

Effects of rice husk biochar and calcium amendment on remediation of saline soil from rice-shrimp system in Vietnamese Mekong Delta: Results from laboratory experiment

ABSTRACT

In a rice-shrimp system in Vietnamese Mekong Delta, more effective techniques are required to remediate the saline soils. The objective of this study was to evaluate the reclamation potential of biochar and calcium in laboratory experiments using a saline soil sample from the rice-shrimp system. Our hypothesized was that the addition of biochar might improve the infiltration rate and more efficiently remove salts, in particular sodium, from the saline soil. The experiment was set up with two kinds of rice husk biochar at rates of 0 and 50 g kg⁻¹ combining with three levels of CaO (0, 0.5 and 2 g kg⁻¹ soil, equivalent to 0, 0.5 and 2 t ha⁻¹, respectively). Results indicated that biochar enhanced significantly drainage speed by 4 times compared to control without biochar. After leaching, exchangeable sodium percentage (ESP) in the soils was significantly lower in biochar treatments than in control. Some other chemical indicators (K:Na and Ca:Na ratios) were also higher in biochar treatments. Although both biochars effectively removed salts in the saline soil, biochar with a lower Na⁺ adsorption capacity, a lower surface area and a higher amount of salts performed better in removing Na⁺ from soil. Combined application of biochar and CaO at the low dose was more effective in improving soil properties related to Na⁺ leaching and ESP.

Keywords: organic amendment, salt leaching, sodium adsorption, soil reclamation

1. INTRODUCTION

Rice-shrimp cultivation has been performed in some decays in the Mekong Delta (MD), Vietnam. In the MD, drought and salinity have been considered to be more important than flood damage to agricultural crops [1]. In some areas, paddy rice has been changed to upland crops in order to adapt to water shortage or changed to a rice-shrimp system in order to adapt to salinity. Rice-shrimp farming has adapted to the natural conditions in brackish zones by growing rice in the wet season, then using the rice fields for growing shrimp in the dry season, when water salinity is too high to grow paddy rice. Under limitation to expand further rice-land and the strong economic value of shrimp, the Vietnamese Government first promoted rice-shrimp cultivation in 2001 [2]. The total areas of rice-shrimp in the MD has increased from 71,000 ha in 2000 to 153,000 ha in 2014 and contributed to 18% of total areas cultivating brackish shrimp in the MD [3]. It is estimated that rice-shrimp cultivation will take over areas of paddy rice having low yields due to salinization and increases to 200,000 ha in 2020 [3].

For rice cultivation in a rice-shrimp system, it is essential to reduce the salinity in the soil to a suitable level for rice growing in the rainy season. Currently, farmers have to pump fresh

water into fields, wait for some days and then pump out the water. This process is repeated several times to reduce salinity from the soil and requires a huge amount of fresh water, in spite that many of these areas do not have enough fresh water during that period. Thus, some techniques to improve this salinity washing process are necessary to save time and water in salinity washing.

Recently, application of biochar (a solid material produced from biomass pyrolysis under low/no oxygen environment) to agriculture has received attention. Biochar amendment to soil has been described as a promising tool to improve soil quality, sequester carbon and mitigate greenhouse gas emissions [4-10]. However, most studies have evaluated benefits of biochar incorporation in non-saline soils while the application of biochar to salt affected soils has received less attention [11-13]. In addition, biochar may improve chemical and physical properties of saline soils since it can be a source of elements such as Ca^{2+} and Mg^{2+} [13-15], which aid in Na^+ exchange and improve soil structure more suitable for sodium leaching. Therefore, application of biochar to salt affected soils needs more attention and further investigation. The objective of this study was to investigate the effects of biochar and calcium amendments on alleviating constraints in saline soil under laboratory conditions.

2. MATERIAL AND METHODS

2.1. Materials

Soil with a high electrical conductivity (EC) value was collected from a rice-shrimp field in the Mekong Delta and used for salinity leaching experiments. Two rice husk biochars, one laboratorial product from College of Environment and Natural Resources, Can Tho University (biochar A) and one commercial product (biochar B), were used. Some characteristics of the soil and biochars are presented in Table 1.

Table 1. Characteristics of soil and biochar used in this study

	Rice-shrimp soil	Biochar A	Biochar B
pH (H_2O) (1:5)	7.6	7.6	9.0
EC mS cm^{-1} (1:5)	1.81	0.50	0.89
Soluble K ($\text{cmol}_c \text{ kg}^{-1}$)	0.72	3.08	4.18
Soluble Na ($\text{cmol}_c \text{ kg}^{-1}$)	8.35	0.21	0.37
Soluble Ca ($\text{cmol}_c \text{ kg}^{-1}$)	1.57	0.38	0.79
Exchangeable K ($\text{cmol}_c \text{ kg}^{-1}$)	1.53	1.74	5.43
Exchangeable Na ($\text{cmol}_c \text{ kg}^{-1}$)	2.67	0.00	0.06
Exchangeable Ca ($\text{cmol}_c \text{ kg}^{-1}$)	5.42	0.98	1.31
Cation exchange capacity (CEC) ($\text{cmol}_c \text{ kg}^{-1}$)	18.4	2.80	5.54
Exchangeable sodium percentage (ESP) (%)	14.5	ND	ND
Iodine number (mg g^{-1})	ND	173	110
Water holding capacity (g water/g dried material)	0.7	5.8	3.4

ND: Not determined. Exchangeable cations were determined by subtracting soluble cations from total extractable cations.

2.2. Salinity leaching design

Soil was air-dried and sieved through a 2 mm mesh before it was used to make a soil column (4 cm diameter, 10 cm in height) with a glass wool layer of 1 mm at the bottom. A filter paper was used to cover the top of the soil columns. The experiment was set up with 8

treatments and with 3 replicates for each treatment: (1) Control, untreated soil; (2) A, Soil + 50 g kg⁻¹ biochar A; (3) B, Soil + 50 g kg⁻¹ biochar B; (4) A+0.5Ca, Soil + 50 g kg⁻¹ biochar A + CaO 0.5 g kg⁻¹; (5) B+0.5Ca, Soil + 50 g kg⁻¹ biochar B + CaO 0.5 g kg⁻¹; (6) A+2Ca, Soil + 50 g kg⁻¹ biochar A + CaO 2 g kg⁻¹; (7) B+2Ca, Soil + 50 g kg⁻¹ biochar B + CaO 2 g kg⁻¹; and (8) 2Ca, Soil + CaO 2 g kg⁻¹. CaO (analytical grade, Wako) was used in the experiment. Rate of biochar was based on dried weight.

After adding 50 ml of deionized water into the soil columns, the column was kept for 5 days by closing the bottom. Then, all the columns were opened for collecting eluent, together with recording the infiltration speed and EC of leachate 4 times per day for the first 3 days and every day until finished. The washing process was repeated until when the EC in the leachate reached the value of 0.5 mS cm⁻¹. The eluents were measured for the major salt ions in order to investigate the leaching sequence of ions. Soil samples were collected after 3 days of washing when EC of leachate in most treatments reached a value of 0.5 mS cm⁻¹. Soil samples were air-dried, sieved through a 2 mm mesh and analyzed for the chemical properties such as pH (H₂O), EC, soluble Na, K and Ca, exchangeable Na, K and Ca and CEC, as described below.

2.3. Data collection and chemical measurements

Speed of drainage: For the leaching speed, data was collected at 24, 27, 30, 33 and 48 hours after opening the soil column. Based on the linearity of infiltration drainage, the slope (coefficient a of the liner function $y = ax + b$, in which y represents for the volume of eluent in ml, x for the time of drainage in hour) was used to compare.

Soil pH and EC: deionized water was mixed with soil at the ratio 1:5 (soil:water) and the mixture was shaken for 2 hours at 120 rpm. Measurement was done using pH and EC meters (pH meter Metrohm 744 and EC meter Horiba B-173, respectively).

Soluble Na, K and Ca: deionized water was mixed with soil at a ratio of 1:10 and the mixture was shaken for 1 hour at 120 rpm. Then, the mixture was passed through filter paper (Advantec 5C) and ions in the filtrate were determined with flame photometry (Flame Photometers, BWB).

Exchangeable Na, K and Ca: Exchangeable cations were obtained by subtracting soluble cations from extractable cations. Extractable cations were analyzed by extracting soil sample (2.5 g) three times with 0.1 M BaCl₂ solution (each time 30 ml) and with 1 hour shaking and determined with flame photometry.

Cation exchange capacity (CEC): Unbuffered salt extraction method was used [16]. A portion (2.5 g) of soil was treated three times with 30 ml of 0.1 M BaCl₂, and then a known amount of 0.02 M MgSO₄ was added to exchange with Ba²⁺ in 2 hours. The remained MgSO₄ was titrated with 0.01M EDTA.

Na adsorption measurement: 0.2 g of biochar was added into 25 ml of Na⁺ solution (made from analytical grade NaCl) with different concentrations (0, 100, 250, 500, 1000, 1500, 2000, 3000, 4000 and 5000 mg Na L⁻¹). The mixture was shaken for 24 hours at 120 rpm. The adsorption capacity of biochar was calculated based on the remained concentrations of Na in the solution [17].

$$AC = \frac{[C_i - C_f]}{m} \times V$$

Where AC is the Na^+ adsorption capacity of biochar, C_i (mg L^{-1}) and C_f (mg L^{-1}) are the initial and final concentration of Na^+ before and after biochar addition, respectively, V is volume of Na^+ solution and m is dosage of biochar (g).

2.4. Data analysis

The ESP (Exchangeable Sodium Percentage) is an important indicator for saline soil. If this value is higher than 6, that soil is considered sodic and if it is higher than 15, that soil is strongly sodic [18].

$$\text{ESP (\%)} = \frac{\text{Na}^+}{\text{CEC}} \times 100$$

Where Na^+ is the content of exchangeable sodium ($\text{cmol}_c \text{ kg}^{-1}$) and CEC is the cation exchange capacity ($\text{cmol}_c \text{ kg}^{-1}$).

Data analysis: The statistical analysis was done by using Minitab software.

3. RESULTS

3.1 Speed of drainage

Of all treatments, applying of biochar significantly ($p < .001$) increased speed of drainage by 4 times compared to that in non-added soil (Fig. 1). There was no significant difference between biochar A and B in the ability to improve speed of drainage. The leachate EC values of all biochar treatments decreased to 0.5 mS cm^{-1} after 3 days while it took 60 days in non-treated soil and 30 days in soil treated with $\text{CaO } 2 \text{ g kg}^{-1}$ (Fig. 2).

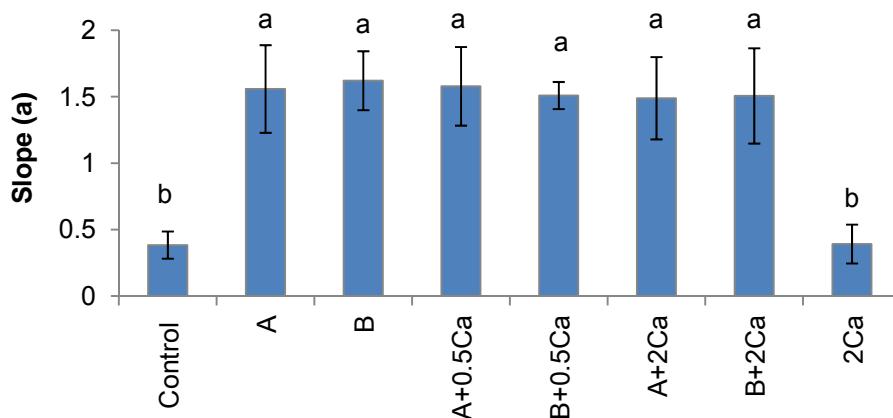


Fig. 1. Comparison of slope values in the infiltration rates from 24 to 48 hours

Difference letters indicate significant differences (Fisher test, $P = .05$) among treatments. Bars represent standard deviation. Control: Untreated soil; A: Soil + 50 g kg^{-1} biochar A; B: Soil + 50 g kg^{-1} biochar B; A+0.5Ca: Soil + 50 g kg^{-1} biochar A + $\text{CaO } 0.5 \text{ g kg}^{-1}$; B+0.5Ca: Soil + 50 g kg^{-1} biochar B + $\text{CaO } 0.5 \text{ g kg}^{-1}$; A+2Ca: Soil + 50 g kg^{-1} biochar A + $\text{CaO } 2 \text{ g kg}^{-1}$; B+2Ca: Soil + 50 g kg^{-1} biochar B + $\text{CaO } 2 \text{ g kg}^{-1}$; 2Ca: Soil + $\text{CaO } 2 \text{ g kg}^{-1}$

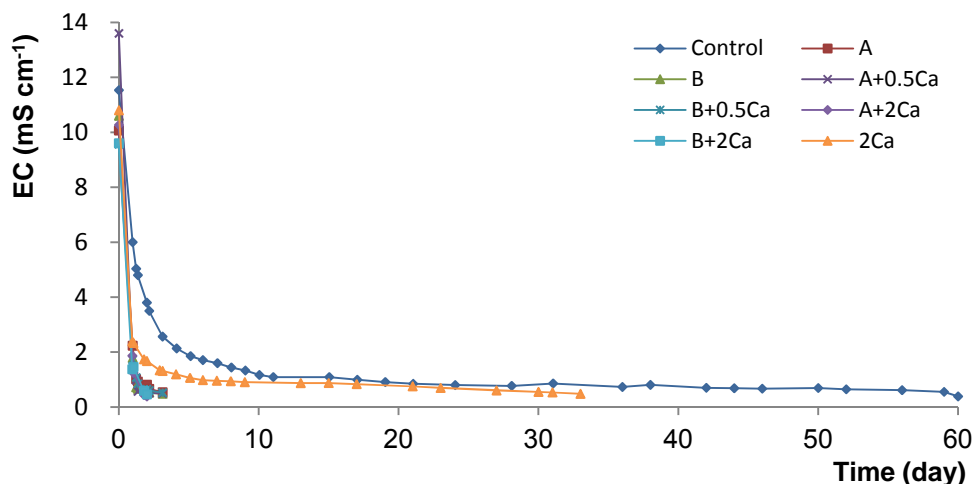


Fig. 2. Periodical change of EC in the eluents from soil columns

Control: Untreated soil; A: Soil + 50 g kg⁻¹ biochar A; B: Soil + 50 g kg⁻¹ biochar B; A+0.5Ca: Soil + 50 g kg⁻¹ biochar A + CaO 0.5 g kg⁻¹; B+0.5Ca: Soil + 50 g kg⁻¹ biochar B + CaO 0.5 g kg⁻¹; A+2Ca: Soil + 50 g kg⁻¹ biochar A + CaO 2 g kg⁻¹; B+2Ca: Soil + 50 g kg⁻¹ biochar B + CaO 2 g kg⁻¹; 2Ca: Soil + CaO 2 g kg⁻¹.

3.2 Chemical parameters of soil after washing

pH of soil: Applying biochar with CaO at the rates of 0 and 0.5 g kg⁻¹ significantly ($P = .05$) decreased the soil pH values (Fig. 3). Applying 2 g kg⁻¹ of CaO significantly ($P = .05$) increased the soil pH values, in both only CaO and combination with biochar A or B.

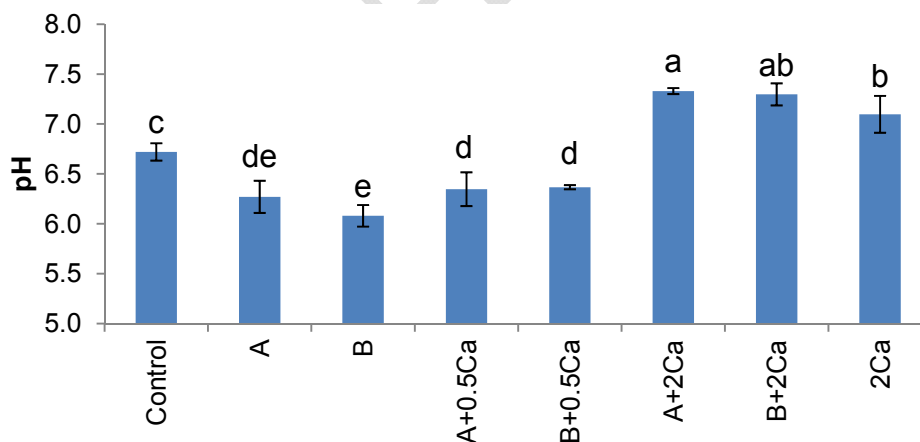


Fig. 3. pH (H₂O) of soil after leaching

Difference letters indicate significant differences (Fisher test, $P = .05$) among treatments. Bars represent standard deviation.

Electrical conductivity (EC) of soil: The initial soil EC values (1.8) decreased to below 1 mS cm⁻¹ in all the treatments after washing and EC values in soil were significantly ($P = .05$) higher biochar treatments without CaO than in untreated soil (Fig. 4).

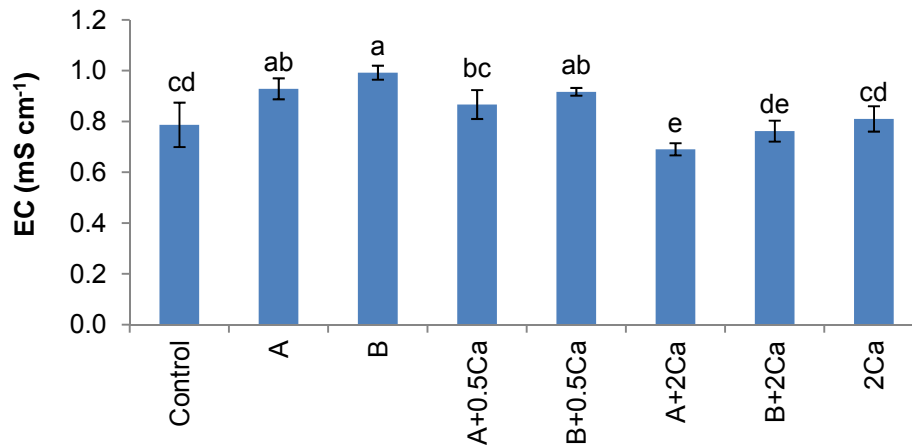


Fig. 4. EC of soil after leaching

Difference letters indicate significant differences (Fisher test, $P = .05$) among treatments. Bars represent standard deviation.

Exchangeable Sodium Percentage (ESP): ESP decreased significantly ($P = .05$) when adding biochars (Fig. 5). The greatest decrease was observed in treatment with 50 g kg⁻¹ biochar B + CaO 0.5 g kg⁻¹, with the decrease of 83% compared to the initial ESP of soil. Comparing to biochar A, reduction in ESP was significantly ($P = .05$) greater in treatment treated with biochar B. Comparison of ESP reducing by three levels of CaO combined with biochar showed that the greatest reduction was at 0.5, following by 0 and the lowest reduction was at 2 g kg⁻¹ CaO level. ESP was the highest in the control treatment, followed by treatment treated with only CaO 2 g kg⁻¹.

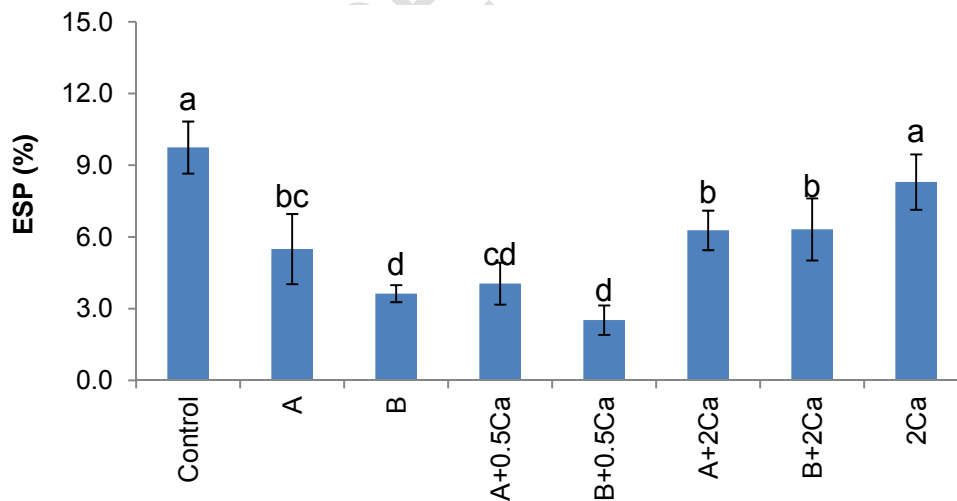


Fig. 5. Exchangeable Sodium Percentage (ESP) of soil after leaching

Difference letters indicate significant differences (Fisher test, $P = .05$) among treatments. Bars represent standard deviation. Soil initial ESP was 14.5.

3.3 Ion concentrations in soil and leachate

Applying biochar (both A and B) significantly ($P = .05$) decreased soluble Na in soil after the leaching experiment (Table 2). Exchangeable Na in soil was the lowest when applying 50 g kg⁻¹ biochar B with a low rate of CaO (0 and 0.5 g kg⁻¹). Exchangeable Na in soil tended to be lower in B and B+0.5Ca than in A and A+0.5Ca.

Biochar B (plus 0 and 0.5 g kg⁻¹ of CaO) and biochar A + CaO 0.5 g kg⁻¹ also showed the highest K:Na ratio (Fig. 6). Combination with 2 g kg⁻¹ of CaO did not enhance the K:Na ratio. In terms of Ca:Na ratio, biochar B with 0 or 0.5 g kg⁻¹ of CaO resulted in the highest value of Ca:Na. Biochar A also presented a higher Ca:Na ratio compared to the control.

Na⁺ sorption capacity of biochar A was double than that of biochar B (Fig. 7). The Na sorption capacity of both biochar increased with concentrations of Na⁺ in solution and reached the peak at 4000 mg Na L⁻¹.

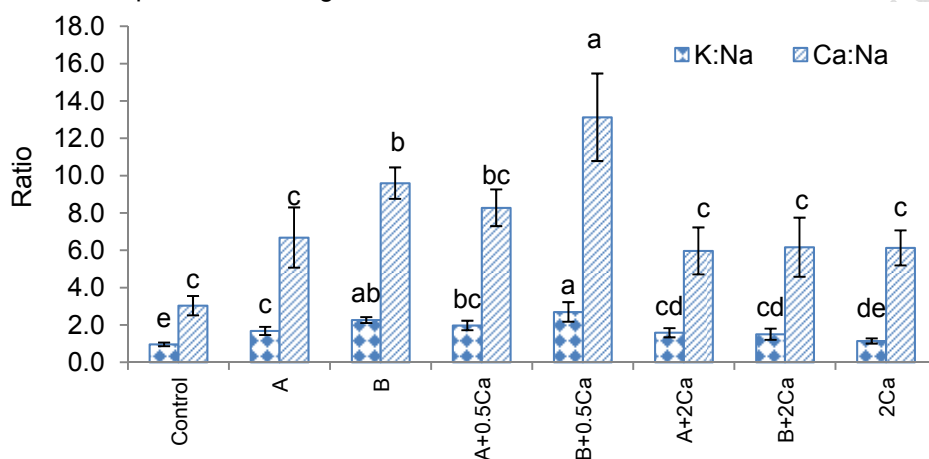


Fig. 6. Ratio of exchangeable K/Na and exchangeable Ca/Na of soil after leaching
Difference letters indicate significant differences (Fisher test, $P = .05$) among treatments. Bars represent standard deviation

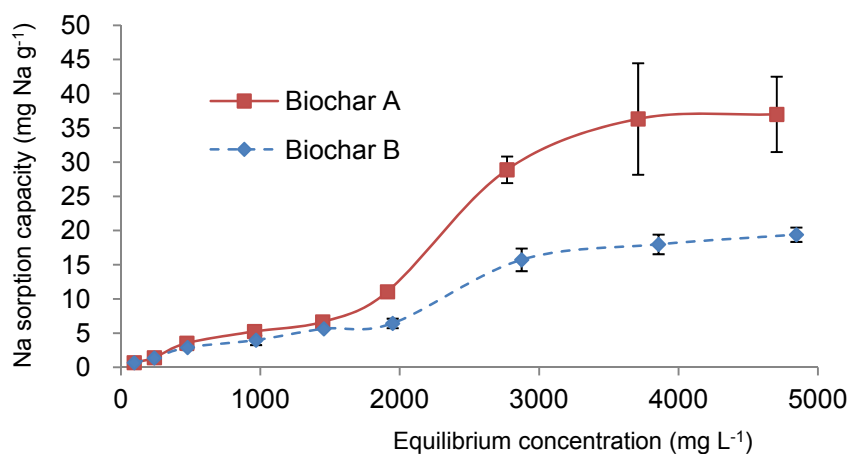


Fig. 7. Sorption isotherm of Na⁺ on two different biochars
($P < .001$). Bars represent standard deviation of $n = 4$.

Table 2. Exchangeable and soluble cations in soil after finishing leaching (3 days)

Treatment	Exchangeable (cmol _c kg ⁻¹)			Soluble (cmol _c kg ⁻¹)		
	Na	K	Ca	Na	K	Ca
Control	1.80 ^a	1.72 ^{abc}	5.40 ^d	3.71 ^b	1.18 ^{b^c}	1.47 ^b
A	1.02 ^{bc}	1.67 ^{abc}	6.50 ^c	2.90 ^d	1.29 ^b	0.64 ^b
B	0.67 ^d	1.52 ^{bcd}	6.42 ^{cd}	3.27 ^c	1.58 ^a	1.16 ^b
A+0.5Ca	0.75 ^{cd}	1.45 ^{cd}	6.10 ^{cd}	2.68 ^d	1.32 ^b	0.75 ^b
B+0.5Ca	0.47 ^d	1.23 ^d	6.00 ^c	2.66 ^d	1.50 ^a	0.99 ^b
A+2Ca	1.16 ^b	1.80 ^{ab}	6.72 ^{bc}	2.70 ^d	1.08 ^c	ND
B+2Ca	1.34 ^b	1.95 ^a	7.92 ^b	2.76 ^d	1.28 ^b	ND
2Ca	1.54 ^a	1.74 ^{ab}	9.32 ^a	4.22 ^a	1.17 ^{bc}	2.68 ^a

Two-way ANOVA comparison between biochar A and biochar B with different CaO levels

Factor	D	P value					
	F*						
Biochar	1	.03	.42	.21	.20	<.001	.23
CaO	2	.001	.001	.004	.01	.001	.92
Biochar x CaO	2	.24	.23	.09	.29	.58	.66

Exchangeable cations were determined by subtracting soluble cations from total extractable cations. Difference letters indicate significant differences (Fisher test, $P = .05$) among treatments. ND: Not detected. *, Degrees of freedom

Table 3. Amount of cations removed from soil into eluent by leaching (3 days)

Treatment	Na	K	Ca
	cmol _c kg ⁻¹		
Control	6.28 ^e	0.29 ^d	1.60 ^c
A	8.00 ^d	0.40 ^{bc}	2.68 ^{ab}
B	8.89 ^{ab}	0.42 ^b	2.55 ^{abc}
A+0.5Ca	8.19 ^{cd}	0.36 ^c	3.10 ^a
B+0.5Ca	9.03 ^a	0.48 ^a	3.15 ^a
A+2Ca	8.85 ^{ab}	0.30 ^d	3.52 ^a
B+2Ca	8.53 ^{bc}	0.34 ^{cd}	3.11 ^a
2Ca	5.59 ^f	0.21 ^e	2.01 ^{bc}

Two-way ANOVA comparison between biochar A and biochar B with different CaO levels

Factor	DF*	P value	
Biochar	1	.001	.40
CaO	2	.25	<.001
Biochar x CaO	2	.001	.62

Difference letters indicate significant differences (Fisher test, $P = .05$) among treatments. *, Degrees of freedom

4. DISCUSSION

4.1 The potential of biochar to enhance speed of salts washing

The drainage results in this study showed that biochar addition accelerated salt leaching through dramatically increased speed of drainage, directly leading to saving time for

removing salts. The improvement in the leaching rate may be caused mainly by the change in the soil physical structure. With porous structure and huge surface area, biochar increases the soil porosity and soil drainage [19, 20]. Depending on the types of soil, biochar, its application rate and size, the effects on saturated hydraulic conductivity are different [19]. When applying biochar, saturated hydraulic conductivity decreases in sand and organic soils, while it increases in clay-rich soil. The soil used in this study and most of soils in a rice-shrimp system in the MD are clay-rich soil [21]. Therefore, it is appropriate to apply biochar as an amendment for quickly removal of salts through increase speed of drainage. It will be proposed that biochar is applied and mixed with the soil bed after shrimp cultivation and fresh water is irrigated to the field to wash out of salts before planting rice. Field studies are now conducted to evaluate the long-term residual effects of biochars on rice crop and soil properties in a rice-shrimp system.

4.2 Effects of biochars on pH and EC of saline soil

Applying 2 g kg⁻¹ of CaO increased pH of soil. The initial soluble plus exchangeable Ca in this soil was high (7.0 cmol_c kg⁻¹) and it was considered as a result of retaining salinity water and applying high amounts of Ca (to maintain the pH of field water above 7.5 and water hardness around 60-250 mg L⁻¹ CaCO₃) in a long period during shrimp cultivation [22]. High cation contents, particularly Ca, increase soil pH. Then, it is not recommended to apply an extra high level of Ca amendment for this soil. With a high pH value of biochar (normally > 7), biochar rises pH of acidic soil. Saline soils show high pH values and therefore, biochar with a low pH value, e.g. biochar A in this study, would be appropriate for this kind of soil and a high value pH of biochar is a concern when applying biochar to saline soil [11]. However, the change in soil pH is not only affected by pH of the used biochars. This study showed that the application of both biochars reduced soil pH possibly due to the removal of high concentrations of salts in the saline soil [23]. Therefore, salt contents and buffering capacity in soil might also be considered when applying biochar to soil.

Many studies have shown that biochar increases the EC of soil through its high salt contents [24-26], and therefore, application of biochar to saline soils is not recommended. This study, however, demonstrated the efficacy of biochar even for saline soil in removing salts. The higher EC values of soil in biochar treatments could be related to adsorption capacity of biochar, leading to retaining high concentration of salts.

4.3 Effectiveness of biochars in removing sodium and other soil chemical properties

Sodium concentration and ESP are the most concerned parameters for saline soils and must be reduced for crop cultivation. The results illustrated that biochar amendment removed more amounts of sodium from saline soil, resulted in lower amounts of soluble and exchangeable Na⁺ in soil and higher amounts of Na⁺ in leachate, indicating accelerated exchange of a part of Na in the saline soil by other cations such as Ca, Mg and K. Increased availability of Ca²⁺ in CaO 2 g kg⁻¹ treated soils saved K in soil, which resulted in higher exchangeable K in soil and lower K⁺ in leachate in high CaO treatments compared to soils with low CaO application. This result agreed with the study of Chaganti and Crohn (2015), who reported that increased availability of divalent cations facilitates efficient exchange of adsorbed Na⁺ into soil solution and reduces exchangeable Na concentration in soil [13]. Current knowledge has also recommended applying potassium fertilizers to alleviate Na⁺ stress in plants under sodic and saline sodic conditions [27, 28]. This study illustrated that instead of applying inorganic fertilizers (such as potassium fertilizers), K:Na and Ca:Na ratios may be improved by applying biochar to saline soil.

ESP of the initial soil in this experiment was 14.5% and it was expected to reduce less than 6% for suitable conditions for rice cultivation [18]. Both biochars A and B with and without CaO achieved this target. Biochar with a porous and loose texture can increase the total porosity of soil [29]. Therefore, more exchangeable Na^+ was leached out in biochar treatments due to higher infiltration rate, which leads to reducing the ESP.

Comparison between biochars A and B in terms of reducing exchangeable Na from soil, biochar B resulted in a better performance. Biochar B contained higher Ca^{2+} and K^+ , which facilitated efficient exchange of sodium into leachate. In addition, the difference in sodium sorption capacity of biochar might be a cause. Some studies showed that the retention/adsorption of Na^+ on biochar surfaces or physical entrapment of salts in fine pores of biochar happens [30-32] and leads to a lower concentration of Na in soil solution. An amount of Na entrapped in fine pores or adsorbed could be different depending on biochar type, aging time and temperature, [12, 31]. This study showed that Na sorption capacity of biochar B was 2 times lower than that of biochar A. Therefore, due to higher adsorption capacity of biochar A, Na^+ was retained and led to higher Na^+ concentration in soil and resulting in higher ESP values in biochar A treatment. Rostamian et al. (2015) showed that textural properties of biochar were the key factor in Na^+ sorption, with the linear correlation between Na^+ sorption and total surface area and total pore volume of rice husk biochar [17]. The higher in Na^+ adsorption capacity with higher in iodine number value of biochar A compared to biochar B supports for this hypothesis. Total surface area and pore volume of biochar is likely depending on pyrolysis temperature. When pyrolysis temperature was above 600°C , the correlation was not clear but below 600°C , lower pyrolysis temperature produced biochar with a smaller surface area and pore volume [17,33,34]. Two biochars used in this study were produced with the pyrolysis temperature around 600°C , but in different methods. Biochar A was a commercial product, and biochar B was produced manually by slow pyrolysis of opened rice husk mound. Therefore, results suggested that the same material but different pyrolysis processes might lead to difference in sorption capacity of biochar.

5. CONCLUSION

This study proved that biochar amendment reduced significantly time for removing salts from a saline sodic soil through soil column. Biochar decreased significantly both exchangeable Na and ESP. Other soil properties rehabilitated by biochar were K:Na and Ca:Na ratios. Biochar with lower sorption Na capacity and lower surface area performed better results in terms of reducing ESP, increasing K:Na and Ca:Na ratios. Applying CaO at the rate of 2 g kg^{-1} soil led to high pH value and also high in soluble and exchangeable Na, resulted in low K:Na, Ca:Na ratios.

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