

Original Research

Mitigating Carbon Dioxide in Atmosphere by Utilizing Biochar as a Fertilizer; A Step Towards Sustainable Agriculture

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Abstract

The use of agricultural waste to produce value-added products has aided in managing waste management difficulties while somehow addressing cost-effectiveness concerns. The current research addresses environmental issues and helps to promote ecologically friendly agricultural practices in Punjab, Pakistan, by using banana and grapefruit peel biomass, converting them to biochar by pyrolysis, and further studying their efficacy as sustainable fertilizer. The return of biochar obtained from agricultural waste to the agricultural field is a sustainable approach for increasing the yield of crop output while reducing the environmental impact of traditional fertilizers. Furthermore, it improves soil condition by regulating pH, water holding capacity, soil organic carbon, and soil ion exchange potential. Zinc oxide loaded biochar was synthesized from banana and grapefruit peel biochar. Pyrolysis was done at 400-500°C as part of the process. Co-precipitation method was used to impregnate ZnO nanoparticles in biochar and proved an efficient and dependable approach. In-situ loading was done. XRD, elemental analysis of carbon, hydrogen, nitrogen, and sulfur (CHNS), FT-IR, and TGA methods were used to characterize synthesized materials. The adsorption ability of ZnO loaded biochar, soil, and raw biochar was investigated using several physical tests such as swelling ratio, water retention, absorbance, and equilibrium water content percentage. As a result, the adsorption capacity of ZnO loaded biochar was shown to be greater than that of raw biochar. Zinc loaded biochar was used as a fertilizer in *Cicer arietinum* (gram). Synthesized nano-fertilizers exhibit enhanced prolonged nutrient release, plant

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growth, and improved soil fertility, providing an environmentally friendly alternative to traditional fertilizers by reducing nutrient loss.

Keywords: Biochar, ZnO loaded biochar, banana biochar, Gram, *Cicer arietinum*, grapefruit biochar, environment friendly fertilizer

Introduction

The agriculture sector is facing a massive challenge to produce an additional 70% of food for the world's growing population, and crop production isn't meeting up with the demand. Any biotic or abiotic stress can impede photosynthesis and reduce plants' ability to convert energy into biomass. Crop yield reduction due to numerous environmental conditions (stress) is a key source of worry in modern agriculture. Similarly, two key stressors, drought and salinity, contribute to a drop in agricultural plant output, lowering yield. First, drought strain is a major threat to crop growth and output around the globe. Second, salinity is a limiting factor, as most crop plants are sensitive to high salt concentrations in arable soil. The influence of salinity can be seen in a variety of physiological, morphological, and biochemical manifestations, such as membrane damage, disrupted enzyme activity, nutritional imbalance, alleviation of seed germination, reduced photosynthesis, oxidative stress, and water relations [1].

According to the circumstances, agricultural production must cope with climatic variability, land degradation, and loss of ecosystem functioning, all while meeting rising global food demand driven by rising population and dietary changes [2]. These factors are well, according to the UN SDGs, related to food security (zero hunger) and climate action. As a result, the agricultural sector's need for resources is rising, resulting in competition in areas where resources are scarce.

Furthermore, the use of conventional fertilizer results in significant economic losses due to leaching difficulties (40-70%), which is crucial for developing countries where agriculture is the backbone of the economy [3]. New fertilizers that gradually deliver nutrients to plants are needed, decreasing nutrient loss and boosting increased crop output, thereby helping economic development [4]. Pathogens, heavy metals, and medicines in manures and composts may cause long-term poisoning of cropland. Furthermore, manures and composts have the potential to emit ammonia and methane, which can exacerbate global warming and cause major nutrient contamination in groundwater and streams [4]. Moreover, the world is exposed to gaseous benzene, varying in extent based on inhalation levels. Megacities are impacted by rising industry and traffic emissions, uncontrolled urban growth, and high concentrations of benzene. This direct negative impact on human health is influenced by its environment and conditions. Kaan Isinkaralar reported the effective removal of benzene with carbon-based adsorbents

obtained from the needles of *Pseudotsuga menziesii* [5], thus reducing the mitigating effect on the environment.

The origin of biochar can be traced back to the Amazon region, when dark earth was created utilizing the slash-and-char process [6, 7]. Currently, this low-cost, carbon-rich organic amendment is produced through high-temperature pyrolysis, gasification, torrefaction, and hydrothermal carbonation of biomass feedstocks [8-11]. Agricultural leftovers, forest residues, byproducts from manufacturing units and waste, solid waste, non-conventional materials, and invasive species are all examples of biochar-producing feedstock [12].

Biochars have several unique qualities that make them appropriate for soil remediation, including a high internal surface area, a negative charge, and resistance to degradation [13]. The surface of biochar has a significant negative charge [14, 15], which attracts positively charged metals and organic molecules from the soil solution to the interior biochar surface. This reduces the quantity of metals and organic pollutants in the soil solution [16, 17] as well as their bioavailability and bioaccessibility [18-21]. Because the negative surface attracts hydrogen ions from the soil solution, the negative charge can also improve soil pH after biochar application to polluted soils.

Higher soil pH increases metal sorption from solution due to the deprotonation of pH-dependent cation exchange sites on soil surfaces [22-24], notably in acidic soils. Some biochars contain a significant amount of mineral ash [25]. Minerals such as carbonates, phosphates, and sulfates can cause some hazardous components to precipitate out of solution; this mechanism can significantly contribute to biochar's remedial potential [26]. Finally, biochar degrades slowly, with C half-lives anticipated to range from 102 to 107 years [27]. As a result, biochar can be considered an inert material for durations ranging from 10 to 100 years. The ability to sequester soil toxins over an extended period of time is one advantage of this recalcitrance. However, as oxygen-containing functional groups on the surface of the biochar are replaced by hydrogen ions, they may release cations into solution over time [28-30].

Moreover, the incorporation of zinc oxide nanoparticles into biochar can enhance the textural features of the carbonaceous material, its porous structure, and the water holding capacity of biochar, which in turn helps with food requirements and supply to plants. Nano-dimensional zinc oxide particles can further improve germination, seedling growth, pigments, sugar, and protein content, and antioxidant enzyme activity in crops. Zinc oxide nanoparticles

invariably increase pigment, protein, and sugar content, as well as nitrate reductase activity [31].

In this study, the biochar was synthesized through the thermal pyrolysis of banana peels and grapefruit peels in the absence of air in a closed container, and ZnO was loaded by the chemical co-precipitation method. Various characterization techniques, such as the Fourier transform infrared spectrometer (FT-IR), X-ray diffractometer (XRD), and thermal gravimetric analysis (TGA), were conducted to illustrate the physicochemical properties of the biochar and help explain its adsorption characteristics for contaminants and its working as an environment friendly fertilizer. The prepared fertilizer was applied to *Cicer arietinum* to check its growth on the plant.

In our current work, we provide an innovative and region-specific strategy for agricultural sustainability in Punjab, Pakistan's rich regions, by using banana and grapefruit biochar as fertilizer. Although the synthesis and characterization procedures have been previously documented, the unique feature is the use of zinc oxide-loaded biochar that is specially sourced from grapefruit and banana peels. This locally produced biochar is not only suited to the unique soil characteristics and agricultural requirements of the Punjab area, but it also provides a sustainable way to handle agricultural waste. The production and use of this biochar as fertilizer are intended to tackle the particular difficulties encountered by nearby farmers, improving crop productivity and supporting ecologically sustainable farming methods. Our research shows that biochar has the potential to be a key component of sustainable agriculture in Punjab, Pakistan's diversified and agriculturally significant environment. It also represents a resource-efficient and regionally appropriate approach.

Materials and Methods

Chemicals

Analytical-grade zinc nitrate hexahydrate ($\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$) was purchased from Simchun. Sodium hydroxide was provided by Sigma-Aldrich.

Synthesis of Zinc Oxide Loaded Biochar

It was synthesized in two steps: in the first step, biochar was prepared by pyrolysis, and in the second step, it was impregnated with zinc oxide.

Preparation of Biochar (BB and GB)

Banana peel biochar (BB) and grapefruit biochar (GB) were prepared by a simple pyrolysis process. Banana and grapefruit peels were procured from local vendors near the University of Punjab, Lahore, washed, dried in open air, and crushed. The crushed peels were placed in the closed container to burn slowly at 400-500°C

for 6h in the absence of air. After burning, biochar was allowed to cool. The resulting biochar was ground in a homogenizer and sieved to obtain a particle size smaller than 0.25 mm. The sieved material was then stored in a zip top plastic bag.

Loading of Zinc Oxide (ZnO BB, ZnO GB)

The produced biochar material from both BB and GB was impregnated with ZnO nanoparticles using the precipitation procedure described by Wu et al. [32]. 10 g of biochar was saturated with 50 mL of a 0.5 M NaOH solution, and the resultant suspension was heated to 60°C while continually stirring. Slowly, 50 mL of zinc nitrate hexahydrate solution (0.5 M) was added dropwise from the burette to the suspension when it reached 60°C. The temperature was then elevated to 80°C for two hours to ensure that $\text{Zn}(\text{OH})_2$ and ZnO nuclei precipitated. When the zinc nitrate solution was added to the suspension, a white precipitate (zinc hydroxide $\text{Zn}(\text{OH})_2$ and ZnO nuclei) emerged at the drop position. After sonicating the suspension for 30 minutes to form ZnO nanoparticles, it was filtered and washed five times with 500 mL of deionized water at room temperature. Finally, the materials were dried overnight in a 60°C oven and sieved manually to get particle sizes smaller than 0.25 mm.

Pot Experiment

The preparation of pots to study the effects of synthesized biochar is given in Table 1.

After preparing the pots, *Cicer arietinum* seeds were sown in each pot, filled with soil, and sprayed with water. These were then placed in a shelter where direct sunlight would not dry them out. They were watered twice a day for 25 days. After 25 days, the pots were shifted, with the contents set into ground soil.

Characterization

The materials' moisture, volatile, and ash contents were evaluated using thermogravimetry (TGA701 analyzer). In a typical oven, moisture was measured using the ASTM E871-82 standard method.

FT-IR (Agilent Technologies, Carry 630) was used to access the organic moieties present, and powder, CHNS (vario micro cube analyzer) was done to check the carbon content of the biochar. XRD (rigaku D/MAX-2550PC X-ray diffractometer) outfitted with Cu K radiation (1.54059 Å), powder X-ray diffraction (XRD) patterns were captured over a 2θ range of 10°-90° to determine phase and crystallinity.

Salt Index (SI)

In separate beakers, 1.0 g of BB, GB, ZnO BB, ZnO GB, and sodium nitrate (NaNO_3) with 200 mL of distilled water were taken. After 24 hours, the conductivities

Table 1. Preparation of pots.

| Sr. no. | Pot label | Soil in grams | Biochar added | Weight of Biochar added in grams |
|---------|-----------|---------------|---------------------------|----------------------------------|
| 1. | 4 | 700 | ----- | 3 |
| 2. | 1 | 700 | Grape fruit biochar (G.B) | 3 |
| 3. | 10 | 700 | Banana biochar (B.B) | 3 |
| 4. | 5 | 700 | ZnO G.B | 3 |
| 5. | 6 | 700 | ZnO B.B | 3 |

of the solutions were tested using a conductivity meter. SI was determined as the ratio of their conductivities [33].

Swelling Ratio (SR) and Equilibrium Water Content (EWC)

1.0 g of BB, ZnO BB, ZnO GB, and GB were submerged in 200 mL of distilled water separately for 24 h, allowed to swell, and then filtered. Calculate SR and EWC using Eqs. (1) and (2), respectively [34].

$$SR = \frac{W_s - W_d}{W_d} \quad (1)$$

$$EWC = \frac{W_s - W_d}{W_s} \times 100 \quad (2)$$

Where, W_d and W_s are the dry and wet weights of the samples taken.

Water Retention Studies (WR)

Water retention studies (WR) were conducted in pre-weighted cups, add 50.0 g of sieved soil in cup 1 (weighed as W_c) as a control or blank, and in the rest of the cups. Add 2.0 g of prepared samples + 50 g of soil. Add 30 mL of distilled water to each cup, allow it to seep, and reweighed after 24 h as W_s . The cups were then retained in a glass box, weighted on a daily basis for 30 days as W_{c1} , W_{s2} [35]. Water retention was calculated using Eq. (3),

$$WR\% = \frac{W_2}{W_1} \times 100 \quad (3)$$

Results and Discussion

Synthesis of BB and GB

The pyrolysis method was utilized to synthesize biochar, which was then used as a support material for macro and micro nutrients. Biochar has a porous structure that promotes and facilitates nutrient impregnation [36]. Earlier research has also

demonstrated the ability of biochar to store nutrients via chemisorption and physisorption [37]. As a result, this property of biochar can be used to employ it as a slow release fertilizer, as it not only improves soil quality but also ensures the availability of nutrients to plants for a longer length of time.

Synthesis of ZnO BB and ZnO GB

Synthesis of ZnO loaded biochar by the precipitation method improved the textural properties of the synthesized biochar.

Characterization

Thermogravimetric Analysis (TGA)

TGA was used to evaluate the thermal stability of the biochar, and the graph shows the relationship between temperature and % weight loss. The moisture and carbon content were evaluated by thermogravimetric analysis.

The first breakdown of grapefruit biochar occurred at over 90°C owing to water loss. The second was lost owing to lignin, cellulose, or hemicellulose breakdown. The deterioration progressed slowly until it reached temperatures of up to 700-800°C, indicating graphitic carbon breakdown with significant weight loss. The TGA plot of banana biochar with respect to temperature and % weight loss revealed that the first deterioration at 85°C was due to water loss because the water molecules were physically connected to the surface. The second was lost owing to lignin, cellulose, or hemicellulose degradation at temperatures close to 750°C. Carbon degradation caused the most weight loss between 750 degrees Celsius [38], as given in Fig. 1.

Fourier Transform - Infrared Spectroscopy (FT-IR)

A comparison of the FT-IR spectra of BB and GB (shown in Fig. 2, parts a and b) revealed that most of the bonds have similar shapes in both biochars. The identified bands are located at 3385 cm^{-1} in the case of BB and at 3380 cm^{-1} assigned to hydroxyl groups' O-H stretching vibrations, and C-H stretching vibration peak in aliphatic carbon compounds, which appeared at 2924 cm^{-1} in the case of BB. Also, the peaks observed in the BB spectra at 1992 cm^{-1} were related

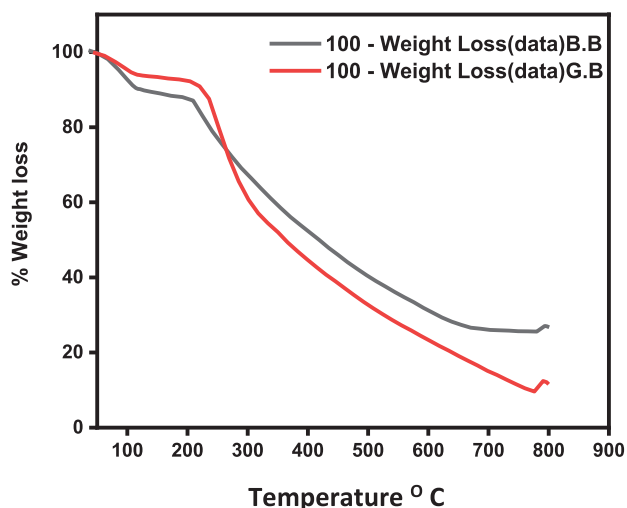


Fig.1. Thermogravimetric analysis of banana biochar (BB), grapefruit biochar (GB).

to CH₃ deformation. In addition, the bonds related to the large aromatic skeleton and O–H bending peak were observed at around 1500 cm⁻¹, as observed in both the BB and Gb spectra. The region between 800 and 1350 cm⁻¹ contains C=C and C=O stretching vibrations [39, 41].

CHNS Analysis

To determine the content of organic materials, an elemental analysis of the sample was done. Carbon,

hydrogen, nitrogen, and sulfur percentages were calculated. Samples were obtained according to weight and wrapped in boats according to standard procedure. The analyzer was used with a combustion temperature of 1050°C and a reduction temperature of 850°C.

The results of the CHNS analysis showed that biochar has a high carbon content, as mentioned in Table 2, which favors its use and role as a soil amender.

Powder X-ray Diffraction (XRD)

The XRD patterns' wide-angle area (10°-90°) enables an assessment of the graphitic nature of the produced carbons. The graphitic carbon XRD patterns shown in Fig. 3(a, b) revealed a single broad peak at 2-theta 21.94 in the case of grapefruit biochar and a single broad peak at 2-theta 22.96 in the case of banana biochar. These data provide credence to an amorphous framework [42].

The XRD patterns (c) in Fig. 3 show significant diffraction peaks at 2 values of 19, 21, 24, 31, 34, 36.2, 47.4, 56.5, 62.7, 66.3, 67.8, 69.0, 74.4, and 76.8. These peaks suit the ZnO with hexagonal wurtzite phase standard JCPDS card no. 89-1397 with a small variation, indicating a modest structural deformation. Predominant diffraction peaks are visible in the XRD patterns (d) of Fig. 3 at 2 theta values of 15, 17, 20, 28, 30, 36.2, 40, and 50. These peaks fit the ZnO with hexagonal wurtzite phase standard JCPDS card no. 89-1397 quite well. [43] The given spectrum demonstrated a clear loading of ZnO on biochar, ensuring the creation of the products.

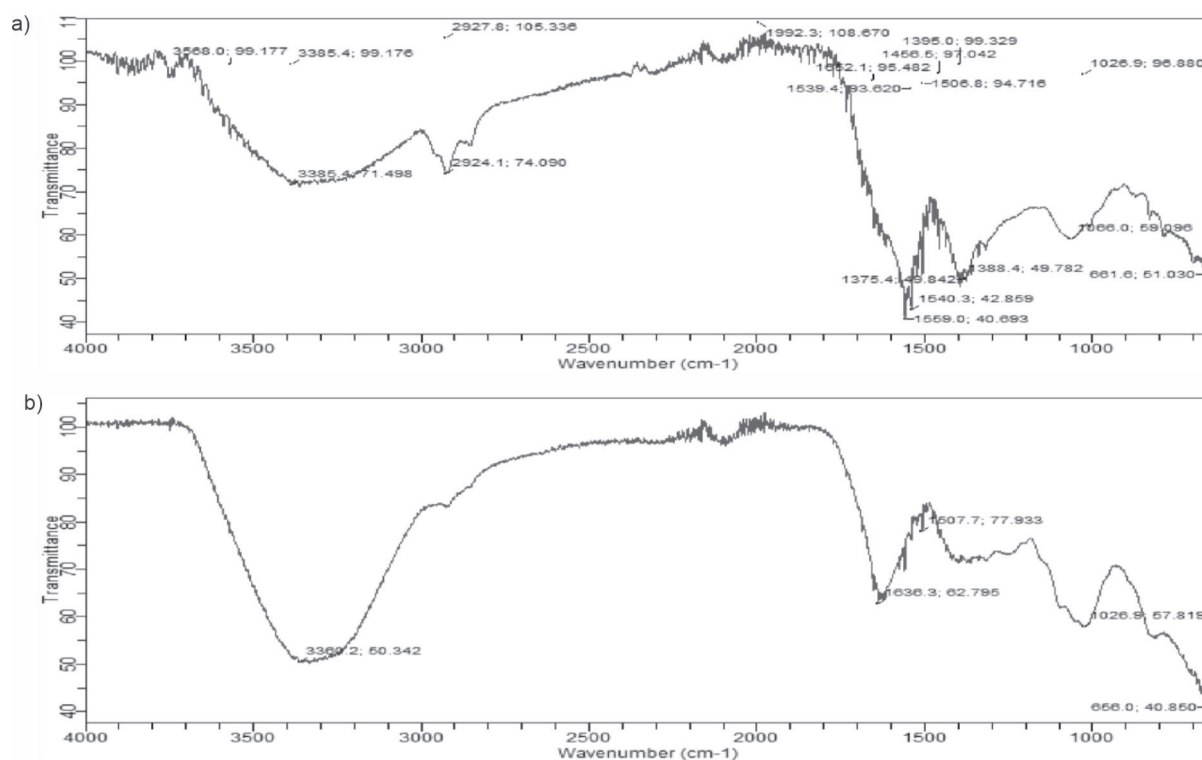


Fig.2. FT-IR spectra of a. Banana Biochar and b. Grapefruit Biochar.

Table 2. Amount of C, H, S and N in banana biochar and grapefruit biochar.

| Composition | %C | %H | %N | %S |
|---------------------|------|------|------|------|
| Banana biochar | 50.8 | 45.9 | 41.5 | 0.05 |
| Grape fruit Biochar | 50.1 | 4.72 | 2.40 | 0.29 |

%C = percentage of carbon, %H = percentage of hydrogen, %N = percentage of nitrogen, and %S = percentage of sulphur.

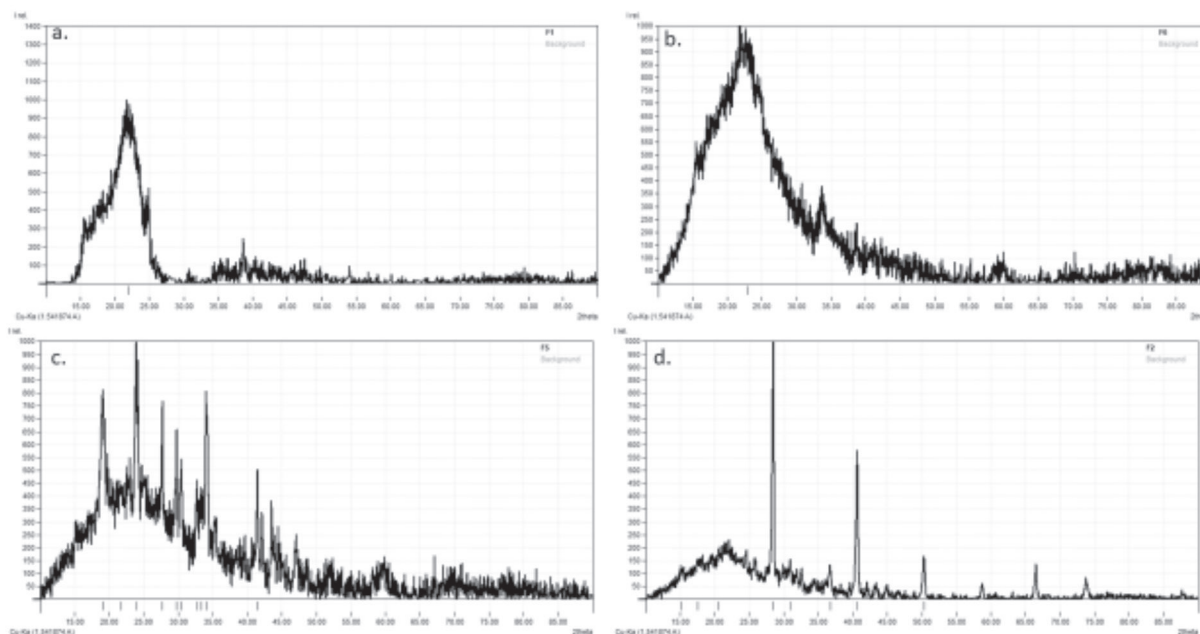


Fig.3. XRD spectra of a. Grapefruit biochar (GB), b. Banana biochar (BB), c. ZnO GB, d. ZnO BB.

Salt Index (SI)

SI measures the probability of a fertilizer causing plant injury. When compared to the acceptable tolerable range of SI, which is 2 mmhos cc^{-1} (in terms of conductivity; reference to NaNO_3 is considered as 100), the value was in range, making it safe for plant usage and, as a result, sustainable agriculture [44]. Higher SI levels in fertilizer have been shown to harm plants and reduce agricultural output.

Swelling Ratio (SR) and Equilibrium Water Content (EWC)

The results of the experiment for BB, GB, ZnO BB, and ZnO GB are given in Table 3, from which it can be observed that there was a small increase in the values of SR and EWC of loaded biochar as compared to pure biochar. In general, ZnO BB is characterized as having a highly porous structure [45] and [46] that can physically adsorb water to be later released to soil or plants, especially in arid areas [37, 47, 48].

The results of the Salt Index, Swelling Ratio, % Equilibrium, and Water Content of the samples are given in Table 3.

Water Retention (WR)

Water retention, as shown in Fig. 5, represents the control (i.e., soil without samples) and experimental samples (GB, BB, ZnO BB, and ZnO GB). Usually, WR decreases with time, as was the case in all samples and controls, due to environmental factors such as temperature. In the present study, the overall effect of biochar and soil for water retention has been studied and compared with the soil where it is applied, rather than separately studying the soil for water holding capacity, to explore the role of biochar as fertilizer. Experimental samples had a higher WR capacity throughout the experimental span of 21 days, as shown in Fig. 4. Due to the high surface area and water holding capacity of biochar itself and the further incorporation of nanoparticles into it, it is a better choice for areas where the availability of water for plant growth is a problem. The response of the experimental samples shows the efficacy of these samples to be used as fertilizer, not only for increasing soil fertility but, in addition to that, to keep the soil hydrated and provide suitable circumstances for plant growth. The retention of water helps in providing water to the soil and, subsequently, to plants [46].

Table 3. Results of Salt Index, Swelling Ratio and % Equilibrium Water Content of samples.

| Properties | BB | GB | ZnO BB | ZnO GB |
|------------|------|------|--------|--------|
| SI | 1.88 | 1.26 | 1.89 | 2.00 |
| SR | 10.2 | 8.92 | 11.04 | 9.8 |
| %EWC | 91.1 | 91.8 | 91.6 | 90.7 |

SI = Salt Index, SR = Swelling Ratio, % EWC = Equilibrium Water Content

Application as a Fertilizer

The use of biochar-based fertilizers or soil amendments is an effective solution, not just a “jackpot,” but even a “multi-win,” in keeping with the circular economy and sustainable development concepts (Fig. 5). Such solutions not only enhance soil qualities (Maikol et al., 2021) and boost agricultural yields, but they are also climatic (Woolf et al., 2010) and natural environment friendly. The same approach was followed in our research. Biochar was synthesized from peels by pyrolysis and impregnated with ZnO to produce

nanocomposite BB and GB loaded with ZnO. Salt index, water absorbance, and retention studies all showed that ZnO loaded biochar has a high potential for application as a nano-fertilizer. These may not only improve plant development by supplying nutrients over a longer period of time, but they can also improve soil fertility while minimizing environmental challenges like global warming and land contamination caused by nitrogen volatilization and leaching from traditional fertilizers. As a result, synthesized fertilizers may be regarded as a cost-effective, practical, and environmentally beneficial material for long-term agriculture.

Water retention studies

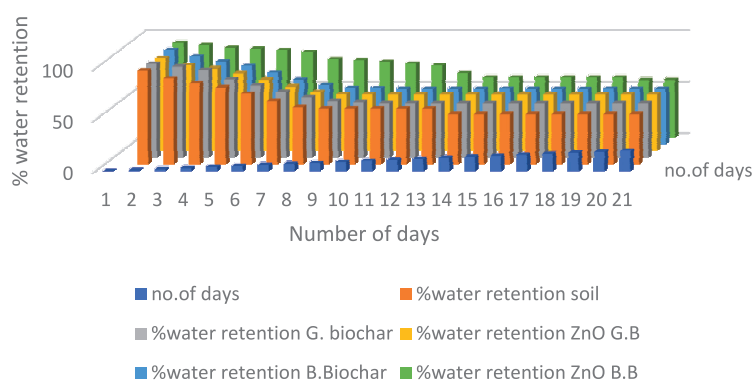


Fig.4. Water retention studies of blank (soil), BB, GB, ZnO BB, ZnO GB.

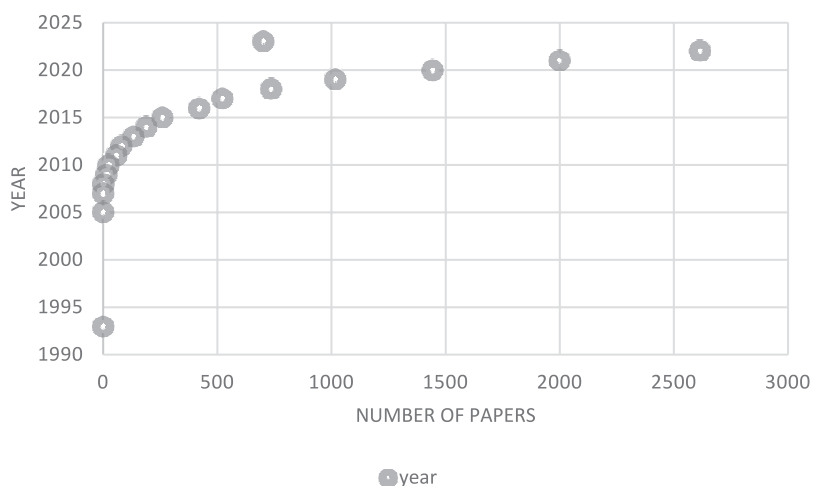


Fig.5. Number of publications according to Elsevier with keyword “biochar fertilizer” from 1993 to 2023.



Fig.6. Visible growth patterns of *Cicer arietinum* in different pots containing different types of samples.



Fig.7. Setup designed for protection from harsh weather.

Different types of biochar were applied in these pots and were compared with a blank (soil). Blank soil was taken in pot 4, GB was applied in pot 1, and BB was applied in pot 10. whereas ZnO GB was applied in pot 5 and ZnO BB was applied in pot 6. After 25 days of growth, the following results were observed, as given in Fig. 6.

After 25 days, the plants were taken out of the pots and put in the soil. A proper setup was designed to protect the plants from harsh weather conditions (Fig. 7). Different visible growth patterns were observed. A visible growth was observed in the case of ZnO loaded biochar as compared to raw biochar and blank soil (Fig. 8).



Fig.8. Growth patterns of *Cicer arietinum*.

Conclusions

Grapefruit biochar and banana biochar were synthesized by pyrolysis at almost 400-500°C. The loading of biochar with metal (ZnO) was done by the chemical co-precipitation method. Biochar was synthesized from banana and grapefruit peels, which is very effective in reducing environmental pollution. Functional group identification, stability of synthesized

samples, structure, and loading were confirmed by Fourier Transform Infrared Spectroscopy (FT-IR), CHNS (elemental analysis), Thermogravimetric analysis (TGA), and X-Ray Diffraction techniques (XRD). Synthesized samples (biochar, metal loaded biochar) showed the ability to be used as nano-fertilizers, according to the findings of investigations on the salt index, swelling ratio, water absorption, and water retention studies. Synthesized nano-fertilizers improved plant growth by giving nutrients to the plant over a long period of time, enhancing soil fertility, and reducing environmental problems. Volatilization from traditional fertilizers results in nutrition loss as well as climate change and land contamination. So, it can be said that synthetic nano-fertilizers are affordable, practical, and environmentally benign. The results of the physical tests confirmed high water absorption and retention capacity for application as nano-fertilizer.

Furthermore, by repurposing agricultural waste, the use of biochar made from banana and grapefruit peels helps reduce environmental pollution. The research results demonstrate these synthetic nano-fertilizers' affordability, usefulness, and environmental friendliness. They represent a viable path forward for sustainable agriculture because of their capacity to increase soil fertility, lessen environmental issues, and offer an affordable substitute for traditional fertilizers. This study offers insightful information about the continuing efforts to create environmentally friendly agricultural practice solutions, ultimately supporting a more resilient and sustainable method of producing food.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.

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