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# Electro-kinetic remediation coupled with phytoremediation to remove lead, arsenic and cesium from contaminated paddy soil

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ABSTRACT

The objectives of this study were to investigate distribution and solubility of Pb, Cs and As in soils under electrokinetic field and examine the processes of coupled electrokinetic phytoremediation of polluted soils. The elevated bioavailability and bioaccumulation of Pb, As and Cs in paddy soil under an electrokinetic field (EKF) were studied. The results show that the EKF treatment is effective on lowering soil pH to around 1.5 near the anode which is beneficial for the dissolution of metal(loid)s, thus increasing their overall solubility. The acidification in the anode soil efficiently increased the water soluble (SOL) and exchangeable (EXC) Pb, As and Cs, implying enhanced solubility and elevated overall potential bioavailability in the anode region while lower solubility in the cathode areas. Bioaccumulations of Pb, As and Cs were largely determined by the nature of elements, loading levels and EKF treatment. The native Pb in soil usually is not bioavailable. However, EKF treatment tends to transfer Pb to the SOL and EXC fractions improving the phytoextraction efficiency. Similarly, EKF transferred more EXC As and Cs to the SOL fraction significantly increasing their bioaccumulation in plant roots and shoots. Pb and As were accumulated more in plant roots than in shoots while Cs was accumulated more in shoots due to its similarity of chemical properties to potassium. Indian mustard, spinach and cabbage are good accumulators for Cs. Translocation of Pb, As and Cs from plant roots to shoots were enhanced by EKF. However, this study indicated the overall low phytoextraction efficiency of these plants.



## 1. Introduction

Heavy metal(loid)s and their pollution are an increasing global concern due to their persistence, high toxicity and potential carcinogenic characteristics (Han, 2007). Heavy metal(loid)s such as lead (Pb) and arsenic (As) are mainly released to soils from anthropogenic activities such as industrial, agricultural activities and mining which have become a serious global environmental threat (Han et al., 2004; Cameselle et al., 2013). It was suggested that top soil could be an permanent sink for anthropogenic Pb and As compounds from the atmosphere or hydrosphere (Salazar and Pignata, 2014). Pb was first largely released to the environment due to coal burning dating from the industrial revolution (Shotyk et al., 1997). The introduction and combustion of leaded gasoline peaked Pb emission during 1950–1980s. In terms of As, it is primarily derived from mining and industrial activities such as electronics, fireworks, ceramics and glasses (Porter and Peterson, 1977). During the 20th century, widespread soil pollution with As has been caused by indiscriminate use of pesticides, herbicides, desiccants and fertilizers in agricultural activities (Mandal, 2002). On the other hand, as a radioactive contaminant, cesium has been released into soils through nuclear wastes, nuclear power plant accidents, and nuclear weapon testing (Giannakopoulou et al., 2007). 137Cs is a radioactive pollutant of great concern with a half life of 30.2 years, high bioavailability and chemical and biological similarity with potassium, an essential element in living organisms. Chernobyl accident released a huge amount of 137Cs and other radionuclides into surrounding soils (Belarus, Ukraine and Russia) and even spread through the entire Northern Hemisphere. Similarly, radionuclides (134Cs, 137Cs) were released during the Fukushima Daiichi nuclear power plant accident in 2011 (Yasunari et al., 2011). Radionuclides were reported to be also present and be transported in colloids of groundwater of nuclear ground detonation sites such as the Nevada Test Site ( Kersting et al., 1999; Yasunari et al., 2011 ).

Phytoextraction, an emerging technology for metal(loid) cleanup, is the process of concentrating metal(loid)s from soil solution

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in the stems and leaves of plants (Raskin and Ensley, 2000). The development of phytoextraction is being driven primarily by the high cost of other soil remediation methods as well as the desire to use an environmental benign process. The success of phytoextraction depends on the tolerance and translocation ability of plants to target metal(loid)s (Lotfy and Mostafa, 2014). Translocation factors (TF), which are ratios of the metal(loid) concentrations in shoots to those in roots, describe the metal(loid) extraction efficiency by plants (Cui et al., 2007). The success of phytoextraction also, is determined by the bioavailability of metal (loid)s in soil. Before metal(loid)s enter into plant systems from soil solution, they must be transported to root surface. This is primarily dependent on the bioavailability of metal(loid)s which are major factors limiting metal(loid) uptake in plant roots (Barber, 1995). The water soluble and exchangeable fractions of metal(loid) s, which are in equilibrium with the solid-phase speciation, are the most bioavailable form for metal(loid)s to plants (Han, 2007). The metals and metalloids are present in many solid-phase fractions including exchangeable, carbonate bound, organic bound, iron/ manganese oxide bound etc (Tessier et al., 1979; Han, 2007; Han and Banin, 1997, 1999; Han et al., 2012). Secretion of $H^+$ ions by plant roots improves the mobility and bioavailability of heavy metal(loid)s in soil by competing the binding site of soil particles with metal(loid) cations. As a result, more metals are transformed into bioavailable forms under acid condition around the rhizosphere (Thangavel and Subbhuraam, 2004).

In addition to plant own strategy, electro-kinetic field (EKF) was also recently introduced to enhance phytoextraction efficiency of metal(loid) contaminated soils (Cameselle et al., 2013). EKF involves using a direct or alternating current with electrodes inserted into contaminated soils. When a low intensity electric field is applied, $H^+$ is generated around the anode electrode through the effect of water electrolysis. As a result, more metal (loid)s are demobilized under the acid condition around the anode electrode (Thangavel and Subbhuraam, 2004). In addition, enhanced mobilization processes occur in soils resulting in the transport of metal(loid) ions from the anode to the cathode electrode (Dermont et al., 2008). Electromigration and electroosmosis are two main mechanisms for the transportation of metals and metalloids (Fig. 1). Water present in soil is able to move towards the cathode through soil pores by electroosmosis while cations move to the cathode through electromigration (Cameselle and Reddy, 2012). The migration of ions makes it possible for the

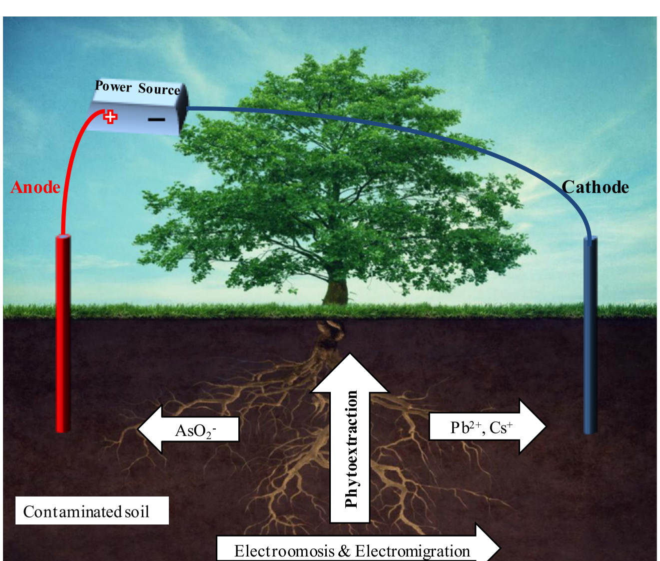


**Fig. 1.** Schematic diagram of electro-kinetic coupled/enhanced phytoremediation.

subsequent removal of soluble metal(loid)s or immobilization with oxides, hydroxide and carbonates during the phytoremediation (Ottosen et al., 2007). However, the detailed mechanisms of releasing/mobilization of metals/metalloids with EKF coupled with phytoremediation are not clearly understood. Especially coupled electro-kinetic phytoremediation has not been applied to remediate Cs contaminated soils. Moreover, with a rapid global urbanization and metropolitanization, the municipal suburb agricultural land plays an increasing role in supplying fresh vegetables to the metropolitan consumption, especially in the developing world. However, municipal suburb vegetable lands are most vulnerable to be contaminated with anthropogenic activities (Han, 2007). Therefore, understanding bioaccumulation and transport of Cs, Pb and As by vegetable plants under electrokinetic treatment is essential to further prevent pollutants into the food chain.

The objectives of this study were: (1) To investigate the coupled electro-kinetic remediation with phytoremediation to remove Pb, As and Cs from polluted soils, (2) To study bioavailability of Pb, As and Cs in Mississippi River Delta paddy soil after a growing season enhanced by EKF, and (3) To determine the bioaccumulation of Pb, As and Cs in Indian mustard, spinach and cabbage plants under EKF treatment.

## 2. Materials and methods

### *2.1. Soil and experimental design*

The surface paddy soils (0–15 cm) were sampled from a rice field in the MS River Delta. All soil samples were air-dried and ground to pass 2 mm sieve. Potted experiment was carried out in greenhouse. Two replicates were set for each treatment. About 1 kg of air-dried soil was weighed and placed into each plastic pot with 6 in. (15.2 cm) diameter and 5.4 in. (13.7 cm) height. Nitrogen, phosphorous and potassium were added as base fertilizers with a ratio of 1:1:1. Chemical grade lead nitrate ($Pb(NO_3)_2$), sodium arsenite ($NaAsO_2$) and cesium chloride (CsCl) were used as Pb, As and Cs sources, respectively. Nitrogen brought from lead nitrate was compensated by nitrate fertilizer. Three levels were applied for each metal(loid). Pb treatment included the control, 200, 600 and 1000 mg $kg^{-1}$; As and Cs treatments were the control, 5, 20 and 100 mg $kg^{-1}$. The control and the middle level treatment were selected for application of EKF: Pb (600 mg $kg^{-1}$), As (20 mg $kg^{-1}$) and Cs (20 mg $kg^{-1}$). Pb, As and Cs salts were ground and mixed gradually with air-dried soil to ensure the homogeneity of mixing the salts with soil. Indian mustard (*Brassica juncea*), spinach (*Spinacia oleracea*) and cabbage (*Brassica rapa*) were planted in each pot. Ten seeds of each plant were sowed in pots after the selection for uniformity. After 7 days, the seedlings of Indian mustard and spinach were thinned to 3 plants per pot while the seedlings of cabbage were thinned to 1 plant per pot. Water moisture was kept at field capacity throughout 7-week growth period of the experiment. Plastic trays were placed under each pot in case of the loss of nutrients and trace elements. Leaches were collected and put back to the respective pots.

### *2.2. EKR setup and determination of metal(loid) solubility and bioaccumulation*

A DC power supplier (0–60 V, 0–3 A) was used as electrical power source. Graphite electrode rod (0.95 cm diameter, 30.5 cm length) was used as both anode and cathode due to its low cost and inertness. A DC electrical field with constant intensity of 1 V $cm^{-1}$ was applied to soil in plastic pots with a medium concentration level of Pb, As and Cs, respectively. A pair of graphite electrode rods were vertically inserted into both sides of each pot