Carbon nanomaterial from watermelon skin waste as liquid supplement for *Lettuce sativa L.* in hydroponics system

N. Hasna Mustofa[a], E. A. Rania Balqist[a], Y. Is Dhiarni[a], Suparno[b], and W. S. Brams Dwandaru[b]

[a]*Magister of Physics Education, Faculty of Mathematics and Natural Sciences, Universitas Negeri Yogyakarta, Jl. Colombo No. 1, Karangmalang, Sleman, Yogyakarta, 55281, Indonesia,*

[b]*Physics Education Department, Faculty of Mathematics and Natural Sciences, Universitas Negeri Yogyakarta, Jl. Colombo No. 1, Karangmalang, Sleman, Yogyakarta, 55281, Indonesia.*

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Carbon nanomaterials have been used in various fields such as agriculture because they have properties that allow them to influence plant growth. This research aimed to determine the effect of carbon nanomaterials made from watermelon skin waste as a plant supplement towards the growth of lettuce (*Lettuce sativa L.*) plants in a hydroponic setting. This research began by making carbon nanomaterial powder based on the two-steps low heating (TSLH) method. The watermelon skin wastes had been dried using an oven and then heated again using a microwave to obtain the carbon nanomaterial sample in the powder form. The carbon nanomaterial samples were characterized using UV-Vis, PSA, and XRD. The effect of the carbon nanomaterial on the lettuce plants was observed in a hdroponic setting. Data collection was carried out by measuring the water height, leaf width, plant height, number of leaves, and wet and gross weights of the lettuce plants. The results showed that the carbon nanomaterials can influence the growth and development of lettuce plants, especially helping plants absorb water and controlling and developing plants' growth so that they experience more stable growth.

Keywords: Carbon nanomaterials; watermelon skin waste; hydroponic system; lettuce plants.

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1. Introduction

Watermelon (*Citrullus vulgaris*) is a fruit that is popular and easy to find in Indonesia because it can grow in various seasons. Watermelon has a fairly high-water content, namely 91.45 g [1]. Some people only use the watermelon flesh for consumption and the watermelon skin is an unused waste material. Organic wastes, such as fruit peels, spices, leaves, and nuts are carbon sources that are rarely utilized [2]. Hence, this watermelon skin waste can be used in the field of nanotechnology, one of which is carbon nanomaterial.

The development of nanotechnology shows broad potential for various applications. One of them is carbon-based nanomaterials, which have been used in various fields, such as agriculture [3,4]. Research regarding the effect of carbon nanomaterials on the germination and growth of rice plants shows that the treated seedlings looked healthier with well-developed root and shoot systems compared to the control seedlings [4]. Apart from that, research conducted on the use of carbon nanomaterials made from mango peel waste to be used as organic fertilizer for rose plants showed that the leaf growth of treated rose plants was better compared to control rose plants [3].

These carbon nanomaterials have properties that allow them to influence plant growth. Carbon-based nanomaterials can be used to improve plant genetic traits, increase plant capacity to deal with biotic and abiotic stress, and protect the environment from harmful pollution [5]. Application of carbon-based nanocarriers can also promote plant growth [6]. Most of the carbon nanomaterials applied can be absorbed by the plants themselves [7]. The absorption of carbon-based nanomaterials depends on their interaction with suspended organic matter, their colloidal properties, and the homo-heterogeneous medium that allows them to have a smooth flow in the plant system [8].

Based on the description above, the aim of this research is to determine the effect of carbon nanomaterials made from watermelon skin waste on plant growth, especially lettuce plants (*Lettuce sativa L.*) in a hydroponic system. Planting with hydroponic system can provide a more controlled growth environment [9]. This is because factors such as nutrition, light, and media can be regulated.

2. Methods

This research aimed to determine the effect of carbon nanomaterials made from watermelon skin waste on the growth of lettuce plants based on the hydroponic setting. This research was conducted at the Nanomaterial Laboratory, Universitas Negeri Yogyakarta, Yogyakarta, Indonesia. The tools used in this research were measuring cups, digital scales, oven, filtering paper, microwave, mortar, hydroponic box, net pot, and flannel cloth. The materials used in this research were watermelon skin waste [Fig. 1a)], aluminum foil, distilled water, and three-week-old lettuce plant seeds.

Preparing the carbon nanomaterials was carried out based on the two-steps low heating (TSLH) method. The method started by first weighing 1.144 g of watermelon skin wastes. Then the watermelon skin wastes were dried in the sun for 3 days to remove the water content [Fig. 1b)]. Then the dried

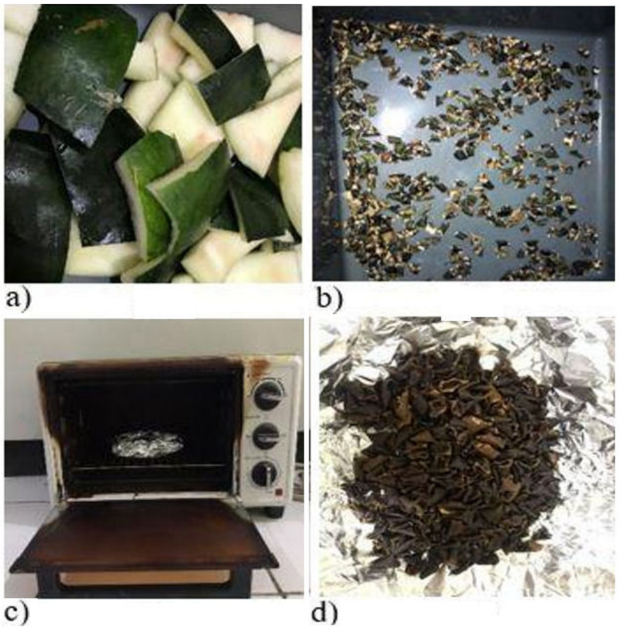

FIGURE 1. Materials for the preparation of carbon nanomaterials, *i.e.*: watermelon skin waste a), watermelon skin waste after drying b), watermelon skin waste in the oven c), and watermelon skin waste after the oven heating process d).

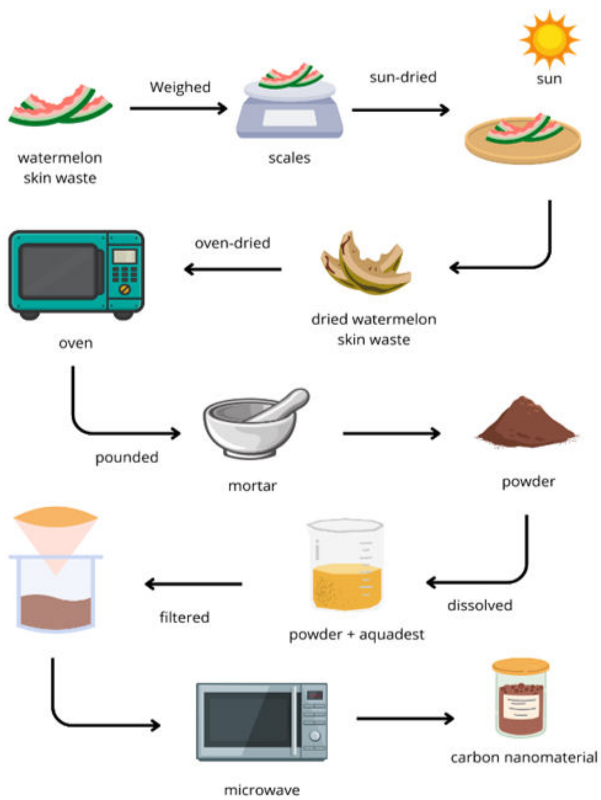

FIGURE 2. Procedure for preparing carbon nanomaterials from watermelon peel wastes.

watermelon skin wastes were heated in the oven at 100°C for 2 hours [Fig. 1c)]. Watermelon skin waste that had been oven-treated produced a weight of 59 g. After that, the dried watermelon skin waste [Fig. 1d)] was ground using a mortar until it became powder. The powder was dissolved in 500 ml of distilled water and left for 2 days. After 2 days, the solution was filtered using filtering papers with 20-micron pore size. The filtered solution was microwaved in stages of 50 ml for 15 minutes to produce a crust, which was then taken in powder form. The steps for preparing the carbon nanomaterials can be seen in Fig. 2.

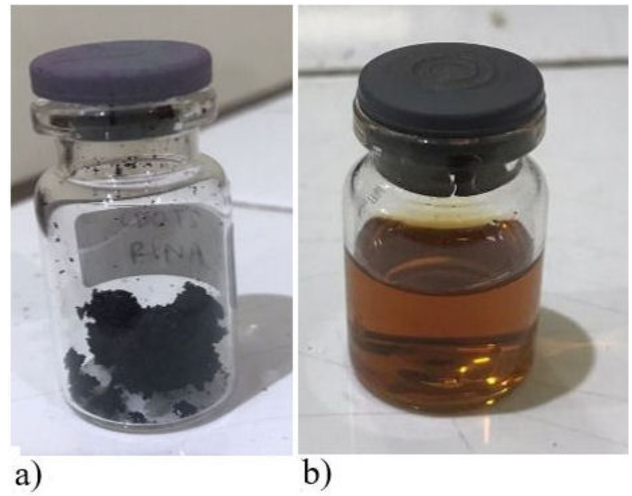

FIGURE 3. Carbon nanomaterial samples from watermelon skin waste in the form of a) powder and b) liquid.

The carbon nanomaterial samples produced in the forms of powder [Fig. 3a)] and solution [Fig. 3b)] were then characterized using ultra violet-visible (UV-Vis) spectrophotometer, particle size analyzer (PSA), and X-ray diffraction (XRD). The characterizations were carried out at the Integrated Laboratory, Faculty of Mathematics and Natural Sciences, Universitas Negeri Yogyakarta, Yogyakarta, Indonesia.

The planting media used in the hydroponic system for growing the lettuce plants used two variations, namely carbon nanomaterial solution (box A) and water (box B). The data collection was carried out to compare the plant growth and harvest weight of the lettuce plants in boxes A and B. The total water medium used in the box was determined to be 6 liters of liquid. Each box was planted with 9 lettuce seedlings that were 3 weeks old. Data collection was carried out for 12 days by measuring plant height, leaf width, number of leaves, and water height reduction in each box as well as weighing the wet and dry weights of the harvested plants at the end of the observation.

3. Results and discussion

The carbon nanomaterial is characterized using a UV-Vis spectrophotometer to determine the absorption pattern at certain wavelengths. The sample is tested in powder form. This test is based on a specific wavelength spectrum range. The testing is carried out with a wavelength range of 200 nm - 800 nm. The result of UV-Vis characterization of the carbon

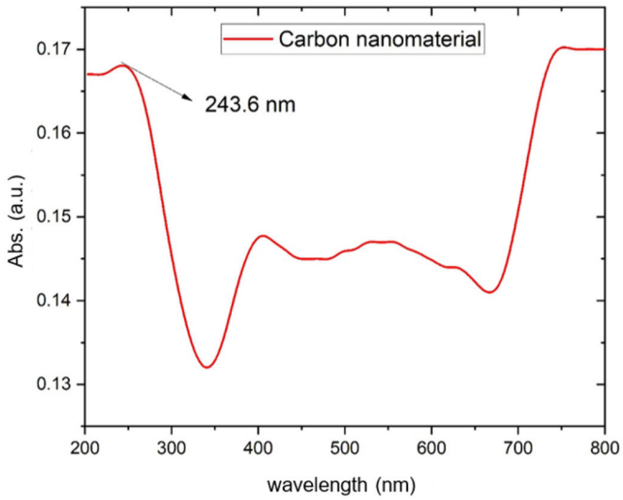

FIGURE 4. Absorption spectrum of the carbon nanomaterial from watermelon skin waste.

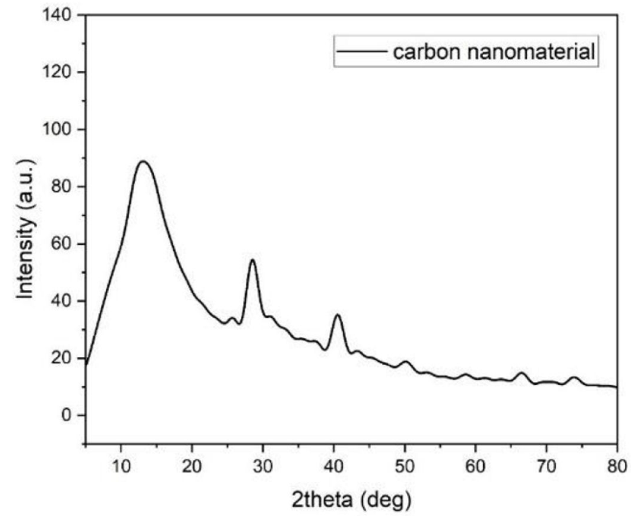

FIGURE 5. Diffraction pattern of the carbon nanomaterial.

nanomaterial is shown in Fig. 4. Based on Fig. 4, the absorption result of the carbon nanomaterial has an absorption peak at a wavelength of 243.6 nm. The presence of this peak indicates that the sample contains carbon material. This is based on a previous study, which produced carbon nanomaterial at a wavelength of 216 nm [10], as well as at 242 nm and 268 nm [11]. Apart from that, based on previous research of sample testing, it can be stated that the absorption peak of carbon nanomaterial is at a wavelength of 200 nm - 400 nm [12]. This wavelength range is in the UV wavelength range [13]. The absorption peak in the graph shows that the sample is experiencing an electron transition (excitation) due to the absorption of UV energy. Absorption occurs because the energy of UV light at a certain wavelength is the same as the excitation energy of the carbon nanomaterial. This electron transition is an excitation from a basic energy level (HOMO) to a higher energy level (LUMO), which is a $\pi \rightarrow \pi^*$ electronic transition [1].

XRD characterization is carried out to determine the crystallinity of the sample [14]. This method is based on X-rays interacting with a material and experiencing diffraction, which is then detected by a detector. This diffraction provides information about the composition and structure of the material. The sample tested is in powder form and the 2θ range used is $4°$ to $80°$. The data obtained are in the form of diffraction angle (2θ) and intensity (I). I is the number of X-rays diffracted by the crystal lattice. The graph produced shows the peaks of the XRD diffraction spectrum. The result of the XRD characterization of the carbon nanomaterial is shown in Fig. 5. Figure 5 is the diffractogram produced from the carbon nanomaterial, which has several peaks. Based on the XRD graph, it can be seen that the sample of the carbon nanomaterial has an amorphous structure. This is because the diffractogram does not produce any sharp peak and only has several broad peaks. Therefore, the distance between atoms does not have a clear pattern and the arrangement of atoms tends to be random. In addition, a less-than-optimal carbonization process when preparing the carbon nanomaterials can cause structures with broad peaks.

The PSA characterization was carried out to determine the particle size distribution of the carbon nanomaterial from watermelon skin waste. This test produces a graph showing $\%$channel and $\%$passing on the Y-axis, as well as particle size on the X-axis. This particle size comes from a group of carbon nanomaterial particles subjected to the Brownian motion. Meanwhile, $\%$passing shows the cumulative percentage of the number of particles that are less than a certain size and $\%$channel shows the percentage of the number of particles that are of a certain size. The results of the PSA characterization of the carbon nanomaterial are shown in Fig. 6. Figure 6 shows that the particle size of the resulting carbon nanomaterial has heterogeneous properties and can be seen from the presentation of particles of a certain size. Based on the PSA results, various particle sizes and their distribution in the samples are obtained as in Table I.

Based on Table I, the carbon nanomaterial has a particle size of 370 nm with a volume of 24.8$\%$. This shows that the particle size of the carbon nanomaterial is relatively large. This happens because the sample experiences clumping, so that the particle size shows large results. Apart from that, this large particle size can occur because the carbonization process is not complete so that there are particles with large sizes.

Observation of the carbon nanomaterial as plant supplement to lettuce plants are carried out for 12 days. The application of carbon nanomaterial solution in the hydroponic

TABLE I. Size distribution of the carbon nanomaterials.

Particle size (nm)	Vol (%)
370	24.8
559	66.5
1517	8.7

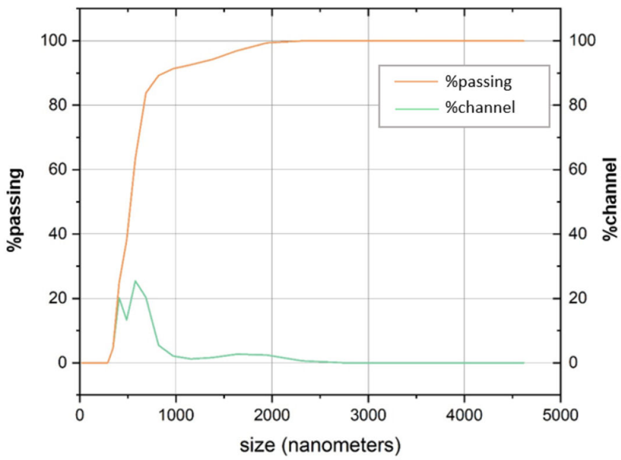

FIGURE 6. Particle distribution of the carbon nanomaterials indicated by cumulative data values (%passing - red line) and percentage of particle sizes (%channel - green line).

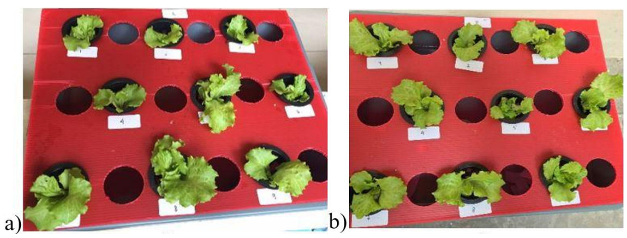

FIGURE 7. Initial conditions of the lettuce plants, *i.e.*: Box A with carbon nanomaterial a) and Box B with water b) media.

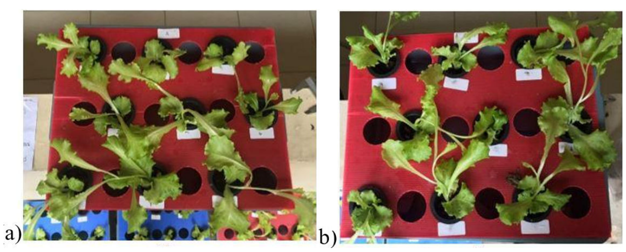

FIGURE 8. Conditions of the lettuce plants on day 12, *i.e.*: Box A with carbon nanomaterial a) and Box B with water b) media.

media is by pouring the carbon nanomaterial mixed with water in one box (box A) and the other box only uses water (box B). During the observation process, water height, number of leaves, plant height, and leaf width are measured. The initial condition and conditions on day 12 of the lettuce plants may be observed in Fig. 7 and 8.

Figure. 9 is a graph of the decrease in the liquid height level in each box. It can be seen that Box A has a lower height media compared to box B. This shows that the lettuce plants tend to absorb more carbon nanomaterial compared to water media. However, the general height level decrease of the two boxes is similar with the height level of Box A is always lower than Box B, except on day 35 where a change of slope is indicated at the 12 days. A somewhat rapid decrease of the height level of the media occurs for Box A compared to Box B before day 5. This means that the absorption of the

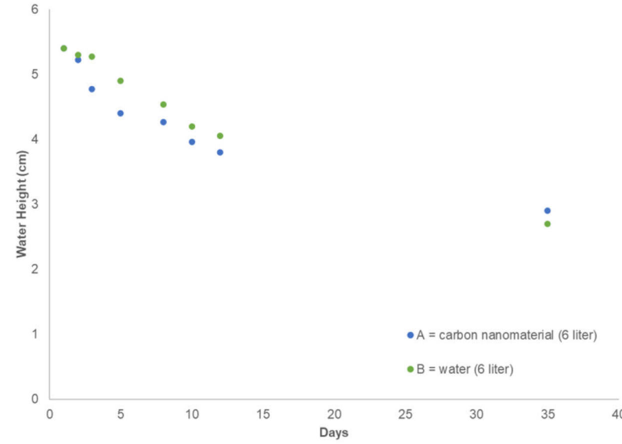

FIGURE 9. Height measurement results of the liquid media.

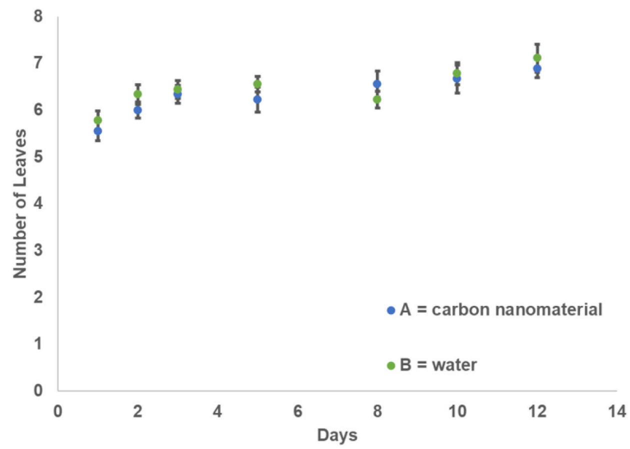

FIGURE 10. Number of leaves measurements.

carbon nanomaterial by the lettuce plants occurs for 5 days since the initial planting. Therefore, the effective absorption of the carbon nanomaterial may only occur for a period of time, *e.g.*: in the case of the lattice plants is 5 days.

Figure. 10 is a graph of the average number of leaves on lettuce plants for boxes A and B. Based on this graph, the average number of leaves in Box A has increased slowly and steadily from day to day. This shows that carbon nanomaterials can support average leaf growth. Meanwhile, the average number of leaves in Box B also experiences slow growth and decreases on day 8. Then after that, it experiences an increase again until the end of the observation. This shows that the average leaf growth on Box B of the lettuce plants experiences unstable growth. Based on the observation, the decrease in the number of leaves on the lettuce plants is due to some of the leaves wilting and then drying out until the leaves fall off the plant. However, it is also seen that some new leaves are growing on some lettuce plants.

Figure 11 is a graph of the average height of the lettuce plants. Based on the graph, the lettuce plants in Box A experience faster average plant growth compared to Box B. It can be seen that the height of the lettuce plants in Box A shows

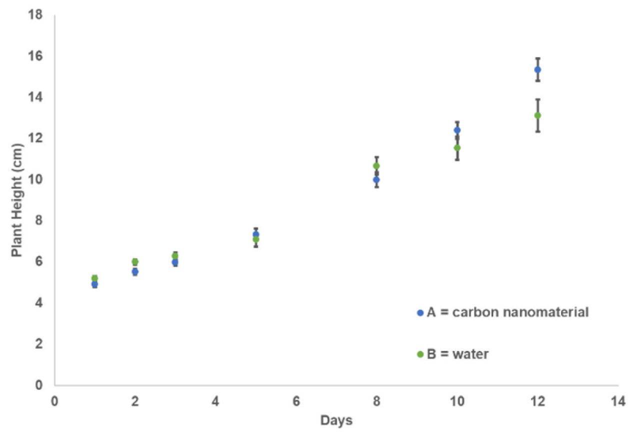

FIGURE 11. Plant height measurements.

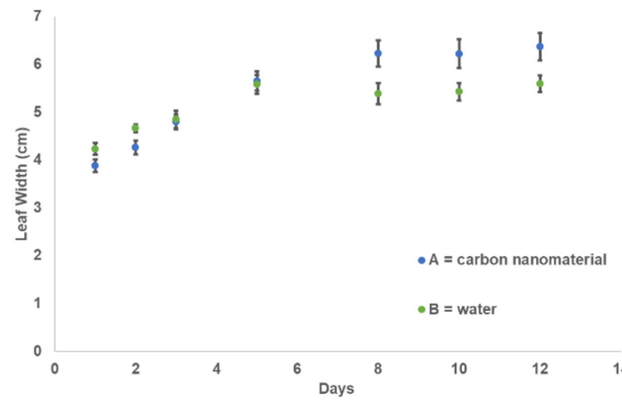

FIGURE 12. Leaf width measurement results.

very stable growth. At the end of the observation, the average plant height in Box A appears to have experienced drastic average height increase. However, the height growth of the lettuce plants in Box B is unstable. This can be shown in the data points, namely that there is a slowdown in the average height growth, such as on the 5th and 10th days. Apart from that, the average height of the lettuce plants in Box B is smaller compared to Box A at the end of the observation.

Figure 12 is a graph of the average leaf width of lettuce plants in each box. Based on the graph, Box A shows a significant increase in average leaf width until the end of the observation compared to box B. Meanwhile, the lettuce plants in Box B show smaller increase in average leaf width. It can be seen that the growth of the average leaf width of the lettuce plants in this box experiences significant increase until the 5th day and thereafter experiences a slowdown and decline on the 8th day. Based on the observation, the decrease in average leaf width on several lettuce plants occurs because the leaves on the lettuce plants wilted. So, when measurements are carried out, the value of the leaf width is smaller than the previous day.

The total wet and dry weights of the lettuce plants at the end of the observation are shown in Table. II. This wet weight is an indicator of the quality of the plant because only certain organs are harvested on the plant [15]. Based on Table II, it can be seen that the heaviest total weight of the lettuce plants is the lettuce plants in Box B, *i.e.*: 39 g. Meanwhile, the total wet weight of the lettuce plants in Box A is 32 g. The difference in total wet weight between the two boxes is 7 g. The increase in wet weight is influenced by the amount of water absorption and accumulation of photosynthesis products. This accumulation of photosynthesis results affects the wet weight of the plants. The greater the photosynthesis process, the more likely it is to form larger organs, which then produce greater wet weight products [16]. In addition, the small amount of water absorbed by plants causes the increase in the size and volume of cells in plants to be hampered, so that plant organs cannot grow properly [17]. Apart from the wet weight, Table II also shows that the heaviest total dry weight of the lettuce plants is also box B, *i.e.*: 10 g and followed by Box A of 8 g. The difference in the total dry weight between these two boxes is 2 g. This dry weight represents the product of the photosynthesis process. The greater the wet weight of the plant, the greater the dry weight of the plants' fiber [17].

The observation and analysis of the results of the plant growths show differences in the plants' development of each box. Box A with carbon nanomaterial as the planting medium shows the most stable results, which means that all growth parameters show the least local decreases. This shows that carbon nanomaterials consistently support plant growth through increasing water absorption [18]. Likewise, Box B, which uses water shows good growth and development, but is not stable because of the slowdown or decline, which may be observed in plant height, number of leaves, and leaf width measurements.

It is worth noting as well that besides carbon nanomaterials affecting the growth of the lettuce plants, the lettuce plants in all of the boxes experienced rather undesirable etiolation condition resulting in unnatural growth. The characteristics of plants experiencing etiolation are seen in plants that have long stems due to the abundant water content in the plant, the stems are not sturdy, the plants look pale, have small leaves, and have less dense roots [19]. This can be shown in Fig. 8, namely the condition of the plants on the 12th day in comparison to Fig. 7, which is the initial condition of the lettuce plants. Etiolation occurs due to insufficient light intensity, so that the plants experience elongation of the stem segments between the leaves [20].

TABLE II. Total weights of lettuce plants after harvest.

Box	Wet Weight ($\pm$ 2 g)	Dry Weight ($\pm$ 2 g)
A	32	8
B	39	10

4. Conclusion

Based on research that has been carried out, carbon nanomaterials affect the growth and development of lettuce plants in the hydroponic setting. In addition, the total weight of the harvested plants shows a lighter weight in lettuce plants that used carbon nanomaterial as the medium. This is probably because the carbon nanomaterials focus on helping water absorption in lettuce plants, as well as controlling the growth and development of lettuce plants so that they experience more stable growth compared to the purely water medium. However, the total wet and dry weights of the plants using the water medium produce higher weights compared to the plants using the nanomaterial medium. The growth and development of the lettuce plants in all the boxes also experienced etiolation because the insufficient light intensity. Further study includes obtaining smaller sizes of the carbon nanomaterials via ultrasonication in between the oven and microwave heating processes as sizes matter for nanomaterials.

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