

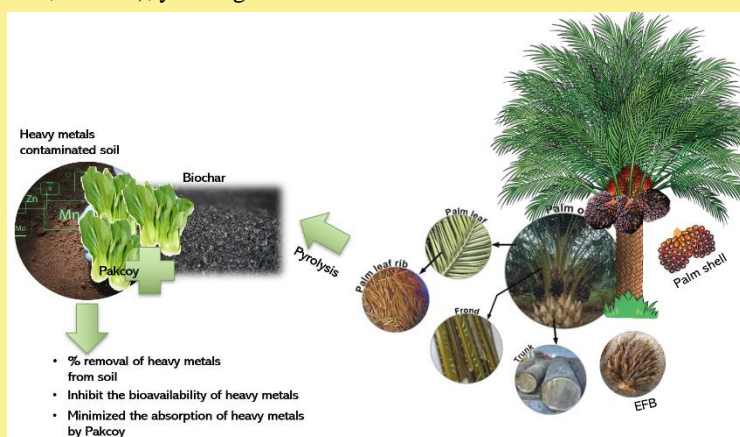
The Effect of Biochar Addition from Empty Bunch Fruits to Heavy Metals Contaminated Soil on the Growth of Pakcoy (*Brassica rapa*)

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Received September 09, 2023; Revised February 10, 2024; Accepted March 12, 2024

DOI: [10.12962/j2964710X.v4i2.18828](https://doi.org/10.12962/j2964710X.v4i2.18828)

Abstract— Production of Crude Palm Oil (CPO) generates waste, one of which is Empty Fruit Bunch (EFB). EFB has a high potential for further utilization due to its carbon and nitrogen content. The abundant carbon content can be utilized and further processed into a value-added product such as biochar. This study investigates the influence of solid waste mixtures from various parts of the oil palm and the effect of temperature on biochar production. A simple furnace pyrolysis method was chosen for biochar production. The biochar produced is subsequently applied to remediate and reduce heavy metal pollution in soil, especially for zinc (Zn) and copper (Cu). The efficacy of biochar application on the contaminated soil is indicated by the percentage removal of heavy metals and the growth of the Pakcoy (*Brassica rapa*). The soil's heavy metals content is conditioned to mimic soil contaminated with micronutrient fertilizer. Solid wastes, such as EFB, trunks, and oil palm shells, are dried until their moisture is ca. 10% -weight. Subsequently, they were crushed and uniformly sized into 50-100 mm. Considering solid waste's proximate and ultimate analysis results, solid waste with the highest carbon content was further processed for biochar production using the furnace pyrolysis method (200, 300, and 400°C for 3 hours). With the best performance, the pristine biochar was subsequently added to contaminated soil media planted with Pakcoy (*Brassica rapa*) in an 80:20-percentage weight ratio. The effectiveness of biochar in the remediation of heavy metal pollution in soil was observed by monitoring the growth of the Pakcoy. The best biochar was produced at furnace pyrolysis (200°C, 3 hours), yielding 36% of biochar and a carbon content of 49.86%. The produced biochar is in category 2 of biochar quality (carbon content of $30\% \leq C < 60\%$). Biochar addition increases the soil's pH in the range of 5-7 and may help plants absorb less copper than zinc. Biochar addition works best on the sample with a high content of Cu (sample C) and the sample mixture of Cu and Zn (sample M). Cuprum removal, in both samples, was significantly decreased (>50%) than sample Z (high content of Zn), which only removed 2%-4% in heavy metal content. Moreover, the Pakcoy grows the best at sample Zn. However, adequate and balanced nutrition can stimulate plant growth.



Keywords— Biochar, Crude Palm Oil production, Waste, Empty Fruit Bunch (EFB), Heavy metals

I. INTRODUCTION

Indonesia is the world's largest producer and exporter of palm oil. In 2022 global palm oil production reached 77.22 million metric tons, with Indonesia contributing 45.50 million metric tons (USDA, 2022). With nearly 60%

of the palm oil industry's production located in Indonesia, there is an urgent need to emphasize the utilization of palm oil waste, one of which is Empty Fruit Bunches (EFB).

EFB is a solid waste generated during palm oil processing, accounting for about 21-23% of the fruit's raw material. EFB utilization in Indonesia involves converting

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it into organic fertilizer, which usually takes 3-4 months for composting. Unfortunately, most of them are not yet utilized, and they are discarded by burning and burying, resulting in suboptimal waste utilization [1]. Hence, concerning Indonesia's status as the largest palm oil industry in the world, there is an urgent to find alternative ways to maximize the potential of EFB waste. One promising method is converting it into biochar.

Biochar is a solid material rich in carbon resulting from the incomplete combustion of organic or agricultural waste. It has a long history of use as a soil amendment in the Amazon basin, where native populations practiced charred vegetation management to enhance soil fertility and crop yields [2]. Research has shown that adding biochar can improve soil fertility and restore degraded soil quality. It is important to note that biochar is not a fertilizer; it acts as a soil conditioner. While its nutrient content is relatively low and cannot directly supply nutrients to plants, its high pH, carbon content, and water retention capacity make it suitable for enhancing organic matter content, increasing water availability, and reducing soil acidity. Good-quality biochar should have a minimum carbon content of 20% [3].

Additionally, biochar can persist in the soil for over 400 years due to its resistance to decomposition. Recent studies have also revealed its potential as a heavy metal immobilizer for soil remediation. Therefore, it is possible to apply the biochar from solid waste of plantation, i.e., palm oil estate, to increase soil fertility.

The issue of soil contamination by heavy metals due to human activities is a global concern. Activities such as mining, industrial processes, and using non-standard pesticides and chemical fertilizers contribute to heavy metal contamination in soil [4]. Heavy metals like Arsenic (As), Lead (Pb), Cadmium (Cd), and Mercury (Hg) are highly toxic based on their frequency of toxicity, occurrence, and exposure to flora and fauna [5]. Contaminated heavy metals can enter the food chain and cause cancer, kidney failure, cardiovascular disorders, neurological issues, and cognitive impairment [6].

Biochar application as a heavy metal immobilizer is highly considered due to its ability to absorb and inhibit the release of heavy metals. The properties of biochar, such as surface area, micro-porosity, surface functional groups, pH, and cation exchange capacity [6], are responsible for the biochar's capacity for absorbing and inhibiting the heavy metals release. Different types of biochar produced from various feedstocks under different processing conditions have been used to immobilize heavy metals like As, Cd, Cu, Pb, Cr, Ni, Co, and Zn in soil [7]. The efficiency of heavy metal immobilization with biochar depends on the type of biochar (production conditions and physicochemical properties), soil properties (pH, organic content, electrical conductivity), and heavy metal properties (valence and ionic radius) [8]. However, the optimum conditions for heavy metal immobilization in soil using biochar are still subjects of further research.

Moreover, a simple method of producing and applying biochar on-site is preferable. The local community needs

to be trained as a primary target for the final application of the resulting biochar. Therefore, a more simple and understandable method of production is mandatory.

Plants need nutrients for their growth, both the macro- and micro-nutrients. Macronutrients, such as nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), and Sulphur (S), are needed in relatively high amounts. At the same time, Boron (Br), chlorine (Cl), Cuprum (Cu), Iron (Fe), Mangan (Mn), Molybdenum (Mo), Nickel (Ni), and Zinc (Zn) are needed only in trace amount, approx. ≤ 100 ppm; therefore, they are micronutrients. Unfortunately, the micronutrients can not be directly added to the soil. Therefore, micronutrients are usually added to the soil as chelated fertilizers. A previous study [9] investigated the effect of micronutrients in organic fertilizers on plants. Adding micronutrients Cu: Zn: EDTA = 1:1.6:3.85 (% w/w/w) was the most effective fertilizer for lettuce growth. However, the application of micronutrient fertilizer may also cause the absorption of heavy metals in the plants. The lettuce contains high copper (Cu) and zinc (Zn) levels, exceeding the maximum allowable limits.

Matching all needs, therefore, a combination strategy consists of a simple furnace pyrolysis method to produce biochar from the solid waste of palm fruits and applying the pristine biochar further to inhibit the bioavailability of heavy metals and minimize their absorption by plants on the contaminated soil seems promising. The strategy is to reduce solid waste and remediate the contaminated soil simultaneously. Moreover, the proposed strategy will help the application of a combination of biochar and micronutrient fertilizers in the coming years, as micronutrient application promotes plant growth. In contrast, the biochar will give the added benefit of reducing heavy metal absorption beyond acceptable levels.

Hence, here, we produce biochar from the solid waste of palm fruits using a simple furnace pyrolysis method and directly apply it to contaminated soil. Observe if the biochar will remove the heavy metals by monitoring the growth of the Pakcoy (*Brassica rapa*).

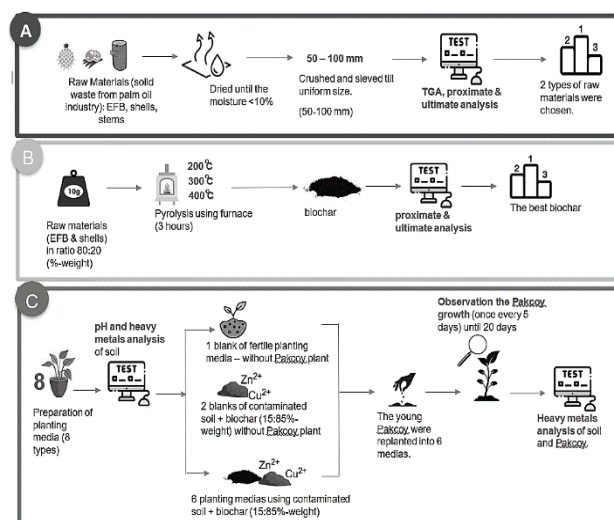


Figure 1. The flow diagram of work stages in this research.

II. METHOD

This research consists of three major stages: the raw material-reducing sizing (A), biochar production through pyrolysis (B), and the application stage to heavy metal-contaminated soil (C) (Figure 1). Each stage will be further explained as follows.

A. Raw Materials Reduction Size

All the solid waste of the palm oil industry, i.e., empty fruit bundles (EFB), shells, and stems, were provided by PT. Agro-Industry is dried until the moisture content is below 10%. Then, it was crushed and sieved until it reached 50-100 mm. Each sample was TGA analyzed, proximate analyzed (water content, ash content, volatile content, fixed carbon content, total Sulphur), and ultimately analyzed (C, H, N, and O content). The proximate and ultimate analysis results were significant for choosing the two raw materials used for biochar production.

B. Biochar Production by Pyrolysis

In the biochar production stage, a simple furnace method for pyrolysis was chosen. The following variables are used:

- The temperatures used in pyrolysis were 200°C, 300°C, and 400°C.
- The raw material ratio used for pyrolysis was (80:20 % w/w) for EFB and shells, respectively.

The steps for biochar production through pyrolysis begin with weighing 10 grams of EFB and shells in a weight ratio of (80:20 - weight %). The obtained biochar was then calculated for the yield (weight % of the raw material used). Finally, the biochar is subjected to proximate and ultimate analysis. The best biochar was determined using both the proximate and ultimate analysis results. Hence, biochar was repeatedly produced to fulfill the amount for remediation of the contaminated soil (third step, C).

C. Application to Soil and Observation

At this step, around three days old, Pakcoy was bought from the seed house of ITS. It was then replanted to the plant media as labeled below. Seven days for adaptation is mandatory. Hence, no observation or pretreatment with NPK addition is required at this period. After seven days of adaptation, the starting day of observation growth was counted, and NPK addition was started. Therefore, the seventh day of Pakcoy planting is a new period (first day) for Pakcoy observation.

The following names of variables and conditions are used. Each label was made in duplicate except for further mention.

- 1) *The blank planting media consists of the following:*
 - (a). Blank 1 - 1 polybag containing fertile soil with Pakcoy (*Brassica rapa*) plants labeled B1-1 and B1-2.
 - (b). Blank 2 - 1 polybag containing fertile soil with biochar and planted with Pakcoy – labeled as B2-1 and B2-2.

- (c). Blank 3 - 1 polybag containing fertile soil labeled B3-1 and B3-2.
 - (d). Blank 4 - 1 polybag containing fertile soil with biochar in a ratio of 85:15 (weight %) – labeled as B4-1 and B4-2.
 - (e). Soil samples contain Cu (3 polybags) – labeled as C1, C2, and C3.
 - (f). Soil samples contain Zn (3 polybags) – labeled as Z1, Z2, and Z3.
 - (g). Soil samples contain mixed Cu and Zn (3 polybags) labeled M1, M2, and M3.
- 2) *The planting media sample and biochar composition ratio is 85:15 (weight %).*
 - 3) *The soil samples are artificially contaminated with heavy metals.*
 - 4) *The Pakcoy plants were grown until the end of the study for 20 days.*

Then, the application stage to the soil begins by preparing fertile soil for planting. Next, heavy metal solutions, i.e., 0.5 M ZnSO₄ and 0.5 M CuSO₄, are prepared, each in a quantity of 1 liter. The solutions are sprayed onto the fertile soil to create artificially contaminated soil samples for each solution and a mixture of the solutions with the same concentration. The sprayed soil is then mixed thoroughly until homogenous. The soil is left to settle and dry for one week. Subsequently, it is ready to use for planting media.

Thirteen 13 polybags for plant test are prepared. The planting media consists of 4 blank polybags and 9 sample polybags of planting media. Pakcoy seedlings are then planted in each polybag of 9 planting mediums. Visual observations of leaf growth, including width, height, leaf count, and color, are observed every five days. Each polybag is watered twice a day. This stage is conducted for 23 days of growth (adjusted according to the plant's maturity until harvest).

III. RESULTS AND DISCUSSION

A. Raw Material Analysis

The first synthesis stage involves selecting the raw materials for biochar production. Five parts of oil palm waste, including Empty Fruit Bunches (EFB), shells, stems, fronds, leaves, and fibers, are tested for their physical properties through proximate and ultimate tests. The test results for each raw material are presented in Table 1.

TABLE 1.
PROXIMATE AND ULTIMATE ANALYSIS OF RAW MATERIALS

Parameter	EFB	Shell	Trunk
Total moisture (%)	16.15	18.84	55.40
Ash (%)	5.22	2.66	2.34
Carbon (%)	41.25	43.59	21.33
Fixed carbon (%)	17.27	17.48	7.48
Total Sulphur (%)	0.22	20.04	0.12

The best raw material for biochar production is a material with the highest fixed carbon value, e.g., EFB and shell. The fixed carbon value affects the mass yield after pyrolysis. The higher the fixed carbon value, the higher the mass yield [10]. EFB and shells appear to have the highest fixed carbon values, 17.27% and 17.48%, respectively.

For the further step of the research, EFB: shells = 80:20 (w/w). A higher composition of EFB was chosen since it has not yet been utilized and is available in abundant amounts in the field. In contrast, the shell raw material has been used for producing electricity, competing with commercially used purposes.

The raw material is also characterized through Thermogravimetric Analysis (TGA). The TGA results indicate that at a temperature of $\pm 340^{\circ}\text{C}$, a significant weight loss of 59% for EFB. On the other hand, at 370°C , the shell material experiences a 66% weight loss. This significant weight loss is likely due to the loss of water, volatile elements, and carbon. These results are used as our initial hypothesis, suggesting that at pyrolysis temperatures higher than 340°C for EFB and 370°C for shells, the biochar yield will decrease, and the resulting biochar will have low moisture content and carbon value. Biochar produced at lower pyrolysis temperatures (200°C) will have the highest carbon content. Therefore, the experimental results we obtained align with our initial hypothesis.

B. Production of Biochar

Biochar is produced through pyrolysis using a furnace at 200°C , 300°C , and 400°C (Table 2). The mixture of EFB: shells = 80:20 (%w/w) is the raw material composition for biochar production. The resulting biochar will then be tested for proximate and ultimate analysis to determine the best biochar quality by examining the carbon (C) and nitrogen (N) content in the biochar.

TABLE 2.
YIELD BIOCHAR AT VARIOUS TEMPERATURES (3 HOURS)

Temp ($^{\circ}\text{C}$)	Initial Weight (g)	Final Weight (g)	yield (%-weight)
200	274.13	98.72	36.01%
300	280.95	32.66	11.63%
400	276.47	16.92	6.12%

The biochar production decreases as the pyrolysis temperature increases. The highest biochar yield, 36% by weight, is obtained at a temperature of 200°C , while the lowest yield is at 400°C , with only 6% by weight.

The proximate and ultimate test results (Table 3) show that biochar produced at higher furnace temperatures will have lower physical properties (total moisture, carbon, nitrogen, and hydrogen) than biochar produced at lower pyrolysis temperatures, except for the ash content. At higher pyrolysis temperatures, volatile components (such as gases and liquids) evaporate, leaving behind solid residues known as ash content, which increases the proportion of ash content [11].

TABLE 3.
PROXIMATE AND ULTIMATE ANALYSIS OF BIOCHAR

Parameter	Furnace temperature		
	200°C	300°C	400°C
Total Moisture	2.16	3.42	3.38
Ash	18.65	44.6	20.32
Carbon	49.86	36.17	14.88
Nitrogen	0.93	0.89	0.52
Hydrogen	4.33	2.03	1.36

Table 4 shows the standard biochar classification according to the International Biochar Initiative (IBI). Biochar is considered good quality if it falls into Class 1, with $\text{C} \geq 60\%$ and an $\text{H}:\text{C}$ ratio ≤ 0.7 . Biochar produced at 200 and 300°C falls in Class 2, while biochar produced at 400°C in Class 3. On the other hand, according to Palansooriya et al. [7], good-quality biochar should have a carbon content within the range of 40-60%. Thus, the biochar considered suitable for our experiment is produced at 200°C .

TABLE 4.
BIOCHAR STANDARD

Parameter	International Standard IBI	Palansooriya et al. (2022)
Total Moisture	-	-
Total Ash	-	-
Carbon	Class 1: $\text{C} \geq 60\%$	$40\% \leq \text{C} \leq 60\%$
	Class 2: $30\% \leq \text{C} < 60\%$	
	Class 3: $10\% \leq \text{C} < 30\%$	
Nitrogen	-	$0.3\% \leq \text{N} \leq 25.9\%$
H: C	Max 0.7	-

C. Contaminated Soil Samples

The heavy metals contaminated soil previously received the micronutrient fertilizers is used as the reference state of the contaminated soil [9]. Micronutrient fertilizers were previously applied to the plants' test by spraying the leaves directly. This method accelerates nutrient absorption compared to the application through the roots.

Unfortunately, the disadvantages of this method are the excessive absorption of micronutrients and the potential contamination of neighboring plants if they are too close [9]. Therefore, to address these issues, biochar is added. The addition of biochar simultaneously with the application of micronutrients is believed to inhibit the movement of heavy metals, thereby minimizing their absorption into the plant roots.

The results of heavy metal-contaminated soil tests (Zn and Cu) from previous studies on using micronutrient fertilizers [9] are shown in Table 5. It is shown that the soil is contaminated with various heavy metals. The highest concentrations of Zn and Cu are 81.7 ppm and 115.3 ppm, respectively. The respective threshold limits for Zn and Cu, according to WHO (1996), are 50 ppm and 36 ppm.

Therefore, artificially contaminated soil samples were made for Zn and Cu with heavy metal contamination concentrations of 82 ppm and 116 ppm, respectively. The artificially contaminated soil samples were mixed with

ZnSO₄ and CuSO₄ solutions with fertile soil planted with pakcoy.

The analysis (Table 6) showed that the initial fertile soil had relatively high Cu and Zn content, with 144.9 ppm and 217.3 ppm, respectively. The soil's pH was relatively low (pH < 7), at pH 5.66. This fertile soil was used as the initial condition of the soil.

TABLE 5.

SOIL MEDIA CONTAMINATED WITH MICRONUTRIENT FERTILIZER

Heavy metal	ppm
As (arsenium)	1.5
Cd (Cadmium)	0.1
Pb (Plumbum)	10.2
Zn (Zinc)	81.7
Cu (Cuprum)	115.3
nilai pH	8.14

Subsequently, the fertile soil was sprayed with ZnSO₄ and CuSO₄ solutions. The artificial soil sample had a Cu content of 3703.2 ppm (an addition of 3558.3 ppm from CuSO₄) with a pH of 4.69. At the same time, the artificial soil sample of Zn had a content of 4215 ppm (an addition of 3997.7 ppm from ZnSO₄) with a pH of 5.21. Meanwhile, the mixed artificial soil sample has a Cu and a Zn content of 4020.6 and 2896.1 ppm, respectively, with a pH of 4.61.

TABLE 6.

THE ARTIFICIALLY CONTAMINATED SOIL SAMPLES WERE USED IN THE STUDY (DAY 0).

Soil Type	Sample Code	Cu (ppm)	Zn (ppm)	pH
Fertile Soil Samples	B	144.9	217.3	5.66
Artificially Soil Sample of Zn	Z	177.3	4215	5.21
Artificially Soil Sample of Cu	C	3703.2	108.3	4.69
Artificially Soil Sample Mix (Zn + Cu)	M	4020.6	2896.1	4.61

Initially, the artificial soil samples went through two planting periods. The first (from 27 April to 2 May 2023) and the second (3-8 May 2023) periods used curly lettuce. Unfortunately, no curly lettuce grew in both periods. Therefore, the Pakcoy plant was chosen as a replacement test plant (starting 11 May 2023).

TABLE 7.

HEAVY METAL CONTENT AT THE INITIAL STAGE OF CULTIVATING POKCOY

Sample	7th-day heavy metal content (ppm)		pH
	Cu	Zn	
Sample Zn (Z3)	169.6	2291.2	7.2
Sample Cu (C1)	3035.8	176	7.32
Sample Mix – Cu+Zn (M1)	3767.9	2995.1	6.76

The Pokcoy plants required a 7-day adaptation period to the new soil medium (11-17 May 2023). After the adaptation period, the growth of Pokcoy plants was observed, and they were given NPK fertilizer twice a day.

Artificial soil samples on the seventh day of Pokcoy planting (17 May 2023) were retested to determine the remaining heavy metal content (Table 7). Afterward, the heavy metal content on the seventh day was considered as the heavy metal content in the new test soil medium. On the seventh day (before spraying with NPK fertilizer), the soil samples were analyzed to determine the heavy metal content in the soil (samples C1, Z3, and M1). The Pokcoy was observed for seven days of planting, from 17 May 2023 to 23 June 2023.

Sample C1 had an 18% decrease in Cu content (pH = 7.32); meanwhile, sample Z1 only had a 4% decrease in Zn content (pH = 7.2). Moreover, sample M1 had a 6.2% decrease in Cu content and, in contrast, increased Zn content. The average decrease in heavy metal content from the initial artificial soil was estimated to be taken up by the plants through phytoremediation. Phytoremediation is using plants to extract and remove pollutants from the soil. This is because plants can absorb ionic compounds in the soil through their root tissues, where the root tissues accumulate heavy metals and reduce the bioavailability of these heavy metals, thus remediating the soil [12].

D. Application of Biochar Addition on the Removal of Heavy Metals on the Contaminated Soil

Overall, the soil media added with biochar experienced an increase in pH from ~5 to ~7. Increasing soil pH can reduce the bioavailability of heavy metals such as copper (Cu) [15].

The increase in pH reduces the solubility of heavy metal ions by forming less soluble ionic form in the soil. Consequently, the ability of heavy metals to move and accumulate in plants or other organisms will be reduced. Hu et al. [13] found that increased soil pH can reduce the mobility of heavy metals such as zinc (Zn) in the soil. The pH increase results in the formation of more stable complex compounds between heavy metals and soil particles, thereby inhibiting the movement of heavy metals into deeper soil layers.

The test plants in sample B1 (fertile soil and Pakcoy) absorbed Cu and Zn, approximately 21% and 56%, respectively. Sample B2 (fertile soil only) reduced Zn content by approximately 54%. Meanwhile, samples B3 and B4 had consecutive reductions in Zn content of 52% and 48%, respectively. The reduction in Cu content was relatively constant in all four samples (B1, B2, B3, and B4) at 20-21%.

Meanwhile, a significant reduction in Cu was observed in the C and M samples, i.e., approximately 50%. In contrast, sample Z showed only a 3% reduction of Cu and a higher reduction of Zn, 49%.

The presence of Cu and Zn mixture together in the soil will result in interactions between Zn and Cu; these interactions include (1) competitive inhibition between Cu and Zn due to both having the exact absorption locations

to plant roots; (2) the presence of Cu will lead to Zn redistribution within the plants [14]. These interaction phenomena may explain why Cu is more removable than Zn in the C and M samples due to Cu's more competitive inhibition than Zn. Notably, Cu is the majority of heavy metal in both sample codes (Table 7).

E. Effect of Biochar Addition on the Growth of Pakcoy in the Contaminated Soil

Figure 2 captures the growth of the Pakcoy in the contaminated soil. Some leaves are wilting, generally occurring on the 13th day (Figure 2). The period when the leaves wither and grow is not uniform, but this occurs after applying NPK fertilizer after the adaptation stage. When the bar chart value is zero (Table 2), it indicates that the leaves are wilting.

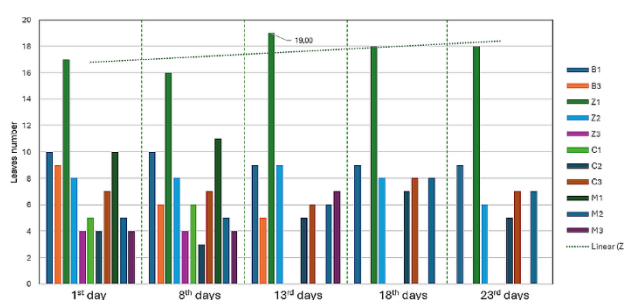


Figure 2. Growth of Pakcoy during the observation period, 20 days of planting.

Sample Z1 shows the highest number of leaves. The speed of leaf growth and color changes can be influenced by the availability of adequate nutrients, especially nitrogen, phosphorus, and potassium. This nutritional deficiency can inhibit leaf growth and result in smaller leaf size. On the other hand, providing adequate and balanced nutrition can stimulate the growth of larger leaves [16].

The presence of Zn and Cu also plays a role in plant growth. Zn plays a role in enzyme activity and is vital in plant metabolic processes, including protein and carbohydrate synthesis. Chlorophyll synthesis in the photosynthesis process also requires Zn. At the same time, Cu plays a role in forming lignin, which provides stability and strength to plant cell walls and is vital for the growth and development of plant tissue.

Therefore, lacking Zn and Cu will inhibit plant growth [14]. The minimum requirement for Cu in plant tissue is 1-5 ppm. Naturally, in plant tissue, Zn is between 15-50 ppm [16]. On the other hand, excess Zn can interfere with the absorption and translocation of other nutrients in plants, such as iron (Fe) and manganese (Mn), which causes other nutritional deficiencies that can affect plant growth and development.

IV. CONCLUSION

The best biochar was produced through pyrolysis using a furnace (200°C, 3 hours), yielding 36% of biochar and a carbon content of 49.86%. Based on the IBI standard, the produced biochar falls into category 2, with a carbon content of $30\% \leq C < 60\%$.

Biochar addition increases the soil pH in the range pH = 5-7), minimizing copper (Cu) bioavailability. Biochar addition works best on the sample with a high content of Cu (sample C) and the sample mixture of Cu and Zn (sample M). Both types of samples experienced a significant decrease in Cu content (>50%) compared to samples labeled Z (the content of Zn), which only showed a decrease of 2%-4% in heavy metal content. With the addition of biochar, plants absorbed less copper than zinc.

V. ACKNOWLEDGMENT

The authors are grateful to acknowledge Hery Wibowo ST., an alumnus of Chemical Engineering of ITS who bridged the communication between authors and PT. Agro Industri, a Goodhope Group member, raw materials provider from the palm oil industry. Direktorat Riset dan Pengabdian Masyarakat, Institut Teknologi Sepuluh Nopember, is also acknowledged under contract funding No. 1301/PKS/ITS/2023, work unit research fund financial year of 2023.

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