

## Effects of Wetting Agents and Approaching Anode on Lead Migration in Electrokinetic Soil Remediation

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**Abstract.** Approaching anode is one of the enhancement techniques in electrokinetic soil remediation. This technique is reported to give promising migration for heavy metals under shorter treatment time and at lower cost in comparison to normal fixed anode system. In the present study, the effectiveness of fixed anode and approaching anode techniques in electrokinetic soil remediation for lead migration under different types of wetting agents (0.01M NaNO<sub>3</sub> and 0.1M citric acid) was investigated. The study showed that the use of citric acid enhanced lead migration in comparison to NaNO<sub>3</sub>. For NaNO<sub>3</sub> tests, lead was found to accumulate in the middle of soil section due to high soil pH, which favoured lead adsorption and precipitation. Approaching anode reduced this effect by compressed high soil pH region and enhanced lead migration at cathode region. The approaching anode only showed technical advantages when NaNO<sub>3</sub> was used whereas the enhancement in citric acid test was insignificant. Nevertheless, this technique reduced electricity usage by 18-20% for both wetting agents.

**Keywords:** Lead, electrokinetic soil remediation, wetting agent, approaching anode

### 1. Introduction

McCartor and Becker [1] and Wuana and Okieimen [2] reported that lead (Pb) has been extensively used in manufacturing processes such as ammunition, batteries, plumbing, dyes, pigments and pesticides and this causes potential environmental pollution and human exposure. Soil contamination is one of the pathways for Pb exposure to humans especially from Pb smelting and mining areas [2-3] as well as from industrial land used for battery and scrap Pb handlings [4]. As Pb is highly toxic and can cause health hazard to living organisms, a proper treatment to these soils is required.

Electrokinetic process is a soil remediation method which uses electricity as driving force for contaminant transport in the soil. This process is initiated by applying low magnitude direct current from the electrodes injected into the soil. During electrokinetic process, electrolysis occurs in both anode and cathode chambers which produce H<sup>+</sup> and OH<sup>-</sup>, respectively. Due to the potential difference between the electrodes, H<sup>+</sup> and OH<sup>-</sup> transport to the respective electrode, and these are named as acid front and base front. These mechanisms create two transport forces in the soil: i) electromigration for ions transport, and ii) electroosmosis for water/neutral compounds transport [5-6]. The forces are responsible for contaminants removal from the soil, whereby the contaminants are concentrated in the electrolyte chambers or enriched in a smaller soil volume. To date, electrokinetic process has been proven as successful method in treating Pb contaminated soil using different types of desorption/flushing agents to enhance Pb mobility via better desorption condition [7-8] or forming stable water soluble complexes [7-12].

However, it is worth noting that the lengthy remediation time and additional cost in power consumption in using electrokinetic process often restricts its wide application [13-15]. Besides that, simultaneous acid and base fronts create a region where H<sup>+</sup> and OH<sup>-</sup> meet and this causes accumulation/focusing of heavy metals in that region [13, 16]. In order to further enhance the transport of heavy metals, approaching anode

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technique was introduced as an enhancement method. Fig. 1 illustrates electrokinetic process using the approaching anode [13-15]. In this technique, extra electrodes are installed along the contaminated soil. The anode is switched to these electrodes from time to time so that the migration distance is reduced. This not only results in progressive soil acidification via compressing high pH region and reduces focusing effect but also provides higher current intensity and acid front for maintaining ion mobility for heavy metals removal [13-15].

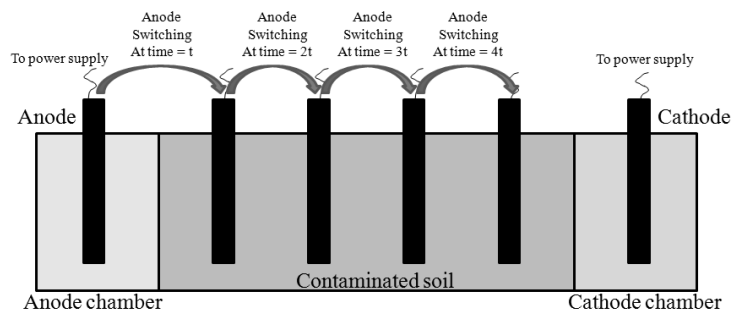


Fig. 1: General diagram for approaching anode electrokinetic process with a total treatment time of  $5t$  [13-15]

In the present study, the feasibility of approaching anode assisted electrokinetic process on Pb migration in soil under different types of desorption/wetting agents was investigated. The study was conducted in a sandbox without electrolyte chamber and the soil was saturated with wetting agent before electrokinetic process. All the electrodes were in direct contact with the soil such that a more consistent electrode environment for both fixed anode and approaching anode tests could be established. The effect of two wetting agents, namely 0.01M  $\text{NaNO}_3$  and 0.1M citric acid on Pb migration were investigated. Moreover, the application of approaching anode in enhancing Pb migration under different types of wetting agents was evaluated from both technical and economical aspects.

## 2. Methodology

### 2.1. Soil characterization and preparation

The soil was collected from Hulu Langat, Malaysia. This soil has high iron content of 3719mg/kg with a maximum contamination level of 1000mg/kg (Unpublished work). The soil was pretreated by drying in open air for one week. Then, it was sieved to a particle size of  $<0.85\text{mm}$ . The soil consisted of fine sand (92% of the soil has particle size of 50-850 $\mu\text{m}$ ) and a pH of 3.97. It had a cation exchange capacity of 5.1Meq and organic matter content of 1.4%. The dried soil was spiked with  $\text{Pb}(\text{NO}_3)_2$  solution to acquire 750mg/kg contaminated soil. The slurry was then mixed thoroughly using spatula and was dried in open air for one week before storing them in dark place prior to use.

### 2.2. Experiment procedure

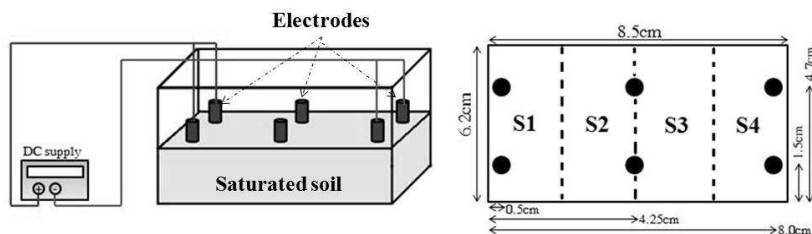


Fig. 2: Schematic diagram for the experimental setup and electrode positions

A mass of 100g contaminated soil was compacted into a polypropylene box with dimensions of 8.5cm x 6.2cm x 5cm. Six graphite rods (0.7cm diameter, 4cm length) were used as the electrodes and were installed into the soil at positions shown in Fig. 2. The anodes (Electrodes in S1 region) and cathodes (Electrodes in S4 region) were then connected to a DC supply source. Experiments were initiated by sprinkling the wetting

agent (0.01M NaNO<sub>3</sub> or 0.1M citric acid) on the soil surface until saturation. Then, a voltage gradient of 1V/cm was applied for 24 hours under room temperature. This operation was named as fixed anode (FA) tests. Similar types of wetting agents were used for approaching anode (AA) tests. In these tests, the anodes were switched from S1 region to the middle electrodes after 12<sup>th</sup> hour operation and the voltage used was adjusted accordingly to maintain 1V/cm.

### 2.3. Analytical methods

The current across the soil during the experiments were determined by Multimeter Sunwa TE-832B. For soil properties, soil pH and contaminants concentration were evaluated. These parameters were analyzed section-by-section, where the soil was divided into four sections after the experiments, as shown in Fig. 2 (S1, S2, S3, S4). Soil pH was determined by USEPA 9045D method using pH meter Crison MM26+. For Pb concentration in the soil, acid digestion was conducted using USEPA 3050b method. The supernatant was filtered through a filter paper and the Pb concentration was analyzed using ICP-OES.

## 3. Results and Discussion

### 3.1. Effect of wetting agent on Pb migration

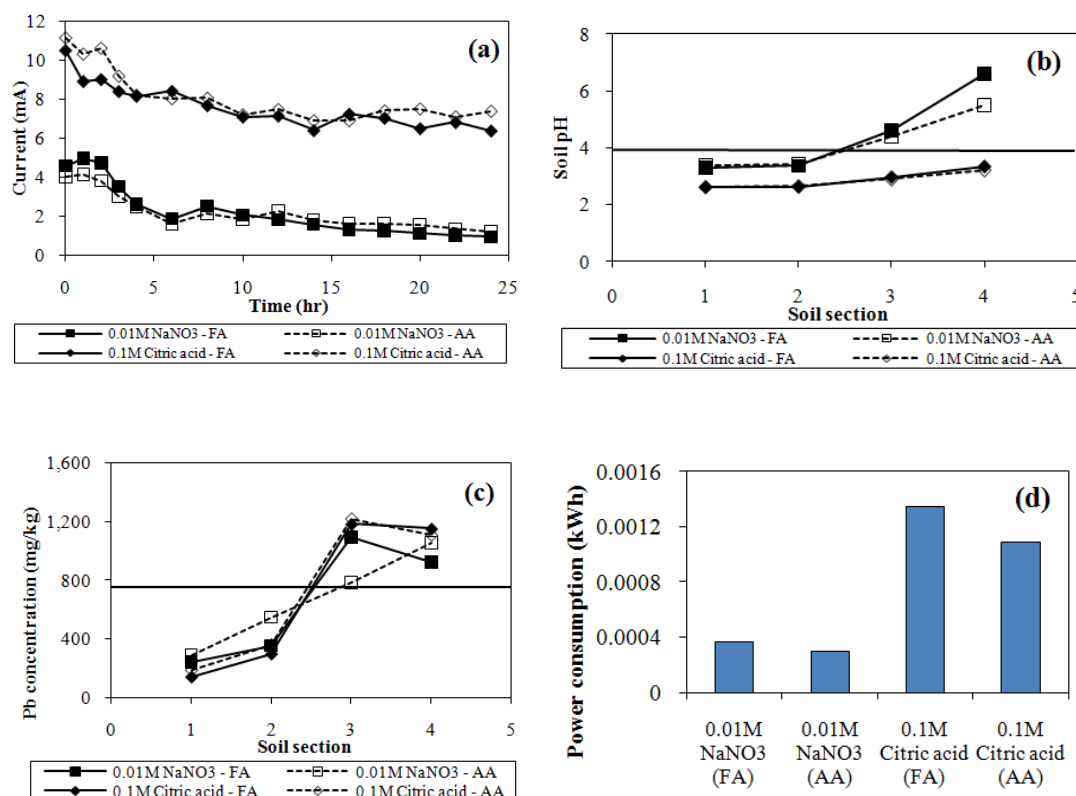


Fig. 3: Properties of the system under different operating conditions: (a) Current variation with time; (b) Soil pH after the experiment; (c) Pb concentration at different soil section after the experiments under different conditions; (d) Power consumption of electrokinetic process under different conditions

Figs. 3a and 3b illustrate the variation in current and soil pH under different wetting agents for both FA and AA tests. Generally, it is found that the use of 0.1M citric acid gives higher current through the soil in comparison to 0.01M NaNO<sub>3</sub>, as shown in Fig. 3a. This could be mainly attributed to the characteristic of citric acid. As an acid, citric acid dissociated and provided additional H<sup>+</sup> for soil acidification which caused a lower soil pH (Fig. 3b) for better Pb desorption [17] and this increased the amount of mobile ions in the system. Besides that, its relatively high concentration in comparison to NaNO<sub>3</sub> also provided more mobile ions and thus yielded better current. High current serves better electromigration force for Pb movement, as

shown in Fig. 3c that Pb concentration is lower in S1-S2 (anode region) and higher at S3-S4 (cathode region) when 0.1M citric acid is used. A lower migration in NaNO<sub>3</sub> test is plausibly to be caused by Pb accumulation in S3 section, as shown in Fig. 3c, and this is mainly due to the relatively high soil pH at S3-S4 region. Unlike citric acid, NaNO<sub>3</sub> served as an electrolyte for conducting electricity only. Its inability to function as buffer solution to nullify OH<sup>-</sup> generated during electrolysis caused higher pH at cathode region and this reduces Pb mobility. Fig. 3c shows that the pH at S3 is 4.61 which is reported to favour Pb adsorption [18-19]. Moreover, a high pH of 6.62 at S4, which favored Pb hydrolysis into Pb(OH)<sub>2</sub> precipitate or even Pb(OH)<sub>3</sub><sup>-</sup> [20] also served as another reason for Pb accumulation in S3.

### 3.2. Effect of approaching anode on Pb migration

AA technique was reported to give better ion migration by providing progressive soil acidification and maintaining high current for electromigration [13-15]. However, the present study shows that the use of approaching anode does not show significant effect in current variation, as shown in Fig. 3a where a stable current as in FA tests are observed for both wetting agents when this technique is applied. Nevertheless, AA showed high impact on soil pH and Pb migration in NaNO<sub>3</sub> test. As the anode was switched to the middle electrodes, H<sup>+</sup> was produced from the middle section of the soil (S2-S3). Since the migration of H<sup>+</sup> is 1.75-2 times faster than OH<sup>-</sup> migration [5-8], soil pH at S3-S4 region is therefore reduced by better acid front and thus high soil pH region is compressed, as shown in Fig. 3b. As the reduction in overall soil pH provides poorer Pb adsorption on soil surface [17], Pb migration in S3-S4 region is enhanced and Pb accumulation/focusing in S3 region is not observed, as shown in Fig. 3c. This is in agreement with Li et al. [13] who claimed that Cr focusing effect was reduced via better soil acidification when AA technique was applied. However, it is worth noting that the shift of anode at the 12<sup>th</sup> hour during the experiment causes lower Pb migration in S1-S2 region as higher Pb concentration is detected, as illustrated in Fig. 3c. This was mainly due to the lack of electricity to maintain electromigration in the regions after electrode switching. From this, it was suggested that the time for electrode switching was important and the 12 hours was not adequate for the migration as much Pb as in FA test in S1-S2 regions when NaNO<sub>3</sub> was used as the wetting agent. A longer experimental duration was required before switching the anode.

In addition, it was worth noting that the effect given by AA was dependent on the types of wetting agents used. As shown in Fig. 3, AA has no effect on current, soil pH and Pb migration when citric acid is used. This could be due to good soil acidification already achieved by 0.1M citric acid even under FA process in which Pb desorption was enhanced. Furthermore, high amount of H<sup>+</sup> ions for strong acid front was also established by citric acid. Thus, the enhancement provided by AA was technically insignificant. Nevertheless, it is worth noting that the use of AA could reduce the power consumption by 18.75% for citric acid test while maintaining the migration, as shown in Figs. 3c and 3d. As majority of Pb ion migrated towards S3-S4 during the 12<sup>th</sup> hours experiment, the shifting of anodes to the middle section could prevent unnecessary electricity consumption in S1-S2 region

## 4. Conclusions

Technical feasibility of approaching anode as enhancement technique for electrokinetic soil remediation on Pb migration was investigated. The study revealed that Pb ion migrated and concentrated to a smaller soil volume under electrokinetic process with the aid of wetting agent. In this study, citric acid showed better migration than NaNO<sub>3</sub> as it provided better soil acidification for better desorption while preventing Pb precipitation in cathode region. Moreover, its higher current also favored electromigration process. In contrast, NaNO<sub>3</sub> which had lower current showed slower Pb migration. It also caused Pb accumulation at S3 region as a result of high soil pH.

Introduction of approaching anode technique enhanced soil acidification in cathode region by providing better acid front. This further enhanced Pb migration in S3 towards S4 via better desorption condition for Pb. However, it was worth noting that approaching anode only enhanced the migration for the case of NaNO<sub>3</sub> whereas there was no effect for the case of citric acid. Nevertheless, this technique could prevent power

wastage by reducing 18.75% of power consumption while maintaining efficient migration when citric acid was used as wetting agent.

## 5. Acknowledgements

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## 6. References

- [1] A. McCartor, and D. Becker, Blacksmith Institute's World Worst Pollution Problem Report 2010. Blacksmith Institute, 2010.
- [2] R.A. Wuana, and F.E. Okieimen. Heavy metals in contaminated soils: A review of sources, chemistry, risks and best available strategies for remediation. *International Scholarly Research Network Ecology* 2011, **2011**: 1-20.
- [3] J.O. Duruibe, M.O.C. Ogwuegbu, and J.N. Ekwurugwu. Heavy metal pollution and human biotoxic effects. *Int. J. Phys. Sci.* 2007, **2** (5): 112-118.
- [4] USEPA. Superfund Engineering Issue: Treatment of lead-Contaminated Soils. 1991 Retrieved on 3rd January 2014, from: <http://www.epa.gov/superfund/remedytech/tsp/download/leadcont.pdf>.
- [5] Y.B. Acar, and A.N. Alshwabkeh. Principles of electrokinetic remediation. *Environ. Sci. Technol.* 1993, **27** (13): 638-2647.
- [6] Y.B. Acar, R.J. Gale, A.N. Alshwabkeh, R.E. Marks, S. Puppala, M. Bricka, and R. Parker. Electrokinetic remediation: Basics and technology status. *J Hazard. Mater.* 1995, **40** (2): 117-137.
- [7] H.I. Chung, and B.H. Kang, Lead removal from contaminated marine clay by electrokinetic soil decontamination. *Eng. Geol.* 1999, **53** (2): 139-150.
- [8] K.-J. Kim, D.-H. Kim, J.-C. Yoo, and K. Baek. Electrokinetic extraction of heavy metals from dredged marine sediment. *Sep. Purif. Technol.* 2011, **79** (2): 164-169.
- [9] M.T. Alcántara, J. Gómez, M. Pazos, and M.A. Sanromán. Electrokinetic remediation of lead and phenanthrene polluted soils. *Geoderma* 2012, **173–174**: 128-133.
- [10] A. Giannis, A. Nikolaou, D. Pentari, and E. Gidarakos. Chelating agent-assisted electrokinetic removal of cadmium, lead and copper from contaminated soils. *Environ. Pollut.* 2009, **157** (12): 3379-3386.
- [11] K.R. Reddy, and P.R. Ala. Electrokinetic remediation of metal-contaminated field soil. *Separ. Sci. Technol.* 2005, **40** (8): 1701-1720.
- [12] E.G. Sumbarda-Ramos, O.X. Guerrero-Gutierrez, B. Murillo-Rivera, I. Gonzalez, and M.T. Oropeza-Guzman. Electrokinetic treatment for clayed and sandy soils. *J. Appl. Electrochem.* 2010, **40**: 1255-1261.
- [13] G. Li, S. Guo, S. Li, L. Zhang, and S. Wang. Comparison of approaching and fixed anodes for avoiding the 'focusing' effect during electrokinetic remediation of chromium-contaminated soil. *Chem. Eng. J.* 2012, **203**: 231-238.
- [14] Z. Shen, X. Chen, J. Jia, L. Qu, and W. Wang. Comparison of electrokinetic soil remediation methods using one fixed anode and approaching anodes. *Environ. Pollut.* 2007, **150** (2): 193-199.
- [15] T. Zhang, H. Zou, M. Ji, X. Li, L. Li, and T. Tang. Enhanced electrokinetic remediation of lead-contaminated soil by complexing agents and approaching anodes. *Environ. Sci. Pollut. Res.* 2013, **21** (4): 1-8.
- [16] Probstein, R.F. and R.E. Hicks, Removal of contaminants from soils by electric fields. *Science* 1993, **260** (5107): 498-503.
- [17] J.Y. Yang, X.E. Yang, Z.L. He, T.Q. Li, J.L. Shentu, and P.J. Stoffella. Effects of pH, organic acids, and inorganic ions on lead desorption from soils. *Environ. Pollut.* 2006, **143** (1): 9-15.
- [18] I. Chaari, E. Fakhfakh, S. Chakroun, J. Bouzid, N. Boujelben, M. Feki, F. Rocha, and F. Jamoussi. Lead removal from aqueous solutions by a Tunisian smectitic clay. *J. Hazard. Mater.* 2008, **156** (1–3): p. 545-551.
- [19] M. Mohapatra, S. Khatun, and S. Anand, Adsorption behaviour of Pb(II), Cd(II) and Zn(II) on NALCO plant sand. *Indian J. Chem. Technol.* 2009, **16** (4): 291-300.
- [20] Y. Niu, R. Qu, C. Sun, C. Wang, H. Chen, C. Ji, Y. Zhang, X. Shao, and F. Bu. Adsorption of Pb(II) from aqueous solution by silica-gel supported hyperbranched polyamidoamine dendrimers. *J. Hazard. Mater.* 2013, **244-245**: 276-286.