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POTENTIAL OF SEVERAL BIOMASS AS BIOCHAR FOR HEAVY METAL ADSORBENT

B Hidayat[1+]
A Rauf[2]
T Sabrina[3]
Ali Jamil[4]

[1,2,3]*Agrotechnology Department, Faculty of Agriculture, University of Sumatera Utara Medan-Indonesia*
[1]*Email: bendayat@gmail.com*
[4]*Director of Cereals of Indonesia Ministry of Agriculture, Indonesia*
Email: jamil_3865@yahoo.com.au

(+ Corresponding author)

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ABSTRACT

Biochar is a negatively charged recalcitrant carbon that has the potential to adsorb heavy metals. This research aim was to identify the best type of biomass with a simple combustion process (Kiln) in producing carbon, base cations, organic acids, the highest surface area and pores with more porous morphology. The type of biomass used was paddy straw, rice husk, coconut fiber, oil palm empty fruit bunch. Instrument to observe the morphology, carbon content and a number of Biochar bases using Scanning Electron Microscope (SEM-EDAX), to observe the surface and pores (m2 / g) using Brunauer Emmet Teller (BET), and to observe functional groups type using Fourier Transform Infrared Spectroscopy (FTIR). The research results showed that coconut fiber biomass had the highest surface area of 23.9145 m2 / g but rice husk had a larger pore volume and pore size of 0.026962 m3 / g and 63.6994 4V / A respectively. The highest percentage of carbon was found in rice husk biochar by 77.18% with an atomic percentage of 86.43%. The functional group was dominated by Phenolic (OH), Carboxyl, Ether and Esters groups with a frequency of 1050-1300 and the highest frequency was in Rice Husk Biochar. Cation in biochar was dominated by K+ with the highest percentage of rice husk by 2.75%, Na+ was also found in rice husk by 1.07%, while Mg2+ was in Biochar of oil palm bunches by 0.63%. Porous morphology was seen in rice husks with > 1000 magnification, so rice husk biochar has the best potential as heavy metals adsorption.

Contribution/ Originality: This study is one of very few studies which have investigated utilization straw, husk, coconut fiber and palm empty bunch as biochar, potential was showed by morphology, surface are, pore size and functional group.

1. INTRODUCTION

Heavy metal pollution is a negative effect of the use of heavy metals in human life. Heavy metals that are naturally found in nature have been utilized in various industrial products hence the waste produced pollutes the environment, especially agricultural land, pollution on agricultural land can be caused by sustainable chemical fertilization as well as factory chemical waste close to agricultural land [1].

Recently the abundant use of organic biomass has been converted into biochar, and has given hope for a reduction in carbon emissions. In addition, biochar which is rich in negative carbon provides a strong ability to adsorb metal such as Cu, Cd, Pb on the soil thereby reducing pollution [2].

The addition of biochar in the soil as an amendment is a deposit of organic carbon which can last in a long-term in the soil without decomposition. This is due to the presence of carbon recalcitrant because of oxygen loss, i.e. carbon no longer binds to oxygen, hence the weathering process in biochar will occur along with an increase in CO bond, and the higher the bonding is the more likely the weathering process will occur Stoyle [3].

Biochar is formed from the result of thermal decomposition of biomass in limited or no oxygen conditions [4]. The physical and chemical properties of biochar are influenced by the properties of raw materials and the pyrolysis temperature, different raw materials such as elemental composition; presence of soil and dust particles; water content; and lignin, cellulose, and hemicellulose content produce different biochar qualities [5].

The pyrolysis process causes mass loss and volume reduction, there is shrinkage and change in the C / N, O / C, and H / C ratios; porosity; surface area; cation exchange capacity (CEC); crystallinity; and functional groups such as increasing aromatic double carbons bond (C = C) and decreasing O-H and CH3 without causing many changes to the original structure of raw materials [6, 7]. These properties has made to have a great potential in metal adsorption hence it is necessary to do research regarding the best types of biomass for the best biochar.

2. MATERIALS AND METHODS

This research was conducted at Faculty Agriculture, University of Sumatera Utara collaborated with McGill University, MacDonald campus, Faculty of Agriculture and Environmental Science, Saint Anne De Bellevue Canada, The biomass used for making Biochar is rice husk and paddy straw, taken from Pantai Labu area, empty bunches are taken from Perbaungan palm oil mill, coconut fiber from the Aksara market. Biochar was pyrolyzed using BT1 tool (Figure 1) with a temperature of 450-500^{0}C with the Kiln system i.e. direct combustion and then closed in order to not having a complete oxidation process that will remove a lot of carbon, after forming a coal then doused with water and dried until the weight does not change. As a comparison of the biochar quality, Azolla compost is used which is obtained from the Laboratory of Soil Biology, Faculty of Agriculture, University of Sumatera Utara (USU). The tool used was BT01 pyrolysis drum, Infrared Thermometer to measure the biochar embers temperature, Cation Exchange Capacity (CEC) with Atomic Absorption Spectroscopy (AAS), the tool to observe the Biochar morphology using the Environmental Scanning Electron Microscopy (ESEM) Quanta 200 Field Emission Gun (FEG) plus EDAX for other nutrients content, The tool for measuring surface area was used **BET TriStar 3000 V6.07 A Serial #: 2134** with analysis of Brunauer Emmet Teller (BET) and Barrett-Joyner-Halenda (BJH), tool to measure Functional Cluster with Fourier Transform Infrared Spectroscopy (FTIR) Spectometer IRPrestige-21 and pH meter.

3. RESULTS AND DISCUSSION

3.1. Biochar Morphology

The pyrolysis process of some biomass using BT01 at a temperature of 450-500^{0}C produces different morphologies of various types of biomass, the best morphology is biomass which has porosity with high carbon percentage [8].

Based on Figure 1 it can be seen that biochar has a more porous morphology compared to Azolla. Biochar of paddy straw (A) and rice husk (B) have a more porous morphology compared to coconut fiber biochar and oil palm empty fruit bunches with 1000-fold magnification, with a pore size of 63.6994 (4V / A), this indicates that paddy straw and rice husk have the potential for metal precipitation to occur in the pore [9].

Based on the BJH analysis performed (Table 1), the pores of all biochar produced by BT01 is meso pore size 17-3000 (4V / Ǎ) or based on IUPAC (International Union of Pure and Applied Chemistry) having a size of 2-50 nm [10] greater than Azolla. One mechanism for decreasing metal concentration is by heavy metal precipitation on the surface of biochar hence the metal can be embedded in biochar's macro pore and for a long time and can be bound by Van der Walls force to biochar walls allowing it to hold heavy metals longer [10].

Figure-1. BT01: pyrolysis tool
Source: a live photo BT01 pyrolysis tool by using canon camera.

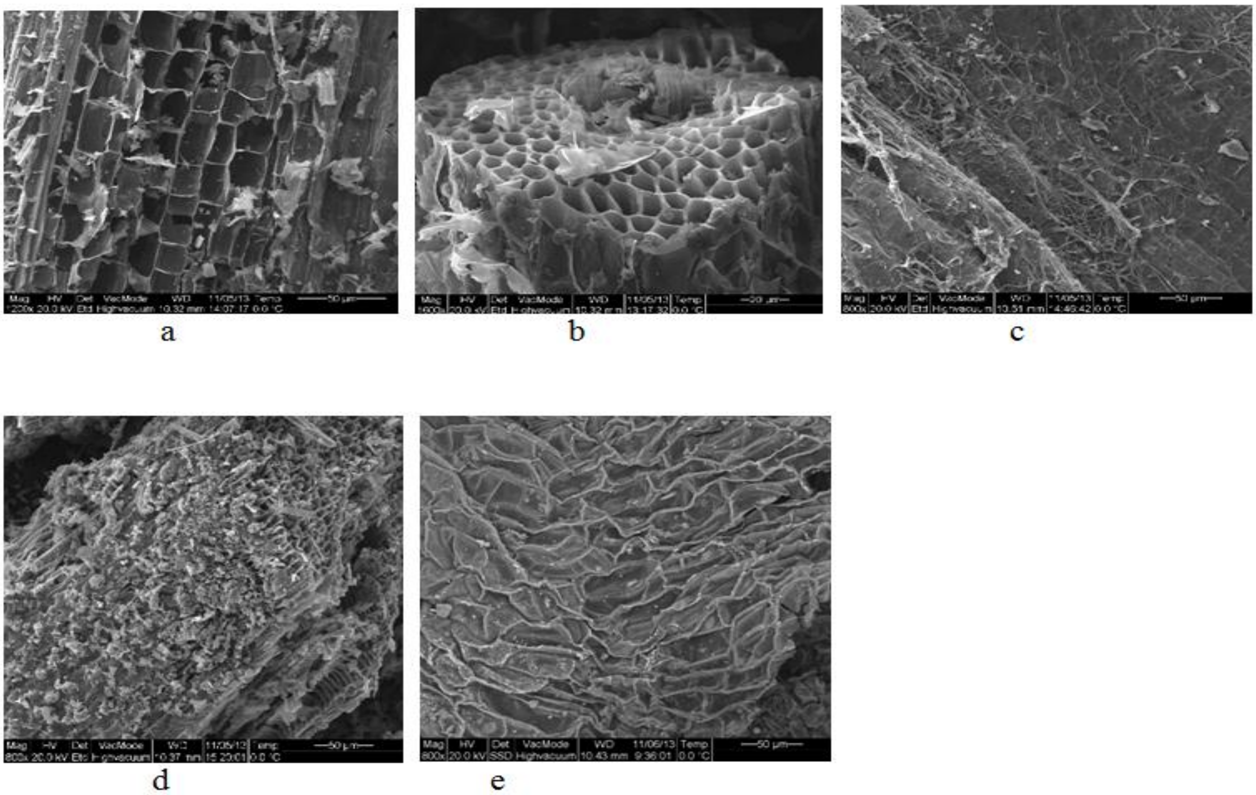

Figure-2. Scanning Electron Microscope (SEM) Paddy Straw (a), Rice Husk (b), Coconut Fiber (c), Oil Palm Empty Fruit Bunches (d), Biomass Azolla (e)
Source: alive photo was taken from Environmental Scanning Electron Microscopy (ESEM) Quanta 200 Field Emission Gun (FEG)

3.2. Biochar Surface Area

Analysis of material surface area is an analysis based on the amount of gas that can be adsorbed by a solid surface at a certain pressure and temperature, if we know the specific volume of gas that can be adsorbed by a material surface at a certain pressure and temperature and we know theoretically the surface area of a gas molecules which is adsorbed, hence the solid total area can be calculated [11].

Based on Table 1 it can be seen that the highest surface area in the 2 adsorption methods was in coconut fiber biochar (B3) with a value of 24.08 m2 / g (BET) and 32.71 m2 / g (Langmuir) and the lowest in oil palm empty fruit bunches (OPEFB) biochar with a value of 8.78 m2 / g (BET) and 11.72 m2 / g (Langmuir) but this value was higher compared to Azolla compost with a value of 6.14 m2 / g in the BET method and 8.12 m2 / g in Langmuir isotherm [11].

The value of Langmuir isotherm which is chemical adsorption has a higher value than the value of BET isotherm which is physical adsorption even though it requires high energy to react [12]. This indicated that the chemical adsorption at biochar has more role compared to its physical adsorption, and this also indicated that biochar has high levels of organic acid due to the pyrolysis process, for details of the two isotherms can be seen in Table 1.

Based on Table 2, the highest pore volume was in rice husk (B2) of 0.027 m3 / g and the lowest was in OPEFB of 0.0056 m3 / g. The highest values of adsorption and release by the Barrett-Joyner-Halenda (BJH) method were found in biochar of rice husks respectively 0.036 m3 / g for adsorption and 0.036 m3 / g for release. The use of BJH as a method of measuring adsorption and desorption because BJH can measure physical absorption in multiple layers [12].

Biochar pore size is far greater than Azolla compost. Biochar's largest pore size was found in rice husk (B2) biochar with a value of 63.70 4V / A, and the smallest in coconut fiber (B3) biochar with a value of 20.74 4V / A but greater when compared to Azolla's pore with a value of 13.34 4V / A. Biochar pores are meso pore with a size value of 17-3000Ă and based on the IUPAC (International Union of Pure and Applied Chemistry) equivalent to nano units having a size of 2- 50 nm, while Azolla includes in micro pore smaller than 17 [12].

Table-1. Differences in Physical Adsorption (BET) and Chemical Adsorption [11]

Physical Adsorption (BET)	Chemical Adsorption (Langmuir)
1. Molecules are bound to adsorbents by physical bonds due to the Van der Walls force	1. Molecules are bound to adsorbents by chemical bonds
2. Has a reaction enthalpy of -4 to 40 Kj / mol	2. Has a reaction enthalpy of -40 to 800 Kj / mol
3. Can form multilayer layers	3. Forming a monolayer layer
4. Does not involve certain activation energies	4. Involves certain activation energies
5. Non-specific	5. Non-specific

Source: IUPAC Technical Report [11]

Table-2. The analysis results of surface area, pore volume and pore size in several methods.

Brunauer–Emmett–Teller (BET)	Straw	Husk	Coconut Fiber	OPEFB	Biomass Azolla
Surface Area					
BET Surface Area (m^2/g)	17.82	17.65	24.08	8.78	6,15
Langmuir Surface Area (m^2/g)	24.17	24.73	32.70	11.72	8,12
Pore Volume					
Single point adsorption total pore volume of pores (m^3/g)	0.026	0.026	0.0124	0.006	0,007
BJH Adsorption cumulative volume of pores (m^3/g)	0.032	0.035	0.0152	0.009	0,009
BJH Desorption cumulative volume of pores (m^3/g)	0.030	0.036	0.014	0.010	0,009
Pore Size					
Adsorption average pore width (4V/A)	58.75	63.69	20.740	25.509	13,345

Source: Original data from BET TriStar 3000 V6.07 A Serial #: 2134

The size of pore and volume of adsorption on rice husk biochar indicated high porosity and potential in heavy metal adsorption [9] stated that one of the mechanisms in reducing the concentration of heavy metals is by precipitation, that is the deposition of heavy metals in the biochar pores, the larger the pore size, the more heavy metal can be deposited even though it is bound weakly by the Van der Walls bond, and in biochar it is not only the Van Der Walls bond but the organic acid also plays a role in holding heavy metals precipitated on biochar and can be retained in a long-term. The organic acid which is contained in biochar will bind to metals and forms strong organometallic bonds and is precipitated on the biochar surface and will last for a long period [9].

Uptake behavior in micro pores (pore width <2 nm) is dominated almost entirely by the interaction between fluid molecules and pore walls, the adsorption potential is in opposite pore walls overlapping [10]. Increasing in the energy interaction of the adsorbent-adsorbate in the center of the pore was very small and the increased in adsorption is mainly due to the presence of adsorbate-adsorbate that interact cooperatively, and the opposite occurred in the macro pore hence the potential of adsorbent-adsorbate interactions on the pore wall is very large [11].

3.3. Functional Group on Biochar

The functional group content in biochar can be seen using the Fourier Transform Infrared Spectroscopy (FTIR) tool, that is by firing energy in the form of infrared light and causing the molecules vibrating where the magnitude of the vibrational energy of each component differs depending on the atom and the strength of the molecular bonds resulting in different frequencies being read using tables [13].

Based on Figure 3, it can be seen that there are 2 functional groups that were dominant in biochar qualitatively, namely wave group A with a frequency of 1500-1600 and wave group B with a frequency of 1050-1300. The analyzing of the FTIR chart based on Skoog, et al. [14] it can be seen that wave group A with a frequency of 1500-1600 indicates an aromatic carbon content with a changing intensity. This showed that biochar produces recalcitrant carbon from the decomposition process hence it can be very long-term carbon storage for even thousands of years [15].

The B wave group namely biochar which has a wave of 1050-1300, based on According to Skoog, et al. [14] about analyze FTIR charts can be understood that wave group A with a frequency of 1050-1300 showed the presence of a phenolic functional group, ether, carboxylic acids, esters, with the highest intensity in rice husk biochar.

The presence of functional groups into biochar has a high Cation Exchange Capacity, thus increasing the adsorption capacity of heavy metals, and with the presence of Phenolic groups, Ether, Carboxylic Acid and Esther also makes biochar does not include as mineral carbon but organic carbon as carbon in Organic Matters, hence biochar also has properties like other organic matters [16].

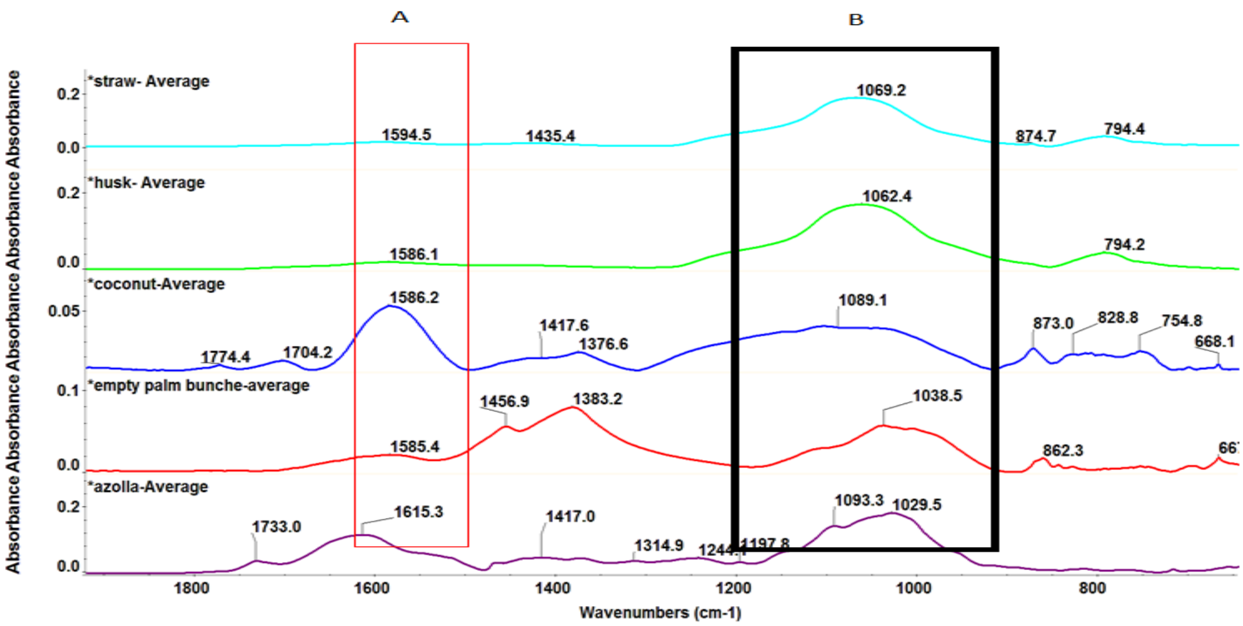

Figure-3. FTIR of Straw, Husks, Coconut Fibers, Coconut Empty Bunches and Azolla

Source: Original figure from FTIR Spectometer IRPrestige-21

Based on Figure 3, it can be seen that the functional group possessed by Azolla compost was also possessed by biochar except for the amide-amine group (CN) at a frequency of 1180-1360 which indicated the high Nitrogen content in Azolla and this is a feature of Azolla compost derived from *Azolla pinnata* who have special abilities in fixing N hence they are able to supply N nutrients up to 45 tons / Ha equivalent to 100 Kg of Urea, hence the use of Azolla in sustainable paddy fields will reduce the use of urea fertilizer [17].

3.4. Biochar pH

Based on Table 2, it can be seen that the highest pH was found in paddy straw with a value of 8.52, then oil palm empty fruit bunches with a value of 8.23 and coconut fibers with a value of 8.13 and the lowest was in rice husks with a value of 6.74. Biochar is an organic carbon that is rich in lime matters such as calcite hence it has a base reaction and increases pH because of the accumulation of base cations due to the loss of H-O [8]. The accumulation of basic cations in biochar causes a high pH value [6] hence application biochar had the same effectiveness as the application of calcite lime at 23% [6].

The pyrolysis process determines the pH of biochar, namely in the presence of oxygen, the more oxygen which enters during the pyrolysis process, the higher the pH content, this is due to an oxidation process in biomass and producing an amount of ash which has a base reaction and this generally occurs in the fast hydrolysis process using the Kiln method. This type of combustible biomass will also produce a high pH. Hence, the making of biochar is adjusted to its utilization [17].

Biochar is a buffered organic carbon because it has high organic acid, as is organic matter, biochar is able to maintain pH at each change, when the pH of solution is high therefore protons in functional groups will release and neutralizes OH in solution, and vice versa when pH drops then the cations that are adsorbed on the surface will be released into the solution hence the pH can be maintained [18].

3.5. Organic Carbon Percentage

Based on SEM-EDAX biochar analysis, it can be seen that the highest Carbon concentration was found in Biochar of rice husk with a value of 77.18%, then oil palm empty fruit bunches with a value of 58.81%, biochar paddy straw with a value of 52.32%, and the lowest biochar coconut fiber with a value of 38.54%. The cations found on many biochar surfaces were dominated by K^+ with the highest percentage of biochar rice husk by 2.75% and the lowest in coconut fiber biochar by 1.06%, Na^+ was also found in rice husk biochar by 1.07%, while Mg^{2+} found in oil palm empty fruit bunch biochar by 0.63%.

Table-2. The Analysis Results of Paddy Straw, Rice Husk, Coconut Fiber and Oil Palm Empty Fruit Bunches Biochars

No	Type of Analysis	Biochar			
		Straw	Husk	Coconut Fiber	OPEFB
1	pH(Gravimetri)	8,52	6,74	8,13	8,23
2	Carbon (%) EDAX	52,32	77,18	38,54	58,81
3	N (%)Kjeldhal	0,00	0,00	0,00	0,00
4	P (%) EDAX	0,00	0,00	0,00	0,00
5	K (%) EDAX	1,77	2,75	1,06	7,20
6	CEC (me/100g)(AAS)	22 ,23	35,45	30,26	33,13
7	Total Pb (AAS) ppm	0,000	0,000	0,00	0,00
11	Na (%) (EDAX)	-	1,07	-	-
12	K (%) (EDAX)	1,77	2,75	1,06	7,20
13	Ca (EDAX)	-	-	-	-
14	Mg (EDAX)	-	-	-	0,63

The high carbon value in biochar is determined by the type of biomass and the pyrolysis process [8]. Biomass containing high lignin has a higher carbon when compared to biomass which contains a lot of cellulose and hemicellulose, this is because the initial process of pyrolysis, elements released from biomass is H and O in the form of water vapor which contains lots of cellulose and hemicellulose, with carbon chains that are Aliphatic while lignin has an Aromatic carbon content [7]. The carbon produced is recalcitrant, this can be seen in the SEM-EDAX analysis, Carbon does not appear to bind in large amounts of oxygen (unit in %) hence it is not detected, recalcitrant is also seen in the presence of chlorine (Cl) on each Biochar [8].

3.6. Cation Exchange Capacity

Biochar results of BT 01 pyrolysis generally have a high Cation Exchange Capacity (CEC), this is seen in Table 2, the highest CEC value was found in biochar of rice husk at 35.45 me / 100g and the lowest in rice straw at 22, 23 me / 100 g. The amount of CEC value in biochar is caused by the high content of organic acids which as seen in the results of FTIR measurements such as carboxyl acids, ether and ester groups and phenolic acids which are rich in negative charges. In addition, biochar is a carbon rich in negative charges hence biochar has a very high ability to reduce metal availability [2]. When compared to Azolla compost, biochar is able to compensate for the presence of organic acids as seen in FTIR analysis, except that biochar does not have a nitrogen-rich Amine-Amide group which is the characteristic of Azolla compost [16].

4. CONCLUSION

Biochar is an organic carbon that has a high ability to adsorb heavy metals. Biochar has a very porous morphology so it can deposit large amounts of heavy metals on its surface. Biochar which has the largest surface, pore volume and pore size is in rice husk biochar 17.65 m2 / g, 0.027m3 / g and 63.70 4V / A, respectively. Biochar which has functional groups in the form of carboxyl, Ether, Esters and Phenolic groups with high intensity and the best is rice husk biochar. Rice Husk Biochar has the best potential in adsorbing heavy metals.

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