Effect of Electrokinetic Pollutant Removal on the Status of Some Macro and Micro Elements in Saline Soil

Ahmed M. Abou-Shady1, Doaa T. Eissa1, Osama M. Abdelmottaleb1 and Rehab H. Hegab2

ABSTRACT
Soil electrokinetic remediation is an appropriate technique to remove pollutants from soils particularly in low permeability soil. Recently, a new variation of soil electrokinetic remediation (SEKR) known as perforated cathode pipe SEKR system (PCPSS) was investigated for heavy metals removal and land reclamation. The PCPSS was enhanced for the removal of heavy metals via introducing the vertical anode/perforated cathode pipe SEKR system (VA/PCPSS). In the present work, the behaviors of associated macro and micro elements were investigated during the removal of heavy metals from soil via either the PCPSS or the VA/PCPSS. The results indicated that calcium (Ca²⁺) depleted from the top surface of soil specimen and accumulated close to the perforated cathode pipes when the PCPSS was applied. The depletion of Ca²⁺ was noticeably detected in the middle of specimen via installing the VA/PCPSS. The removed magnesium (Mg²⁺) was lower than Ca²⁺, and it tended to desorb from the soil layer around anode and re-absorbed again in the subsequent layer during the application of the PCPSS. This accumulation disappeared when the VA/PCPSS was applied. The removal of potassium (K⁺) was lower in the top layer of soil when the VA/PCPSS was installed that may increase its applicability during soil reclamation. Boron accumulated around anode in the PCPSS system. On the other hand the application of the VA/PCPSS shunned this behavior. Molybdenum (Mo) tended to oscillate during the application of the PCPSS, however the application of the VA/PCPSS resulted in high removal rate of Mo at the end of anodes and around cathode pipes.

Keywords: Electrokinetic remediation; PCPSS; VA/PCPSS; Macro elements; Micro elements

INTRODUCTION
Soil pollution with heavy metals has been widely increased due to industrial revolution particularly in last decades. Also, reusing of wastewater in agriculture purpose has negatively increased the concentrations of organic and inorganic pollutants containing agricultural soil. There are several approaches have been taken to remediate polluted soils including physical, chemical, and biological treatments. Soil electrokinetic remediation (SEKR) is one of physical remediation approach that fits low permeability of the soil polluted with heavy metals, organic pollutants, and radioactive materials (Abou-Shady, 2012, Abou-Shady, 2016a, Abou-Shady, 2017).

Recently, a modern technology have been introduced for land reclamation and heavy metals removal known as perforated cathode pipe SEKR system (PCPSS) to remediate heavy metals containing polluted soils with high efficiency. Also, the PCPSS was investigated as a possible technique that may be used to achieve land reclamation to avoid the consumption of large amounts of water and to ensure the sustainability (Abou-Shady, 2012; Abou-Shady and Peng, 2012; Abou-Shady, 2016b). The performance of the PCPSS has been recently improved via introducing five new designs to remove eight heavy metals from saline clay soil. The most convenient design proposed to improve the performance of the PCPSS was the vertical anode/perforated cathode pipe SEKR system (VA/PCPSS) in which several goals have been achieved such as preventing the formation of a pH jumping zone, prevention of the formation of an unsaturated zone, and consumption of a comparatively low amount of water (Abou-shady et al., 2018).

The aim of this study was to evaluate the behavior of some macro and micro elements including calcium (Ca²⁺), magnesium (Mg²⁺), sodium (Na⁺), potassium (K⁺), boron (B), and molybdenum (Mo) during soil electrokinetic remediation in saline soil using either a perforated cathode pipe SEKR system (PCPSS) or the vertical cathode/perforated cathode pipe SEKR system (VA/PCPSS). Based on literature survey there are no available articles focused on the effects of soil electrokinetic remediation on the behavior of such associated elements that may be affected with the passed current. This evaluation is very important to ensure the rehabilitation of polluted soils particularly those under agriculture uses.

MATERIALS AND METHODS
Soil properties
Saline clay soil was contaminated with different heavy metals and treated using the PCPSS and the VA/PCPSS according to Abou-shady et al., (2018). The chemical and physical properties of soil are listed in Table 1. Soil electrical conductivity was 9.18 dS m⁻¹ for

1Laboratory of Water & Soil Chemistry, Water Resources and Desert Soils Division, Desert Research Center, El-Matariya 11753, Cairo, Egypt.
2Soil Fertility and Microbiology Department, Water Resources and Desert Soils Division, Desert Research Center, El-Matariya 11753, Cairo, Egypt.
Received February 14, 2018, Accepted March 14, 2018
supernatant extracted from soil water ratio 1:1. Soil pH was close to neutral condition. The concentrations of Na\(^+\) represented the highest values among cations followed by Ca\(^{2+}\) > mg\(^{2+}\) > k\(^+\) (Table 1). On the other hand, Cl\(^-\) represented the highest concentration among anions followed by sulfate. This indicated that, the saline soil was rich in NaCl content. The hydraulic conductivity was \(1.83 \times 10^{-4}\) cm s\(^{-1}\).

**Table 1** The main soil chemical and physical properties of the used soil (Abou-shady et al., 2018)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Natural Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Texture</td>
<td>Clay</td>
</tr>
<tr>
<td>Electrical Conductivity (1:1) (dS m(^{-1}))</td>
<td>9.18</td>
</tr>
<tr>
<td>pH</td>
<td>7.56</td>
</tr>
<tr>
<td>Ca(^{2+}) (ppm)</td>
<td>780</td>
</tr>
<tr>
<td>K(^+) (ppm)</td>
<td>109.5</td>
</tr>
<tr>
<td>Na(^+) (ppm)</td>
<td>2240</td>
</tr>
<tr>
<td>Mg(^{2+}) (ppm)</td>
<td>585</td>
</tr>
<tr>
<td>Cl(^-) (ppm)</td>
<td>2441.5</td>
</tr>
<tr>
<td>SO(_4^{2-}) (ppm)</td>
<td>1031.3</td>
</tr>
<tr>
<td>Hydraulic Conductivity (cm s(^{-1}))</td>
<td>1.83 \times 10^{-4}</td>
</tr>
</tbody>
</table>

Recently, we have invented a new variation of soil electrokinetic remediation known as perforated cathode pipe SEKR system (PCPSS) as shown in Figs 1a and 1b. The main purpose of the PCPSS was to enhance the vertical electro-migration of heavy metals and soil elements. As it depicted in Figs 1a and 1b, the PCPSS approach will force electro-migration and electro-osmosis in one-way flow towards the perforated cathode pipes. This allows to collect heavy metals containing wastewater in an underground drainage system that is already exist in Egyptian clay soil. The details information about the PCPSS may be found in our previous studies (Abou-Shady, 2012; Abou-Shady and Peng, 2012; Abou-Shady, 2016b).

As a new generation of SEKR there were several technical problems appeared with the primary investigation of the PCPSS. This motivated us to improve the original design of the PCPSS with a five new designs. The vertical anode/perforated cathode pipe SEKR system (VA/PCPSS) was recommended as the most alternative design to overcome drawbacks raised during the operation of the PCPSS as shown in Fig. 1c (Abou-shady et al., 2018).
Methodology

Soil cations and anions were determined in soil solution 1:1 using ion chromatography (Dionex ICS-1100). After terminating the treatment period (23 day), Ca\(^{+2}\), Mg\(^{+2}\), B, and Mo were detected in soil digest solution simultaneous with heavy metals detection using Inductivity Coupled Argon Plasma (ICAP 6500 Duo, Thermo Scientific England). In the same digest solution, the concentrations of Na\(^{+}\) and K\(^{+}\) were measured using Flamephotometer (CL378, India). Fixed applied potential 40 V (20 V cm \(-1\)) was set for either the PCPSS or the VA/PCPSS. Fifty samples were taken to represent the whole specimen. The contour maps were drawn using (Surfer 10).

RESULTS AND DISCUSSION

Ca\(^{+2}\) behavior during the remediation of heavy metals containing soil using the PCPSS and the VA/PCPSS

Calcium ion is a vital element for plant growth and also important for soil structure, it plays an important role for creating soil aggregates that eventually improves soil physical and chemical properties (Dontsova and Norton, 1999; White and Broadley, 2003; Warton and Matthiessen, 2005; Wuddivira and Camps-Roach, 2007). The studied soil contained Ca\(^{+2}\) at concentration of 780 mg kg\(^{-1}\). During electrokinetic pollutant removal of heavy metals, Ca\(^{+2}\) containing saline soils will migrate towards cathode pipe via electro-migration, electro-osmosis, and diffusion using either the PCPSS or the VA/PCPSS. The continuously depletion of Ca\(^{+2}\) from saline soil may reflect a negative impact on soil aggregate that eventually decreases soil hydraulic conductivity and electro-osmosis during the operation of soil electrokinetic remediation (Abou-Shady, 2016b). Previous investigations indicated that the VA/PCPSS overcome the formation of pH jumping and unsaturated zone as it presented in Figs. 2a and 2b (Abou-shady et al., 2018). Data presented in Fig. 3a shows that Ca\(^{+2}\) completely removed from the upper surface of soil specimen when the PCPSS was installed. In the pH jumping zone, the removed Ca\(^{+2}\) was achieved approximately 50%. When the PCPSS was used, Ca\(^{+2}\) concentrations around perforated cathode were almost constant and the lowest values were notified close to anode. Applying the VA/PCPSS did not markedly change Ca\(^{+2}\) concentrations in the top surface of soil specimen. However, Ca\(^{+2}\) was depleted from the middle of specimen when the VA/PCPSS was used. It was clear that, Ca\(^{+2}\) accumulated adjacent to cathode pipes. We suggest that, to ensure high performance during the reclamation of saline clay soil the PCPSS should be used firstly as a primary treatment that may be followed by the VA/PCPSS.

---

Fig. 2. pH distribution in the soil electrokinetic specimen A) the PCPSS and B) the VA/PCPSS (Abou-shady et al., 2018)
Mg$^{2+}$ behavior during the remediation of the PCPSS and the VA/PCPSS

Mg$^{2+}$ existed in saline soil with relatively low concentrations (585 mg kg$^{-1}$) compared with Ca$^{2+}$ and Na$^+$ (Table 1). In general, the effect of Mg$^{2+}$ concentrations on the formation of soil aggregates was lower than Ca$^{2+}$ (Dontsova and Norton, 1999). Mg$^{2+}$ containing soil should be adequate for plant requirements otherwise several physiologic functions will be appeared owing to the interrelated processes (Kirkby and Mengel, 1976). Fig. 4a shows that Mg$^{2+}$ depleted from the area close to the horizontal anode in the PCPSS regular design and re-adsorbed in subsequent layer (upper half of the PCPSS specimen). The same tendency was observed in the lower half of the PCPSS specimen. The removed Mg$^{2+}$ was comparatively lower than Ca$^{2+}$. In the depletion zone, the removed Mg$^{2+}$ was close to 50%. The accumulation of Mg$^{2+}$ was observed in the gap between cathode pipes. Applying the VA/PCPSS enhanced the removed Mg$^{2+}$ from the right part of top surface (around vertical cathode) and accumulated in the left part as shown in (Fig. 4b).
Ahmed M. Abou-Shady, et al.: Effect of Electrokinetic Pollutant Removal on the Status of Some Macro and Microelements

The VA/PCPSS succeeded in preventing the re-adsorption of Mg\(^{2+}\) in middle of specimen in the right part of specimen. Inserting vertical anode in the VA/PCPSS design induced the movement of Mg\(^{2+}\) from the gap between cathode pipes to outside. Accordingly, to ensure the best removal of Mg\(^{2+}\) during saline soil electro-reclamation, the installation of the PCPSS should be followed by the VA/PCPSS.

Na\(^+\) behavior during the remediation of the PCPSS and the VA/PCPSS

Sodium ion in saline soils is considered the dilemma in arid and semi-arid countries owing to its negative impact on the formation of soil aggregates that eventually decreases hydraulic conductivity (Abou-Shady, 2016b). Relatively high concentrations of Na\(^+\) (2240 mg kg\(^{-1}\)) was measured in soil solution compared with Ca\(^{2+}\) and Mg\(^{2+}\). Generally, the removed Na\(^+\) was more than 50% in either the PCPSS or the VA/PCPSS, as it depicted in Fig. (5). The removed Na\(^+\) was much better in the VA/PCPSS than the PCPSS particularly close to perforated cathode pipe. Na\(^+\) accumulated close to cathode pipe in the PCPSS regular design. The accumulation of Na\(^+\) in the VA/PCPSS was much lower than the PCPSS and depleted from the horizontal zone above cathode pipe. The removed Na\(^+\) was much better with the VA/PCPSS technique than the PCPSS. Ongoing investigation focusing on improving the removal rate of Na\(^+\) over Ca\(^{2+}\) and Mg\(^{2+}\) from saline soils via improving the VA/PCPSS technique.

K\(^+\) behavior during the remediation of the PCPSS and the VA/PCPSS

From agricultural point of view, K\(^+\) is considered as one of the three major nutrients (NPK) essential elements for plant growth (Wang et al., 2013). K\(^+\) showed comparatively low concentrations levels in saline clay soil 190.5 mg kg\(^{-1}\) compared with Ca\(^{2+}\), Mg\(^{2+}\), and Na\(^{2+}\). The removal of K\(^+\) was high when the PCPSS was installed compared with the VA/PCPSS in the upper half of electrokinetic specimen as presented in Figs. (6 a and b). Accordingly, the VA/PCPSS is highly recommended to avoid the depletion of K\(^+\) and to ensure soil sustainability for agricultural purpose. The lower removal rate of K\(^+\) may be owing to the capture of K\(^+\) inside clay layers. On the other hand, the depletion of K\(^+\) in the lower half of soil specimen was comparatively high when the VA/PCPSS was installed. This is may be due to the relatively high pulling force close to the cathode pipes (Abou-Shady and Peng, 2012).

Boron behavior during the remediation of the PCPSS and the VA/PCPSS

If born exist in traces amounts, it may vital for plant maturity, flower set, and water balance (Whittington, 1957; Bhat, 2013; Ganie et al., 2013; Ag-Info Centre). Boron existed in saline clay soil with total amount of 48.7 mg kg\(^{-1}\). Boron depleted from the middle of the PCPSS specimen and accumulated around anode electrode because of the negatively charged atom surface, as shown in Fig. (7a). Accordingly, plants grown in polluted soil treated with the PCPSS will...
suffer from boron toxicity. The VA/PCPSS overcame boron depletion from the middle of soil specimen as it shown in Fig. 7b. Applying the VA/PCPSS did not affect negatively on the distribution of boron throughout soils. Accordingly, the VA/PCPSS will be more appropriated with boron heavy metals containing polluted soil with heavy metals.

**Mo behavior during the remediation of the PCPSS and the VA/PCPSS**

Molybdenum may be a vital element for plant growth at low concentrations (Zimmer and Mendel, 1999; Kaiser et al., 2005). The total concentration of Mo in saline clay soil was as low as 0.88 mg kg\(^{-1}\). Mo distribution inside the PCPSS system is shown in Fig. 8a. It is clear that, Mo removal tended to osculate throughout soil specimen, this may be because of its comparatively low concentrations in the treated soil. The application of the VA/PCPSS resulted in the depletion of Mo from the area adjacent to anodes end and cathode pipes as presented in Fig. (8b). Accordingly, Mo re-distribution after electrokinetic remediation did not negatively affect by neither the PCPSS nor the VA/PCPSS.

![Fig. 6. Distribution of K\(^+\) in the treated soil using A) the PCPSS and B) the VA/PCPSS](image)

![Fig. 7. Distribution of B in the treated soil using A) the PCPSS and B) the VA/PCPSS](image)
Ongoing researches will be focused on improving the performance of the VA/PCPSS to treat heavy metals containing sewage sludge in which pilot scale experiments will be established using continuously-reoriented electric field (Almeria et al., 2012; Peng et al., 2013). The heavy metals containing outlet discharge will be treated simultaneously using integrated electrodialysis, electrolysis, and adsorption (Abou-Shady et al., 2011; Bi et al., 2011; Peng et al., 2011; Abou-Shady et al., 2012a; Abou-Shady et al., 2012b; Jin et al., 2102) Also, the redistribution of humic substances during soil electrokinetic remediation will be taken into consideration (Aboushady, 2008; Khalil et al, 2009).

Conclusions

Two different techniques were developed to remediate heavy metal containing polluted soil. The first technique was perforated cathode pipe SEKR system (PCPSS), and the second technique was the vertical anodes/perforated cathode pipe SEKR system (VA/PCPSS). In the present work, the behavior of some macro and micro element was investigated during the remediation of heavy metals containing polluted soil. The obtained resulted are summarized as follows:

1) High removal of Ca$^{2+}$ was observed in the top layer close to anode when the PCPSS was applied and tended to accumulate close to cathode pipes. On the other hand, in the VA/PCPSS Ca$^{2+}$ was depleted from the middle of soil specimen.

2) The removal percentage of Mg$^{2+}$ was lower than Ca$^{2+}$. The Mg$^{2+}$ desorbed from the layer close to anode and re-adsorbed in the subsequent layer in the PCPSS technique. On the other hand, the application of the VA/PCPSS shunned this accumulation.

3) The removed Na$^+$ was more than 50% in either the PCPSS or the VA/PCPSS. In general, the removal rate using the VA/PCPSS was higher than the PCPSS.

4) The removal rate of K$^+$ was high during the PCPSS compared with the VA/PCPSS.

5) Boron depleted from the middle of the PCPSS and migrated toward the anode. The VA/PCPSS avoided this accumulation that may be considered as an agricultural value.

6) Molybdenum removal tended to osculate throughout soil specimen, this may be because of its comparatively low concentration in the treated soil.

Acknowledgments

This work was funded by the Desert Research Center (DRC), Egypt. Research No. 1546.

REFERENCES


Ag-Info Centre. Data was obtained from the following website: (http://www1.agric.gov.ab.ca/$department/deptdocs.nsf/all/agedex789).
تأثير المعالجة الكهربائية للملوثات على حالة بعض العناصر الكبرى والصغيرة في الأرض الملحية
أحمد أبو شادي، دعاء عيسى، أسماء عبد المطلب، رحاب جلاب

الملخص العربي

تعتبر المعالجة الكهربائية من التقنيات الملائمة لإزالة الملوثات من الأراضي ذات الظروف المتخصصة. قدمنا حديثاً تطوير جيل جديد من المعالجة الكهربائية معرف حالياً باسم أنوية الكاذود المثبتة. وقد تم اختبار هذه الطريقة لإزالة النفايات الثقيلة وكذلك إصلاح الأراضي الملحية. تم تحديد نظام أنوية الكاذود المثبتة لمعالجة الثقيل لإزالة النفايات الثقيلة وذلك بتقديم نظام جديد يوفر نظام إطلاعات النفايات المشارك لأنوية الكاذود المثبتة. من البحث الحالي تم دراسة سلوك بعض العناصر الكبرى والصغيرة أثناء إزالة الفيزاء الثقيلة الموجودة في الأرض باستخدام نظام أنوية الكاذود المثبتة لمعالجة الثقيل ومن نظام إطلاعات النفايات المشارك لأنوية الكاذود المثبتة. أوصيت النتائج المترتبة عليها أن

قد تم إزالة الكاذود من أعلى سطح التربة وتراكم بالقرب من أنوية الكاذود المثبتة وذلك في نظام أنوية الكاذود المثبتة. وعندما قمنا باستخدام نظام إطلاعات النفايات المشارك لأنوية الكاذود المثبتة فقد تراكم الكاذود في منتصف عمود التربة. وبصفة عامة وجد أن كمية الملوثات الموجود بالثنيين يمكن أن تكون أكبر بالمقارنة بالكاذود. كما وجد أن في نظام أنوية الكاذود المثبتة أن

المغشكن السالب

المغشكن المزال قد تم إزالة من طبقة وتركازة في الطبقة التالية عندما تم استخدام نظام أنوية الكاذود المثبتة ولكن هذه الملاحظة لم تظهر عندما قمنا باستخدام نظام إطلاعات النفايات المثبتة لأنوية الكاذود المثبتة. بالنسبة للإطلاعات المزار من الطبقة السطحية فإنها كان نكمية أقل من تلك الموجودة في طبقة التربة. في حالة استخدام نظام إطلاعات النفايات المثبتة لأنوية الكاذود المثبتة مما يشجع استخدام هذا النظام في الظروف المحتاجة مرة أخرى بعد المعالجة الكهربائية لها. بالنسبة للإطلاعات المزار فإنها قد تراكم في الطبقة السطحية في نظام أنوية الكاذود المثبتة. هذه الملاحظة قد تم تفديها باستخدام نظام إطلاعات النفايات المثبتة لأنوية الكاذود المثبتة. وأوضحت النتائج المترتبة عليها والخاصة بالمغشكن المزال بإعادة توزيعها في عمود التربة نتيجة استخدام نظام أنوية الكاذود المثبتة لمعالجة الثقيل سالف الذكر قد تلبيت مقاتلت من مكان إلى آخر. ولكن باستخدام نظام إطلاعات النفايات المثبتة لأنوية الكاذود المثبتة فإنها لوحظ زيادة كمية المزار من المغشكن المزال بالقرب من نهاية إطلاعات النفايات المثبتة