

BIOCHAR FROM DURIAN SHELLS: A NEW APPLICATION IN SUSTAINABLE AGRICULTURE DEVELOPMENT

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ARTICLE INFO		ABSTRACT
Received:	16/01/2025	This study aimed to repurpose durian shells into biochar for sustainable fertilizer production, addressing agricultural waste management while promoting plant growth. The biochar was prepared through anaerobic pyrolysis, with varying modification durations to identify the optimal sample. Experiments on water spinach and green mustard demonstrated that the fertilizer significantly enhanced plant growth. Characterization using FTIR, SEM, and EDX confirmed the material's morphology and composition. The optimal ratio (70% biochar, 15% chitosan nanoparticle solution, 15% shallot juice) contains nutritional elements of C, O, P, K, N, and Mg that effectively support plant growth comparable to urea fertilizer, achieving a height of 9.5 cm after 14 days on scallion plants while maintaining low moisture content (1.11%). Thus, the combination of biochar and nutrients significantly boosts plant tolerance and growth. This study suggests that generating organic fertilizer from durian shells offers an effective solution to manage agricultural waste while enhancing the economic value of this type of organic biomass.
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THAN SINH HỌC TỪ VỎ SẦU RIÊNG: MỘT ỨNG DỤNG MỚI TRONG PHÁT TRIỂN NÔNG NGHIỆP BỀN VỮNG

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THÔNG TIN BÀI BÁO		TÓM TẮT
Ngày nhận bài:	16/01/2025	Nghiên cứu này nhằm tái sử dụng vỏ sầu riềng để chế tạo than sinh học phục vụ sản xuất phân bón bền vững, giải quyết vấn đề quản lý chất thải nông nghiệp và thúc đẩy sự phát triển của cây trồng. Than sinh học được chế tạo thông qua quá trình nhiệt phân yếm khí, với thời gian xử lý khác nhau để xác định mẫu tối ưu. Thử nghiệm trên rau muống tàu và cải xanh cho thấy phân bón này cải thiện đáng kể sự phát triển của cây trồng. Việc phân tích bằng FTIR, SEM và EDX xác nhận hình thái và thành phần của vật liệu. Tỷ lệ tối ưu (70% than sinh học, 15% dung dịch nano chitosan, 15% nước ép hành tím) với các thành phần dinh dưỡng C, O, P, K, N, và Mg đảm bảo hỗ trợ sự phát triển của cây trồng tương đương với phân urê, đạt chiều cao 9,5 cm sau 14 ngày trên cây hành lá và duy trì độ ẩm thấp (1,11%). Do đó, sự kết hợp giữa than sinh học và các thành phần dinh dưỡng giúp cải thiện khả năng chống chịu và sự phát triển của cây trồng. Nghiên cứu này gợi ý rằng việc tạo ra phân bón hữu cơ từ vỏ sầu riềng là một giải pháp hiệu quả để quản lý chất thải nông nghiệp đồng thời nâng cao giá trị kinh tế của loại sinh khối hữu cơ này.
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1. Introduction

Durian (*Durio zibethinus*), belonging to the family Bombacaceae and genus *Durio*, is a seasonal tropical fruit tree. It is an economically significant crop in Southeast Asian countries such as Thailand, Malaysia, Indonesia, and Vietnam. The durian fruit is characterized by its large size, strong odor, hard shell, and numerous spines [1]. On average, the edible flesh of a durian comprises only 15-30% of the total weight of fruit, with the remaining 70-85% consisting of the husk [2]. Currently, durian shell waste is often incinerated or sent to landfills without consideration for the environment, and there is a lack of treatment measures to prevent pollutants from leaching into the soil and water [3].

Many studies worldwide have focused on the processing methods and applications of durian shells. In 2003, Khedari et al. [4] studied the production of thermal insulation particle boards from durian shells and coconut fiber. The main variables investigated were the type of binder (urea formaldehyde 12%, phenol formaldehyde 6%, and isocyanate 3%) and density. The study found that the mechanical strength of the particle boards increased with density, and the boards exhibited low thermal conductivity suitable for use as ceiling and wall insulation. In 2009, Chandra et al. [5] successfully synthesized activated carbon from durian shells for dye adsorption, specifically for removing methylene blue from aqueous solutions. The activated carbon was produced through chemical activation with KOH at a temperature of 673.15 K for 1 hour, with an activator-to-durian shell ratio of 1:2. Kinetic and isotherm tests were conducted to evaluate the adsorption properties of the activated carbon. In 2012, K.Y. Foo and B.H. Hameed [6] investigated the production of activated carbon from durian shells using NaOH with microwave assistance, examining parameters such as the chemical impregnation ratio (0.25 – 2.0), microwave power (90 - 800 W), and irradiation time (4 - 8 minutes). The results indicated a maximum adsorption capacity of 410.85 mg.g⁻¹, a BET surface area of 1475.48 m².g⁻¹, and a pore volume of 0.841 m³.g⁻¹. In 2023, Manmeen et al. [7] researched the production of biochar from durian shells using a slow pyrolysis process, with variables including pyrolysis temperature, cooling temperature, and residence time. Variance analysis showed that only the pyrolysis temperature had a significant effect on biochar yield. The highest yield (56.11%) was obtained at a pyrolysis temperature of 300 °C, while a high calorific value (26.55 MJ.kg⁻¹) was achieved at 600 °C with a residence time of 30 minutes. Economic analysis showed that converting 60 tons of durian shells per year into biochar and pyrolysis liquid had an estimated internal rate of return (IRR) of 25.91% and a payback period of 1.58 years, confirming the feasibility of large-scale pyrolysis. With the increasing demand for food, optimizing both yield and quality on limited agricultural land is crucial. Nutrient management plays a vital role in crop yield and quality. However, long-term agricultural land often suffers from nutrient depletion, leading to the use of chemical fertilizers and pesticides to protect crops and maximize yield. The use of chemical fertilizers not only causes environmental pollution but also poses health risks to humans [8].

This paper focuses on the synthesis of organic fertilizer from biochar derived from durian shells, combined with macronutrients and micronutrients to enhance its ability to promote plant growth. The characteristics of the biochar were analyzed using Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). The production of organic fertilizer from durian shells has significant potential for managing agricultural waste, utilizing biomass, and promoting sustainable agriculture for the present and future.

2. Materials and methods

2.1. Materials

Phosphoric acid (H₃PO₄, 85%), acetic acid (CH₃COOH; 99%) were purchased from Xilong Scientific Co., Ltd, China; chitosan (DD ≥ 90%) was bought from a Vietnamese company; while

diaminomethanone urethane ($\text{CO}(\text{NH}_2)_2$) was purchased from Merck, Germany. Durian shells and purple onions were collected from An Binh market, Ninh Kieu district, Can Tho city. Sodium tripolyphosphat (STPP, 99%) was purchased from Himedia Laboratories Pvt. Ltd. (India). All solutions were prepared with deionized (DI) water from a MilliQ system.

2.2. Activation of durian shells using a phosphoric acid (H_3PO_4) solution

Fresh durian shells were cut into pieces and thoroughly washed with water. The shells were dried in an oven at 105 °C for 16 hours. The dried durian shells were then placed in a container containing a mixture of 4.97 L of water and 30 mL of phosphoric acid (H_3PO_4) solution and soaked for 24 hours. After soaking, the shells were removed and drained for 10 minutes, then further dried in an oven at 105 °C to eliminate moisture before proceeding to the anaerobic pyrolysis process. The next stage involved anaerobic pyrolysis, where the durian shells were subjected to pyrolysis under anaerobic condition for varying durations (30, 45, 60, and 75 minutes). At the end of the experimental process, the biochar samples were analyzed for surface morphology, characteristics, and composition using appropriate material analysis methods.

2.3. Activation of durian shells using warm water

The conditions and steps for implementation are similar to the procedure using H_3PO_4 mentioned above; replace the H_3PO_4 solution with warm water during the activation process. At the end of the experimental process, the biochar samples were analyzed for surface morphology, characteristics, and composition using appropriate material analysis methods.

2.4. Preparation of chitosan nanoparticles solution

Chitosan nanoparticles solution (CTS NPs) were simply synthesized by using STPP (sodium triphosphate) as a cross-linking agent. First, 1.0 g of chitosan (CTS) was completely dissolved in 100 mL of acetic acid (1.5 wt%) solution under magnetic stirring at 60 °C for 30 min. Then, 2 mL of 1 wt% STPP was added to 40 mL of as-prepared CTS solution with strongly stirring at 60 °C for 60 min. The as-prepared products were centrifuged for 15 min and washed several times with DI H_2O to remove excess chemicals un-reaction. Finally, CTS NPs were obtained.

2.5. Fabrication of organic fertilizer from biochar, chitosan nanoparticles solution (CTS NPs) and purple onion (shallot juice)

Table 1. Compositions and mixing ratios of organic fertilizers

Sample	Biochar (w%)	Chitosan nanoparticles solution (CTS NPs) (1% of chitosan in acetic acid 1.5%) (w%)	Purple Onion (shallot juice) (w%)
No.1	70	20	10
No.2	70	15	15
No.3	70	10	20

Biochar from durian husks was pyrolyzed under anaerobic conditions for 60 minutes and then ground into a fine powder. After grinding, 50 g of the powder was mixed with a specific ratio as detailed in Table 1 and thoroughly blended for 10 minutes. The 50 g mixture was then pelletized using a manual pellet press. The resulting pellets had dimensions of (1.5 x 1 cm) and a weight of 0.7 g. Following palletization, the samples were dried at 70 °C for 30 minutes to ensure that the solid components and bonds remained intact and did not crumble upon handling.

At the end of the process, the samples were analyzed for their components, morphology, and suitability for use in crop applications. This procedure is similarly applied to the remaining samples with the ratios specified in Table 1.

2.6. Evaluation of modified biochar fertilizer organic fertilizer samples made from durian husk biochar on onion growth

The experiment was conducted using garden soil sourced from Can Tho University campus with an initial pH of 6.5. Each experimental pot was filled with a 2-kg soil sample. Twenty grams of biochar pellets (each pellet weighed 0.7 g) were top-dressed after seeding. Soil moisture content was maintained at a constant 60%. Soil pH was determined using a pH meter at the start of the experiment, at 3, 7 and 14 days post-seeding. Each measurement was replicated three times, and the mean was calculated. Concurrently, plant growth was assessed by measuring plant height from base to apex using a ruler. This measurement was replicated five times, and the mean was calculated.

2.7. Methods for analyzing properties and the process of plant cultivation experiments

To analyze the synthesized material samples, various analytical tests were performed, including Scanning Electron Microscopy (SEM) which was used to measure the particle size and surface morphology of the material samples using a JEOL JCM-7000 (Japan) with an accelerating voltage of 15kV. Additionally, functional groups present in durian husk biochar were analyzed using a Renishaw 2000 confocal Raman microscope on a Fourier-transform infrared spectroscopy (FTIR; PerkinElmer Frontier FT-NIR Spectrometer). Furthermore, the phase structure of the films was determined by X-ray diffraction (Empyrean; PANalytical; UK) with Cu K α radiation (operating at 40 kV and 100 mA). A scan rate of 0.05 degree⁻¹ was used for 2 θ (between 10^o and 80^o). The experimental setup for organic fertilizer samples made from durian husk biochar, with varying component concentrations, was tested on green onion plants at 3, 7, 10, and 14 days. Soil Moisture Meter (EXTECH MO750, USA) was employed to control soil moisture measurement.

3. Results and discussions

3.1. Results of morphology and characterization analysis

The FTIR spectra of durian husk biochar (Figure 1a) reveal functional groups influencing fertilizer properties. The vibration at 3614 cm⁻¹ indicates covalent O-H bonds, essential for adsorption and catalytic abilities. Peaks at 2345 cm⁻¹ and 2322 cm⁻¹ correspond to C-H stretching in aliphatic formations [9], confirming the presence of cellulose, hemicellulose, and lignin. The higher peak intensities in biochar compared to organic fertilizers (Figure 1b-1d) suggest the decomposition of aliphatic hydrocarbons into carbon dioxide, methyl hydride, or aromatics during anaerobic pyrolysis. Peaks at 1558 cm⁻¹ and 1982 cm⁻¹ indicate silica (Si-O) and aromatic C-H groups, respectively, suggesting a honeycomb-like structure [10]. In the organic fertilizer FTIR spectra (Figure 1b-1d), characteristic peaks of durian husk persist with shifts due to chitosan and onion juice. The O-H peak shifts from 3614 cm⁻¹ to 3855 cm⁻¹, indicating reduced hydrogen bonding. The C-H peak shifts to 2347 cm⁻¹ with decreased intensity, reflecting shortened organic chains. Peaks at 1560 cm⁻¹ and 1541 cm⁻¹ correspond to CONH₂ and NH₂ groups from chitosan, while 1508 cm⁻¹ indicates interactions between NH₃⁺ and phosphate. Additional peaks at 1072 cm⁻¹ (P=O) and 3568 cm⁻¹ (N-H groups) confirm polyphosphate formation and onion juice content. The alcohol group (-C-O, C-OH, or C-O) appears at 669 cm⁻¹ [11]. The results show that the organic fertilizer retains its functional groups and nutrients after synthesis. FTIR analysis indicates that the fertilizer exhibits higher intensity peaks compared to H₃PO₄-treated durian husk biochar, suggesting that the activation process enhances surface area and absorption capacity due to the biochar's porous structure.

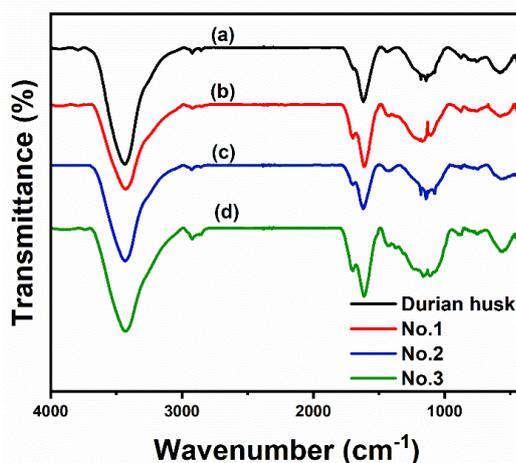


Figure 1. Fourier Transform Infrared (FTIR) spectrums of: (a) Durian husk biochar sample, Organic fertilizer sample made from durian husk biochar with the weight ratio of (b) Sample No.1: (70% biochar, 20% of Chitosan nanoparticles solution (CTS NPs) (1% of chitosan in acetic acid 1.5%), 10% of shallot Juice), (c) Sample No.2: (70% biochar, 15% of CTS NPs, 15% of Shallot Juice), and (d) Sample No.3: (70% biochar, 10% of CTS NPs, 20% of shallot Juice), respectively

The SEM results (Figure 2(I)) illustrate the structural evolution of durian husk biochar during pyrolysis at 30, 45, 60, and 75 minutes. Pyrolysis reduces water and oxygen, forming 13–18 μm pores and a honeycomb-like structure [12]. At 60 minutes, the biochar exhibits uniform pores and thinner walls, indicating optimal porosity, surface area, and adsorption capacity [13]. Shorter pyrolysis times (30 and 45 minutes) yield underdeveloped pores, while 75 minutes results in structural collapse, reduced surface area, and brittleness due to over-decomposition. Figure 2 (II) show activated carbon samples derived from durian peel after anaerobic pyrolysis at 30, 45, 60, and 75 minutes. The biochar pre-treated with warm water exhibits a broad pore size distribution (5–18 μm) with thicker pore walls (1–5 μm). The 75-minute pyrolyzed sample shows pore collapse due to prolonged pyrolysis, causing carbon chain breakdown. In the 60-minute pyrolyzed sample, smaller pores are observed on the inner surface of the main pores (Figure 2 IIB(c)). This phenomenon is believed to result from the warm water pre-treatment, which allows a certain amount of water to penetrate the initial pores of the durian peel, combined with the residual chemically bound water in the sample (which cannot evaporate during the drying process), causing increased pressure inside the small pores during high-temperature pyrolysis, leading to structural breakdown. In contrast, H_3PO_4 -treated samples avoid this issue, as the acid's hygroscopic properties remove water from the pores. The 60-minute pyrolyzed biochar was identified as the optimal sample. The durian peel biochar treated with H_3PO_4 and pyrolyzed anaerobically for 60 minutes exhibits superior properties compared to warm water-treated samples. It has a cleaner surface, numerous honeycomb-like pores, enhanced adsorption capacity, and tightly bonded carbon chains, making it ideal for organic fertilizer production.

The SEM analysis (Figure 3) reveals that the organic fertilizer samples derived from durian peel biochar, when combined with varying ratios of chitosan and shallot juice, exhibit similar block-like structures with sizes ranging from 45 to 83 μm . In contrast, sample No.3 (containing the weight ratio of: 70% durian peel biochar, 10% CTS NPs, 20% shallot juice) displays a less stable structure due to the high shallot juice content, resulting in insufficient pellet compaction for prolonged use. However, this structure can retain additional nutrients during plant growth. Sample No.2, dried at 70 $^\circ\text{C}$ for 30 minutes (Figure 3B(b)), demonstrates strong inter-component bonding, enhancing its reactivity and nutrient release efficiency upon water contact, performing slightly below sample No.4, which contains urea. From these results, it can be concluded that

organic fertilizers made from durian peel biochar combined with other organic components have the potential to replace inorganic or industrial fertilizers currently available on the market [14].

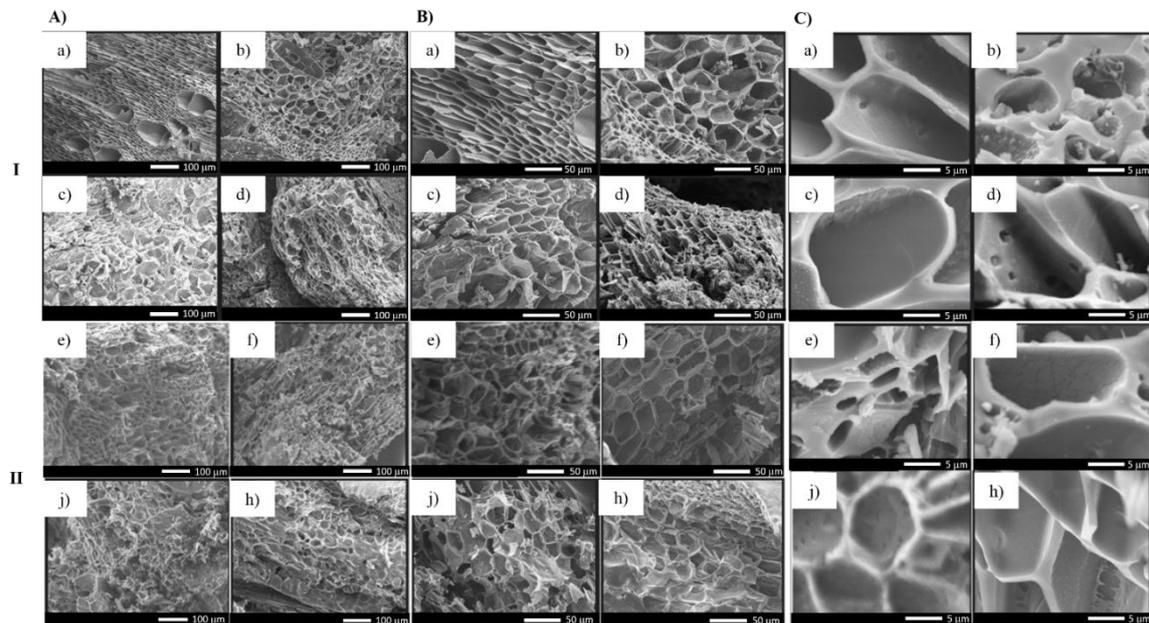


Figure 2. SEM images of biochar samples from durian husk treated with (I) H_3PO_4 acid and pyrolyzed under anaerobic conditions for different durations: (a) 30 minutes; (b) 45 minutes; (c) 60 minutes; (d) 75 minutes, (II) warm water and calcined for different times: (e) 30 minutes; (f) 45 minutes; (j) 60 minutes; (h) 75 minutes, corresponding to scale bars of A) 100 μm , B) 50 μm , C) 5 μm

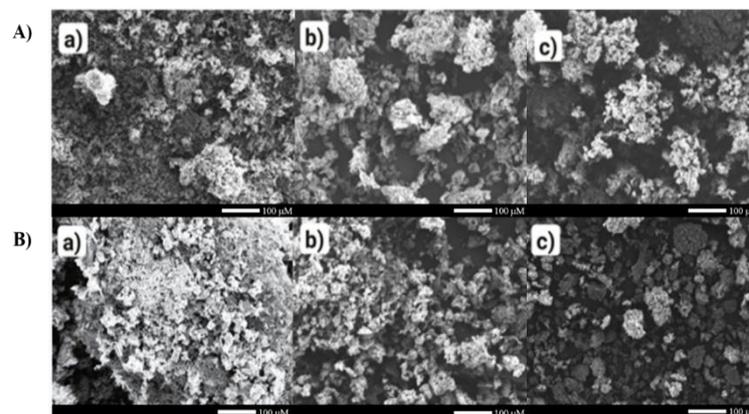


Figure 3. SEM images of the organic fertilizer samples mixed with different amounts: A) before drying and B) after drying, with (a) No.1; (b) No.2; and (c) No.3, respectively

Energy Dispersive X-ray Spectroscopy (EDX) analysis (Figure 4) revealed the elemental composition of durian peel biochar after pyrolysis: C (77.66%), O (18.56%), P (1.32%), K (1.3%), N (0.72%), and Mg (0.43%) (from durian peel biochar powder). In the synthesized organic fertilizer, which includes chitosan nanoparticles solution (CTS NPs) and shallot juice, the composition shifted to C (74.26%), O (20.23%), K (2.03%), P (1.67%), N (1.41%), and Mg (0.4%). The nitrogen content increased to 1.41% due to chitosan and shallot juice, which significantly increased the percentages of phosphate and potassium. These results confirm that the fertilizer retained the properties of biochar during synthesis, aligning with FTIR findings, and that the addition of chitosan and shallot juice enriched key nutrients (N, P, K) for plant growth.

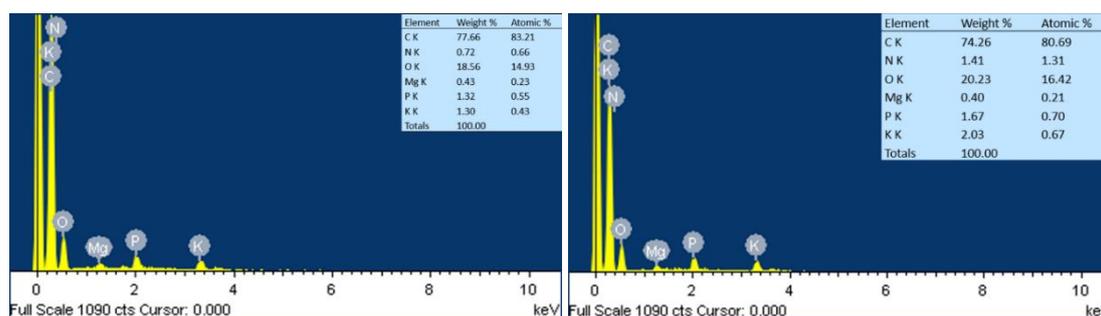


Figure 4. Energy dispersive X-ray spectra (EDX) of biochar powder samples from durian peel (a) and organic fertilizer No.2 (b), respectively

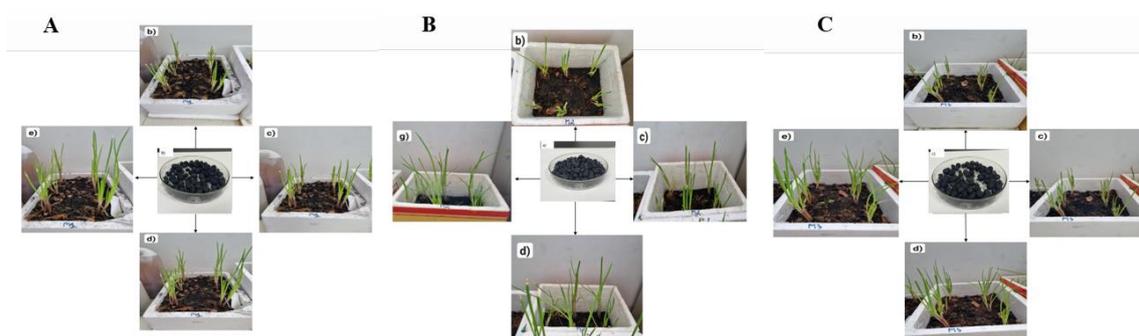


Figure 5. Results of fertilizer samples A) No.1, B) No.2, C) No.3 at different time intervals: (a) sample No.1, (b) 3 days, (c) 7 days, (d) 10 days, (e) 14 days, respectively

Table 2. Survey results of average height/growth of fertilizer samples made from durian shell charcoal for green onion plants

Sample	3 days (cm)	7 days (cm)	10 days (cm)	14 days (cm)
No.1	1.6	3.4	7.2	8.4
No.2	2.5	4.6	8.3	9.5
No.3	2.1	4.2	7.6	9.1

The experimental results of organic fertilizer samples made from durian peel biochar with different component ratios were tested on scallion plants at 3 days, 7 days, 10 days, and 14 days. The survey results (Figure 5) show that fertilizer samples tested on scallion plants over 3, 7, 10, and 14 days demonstrated that sample No.4 enhanced plant growth more effectively than the others. However, since sample No.4 contains a combination of Vietnamese-Russian factory-produced urea (black urea) and durian peel biochar, its superior performance is expected due to the well-established effectiveness of black urea. Notably, sample No.2 (composed of 70% of durian peel biochar, 15% of chitosan nanoparticles solution (CTS NPs), and 15% of shallot juice) also showed a relatively fast growth rate comparable to No.1 (Table 2), suggesting it could partially replace urea in current fertilizers with its organic components (hydroxyl groups, nitrogen, chitosan, aromatic rings, etc.). Although the growth rate of sample No.2 was slightly slower than that of inorganic fertilizers, it offers a safer and more environmentally friendly alternative, free of harmful functional groups. Thus, the eco-friendly organic fertilizer made from durian peel biochar shows great potential and feasibility for further development [11].

3.2. Results of testing synthetic organic fertilizer from durian shell charcoal on short-term vegetable crops

The results of the application survey of organic fertilizer sample No.2 on vegetables are shown through Figure 6. The application results of fertilizer sample No.2 on green mustard plants

(Figure 6A) show a favorable growth rate, with the plants appearing robust, with large and healthy leaves. The fertilization method involves diluting the fertilizer with water at a ratio of 0.015 g/mL (according to Official Dispatch No. 7075/BNN-KHCN (2018) [15] for vegetables grown at a household scale, such as in foam boxes or pots with a diameter of less than 50 cm. Fertilizer sample No.2 was applied on the 7th day, a critical period when the plants require sufficient leaf area for photosynthesis and well-developed roots to anchor in the soil, ensuring efficient nutrient absorption. However, a few considerations should be made during the application process on the 7th day: if there is continuous sunlight, additional clean water should be provided in the afternoon to enhance root absorption. A second application can be made 3 days after the first harvest [15]. The experimental application on Chinese spinach was conducted over 18 days (Figure 6B). The results indicated that plant growth began on the 3rd day, with rapid development observed from the 7th to the 18th day following the application of organic fertilizer (using the same fertilization method as for green mustard). Seven days after applying the organic fertilizer, the soil pH increased to 6.0 from an initial pH of 4.5, demonstrating the benefits of fertilize in balancing pH and supplying essential nutrients, thereby enhancing plant productivity and yield. Furthermore, the growth potential of the plants also depends on weather conditions and the grower's care. Therefore, the use of fertilizer primarily shortens the plant growth period and promotes healthier growth compared to natural development.

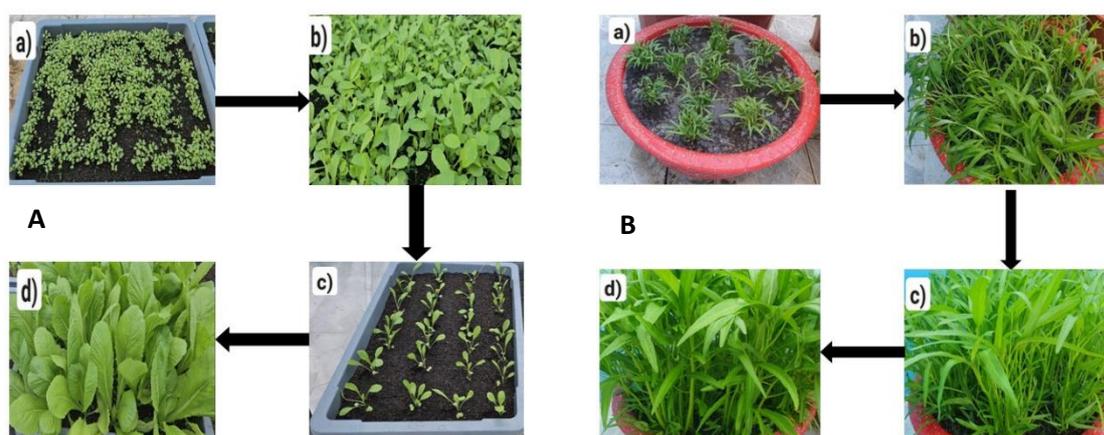


Figure 6. Sample of organic fertilizer No.2 on plants A) green mustard, B) Chinese spinach at different time points: (a) 3 days; (b) 7 days; (c) 10 days; (d) 18 days, respectively

4. Conclusion

Biochar was successfully prepared from durian peel by anaerobic pyrolysis for 60 minutes with H_3PO_4 pre-treatment to remove lignin, yielding optimal porosity (~13-18 μm pores, SEM). The resulting biochar was used to fabricate organic fertilizer by combining it with chitosan nanoparticle solution and shallot juice. FTIR analysis confirmed the retention of functional groups (O-H, C-H, N-H, P-O-P), ensuring the fertilizer maintained its properties. During testing, the organic fertilizer (No.2) with a weight ratio of durian peel biochar (70%), chitosan nanoparticles solution (15%) (containing 1% of chitosan in acetic acid 1.5%), and shallot juice (15%) supported plant growth comparable to market urea fertilizer, achieving a height of 9.5 cm after 14 days on scallion plants and maintaining low moisture content (1.11%). Trials on green mustard and water spinach over 18 days showed effective growth promotion. This study primarily focused on small-scale laboratory experiments and a limited number of crops. However, the organic fertilizer derived from durian peel still demonstrated significant performance, indicating great potential in the field of organic fertilizers, benefiting agriculture and environmental management. In the future, large-scale

field trials, simulating real agricultural conditions, will be conducted to confirm the performance and effectiveness of the durian peel biochar.

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