

Behavior of V, Cr, Li, and Ba during electrokinetic pollutant removal: Comparison of PCPSS and VA-PCPSS

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ABSTRACT

Soil pollution with heavy metals is considered a serious issue affect human, animal, and plant. Owing to the deficiency of water supply in arid and semi-arid areas wastewater may be used in agricultural sector without carrying out the appropriate remediation that may increase pollutants content. Recently, we have introduced a new variation of soil electrokinetic remediation (SEKR) known as vertical anode-perforated cathode pipe SEKR system (VA-PCPSS) to overcome obstacles found in the regular PCPSS design. In the present study, the behavior of associated elements existed in anionic and cationic forms such as vanadium (V), chromium (Cr), Lithium (Li), and barium (Ba) during electro-remediation using the PCPSS and the VA-PCPSS techniques was investigated. The results indicated that, the VA-PCPSS did not affect negatively on vanadium distribution throughout soil specimen compared with sever accumulation adjacent to horizontal anode in the PCPSS design. Chromium showed the same behaviors of vanadium during SEKR of heavy metals. Lithium accumulated in the middle of specimen in either the PCPSS or the VA-PCPSS. Barium removal was 50% in the zone adjacent to anode, however sever removal was observed in the subsequent layers of the PCPSS. The application of the VA-PCPSS decreased the removed barium throughout soil, however it accumulated in the zone adjacent to specimen surface.

Keywords: Soil electrokinetic; Pollution; Remediation; PCPSS; VA-PCPSS

INTRODUCTION

Remediation technologies for organic and inorganic pollutants containing soils may be classified into physical, chemical, and biological methods. Soil electrokinetic remediation (SEKR) is belong to the physical treatment that may be suitable for treating heavy metals, organic pollutants, and radioactive metals particularly in soils possess low hydraulic conductivity (Abou-Shady, 2012). Primary studies set the principles and basics of SEKR in which pollutants are removed from polluted soil via four mechanisms including

electro-migration, electro-osmosis, diffusion, and electro-phoresis (Acar and Alshawabkeh, 1993; Probststein and Hicks, 1993). SEKR has been classified into vertically and horizontally systems according to electrode installation. The application of SEKR may be undergoing different obstacles such as: a) a pH jumping zone that continuously exist in the middle of specimen and b) the formation of an unsaturated zone that negatively hinder the applications of SEKR. There are several attempts were carried out to overcome SEKR obstacles and maximize the performance. A review of researcher's attempts to introduce a suitable solutions could be found in our previous study (Abou-Shady, 2012; Abou-Shady and Peng, 2012).

Previously, we introduced a new variation of SEKR known as perforated cathode pipe SEKR system (PCPSS). The PCPSS was first investigated with the removal of heavy metals such as Zn^{2+} and Pb^{2+} containing polluted soil, further study investigated its suitability to reclaim highly saline soils (Abou-Shady and Peng, 2012; Abou-Shady, 2016).

The aim of this study was therefore to evaluate the behavior of V, Cr, Li, and Ba that naturally existed during electrokinetic pollutants removal using either the perforated cathode pipe SEKR system (PCPSS) or the improved design known as vertical anode-perforated cathode pipe SEKR system (VA-PCPSS) (Abou-Shady, 2018). Based on literature review, the behaviors of associated elements during soil electrokinetic were not investigated in details, although it may be vital for plant growth that eventually affect negatively on agriculture and ecosystem. In general, these elements were found with high concentration (vanadium 330 mg kg^{-1}), moderated concentration (chromium 50.8 mg kg^{-1}), and low concentration (lithium 3.5 mg kg^{-1}).

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MATERIALS AND METHODS

Soil properties

Natural saline clay soil were artificially contaminated with heavy metals including Zn²⁺, Cd²⁺, Co²⁺, Mn²⁺, Pb²⁺, Sr³⁺, and Cu²⁺ to evaluate five new designs proposed to enhance the performance of the PCPSS (Abou-Shady, 2016). The treated soil was naturally contaminated with vanadium (total vanadium

330 mg kg⁻¹), which may be owing to using untreated wastewater for irrigation purpose (Abou-Shady, 2016a, Abou-Shady, 2017). Chromium was existed naturally in the treated soil at total concentration (50.8 mg kg⁻¹). Lithium represented the lowest concentration (3.5 mg kg⁻¹). The physical and chemical properties of the treated soil are shown in Table 1.

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

Properties	Natural Soil
Texture	Clay
Electrical Conductivity (1:1) (dS m ⁻¹)	9.18
pH	7.56
Ca ²⁺ (ppm)	780
K ⁺ (ppm)	109.5
Na ⁺ (ppm)	2240
Mg ²⁺ (ppm)	585
Cl ⁻ (ppm)	2441.5
SO ₄ ²⁻ (ppm)	1031.3
Hydraulic Conductivity (cm s ⁻¹)	1.83 × 10 ⁻⁴

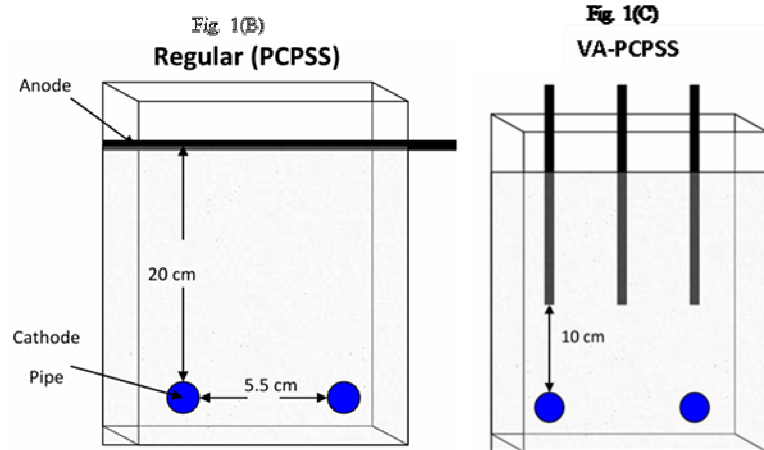
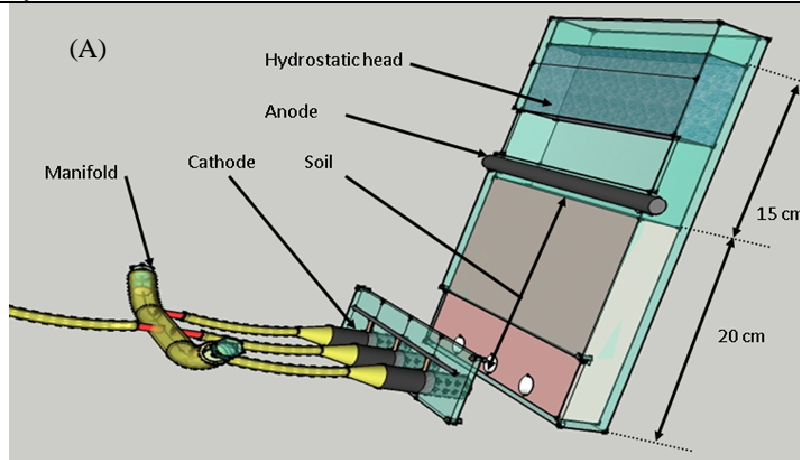


Fig. 1. A. and b. Schematic photographs of perfluorinated cathode pipe SEKR system (PCPSS) and C) Schematic photograph of the vertical anode/perfluorinated cathode pipe SEKR system (VA/PCPSS) (Abou-shady *et al.*, 2018a and b)

Methodology

Vanadium, chromium, lithium, and barium were detected in soil digest using Inductivity Coupled Argon Plasma (ICAP 6500 Duo) Thermo Scientific England simultaneously during heavy metals detection. Supernatant of soil solution ratio 1:1 was used to measure cations and anions from the extracted saline clay soil using ion chromatography (Dionex ICS-1100). pH was measured using pH meter (6101N, USA).

The PCPSS and the VA-PCPSS designs

Abou-Shady and Peng 2012 have introduced a new variation of soil electrokinetic remediation known as perforated cathode pipe SEKR system (PCPSS) as it presented in schematic photographs in Figs 1a and b to treat heavy metals containing soils. Beside the removal of heavy metals, the PCPSS has been evaluated for reclaiming highly saline soils (Abou-Shady, 2016b). The main objective of the PCPSS was to maximize the migration of heavy metals, containing soil, towards cathode pipes and eventually dispose to underground drainage system. The principles and basics information of the PCPSS has been mentioned in our previous articles (Abou-Shady, 2012; Abou-Shady and Peng, 2012; Abou-Shady, 2016b). The PCPSS has some problems appeared during the treatment of heavy metals containing soils. This was our motivation to introduce the improved design that known as the vertical anode-perforated cathode pipe SEKR system (VA-PCPSS) (Abou-shady *et al.*, 2018).

Operation of PCPSS and the VA-PCPSS

The experimental period was set during the comparison between PCPSS and AV-PCPSS for 23 days. After that experiments were terminated, soil

samples were taken in 2 cm intervals. The samples were air dried and ground for digest. The applied electrical potential was fixed to 40 V (20 V cm⁻¹) for either the PCPSS or the VA-PCPSS during the 23 days.

RESULTS AND DISCUSSION

Vanadium behavior during the remediation of the PCPSS and the VA-PCPSS

The studied saline clay soil contained vanadium with relatively high levels (330 mg kg⁻¹). Soil pH may control vanadium adsorption capacity on soil clay minerals. At pH among 5.0 and 9.0 the adsorption of vanadium reached to maximum. pH lower than 5 and higher than 9 decreases the adsorption capacity. The effect of pH may be relevant to the changes in zeta potential values. Also, the existing of electrostatic repulsion between VO₂⁻ and soil positive charge might occurs at pH lower than 5. In the high pH values, the natural competition between OH⁻ and anionic vanadate may occur (Luo *et al.*, 2017). Vanadium pollution in soils become noticeable nowadays particularly those found in industrial areas (Eissa *et al.*, 2017). The schematic photographs of the PCPSS and the VA-PCPSS are shown in Fig.1.

In the PCPSS, the low pH prevails adjacent the horizontal anode, high pH around cathode pipe, and pH jumping zone in the middle of specimen as it shown in Fig. 2a. In the VA-PCPSS the distribution of pH markedly changed and there was no significant changes of soil pH around cathode. The pH jumping zone observed in the PCPSS is replaced with low pH in the VA/PCPSS as it depicted in Fig. 2b.

The distribution of vanadium during electrokinetic heavy metal removal using the PCPSS and the VA-PCPSS is shown in Fig. 3.

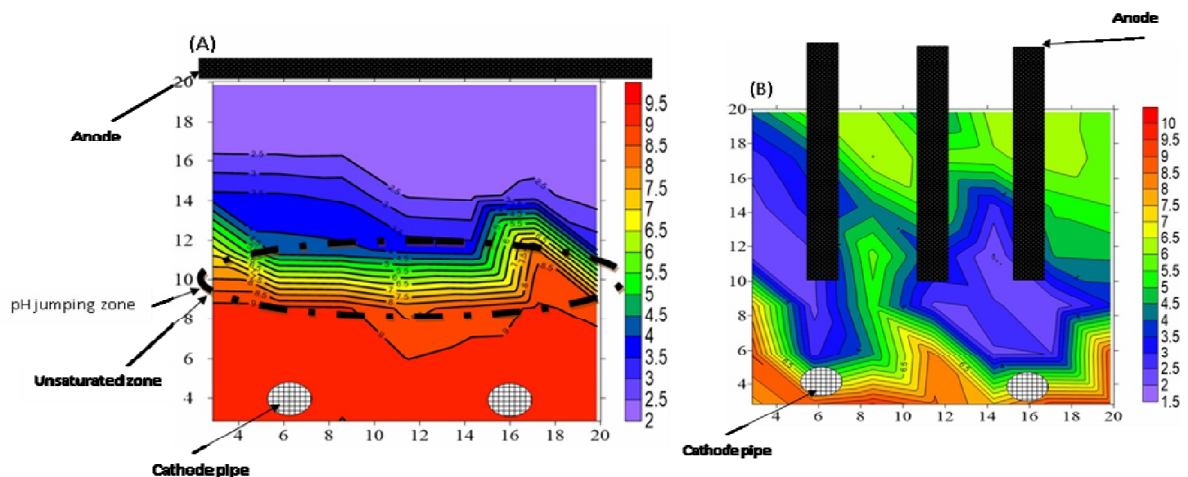


Fig. 2. pH distribution in soil electrokinetic specimen A) the PCPSS and B) the VA-PCPSS (Abou-shady *et al.*, 2018a and b)

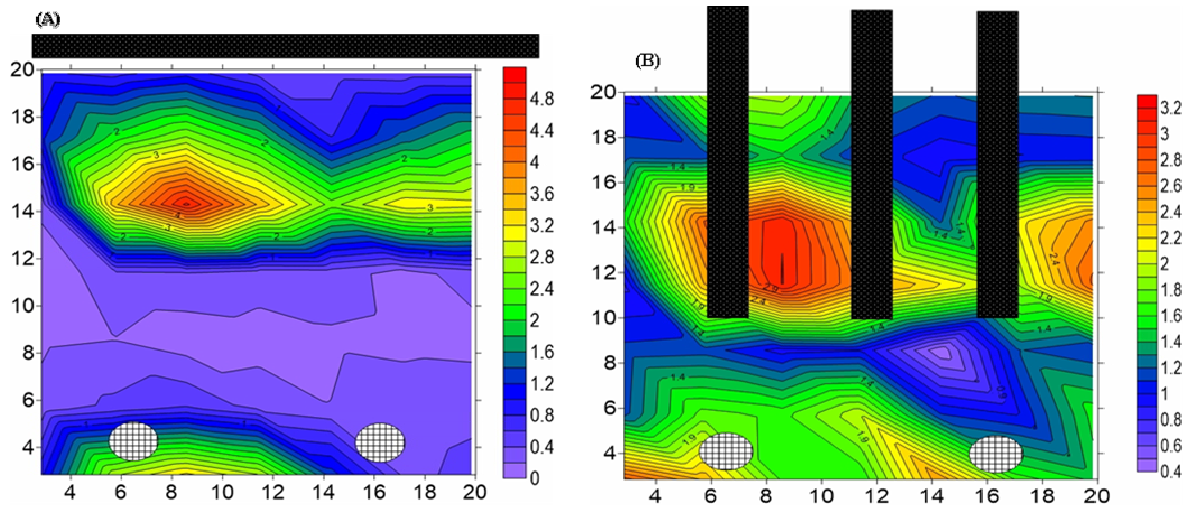


Fig. 3. Distribution of vanadium in the treated soil using A) the PCPSS and B) the VA-PCPSS

Vanadium accumulated near to the horizontal anode in the low pH zone and depleted markedly throughout the PCPSS. Small amount of vanadium was accumulated adjacent the left cathode. Vanadium did not accumulated directly in touch with horizontal anode. This may be due to the effect of electro-osmotic flow in the PCPSS that may prevails the electro-migration effect. The depletion of vanadium in the VA-PCPSS was not sever as it observed using the PCPSS. Based on literature survey, there are no study focused on electrokinetic vanadium removal. From agricultural pint of view, vanadium may be beneficial for pants and green algae at trace concentrations (Luo et al., 2017). Accordingly, the VA-PCPSS may fit heavy metals containing polluted soils electrokinetic remediation without reflecting negative impact on plant requirement of trace elements such as vanadium. Ongoing researches will be focused on electrokinetic vanadium removal of from industrial areas as it reported in our previous study (Eissa et al., 2017), and the suggested mechanisms will be reported.

Chromium behavior during the remediation of the PCPSS and the VA-PCPSS

Chromium was found in saline clay soil at moderated concentrations (50.8 mg kg^{-1} - total chromium) compared with vanadium. Generally, there are two forms of chromium exist in soil; Cr^{6+} and Cr^{3+} . Desorption of Cr^{3+} occurs at low pH, while Cr^{6+} adsorption prevails. Several oxyanions forms of Cr^{6+} such as HCrO_4^- , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$ may exist as a very mobile form in contaminated soils. Previous study showed that the removed of chromium was lower than 12% from contaminated soil using SEKR (Cameselle and Pena 2016; Fu et al., 2017). Converting Cr^{6+} to Cr^{3+} is commonly occurs using soil oxidizing agent. Soil pH plays an important role for oxidation and reduction of

chromium. Increasing soil pH catalyze oxidation reactions, and in contrast at low pH values. Accordingly, Cr^{6+} may converted to Cr^{3+} adjacent to cathode and Cr^{3+} may converted to Cr^{6+} adjacent to anode. Data presented in Figs 4 a and b shows the variations of chromium during electrokinetic heavy metals removal. Chromium migrated towards anode and accumulated directly under horizontal anode in the PCPSS. Soil layers around anode is characterized with low pH in the PCPSS. In such environment Cr^{3+} may converted to Cr^{6+} and migrated from anode towards cathode. Also, this may be due to the effect of electro-osmotic flow that overcome the role of electro-migration. However, in the middle of the PCPSS specimen chromium may existed in anionic forms such as HCrO_4^- , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$. It was clear that small amount of chromium accumulated adjacent to left cathode pipe. The distribution of chromium in either the PCPSS or the VA/PCPSS was identical with the behavior of vanadium. The VA-PCPSS decreased the depletion of total chromium from the middle of specimen. Although, the role of chromium in plant is still unknown, chromium is vital for animal and human being (Ag-Info Centre). Accordingly, the implement of the VA/PCPSS is convenient with chromium containing soils.

Lithium behavior during the remediation of the PCPSS and the VA-PCPSS

Low concentrations of lithium in soil may enhance markedly yield productivity, elevate it resistance to disease, and decrease maturation period. Lithium may compete the uptake of Ca^{2+} (Yalamanchali, 2012). In our study, total lithium concentration exists in saline clay soil at very low levels (3.5 mg kg^{-1}). The depletion of lithium in the PCPSS was more severe than the

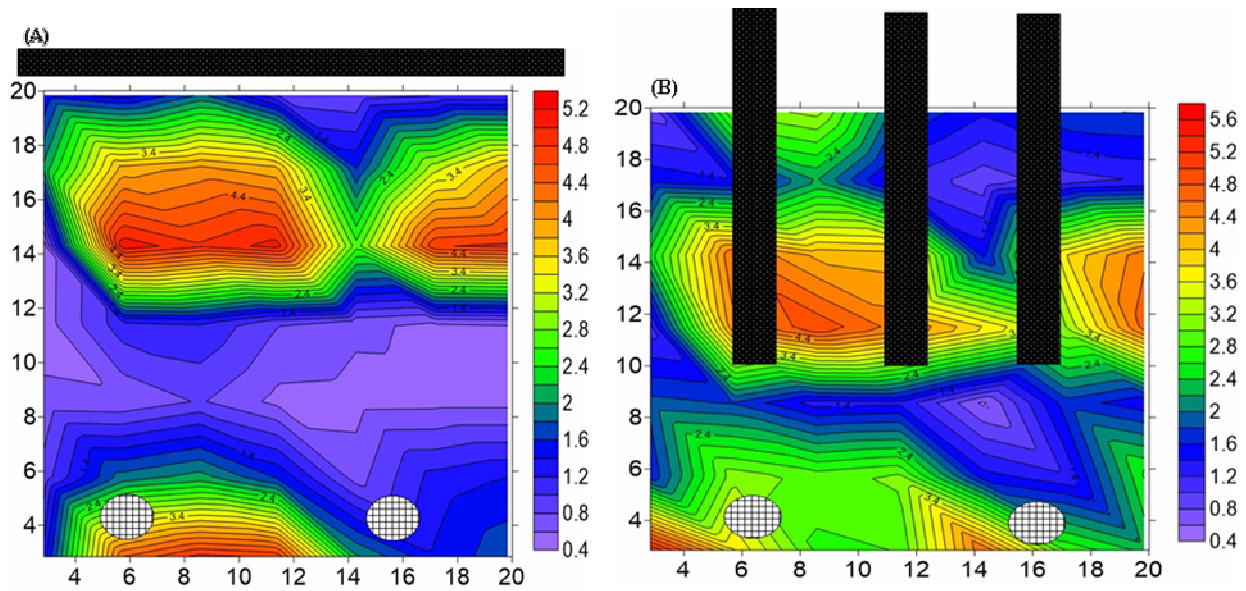


Fig. 4. Distribution of chromium in the treated soil using A) the PCSS and B) the VA/PCSS

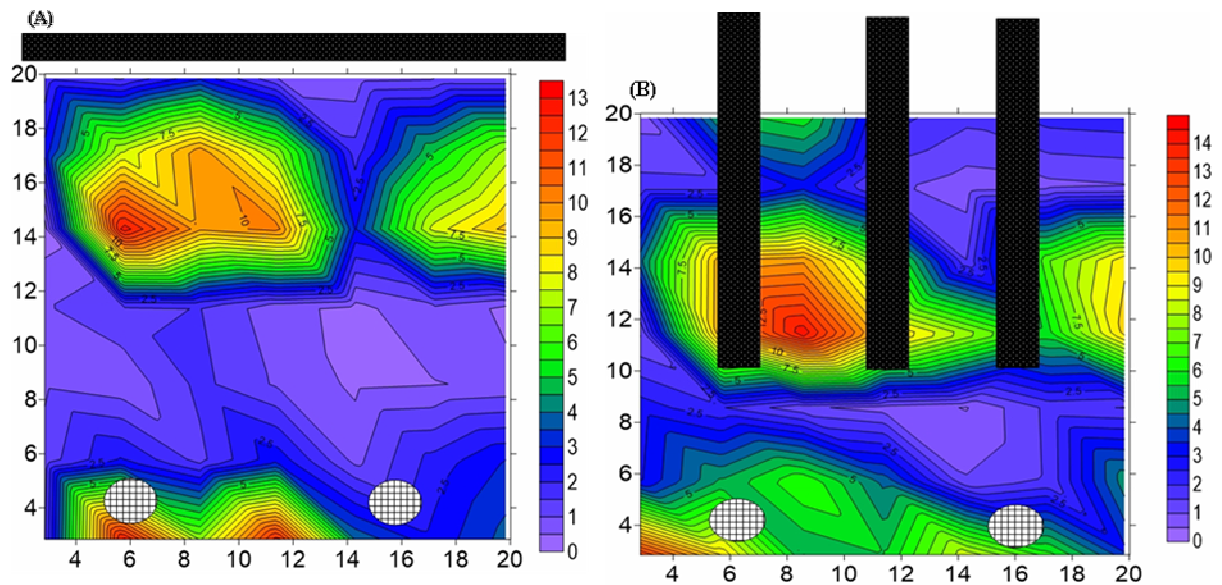


Fig. 5. Distribution of lithium in the treated soil using A) the PCSS and B) the VA-PCSS

VA/PCSS as it shown Figs. 5a and b. Generally, lithium accumulated with high levels downward anode in either the PCSS or the VA/PCSS. This may be because of lithium exists in the treated soil at low concentration and the desorption may be occurred around anode zone and re-adsorbed again in the middle of specimens.

Barium behavior during the PCSS and the VA-PCSS remediation

Barium exists in saline clay soil at concentration of 55.1 mg kg⁻¹. Barium may play an important role in ameliorating Na⁺ negative effect on leave

photochemistry (Abreu *et al.*, 2012). It is clear seen that, about 50% of barium in the top surface of the PCSS system was removed successively as it depicted in Fig. 6a. The best removal of barium was observed at the rest 2/3 of the PCSS. The application of the VA/PCSS decreased barium removal throughout specimen as it shown in Fig. 6b. This is may be due to, in the basic and neutral pH levels developed by the VA/PCSS the precipitations of barium occur in carbonate and sulfate forms. The VA/PCSS reflects low removal of barium during electrokinetic of highly polluted soil contaminated with heavy metals.

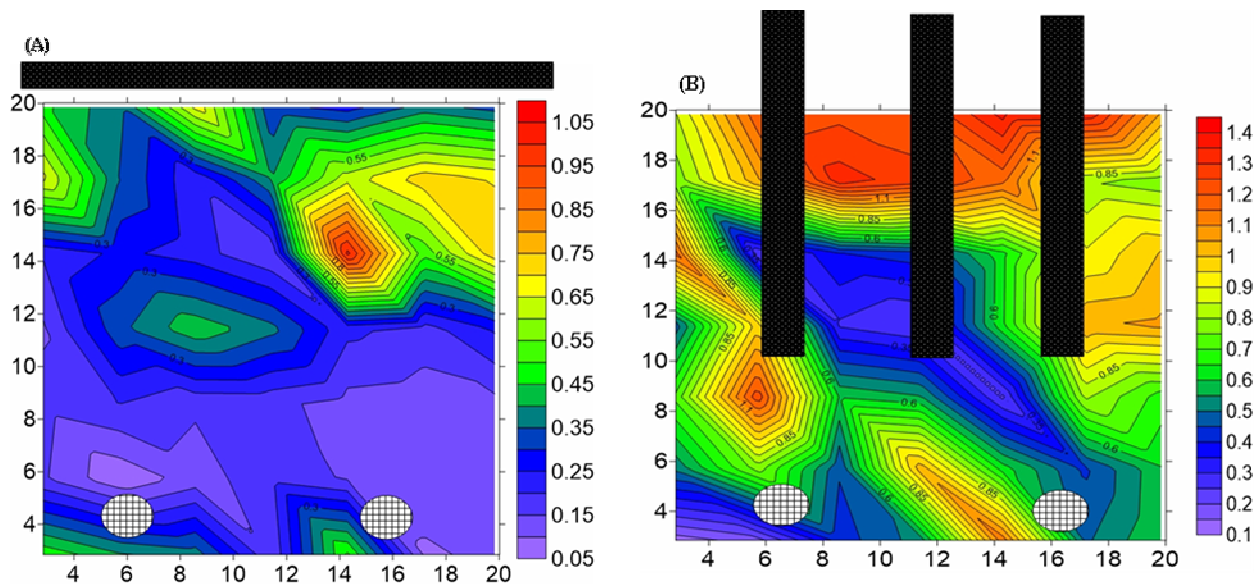


Fig. 6. Distribution of barium in the treated soil using A) the PCPSS and B) the VA-PCPSS

Perspective for further approaches and large scale application

Based on literature survey, SEKR technology has been carried out to treat heavy metals, radioactive materials, organic pollutant, reclaim salty soils, and remove soil anions. The effect of SEKR on soil humic substances did not take into consideration, although its play the major role of elements chemistry (Aboushady, 2008; Khalil *et al.*, 2009). Our future researches will be focused on the role of humic substances including humic and fulvic acids during SEKR. For large scale application of PCPSS, the fixed anodes will not fit. So that, the continuously -reoriented electric field will be installed (Almeria *et al.*, 2012a; Peng *et al.*, 2013). The outlet discharge will be connected directly to the underground drainage in which at the end of manifold pipe the outlet wastewater will be treated using electro dialysis (Abou-Shady *et al.*, 2011; Abou-Shady *et al.*, 2012a), electrolysis (Peng *et al.*, 2011; Jin *et al.*, 2102), adsorption on cation and anion exchange membrane (Abou-Shady *et al.*, 2012b), and electrodeionization simultaneously (Bi *et al.*, 2011; Almeria *et al.*, 2012b).

CONCLUSION

The behavior of V, Cr, Li, and Ba using two different SEKR systems known as the perforated cathode pipe SEKR system (PCPSS) and the vertical anode/ perforated cathode pipe SEKR system (VA-PCPSS) was investigated. The resulted may be summarized in the following points:

- 1) Vanadium distribution did not markedly influence with SEKR when the VA-PCPSS was installed.

Accumulation of vanadium close to horizontal anode was clear seen in the PCPSS which may present high toxicity for plant growth.

- 2) Chromium behavior was identical with vanadium using either the PCPSS or the VA-PCPSS.
- 3) Lithium accumulated in the middle of either the PCPSS or the VA-PCPSS, but the removal was more sever with the PCPSS.
- 4) The removed barium was close to 50% in the zone adjacent to anode, and sever removal was observed in the rest of the PCPSS. The VA-PCPSS decreased the removed barium throughout soil, but accumulated in the zone adjacent to specimen surface.

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الملخص العربي

سلوك الفناديوم والكروميوم والليثيوم والباريوم اثناء إزالة الملوثات بالطرق الكهربائية: مقارنة بين نظام VA-PCPSS وPCPSS

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اقطاب الانود العمودية المصاحبة لانبوبة الكاثود المتقبة. وقد اوضحت النتائج المتحصل عليها ان، نظام اقطاب الانود العمودية المصاحب لانبوبة الكاثود المتقبة لم تؤثر بالسلب على توزيع الفناديوم فى قطاع التربة وذلك بالمقارنة بالتراكم الكبير بجوار الانود فى نظام انبوبة الكاثود المتقبة للمعالجة الكهربائية. بالنسبة للكروميوم فقد اظهر نفس السلوك الملاحظ مع الفناديوم. وقد ادى استخدام نظام انبوبة الكاثود المتقبة الى جعل معدل الازالة للباريوم حوالى ٥٠% فى المنطقة الملاصقة للانود، كما ان معدل الازالة كان عالى جدا فى الطبقات التالية لهذه الطبقة. كما وجد ان استخدام نظام اقطاب الانود العمودية المصاحبة لانبوبة الكاثود المتقبة قلل من كمية الباريوم المزال من قطاع التربة وتراكمها بالقرب من الطبقة السطحية.

يعتبر التلوث بالفلزات الثقيلة من المشكلات الخطيرة والتي تؤثر بالسلب على كل من النبات و الحيوان و الانسان. ونتيجة لنقص المياه المخصصة للزراعة فى المناطق الجافة ونصف الجافة، فقد استخدمت مياه المصارف الملوثة فى الري بدون اى معالجة والتي تتسبب فى زيادة تركيز الملوثات فى هذه الاراضى. حديثا تم تقديم جيل جديد من المعالجة الكهربائية للاراضى يعرف باسم نظام الاقطاب العمودية المصاحب لانبوبة الكاثود المتقبة وذلك للتغلب على المعوقات الموجودة فى الجيل السابق والمعروف باسم انبوبة الكاثود المتقبة. فى هذا البحث، تم دراسة سلوك بعض العناصر المصاحبة للفلزات الثقيلة وهى الفناديوم و الكروميوم و الليثيوم و الباريوم اثناء المعالجة الكهربائية باستخدام انبوبة الكاثود المتقبة ونظام