DOI https://doi.org/10.18551/rjoas.2020-09.15

BIOCHAR AND AZOLLA APPLICATION ON FERTILITY OF LEAD CONTAMINATED SOIL

Hidayat Benny*
Doctoral Program of Agricultural Sciences, Faculty of Agriculture,
University of Sumatera Utara, Indonesia

Rauf A., Sabrina T.
Program Study of Agrotechnology, Faculty of Agriculture, University of Sumatera Utara, Indonesia

Jamil Ali
Head of Indonesia Quarantine Agriculture, Jakarta, Indonesia

*E-mail: bendayat@gmail.com

ABSTRACT
Potential for lead pollution does not only come from factory pollution but also from the air and the negative effects of fertilization. Rice is a hyper-accumulator plant that has the ability to store heavy metals without experiencing physiological disturbance, and this is very dangerous because rice is a staple food, especially in Indonesia. Biochar and Azolla are one of the solutions to produce quality rice even in heavy metals polluted land because of its ability to absorb heavy metals, especially Pb. This research aim was to explore the potential of several types of biochar from biomass abundance and combine it with azolla which is known as the best source of Nitrogen and organic matter. This research used factorial randomized block design (RBD) with 2 treatments and 3 replications. The first treatment is the use of various types of biochar namely; without Biochar (B0), rice straw biochar (B1), rice husk Biochar (B2), coconut fiber biochar (B3) and oil palm empty fruit bunches (B4). The second treatment using Azolla, namely; Without Azolla (A0), *Azolla pinnata* (A1) and *Azolla mycrophylla* (A2). The results showed that the best biochar for increasing soil organic content, N, P, K, soil CEC was rice husk biochar (B2) and the best azolla was *Azolla microphyllla* (A2) and both had the best interaction in increasing C organic and soil CEC.

KEY WORDS
Biochar, azolla, lead, soil fertility.

Lead (Pb) is a very dangerous element when accumulated in the human body, it can damage the human nervous system and affect cognitive function, learning ability, shortening height, decreased hearing function, affecting behavior and intelligence, and could damage the function of organs, such as kidney (Sudarmaji, 2006). This metal has a very large source of liquid waste, solids, or in the form of gas (TEL), and is also widely used as a coating agent for various fertilizers and naturally form of rocks, hence efforts to control Pb pollution are needed.

The establishment of factories in agricultural areas, especially paddy fields, is a threat of land quality degradation by waste which directly or indirectly affects the quality of agricultural production produced. The waste formed in organic or inorganic compounds. Organic compounds will be decomposed into simpler forms or lost to the air, but inorganic compounds such as heavy metals cannot be decomposed but will accumulate. If Pb accumulates in food crops such as rice it will be a big problem especially for humans because it is a universal consumer and the top of the food pyramid, and the application of biochar and azola would be a solution for heavy metal problems in paddy field (Hidayat, 2015).

Biochar is derived from biomass combustion at a temperature of 600 ^{0}C, resulting in changes of carbon structure and has good improving ability for soil properties, solving organic or un organic polluted soils, reducing the greenhouse effect and increasing production (Zhang et al. 2012). Biochar has a broad surface, porous, and contains negative C that can bind metals, so as to stabilize heavy metals in polluted soils by significantly reducing the absorption of heavy metals by plants and can improve soil quality by improving the physical and chemical-physical properties of soils (Ippolito et al. 2012; Komarek et al. 2013).

The ability of Biochar is largely determined by the origin of the material and its pyrolysis process, high density biomass required high temperatures of 400^{0}C-600^{0}C and low density biomass required a temperatures of 200^{0}C, high temperature biomass has a higher surface area advantage, but low nutrient content (Sohi et al. 2010), Biochar is easy to product and could be applied by farmers and has potential to be developed in increasing the utilization of organic biomass which is very abundant and increases lowland rice production especially on polluted land.

Azolla is a fern, generally has the ability to supply nitrogen of 30-40 tons/ha, but Azolla also has the ability to absorb heavy metals (hyper accumulator), each type of Azolla has a different ability, *Azolla pinnata* has finer roots compared to *Azolla macrophylla* hence has a broader surface area and its ability to absorb heavy metals is much greater but *Azolla macropylla* has high biomass and is very active to the environment hence plants can be in extreme conditions even though it has great potential to grow in polluted areas (Hidayat, 2011). Azolla accumulated Pb in roots more than in other parts (Hidayat, 2011). Azolla biomass which accumulated Pb will undergo a process of decomposition and release a number of nutrients, especially nitrogen needed by plants, and increasing the total Pb in the soil, not increasing the amount of Pb available, because Pb is strongly bound in Azolla's organic material, hence the continue used of Azolla will maintain Pb organic bonds and potentially become a phytoremediation plant for heavy metals in paddy soils (Abror et al, 2012).

Azolla biomass accumulated by Pb will undergo a process of decomposition and release a number of nutrients, especially nitrogen needed by plants, it turns out that this only increases the soil total Pb but does not increase the amount of the available Pb, because Pb is strongly bound to Azolla's organic material, hence with the continue used of Azolla, it will maintain organic Pb bonds hence it has the potential to become phytoremediation plants for heavy metals in paddy field soils (Abror et al, 2012).

Indonesia is a country that is rich in biomass that has not been maximally utilized and even has great potential as a source of greenhouse gases that will increase the temperature of the earth. Utilization of biomass in the form of biochar and Azolla sp is the right choice to control heavy metal pollution, therefore research is needed on the best biomass and Azolla and the combination of both in controlling heavy metal pollution in paddy plants.

METHODS OF RESEACH

This research was conducted at the Growth center of region I Kopertis (Coordination of Private Universities) Jl. Pancing, Sumatera Utara with an altitude of 25 meters above sea level, and in a standardized laboratory of KAN (National Accreditation Committee) at BPTP-RISPA. Biochar material is in the form of paddy husk and paddy straw was taken from Pantai Labu area. Empty palm bunches (EPB) are taken at the Perbaungan palm oil mill, coconut fibers from the Medan-Aksara market. The tools used were large buckets for irrigation water containers, plastic buckets, large plastic for ground containers, hoes, Global Positioning System (GPS), pyrolysis in the form of a drum which is perforated at the bottom and given an inlet and outlet air pipe (Figure 1) and applied water cooling hence the ash content is not high. The method used was a factorial Randomized Block Design with 3 replications. The first factor is the type of biochar used, namely; without biochar (B0), rice straw biochar (B1), rice husk biochar (B2), coconut fiber biochar (B3) and oil palm empty fruit bunch biochar

(B4). The second factor is the application of azolla, namely; without azolla (A0), *Azolla pinnata* (A1) and *Azolla microphylla* (A2).

Biomass of straw, husk, empty bunches and coconut fibers chopped to 1-2 cm size and dried. Biochar is made by the Kiln method, namely by inserting the biomass into a reator biochar BT 01 (Figure 1) which is self-assembled with a heat source from below, with limited ir conditions, temperatures up to 400-600 ^{o}C with a combustion time of 2-3 hours, then cooled (Jiang, 2012). The biochar formed was sieved with a 40 mesh sieve. The parameters observed were the pH of incubation soils for the first and second weeks, Soil organic Carbon, total Nitrogen content, Phosphate and Kalium available and total respiration.

Figure 1 – Reactor BT01

Table 1 – Preliminary analysis of soil, water, biochar and azolla

No	Analysis	Soil[1]	water	Biochar[2]				Azolla
				Straw	husk	Coconut fiber	EPB	
1	pH (Gravimetric)	6,84	7,36	8,52	6,74	8,13	8,23	-
2	Carbon (%) Spectrophotometry	1,31	-	52,32	77,18	38,54	58,81	55,59
3	N Total (Kjeldhal Method) (%)	0,15	4,89	0,00	0,00	0,00	0,00	0,43
4	P (HCl 25%)	0,087	0,045	0,00	0,00	0,00	0,00	0,027
5	K (HCL 25%)/Edx	1,03	19,45	1,77	2,75	1,06	7,20	0.38
6	Pb Total (AAS) ppm	77,21	31,00	0,000	0,000	0,00	0,00	0,00
7	Pb Available (AAS) ppm	28,96	31.00	-	-	-	-	-
8	Texture	Sandy Clay Loam						

Note:
1. *USDA*
2. *IBI, 2014*

RESULTS AND DISCUSSION

Changes in soil pH due to the application of biochar and azolla in polluted soils and water. Based on the data analysis, it can be seen that the application of biochar significantly increases soil pH but not with the application of azolla or its interactions, with the highest pH being in the treatment of B1 (biochar of rice straw) with a pH value of 8.69 and the lowest was in the control treatment (B0) worth as 6.66 pH value. The application of rice straw biochar (B2) was not significantly different from the control with a pH value of 6.75.

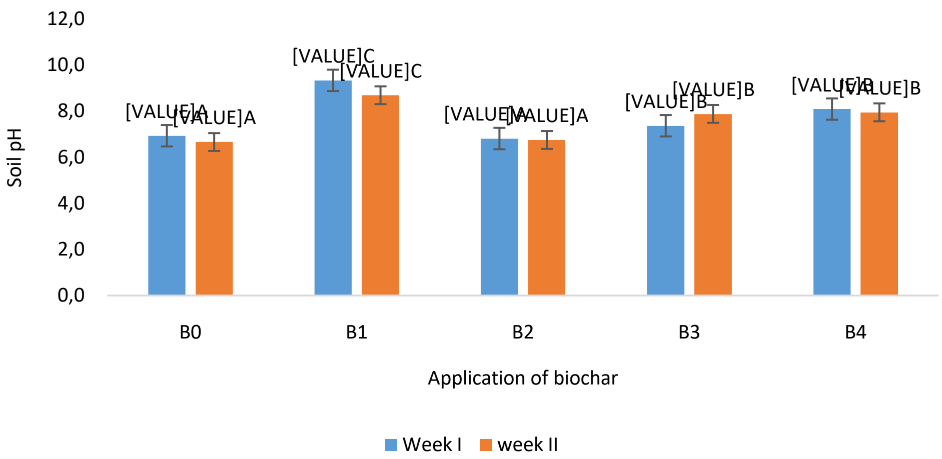

Figure 2 – Soil pH values due to the application of several types of biochar (Note: The number followed by the lower case is significantly different at the 5% level and the uppercase letter is very significantly different at the 1% level according to the Duncan test (DMRT)

The increase in pH through the application of biochar is because biochar has an alkaline reaction that is the presence of ash and most of the biochar is an alkaline material and has a liming effect, and the high alkali material in biochar is caused by many cations (Sheng et al. 2005; Wu et al. 2012) hence the base saturation becomes high and increases the pH, if the base component increases (such as $CaCO_3$), the H^+ ion will be neutralized. With the addition of a continuous base will become a buffer on Al^{3+} hydrolysis which releases a lot of H^+ and finally the soil pH does not increase to the appropriate limit on the addition of alkaline components to biochar which will reduce the solubility of Al^{3+}, finally $Al(OH)_3$ will settle to pH 6.5, the amount of Al^{3+} solubility will decrease and soil pH will increase (Plaster, 2004).

Biochar and azolla potential in the total value of Soil Organic Carbon. Based on the data analysis, it was identified that the interaction of biochar and azolla produces a numerous significant effect on changes in total organic carbon, with the highest total soil carbon value in the treatment of biochar and *Azolla microphylla* (B2A2) with organic carbon value of 4.9% and the lowest value of 1.8% in the treatment of Biochar of rice straw and *Azolla microphylla* (B3A2) which were not significantly different from the control of 1.7%.

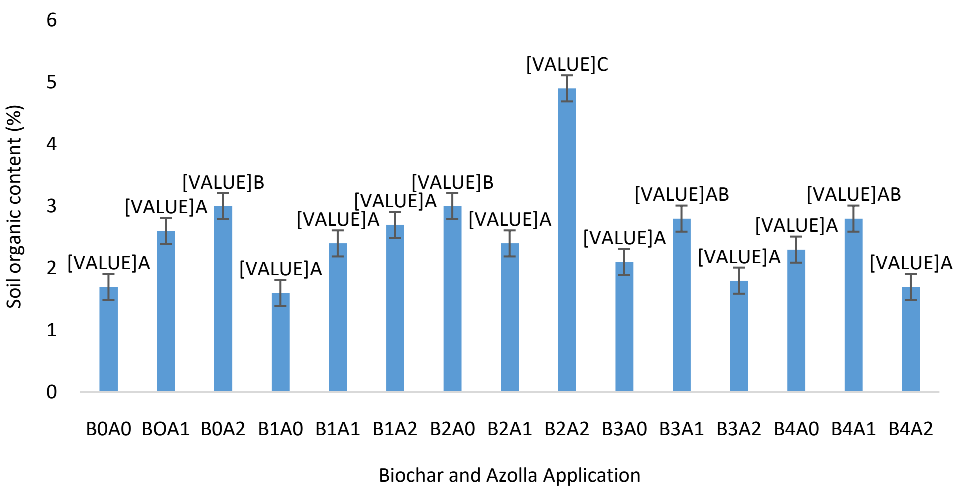

Figure 3 – The value of organic soil content in the several types of biochar application (Note: The number followed by the lower case is significantly different at the 5% level and the uppercase letter is very significantly different at the 1% level according to the Duncan test (DMRT)

Biochar and azolla application in this research significantly increased soil organic content, this is because both are high carbon sources. The making process of biochar in hydrolysis aims to maintain the amount of organic carbon present in biomass and also the organic acids present in it, with its porous structure making biochar very suitable for microbial growth in it, for remediating polluted soils (Park, 2011, Hidayat, 2018). Thus, *Azolla microphylla* which can double three times a week able to contribute high carbon to the soil. *Azolla microphylla* also has a high adaptation and duplication compared to *Azolla pinnata* which has a low adaptation (Arora and Singh 2002; Hidayat et al. 2017).

Biochar and Azolla potential in total N values of soil. Application of biochar and azolla has a very significant effect on changes in soil N total but not with their interactions. Based on Fig 4, it can be seen that the application of biochar has a significant effect on the change in soil N total, with the highest N value in the biochar application of rice husk (B2) of 0.23% and the lowest in the control treatment and rice straw treatment of 0.14%. Azolla application has a significant effect on the changes of soil N total value with the highest N value in the treatment of A2 (*Azolla microphylla*) of 0.21% and the lowest in A0 (control) of 0.15%.

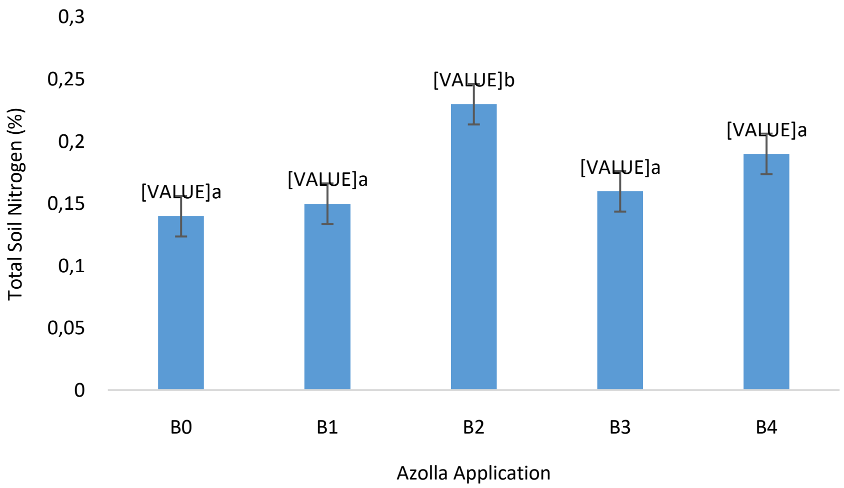

Figure 4 – The total value of soil nitrogen in several types of biochar application (Note: The number followed by the lower case is significantly different at the 5% level and the uppercase letter is very significantly different at the 1% level according to the Duncan test (DMRT)

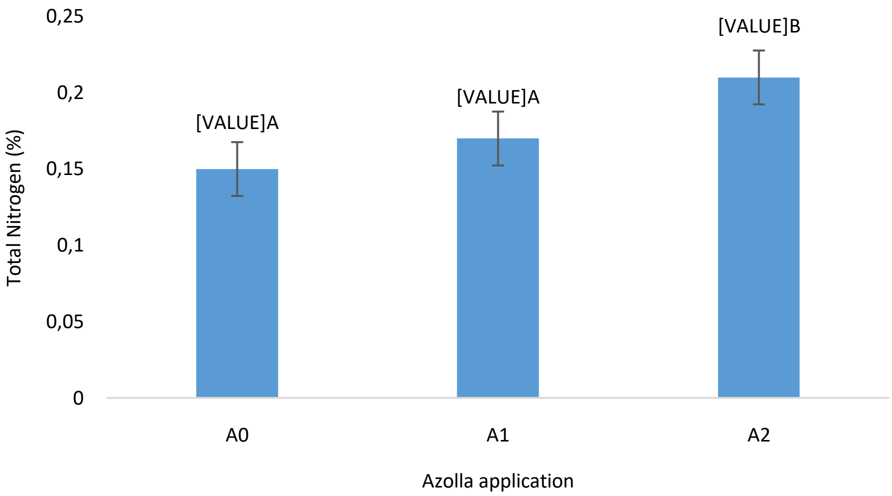

Figure 5 – Soil N values due to several types of Azolla application (Note: The number followed by the lower case is significantly different at the 5% level and the uppercase letter is very significantly different at the 1% level according to the Duncan test (DMRT)

Biochar is an organic material that can absorb ammonium that is available from the decomposition of organic material, not only that but it also can manipulate the presence of N in the soil hence it is more resilient by increasing cation exchange capacity (Clough and Condron, 2010). Azolla is a fern plant known as Nitrogen nutrient supply in the presence of symbiosis with Anabaena azolla, which is able to fixate N in the air to become N available to plants in the form of ammonium after a decomposition process with a supply reaching to 240 kg/ha and *Azolla microphylla* has a higher adaptability than *Azolla pinnata* hence it can develop and duplicate itself and produce more organic matter and nitrogen (Arora and Singh, 2002; Arora et al. 2005).

Biochar potential on the Soil P available value (ppm). Application of biochar has a very significant effect on changes in the soil P. In Fig 6, it can be seen that the application of biochar has a very significant effect on increasing soil P available, with the highest P available value in treatment B2 (rice husk) of 32.17 ppm and the lowest value in control treatment (B0) of 23.07 ppm and not significantly different from other biochar treatments.

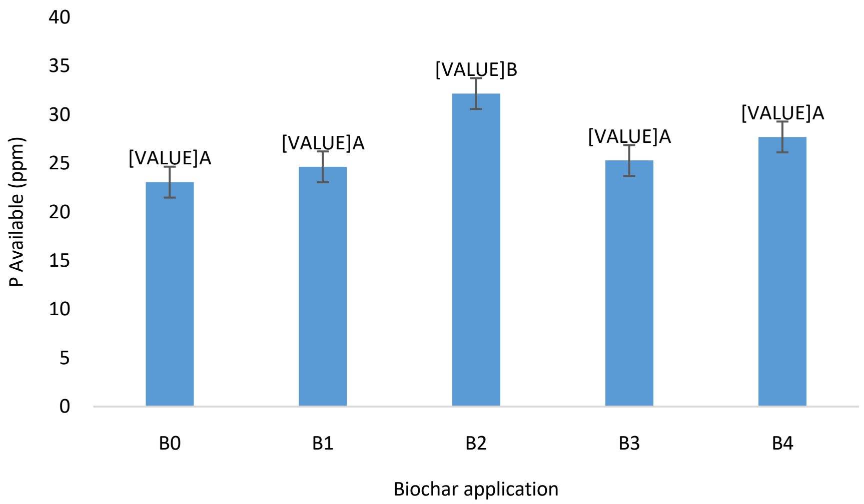

Figure 6 – Soil P available value due to several types of biochar application (Note: The number followed by the lower case is significantly different at the 5% level and the uppercase letter is very significantly different at the 1% level according to the Duncan test (DMRT)

The increasing of P availability in the biochar application is highly dependent on the type of biochar biomass and temperature during the pyrolysis process, at low temperatures (300^0C-400^0C) the availability of P is much higher than at high temperatures (500^0C- 600^0C), the increase in pH also affects P availability (Zheng et al. 2013).

Biochar and azolla potential in soil K values (me/100 g). In general, the application of biochar and azolla produced a significant effect on changes in K exchange rates, In Fig 7, it can be seen that the application of biochar has a significant effect on the increase in K exchange rate, with the highest value in the treatment of rice husk biochar (B2) of 3.00 me/100 g and the lowest was in the control treatment of 1.58 me/100 g.

Azolla application has a very significant effect on changes in K exchange rate, with the highest value on *Azolla microphylla* treatment with an average value of 2.30 me/100 g and the lowest was in the control treatment of 1.79 me/100 g.

Biochar has a high potassium content, and its availability depends on the pyrolysis process, in the high-temperature pyrolysis process (500^0C-600^0C), the availability of potassium is much higher than the low-temperature process, the availability of K will increase with the increasing of pyrolysis temperatures and vice versa the availability of N and P will decrease with the increasing of temperature, and oil palm empty fruit bunches (B4) are produced with temperatures between 500^0C - 600^0C hence it produce high potassium values (Zheng et al. 2013).

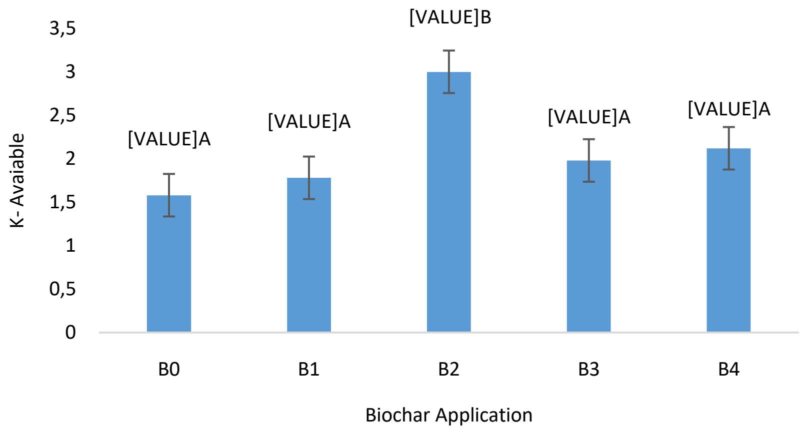

Figure 7 – Soil K exchange value due to several types of biochar application (Note: The number followed by the lower case is significantly different at the 5% level and the uppercase letter is very significantly different at the 1% level according to the Duncan test (DMRT)

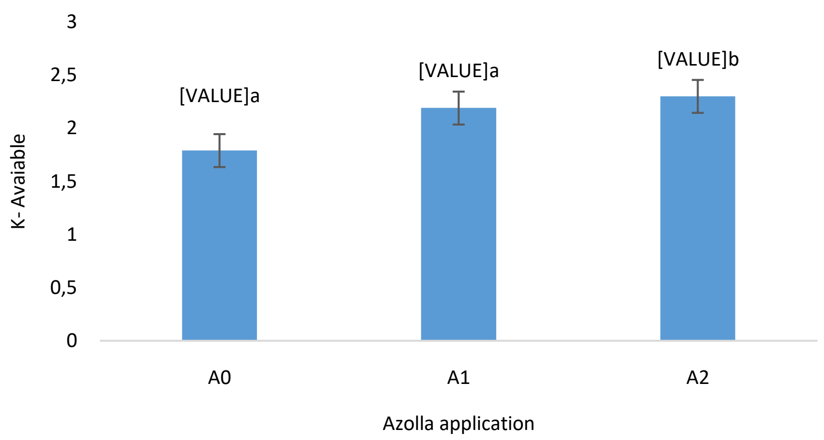

Figure 8 – Soil K Exchange value due to 2 types of azolla application (Note: The number followed by the lower case is significantly different at the 5% level and the uppercase letter is very significantly different at the 1% level according to the Duncan test (DMRT)

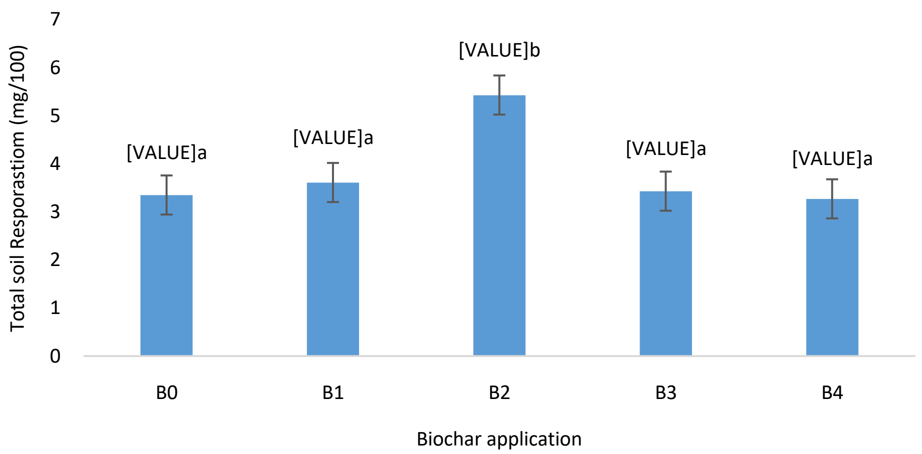

Figure 9 – The total value of soil respiration due to several types of biochar application (Note: The number followed by the lower case is significantly different at the 5% level and the uppercase letter is very significantly different at the 1% level according to the Duncan test (DMRT)

Biochar and Azolla potential in total respiration values (mg CO2/100 g soil). The application of biochar and azolla in general has a very significant effect on changes in the total respiration value of the soil. The application of biochar in Fig 9 showed significant results in changes in the total respiration value of polluted soils, with the highest value in the treatment of rice husk biochar (B2) of 5.43 mg/100 g of soil and the lowest in the treatment of oil palm empty fruit bunches (B4) biochar of 3.27 mg/100 g of soil.

The application of azolla has a very significant effect on changes in respiration value of Pb-contaminated soil and water, with the highest value was in the *Azolla microphylla* treatment of 5.11 mg/100 g of soil and the lowest value was in the control treatment of 2.91 mg/100g soil.

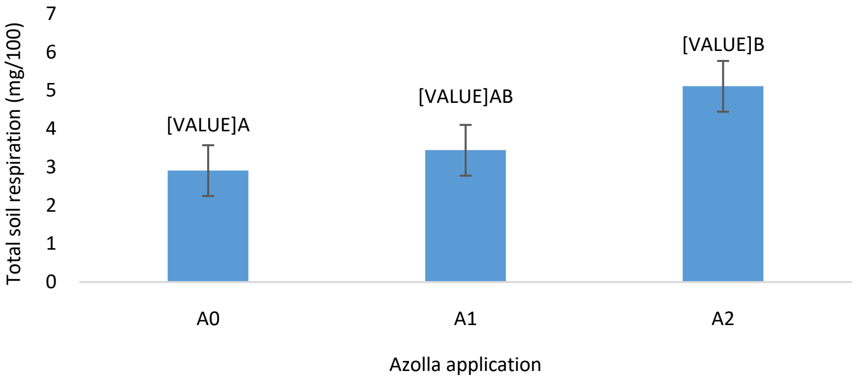

Figure 10 – The total value of soil respiration due to 2 types of azolla application (Note: The number followed by the lower case is significantly different at the 5% level and the uppercase letter is very significantly different at the 1% level according to the Duncan test (DMRT)

Biochar is the best home for soil microbes because it has a porous structure and is also relatively rich in nutrients and stable in the degradation process (Ladygina and Francois, 2013). The porosity of the biochar and nutrient content is highly dependent on the type of biomass it originates from and the pyrolysis process, on the high pyrolysis process >6000C resulting in a high surface area, up to hundreds of m2/g (Warnock et al. 2007), hence it has the ability to retain high water and inviting a number of microbes, fungi are microbes that make biochar as their habitat because they have a pH range that is more tolerant than bacteria (Ladygina and Francois, 2013).

Planted Azolla will undergo a decomposition process with the help of several heterotrophic microbes, there is a positive correlation between the number of microbes and with a large amount of Azolla biomass (Arora et al. 2006).

CONCLUSION

Biochar and Azolla, respectively, can increase the fertility of polluted soils by increasing the C organic concentrations of N, P and K of the soils and increasing soil total respiration. The best biochar in increasing nutrient concentrations of N, P, K and total respiration is rice husk biochar. Azolla which is the best in increasing soil N and K nutrients and total respiration is Azolla microphylla. The interaction of biochar and azolla has the best ability to increase total soil carbon.

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