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Reclaiming saline-sodic soils using electrochemical processes: a case study from Sahl El-Tina plain, Egypt

Abstract: A leaching experiment was conducted using column techniques assessing efficiency of electrochemical process to reclaim saline-sodic soils. Soil material was collected from Sahl El-Tina plain, which located in North West coast of Sinai, Egypt. The experiment was designed as factorial randomized complete block and all treatments were replicated three times. Two 2.5 cm diameter×30 cm height mild stainless steel tubes were inserted into the soil matrix to serve as electrodes (i.e. cathode and anode). Distance between cathode and anode was 10 cm. Electrodes were supplied by a direct current (DC) power supply; Volt ages of 0.3 or 9 Volt. Leaching was done using the intermittent method so as to add portions to the already saturated soil columns, and obtain leachates equal to the added portions. Pore volume 0.1 PV was used in the leaching processes which are equal 498.4 cm³, i.e. PV being volume of pores per column, thus 1 PV equals volume of pores (cm³) expressed as water quantity. Electric remediation increased ionic mobility and separated salts from soil. All treatments decreased soil EC and soil sodicity expressed as SAR and ESP. Results showed that 9 Volt treatment was more effective in decreasing the soil EC and soil sodicity than the other treatments. Efficiency of treatments were 9-Volt > 3-Volt > leaching alone (non-DC treatment). This study suggests that leaching using direct current (DC) led to improvement of the chemical properties of saline sodic soils and required a short time to reclaim saline-sodic soils compared with leaching alone.

Keywords: saline-sodic soils, salt-affected soils, soil reclamation, electrochemical remediation, leaching, Egypt

INTRODUCTION

Electrochemical remediation technology is part of a boarder class of technology known as direct current technologies. This technology uses an electric current in the treatment process to either mobilize or break down contaminants in soils or sediments (Niroumand et al. 2012). Jayasekera and Hall (2007) observed that the soil dispersion, otherwise known as soil sodicity (measured as exchangeable sodium percentage and sodium adsorption ratio) decreased by up to 90% in most regions of the soil between the electrodes. Electrokinetic restoration has successfully been used to increase ionic mobility and separate pollutants from soil fields (Acar and Alshawabkeh 1993; Acar et al. 1995; Zhou et al. 2005; Altaee et al. 2008; Ryu et al. 2009; Park et al. 2009; Kim et al. 2009a, 2009b; Baek et al. 2009). Salts have higher ionic mobility than heavy metals and many studies have been reported to remove and retain salts using the electrokinetic process (Eid et al. 2000a, 2000b; Manokararajah and Sri Ranjan 2005a, 2005b; Jia et al. 2005; Jia et al. 2006; Cho et al. 2009).

Electrokinetic restoration involves application of a low current or Volt age gradient between the electrodes installed at the contaminated site. Electromi-

gration, namely the transportation of ions toward oppositely charged electrodes, is the major mechanism for separating and removing salts (Ryu et al. 2009). Electrokinetic process was performed by Cho et al. (2011) to restore sulfate-originated saline soil and to evaluate the effect of treatment duration, and found that after electrokinetic treatment, the electrical conductivity (EC) of the soil, an indicator of soil salinity, decreased to 1.93 dS·m⁻¹ from an initial value of 5.3 dS·m⁻¹ and the distribution of sulfate was similar to that of EC. By using column techniques the present study has been conducted to assess efficiency of electrochemical process to reclaim saline-sodic soils using. The main objective of this study was to evaluate the efficiency of leaching using direct current (DC) for remediation of saline-sodic soils in Egypt.

MATERIALS AND METHODS

Soil sampling

A leaching experiment was conducted using column techniques at the laboratory of Soil Science Department, Faculty of Agriculture, Zagazig University (Egypt) in 2012. The area from where the soil material was collected to conduct for the current column experiment was Sahl El-Tina plain located in North

West coast of Sinai, Egypt. Soil material used for the experiment was collected from the top 30 cm. Samples were air dried, crushed, mixed and passed through a 2 mm sieves. Table 1 shows physical and chemical properties of the saline-sodic soil.

Soil columns design and preparation

Nine polyvinyl chloride (PVC) cylindroids tubes of 40 cm height and 16 cm inside diameter were used. The bottom of each tube was sealed with perforated a mesh nylon screen and glass wool. Acid-washed inert sand (pre-washed with HCl and water) was placed on the tube bottom to make a 5 cm layer of the column. Soil was packed in tubes so that the soil column was 30 cm height and a bulk density of $1.4 \text{ Mg}\cdot\text{m}^{-3}$. This required a quantity of soil of 8 kg of soil per column. Such arrangement allowed to give sufficient space (5 cm on top of soil column) for addition of water for the leaching process. Figure 1 illustrates a schematic drawing of the electric cell used in this study. Two

FIGURE 1.
Schematic drawing
of the soil column
and electrochemical
experimental system

2.5 cm diameter×30 cm height mild steel tubes were inserted on the soil matrix to serve as electrodes (i.e. cathode and anode). Distance between cathode and anode was 10 cm. Electrodes were contacted to a direct current power supply (DC). The voltage treatments were 3 and 9 V. An additional treatment using no electric treatment was conducted. In this treatments water having EC $1.5 \text{ dS}\cdot\text{m}^{-1}$ was used for the leaching.

Leaching process

The leaching procedure was conducted using the intermittent method adding water portions to the already saturated soil columns. Leachates were collected until obtaining volume equals to the one added. Portions of 0.1 pore volume (PV) were used in the leaching processes. The PV equals 4984 cm^3 (i.e. volume of pores per column). The water was added in increments. Leachates were collected and analyzed for salinity. Leaching termination was done after passing 1 PV through soil columns (i.e. ten increments of 0.1 PV). Each leachate was analyzed for the total soluble salts and soluble ions.

Methods used for analysis

After the termination of leaching, soil columns were separated into two segments as follows: 0–15 and 15–30 cm. Soil from each segment was air dried, crushed, mixed and passed through a 2 mm sieves and analyzed according to the methods described by Richards (1954) and van Reeuvijk (2002).

- Particle size distribution was determined according to the pipette method. Sodium hexametaphosphate was used for dispersion after leaching the soluble salts.
- Calcium carbonate content was determined using the calcimeter.

TABLE 1. Physical and chemical properties of studied soil

Property	Value
Particle size distribution [%]:	
– Clay	46.5
– Silt	35.2
– Fine sand	15.6
– Coarse sand	2.7
– Texture class	Clayey
Soil moisture characteristics [%]:	
– Saturation percent	62.3
– Field capacity	31.2
– Wilting point	15.6
Density:	
– Bulk density [$\text{Mg}\cdot\text{m}^{-3}$]	1.4
– Total porosity [%]	49.1
Organic matter [$\text{g}\cdot\text{kg}^{-1}$]	5.3
CaCO_3 [$\text{g}\cdot\text{kg}^{-1}$]	94
pH [soil suspension 1:2.5]	8.6
Soil saturation paste extract:	
– EC_e ($\text{dS}\cdot\text{m}^{-1}$)	51.2
– Soluble ions ($\text{mmol}\cdot\text{dm}^{-3}$)	
Na^+	589
K^+	26.4
Ca^{2+}	152
Mg^{2+}	564
Cl^-	1126
HCO_3^-	9.7
SO_4^{2-}	195
SAR	31.0
Exchangeable cations and CEC ($\text{cmol}_c\cdot\text{kg}^{-1}$):	
Na^+	11.3
K^+	2.8
Ca^{2+}	7.4
Mg^{2+}	10.0
CEC ($\text{cmol}_c\cdot\text{kg}^{-1}$)	31.5
ESP	35.9

- Organic matter content was determined using Walkley-Black method.
- Electric conductivity (EC_e) and the main ion composition were determined in the saturation soil-paste extract as follows:
 - 1 – EC_e by conductometric method.
 - 2 – CO_3^{2-} and HCO_3^- content by titration with a standard solution of sulphuric acid using phenolphthalein as an indicator for former and methyl orange for latter.
 - 3 – Cl^- content by argentometric method.
 - 4 – Ca^{2+} and Mg^{2+} content were determined by titration with sodium versinate solution
 - 5 – Na^+ and K^+ content using flame photometer.
- The pH value was measured using a pH-meter in soil suspension 1:2.5.
- Cation exchange capacity and exchangeable cations were determined by 1M ammonium acetate extraction at pH 7.

RESULTS AND DISCUSSION

Chemical composition of leachates

Salt and ion removal as affected by leaching and electric treatments are shown in Figure 2. Generally, results show that all treatments receiving direct current (DC) gave greater salt removal. Salt removal by

treatments was in the following order: 9-Volt > 3-Volt > leaching alone (i.e. non-DC). The main effect shows that 9 Volt gave the highest salt removal ($49.5 \text{ dS}\cdot\text{m}^{-1}$) whereas non-DC treatment gave the lowest ($38.2 \text{ dS}\cdot\text{m}^{-1}$). This shows the high efficiency of electric current in salt removal from saline sodic soils. At start of leaching and after collection of first leachate, the EC values of the leachates were 187, 178 and $210 \text{ dS}\cdot\text{m}^{-1}$ for the 3, 9 Volt and the non-DC, respectively. For the second and third leachates, the DC-treatments were of markedly greater efficiency in removing salts. The 3 Volt and 9 Volt treatments surpassed the non-DC treatment by 13 to 46% for the 3Volt and 28 to 79% for the 9 Volt. From the fourth leachate onwards, both DC-treatments maintained their superiority, though by smaller margins. Imposition of electrical field in such soil of low permeability causes ions to move towards electrode of opposite. It follows that most of the readily soluble salts, originally present in the soil, were leached out with the leachate. Such mechanism was considerable during the first 3 leachates and decreased sharply afterwards. Athmer et al. (2013) reported that a series of anode and cathode wells placed in the soil can be used to separate and remove chloride (Cl^-) and sodium (Na^+), respectively. Clear from the results that the higher electric current, the more decomposition of salts and therefore it was easier to leach ions from the soil. Similar results have been

FIGURE 2. Change on EC of the leachate as a function of pore volume

reported by others authors (Park et al. 2009; Kim et al. 2009a, 2009b; Baek et al. 2009; Altaee et al. 2008; Zhou et al. 2005; Acar and Alshawabkeh 1993; Acar et al. 1995).

Soil salinity

Soil salinity as affected by leaching and electric treatments is shown in Table 2. Data reveal the effect of treatments throughout the depth of soil columns was significantly. Also the interaction between treatments and depth of soil was statistically significant. Soil EC was decreasing upon leaching in all depths. The results revealed that, salinity of soil was significantly decreased by 9 Volt and 3 Volt treatments compared with control in the two depths. The efficiency in decreasing soil salinity was higher with 9 Volt than 3 Volt treatments and lowest with the non-DC treatment. Salinity relative to initial status decreased by 94, 76 and 73% due to 9 Volt, 3 Volt and non-DC treatments, respectively. The pattern of rating regarding the treatments was similar in each of the two soil depths. In general, there was greater salinity with soil depth. You-Jin et al. (2013) reported that the soil EC was reduced 56% using electrokinetic direct current (DC). Commonly, when a Volt age gradient is applied to a soil, the resulting current flowing is found to be decreasing with time after an initial period of increase, which may last for several hours (Virukuttyte et al. 2002; Kim et al. 2005; Lynch et al. 2007). In fact, the initial current increase is due to an increase in the salt concentration in the soil pore water,

due to the salt dissolution from soil particles (Mitchell 1993). As time elapses, the pore water ionic concentration decreases due to the gradual depletion of solutes, to the precipitation of non-conductive solids from the pore water salts and the polarization of the electrodes (Acar and Alshawabkeh 1993; Acar et al. 1995; Yu and Nereitnieks 1997; Virukuttyte et al. 2002; Reddy and Chinthamreddy 2004; De Gioannis et al. 2007; Lynch et al. 2007). In particular, during the unenhanced electrochemical treatment, the current flowing is gradually decreased because of the formation of high electric resistivity zone near the cathode, due to the precipitation of metal hydroxides under the local basic conditions (Acar et al. 1995; Amrate et al. 2005; Kim et al. 2006). Therefore, it is common for the current to reduce with time, unless amendments, such as ionic solutions, are supplied to provide new charge carriers in the soil-solution system (Reddy and Chinthamreddy 2004). Usually, in bench-scale electrokinetic tests, the electrical currents are found to increase rapidly after the application of the Volt age gradient, to reach a peak value within 1–24 h, and then to decrease and stabilized at a nearly constant steady state value (Reddy and Chinthamreddy 2004; Kim et al. 2005). Various salts can contribute to the ionic conductivity of the pore water solution. HCO_3^- and CO_3^{2-} may be released from soil. The addition of ionic solutions (e.g. NaCl, H_2SO_4) can allow for an additional salt release and improve the soil conductivity. Also the addition of hydrogen peroxide could enhance the ionic conductivity, by providing anions deriving from its decomposition, such

TABLE 2. Chemical soil properties of soil at the end of leaching

Treatment (A)	SD (B)	EC_e $\text{dS}\cdot\text{m}^{-1}$	pH	Cations ($\text{mmol}\cdot\text{dm}^{-3}$)				Anions ($\text{mmol}\cdot\text{dm}^{-3}$)				SAR	ESP
				Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}		
Leaching alone (non-DC)	0–15	13.9	8.1	78.3	4.3	17.0	53.0	87.7	14.1	7.1	43.6	13.2	19.4
	15–30	14.0	8.0	57.5	4.2	36.5	55.7	57.7	28.6	14.4	53.3	8.5	14.1
	Mean	13.9	8.1	67.9	4.2	26.7	54.3	72.7	21.3	10.7	48.4	10.9	16.8
3-Volt	0–15	12.2	8.0	50.9	3.6	31.0	48.4	52.4	35.9	18.0	27.5	8.1	13.6
	15–30	12.5	8.2	41.1	3.7	43.6	48.6	49.0	19.9	10.0	57.9	6.6	11.8
	Mean	12.4	8.1	46.0	3.6	37.3	48.5	50.7	27.9	14.0	42.7	7.3	12.7
9-Volt	0–15	2.8	8.0	24.0	1.8	16.6	23.8	22.3	10.4	5.2	28.2	3.7	8.0
	15–30	3.0	7.9	11.1	0.8	6.6	10.5	12.4	5.0	2.5	9.1	3.9	8.3
	Mean	2.9	7.9	17.6	1.3	11.6	17.1	17.4	7.7	3.9	18.7	3.8	8.1
Means of soil depth (B)													
Soil Depth (cm)	0–15	9.6	8.0	51.0	3.2	21.5	41.7	54.2	20.1	10.1	33.1	8.3	13.7
	15–30	9.8	8.0	36.6	2.9	28.9	38.2	39.7	17.8	9.0	40.1	6.3	11.4
	Mean	9.7	8.0	43.8	3.0	25.2	40.0	46.9	19.0	9.5	36.6	7.3	12.5
LSD 0.05	A	0.24	NS	3.61	0.20	2.65	3.20	8.06	4.72	2.37	13.11	0.75	0.86
	B	0.20	NS	2.95	NS	2.17	NS	6.58	NS	NS	10.70	0.61	0.70
	AB	0.34	NS	5.11	NS	3.75	NS	11.39	6.68	3.35	18.54	1.06	1.21

Notes: SD – soil depth (cm); EC_e – electrical conductivity; pH was measured in soil suspension 1:2.5; SAR – sodium adsorption ratio; ESP – exchangeable sodium percentage; A: – treatments, B – soil depth and AB – interaction between treatments and soil depth.

FIGURE 3. EC_e in the soil segments after termination of experiment

as O_2^- and HO_2^- (Kim et al. 2006). In the electrokinetic processes, the decrease in the current flowing may be counterbalanced by the addition of proper ionic solutions as the electrolyte, to compensate the exhaustion rate of the electrolyte solution by electromigration (Park et al. 2005). These processes are designed in order to balance the ionic extraction rate due to electromigration and the supplementation of salts in the electrolyte solution, therefore the resulting current may be constant.

Soil pH

Electrolysis of the water, under the applied Volt age caused a change in pH. Reactions can be described as follows:

At anode (oxidation): $2H_2O \rightarrow O_{2(gas)} + 4H^+_{(aq)} + 4e^-$

At cathode (reduction): $4H_2O + 4e^- \rightarrow 2H_{2(gas)} + 4OH^-_{(aq)}$

Hydrogen and hydroxide ions generated at the anode and cathode were transported toward the opposite charged electrodes by electromigration. Thus, soil pH would decrease at the anode and increase at the cathode. Results of pH are presented in Table 2

and Figure 4. Results reveal that there was no significance between all treatments. The interaction between treatments and depth of soil were not significant as well. There was a tendency for a decrease in pH values due to treatments of electric remediation. The pH values ranged from 8.0 to 8.2 (Fig. 4). The soil must have had high buffering capacity due to the heavy clayey texture and high $CaCO_3$ content (Table 1). Kim et al. (2011) observed that the pH values ranged from 4.8 to 6.6 due to the high buffering capacity of the soil upon high organic content and considerable silt content.

Soil sodicity

Sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP) were estimated by using the following equation where ionic concentration of the saturation extracts are expressed in $mmol_c \cdot dm^{-3}$

$$SAR = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}}$$

$$ESP = \frac{100(-0.0126 + 0.01475 \times SAR)}{1 + (-0.0126 + 0.01475 \times SAR)}$$

FIGURE 4. pH in the soil segments after termination of experiment

The results of ESP and SAR are presented in Table 2, and Figs. 5 and 6. The decrease of sodicity upon leaching is shown by very high decrease in SAR (being ranging from less than 1 to 13 compared with 31 before leaching) and also very high decrease in ESP (being less than 1 to 19 as compared with about 36 before leaching). The comparative efficiency rating of treatments is as follows: 9 Volt>3 Volt>leaching alone (i.e. non-DC). The decrease in soil SAR upon leaching amounted to 65.0, 76.5 and 87.5%, for the non-DC, 3- Volt and 9-Volt treatments, respectively. Regarding ESP, respective decreases were 53.2, 64.6 and 76.9% for the non-DC, 3 Volt and 9 Volt treatments, respectively. The pattern of rating regarding the treatments was similar in each of the two soil depths. In general there was a greater ESP and SAR value with soil depth. The results showed that sodicity of soil significantly decreased by 9 Volt and 3 Volt treatments compared with control in the two depths. This may be explained by soluble ions removal process by leaching which makes it easy for exchangeable sodium

ions released from the exchange complex to the soil solution upon equilibrium between soluble and exchangeable ions and then the removal of exchangeable ions become easier. Also, presence of calcium carbonate could be helpful in reducing ESP of the soil columns.

CONCLUSIONS

A leaching experiment was conducted using column techniques assessing efficiency of electrochemical process to reclaim saline-sodic soils. All treatments significantly decreased soil EC, pH and soil sodicity expressed as SAR and ESP. Efficiency of treatments was in the following order: 9-Volt>3-Volt> leaching alone (non-DC treatment). Leaching using direct current (DC) led to improvement of the chemical properties of saline sodic soils and required a shorter time to reclaim saline-sodic soils comparing with leaching.

FIGURE 5. SAR in the soil segments after termination of experiment

FIGURE 6. ESP [%] in the soil segments after termination of experiment

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