-treated biochar in the mortar mixtures increases, the carbonation profiles of the samples also show an increase. Samples containing 0.5 % by weight of biochar exhibit nearly complete carbonation within the initial 7 d of exposure (Flórez et al., 2019).

Several research found that biochar of different feedstocks significantly increases the compressive strength of the concrete. Dried wood sawdust biochar as partial substitute for cement led to the enhancement in compressive strength at 7 d and 28 d (Gupta et al., 2020). Rice husk and sugarcane bagasse biochar with dosage of 5 % improves the compressive strength by 36 % (Zeidabadi et al., 2018). 5 % biochar replacement level was found to be the optimal percentage (Sirico et al., 2021).

This objective of this study is to develop a concrete mixture design with Sodium Hydroxide (NaOH) – activated bamboo biochar as partial cement replacement. Specifically, this study aims to produce activated biochar using NaOH chemical impregnation to optimize the CO_2 uptake capacity. It aims to evaluate the mechanical property of concrete in terms of its compressive strength. It also aims to investigate the CO_2 adsorption capacity of bamboo biochar as partial cement replacement in concrete by recording CO_2 concentration in a closed chamber over a period of time using MQ135 gas sensor. And lastly, it aims to investigate the CO_2 sequestration capability of concrete by determining the carbonation depth on its cross-sectional surface using phenolphthalein solution.

2. Materials and methods

The methodology used in this study is divided into three (3): compressive strength test (ASTM C39), MQ135 gas sensor test, and phenolphthalein solution test. These aim to assess the mechanical properties, CO_2 adsorption capacity and sequestration of concrete with biochar, respectively.

2.1 Biochar production and activation

Bambusa blumeana (kawayang tinik), aged between 3 to 5 y from a landfill situated in Consignacion, Orani, Bataan, Philippines, was used as the feedstock for biochar production. The shredded bamboo was sun-dried for a 5-hour period to remove excessive moisture. Biochar was produced by subjecting bamboo in slow pyrolysis at 300 °C in a biochar furnace-type pyrolyzer of the BPSU Mechanical Engineering Department. The biochar was activated using a 32 % sodium hydroxide (NaOH) solution for 3 h, and oven-dried set at 105 °C for 4 h. It was then washed with deionized water to achieve a pH range of 6 to 7. Upon visual inspection, impurities such as non-black biochar pieces were removed. The processed biochar was pulverized and sieved through Sieve No. 200.

2.2 Mixing, casting, and curing of concrete

Table 1 presents the design mixture of this study. 2 %, 5 %, 8 % biochar replacement by weight of cement were used. Mixtures were poured in a 6"x12" cylindrical mold and is tamped 25 times to minimize the formation of voids within the specimen.

Table 1: Design Mixture

Mix ID	Cement: Aggregate Ratio	Water: Cement Ratio	Bamboo Biochar (%)
Control	1:2:4	0.57	0
BC2	1:2:4	0.57	2
BC5	1:2:4	0.57	5
BC8	1:2:4	0.70	8

The specimens for compressive strength testing underwent water curing for 7 and 28 d, while the specimens for the MQ135 gas sensor test and phenolphthalein solution test were demolded after 24 h. The phenolphthalein solution test specimens were then exposed to CO_2 for 30 d in a specialized tank.

2.3 Slump test (ASTM C143)

The mold was positioned on a level, damp, non-absorbent, and vibration-free surface. The filling of the mold occurred in three levels, each uniformly tamped twenty-five times across the cross-section using a rod. The mold was then cautiously lifted vertically, ensuring a continuous upward motion without any lateral or torsional movements. This lifting process involved raising the mold by approximately 12 inches (300 mm) within a time frame of 5 ±2 s. Immediately after removing the mold, the vertical difference between the top of the mold and the original center of the concrete's top surface was measured and recorded.

2.4 Compressive strength test (ASTM C39)

The test was carried out by placing the top and bottom faces of the specimen in a flat and level surface of the universal testing machine (UTM). Gradually increasing load was applied to the concrete specimen until failure occurred. The compressive strength of each specimen was determined by dividing the highest recorded applied load by the area of the specimen. The results were then recorded in pounds per square inch (psi) as the units of measurement.

2.5 CO_2 adsorption capacity test using MQ135 gas sensor

To investigate the CO_2 adsorption capacity of bamboo biochar as partial cement replacement in concrete, MQ135 CO_2 sensor test was conducted, patterned to the study of (Nair et al., 2020). The MQ135 gas sensor utilizes a stannic oxide (SnO_2) semiconductor to detect CO_2. The candle/s and concrete specimens were placed one at a time inside the airtight chamber. Candle/s were then burned to generate CO_2. The chamber opening was immediately sealed to ensure that CO_2 will not escape nor penetrate the airtight chamber during the actual test. This study utilized two setups: single burning candle, and double burning candle.

CO_2 concentration recording of MQ135 gas sensor setup commenced 10 s before burning the candle to determine its initial concentration. The recording continued over a 10 mins duration period. Various data such as the initial (I), peak (P) and final (F) CO_2 concentration were recorded. The equation used in the calculation of the percentage adsorption of biochar is as Eq(1):

$$\%CO_2\ sorption = \frac{P-F}{P-I}(100\%) \tag{1}$$

2.6 Phenolphthalein solution test

The phenolphthalein test was conducted to evaluate the carbon sequestration capacity of concrete. After a 1-month CO_2 exposure of specimens, the specimens were horizontally cut using a grinder, approximately 4 inches from the top. Phenolphthalein solution was sprayed onto each specimen 40 times, ensuring comprehensive coverage of the surface area. The reaction between the phenolphthalein solution and the concrete's cross-sectional area was then observed and interpreted. The emergence of a pink color indicated a non-carbonated region on the surface, a colorless region denoted a carbonated area, and light pink surfaces indicated a semi-carbonated region. In order to ensure an objective evaluation of the results obtained during the phenolphthalein test, this study employed the use of ImageJ software.

3. Results and discussion

3.1 Workability

Table 2 presents the slump values of four (4) different mixtures with varying ratios of biochar replacement to cement. The recommended range of slump according to ACI 211.1-91 for various construction types is between 1 inch and 3 inches. In this study, the results of the slump test indicate that the workability of all the mixtures meets the required standard.

Table 2: Slump of fresh concrete

Mix ID	Bamboo Biochar (%)	Slump (inches)
Control	0	2
BC2	2	2.25
BC5	5	2.5
BC8	8	1.5

The workability of fresh concrete was significantly influenced by the increase in the proportion of biochar as a partial replacement for cement. The reduction in workability was particularly evident when employing the highest ratio of 8 percent, resulting in a deviation of one inch from the slump value observed in the BC5 mixture. This decline can be attributed to the incorporation of a larger amount of water in the BC8 mixture, which utilized a water-cement ratio of 0.7, as opposed to the other biochar mixtures with a water-cement ratio of 0.57. The large surface area of the biochar material contributes to an increased demand for water, as the pores of biochar possess a considerable capacity for water absorption, and the biochar particles tend to retain water on their surfaces.

3.2 Compressive strength

Table 3 presents the result of the compressive strength of cylindrical sample on the average of three specimen per mixture at 7 and 28 d.

Table 3: Compressive Strength of Cylindrical Sample

Mix ID	Bamboo Biochar (%)	Day 7 (psi)	Day 28 (psi)
Control	0	2526.67	3558.50
BC2	2	2173.33	3174.33
BC5	5	1829.33	3801.33
BC8	8	1764.33	2548.67

A significant reduction in the compressive strength of concrete specimens was observed after 7 d of curing. The same trend was observed in the study of Dixit et al. (2019) where 2 % and 5 % replacement level led to decrease in strength. The inherent characteristics of biochar, including its porous structure and comparatively lower pozzolanic activity, contribute to this decline in compressive strength (Dixit el al., 2019). As the proportion of cement replaced by biochar increases in the concrete specimens, these properties of biochar act relatively to result in a discernible downward trend in the compressive strength.
At the 28 th d of curing the concrete specimens, a significant improvement in compressive strength was observed, particularly in the case of the 5 % biochar partial cement replacement, which demonstrated the highest increase percentage of 7 % against control specimen. In similarity, Choi et al. (2012) stated that 5 % biochar replacement increases the strength at 28 d (Choi et al., 2012). This can be attributed to the water absorption and retention capabilities of the biochar particles over an extended period.
In contrast, the disparity between the control specimen and the other mixtures diminished in terms of compressive strength when compared to the results obtained at 7 d. A reduction of 11 % and 29 % in relation to the control specimen was observed for the BC2 and BC5 mixtures, respectively, which was slightly lower than the corresponding 14 % and 30 % decreases in strength observed at 7 d. These findings provide validation for the self-curing mechanism of concrete incorporating biochar.

3.3 Carbon Dioxide Adsorption

Figure 1 presents the model graph of the results obtained from the MQ135 CO_2 test in a single and double burning candle setup, respectively, on the average of three specimen per mixture.

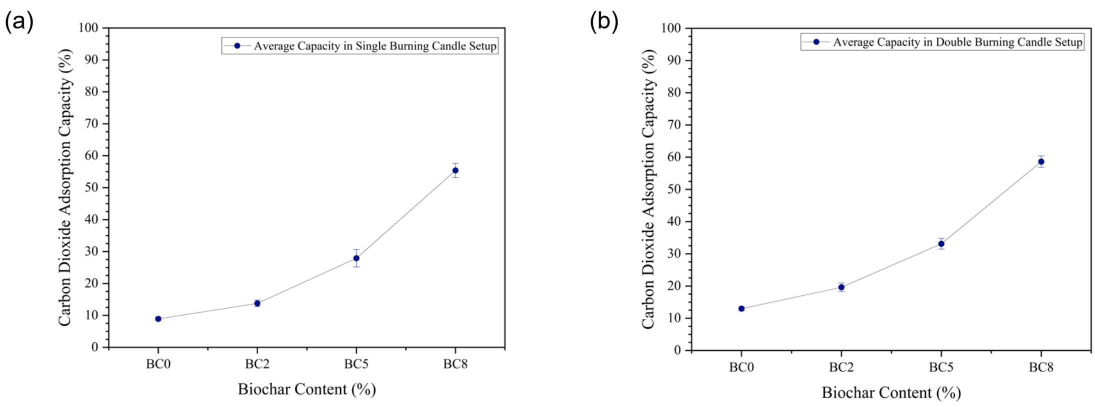

Figure 1: CO_2 adsorption capacity of concrete in (a) single candle setup, and (b) double candle setup

The MQ135 gas sensor detected a decline in the CO_2 concentration within the sealed chamber during the 10-minute duration, signifying the capacity of the concrete specimens to adsorb CO_2. The CO_2 adsorption capacity of the concrete specimens exhibits a direct correlation with the biochar content. As the biochar content increases, the adsorption capacity of the concrete also increases, showcasing a proportional relationship.
The adsorption capacity for the BC0, BC2, BC5, and BC8 mixtures was determined to be 8.91 %, 13.79 %, 27.91 %, and 55.40 %, respectively, in the single burning candle setup. In the double burning candle setup, the adsorption capacity for the BC0, BC2, BC5, and BC8 mixtures was found to be 12.97 %, 19.64 %, 33.11 %, and 58.63 %, respectively. These results reveal a consistent trend, indicating that as the biochar ratio increases, the CO_2 adsorption capacity of the concrete specimens also increases.
A comparable pattern was identified in the research conducted by Nair et al. (2020). The findings demonstrated that as the biochar content increased, there was a corresponding rise in the percentage of CO_2 sorption (Nair et al., 2020).

3.4 Carbon Dioxide Sequestration

Table 4 presents the results of the carbonation depth of specimens subjected to phenolphthalein test on the average of three specimen per mixture.

Table 4: Carbonation Depth

Mix ID	Bamboo Biochar (%)	Carbonation Depth (mm)
Control	0	8.83
BC2	2	12.43
BC5	5	19.20
BC8	8	20.02

Carbonation in cementitious systems develops when ambient CO_2 disperses into the concrete and dissolves in the cement paste pore solution (Taylor, 1997). Carbonation depth in concrete serves as an indicator of its ability to sequester CO_2. During the carbonation process, CO_2 infiltrates the pores of the concrete and reacts chemically with calcium hydroxide ($Ca(OH)_2$) in the matrix. This reaction results in the formation of calcium carbonate ($CaCO_3$), which permanently deposits within the concrete.
The results of this study revealed that all concrete mixtures containing biochar exhibited notably higher carbonation depths compared to the control specimen. BC2, BC5, and BC8 displayed increases of 28.96 %, 54.01 %, and 55.89 % in carbonation depth, respectively.
This phenomenon can be attributed to the porous structure of biochar, which facilitates its capacity to adsorb CO_2 and initiate the carbonation process within the concrete. The increased availability of CO_2 due to the presence of biochar contributes to greater carbonation depth, ultimately enhancing the CO_2 sequestration capability of the concrete mixture.
In the investigation conducted by Flórez et al. (2019), the carbonation profile of the samples deepens with the increasing quantity of pre-treated biochar. In the initial 7 d of exposure with CO_2, concrete samples with 0.5 % by weight of biochar have almost completed the carbonation process. Accelerated carbonation was also found in the samples with 0.1 % biochar (Flórez et al., 2019). This shows that the addition of biochar in the concrete matrix can effectively increase its CO_2 sequestration capability.

4. Conclusions

As this study's objective is to design concrete mixture with biochar as partial cement replacement, the researchers aimed to produce an activated biochar. To attain this, the bamboo waste was collected and processed through slow pyrolysis at 300 °C to produce the biochar. In order to develop its porosity and surface area for an optimized CO_2 uptake capacity, the biochar was soaked in a 32 % NaOH solution and oven-dried.
The evaluation of the compressive strength of the biochar-incorporated concrete was necessary to determine its applicability in the construction setting. In this study, a 7 % increase in the 28-d compressive strength of the mixture with 5 % biochar was observed. Workability of the concrete mixture was not compromised.
In terms of the CO_2 adsorption capacity of biochar-incorporated concrete, MQ135 gas sensor was developed and employed. The result showed that the concrete mixture containing 8 % biochar content demonstrates the highest CO_2 adsorption capacity. In comparison to the control specimen, it is significantly higher by 83.92 % and 77.88 % for the single and double candle setup, respectively.
This study measured the carbonation depth of the concrete with biochar to evaluate its potential to sequester CO_2. Phenolphthalein solution was sprayed in the cross-sectional surface of the concrete and carbonation depth

was measured using ImageJ software. Concrete mixture containing 8 % biochar has the most significant carbonation depth which is 55.89 % higher than the control specimen.

For future research, a comprehensive analysis of the bamboo biochar must be performed including its water absorption capacity, surface area, and alkalinity. It will provide more insights on the effects of biochar in the workability, strength, and CO_2 sequestration capacity of concrete. Given the time constraints in this study, the concrete specimens were exposed to CO_2 specialized tank for only one month. It is recommended to subject the concrete specimens in CO_2 exposure for a longer period of time. In this study, the water-cement ratio was adjusted to let the mixture be physically flowable to be mixed. Using plasticizers can be considered for future research to maintain a constant water-cement ratio for all concrete mixtures.

In summary, bamboo biochar as partial cement replacement in concrete has the capacity in adsorbing and sequestering CO_2 without compromising its compressive strength. The necessity to reduce the dependence in cement aligns with this innovation – a low-cost adsorbent made from heavily abundant agricultural waste. With the alarming increase in the atmospheric CO_2 concentration, materials for CO_2 sequestration are indeed necessary. The use of biochar in concrete is a potential solution to this pressing concern.

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