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Running Title: THE RECLAMATION OF SALINE-ALKALI SOIL

Short-Term Effects of Biochar and Gypsum on Soil Hydraulic Properties and Sodicity in a Saline-Alkali Soil

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ABSTRACT

Salt and sodicity of saline-alkali soil adversely affect the construction of ecological landscapes and impacts on crop production. The reclamation potential of biochar (BC, wheat straw biochar and applied at 1% by weight), gypsum (G, 0.4% by weight) and gypsum coupled with biochar (GBC) are examined in this laboratory-based study by evaluating their effects on a saline-alkali soil (silt loam). Saline ice and fresh water (simulated rainfall) were leached through soil columns to investigate changes of salt content, sodium adsorption ratio (SAR), alkalinity and pH of the leachate and the soil. Results show that saturated water content and field water capacity (FWC) significantly increased by 4.4% and 5.6% separately in biochar treated soil after a short incubation time. Co-application of biochar and gypsum increased soil saturated hydraulic conductivity (Ks) by 58.4%, which was also significantly higher than solely addition. Electrical conductivity (EC) of the leachate decreased sharply after saline ice leaching; subsequent freshwater leaching accelerated the removal of the rest of the salts, irrespective of the amendment application. However, the application of gypsum significantly enhanced the effect in removing exchangeable Na^+ and reduced leachate SAR. After leaching, the soil salt content decreased significantly for all treatments. The application of gypsum resulted in a significantly lower soil pH, exchangeable sodium percentage (ESP), SAR and alkalinity values than those recorded by the control and biochar amended soil. These results demonstrate that co-application of gypsum and biochar can improve saline-alkali soil hydraulic conductivity and decrease leaching induced sodicity over a short period.

Key Words: saline ice; field water capacity; saturated hydraulic conductivity; sodium adsorption ratio; soil alkalinity

INTRODUCTION

Soil salinity and sodicity are the two major environmental hazards resulting from land degradation in arid and semi-arid regions (Qadir *et al*., 2000; Rengasamy, 2006). Saline-alkali soil is characterized by high electrical conductivity values (EC; >4 dS m^{-1}), high sodium adsorption ratios (SAR; >13) of the saturation extract and an exchangeable sodium percentage (ESP) >15 (Richards, 1954). Generally, saline-alkali soil presents severe structural degradation and they have limited productivity due to the simultaneous detrimental effects of salinity and sodicity (Rengasamy and Olsson, 1991). Reclamation of a saline-alkali soil not only requires the removal of excessive salts from the upper layers of the soil by leaching (Da Silveira *et al*., 2008; Chaganti *et al*., 2015), sodicity of the soil needs to be eliminated and overall soil physical properties need to be improved (Gharaibeh *et al*., 2010; Yu *et al*., 2010).

With rapid industrialization and urbanization in coastal saline regions, there is an urgent need to improve the local environment to satisfy increasing demands from cities and districts. In Hebei province, China, the distribution of saline-alkali soil in coastal regions covers an area about 200 km^2, with the majority of the coastal wasteland region not being used (Lin *et al*., 2012). However, the lack of available fresh water in this region is a limiting factor to reclaiming these soils using traditional leaching techniques, techniques which have been found to be ineffective in creating a habitat suitable for good plant growth in a short time period. Recent developments in the use of saline ice treatment methods have resulted in this method becoming a practical alternative solution to remove excessive salt in saline-alkali soils (Guo *et al*., 2010, Zhang *et al*., 2016). The saline ice treatment method includes freeze separation where dissolved solutes in aqueous solutions are concentrated in brine pockets during freezing processes (Cole and Shapiro, 1998). When temperatures subsequently increase, brine drainage channels in the ice are opened, allowing brine to be flushed from the ice (Oertling and Watts, 2004); this process also provides fresh water to leach the soil. Zhang *et al*. (2012) reported that saline ice irrigation could decrease soil salinity and increase the germination rate and productivity of cotton in coastal saline-alkali soils. Previous studies have also shown that saline ice irrigation increased soil moisture and reduced soil salinity in the spring, and soil salinity was further reduced during the summer rainy season (Zhang *et al*., 2012; Guo *et al*., 2010; 2014). In contrast to soil salinity, limited information exists concerning the effects of sodicity on soil degradation. A laboratory study by Zhang *et al*. (2016) reported that soil pH and alkalinity significantly increased after saline ice leaching. Previous investigations have also shown that a deterioration of saline-alkali soil can be induced by sodicity. Rengasamy and Olsson (1991) found that high concentrations of Na^+ in the soil solution, or at exchange sites, destroys the soil physical structure by aggregate slaking, soil swelling and clay dispersion, and Tang *et al*. (2013) reported that a noticeable increase of soil pH leads to the degradation of many soil properties, such as low organic matter content, poor permeability and an imbalance of nutrition and water supply.

Increases of pH or alkalinity are due to the disequilibrium of ion composition, usually due to an excess of Na^+ (Chen *et al*., 2000; Zhang *et al*., 2016). The addition of divalent ions into a soil, usually Ca^{2+}, can effectively prevent an increase of soil pH after leaching (Da Silveira *et al*., 2008; Wang *et al*., 2012; Tao *et al*., 2014). Due to its low cost and abundance, gypsum is one of the most commonly used amendments for sodic soil reclamation (Mace and Amrhein, 2001; Aydemir and Najjar, 2005; Gharaibeh *et al*., 2009). The use of gypsum can potentially supply substantial amounts of Ca^{2+} into a soil solution to facilitate efficient replacement of Na^+ on the exchange site (Gharaibeh *et al*., 2009; Chaganti *et al*., 2015). Thus, the effects of gypsum in the reclamation of a saline-alkali soil leached by saline ice and simulated rainfall are evaluated in this study.

Biochar, produced by slow pyrolysis of biomass, is increasingly seen as an organic amendment to soil physical properties (Sun *et al*., 2016). Previous studies have shown that biochar is an effective organic amendment to improve soil aggregate stability and hydraulic conductivity (Almaroai *et al*., 2013; Wu *et al*., 2014; Chaganti and Crohn, 2015; Chaganti *et al*., 2015). In addition, biochar can supply an abundance of Ca^{2+} and Mg^{2+} ions, and enhance their availability in replacing Na^+ (Cao and Harris, 2010; Tsai *et al*., 2012). However, the application of biochar as a soil amendment for remediating saline-alkali soil sodicity has not been widely investigated. The benefits of combined applications of biochar and gypsum on soil hydraulic properties and sodicity after leaching are currently unknown and require investigation.

The main objective of this study therefore is to evaluate the effects of biochar and gypsum (individually and as a combination) applications on soil water retention curves and leaching induced sodicity of a saline-alkali soil. Our hypothesis is that the combined application of gypsum and biochar will accelerate the reclamation process of a saline-alkali soil more than then that attained when gypsum and biochar are applied separately.

MATERIALS AND METHODS

Materials

Nearly 10 kg saline-alkali soil samples (0-20 cm) were collected from the coastal area of Haixing County of Hebei Province, China (38° 10′ 56″ N, 117° 34′ 45″ E). This area is a typical monsoon region which is characterized by wet summers, dry-windy springs and autumns, and dry-cold winters. Soil salinization in this area is a result of shallow groundwater having a high salinity. Collected soil samples were air-dried, ground, passed through a 2 mm sieve, thoroughly mixed, labeled, and stored in plastic bags for analysis. The soil physical and chemical properties examined in our investigation are listed in Table 1. Water from the study area was collected from ditches and analyzed to identify the main ions in solution; this information was used to make a saline water stock solution of similar ions composition using NaCl dissolved in distilled water with $CaSO_4$ and $MgCl_2$ (Table 2).

TABLE 1

Soil physical and chemical characteristics

Soil characteristics					
Particle size distribution (%)		Soluble ions (cmol kg^{-1})		Exchangeable cation (cmol kg^{-1})	
>0.05 mm	16.8	K^+	0.09	Cation exchange capacity	8.77
0.05～0.002 mm	76.1	Na^+	20.0	Exchangeable Na^+	4.28
<0.002 mm	7.10	Ca^{2+}	0.67	Exchangeable K^+	0.07
soil classification	Silt loam	Mg^{2+}	1.38	Exchangeable Ca^{2+}	0.78
Soil EC (ds m^{-1})	5.37	Cl^-	20.7	Exchangeable Mg^{2+}	1.43
pH	8.58	SO_4^{2-}	1.26		
$CaCO_3$ (g kg^{-1})	106	$CO_3^{2-}+HCO_3^-$	0.35		
Organic matter (g kg^{-1})	7.69				

TABLE 2

Chemical properties of saline water collected from the study area and used in this experiment

Item	EC (dS m^{-1})	pH	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-
			(cmol l^{-1})							
Shallow groundwater	17.0	8.16	0.03	15.6	0.38	1.88	22.3	0.34	0	0.75
Experimental water	17.0	5.82	0	13.0	0.35	1.75	16.5	0.35	0	0

Two types of amendments were used in this experiment: gypsum ($CaSO_4 \cdot 2H_2O$; reagent grade) and commercial biochar. Biochar used was supplied by the Shangqiu Sanli New Energy Company in Henan, China.

This biochar was made from wheat straw using vertical continuous biomass carbonization equipment, and the average pyrolysis temperature was 450 ℃ (Bian *et al*., 2014). The biochar was ground and sieved on a 2 mm sieve before analysis and application. This preprocessing of biochar addition was to mix it homogeneously with soil, and correspond with the United States Department of Agriculture (USDA) textural limit for soil. The chemical properties of the biochar are presented in Table 3.

TABLE 3

Chemical properties of the biochar used in this experiment.

EC	pH	Soluble ions (cmol kg^{-1})							
(dS m^{-1})		K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-
9.46	7.53	10.2	21.5	2.11	1.42	38.2	1.45	0	0.70

For most researches on biochar, the application rates were sat among 0.5%-5% by weight (Chaganti *et al*., 2015; Laghari *et al*., 2015; Burrell *et al*., 2016). In this research, biochar (BC) amendment was applied at a rate of 27 t ha^{-1} on a dry weight basis (≈1% by weight, assuming a 20 cm plough depth and a generic soil bulk density of 1.35 g cm^{-3}). Gypsum (G) was applied at a 100% soil gypsum requirement (nearly 0.4% by weight in this experiment); the gypsum requirement was estimated according to the report of Amezketa *et al*. (2005). For the biochar combined with gypsum (GBC) treatment, the same application rates of gypsum and biochar were used. The high amendment application rate was chosen to simulate a one-time application and the significant effects of addition of these amendments. A soil control (CK) was established which did not have any amendments applied to it. For all of the amendments, soil samples were mixed under dry conditions. During the mixing process it was ensured that a homogeneous mixture was prepared. The soil mixtures were then stored in plastic bags before soil columns were prepared.

Soil water retention analysis

To investigate soil water retention, soil columns were prepared by uniformly packing the soil mixtures into steel cylinders (internal diameter: 5.04 cm; height: 1.50 cm) until a bulk density of 1.35 Mg m^{-3} was attained. The soil columns were then sprayed with the distilled water until they attained a gravimetric water content of 0.15 g g^{-1}. The samples were then immediately wrapped in cling film to reduce moisture loss. It was reported that many important changes between soil particles, gypsum and lime, such as cation exchange, flocculation and agglomeration, quickly occurred at curing period of the first week (YiLmaz and CiVelekoglu, 2009; Al-Mukhtar *et al*., 2010). Thus in this experiment, the soil samples were cured at 20℃ for 7 days for all treatments before soil water retention curves (SWRCs) were determined using suction measurements via pressure plate apparatus. Before determining the SWRCs, soil samples were saturated with distilled water at room temperature (20℃) for 12 hours. After soil samples were saturated, they were promptly removed to pressure chambers. The pressure chambers were equilibrated at the pressures of 1, 2, 3.5, 4, 8, 15, 30, 50, 100 and 150 m H_2O. All the equilibrations were generated at room temperature (20℃) and each treatment was repeated four times.

Leaching experiment

To investigate leaching through the soil sample, 16 steel cylinders (10 cm length and 5.04 cm internal diameter) were prepared. The bottom of each cylinder was initially cover with a cotton gauze (mesh=1 mm) to retain the soil. The soil mixtures were then packed into the cylinders to a depth of 5 cm, having a bulk density of 1.35 Mg m^{-3}. The leaching columns were pre-wetted and cured as the same condition of section 2.2. After a week curing period, all soil columns were leached six times. A glass funnel (diameter: 10cm) was placed under each cylinder to direct the leachate into plastic collection bottles. Firstly, two pore volumes (PVs) of saline ice were placed on the surface of the soil columns and the melting water was used to leach the soil. The saline ice was obtained by freezing saline water below -16℃ for 12 hours. The next five leaching experiments were undertaken using distilled water (1 PV each time). The PV is the volume of water required to saturate all soil pores, and this averaged approximately 46 ml for each soil column. Irrigation was undertaken when the previous experiment had successfully been completed. Saturated hydraulic conductivity (Ks) measurements were conducted during the distilled water leaching using falling head method, which required an individual to manually read the change in leachate volume across time. The readings were taken every 5 minutes and Ks was calculated according to the report of Johnson *et al.* (2005). For every treatment, four replicates were used and the leaching experiments were undertaken at room temperature (20 ±2℃). The leachate was collected for every pore volume in bottles and continuously analyzed for EC, Na^+, Mg^{2+} and Ca^{2+}. After the completion of leaching, all columns were allowed to drain freely. Then a 1.5 cm length and 5.04 cm internal diameter soil cores was carefully removed from each column. These soil cores were saturated with distilled water for 12 hours and then were used to determine field water capacity (FWC) using a pressure plate apparatus at the pressure of 3.3 m H_2O. Residual soil samples were collected and analyzed for EC, pH, soluble Na^+, Ca^{2+}, Mg^{2+}, CO_3^{2-} and HCO_3^-. Soil EC, pH and soluble ions were determined in 1:5 soil: water extracts, as per Rayment and Higginson (1992). EC and pH were measured by Seven Excellence (METTLER TOLEDO, Shanghai, China). Soluble Na^+ and K^+ were analyzed by flame photometry (FP650, Aopu analytical instruments, Shanghai, China). Soluble Ca^{2+}, Mg^{2+}, Cl^-, CO_3^{2-} and HCO_3^- were estimated by potentiometric titration. The same method was used to determine the properties of the biochar. The chemical composition of exchangeable phases was determined by treating the soils with the mixture of 1 mol l^{-1} NH_4OAc, 70% CH_3CH_2OH and buffered at pH=9.0 by ammonium hydroxide (Hong et al., 2014).

Data analysis

The SAR of the soil solution and leachate was calculated as:

$$\mathrm{SAR} = Na^{+}/\sqrt{(Ca^{2+} + Mg^{2+})/2} \qquad (1)$$

where, Na^+, Ca^{2+} and Mg^{2+} are the soluble cation concentrations (cmol l^{-1}).

The alkalinity (A) of the soil solution and leachate was calculated as:

$$\mathrm{A} = CO_3^{2-} \times 2 + HCO_3^{-} \qquad (2)$$

where, CO_3^{2-} and HCO_3^- are respective soluble anion concentrations (cmol l^{-1}).

In this experiment, the equation of Brooks and Corey (1964) was used to describe $\theta(h)$, further referred to as the following equation:

$$\theta(h) = \begin{cases} (\theta_s - \theta_r)/(\alpha h)^{\lambda} + \theta_r & (\alpha h > 1) \\ \theta_s & (ah \leq 1) \end{cases} \qquad (3)$$

where, θ is the volumetric water content; $\theta(h)$ is to emphasize that it is a function of h; θ_r and θ_s are the residual and saturated water contents, respectively; the reciprocal of α is often referred to as the air entry value or bubbling pressure; and λ is a pore-size distribution parameter affecting the slope of the retention function.

The Ks was calculated by using a derivation of Darcy's law (Johnson *et al.*, 2005):

$$H_i = H_0 - \frac{V_i}{A} \tag{4}$$

$$K_s = \frac{L}{(t_i - t_{i+1})} \ln \frac{H_i}{H_{i+1}} \tag{5}$$

where H_0 and H_i are the pressure heads (cm) at initial time and t_i, respectively; V_i is the leachate volume (cm^3) at time t_i; A is the area of the core (cm^2); L is the length of soil sample (cm) and t is time (s).

Field water capacity was calculated as:

$$\mathrm{FWC} = \frac{m_w}{m_s} \tag{6}$$

where, m_w is the mass of water retained in the soil at -3.3 m of hydraulic head or suction pressure; and m_s is the oven-dried soil mass.

Significance between the treatments was tested using Duncan's test in SPSS18.0 at the 95% significance level (P<0.05). All figures were created using SIGMAPLOT 12.5.

RESULTS AND DISCUSSION

Effects of amendments on SWRCs

Although there were slight differences between the SWRCs for the four amendments, overall results showed similar retention curves (Fig. 1). Soils with the biochar application recorded the highest water retention at near saturation conditions, a finding which might be attributed to the abundant macro-pores presented in the biochar pyrolysed at approximately 500 ℃ (Herath *et al.*, 2013; Sun *et al.*, 2015). The parameters presented in Table 4 show that differences of θ_r and λ between treatments, however, were statistically not significant. The saturated water content was identified to increase by 4.4% for soils treated with biochar, a result confirmed by the SWRCs (Fig. 1). The application of gypsum did not have a significant effect on θ_s, however, an increase of α was observed.

TABLE 4

The short-term effects of treatments on soil water retention curve parameters in coastal saline-alkali soil. CK: no amendment; G: 100% gypsum requirement application; BC: 1% biochar application; GBC: G + BC.

Treatments	θ_r [b)]	θ_s	a	λ	R^2
CK	0.118a [a)]	0.453b	0.007b	0.568a	0.997
G	0.103a	0.445b	0.010a	0.416a	0.999
BC	0.124a	0.473a	0.007b	0.613a	0.999
GBC	0.113a	0.447b	0.007b	0.578a	0.998

[a)] Same letters within a column indicate no significant differences among treatments (P <0.05, Duncan's test).
[b)] θ_r and θ_s are the residual and saturated water contents, respectively; the reciprocal of α is often referred as the air entry value; λ is a pore-size distribution parameter; R^2 is the correlation coefficient.

Results for the mean field water capacity for different treatments before and after leaching (Fig. 2) showed that prior to leaching, FWC for the biochar amended soil had an increase of approximately 5.6% compared with the mean value of the control. Post-leaching, the FWC of all treatments recorded an insignificant decrease compared to initial FWC values, however the BC treatment still had a higher FWC value than the CK and other treatments. Before leaching, the application of gypsum resulted in a soil FWC decrease of 3% compared with the CK; this reduction was more noticeable post leaching. Biochar combined with gypsum decreased its effects on improving soil water retention compared to soils that received using only biochar. This is because the solubility of gypsum is small in soil solution, and the undissolved gypsum particles could enter into the biochar and soil pores, which changed the distribution of the biochar and soil porosity (Al-Kayssi and Mustafa, 2016; Liang *et al*., 2016).

Overall, over the short curing period, biochar was found to significantly improve soil field water capacity and saturated water content. This result might be attributed to the high specific surface area and porosity of the biochar which would result in a decrease of bulk density and an increase of field capacity for the soil (Peake *et al*., 2014; Hansen *et al*., 2016). The gypsum treated soil after 7 days of incubation showed insignificant effects on improving water holding capacity before or post leaching. This result is in contrast with that of Aldaood *et al*. (2014) who reported that water holding capacity of soil samples increased after more than 28 days of curing periods. This increase was attributed to the formation of calcium silicate hydrate and ettringite minerals during longer curing periods, which contributed to changes in pore size distribution in the soil samples (Aldaood *et al*. 2014; Al-Mukhtar *et al*., 2010). It was likely that only cation exchange, flocculation occurred between gypsum and soil particles at the short curing period (7 days), which resulted in unnoticeable effects on water holding capacity.

Fig. 1 Soil water retention curves using the Brooks-Corey equation for the different treatments. CK: no amendment; G: 100% gypsum requirement application; BC: 1% biochar application; GBC: G + BC.

TABLE 4. The short-term effects of treatments on soil water retention curve parameters in coastal saline-alkali soil.

Fig. 2 Field water capacity for the different treatments before and after leaching. The same letters in a column series indicate no significant differences among treatments ($P < 0.05$, Duncan's test). CK: no amendment; G: 100% gypsum requirement application; BC: 1% biochar application; GBC: G + BC.

Saturated hydraulic conductivity (Ks)

Mean Ks measurements after ice melt-water leaching are shown in Figure 3. Ks values of the control soil were the lowest, biochar addition slightly increased soil Ks but the differences were not statistically significant ($P > 0.05$). Chaganti *et al*. (2015) reported that the soil Ks of one month incubation of biochar treated soil was 127% higher than CK. But their soil type belonged to clay loam texture, which might induce the more significant effects on soil Ks compared with this research. Barnes *et al*. (2014) also found that biochar application decreased the Ks of sandy soils but significantly increased Ks in clay-rich soil. On the other hand, longer incubation of biochar treated soils facilitated the biological activity, which enhanced formation of macro aggregates (Herath *et al*., 2013), and therefore helped to increase soil hydraulic conductivity. The addition of gypsum increased soil Ks by 51.2% relative to CK, and gypsum combined with biochar resulted in an even greater increase in soil Ks. There are two reasons attributing to this effect of gypsum on Ks: Firstly, the addition of gypsum increased electrolyte concentration of the leaching solution, and therefore helped to increase soil Ks (McNeal and Coleman, 1966); Secondly, high Ca^{2+} released from the gypsum preferentially exchanged Na^{+} and facilitated its loss from soil, which could prevent soil swelling and dispersion by Na^{+} exchange (Mace and Amrhein, 2001).

Therefore, the addition of gypsum combined biochar after a week of incubation not only increased soil water holding capacity (Fig. 1) by the effects of biochar, it also improved soil hydraulic conductivity through gypsum application, and an important improvement which enhances rainwater utilization.

Fig. 3 The saturated hydraulic conductivity for the different treatments after ice melt-water leaching. The same letters in a column series indicate no significant differences among treatments ($P < 0.05$, Duncan's test). CK: no amendment; G: 100% gypsum requirement application; BC: 1% biochar application; GBC: G + BC.

Leachate EC

Results for mean leachate EC (Fig. 4) show that leachate EC peaked with the first leaching episode (about 80～90% of total salt was removed from the soil columns after the saline ice treatment), after which subsequent leaching episodes with fresh water had lower values. Under the force of gravity in low temperature environments, saline ice can remove the majority of salts during the first half of the melting process, after which the melt-water contains low salt concentrations (Guo and Liu, 2014), which also removes soluble salts out of the soil columns. Our results showed that more salt was leached out of the columns for G, BC and GBC compared to CK during the first leaching episode. This increase was attributed to the large volume of soluble salt contained in the biochar (Table 3) and the dissolution of gypsum. After the first leaching episode, leachate EC decreased at a very slow rate. These results demonstrate that 2 PVs of saline ice can remove the majority of soluble salts from the soil while subsequent additions of fresh water can enhance additional leaching of the salts. No significant difference was identified between CK and BC after the first leaching episode, thus indicting that only the biochar amendment had little effect on leachate EC after its own salt was removed. Our results show that gypsum significantly increased leachate EC through the whole leaching process, an increase that can be associated to not only the dissolution of gypsum, but also to the increase of Na^+ replacement from exchange sites into the soil solution (Gharaibeh *et al*., 2009). Similar effects of biochar and gypsum on soil leachate EC were also reported by Jalali and Ranjbar (2009) and Chaganti *et al*. (2015). It should be noted that the leachate EC of CK and BC increased slightly after four leaching episodes (Fig. 4), an occurrence that was possibly due to the enhancement of the solubility and exchangeability of salts when soil temperature increased after the saline ice treatment, an occurrence which aided further removal of salt.

Fig. 4 Mean leachate salt content for the different treatments. The same letters in a column series indicate no significant differences among treatments ($P < 0.05$, Duncan's test). CK: no amendment; G: 100% gypsum requirement application; BC: 1% biochar application; GBC: G + BC.

Leachate SAR

The concentration of Na^+ of the leachate decreased sharply after the first leaching episode for all treatments (Fig. 5a). The amounts of Na^+ in the leachate were higher for G and GBC before the third leaching episode, but they decreased rapidly and were significantly lower than those in the CK and BC during the following leaching episodes. Therefore, the application of gypsum could facilitate Na^+ leaching compared to the control soil and sole biochar application treatments. Although the addition of biochar increased the removal of Na^+ from the soil samples in the first two leachate episodes, this increase was partly derived from the biochar itself (Table 3).

Mean leachate SAR results for the different treatments (Fig. 5b) showed a significant decline for the first two leaching episodes, then a gradual decline for the other leaching episodes. Saline ice preferentially enhanced the losses of Na^+ relative to Ca^{2+} and Mg^{2+}. The leachate of CK and BC presented the same values of SAR, which were significantly higher than G and GBC. The application of gypsum therefore could efficiently decrease SAR of the leachate. This finding may be attributed to the dissolution of gypsum which could supply enough Ca^{2+} to the effluent and accelerate the losses of Na^+ (Qadir *et al*., 2001; Gharaibeh *et al*., 2009). Our results showed that the application of biochar had little effect on the SAR of the leachate, a result that was in contrast with the results of Chaganti *et al*. (2015) who reported that woodchip biochar application could increase Na^+ loss from soil leached with moderate SAR water. It is likely that the biochar used in this experiment contained an abundance of Na^+ (Table 3), and the short curing time decreased its Ca^{2+} and Mg^{2+} availability in soil, therefore decreasing its effects in reducing leachate SAR.

Fig. 5 The effects of different treatments on leachate Na^+ content (a) and SAR (b). The same letters in a column series indicate no significant differences among treatments ($P < 0.05$, Duncan's test). CK: no amendment; G: 100% gypsum requirement application; BC: 1% biochar application; GBC: G + BC.

Soil desalination and desodification

Soil chemical properties for the different treatments after leaching are shown in Table 5. Compared to the initial characteristics of the soils, soil EC represented the greatest decrease. Saline ice leaching coupled with fresh water could significantly reduce the soil salt content, irrespective of the amendment treatment. After leaching, soil EC of G and GBC treatments were higher than those for the CK and BC treatments, a result which may be due to the dissolution of gypsum. A similar increase in post-leaching soil EC was reported by Yu *et al*. (2015) who used flue gas desulfurization gypsum to amend alkaline clayey soil. Our results indicate that the addition of biochar did not increase soil EC after leaching, even though it contained a large volume of soluble salts (Table 3). Chaganti *et al*. (2015) reported a reduction in post leaching soil EC after the addition of biochar, a finding they proposed was due to an improvement of the soil structure and permeability, thus enhancing the leaching of salts.

TABLE 5

Soil chemical properties for different treatments after six leaching episodes. CK: no amendment; G: 100% gypsum requirement application; BC: 1% biochar application; GBC: G + BC.

Treatments	Soil EC $dS\ m^{-1}$	pH	ESP[b] %	SAR [c] $cmol^{0.5}\ kg^{-0.5}$	Alkalinity $cmol\ kg^{-1}$
CK	0.16b[a]	9.45a	14.1b	2.44a	1.74b
G	0.82a	8.31c	8.55d	0.72b	0.39c
BC	0.17b	9.32b	17.9a	2.54a	1.93a
GBC	0.83a	8.27c	12.0c	1.05b	0.31c

[a]Same letters within a column indicate no significant differences among treatments ($P < 0.05$, Duncan's test); [b]ESP: exchangeable sodium percentage; [c]SAR: sodium adsorption ratio.

Due to an increase of Na^+ loss after leaching, results after the leaching episodes (Table 5) show that all treatments recorded reductions in soil SAR. SAR results for treatments G and GBC showed a greater decrease than those for treatments CK and BC, a finding attributed to more Ca^{2+} being dissolved in the soil solution from the gypsum, thus enhancing Na^+ displacement from exchange sites into the soil solution. This would therefore promote a greater reduction of soil SAR in these treatments (Gharaibeh *et al.*, 2009). The addition of biochar was not beneficial for decreasing soil SAR during leaching compared with the CK, and it did not have any significant improvement when combined with gypsum in reducing post-leaching soil SAR values. ESP results in post-leaching soil for the G and GBC treatments were significantly lower than those for the CK and BC treatments. This result was probably due to high volumes of Ca^{2+} (from the gypsum) being exchanged by Na^+, thus facilitating its release into the soil solution, and thereby being subsequently leached (Gharaibeh *et al.*, 2009; Chaganti *et al*., 2015).

Results for pH after the leaching experiment recorded a 1.14 unit decrease for soil treated with gypsum, indicating that the application of gypsum could efficiently maintain soil pH after successive leaching. This occurrence was attributed to the fact that more exchangeable Na^+ was removed from soil amended by gypsum (Misra *et al*., 2007; Chaganti *et al*., 2015). A significant increase of pH for soil with or without the addition of biochar after leaching indicated that biochar presented a slight effect in reducing soil pH. This result was in accordance with that of Chaganti and Crohn (2015) who also reported an insignificant effect of biochar on soil pH after leaching with brackish water. Alkalinity results after the leaching experiment recorded an increase of 79.86% and 81.87% for CK and BC, respectively. However, soils amended with gypsum presented an insignificant increase in alkalinity after leaching compared with the initial value (0.39 and 0.31 for G and GBC, respectively). It is likely that gypsum can eliminate dissolved CO_3^{2-} and HCO_3^- by forming insoluble $CaCO_3$ (Nayak *et al*., 2008), therefore maintaining a reduced soil alkalinity.

CONCLUSION

This study evaluated the reclamation potential of biochar and gypsum over a short time period, applied individually or together, to remediate a saline-alkali soil leached with saline ice and fresh water. Our results demonstrated that the addition of gypsum combined with biochar increased soil saturated water content and field water capacity, as well as saturated hydraulic conductivity. Most of salt present in the soil samples was leached out after the saline ice leaching episode, with more soluble content and Na^+ being leached from the soil treated with gypsum. The addition of gypsum to the soil samples, however, performed better on reducing soil SAR, pH and alkalinity compared to the non-amended soil, or soil with only the addition of biochar. The application of gypsum therefore with biochar amendments produced synergistic effects in improving soil physical and chemical properties during the leaching experiment.

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Figures

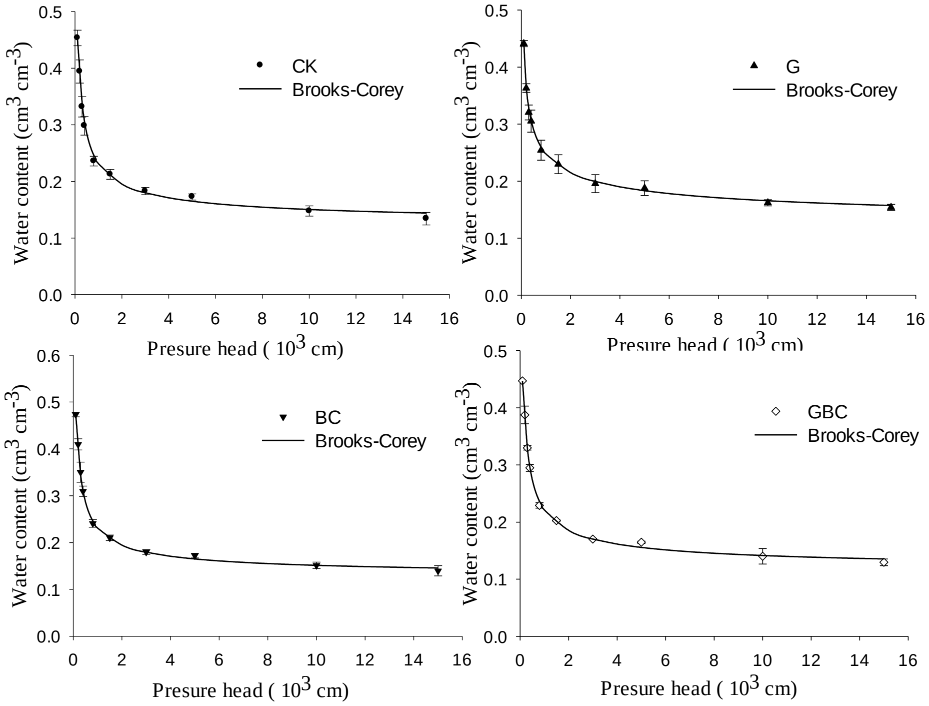

Fig. 1 Soil water retention curves using the Brooks-Corey equation for the different treatments. CK: no amendment; G: 100% gypsum requirement application; BC: 1% biochar application; GBC: G + BC.

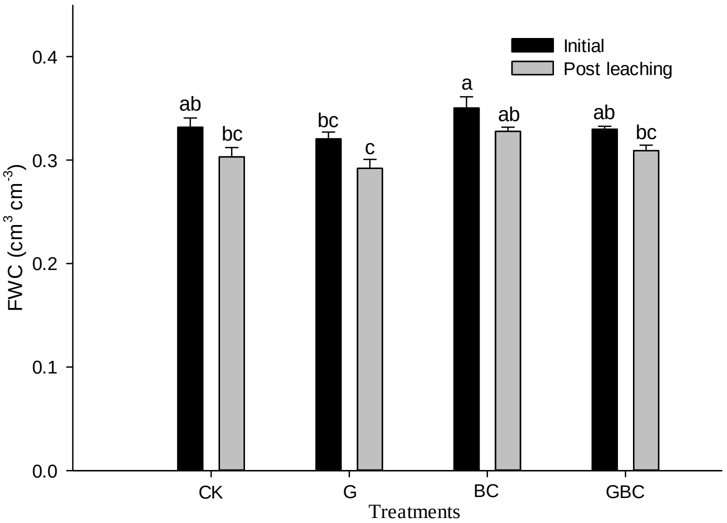

Fig. 2 Field water capacity for the different treatments before and after leaching. The same letters in a column series indicate no significant differences among treatments ($P < 0.05$, Duncan’s test). CK: no amendment; G: 100% gypsum requirement application; BC: 1% biochar application; GBC: G + BC.

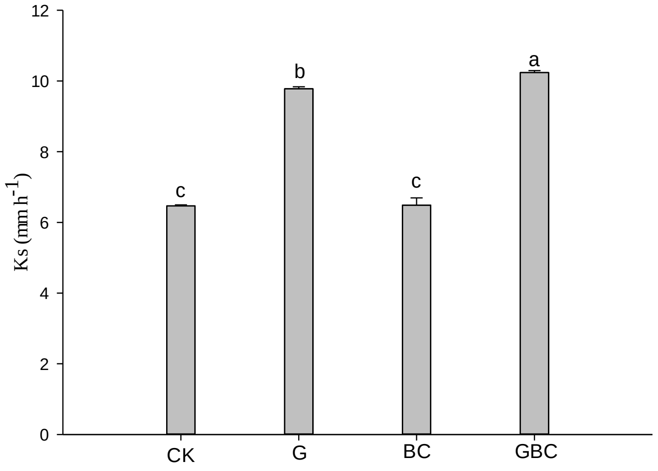

Fig. 3 The saturated hydraulic conductivity for the different treatments after ice melt-water leaching. The same letters in a column series indicate no significant differences among treatments ($P < 0.05$, Duncan's test). CK: no amendment; G: 100% gypsum requirement application; BC: 1% biochar application; GBC: G + BC.

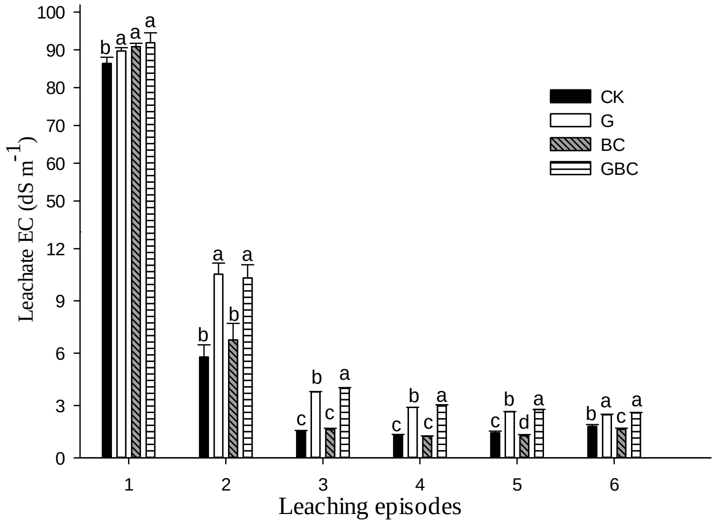

Fig. 4 Mean leachate salt content for the different treatments. The same letters in a column series indicate no significant differences among treatments (P <0.05, Duncan's test). CK: no amendment; G: 100% gypsum requirement application; BC: 1% biochar application; GBC: G + BC.

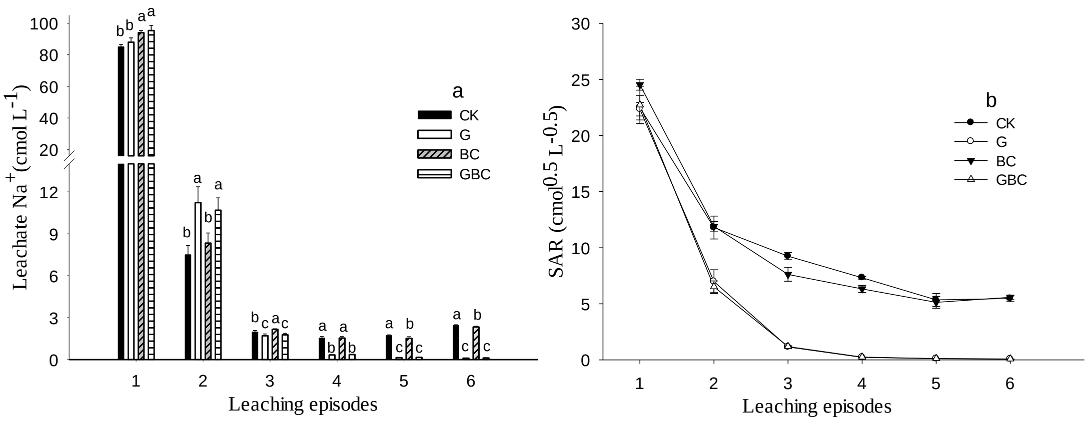

Fig. 5 The effects of different treatments on leachate Na^+ content (a) and SAR (b). The same letters in a column series indicate no significant differences among treatments (*P* <0.05, Duncan's test). CK: no amendment; G: 100% gypsum requirement application; BC: 1% biochar application; GBC: G + BC.