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Potential solution in sustainable agriculture: improving the pH and pH buffering capacity of gray soil Acrisol from Cu Chi, Ho Chi Minh City, Vietnam using biochar combined with bentonite

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ABSTRACT

The acidification of agricultural soils should be avoided, and low pH soils should be corrected for better productivity. Soil improvement by applying biochar from agricultural byproducts combined with bentonite, a rich source in Vietnam, is a trend in green agriculture in the country. The current study is important in assessing the potential influences of biochar and bentonite on the pH and pH buffering capacity (pHBC) of low pH soil collected in Cu Chi, Ho Chi Minh City, Vietnam. Experimental methods, including biochar preparation (pyrolysis at 300°C, retention time: 2 h), soil incubation (time: 30 days, temperature: 27°C), and pH and pHBC determination, were performed. Research results have shown that biochar and bentonite have contributed to improving the pH and pHBC of gray soil samples. Using 1% bentonite and 1% biochar raised the pH to 6.21 and improved the pHBC of Cu Chi gray soil to 24.1 mmolH^+/OH^- kg^{-1}. This dose is currently suitable for agricultural production in Vietnam. The study confirmed the applicability of biochar derived from cow manure prepared at a low pyrolysis temperature in combination with bentonite to improve soil parameters such as pH and pHBC in Cu Chi gray soil.

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1. INTRODUCTION

Through various activities, such as intensive farming and excessive use of fertilizers, acid rain has accelerated the acidification of agricultural land, leading to reduced crop yields (Xu et al., 2012). These soils typically have low pH but high pH buffers, making them more difficult to improve and more expensive. The pH needed to ensure plant growth usually ranges from 6.0 to 7.0 (Penas & Lindgren, 1990). The pH buffer capacity (pHBC) of the soil is the main parameter that determines the rate of pH change during soil acidification. Greater pH buffering will result in slower pH changes, and pHBC can be used to predict soil acidification trends (Shi et al., 2017; Xu et al., 2012).

Soil pH affects the properties and the biological, chemical, and physical processes of the soil, there by affecting the growth of plants. Changing pH and pHBC depends on many factors, including cation exchange capacity (CEC), organic matter content (total organic carbon (TOC)), and the dissolution/precipitation and protonation/deprotonation reactions of minerals with variable electrical charges already present in the soil (Shi et al., 2017). Biochar is a product prepared from agricultural by products by pyrolysis in anaerobic conditions at temperatures of > 300°C. The common raw material for biochar is mainly waste from various sources, including cow dung (Piash et al., 2017; Yang et al., 2019). Currently, Cu Chi district, Ho Chi Minh City, Vietnam, has more than 26,870 cows, and the amount of cow manure is estimated at 50 tons/day; this will be a very valuable source of raw materials for producing biochar. In recent years, biochar has received attention for its potential to sequester carbon, improve soil fertility, and amend soil (Shi et al., 2017). Using biochar can increase soil pHBC and reduce soil acidity due to the contribution of organic salts present in biochar (Shi et al., 2017). Biochar is alkaline; however, its alkalinity varies depending on the characteristics of the raw materials and the pyrolysis temperature (Neina, 2019).

Bentonite, which mainly contains montmorillonite (a clay mineral of the smectite group), is considered a very good material for improving the characteristics of degraded soils (Czaban & Siebielec, 2013). Specifically, bentonite has the ability to increase clay content, porosity, water holding capacity, and pHBC significantly for soil (Hassan & Mahmoud, 2013). Vietnam has a rich and diverse source of bentonite. Monmontmorillonite reserves in Vietnam are very abundant, at about 5 million tons (grade 1) and 42 million tons (grade 2), and forecasted resources are about 350 million m^3. The gray soil of Cu Chi district formed mainly on pleistocene sediment. The soil layer is usually very thick, with a light mechanical composition and a very high percentage of sand grains (40%–90%). Furthermore, it is acidic, with a pH (H_2O) of < 5.5 and a pH (KCl) of approximately 4.0, so it is necessary to invest in improving its characteristics, especially the pH.

Soil pH plays an important role in providing nutrients needed for plant growth (Horrocks & Vallentine, 1999). To ensure optimum nutrient availability, the soil pH should be between 6.0 and 7.0. To consider the pH stabilization factor of Cu Chi gray soil, it is necessary to further investigate the pHBC of the soil when using biochar, bentonite, or a combination of both as an amendment. However, studies on this issue are still very lacking. Therefore, this study was carried out and aimed to determine the appropriate solution between using biochar, bentonite, or their combination to improve the soil pH and pHBC of Cu Chi gray soil.

2. MATERIALS AND METHODS

2.1. Materials

Cow dung samples were taken from a cow farm in Cu Chi province, Ho Chi Minh City, Vietnam. The location of the sampling site is 10˚58′17,8″N; 106˚34′29,8″E. The samples were let out to dry and were cut into smaller portions under 5 mm. They were then baked in an oven at 60°C for 24 hours (h) (Kiran et al., 2017).

2.2. Preparing biochar

The prepared cow dung samples underwent pyrolysis in a Nabertherm P330 furnace at 300°C. The heating rate was set to 10°C min^{-1}. Once the desired temperature was reached, the temperature was kept constant for 2 hours, and the samples were left to cool in the oven overnight. The biochar was then pressed through a plastic sieve (hole diameter of 1 mm) to make it homogeneous and stored separately in polyethylene (PE) containers in the dark at 4°C (Yoo et al., 2014).

Analyses were conducted on these biochar samples to determine the characteristics of surface functional groups, such as pH and pH_{pzc} (Trần, 2016), TOC (Walkley & Black, 1934), H^+/OH^- (Cheung et al., 2012), and the CEC based on the Vietnamese Standards (TCVN 8568:2010). Changes in the biochar's functional groups were analyzed using reflectance spectroscopy (FT/IR-4700 type A) with a 350–4000cm^{-1} resolution.

Soil samples were then taken to the Tan Thanh Dong Ward of Cu Chi district in October 2020 (Yoo et al., 2014). The bulk density, pH, and TOC of the soil were determined according to TCVN 8305:2009, ISO 10390:1993, and TCVN 8941:2011, respectively.

Table 1. Chemical composition of bentonite

Composition	Units	Content
pH	-	6.4
SiO_2	%	55.9
Al_2O_3	%	17.6
Fe_2O_3	%	2.85
$Na_2O + K_2O$	%	4.04
CaO + MgO	%	2.02
CEC	cmol/kg	70.3

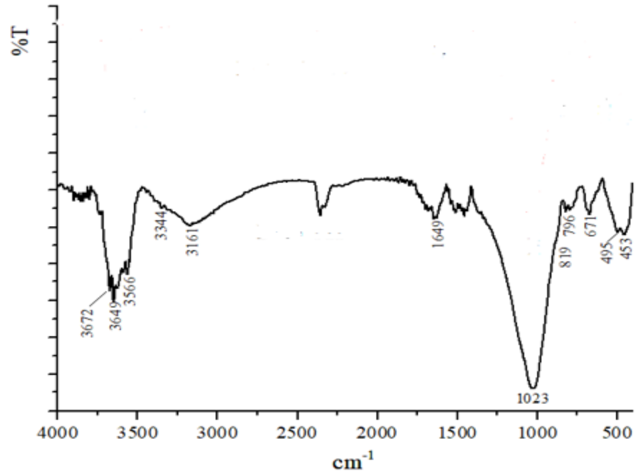

Figure 1. FTIR spectrum of bentonite samples (supplied by the company)

Soil samples were selected from the post-harvest vegetable growing area. Soil samples were taken at a depth of 0–10 cm, and the sampling area was 10 m in diameter. Five samples from the four corners and one sample from the diagonal center position were taken. These were mixed, and a composite sample was taken. Then, the soil sample was air-dried, crushed, passed through a 2-mm sieve, and stored at 4°C.

Bentonite was provided by Thanh Phuong Chemical Company Limited and the chemical parameters are presented in Table 1 (analysis sheet provided by the company).

Figure 1 shows that the 3672 and 3649 cm^{-1} peaks are typical for the valence vibrations of the -OH group associated with the metals in the clay layer (Al^{3+}, Fe^{3+}, Mg^{2+},...) of the octahedron. Oscillations of the -OH group in free or adsorbed water molecules on the surface or in the middle of the layer appear at positions 3161 and 1649 cm^{-1}. The peak at 1023 cm^{-1} characterizes the Si–O valence vibrations in the tetrahedron. Figure 1 shows the existence of -OH groups and Si-O groups, which will contribute to the increase of pHBC. Moreover, basic cations such as Ca^{2+} and Mg^{2+} of bentonite can adhere to the soil surface and participate in exchange reactions, replacing Al^{3+} and H^+, which reduce pH fluctuations (Becerra-Agudelo et al., 2022). Therefore, the use of this bentonite sample for the pH and pHBC improvement of soil is appropriate.

2.3. Chemicals

All chemicals used in the study were analytically pure chemicals (Merck), which include KCl, HCl, NaH_2PO_4, NaOH, HNO_3, NaOH, and H_2O_2. Distilled water used in the experiments was produced with an ultra-clean water purifier (EASYpure II RF from Thermo Scientific, USA).

2.4. Experimental design

2.4.1. Incubation Experiment

The incubation process is simulated according to Shi et al. (2017) and the treatments include: 0. Soil (control sample); 1. Soil and biochar (ratios: 1%, 3%, and 5%); 2. Soil and bentonite (ratios: 1%, 3%, and 5%); 3. Soil, 1% bentonite, and biochar (ratios: 0.5%, 1%, 3%, and 5%).

The soil sample (120 g) was air-dried, placed in a PE beaker, and mixed with biochar or bentonite according to the listed treatments. All mixtures were wetted with deionized water to 60% soil moisture at an ambient temperature (27°C), and covered with a lid with a small hole perforated to prevent excessive water loss. The samples were incubated for 30 days. The samples were weighed and watered throughout the incubation period to maintain constant 60% moisture content at 3-day intervals. The experiment was repeated three times for each treatment. After incubation, the soil samples were air-dried and ground through a 2-mm sieve to determine the pH and pHBC (Shi et al., 2017; Xu et al., 2012).

2.4.2. Determination of pH and pHBC of soil samples

2.4.2.1. Determination of pH

The pH of the treated soil samples was determined using Hanna's pH meter, HI98190, when they were equilibrated with distilled water in a 1:5 solid-to-liquid ratio by shaking and standing both for 1 h (ISO 10390:2005).

2.4.2.2. Determination of pHBC of soil samples

The experimental model is simulated from the study of Xu et al. (2012), and the pH buffer of the soil sample was determined by the titration technique. Soil samples were established by adding a series of standard concentrations of HCl or NaOH of known concentrations to the soil suspension at a 1:5 solid-to-liquid ratio. The addition of HCl or NaOH was adjusted, depending on the initial soil pH, to make the titration curve range from 4.0 to 7.0. Specifically, 4 g of the soil sample were transferred into six 50-mL PE tubes, and deionized water was added to a final volume of 20 mL after adding 0.04 M HCl or NaOH (standard solution) to have a chain of tubes with a pH range of 4.0–7.0. To increase dissociation and inhibit microbial activity, 1.0 mL of 0.04 M $CaCl_2$ and 0.25 mL of chloroform were added to each tube.

The suspensions were shaken for 24 h at 25°C and equilibrated for another 6 days. During that time, the suspensions were shaken daily for 2 min. At the end of 6 days, the pH of the solution was measured. The pHBC of soil samples was calculated from the slope of the linear part of the acid–base titration curves (Shi et al., 2017; Wang et al., 2015; Xu et al., 2012).

2.5. Data processing

The collected data were statistically processed using Excel. To minimize the sources of error, duplicate samples were used in the analysis to evaluate accuracy and bias. Experiments and analyses were repeated three times. SPSS 22.0 was used to determine the homogeneity of variance, and Tukey's test post hoc was used to determine the difference in mean values between experiments with $p < 0.05$ by when Sig > 0.05 or Tamhane when Sig < 0.05.

3. RESULTS

3.1. The properties of soil and biochar

Table 2 shows the results of some properties of the soil sample, as follows: the soil sample had a pH of 5.5 in the form of medium-acidic soil; bulk density and density were 1.40 and 2.54 g/cm^3, respectively, in the group with a light-medium mechanical composition.

The results from the analysis on a FT/IR-4700 type A spectrometer (Fig. 2) showed a peak at 3500–3000 cm^{-1} for biochar produced at 300°C. This suggests the presence of a large -OH functional group. The peak at 1590–1520 cm^{-1} happened due to COO- bonds. The peak at 1160–1020 cm^{-1} is speculated to be caused by the vibration of polysaccharide or carbonate (CO_3^{2-}) C-O-C bonds.

The results of the study on biochar recovery efficiency and some surface physicochemical components of biochar are detailed in Table 3. The results showed the pyrolysis temperature of 300°C, the TOC content were 36.7 %; pH 7.91; pHpzc 7.43, number of acid functional groups (H^+) were 5.14 mmol H^+ g^{-1} and number of basic functional groups (OH^-) 11.3 mmol OH^- g^{-1}, CEC was determined as 313 mmol kg^{-1}.

3.2. Effect of biochar addition on soil pH and pHBC

As shown in Figure 3, acidic soil samples (low pH) improved when biochar was added. Specifically, the soil without biochar had a pH of 5.5 and 5.3; 6.0 and 6.5 corresponding to the amount of biochar added to the soil at 0%, 1%, 3%, and 5%, respectively.

Table 2. Some properties of soil

Element	Unit	Results	SD
Particle Density	g/cm^3	2.54	0.08
Bulk density	g/cm^3	1.4	0.1
pH	pH	5.5	0.1
TOC content	%	3.2	0.5
Clay content	%	8.8	0.2
CEC	cmol/kg	8.3	0.1

Remark: SD: standard deviation

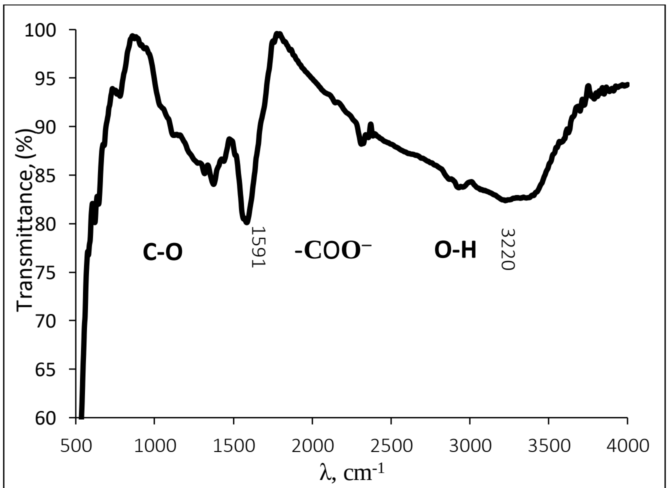

Figure 2. FTIR spectrum of biochar 300°C

Table 3. Recovery efficiency and some surface physicochemical components of biochar

t °C	%H	pH	pHpzc	mmol H^+ g^{-1}	mmol OH^- g^{-1}	%TOC	CEC, mmol kg^{-1}
300	63.0	7.91	7.43	5.14	11.3	36.7	113
SD	1.7	0.03	0.1	0.1	0.1	5.3	12

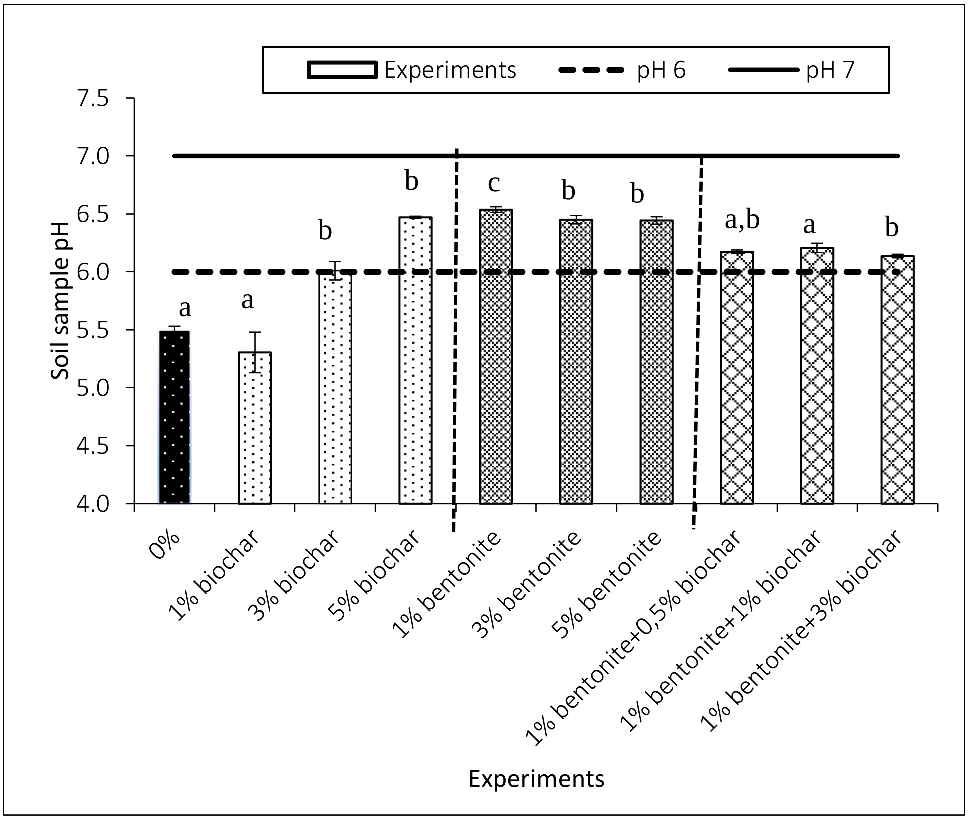

Figure 3. pH of the treatments
Remark: letters [a, b, c, d] and d represent statistically significant differences

In addition, according to the research results, when 1% biochar is added, its pH decreased compared with that of the control sample. This confirms that the alkaline content of biochar is not the only parameter that changes the pH of the soil, but there may also be mineralization of organic compounds containing N. Similar results were found in Shetty & Prakash's study for bamboo-derived biochar (10 tons ha^{-1} application) (Shetty & Prakash, 2020).

When adding 300°C biochar to the soil (Fig. 4), the pHBC of the soil sample increased. Specifically, when biochar was not added, the soil had a pHBC of 12.3, but when biochar was added at ratios of 1%, 3%, and 5%, the pHBC was 10.1, 12.1, and 12.4 mmolH^+(OH^-) kg^{-1}, respectively.

3.3. Effect of bentonite addition on soil pH and pHBC

As shown in Figure 4, the pH of the soil sample increased when bentonite was added. Specifically, the soil without bentonite had a pH of 5.5 and 6.5, 6.4 and 6.4, when the amount of added bentonite increased by 0%, 1%, 3%, and 5%, respectively. At the 1% bentonite ratio, the pH value of the soil sample was highest compared with no addition, the rate of 3 or 5%. Its pH value differs statistically.

As shown in Figure 3b, in the soil supplemented with bentonite, increasing the amount of bentonite from 1% to 3% significantly increased the pHBC; however, there was no significant increase between 3% and 5%. Specifically, the pHBC increased by 11.3, 31.2, and 41.4 mmol H^+(OH) kg^{-1} corresponding to 1%, 3%, and 5%.

3.4. Effects of the addition of 1% bentonite combined with biochar

Research results on the addition of 1% bentonite to the soil combined with biochar at the rates of 0.0%, 0.5%, 1.0%, and 3.0% are presented in Figure 3. All treatments gave a suitable pH for plant growth (Horrocks & Vallentine, 1999). When increasing the rate of biochar by 0.5% and 1%, the pH decreased significantly compared with no addition of biochar. Only when the amount of biochar was increased to 3% did the pH increase significantly compared with 0.5% and 1%, but the pH remained lower than when not adding biochar. This can be explained by the mineralization of organic compounds containing N (Shetty & Prakash, 2020). In addition, bentonite has the ability to adsorb both cations and anions because the silicate structure is negatively charged on the outside surface and Al_2O_3 is positively charged on the inside surface (El-Nagar & Sary, 2021), which has the effect of reducing the pH of the soil when biochar is added.

Unlike the process of improving pH, when 1% bentonite combined with 0%, 0.5%, 1.0%, and 3.0% biochar were added to the soil (Fig. 4), the pHBC increased significantly (11.3, 17.2, 24.1, and 31.9 mmol H^+(OH^-) kg^{-1}, respectively).

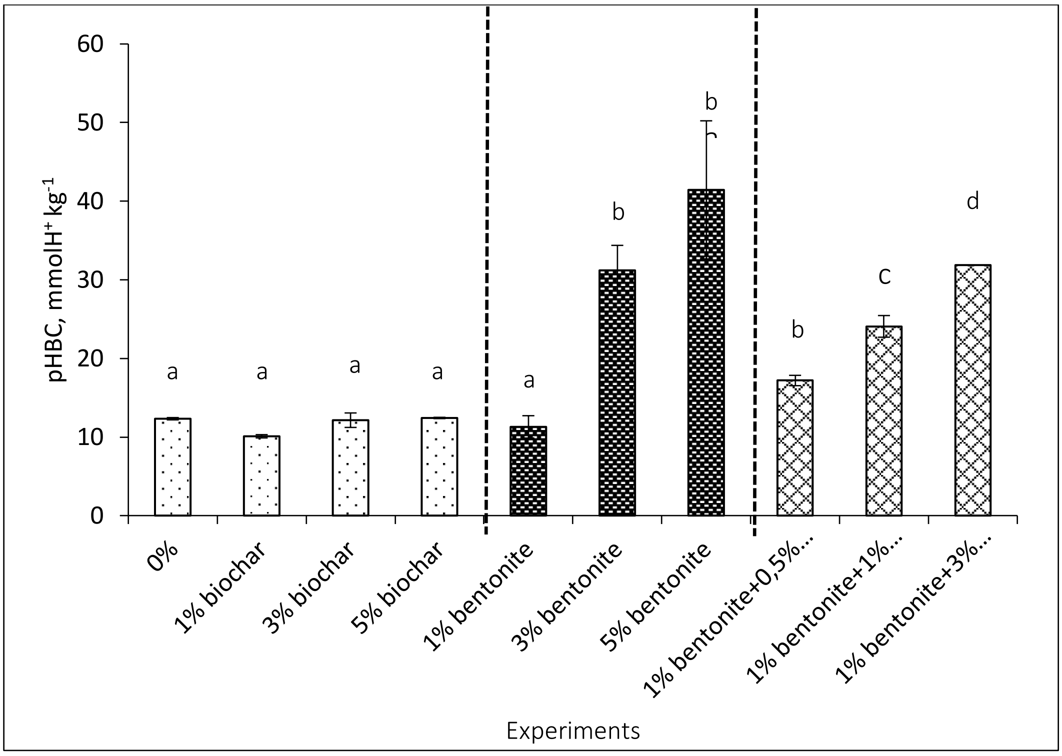

Figure 4. pHBC of the treatments
Remark: letters [a, b,c, d] and d represent statistically significant differences.

4. DISCUSSION

4.1. The properties of soil and biochar

The results shown in Table 2 (bulk density of 1.53 g cm^{-3}) are similar to the results of the study of Duong et al. (2017). The TOC content in the soil was 3.2%, which is within the average organic content according to the Vietnam Soil Science Association. The results showed that the soil has a low clay content (10%) and low CEC (<10 cmol kg^{-1}), which indicate that the soil is susceptible to leaching, has a low moisture, and has a low nutrient holding capacity (Table 2).

The results from the analysis on a FT/IR-4700 type A spectrometer (Fig. 2) showed the presence of a large -OH functional group, COO- bonds, and C-O-C bonds in polysaccharide or carbonate (CO_3^{2-}) compounds. These results have shown that the use of biochar pyrolysis at 300°C, which contains OH, COO- groups on the surface, can improve the pH and pH buffering capacity of the soil (Shi et al., 2017).

4.2. Effect of biochar addition on soil pH and pHBC

The results in Figure 3 show that when adding biochar to the soil, pH improved. Similar research results were also found in the study of Yuan et al. (2011), suggesting that the increase in pH of the treatments when increasing the amount of biochar could be due to an increase in the alkalinity of the biochar. Analysis of the average values of pH when adding biochar showed that with the addition of 0% and 1% biochar, the difference was not statistically significant, except for 3% (Fig. 3), although the difference was not significant between 3% and 5%. Similar results were found in Shetty and Prakash (2020) for biochar derived from bamboo and rice husk at rates of 10 and 20 tons ha^{-1}. The obtained results show that the addition of 3%–5% biochar to the soil is suitable for the growth of vegetables in Cu Chi (pH 6.0–7.0) (Penas & Lindgren, 1990).

The results in Figure 4 show that when adding biochar to the soil, the pHBC of the soil sample increased. Analysis of the difference in mean values of pHBC when adding biochar showed that the difference in treatments was not statistically significant. Research results showed that using biochar at the rates of 3% and 5% improved pH but did not show a significant improvement in pHBC.

Biochar derived from cow dung pyrolysis at 300°C, when used to amend Cu Chi gray soil, showed a positive correlation with pH and pHBC. However, the degree of correlation with pH is stronger than pHBC. There is also a positive correlation between pH and pHBC in the use of biochar (Table 4).

Table 4. Correlation between biochar, pH, and pHBC

	Biochar	pH	pHBC
Biochar	1	0.939**	0.887**
pH		1	0.809**
pHBC			1

Remarks: ** Correlation is significant at the 0.01 level (2-tailed).

Table 5. Correlation between bentonite, pH, and pHBC

	Bentonite	pH	pHBC
Bentonite	1	0.615*	0.932**
pH		1	0.432
pHBC			1

Remarks: * Correlation is significant at the 0.05 level (2-tailed);
** Correlation is significant at the 0.01 level (2-tailed).

Research results confirm that the use of biochar derived from cow dung pyrolysis at 300°C can both improve pH and increase the pHBC of Cu Chi gray soil. However, the degree of improvement and the amount of biochar used are factors to consider. With a rate of 3%, the amount of biochar needed is approximately 40 tons ha^{-1}, which is too large and very difficult to do. Therefore, the study of using bentonite was considered.

4.3. Effect of bentonite addition on soil pH and pHBC

The results showed that the alkalinity from bentonite has the ability to improve pH (Fig. 3). This is explained by the presence of -OH groups on the bentonite surface, and these groups are able to accept protons from the soil. When the percentage of bentonite was increased to 3.5%, the pH of the soil sample did not increase. This is explained by the increase of free cations such as Ca, Mg, Fe, or Al that exchanged the protons of some organic substances in the soil and caused the soil pH to decrease a little. On the other hand, it is also possible that high-valence cations such as Fe^{3+} or Al^{3+} are hydrolyzed. Similar results are found in the report of Chittamart et al. (2018), who found that bentonite can only raise the pH up to 6.0. This pH value is recommended to limit the dissolution of Al, which can be toxic to plant roots.

With soil supplemented with bentonite (Fig. 4), when increasing the amount of bentonite from 1% to 3%, the pH buffering capacity increased significantly; however, between 3% and 5%, there was no significant increase. Specifically, the pHBC increased by 11.3, 31.2, and 41.4 mmol $H^+(OH^-)$ kg^{-1} corresponding to 1%, 3%, and 5%. This can be explained by the fact that on the bentonite surface, there are -OH groups that have the ability to accept or donate protons. The basic characteristic of bentonite is its ability to exchange ions because, on the surface of the clay layers, there are negatively charged (O, OH) centers, which are capable of adsorbing and exchanging cations. A similar explanation was also found in the study of Shi et al. (2017)., who suggested that pHBC changes depend on many factors, such as CEC and the protonation/deprotonation reactions on variable charge-containing minerals. The Al content on the bentonite surface is directly related to CEC and has a great influence on pHBC (Chittamart et al., 2018).

However, the level of 3%, corresponding to about 45 tons ha^{-1}, is not feasible for the application. Moreover, the increase in bentonite percentage means an increase in clay content, which will increase soil bulk density and reduce soil porosity, which, in the long run, will be detrimental to plant growth. A similar explanation has also been found in the results of El-Nagar and Sary (2021). Therefore, the selection of 1% bentonite combined with biochar with the desire to increase the pHBC was made.

Using bentonite to improve Cu Chi gray soil showed that the percentage of bentonite addition was positively correlated with pH and pHBC, but the degree of correlation with pH was not high. The correlation between pH and pHBC in the process of using bentonite is also proportional but low.

Research results have confirmed that bentonite can partially improve pH and can improve the pHBC of Cu Chi grey soil very well.

Table 6. Correlation between biochar, pH, and pHBC when the soil has pre-added 1% bentonite

	Biochar	pH	pHBC
Biochar	1	−0.465	0.939**
pH		1	−0.701*
pHBC			1

Remarks: * Correlation is significant at the 0.05 level (2-tailed); ** Correlation is significant at the 0.01 level (2-tailed).

4.4. Effects of the addition of 1% bentonite combined with biochar

Unlike the process of improving pH, when 1% bentonite combined with 0%, 0.5%, 1.0%, and 3.0% biochar were added to the soil (Fig. 3), the pHBC increased significantly. The pHBC is attributed to the protonation and deprotonation of the oxygen-containing functional groups of biochar as they interact with bentonite. This process increases the pH buffering capacity of the soil (Xu et al., 2012).

In the analysis of the correlation between the percentage of biochar, pH, and pHBC when the soil contains 1% bentonite to improve Cu Chi gray soil shows that biochar is negatively related to pH but at a low level and positively related to pHBC at very hight levels. There is also a positive correlation between the pH and pHBC only at a tight level (Table 5).

The correlation analysis results confirmed that using 1% bentonite combined with biochar at different ratios slightly reduced the pH but increased the pHBC of the Cu Chi gray soil very significantly (Table 6).

In general, all treatments gave a pH in the range of 6.0–7.0 suitable for plants, except for the treatments without adding and adding 1% biochar (Fig. 3).

However, the treatments, including 3% and 5% biochar, 3% and 5% bentonite, and 1% bentonite combined with 3% and 5% biochar were not suitable because the amount used was too large when applied in the field (range: 40–65 tons ha^{-1}).

The treatments of 1% bentonite and 1% bentonite combined with 0.5% and 1.0% biochar were further reviewed to evaluate the pHBC. The results in Figure 3 and Figure 4 show that the treatment of 1% bentonite combined with 1% biochar was suitable for improving the pH and pHBC of Cu Chi gray soil.

5. CONCLUSION

Gray soil and cow manure (Cu Chi District, HCMC) were collected. Cow manure has been prepared at temperatures of 300°C. The physicochemical properties of the soil (bulk density, density, pH, TOC) and biochar (recovery yield, TOC, pH, pHpzc, the number of H^+/OH^- groups, OH-, CEC) were determined. Research results show that biochar derived from cow dung pyrolysis at 300°C and bentonite both improve the pH and pHBC of Cu Chi gray soil. The process of combining 1% bentonite and 1% biochar both improves soil pH and increases pHBC, which is suitable for cultivation conditions. Research results have confirmed that the combination of bentonite and biochar derived from cow dung pyrolysis at 300°C to amend Cu Chi gray soil is based.

Declaration of Competing Interest

The authors declare that no competing financial or personal interests that may appear and influence the work reported in this paper.

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