

# Application of humic substances and bottom ash compounds in improving soil quality in limestone post-mining land

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**Submission date:** 19-Jan-2022 04:21PM (UTC+0700)

**Submission ID:** 1744054713

**File name:** Musfira\_2021\_IOP\_Conf.\_Ser.\_Earth\_Environ.\_Sci.\_807\_022038.pdf (584.89K)

**Word count:** 4249

**Character count:** 20582

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To cite this article: Musfira *et al* 2021 *IOP Conf. Ser.: Earth Environ. Sci.* **807** 022038

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**Application of humic substances and bottom ash compounds  
in improving soil quality in limestone post-mining land**

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**Abstract.** Limestone mining leaves the ex-mine land with poor soil chemical quality. Humic substances can be used as fertilizer to increase macronutrient availability in the soil and improve pH. The application of coal ash can improve the soil's chemical, physical, and biological properties because it has a pH value, high organic C content, available P, and basic cations such as K, Na, Ca, and Mg. This research aims to determine the effect and interaction of humic substances and bottom ash interaction with different doses to improve soil quality after a limestone quarry. This research uses a randomized block design in a factorial pattern. This experiment consisted of humic substances (H) with 4 levels H0, H1 (0.09%), H2 (0.12%), and H3 (0.15%), and bottom ash (B) with three levels: B0, B1 (400 grams), B2 (600 grams). Humic substances at H2 concentration (0.15%) significantly increased C-organic, K, P-available, Mg-dd, and increased plant height. In contrast, bottom ash treatment at a B2 (600 grams) dose significantly affected the increase in C-organic, P-available, and Mg-dd. The treatment of humic substances with concentrations of H3 (0.15%) and bottom ash at a dose of 600 grams is the best interaction characterized by an increase in soil pH, CEC, Ca-dd, K, and Na. The application of a concentration of H3 (0.15%) and the provision of a dose of B2 (600 grams) or 120 tons/ha significantly affect the chemical properties of post-mining soils limestone and increase plant height.

## 1. Introduction

PT. Semen Bosowa has a limestone mining location with a mining business permit area of 749.14 ha, open land area for limestone which is 171,125 ha, the area of open land for marble is 48,375 ha. The area of land that has reclaimed until 2012 is 15,961 ha. The area of open land (the remaining land to be reclaimed) is 203,539 hectares [1].

Limestone mining leaves ex-mining land with poor physical, chemical, and biological soil conditions. This mining activity's impact causes the topsoil layer lost, and the available nutrient content is low and acidic pH of soil. The high rainfall activity caused nutrient leaching, low C-organic levels, high soil temperature, and decreased microbial diversity. Thus, the ex-limestone mining land has low soil fertility characteristics, both physically, chemically, and biologically. For this reason, management is needed as an effort to conserve the environment so that further damage does not occur. These efforts can be pursued by improving the quality of the soil. Soil conservation commonly used to increase fertility and soil improvement are cover crops, compost, manure, and green manure [2].



One form of compost that is currently widely used is humic compounds, which contain high nutrients. Humic compounds and coal ash can be used as fertilizer and soil amendment [3], especially in improving pH and increasing macronutrient availability in the soil. The higher the humic content in organic matter, the greater the ability to improve acidic soil pH and increase nutrient availability in the soil. Also, humic materials can form complex bonds with metal ions to reduce nutrient leaching through irrigation water and increase fertilizer efficiency [4].

Soil amendment from coal resulting from burning coal will produce bottom ash and fly ash. A mixture of fly ash and bottom ash is known as coal ash. About 5% of solid waste is generated from coal combustion in fly ash and bottom ash, about 10-20% is fly ash, and about 80-90% is bottom ash. The total ash produced beside is coal ash is one of the abundant materials available in abundance and abundance at mine sites. Therefore, coal ash is expected to improve the chemical, physical and biological properties of ex-mining land for planting with to support the success of reclamation activities [5].

Based on the description above, this research aimed to determine the effectiveness of humic compounds and coal ash with different doses on improving soil quality after limestone mining.

## 20. Methods

This research was conducted at Experimental Farm, Faculty of Agriculture, Hasanuddin University from September 2019 to January 2020; soil analysis was carried out at the Laboratory of Chemistry and Soil Fertility, Department of Soil Science, Faculty of Agriculture, Hasanuddin University, Makassar. Soil samples were taken from PT Semen Bosowa, in Baruga Village, Bantimurung District, Maros Regency, coal ash taken from PLTU Barru, in Lampoko Village, Balusu District, Barru Regency.

This research design using a two-factor factorial (F2F). This experiment consists of factors Humic (H) with 4 levels namely H0, H1 (0.09%), H2 (0.12%), and H3 (0.15%) or equivalent concentrations of 900, 1,200, and 1,500 ppm and the coal ash factor (B) with three levels: B0, B1 (400 grams), B2 (600 grams), equivalent to 0, 80, and 120 tons/ha. We have 12 total treatment combinations because each treatment combination repeated three times; the number of experimental units was 36 experimental units.

The research goes through two stages, namely the initial analysis and the final analysis. The initial study prepared humic compounds and coal ash with the Ahmad method [3] and soil sampling for post-mining soil. After that, planting is carried out for the final analysis stage, applying humic compounds and coal ash, sample analysis, to the conclusion stage. The first stage of extraction of humic compounds, namely, refines the source of humic compounds to 400 grams. It dissolved the source of humic compounds into KOH (0.1 / L) with a ratio of 1:10, which is 100 grams of compost and KOH solution 1,000 ml into Erlenmeyer. Shake the suspension using a shaker for the duration  $\pm$  3 hours so that the humate source is wholly dissolved, stirred, and let stand for 24 hours. The humate source solution is then filtered using filter paper. It separates the filtrate and the sediment by centrifuging it at 2,500 rpm for 15 minutes and then filtering it again using Whatman filter paper into a volumetric flask. The coal ash that has been taken then tested using the XRF method to determine the component elements.

The stages of preparation for planting include post-mining soil sample preparation, soil incubation, planting indicator crops, application of humic compounds and coal ash, and basic fertilizers. Observation Parameters Observation parameters for soil properties used in this study were: soil pH, soil organic C, Cation Exchange Capacity (CEC), available K, available P, cation bases (Ca, Mg, Na). The plant parameters used were plant height, number of leaves, plant dry weight, root dry weight, and root length.

### 3. Results and discussion

#### 3.1. Analysis of soil chemical properties characteristics before treatment

Soil analysis before treatment showed that pH value was considered acidic, C-organic with low criteria, CEC classified as moderate, cations such as Ca, Mg, K, and Na classified as low to moderate and available P classified as moderate (table 1). This is following the opinion of [6] that the negative impact of mining group C (limestone) minerals, among others, is that the soil layer becomes mixed with rock, an increase in bulk density (compaction) and soil moisture, as well as a decrease in soil permeability and fertility.

**Table 1.** Results of soil analysis before treatment.

Soil chemical properties	Value	Criteria
C-Organic	1.79%	* Low
Cation exchange capacity	18.4 mol / kg	* Medium
•Ca	5.09 cmol / kg	* Low
•Mg	1.14 cmol / kg	* Medium
•K	0.14 cmol / kg	* Low
•Na	0.15 cmol / kg	* Low
pH H <sub>2</sub> O	5.44	*acid
Available P(olsen)	15.67 ppm	* Moderate

#### 3.2. Analysis of the characteristics of soil chemical properties after treatment

3.2.1. *Soil pH.* Even though there was an increase in the pH of each treatment (table 2), it can be seen that the higher the dosage of humic substances and bottom ash, the increase in the pH value, although not significant. Ex-limestone mining area has undergone high and intensive washing and has poor soil chemical properties resulting in a high buffering capacity. It is recommended that ameliorants with high doses on the soil increase pH significantly [7].

**Table 2.** Soil pH after treatment.

Humic substances	Bottom ash			NP BNJ 0.05%
	BO (0 g)	B1 (400 g)	B2 (600 g)	
H0 (0%)	5.44 <sup>d</sup>	6.58 <sup>b</sup>	6.81 <sup>ab</sup>	
H1 (0.09%)	6.40 <sup>b</sup>	6.51 <sup>b</sup>	6.88 <sup>a</sup>	0.26
H2 (0.12%)	6.07 <sup>c</sup>	6.79 <sup>ab</sup>	6.91 <sup>a</sup>	
H3 (15%)	5.84 <sup>c</sup>	6.86 <sup>a</sup>	6.97 <sup>a</sup>	

Note: The numbers followed by the same letter in the rows and columns (a, b, c, d) are not significantly different on the BNJ level test  $\alpha$  0.05.

3.2.2. *C-organic.* The amount of C-organic content is in line with the content of the humic substance (table 3). The higher the humic substance of each treatment, the higher the C-organic content in the soil [8]. Straw can increase production by improving soil's chemical and physical properties, increasing levels of organic C, exchangeable K and Mg, soil cation exchange capacity (CEC), and available Si in the soil [9].

3.2.3. *Cation exchange capacity (CEC).* The addition of doses of humic substances and bottom ash tends to increase the value of soil CEC. The high cation exchange capacity (CEC) indicates that the treatment of humic substances and bottom ash on the post-mining limestone soil has increased cations such as Ca<sup>++</sup>, Mg<sup>++</sup>, K<sup>+</sup> (table 4). The CEC value is influenced by the decomposition process of each organic material, which produces humic substances that contribute to soil colloids so that the soil CEC will increase; this increase is also caused by the increase in the negative charge of soil colloids [10].

**Table 3.** C-organic soil after treatment.

Humic substances	Bottom ash			Average	NP. BNJ 0.05%
	B0 (0 g)	B1 (400 g)	B2 (600 g)		
H0 (0%)	1.79	2.20	2.11	2.04 <sup>b</sup>	0.12
H1 (0.09%)	1.36	1.86	2.25	1.82 <sup>c</sup>	
H2 (0.12%)	1.93	2.50	2.44	2.29 <sup>a</sup>	
H3 (0.15%)	2.04	2.63	2.56	2.41 <sup>a</sup>	
Average	1.78 <sup>y</sup>	2.30 <sup>x</sup>	2.34 <sup>x</sup>		
NP. BNJ 0.05%	0.09				

Note: The numbers followed by the same letter in columns (x, y) and rows (a, b, c) are not significantly different in the BNJ further test with confidence level  $\alpha$  0.05.

**Table 4.** Soil CEC after treatment.

Humic substances	Bottom ash			NP BNJ 0.05%
	B0 (0 g)	B1 (400 g)	B2 (600 g)	
H0 (0%)	18.41 <sup>d</sup>	19.50 <sup>d</sup>	20.68 <sup>cd</sup>	1.72
H1 (0.09%)	19.50 <sup>d</sup>	22.70 <sup>bc</sup>	22.13 <sup>c</sup>	
H2 (0.12%)	16.26 <sup>e</sup>	24.43 <sup>b</sup>	25.36 <sup>ab</sup>	
H3 (0.15%)	22.88 <sup>bc</sup>	25.36 <sup>ab</sup>	26.89 <sup>a</sup>	

Note: The numbers followed by the same letter in the row and column (a, b, c, d) are not significantly different in the BNJ level  $\alpha$  0.05.

3.2.4. *Available phosphorus (P<sub>2</sub>O<sub>5</sub>)*. The factor of giving humic substances the highest analysis results was treating H3 (humic substances 0.15%) with a P concentration of 20.10 ppm, which was classified as very high (table 5). According to Dariah and Nurida [11], the increase in P occurs due to the formation of complex Al compounds by decomposition of organic compounds, reducing Al-dd content, and reducing P adsorption by Al to increase P availability. Consequently, inorganic phosphorus ions will be released into the soil solution that plants will then absorb.

**Table 5.** Available phosphorus soil after treatment.

Humic substances	Bottom ash			Average	NP BNJ 0.05%
	B0 (0 g)	B1 (400 g)	B2 (600 g)		
H0 (0%)	15.67	17.98	18:21	17:29 b	2:20
H1 (0:09%)	15.81	19:32	17.71	17.61 b	
H2(12:12%)	15.88	19:17	20.70	18:59 ab	
H3-on (0.15%)	17:19	21:13	21.98	20:10a	
average	16:14y	19:40xy	x 19.65		
NP BNJ 0.05%	1.90				

Note: The number followed by the same letter in the column (x, y) and row (a, b, c) is not significantly different in the BNJ continued to test for the confidence level  $\alpha$  0.05.

3.2.5. *Exchangeable calcium (Ca-dd)*. The interaction with coal ash treatment maximizes the function of humic substances (table 6). Generally, coal ash is alkaline (pH 8-12); chemically, coal ash is an aluminosilicate mineral containing many elements such as Ca, K, and Na besides containing small amounts of elements C and N [12]. Other nutrients in coal ash that plants need include boron (B), phosphorus (P), and elements such as Cu, Zn, Mn, Mo, and Se and [6].

3.2.6. *Interchangeable magnesium (Mg-dd)*. The increase of Mg-dd value before treatment, the Mg-dd value of the soil was 1.14 cmol/kg, which was in the medium category, and after treatment was in the high category (table 7). The presence of bases causes the increased base's value to be exchanged through coal ash contributed by coal into the soil [13].

**Table 6.** Exchangeable calcium (Ca-dd) of soil after treatment.

Humic substances	Bottom ash			NP BNJ 0.05%
	B0 (0 g)	B1 (400 g)	B2 (600 g)	
H0 (0%)	5.09 <sup>d</sup>	6.72 <sup>cd</sup>	5.73 <sup>d</sup>	2.45
H1 (0.09%)	4.76 <sup>d</sup>	8.40 <sup>c</sup>	10.70 <sup>bc</sup>	
H2 (0.12%)	6.73 <sup>cd</sup>	10.68 <sup>bc</sup>	15.65 <sup>a</sup>	
H3 (0.15%)	8.76 <sup>c</sup>	12.07 <sup>b</sup>	13.69 <sup>ab</sup>	

Note: The numbers followed by the letters in the same rows and columns (a, b, c, d) are not significantly different in the BNJ level  $\alpha$  0.05.

**Table 7.** Interchangeable magnesium (Mg-dd) soil after treatment.

Bottom ash	Average	NP BNJ 0.05%
B0 (0 g)	2.00 <sup>a</sup>	0.37
B1 (400 g)	2.31 <sup>a</sup>	
B2 (600 g)	2.11 <sup>a</sup>	

Note: Numbers followed by the same letter in column (a) mean no significant difference in the BNJ level  $\alpha$  0.05.

3.2.7. *Potassium (K)*. The factors of humic substances and bottom ash significantly affect the concentration of potassium available in the soil. In giving coal ash, it can be said that the higher the dosage of humic substance and bottom ash, it can increase the potassium content in the soil (table 8). According to Arifin [14], coal ash is an aluminosilicate mineral containing Ca, K, and Na elements. Also, it contains small amounts of elements C and N. The Micronutrients in bottom ash that are needed in the soil included Cu, Zn, Mn, Mo, and Se. The potassium level available in the soil can be reduced because it is absorbed by plants [15].

**Table 8.** Potassium (K) available soil after treatment.

Humic substances	Bottom ash			Average	NP BNJ 0.05%
	B0 (0 g)	B1 (400 g)	B2 (600 g)		
H0 (0%)	0.14	0.18	0.21	0.18 <sup>d</sup>	0.018
H1 (0.09%)	0.20	0.21	0.25	0.22 <sup>c</sup>	
H2 (0.12%)	0.20	0.28	0.26	0.25 <sup>b</sup>	
H3 (0.15%)	0.21	0.31	0.30	0.27 <sup>a</sup>	
Average	0.19 <sup>y</sup>	0.24 <sup>x</sup>	0.25 <sup>x</sup>		
NP BNJ 0.05%	0.014				

Note: The number followed by the same letter in the column (x, y) and row (a, b, c) is not significantly different in the BNJ continued to test for the confidence level  $\alpha$  0.05.

3.2.9. *Sodium (Na)*. There was an increase in the available sodium value with the increase in the dosage of humic substances and bottom ash. However, the increase in available sodium concentration was not very significant (table 9). Soils that are dominated by alkaline cations such as Ca, Mg, K, and Na with high concentrations (high base saturation) will increase soil fertility because these nutrient elements are not easily leached by water [16].

### 3.3. Plant growth

3.3.1. *Average plant height (cm)*. The humic substances factor gave significant results on the height of maize plants, while the bottom ash factor did not give accurate results (table 10). When viewed from the physical condition of the plant, plants are stunted or slow to grow, both from the top (shoots) and bottom (roots) growth. Humic substances containing many micronutrients such as nitrogen can significantly affect plant weight, plant height, and leaf width [9].

**Table 9.** Sodium (Na) soil after treatment.

Humic Substances	Bottom ash			NP BNJ 0.05%
	B0 (0 g)	B1 (400 g)	B2 (600 g)	
H0 (0%)	0.15 <sup>d</sup>	0.23 <sup>c</sup>	0.25 <sup>bc</sup>	0.06
H1 (0.09%)	0.15 <sup>d</sup>	0.31 <sup>b</sup>	0.27 <sup>bc</sup>	
H2 (0.12%)	0.27 <sup>bc</sup>	0.36 <sup>ab</sup>	0.38 <sup>ab</sup>	
H3 (0.15%)	0.20 <sup>cd</sup>	0.40 <sup>a</sup>	0.40 <sup>a</sup>	

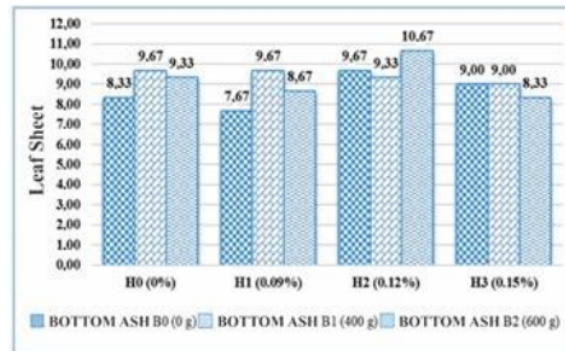
Note: The numbers followed by the same letter on the line and column (a, b, c, d) mean no significant difference in the BNJ level test  $\alpha$  0.05.

**Table 10.** Average plant height.

Humic substances	Bottom ash			Average	NP BNJ 0.05%
	B0 (0 g)	B1 (400 g)	B2 (600 g)		
H0 (0%)	26.00	26.33	23.00	25.11 <sup>b</sup>	3.40
H1 (0.09%)	16.87	34.00	24.33	24.87 <sup>b</sup>	
H2 (0.12%)	27.83	29.67	29.33	28.94 <sup>a</sup>	
H3 (0.15%)	19.83	30.67	24.00	24.38 <sup>b</sup>	

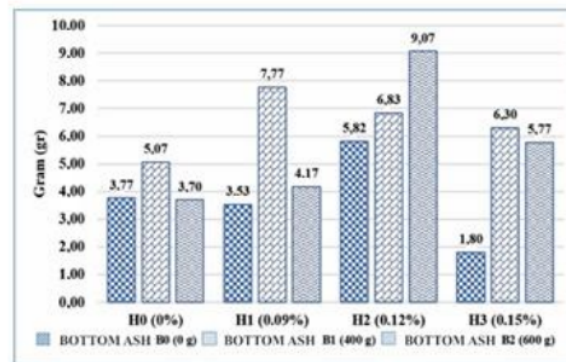
Note: The numbers followed by the same letter in rows and columns (a, b, c, d) are not different real at the BNJ level  $\alpha$  0.05.

3.3.2. *Plant leaves.* Based on the analysis of variance in the number of leaves after treatment, humic substances and bottom ash have no significant effect on the average number of plant leaves (figure 1). Soil analysis after treatment shows that the interaction between humic substances and bottom ash. Bottom ash shows significant results in the phosphorus in the soil, which is categorized as high enough, affecting the number of leaves in plants. Phosphorus plays a role in forming nucleic acids, energy transfer, and stimulation of enzyme activity. Therefore, an adequate supply of phosphorus can increase plant growth and production [17].



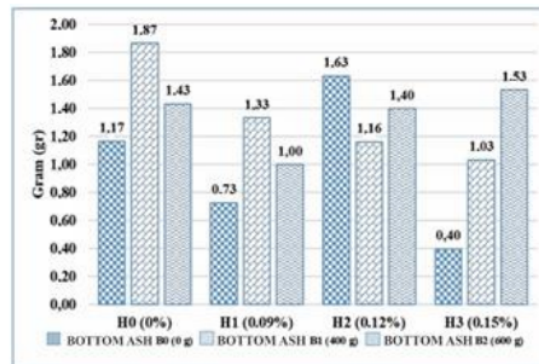
**Figure 1.** Average number of leaves.

3.3.3. *Plant dry weight.* The application of humic substances and bottom ash did not significantly affect the average dry weight of maize plants (figure 2). It can be seen that increasing the dosage of humic substances and bottom ash in mixing the composition of the planting medium can meet the nutrients needed by plants, such as plant weight and photosynthesis. The photosynthesis was indirectly influenced by nutrient availability [18].



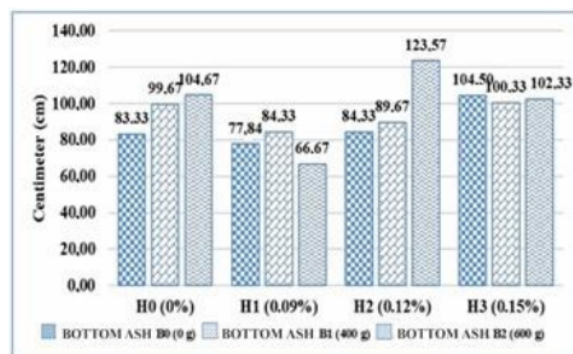
**Figure 2.** Average dry weight of maize plants.

*3.3.4. Dry weight of roots.* Application of humic substances and bottom ash did not significantly affect the average dry weight of plant roots (figure 3). Bottom ash can increase the pH value of the soil, which is positively correlated with plants, for example, with plant growth or plant weight. The application of humic substances triggers to increase nutrients in soil because it can activate soil microbes that function to accelerate the humification of stem and nitrogenase activity. It can help accelerate humus formation in plant root areas, changing nutrients in the form of organic metals that are more easily absorbed by plants through mass flow and diffusion processes and can improve physical soil conditions and accelerate plant root development [9].



**Figure 3.** Average dry weight of corn roots.

*3.3.5. Root length.* The application of humic substances and bottom ash did not significantly affect the average length of plant roots (figure 4). Humic compounds from organic matter indirectly increase soil porosity by increasing the activity of microorganisms so that it can stimulate root growth which will form a loose and crumbly structure, this is the physical condition of the soil that is good for root growth media, both mass and root length [18].



**Figure 4.** Average root length of maize plants.

#### 4. Conclusions

- Provision of humic substances of the straw compost had a significant effect on improving the chemical properties of soil from post-mining limestone soil by increasing C-Organic, P<sub>6</sub> available, K-dd, and increasing plant height. Application of bottom ash has a significant effect on improving the chemical properties of soil after limestone mining by increasing C-organic, P-available, Mg-dd and K.
- The combination of H3 (0.15%) and bottom ash with a B2 (600 grams) dose was the best interaction as amelioration material for soil from post-mining limestone.

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