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Research Article

The potential of organomineral amendments in increasing the adsorption of lead (Pb) and cadmium (Cd) in a sandy loam soil

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Abstract

Sandy loam soils contain low organic carbon and have low ion adsorption capacity. Under certain conditions, the soils contain heavy metals that are harmful to plants. Soil amendments such as biosilica and humic acid from natural sources are expected to increase the soil adsorption capacity to heavy metals. A simulation experiment consisting of two factors was conducted to explore the effectiveness of humic and biosilica, as soil amendments, in adsorbing heavy metals from soils. The first factor was biosilica dose composing 0 t ha^{-1} (S0), 0.5 t ha^{-1} (S1), 1 t ha^{-1} (S2), and 1.5 t ha^{-1} (S3). The second factor was the humic acid dose composing 0 kg ha^{-1} (H0), 20 kg ha^{-1} (H1), 40 kg ha^{-1} (H2), and 60 kg ha^{-1} (H3). The humic acid and biosilica were applied to soil contaminated with Pb and Cd. The results showed that the combination of 0.5 t biosilica ha^{-1} (S1) and 20 kg humic acid ha^{-1} (H1) significantly increased soil pH, organic C content, cation exchange capacity, and reduced the availability of Pb and Cd at 90 days after treatment. The Pb and Cd contents in plant tissue decreased from roots to grains. Humic acid treatment was more effective in absorbing Pb of 86.89-90.49% and Cd of 71.47-76.33% than other treatments.

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Introduction

The characteristics of sandy soil are low organic carbon content, low fertility, and low water holding capacity (Weber et al., 2007; Hamid et al., 2017). Sandy soil management is very important for agricultural land management. The potential for heavy metal contamination will also worsen sandy soil conditions. This condition causes the sandy soil to be poor in nutrients and not widely used for agricultural land (Darlita et al., 2017). Therefore, the adsorption capacity of water in sandy soil is very small.The presence of excessive sand fraction in the soil causes the soil to lose water easily due to its low adsorption capacity (Mirdat et al., 2013). Plant growth requires soil with stable soil aggregation characteristics; this is important in preventing the loss of water and available nutrients in the soil (Kusuma et al., 2016). Soils with low soil organic matter content are very susceptible to loss of water and available nutrients. This condition is caused when there is a washing process; the soil is prone to decreased fertility (Sukartono and Utomo, 2012).

Heavy metals in the soil through various sources can be caused by the addition of fertilizers, pesticides, the addition of organic matter or organic matter, waste residues and others (Chairiyah et al., 2013). Agricultural activities contribute to pollution through fertilization. It is known that excessive fertilization has an impact on the accumulation of heavy metals, for example, found in several fertilizers, namely P fertilizer (0.1-170 mg Cd kg^{-1}), N fertilizer (0.05-8.5

mg Cd kg^{-1}), lime (0.04-0.1 mg Cd kg^{-1}), and compost (0,01-100 mg Cd kg^{-1}) (Wihardjaka and Harsanti, 2018). The condition of heavy metal forms in the soil varies with the biochemical activity in the soil. Some forms of metal found in the soil (Bruemmer et al., 1986; Notohadiprawiro, 2006), (1) water-soluble, present in soil solution, (2) exchangeable, bound to adsorption sites on soil colloids and can be liberated by ion-exchange reactions, (3) bound organically, associated with humus compounds that do not dissolve, (4) occluded in iron and manganese oxides, (5) certain compounds, such as carbonates, phosphates, and sulfides, and (6) structurally bound in silicate minerals or primary minerals.

Improvements to rice fields contaminated with heavy metals can be made using several methods, using soil improvers, planting accumulators and using microbes to reduce contamination (Wihardjaka and Harsanti, 2018). Humic acid and silica are soil amendments used for the remediation of metal-polluted soils. The research showed that sub-alkali humic acid was able to adsorb on Cu, Pb, Zn, Cd, and Cr (Piccolo et al., 2019). It is also known that silica has the ability as an adsorbent for heavy metals and is able to reduce the Pb content in the soil (Lei et al., 2018).

Humic compounds have the ability to adsorb heavy metals through the mechanism of interaction of metals or other cations with functional groups (Fahmi, 2011). Humic compounds have great potential to be used as bioremediation because they have been shown to be able to reduce heavy metal content due to tailings soil contamination (Wang and Mulligan, 2009). The use of compost as a source of humic acid has a lower economic value with the same level of effectiveness as leonardite (Piccolo et al., 2019). The optimal dose of soil remediation by humic acid is in the range of 10-20 kg ha^{-1} and combined with vetiver plants. The application of humic acid at that dose was able to reduce the available Cu content in the soil up to 47.13%-76.79% (Vargas et al., 2016). The application dose of 40 mg kg^{-1} with a pH of 7 increased the –COOH and –OH contents and formed an adsorption complex with Fe-metal (Boguta et al., 2019). The application of a dose equivalent to the use of humic acid is as much as 80 kg ha^{-1}. Humic acid applied to soil also affects plant root tissue. It is known that given humic acid, more heavy metals will be accumulated in the roots and limited for translocation to other tissues (Vargas et al., 2016).

Silica obtained from rice husk ash extraction can be used as a good adsorbent (Peres et al., 2018). Besides being an adsorbent, biosilica is able to increase the productivity of rice plants. The production of rice plants treated with colloidal biosilica at concentrations of 20 and 30 mg kg^{-1} gave a positive response to plant growth and productivity (Amrullah et al., 2014). The application of silica in lowland rice was able to reduce the available Cd by 11.4%-25.8% compared to polluted soil and increase the heavy metal in the form of residue (Ning et al., 2016). The treatment used 10 t husk ash ha^{-1} and the equivalent of 1.5 t biosilica ha^{-1}. Application of biosilica with a dose of 1-2 t ha^{-1} can reduce the availability of Pb in the soil (Imtiaz et al., 2016). Silica binds heavy metals through an adsorption system; the mechanism of heavy metals such as Pb will bind the –OH present in the Si-OH group (Lei et al., 2018). Biosilica treatment in liquid form will increase the adsorption capacity of metals (Chuah et al., 2005).

The objectives of this study were to elucidate the effect of the application of biosilica and humic acid, as soil amendments, on the availability of Pb and Cd in a sandy loam soil and Pb and Cd uptake by rice plants.

Materials and Methods

The study was conducted using a pot model with rice plants grown on a sandy loam Entisol that had been injected with Pb and Cd. The study was conducted in the greenhouse of the Faculty of Agriculture, UPN "Veteran" East Java, from May to September 2021. The soil that was collected from Purwosari District of Kediri Regency is slightly acid with very low organic C content and low cation exchange capacity (CEC). The low CEC of the soil is probably due to the low organic C content of 0.79% and the high sand fraction content of 55% (Table 1). The soil was air-dried and sieved to pass through a 2 mm sieve. Soil amendments used for this study were humic acid extracted from compost and biosilica extracted from rice husks.

Table 1. Characteristics of soil used for this research.

Parameters	Value	Criteria
pH	5.73	slightly acid
Organic C (%)	0.79	very low
CEC (cmol(+) kg^{-1})	13.89	low
Sand (%)	55	sandy loam
Silt (%)	32	
Clay (%)	13	

Note: Criteria based on Soil Research Institute (2009).

Extraction of soil amendments

Humic acid

Humic acid was extracted from compost using a modified method by Stevenson (1994). 10 g of compost was extracted using 100 mL of 0.5 N KOH solution (1:10) and soaked for up to 24 hours, and refrigerated for 16 hours with occasional shaking. The substance was then separated using Whatman 41 filter paper to obtain humic compounds. The substance was then added with H_2SO_4 6 N until the pH of the solution reached 2. The addition of H_2SO_4 6 N formed two layers. The solution was separated again with Whatman 41 filter paper. The precipitate obtained was rinsed using CO_2-free distilled water to remove residual chloride in humic acid (Stevenson, 1994). The supernatant obtained was then titrated to pH 7 using 0.1 N KOH (Piccolo et al., 2019).

Biosilica

Rice husks were dried in open dry air and cleaned of adhering impurities such as rice leaves, sand, gravel and so on. The husks were then burned manually to produce ash. The resulting ash was ground and then sieved to pass a 200 mesh sieve. The KOH solution was made with a concentration of 10% w w^{-1}, then 60 mL of the KOH solution was added to 10 grams of husk ash, then heated to a temperature of 85 ºC while stirred for 90 minutes. After cooling, it was filtered, and the residue was extracted again as before, and the filtrate was combined with the first filtrate as a silicate solution. The 1 N HCl solution was slowly added to the extracted silicate solution until its pH reached 9 (Agung et al., 2013).

pH, organic C, total Pb, and total Cd of humic acid and biosilica were determined using the methods developed by Soil Research Institute (2009), while total acidity, carboxyl groups and phenolic groups of the amendments were determined using the method of Schnitzer and Desjardins (1965). The characteristics of the humic acid and biosilica are presented in Table 1.

Table 1. Characteristics of humic acid extracted from compost and biosilica extracted from rice husks.

Parameters	Humic acid	Biosilica
pH	7.21	9.65
Organic C (%)	0.32	0.01
Total acidity (meq g^{-1})	2.78	2.55
Carboxyl group (meq g^{-1})	0.03	nd
Phenolic group (meq g^{-1})	2.75	2.55
Total Pb (mg kg^{-1})	5.07	0.01
Total Cd (mg kg^{-1})	nd	nd

Note: *nd = not detected

Addition of heavy metals

Heavy metals (Pb and Cd) were introduced to the soil with a concentration of 40 mg Cd kg^{-1} and 400 mg Pb $kg^{-1,}$ referring to the heavy metal contents of polluted soil (Alloway, 2012). Lead was added in the form of $PbSO_4.7H_2O$, and cadmium was in the form of $CdCl_2.2H_2O$. The addition of the Pb and Cd was carried out simultaneously with the application of humic acid and biosilica to evenly distribute Pb and Cd in the soil. The addition of Pb and Cd made the soil contain available Pb of 328.31 mg kg^{-1} and available Cd of 45.97 mg kg^{-1}. According to Soil Research Institute (2009), the critical contents of Pb and Cd are 100-400 mg kg^{-1} and 3-8 mg kg^{-1}, respectively.

Treatments

Treatments tested in this study consisted of four doses of biosilica, i.e. 0 t ha^{-1} (S0), 0.5 t ha^{-1} (S1), 1 t ha^{-1} (S2) and 1.5 t ha^{-1} (S3), and four doses of humic acid, i.e. 0 kg ha^{-1} (H0), 20 kg ha^{-1} (H1), 40 kg ha^{-1} (H2) and 60 kg ha^{-1} (H3). The treatments were arranged in a factorial, completely randomized design with three replications. Each treatment of soil amended with humic acid and biosilica was incubated for seven days before planting rice seeds of Cibogo variety. The rice seedlings were planted after 15 days of seeding in trays. Before planting, each treatment received 120 kg N ha^{-1} (260 kg urea ha^{-1}), 22 kg P ha^{-1} (61 kg SP36 ha^{-1}), and 41.5 kg K ha^{-1} (69 kg KCl ha^{-1}) as basal fertilizers (Bijay-Singh et al., 1991). Each treatment pot was given 1.08 g of urea, 0.25 g of SP36 and 0.29 g of KCl. The fertilizers were applied in a circular manner at a distance of 10 cm from the center of the diameter of the pot (Nazirah and Damanik, 2015).

The rice plants were harvested 90 days after planting by slowly dismantling the plant from the pot (destructive). The harvesting process separated the plant into three parts: rice grains, rice stalks, and rice plant roots. Soil samples were taken using the sample destruction method. The plant samples were analyzed for total Pb and total Cd contents using the method of Soil Research Institute (2009). Soil samples were taken from the experimental pot at 7 and 90 days after applying amendments, with three repetitions per pot to represent the sample. Rice plants were harvested 75 days after planting or 90 days after applying amendments. The soil samples were analyzed for pH and contents of organic C, Pb, and total Cd using the method of Soil Research Institute (2009).

Data analysis

Data obtained from the experiment were subjected to analysis of variance (ANOVA) at an error rate of 5%. Tukey's HSD (Honestly Significant Difference) test at an error rate of 5% was performed to determine the effect of the applied treatments. Correlation analysis was also conducted to test the closeness and influence of each observed variable.

Results and Discussion

Observational data at 7 days (Table 3) showed that the results were not significantly different in Tukey's HSD test at $p<0.05$. Only pH and CEC data showed significantly different results with the treatment combination. The combination treatment did not have a significant impact on the soil after 7 days. There were significantly different results for soil pH and soil CEC. The maximum soil CEC value in the S1 treatment was 17.35 cmol(+) kg^{-1}. The CEC value of the soil changed from low to medium after the application of the amendments (Soil Research Institute, 2009). The effect of humic acid on soil pH was not significantly different at 7 days on the Tukey's HSD test at $p<0.05$, so the use of biosilica at a dose of 0.5 t ha^{-1} at 7 days was the optimal treatment. Biosilica tends to be more alkaline than humic acid, which has a pH value of 7.21.

However, the overall biosilica and humic acid treatments were able to increase the pH value. According to Gu et al. (2011), silica can increase the pH value from 4.0 to 6.2. The ability of silica to neutralize acidic pH is due to its ability to bind H^+ions which will form monosilicic acid compounds (H_4SiO_4) (Siregar et al., 2020). The application of biosilica and humic acid only increased the CEC value, but biosilica gave a significant response to the HSD test at $p<0.05$. The combination of biosilica and humic acid did not show any interaction, meaning that the effect of biosilica on CEC had appeared in 7 days. The biosilica treatment produced the highest CEC value at a dose of 0.5 t ha^{-1}. Silica treatment obtained from corn plant extract at a dose of 5% (w w^{-1}) also increased the initial soil CEC from 94 cmol(+) kg^{-1} to 100.3 cmol(+) kg^{-1} (Shim et al., 2014). However, the increase in soil CEC at the beginning of 7 days did not impact the entrapment of Pb and Cd. Evidence of heavy metal availability is not significant in each treatment. The interaction between biosilica and humic acid treatment after 90 days only affected the pH, organic C, and soil CEC with a significant difference at $p<0.05$. Humic acid treatment significantly affected soil chemical properties (pH, organic C, CEC, available Pb, and available Cd (Table 4). Treatments with 0.5 t biosilica ha^{-1} and 20 kg humic acid ha^{-1} gave optimal pH changes of 6.82 and 6.84. The last observation of soil media was carried out at 90 days. Several observation parameters showed significantly different results on Tukey's HSD test at $p<0.05$. Biosilica and humic acid treatments had different effects.

Table 2. Soil characteristics at 7 days after applying amendments.

Treatments	**pH**	**Organic C (%)**	**CEC (cmol(+) kg^{-1})**	**Available Pb (mg kg^{-1})**	**Available Cd (mg kg^{-1})**
Biosilica					
S0 = 0 t ha^{-1}	6.04 a	0.54	13.37 a	85.04	20.36
S1 = 0.5 t ha^{-1}	6.20 b	0.50	17.35 b	58.40	17.96
S2 = 1.0 t ha^{-1}	6.20 b	0.50	16.59 b	70.68	19.91
S3 = 1.5 t ha^{-1}	6.23 b	0.52	16.01 ab	63.66	17.13
Tukey's HSD at p<0.05	0.10	ns	2,73	ns	ns
Humic acid					
H0 = 0 kg ha^{-1}	6.15	0.54	15.58	99.12	22.11
H1 = 20 kg ha^{-1}	6.19	0.51	14.71	57.97	17.22
H2 = 40 kg ha^{-1}	6.18	0.52	16.66	61.27	18.54
H3 = 60 kg ha^{-1}	6.14	0.50	16.37	59.43	17.50
Tukey's HSD at p<0.05	ns	ns	ns	ns	ns

Note: numbers followed by the same letter show that the results are not significantly different in Tukey's HSD test $p<0.05$, ns = not significant, CEC (cation exchange capacity, HSD (Honestly Significant Difference).

Tukey's HSD test results at $p<0.05$ showed significantly different values in the biosilica treatment, including pH, organic C and CEC parameters. The humic acid treatment gave another response to Tukey's HSD test at $p<0.05$, in which all parameters pH, organic C, CEC, available Pb, and available Cd showed significant differences (Table 4). However, the interaction between biosilica and humic acid treatment did not occur in all parameters. Treatment of biosilica dose of 0.5 t ha^{-1} and humic acid dose of 20 kg ha^{-1} gave optimal changes in pH with values of 6.82 and 6.84 (Table 4). This is based on Tukey's HSD test at $p<0.05$ between all treatments. Soil organic C experienced a significant change at 90 days (Table 4), biosilica at a dose of 1.5 t ha^{-1} gave a maximum value of 1.04% and humic acid at 20 kg ha^{-1} gave an optimal yield of 0.92%. Changes in the organic C content impacted the cation exchange capacity of the soil. The increase in CEC value was due to the increased availability of soil organic C, which would form carboxyl groups and increase the adsorption complex (Bakri et al., 2016). This condition is supported by a regression graph (Figure 1) which produced R^2=0.6994, which means that organic C affected 69.94% of the CEC value of the soil. The increase in soil CEC was a sign of the effect of amendment application on increasing the absorption of Pb and Cd.

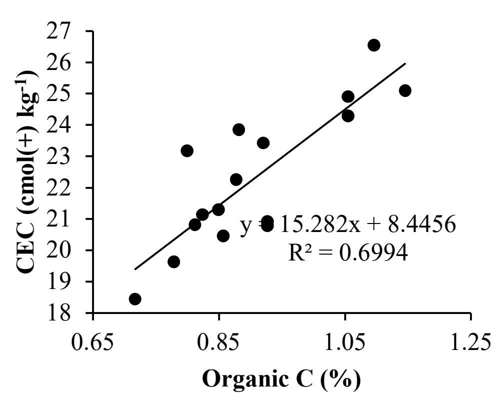

Figure 1. Effect of organic C on soil CEC.

The data obtained from the treatment of biosilica and humic acid gave different responses (Table 4). Humic acid treatment in one factor was able to provide a significant value to the availability of Pb and Cd metals. Although overall, the biosilica treatment also had an impact on decreasing the value of available heavy metals.

Humic acid dose of 40 kg ha^{-1} had the lowest effect on the availability of heavy metals Pb and Cd. Meanwhile, biosilica with a dose of 1.5 t ha^{-1} was the lowest for the availability of heavy metals. Changes in soil pH values are one of the causes of differences in the availability of heavy metals Pb and Cd. Increasing the CEC value and soil pH will affect the availability of heavy metals, where heavy metals will be deposited in alkaline soil pH conditions (Mahendra et al., 2018). Biosilica and humic acid treatments impacted changing the pH value of the soil from 5.73 to 6.41-6.84. The pH value, which changed from the initial criteria from slightly acidic to neutral, can cause changes in the formation of heavy metals. Soil heavy metals in available form occur at low soil pH conditions. Conditions and forms of availability of heavy metals vary according to the type of heavy metal. Cd has a low concentration when the soil pH is 7-8 but high when the soil pH is below pH 6 (Bruemmer et al., 1986). Pb concentration is minimal when the soil pH is between 5-6 and increases when it is below pH 4. Therefore, in general, the availability of heavy metals increases in soil conditions with very acidic pH values or extremely low pH (Bruemmer et al., 1986). The difference in the response of the two treatments could be caused by the characteristics of the amendments (Table 1). This is due to differences in the compound content of the carboxyl and phenolic groups of the two amendments.

Table 3. Soil characteristics at 90 days after applying amendments.

Treatments	pH	Organic C (%)	CEC (cmol(+) kg^{-1})	Available Pb (mg kg^{-1})	Available Cd (mg kg^{-1})
Biosilica					
S0 = 0 t ha^{-1}	6.41 a	0.78 a	20.60 a	50.63	14.63
S1 = 0.5 t ha^{-1}	6.82 b	0.86 a	20.84 a	42.47	12.19
S2 = 1.0 t ha^{-1}	6.83 b	0.95 b	24.62 b	39.58	12.95
S3 = 1.5 t ha^{-1}	6.72 b	1.04 c	24.70 b	37.77	12.04
Tukey's HSD at $p<0.05$	0.20	0.08	3.46	ns	ns
Humic acid					
H0 = 0 kg ha^{-1}	6.44 a	0.83 a	21.25 a	58.02 b	16.57 b
H1 = 20 kg ha^{-1}	6.84 b	0.92 b	21.56 a	38.17 a	13.12 ab
H2 = 40 kg ha^{-1}	6.77 b	0.92 b	25.11 b	31.23 a	10.88 a
H3 = 60 kg ha^{-1}	6.72 b	0.96 b	22.84 ab	43.04 ab	11.23 a
Tukey's HSD at p<0.05	0.20	0.08	3.46	19.27	4.52

Note: numbers followed by the same letter show that the results are not significantly different in Tukey's HSD test p<0.05, ns = not significant, CEC (cation exchange capacity), HSD (Honestly Significant Difference).

The content of the carboxyl group in humic acid is higher than that of biosilica, which has no carboxyl content detected. The carboxyl group is the main organic acid and is followed by other weak acid groups in humic acids (Jeong et al., 2007). The formation of carboxyl groups was higher in humic acid at pH 5 than at pH 7; this was a determinant of the ability of humic acids to bind heavy metals in the adsorption complex group (Boguta et al., 2019). The phenolic group became higher when the humic acid was at pH 7 (Table 1) than the carboxyl group. The phenolic group in biosilica was lower than that of humic acid (Table 1) and did not have a carboxyl functional group that has an important role in heavy metal absorption. At pH 2.5-7, the role of the carboxyl group is very important in metal adsorption, and at pH 8-13.5, the role of the phenolic -OH group in metal binding, but the bond is weak(Wang and Mulligan, 2009). While the bond in biosilica only occurs in the –OH group bond which will bind heavy metals (Lei et al., 2018). This makes the ability to bind biosilica lower than humic acid.

Pb and Cd uptake by the plant

The absorption of heavy metals in plant tissues occurs due to the pH value, organic C, and the availability of metals. Heavy metals are readily available under low pH conditions. Meanwhile, the high organic C content will cause heavy metals bound in the adsorption complex (Ismail et al., 2009). Accumulation of heavy metals in tissues occurs in 3 stages, (1) absorption by roots, (2) translocation of metals from roots to other parts, and (3) localization of metals in cells and tissues (Hardiani, 2009). Metal localization in plant cells and tissues explained that plants have the natural ability to accumulate heavy metals in certain parts, such as plant roots (Hardiani, 2009). This is evident in the graph showing the value of heavy metal uptake decreased from the roots to the grain of the plant. The concentrations of Pb and Cd in plant roots were higher than in other plant parts (Figures 2 and 3). In addition to the ability of plants, the application of amendment also supports the formation of a heavy metal isolation system in plant roots. The application of 0.5 t biosilica ha^{-1} and 1.5 t biosilica ha^{-1} significantly affected Cd uptake by plant roots. This dose gave no significant difference in the HSD test at $p<0.05$, so it can be conveyed that the use of a dose of 0.5 t ha^{-1} was more effective and efficient in treatment. These results are also the same as the conditions for Pb uptake in the roots.

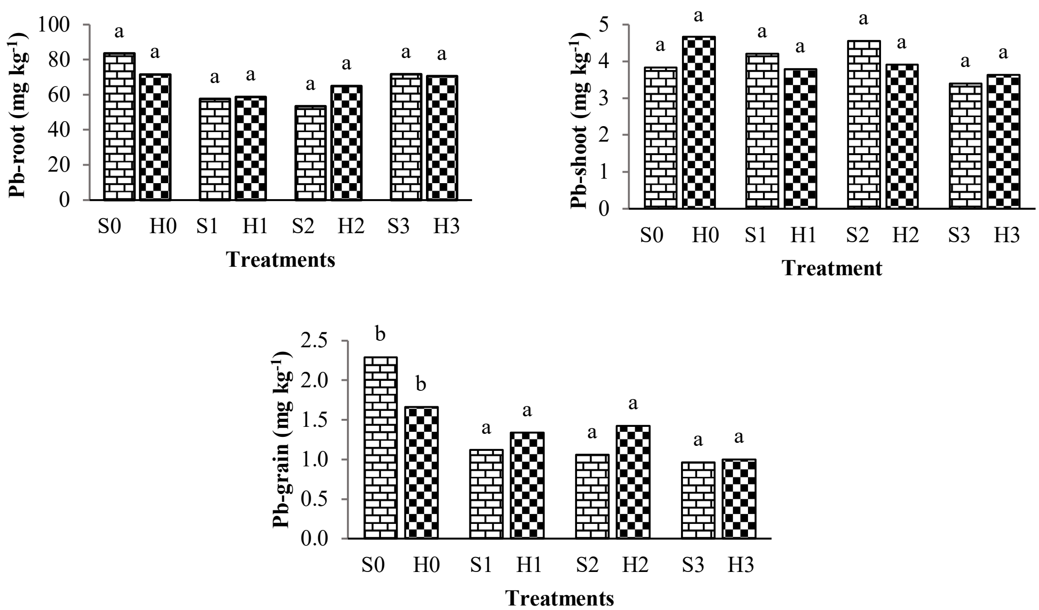

Figure 2. Effect of humic and silica on Pb uptake in roots, stem, and grains. Note: numbers followed by the same letter show that the results are not significantly different in Tukey's HSD test at $p<0.05$. S0 = 0 t ha^{-1}, S1 = 0.5 t ha^{-1}, S2 = 1 t ha^{-1}, S3 = 1.5 t ha^{-1}, S0 = 0 kg ha^{-1}, S = 20 kg ha^{-1}, S2 = 40 kg ha^{-1}, S3 = 60 kg ha^{-1}.

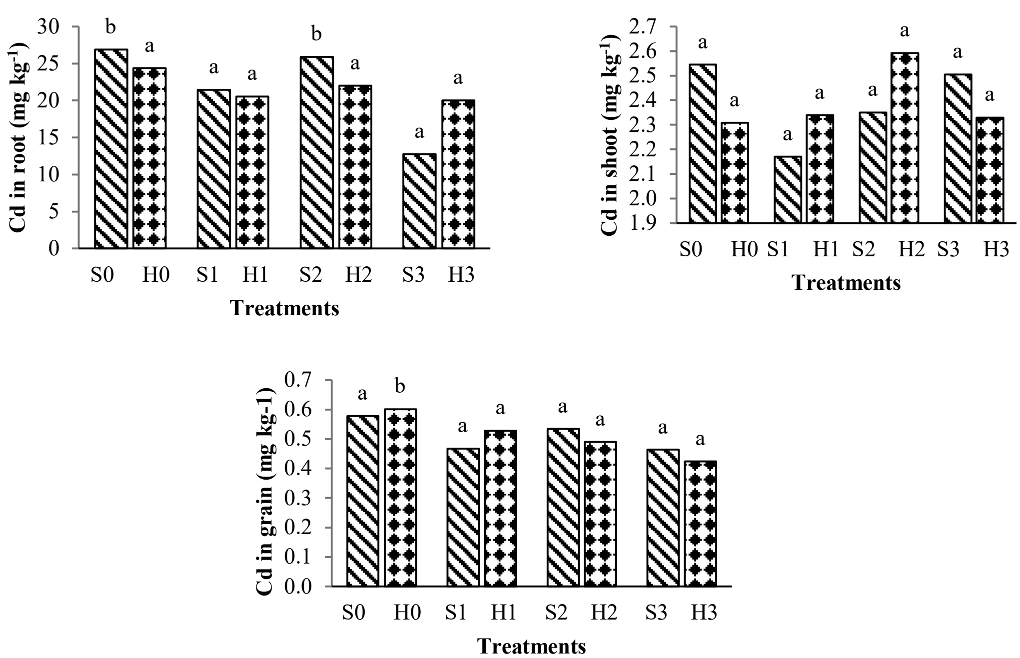

Figure 3. Effect of humic and silica on Cd uptake in roots, stem, and grains. Note: numbers followed by the same letters show that the results are not significantly different in Tukey's HSD test at $p<0.05$. S0 = 0 t ha^{-1}, S1 = 0.5 t ha^{-1}, S2 = 1 t ha^{-1}, S3 = 1.5 t ha^{-1}, S0 = 0 kg ha^{-1}, S = 20 kg ha^{-1}, S2 = 40 kg ha^{-1}, S3 = 60 kg ha^{-1}.

The absorption of heavy metals did not show a significant difference in both biosilica and humic acid treatments. Although the application of the soil amendments did not give significant results, it reduced the accumulation of Pb and Cd in the roots. This is in accordance with the research of Shafigh et al. (2016) that humic acid treatment is quite efficient in phytoextraction and translocation as well as increasing the absorption of Pb. Silica in plant root tissue has a role in increasing the production of root exudates, which will entrap the roots in the root area (Adrees et al., 2015; Imtiaz et al., 2016). The treatment of biosilica and humic acid was not significantly different to the Cd concentration in the stem on Tukey's HSD test at $p<0.05$ (Figure 3). However, the concentration of Pb and Cd in rice grains was significantly different in the 5% of Tukey's HSD test. The optimal dose of biosilica was 0.5 t ha$^{-1,}$ and humic acid was 20 kg ha^{-1} (H1). The decrease in the concentration of heavy metals in stems is due to the role of silica which is able to reduce the concentration of heavy metals so that they are not included in the xylem tissue and accumulate heavy metals in the endodermis so that they can suppress the mobility of heavy metals (Gu et al., 2011; Adrees et al., 2015). Cd in rice grains showed significant results in humic acid treatment, while biosilica did not show different results in each treatment. The application of humic acid can reduce the content of Cd in plant grains up to 11-30% compared to without humic acid (H0) treatment.

The optimal dose of AH was 60 kg ha^{-1} (H3) with the lowest Cd content. Biosilica could only reduce the Cd content from 8.62 to 20.68% compared to that without soil amendments (S0). Cd content in rice grains showed significantly high in humic acid treatments, while the application of biosilica did not show different effects in each treatment. Humic acid reduced Cd content in rice grains up to 11-30% compared to without humic acid (H0) treatment. Treatments of H1 to H3 did not give significant effects, so a dose of 20 kg ha^{-1} (H1) was taken as the optimal dose and 60 kg ha^{-1} (H3) as the dose that yielded the lowest Cd content. Biosilica was only able to reduce the Cd content from 8.62 to 20.68% compared to the value without soil amendments (S0).

Effectiveness of amendments for increasing Pb and Cd adsorption

The Pb and Cd adsorption abilities of the two soil amendments were different (Figures 4 and 5). At 7 and 90 days, the percentage of adsorption Pb and Cd increased for each treatment. The biosilica treatment at 7 days gave an insignificant difference in Pb and Cd adsorption with the control (S0) (Figures 4 and 5). In contrast, the application of humic acid showed a significant difference compared to the control (H0) on Pb adsorption (Figure 4) but not significant for Cd adsorption (Figure 5). The application of 20 kg humic acid ha^{-1} (H1) yielded the highest percentage of Pb adsorption of 82.34% (Figure 4), followed by humic acid treatments at 40 kg ha^{-1} (H2) of 81.34% and 60 kg ha^{-1} (H3) of 81.90%. This condition also occurred for Pb adsorption at 90 days (Figures 4 and 5), which showed that the biosilica treatment did not significantly affect Pb adsorption in the HSD test at $p<0.05$. The percentage of biosilica adsorption at 90 days ranged from 84.58 to 88.50% for Pb and from 68.19 to 73.49% for Cd. These values were still below that of the humic acid treatments. At 90 days, the humic acid treatments showed significant differences from each treatment (Figures 4 and 5). The uptake of Pb in the humic acid treatment of 20 kg ha^{-1} (H1) showed the optimal adsorption value because it was not significantly different from the dose of 40 kg humid acid ha^{-1} (H2) in the HSD test at $p<0.05$, although the percentage value of H2 (90.49%) was higher than H1 (88.37%). Vargas et al. (2016) reported a decrease in Cu after humic acid treatment to 47.13-76.79% at a dose of 10-20 kg ha^{-1} (Vargas et al., 2016). In addition, the use of humic acid extracted from compost is a cheap and environmentally friendly remediation technique (Piccolo et al., 2019). Although it did not show significant results in the percentage of adsorption, the addition of biosilica also supported the decrease in the availability of heavy metals.

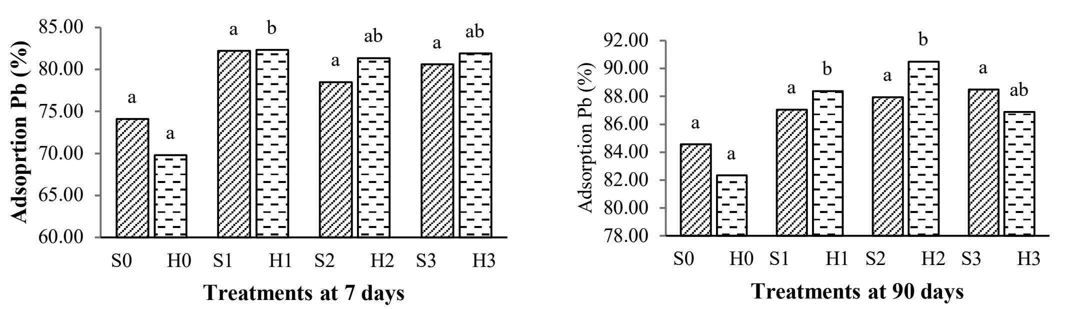

Figure 4. Adsorption of Pb at 7 and 90 days. Note: numbers followed by the same letters show that the results are not significantly different in Tukey's HSD test at $p<0.05$. S0 = 0 t ha^{-1}, S1 = 0.5 t ha^{-1}, S2 = 1.0 t ha^{-1}, S3 = 1.5 t ha^{-1}, S0 = 0 kg ha^{-1}, S = 20 kg ha^{-1}, S2 = 40 kg ha^{-1}, S3 = 60 kg ha^{-1}.

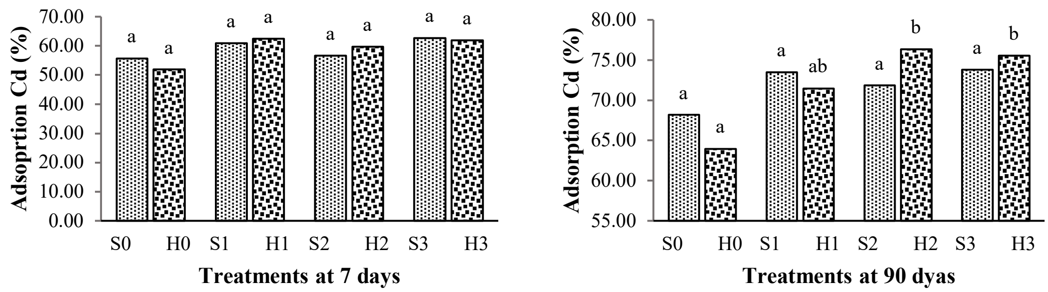

Figure 5. Adsorption of Cd at 7 and 90 days. Note: numbers followed by the same letters show that the results are not significantly different in Tukey's HSD test at $p<0.05$. S0 = 0 t ha^{-1}, S1 = 0.5 t ha^{-1}, S2 =1.0 t ha^{-1}, S3 = 1.5 t ha^{-1}, S0 = 0 kg ha^{-1}, S = 20 kg ha^{-1}, S2 = 40 kg ha^{-1}, S3 = 60 kg ha^{-1}.

The biosilica treatment decreased the availability of Pb by16.11-21.82% and Cd by 11.48-16.67% compared to the soil without amendments. These results are in line with the research carried out by Imtiaz et al. (2016) and Ning et al. (2016) that silica treatment with a dose of 1-2 t ha^{-1} can reduce the availability of Cd from 11.40 to 25.80%. The ability of humic acid to adsorb available metals is due to the very complex constituent factors of humic acid. Humic acid contains organic acid groups, which are complex and come from the final decomposition of organic matter (Tan, 2014). The bonding model of humic acid with heavy metals has 4 bonding models, namely (1) one of the –COOH groups reacts with metal ions to form an inorganic salt or monodentate complex. Reaction equation (2) describes a reaction in which one –COOH group and one –OH group react simultaneously with metal ions to form bidentate complexes. Reaction equation (3) Two nearby –COOH groups react simultaneously with metal ions to form bidentate complexes.

Equation (4) shows a situation where metal ions are bound due to electrostatic forces on water molecules which are bound to the C=O group of humic acid through hydrogen bonds (Yuliyati et al., 2016). The heavy metal adsorption method with silica is simpler than that of humic acid. It is known that biosilica has only –OH group in its compound. Silica binds to heavy metals through an adsorption system, which is a mechanism where heavy metals such as Pb will bind to the –OH present in the Si-OH group (Lei et al., 2018). The bonding conditions will make Pb metal which was initially available to be unavailable to plants. This is evidenced by the compound bond formula as follows (Vareda and Durães, 2017):

(1) $\equiv Si–OH + PbOH^{+} \rightarrow \equiv Si–OPbOH + H^{+}$;
(2) $\equiv Si–OH + Pb^{2+} \rightarrow \equiv Si–OPb^{+} + H^{+}$;
(3) $2(\equiv Si–OH)\ Pb^{2+} \rightarrow (\equiv Si–O–)_2Pb^{2+} + 2H^{+}$

The high phenolic –OH content without the presence of a carboxyl group makes the biosilica ability lower than humic acid. The carboxyl group will readily form bonds with metals in the pH range of 2.5-7 and form carboxylic bonds, while the phenolic OH groups will react at pH 8-13.5, but these bonds are weak to metals (Wang and Mulligan, 2009) and in particular, Pb will be easily bound to humic acid at neutral pH (Zhu et al., 2020).

Conclusion

The application of biosilica and humic acid showed positive results in increasing Pb and Cd sorption on a sandy loam soil. The role of amendment can be seen in the changes in the chemical properties of sandy soil. Treatment of biosilica 0.5 t ha^{-1} (S1) and humic acid 20 kg ha^{-1} (H1) was optimal for changes in soil chemical properties at 7 to 90 days. The value of pH, CEC, and organic C increased, and the availability of Pb and Cd decreased. The absorption of Pb and Cd in roots, stems, and grains of rice plants decreased. The combination of biosilica and humic acid was less effective for the effectiveness of metal adsorption. Humic acid treatment of 40 kg ha^{-1} (H2) had maximum effectiveness of Pb adsorption by 90.49% and Cd adsorption by 76.33%. The humic acid treatment of 20 kg ha^{-1} (H1) had optimal effectiveness of Pb adsorption value by 88.37% and Cd adsorption by 71.47%.

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