Heliyon 7 (2021) e07736

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Research article

The combination of phytoremediation and electrokinetics remediation technology on arsenic contaminated remediation in tailing storage facilities from gold mine

Kitsadee Wanitsawatwichai [a], Pantawat Sampanpanish [b,*]

[a] Interdisciplinary Program in Environmental Science, Graduate School, Chulalongkorn University, 254 Phayathai Road, Pathumwan, Bangkok 10330, Thailand
[b] Environmental Research Institute, Chulalongkorn University, 254 Phayathai Road, Pathumwan, Bangkok 10330, Thailand

HIGHLIGHTS

- Plants treated with 1 V/cm electromagnetic field for 120 days had the highest arsenic accumulation.
- Treatment with 4 V/cm electromagnetic field can inhibit plant growth.
- Napier grass accumulated more arsenic in its roots than in its stems and leaves.
- Treatment with 1 V/cm electromagnetic field stimulated toxin uptake by plants.

ARTICLE INFO

Keywords:
Arsenic
Electrokinetic
Micro-X-ray fluorescence
Mott dwarf Napier grass
Mine tailings
Phytoremediation

ABSTRACT

This research aims to study the effects of combining Mott dwarf Napier grass cultivation and electrokinetic (EK) treatment on arsenic (As) mobility and remediation of As-contaminated mine tailings. Experimental groups were treated with 0, 1, 2, and 4 V/cm for 15 days–120 days. Groups treated with 1 and 2 V/cm electromagnetic field had better As remediation efficiency than the control group with no electromagnetic field treatment. However, electromagnetic field treatment at 4 V/cm inhibited plant growth and had an effect on As uptake in the form of solution at a low level. Plants in experimental group treated with 1 V/cm electromagnetic field for 90 days had significantly high As accumulation (7.69 ± 0.16 mg/kg) in their roots. Their relative growth rate was close to that of the control group with the highest biomass (15.09 ± 0.65 g) recorded on day 120. Mobility and accumulation of As and other elements in the plants were investigated using micro-X-ray fluorescence technique (Beamline BL6b). It was found that very low As concentrations could not be detected although energy emitted from its innermost electron shell (K alpha ($K\alpha 1\&2$) and K beta ($K\beta 1$)) were equal to 10.54 and 11.72 keV. In general, As accumulation in plants occurs primarily in the roots and stems, with greater accumulation around the cortex, epidermis, and xylem. This is similar to the patterns of iron and phosphate accumulation, which occurs through phosphate transporters. In addition, high aluminum mobility and accumulation were found in the stems and leaves of Mott dwarf Napier grass. However, As accumulation in the roots of Mott dwarf Napier grass was higher than in the stem and leaves.

1. Introduction

Mine tailings are byproducts from processing activities of the mining industry and are most likely stored in open tailings storage facility (TSF) without remediation (Babel et al., 2016). They are comprised of very small sand particles and are contaminated with large quantities of heavy metals (Santibanez et al., 2011). With the inappropriate storage and disposal of mine tailings, a risk of adverse effects on human health and environment might be occurred (Yang et al., 2012; Sanchez-Lopez et al., 2015). Since the advent of mining, pollution and environmental problems, especially heavy metal contamination in areas with and near mining activities, have become more likely. High levels of heavy metals can inhibit plant growth and decrease plant biomass (Jadia and Fulekar, 2009), and ultimately affect the food chain.

---

* Corresponding author.
E-mail address: pantawat.s@chula.ac.th (P. Sampanpanish).

https://doi.org/10.1016/j.heliyon.2021.e07736
Received 27 April 2021; Received in revised form 26 July 2021; Accepted 4 August 2021

As is considered a highly toxic element and creates hazardous living conditions for humans, animals, and plants. As contamination across the world is attributable to the expansion of the gold mining industry (Chung et al., 2014), especially to leakage from deteriorated or unstandardized tailings storage facilities to groundwater (Abdul et al., 2015). There are various remediation methods for As-contaminated soils, such as EK remediation, which can be performed in-situ to remove As from contaminated soils and mine tailings (Baek et al., 2009). Besides, this remediation technology is suitable for areas with clay and sandy soils and is useful for widespread areas with decreasing contamination levels (Suied et al., 2018). If the EK remediation method is combined with the phytoremediation technologies, the remediation efficiency might be increased. The effects of As mobility and accumulation in different part of plants and the atomic compounds of samples of substances can be identified using synchrotron radiation (synchrotron light) micro-X-ray fluorescence (Micro-XRF) technique, Beamline BL6b (Aida et al., 2017). This technology can be used to study mechanisms of heavy metal mobility, distribution, and accumulation in plant tissues.

Therefore, in this research, EK and phytoremediation technologies were combined for the treatment of contaminated mine tailings from tailing storage facility (TSF). The effects of different levels of electromagnetic field on As uptake by Mott dwarf Napier grass (*Pennisetum purpureum* cv. Mott) were studied. This will potentially help in the reutilization of contaminated areas for other activities in a more efficient and safer manner.

2. Materials and methods

2.1. Preparation of mine tailings and P. purpureum cv. Mott

Mine tailings used in the study were collected from tailing storage facilities (TSFs) in areas with gold mining capacity at depths of 0–30 cm. Pieces of wood, stones, plants, and unwanted materials were removed. The initial physical and chemical characteristics of the mine tailings are shown in Table 1.

The plant used in the study is Mott dwarf Napier grass from Animal Nutrition Research and Development Center, Pak Chong sub-district, Pak Chong district Nakhon Ratchasima province. The experimental plants were grown using the cutting method and plants of the same age, size, and fresh weight were selected. Analysis of As accumulation in the experimental plants was conducted prior to the experiment.

2.2. Experimental design

2.2.1. Study on As accumulation in mine tailings in conjunction with the use of EK

Experimental groups were prepared by growing plants in a greenhouse (ex-situ). Cylindrical pots measuring 30 cm in height and 25 cm in diameter were used to grow the plants. Each pot cultivated one plant in a 11-kg of mine tailings contaminated with 68.70 mg/kg of As. Seven stainless steel 316L electrodes were placed hexagonally in the mine tailings around the edge of each pot at a suitable distance from each other as shown in Figure 1 (a) and (b). The electrode in the center was an anode while the other six were cathodes. Plants were watered with 200 ml water every two days (moisture content of the mine tailings was maintained at 15% prior to the electromagnetic field treatment). No fertilizers were added during the experimental period and there were four experimental groups: 1) experimental group without electromagnetic field treatment; 2) experimental group with 1 V/cm electromagnetic treatment; 3) experimental group with 2 V/cm electromagnetic treatment; and 4) experimental group with 4 V/cm electromagnetic treatment. Duration of the electromagnetic field treatment was 3 hours per day (09.00–12.00 h). Samples of plants and mine tailings were collected on days 15, 30, 45, 60, 75, 90, 105, and 120.

An High Density Polyethylene (HDPE) pipe was used to collect samples of mine tailings near the anodes and cathodes; samples were collected at three points around the anodes at a depth of 20 cm. The mine tailing samples were dried at room temperature and extracted according to USEPA method 3051A (USEPA, 2007), via microwave assisted acid digestion using an Ultrawave single reaction chamber (SRC) invented by Milestone Helping Chemist. The solutions were analyzed to determine total As (TAs) content via inductively coupled plasma-optical emission spectrometry (ICP-OES), using PlasmaQuant PQ 9000 Elite invented by Analytik Jena AG.

Plant samples were washed with tap water three-four times and once with de-ionized water. Next, the aboveground parts (stems and leaves) and underground parts (roots) were separated, their fresh weight was measured, and then oven dried at 105 °C for 24–48 h. Subsequently, the dry weight of each part was measured. A portion of the plant samples were ground and extracted according to USEPA method 3052 (USEPA, 1996) via microwave-assisted acid digestion. The samples were then analyzed to determine total As concentration using ICP-OES.

2.2.2. Study on element mobility through roots, stems, and leaves of Mott dwarf Napier grass

Plant samples in the experimental groups, 1) with electromagnetic field treatment; 2) with 1 V/cm electromagnetic treatment; 3) with 2 V/cm electromagnetic treatment; and 4) with 4 V/cm electromagnetic treatment, were collected at the time As uptake and accumulation by plants were the highest.

Plant samples were prepared by dividing them into three parts: 1) root, 2) stem, and 3) leaf. The plant samples in each experimental group were collected and cross-sectioned into three parts. Plant specimens were then stored at -60 °C for 48 h and freeze dried for 24 h. The prepared plant samples were analyzed via synchrotron radiation (synchrotron light) micro-X-ray fluorescence (Micro-XRF) technique, using Beamline BL6b. The PyMCA program (Solé et al., 2007) was used to plot a graph of appropriate fundamental parameters including energy lines of ejected elements (Alfeld and Janssens, 2015).

2.2.3. Data analysis

ANOVA was used to analyze variance in data obtained experimentally and the F-value at the 95% confidence level was determined. Statistical Package for the Social Sciences (SPSS) was used for calculating if the data were highly different, and Duncan's New Multiple Range Test (DMRT) was used to compare data differences.

Table 1. Physical properties and basic chemical properties of the mine tailings used in the experiment.

Property of the mine tailings	Analysis method	Value
Sand: Silt: Clay	Hydrometer	83.8:15.2:1.0
pH	1:2 (v/v) soil: water mixture	7.68 ± 0.07
Electrical conductivity (μS/cm)	1:2 (v/v) soil: water mixture	1,654 ± 8.39
Oxidation reduction potential (mV)	1:2 (v/v) soil: water mixture	170.78 ± 5.09
Cation exchange capacity ($cmol_c$/kg)	Ammonium acetate saturation	3.0 ± 0.19
Organic matter (%)	Walkley and Black	0.916
Total nitrogen (%)	-	0.029
Phosphorus (mg/kg)	-	35.10
Potassium (mg/kg)	-	102
Al (mg/kg)	USEPA 3051A	9,292.96 ± 91.32
Fe (mg/kg)	USEPA 3051A	18,792.40 ± 2,435.61
Mn (mg/kg)	USEPA 3051A	989.42 ± 19.15
As (mg/kg)	USEPA 3051A	68.70 ± 0.18

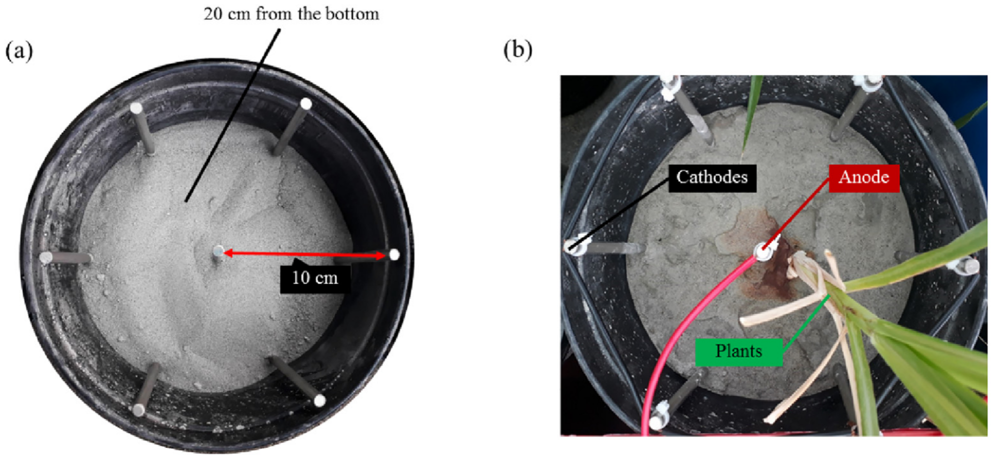

Figure 1. Experimental design for growing Mott dwarf Napier grass in mine tailings in conjunction with EK treatment. (a) Stainless steel 316L electrodes placed hexagonally and (b) Top view of the experimental groups involving plant cultivation.

3. Results and discussion

3.1. Initial properties of mine tailings

3.1.1. pH of mine tailings

Acidity and alkalinity measurements of the mine tailings at the end of the experiment on days 15–120 could be divided into two parts. pH of mine tailings near the anode before the experiment was 7.68 ± 0.01 (Table 1). Mine tailings in the experimental groups with electromagnetic treatment (1, 2, and 4 V/cm) had statistically ($P \leq 0.05$) different pH values on days 15–120 of the experiment. The pH of mine tailings near the anode tended to decrease with increase in the duration of the experiment (Table 2), while the pH of the mine tailings near the cathode appeared to increase significantly ($P \leq 0.05$) with increase in the duration of the experiment (Table 2). As for the control group (0 V/cm), there was no statistically significant difference in pH values from the beginning till the end of the experiment. Changes in pH values in the experimental groups with electromagnetic field treatments could be because the presence of electromagnetic field and increase in the duration of electromagnetic field treatment facilitate hydrolysis reactions between water and mine tailing particles near the anode and cathode. Mine tailings near the anode tend to have lower pH values while mine tailings near the cathode tend to have higher pH values (Tang et al., 2018). The anode is where oxidation reactions takes place, contributing to an increase in hydrogen ions (H^+) from the splitting of water (H_2O). This reaction is enhanced by the intensification of electromagnetic field treatment. When there is high accumulation of hydrogen ions, pH values drop significantly. The cathode is where reduction reactions takes place, leading to high accumulation of hydroxide ions (OH^-), which in turn causes pH to increase. Besides, hydrogen ions (H^+) can move faster than hydroxide ions (OH^-), making expansion of acidic areas more rapid than that of alkaline areas. Furthermore, hydroxide ions (OH^-) may cause precipitation of metal oxides around the cathode (Cameselle et al., 2013; Cang et al., 2012; Paz-Garcia et al., 2012; Peng et al., 2012).

3.1.2. Oxidation reduction potential of the mine tailings

The oxidation reduction potentials (ORPs) of mine tailings near the anode and cathode increased and decreased, respectively, during the experiment (Table 3). ORP values of the mine tailings before the experiment were in the range of 165.34–175.42 mV (average: 170.78 ± 5.09 mV; Table 1). In the experimental groups without electromagnetic field treatment or the control (0 V/cm) and the experimental groups with electromagnetic treatment (1, 2, and 4 V/cm), ORP of the mine tailings around the anode increased significantly ($P \leq 0.05$) as the experiment progressed (Table 3). The ORP of the mine tailings around the cathode in all the experimental groups exhibited an opposite trend, decreasing with time (Table 3). Experimental results showed that the ORP around the anode was significantly higher than that around the cathode. This is because electrolysis reaction at the anode occurs faster and in the same direction as the pH values of mine tailings around the anode. The ORP values of mine tailings around the cathode tended to decrease as the experimental time increased. During electrolysis, oxidation took place at the anode causing the reducing agent (i.e., water present in the mine tailings) to lose electrons. The reducing agent is the primary electron donor for the hydrolysis reaction at the anode which contributing to higher oxygen levels and higher ORP of mine tailing around the anode than around the cathode (Reddy et al., 2011). In addition, ORP values of soils which were exposed to the air or oxygen were generally higher. Meanwhile, more negative ORP values were observed for soils or sediments piled in areas deeper than the depth of soil surface, as they are not

Table 2. pH of mine tailings around the anode and cathode.

Trial period (d)	Anode				Cathode			
	0 V/cm	1 V/cm	2 V/cm	4 V/cm	0 V/cm	1 V/cm	2 V/cm	4 V/cm
15	7.68 ± 0.02^{a}	7.56 ± 0.09^{a}	7.35 ± 0.05^{b}	7.16 ± 0.04^{c}	7.65 ± 0.10^{l}	7.89 ± 0.02^{kl}	7.86 ± 0.09^{kl}	7.95 ± 0.03^{k}
30	7.67 ± 0.02^{a}	6.73 ± 0.04^{d}	6.15 ± 0.05^{fg}	5.71 ± 0.07^{h}	7.65 ± 0.09^{l}	8.00 ± 0.06^{k}	8.00 ± 0.06^{k}	8.03 ± 0.27^{k}
45	7.68 ± 0.02^{a}	6.41 ± 0.14^{e}	5.73 ± 0.35^{h}	5.33 ± 0.04^{j}	7.64 ± 0.07^{l}	8.75 ± 0.26^{j}	9.00 ± 0.12^{i}	9.03 ± 0.04^{hi}
60	7.66 ± 0.02^{a}	6.21 ± 0.03^{f}	5.52 ± 0.05^{i}	4.92 ± 0.04^{l}	7.65 ± 0.04^{l}	9.13 ± 0.17^{ghi}	9.16 ± 0.21^{fghi}	9.38 ± 0.31^{efg}
75	7.67 ± 0.01^{a}	6.07 ± 0.03^{g}	5.20 ± 0.04^{k}	4.49 ± 0.04^{n}	7.65 ± 0.02^{l}	9.21 ± 0.09^{fghi}	9.23 ± 0.07^{fghi}	9.50 ± 0.07^{de}
90	7.65 ± 0.01^{a}	5.83 ± 0.03^{h}	4.96 ± 0.08^{l}	3.90 ± 0.01^{o}	7.66 ± 0.03^{l}	9.20 ± 0.13^{fghi}	9.22 ± 0.10^{fghi}	9.77 ± 0.31^{bc}
105	7.67 ± 0.02^{a}	5.55 ± 0.05^{i}	4.71 ± 0.03^{m}	3.45 ± 0.04^{p}	7.68 ± 0.01^{l}	9.28 ± 0.14^{efgh}	9.40 ± 0.07^{def}	9.92 ± 0.04^{b}
120	7.67 ± 0.01^{a}	5.21 ± 0.04^{k}	4.42 ± 0.04^{n}	2.94 ± 0.05^{q}	7.67 ± 0.02^{l}	9.32 ± 0.08^{efg}	9.63 ± 0.05^{cd}	10.15 ± 0.23^{a}

Data are shown as mean ± 1 SD, derived from triplicate measurements. Means with a different letter are significantly different ($p < 0.05$; DMRT).

Table 3. ORP of mine tailings around the anode and cathode.

Trial period (d)	Anode				Cathode			
	0 V/cm	1 V/cm	2 V/cm	4 V/cm	0 V/cm	1 V/cm	2 V/cm	4 V/cm
15	172.50 ± 2.80^{m}	173.28 ± 2.02^{m}	178.23 ± 0.21^{m}	197.93 ± 2.69^{l}	171.63 ± 3.79^{a}	170.33 ± 1.42^{ab}	168.08 ± 2.80^{abc}	160.33 ± 1.42^{ef}
30	171.57 ± 2.20^{m}	199.60 ± 1.47^{l}	207.66 ± 2.71^{kl}	225.70 ± 3.83^{ij}	171.23 ± 5.32^{a}	163.73 ± 1.59^{cdef}	159.67 ± 3.60^{ef}	151.87 ± 1.39^{gh}
45	171.65 ± 5.43^{m}	204.31 ± 2.91^{l}	209.11 ± 5.98^{kl}	239.65 ± 1.59^{gh}	169.90 ± 4.10^{ab}	162.56 ± 2.31^{def}	160.23 ± 1.51^{ef}	146.11 ± 1.98^{i}
60	170.75 ± 5.03^{m}	218.10 ± 2.86^{jk}	234.32 ± 3.86^{hi}	256.70 ± 4.33^{de}	170.29 ± 1.42^{ab}	164.23 ± 1.06^{cde}	154.63 ± 3.35^{g}	145.16 ± 2.44^{i}
75	171.47 ± 2.63^{m}	223.80 ± 1.59^{ij}	241.91 ± 0.26^{fgh}	272.58 ± 2.48^{c}	170.05 ± 2.58^{ab}	159.15 ± 2.47^{f}	163.15 ± 1.18^{def}	139.73 ± 3.07^{j}
90	173.42 ± 2.00^{m}	231.27 ± 0.90^{hi}	252.93 ± 2.44^{def}	288.15 ± 2.78^{b}	170.74 ± 2.78^{ab}	151.70 ± 2.73^{gh}	146.55 ± 2.85^{i}	127.94 ± 2.14^{k}
105	169.31 ± 3.65^{m}	248.51 ± 2.48^{efg}	262.01 ± 2.70^{cd}	308.44 ± 3.77^{a}	167.01 ± 3.42^{abcd}	149.80 ± 2.56^{hi}	145.56 ± 3.34^{i}	124.13 ± 2.03^{kl}
120	167.71 ± 4.79^{m}	254.99 ± 2.11^{de}	270.41 ± 2.39^{c}	319.62 ± 2.09^{a}	165.81 ± 3.04^{bcd}	146.53 ± 1.21^{i}	137.23 ± 1.30^{j}	122.29 ± 0.82^{l}

Data are shown as mean ± 1 SD, derived from triplicate measurements. Means with a different letter are significantly different ($p < 0.05$; DMRT).

exposed to air (Lageman et al., 2005). Therefore, the depth of the soil during the plant growing experiment should be deeper than 20 cm. In addition, the water content should be regulated throughout the experiment so that water does not accumulate at the bottom of the container as mine tailings can be affected by air or oxygen. In this regard, ORP values of mine tailings around the cathode are positive though they tend to decrease as the duration of the experiment increases.

3.2. Uptake and accumulation of As by Mott dwarf Napier grass in EK-assisted treatment

3.2.1. Relative growth rate (RGR)

The RGR of Mott dwarf Napier grass in the four experimental groups on days 15–120 was analyzed. This part of the text can be shortened to simply "The RGRs of Mott dwarf Napier grass in the experimental groups with electromagnetic field treatments (1, 2, and 4 V/cm) decreased significantly ($P \leq 0.05$) and continuously as the experiment progressed (Figure 2).". Besides, RGRs of the experimental group without electromagnetic field treatment (or the control group) and the experimental groups with electromagnetic field treatments (1, 2, and 4 V/cm) were statistically different ($P \leq 0.05$). The control group had the highest RGR, and good growth of Mott dwarf Napier grass was observed at all experimental durations. However, RGRs in the experimental groups with electromagnetic treatment declined more than usual or were lower than that in the control group. For the experimental groups with electromagnetic field treatments, RGR decreased with increase in electromagnetic field strength. The experimental group with 4 V/cm electromagnetic field treatment had the lowest RGR. Under normal circumstances, the mean RGR of plants is similar to that of monocotyledonous trees growing in nature at the same latitude (Haider et al., 2012) in soil that has similar elemental composition and fertility. However, the mine tailings used in the experiments had low fertility and thus were not suitable for plant growth. This explains why plants in the control group, without electromagnetic field treatment, had a mean RGR that was much lower than that of plants growing in normal soil from day 15–120 of the experiment (Read et al., 2009). In addition, in the experimental groups with electromagnetic field treatments, good plant growth was not observed. This could be because long and intense electromagnetic field treatment (for example, the 4 V/cm treatment) affect the properties of mine tailings, such as porosity, moisture content, chemical forms of elements, pH, and electrical conductivity. This may successively lower the fertility of mine tailings or soil, and high voltage may affect the nutrient uptake ability of plant root cells (Wawrecki and Zagorska-Marek, 2007).

3.2.2. Biomass

The plants in all of the four experimental groups had significantly ($P \leq 0.05$ at the 95% confidence level) higher biomass at the end of the experiment than at the beginning (Table 4). At the end of the experiment, plant biomass in the control group (0 V/cm) and experimental group with 1 V/cm electromagnetic field treatment were significantly higher ($P \leq 0.05$) than that in experimental groups with 2 and 4 V/cm electromagnetic field treatments, especially on day 120 of the experiment. The experimental group with 1 V/cm electromagnetic field treatment showed the best biomass growth among the experimental plants. This is consistent with the results of Cang et al. (2011), who studied the effects of electromagnetic field treatment on the remediation of soil contaminated with cadmium, copper, lead, and zinc using brown lettuce. They found that applying a low electromagnetic field for 4–5 hours per day enhanced the growth of experimental plants. However, in this study, plant biomass

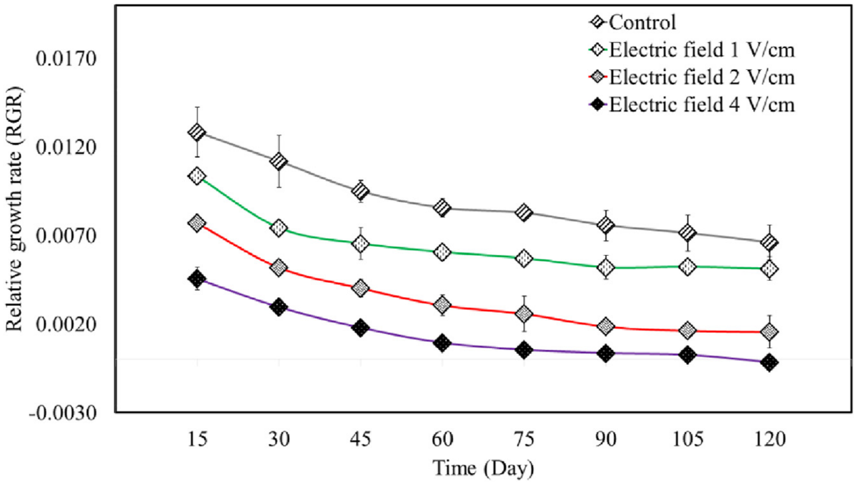

Figure 2. Relative growth rate (RGR) of Mott dwarf Napier grass.

Table 4. Biomass of roots, stems, and leaves of *Pennisetum purpureum* cv. Mott.

Trial period (d)	Biomass (g)			
	0 V/cm	1 V/cm	2 V/cm	4 V/cm
15	4.05 ± 0.26^{n}	4.11 ± 0.11^{n}	4.74 ± 0.70^{mn}	5.28 ± 0.72^{lmn}
30	7.78 ± 1.19^{fghijk}	6.89 ± 0.02^{ijklm}	4.95 ± 0.84^{lmn}	5.02 ± 0.49^{lmn}
45	7.13 ± 0.13^{hijkl}	7.85 ± 0.21^{fghijk}	6.57 ± 0.67^{jklm}	4.95 ± 1.10^{lmn}
60	9.98 ± 0.91^{def}	8.22 ± 0.01^{efghij}	9.49 ± 0.72^{defg}	5.83 ± 0.05^{klmn}
75	9.45 ± 0.76^{defg}	7.56 ± 0.32^{ghijk}	8.09 ± 0.30^{efghij}	6.41 ± 0.52^{jklm}
90	10.29 ± 0.24^{cde}	9.75 ± 0.09^{defg}	8.59 ± 0.35^{defghij}	6.54 ± 0.20^{jklm}
105	12.22 ± 0.22^{bc}	10.65 ± 1.18^{cd}	9.17 ± 0.34^{defgh}	8.82 ± 0.46^{defghi}
120	13.49 ± 0.75^{ab}	15.09 ± 0.65^{a}	13.37 ± 0.43^{ab}	8.82 ± 0.57^{defghi}

Data are shown as mean ± 1 SD, derived from 3 repeats. Means with a different letter are significantly different ($p < 0.05$; DMRT).

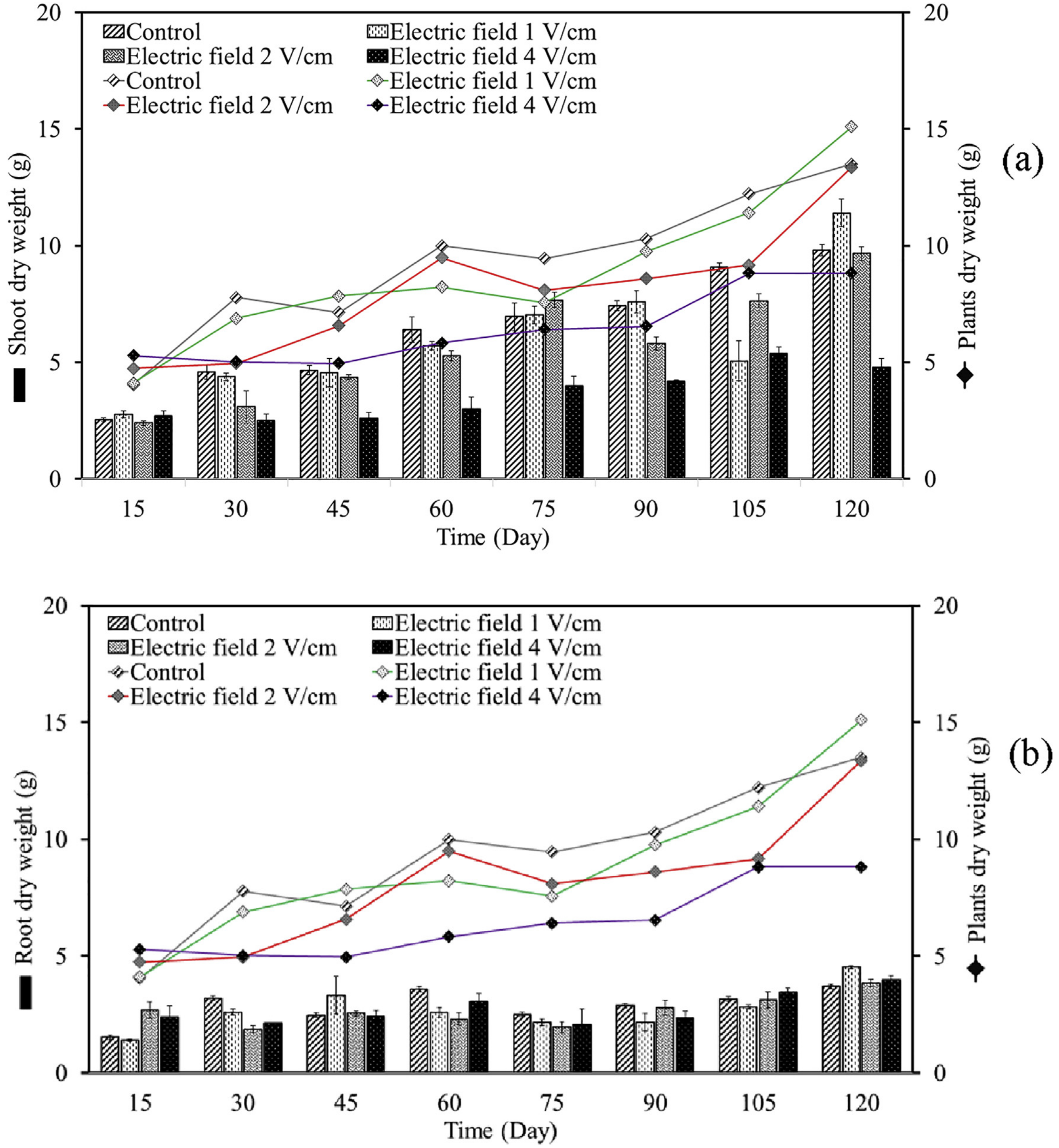

Figure 3. Dry weight of experimental plants: (a) aboveground parts (stems and leaves) and (b) underground part (roots) at different experimental durations.

Table 5. Amount of As in the aboveground parts (stems and leaves) and underground part (roots) of Mott dwarf Napier grass.

Trial period (d)	Aboveground parts (stems and leaves) As (mg/kg)				Underground part (roots) As (mg/kg)			
	0 V/cm	1 V/cm	2 V/cm	4 V/cm	0 V/cm	1 V/cm	2 V/cm	4 V/cm
15	1.14 ± 0.10^{j}	1.72 ± 0.70^{ghi}	1.60 ± 0.19^{hij}	1.54 ± 0.19^{ij}	1.92 ± 0.19^{k}	1.98 ± 0.52^{k}	2.27 ± 0.50^{klm}	2.05 ± 0.55^{kl}
30	1.57 ± 0.04^{ij}	1.62 ± 0.44^{hij}	1.66 ± 0.17^{hij}	2.02 ± 0.31^{efghi}	2.21 ± 0.14^{klm}	2.48 ± 0.17^{lmno}	2.81 ± 0.29^{nopq}	2.59 ± 0.09^{mno}
45	1.71 ± 0.21^{ghi}	1.81 ± 0.12^{fghi}	1.92 ± 0.18^{efghi}	1.97 ± 0.06^{efghi}	2.41 ± 0.08^{klmn}	2.69 ± 0.13^{mnop}	2.93 ± 0.21^{opq}	4.62 ± 0.42^{tu}
60	1.73 ± 0.17^{ghi}	1.92 ± 0.27^{efghi}	2.29 ± 0.09^{cdefg}	2.85 ± 0.14^{abc}	3.11 ± 0.05^{pqr}	4.64 ± 0.10^{tu}	4.50 ± 0.28^{tu}	4.74 ± 0.09^{tu}
75	1.84 ± 0.11^{fghi}	2.32 ± 0.22^{cdef}	3.12 ± 0.17^{a}	2.79 ± 0.29^{abc}	3.19 ± 0.08^{qrs}	5.61 ± 0.14^{v}	4.66 ± 0.09^{tu}	4.92 ± 0.30^{u}
90	1.94 ± 0.02^{efghi}	2.60 ± 0.04^{abcd}	3.10 ± 0.06^{a}	1.78 ± 0.20^{fghi}	3.43 ± 0.39^{rs}	7.69 ± 0.16^{z}	6.48 ± 0.22^{xy}	4.85 ± 0.28^{tu}
105	2.16 ± 0.06^{defgh}	2.64 ± 0.73^{abcd}	2.92 ± 0.51^{ab}	2.29 ± 0.53^{cdefg}	3.64 ± 0.16^{s}	6.91 ± 0.09^{y}	6.02 ± 0.19^{vw}	4.90 ± 0.23^{u}
120	2.43 ± 0.36^{bcde}	2.49 ± 0.39^{bcde}	2.34 ± 0.33^{cdef}	2.73 ± 0.15^{abcd}	4.38 ± 0.20^{t}	6.69 ± 0.13^{xy}	6.26 ± 0.49^{wx}	2.61 ± 0.22^{mno}

Data are shown as the mean ± 1 SD, derived from 3 repeats. Means with a different letter are significantly different ($p < 0.05$; DMRT).

in the experiment groups with 2 and 4 V/cm electromagnetic field treatments were lower than that in the control group and the experimental group with 1 V/cm electromagnetic field treatment. This indicates that the existence of a high electromagnetic field can hinder plant growth (Aboughalma et al., 2008).

Comparison of the biomass of the aboveground (stems and leaves) and underground (roots) parts showed that root biomass is lower than stem and leaf biomass as shown in Figure 3(a). In this study, electromagnetic field was applied for 3 hours per day so that growth of experimental plants is not majorly affected. Root, stem, and leaf biomass increased as the experiment progressed. Prolonged electromagnetic field treatment can negatively impact the plant roots to which they are directly exposed. Hence, roots are more affected by an electromagnetic field than stems and leaves (Sanchez et al., 2018). However, when electromagnetic field was applied for 3 hours per day, biomass of the experimental plants, especially plant root biomass was maintained as shown in Figure 3(b). Plant growth was higher in the 2 and 4 V/cm electromagnetic field treatments. Moreover, biomass of plants from certain experimental periods were not statistically different. In contrast, a high electromagnetic field had an obvious negative effect on the growth of stems and leaves as observed in the experimental group with 4 V/cm electromagnetic field treatment was given. It can be said that high levels of electromagnetic fields may affect plant uptake ability of elements and nutrients including reducing efficiency of heavy metal contamination to soils. Based on the relationship among the stem, leaf, and root biomass observed in this study, the results were different from those of Sánchez et al. (2019), who treated atrazine-contaminated soil using EK in conjunction with phytoremediation. Sánchez et al. (2019) applied an electromagnetic field to plants for 6 consecutive hours for 14 days (alternating between the anode for 4 hours and cathode for 2 hours). They found that, over time, strong electromagnetic fields reduced plant root biomass.

3.2.3. *Effects of EK on remediation of As-contaminated mine tailings using Mott dwarf Napier grass*

As uptake and accumulation in the 1) aboveground parts (stems and leaves) (Table 5) and 2) underground part (roots) (Table 5) of Mott dwarf Napier grass used in conjunction with EK for remediation of As-contaminated mine tailings were determined. As accumulation in the aboveground and underground parts of the control and experimental (1, 2, and 4 V/cm electromagnetic field treatment) group plants were significantly different ($P \leq 0.05$). On day 30, no major difference in As levels of the underground part (roots) was observed. Statistically significant As accumulation ($P \leq 0.05$) began on day 60, especially in the experimental groups with 1–4 V/cm electromagnetic field treatments, and the highest As accumulation ($P \leq 0.05$) was observed in the roots. Although statistically insignificant, a small amount of As accumulation was observed in the aboveground parts (stems and leaves). This is consistent with the study conducted by Mao et al. (2016) on remediation of As-contaminated rice field soils using phytoremediation and EK. They found that plants treated with electromagnetic field showed higher As uptake than plants without electromagnetic field treatment. Moreover, more As was accumulated in the roots than in the stems. Based on the pH values of mine tailings around the anode and As accumulation in plants, the experimental groups with 1 and 2 V/cm electromagnetic field treatments for 90–120 days had the best As remediation efficiency, especially on day 90 when As accumulation in the roots was the highest. The highest As uptake by plants occurred when the pH of the mine tailings was in the range of 5.20–5.80. Increased As distribution, mobility, and accumulation in plant roots was observed with acidic (approximately 5.5) soil or mine tailings (Signes-Pastor et al., 2007).

Generally, soils that are slightly acidic will increase levels of As in solution. In addition, changes in pH of soils or mine tailings affect As distribution, mobility, and form (arsenate or As (V) and arsenite or As (III)) (Adra et al., 2016). Potential mechanism of As distribution in mine tailings compartment after the electrokinetic experiment. As exists mainly as arsenate in a natural and oxidative state, and the speciation of the arsenate oxyanion is classified as $H_2AsO_4^-$, $HAsO_4^{-2}$, or AsO_4^{-3} for a given pH. These anionic metals can be desorbed from mine tailings by anion exchange with hydroxide ions in the pore solution. Therefore, an alkaline condition can increase desorption and the removal efficiency of As in electrokinetic remediation. Considering the initial fractionation of As, these results were not inferior because the predominant species of As, nearly 95%, was detected in the residual fraction, which is strongly bound. This result means that strongly bound fractions such as the residual form can be removed by electrokinetic remediation assisted by an acidic and basic electrolyte. In mine tailings, most of the As is surrounded by iron oxides (FeO) and manganese oxides (MnO_2). This is consistent with concentrations of aluminum (9,292.96 mg/kg), iron (18,792.40 mg/kg), and manganese (989.42 mg/kg) in the mine tailings used in this study (Table 1). Consequently, decrease in pH values of mine tailings is a major factor increasing As solubility (Han et al., 2004) in water. Moreover, increasing the acidity or alkalinity of mine tailings will affect As absorption and precipitation with other metals in soils or mine tailings. Besides, in highly acidic or alkaline soils or mine tailings, As can easily capture and precipitate with calcium or sulfate, while in slightly acidic or alkaline soils or mine tailings, As will likely capture iron oxide (Iron(II) oxide) and aluminum oxide (Moreno-Jimenez et al., 2013). In addition, plants generally take up As in the form of arsenate via phosphate transporters located in the cells of the outer layer of roots. Under low oxygen conditions, such as in inundated lands, As is present as arsenite, which can be more readily absorbed by plants than arsenate through aquaporin proteins (Zhao et al., 2009).

3.2.4. *Effects of element mobility in roots, stems, and leaves of Mott dwarf Napier grass*

Elemental mobility, distribution, and accumulation of As in roots, stems, and leaves of Mott dwarf Napier grass were analyzed using micro-X-ray fluorescence (Micro-XRF) technique, Beamline BL6b. Plants from

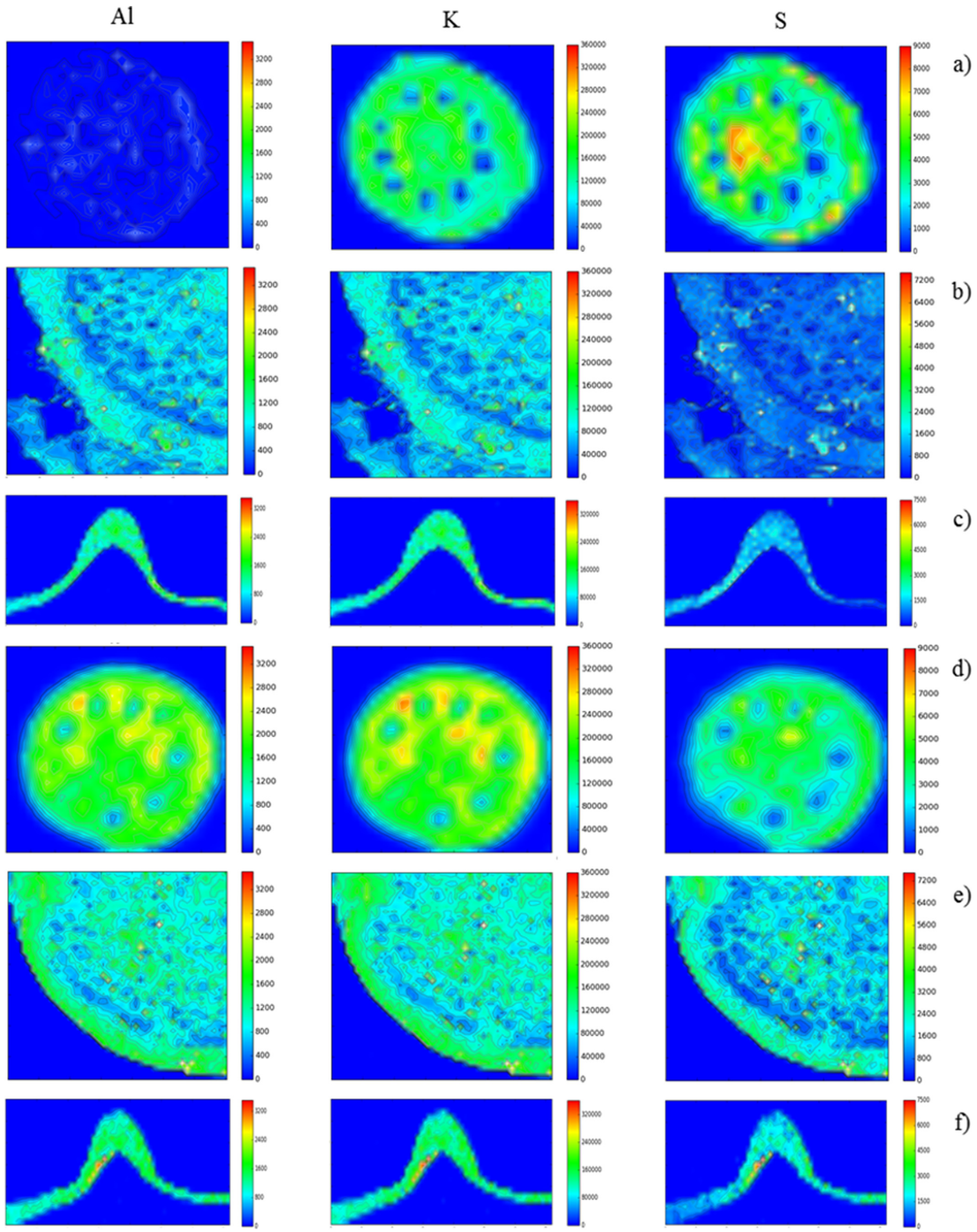

Figure 4. Element accumulation in different parts of Mott dwarf Napier grass: a) root part of the control group; b) stem part of the control group; c) leaf part of the control group; d) root part of the experiment group in which 1 V/cm electromagnetic field treatment was given; e) stem part of the experiment group in which 1 V/cm electromagnetic field treatment was given and f) leaf part of the experiment group in which 1 V/cm electromagnetic field treatment was given.

experimental group with 1 V/cm electromagnetic field treatment harvested on day 120 had the highest As accumulation. As concentrations in the underground (roots) and aboveground (stems and leaves) parts were too low to be detectable by Beamline BL6b or synchrotron light; this instrument can analyze only in the energy range of 2–12 keV. However, when electron vacancy in the innermost shell of As is filled, the characteristic K alpha (Kα1&2) and K beta (Kβ1) spectral lines of the emitted photon with the energies equal to 10.54 and 11.72 keV, respectively. Further, when electrons in the second or sub energy level are substituted, photons were emitted (Lα1&2) with energy equal to 12.82 keV. It can be seen that energy emitted during analysis of As is close to the detection limit of the instrument. Plant roots assimilate As in the form of arsenate or As (V) and arsenite or As (III) via phosphate transporters (Abbas et al., 2018). As mobility depends on the type of monocotyledonous plants, which can be non-hyperaccumulators or hyperaccumulators (Rosas--Castor et al., 2014). In non-hyperaccumulators, As accumulation is higher in the roots than in the stems and leaves, while hyperaccumulators assimilate more arsenate via roots, where they are converted to more mobile arsenite (Awasthi et al., 2017). Therefore, in hyperaccumulators, As accumulation in stems and leaves and the ratio of As concentration in whole of stems biomass are higher. Mott dwarf Napier grass (*Pennisetum purpureum* cv. Mott) is a non-hyperaccumulator as indicated by the higher As accumulation in its roots than in its stems and leaves. In general, high As accumulation is found in the cortex, epidermis, and xylem of plant roots and stems, similar to iron and phosphate accumulation via phosphate transporters (Seyfferth et al., 2017). As accumulation in leaves occurs only in hyperaccumulators and not in non-hyperaccumulators; As accumulation behavior is similar to that of sulfur, with high accumulation in the collenchyma and lower epidermis and movement through xylem (Datta et al., 2017).

The mobility and distribution of aluminum (Al), calcium (Ca), chromium (Cr), potassium (K), manganese (Mn), phosphorus (P), sulfur (S), and zinc (Zn) in the roots, stems, and leaves of Mott dwarf Napier grass were determined to be different (Figure 4). All these elements were detected at higher concentrations than As; Aluminum concentrations in roots, stems, and leaves were especially high, followed by potassium and sulfur. Energy emitted from its innermost electron shell, K alpha(Kα1&2) and K beta (Kβ1) and second shell (Lα1&2) were equal to 1.48 and 1.55 keV, respectively. This energy emitted is lower than the detection limit of the instrument (2 keV). However, aluminum could be detected as it was accumulated at high concentrations in the plants, which may be attributable to the high initial aluminum concentration in mine tailings (9,296.96 mg/kg; Table 1). Electromagnetic treatment changed aluminum to a soluble form. Once plants take up aluminum, it moves into the xylem and accumulates in plants better than As, iron, and manganese. Furthermore, potassium accumulation was the highest in the plant roots, followed by stems and leaves, respectively. The low amount of potassium accumulation was displayed by blue color and the high amount of potassium accumulation was displayed by red color (Limit of detection = 150–200 ppm). Overall, it is noticeable that with 1 V/cm electromagnetic field treatment (this electromagnetic field level does not affect the inhibition of plant growth.), the uptake, mobility, and accumulation of elements by plants were better than those of the control group in which no electromagnetic field treatment was given.

4. Conclusion

The remediation of As-contaminated mine tailings using Mott dwarf Napier grass in conjunction with EK can be concluded that the experiment group in which 1 and 2 V/cm electromagnetic fields were more efficient for As remediation than the control group no electromagnetic field treatment. Further, electromagnetic field treatment at 4 V/cm strongly affected plant growth as As uptake and accumulation by Mott dwarf Napier grass were greater in the roots than in the stems and leaves. Plant roots of the experimental group treated with 1 V/cm electromagnetic field for 90 days showed the highest As uptake (7.69 ± 0.16 mg/kg). As accumulation in plant biomass was the highest in the experimental group treated with 1 V/cm electromagnetic field for 120 days. However, considering other factors, such as plant growth rate, oxidation-reduction, anode deterioration, and acidity-alkalinity, the experimental duration of 120 days was determined to be unsuitable as it caused major changes in the properties of the mine tailings; for instance, pH around the anode was very low. Therefore, if applied to agricultural soils, soil fertility will be affected. In terms of elemental mobility and distribution in different plant parts, electromagnetic field treatment at 1 V/cm was suitable as it stimulated uptake of essential nutrients by plants and hence their growth. Further, plants treated with 1 V/cm electromagnetic field showed better heavy metal uptake than plants without electromagnetic field treatment and those treated with 4 V/cm electromagnetic field. Thus, elemental mobility and accumulation in different parts of monocotyledonous plants (roots, stems, and leaves) are influenced by plant type and habitat.

Declarations

Author contribution statement

Kitsadee Wanitsawatwichai: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Pantawat Sampanpanish: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Funding statement

This work was supported by the 90th Anniversary of Chulalongkorn University Fund (Ratchadaphiseksomphot Endowment Fund) and the Ratchadaphiseksomphot Endowment Fund, Chulalongkorn University, for the Research Unit.

Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Acknowledgements

We would like to express our sincere thanks to the Environmental Research Institute (ERIC), the Center of Excellence on Hazardous Substance Management (HSM), Research Program (RP) and Green Mining Management (GMM-RU) and the Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima Province, for providing courtesy facilities, equipment, and analytical tools, facilitating the successful completion of our research studies.

References

Abbas, G., Murtaza, B., Bibi, I., Shahid, M., Niazi, N.K., Khan, M.I., et al., 2018. Arsenic uptake, toxicity, detoxification, and speciation in plants: physiological, biochemical, and molecular aspects. Int. J. Environ. Res. Publ. Health 15 (1).

Abdul, K.S., Jayasinghe, S.S., Chandana, E.P., Jayasumana, C., De Silva, P.M., 2015. Arsenic and human health effects: a review. Environ. Toxicol. Pharmacol. 40 (3), 828–846.

Aboughalma, H., Bi, R., Schlaak, M., 2008. Electrokinetic enhancement on phytoremediation in Zn, Pb, Cu and Cd contaminated soil using potato plants. J. Environ. Sci. Health A Tox. Hazard Subst. Environ. Eng. 43 (8), 926–933.

Adra, A., Morin, G., Ona-Nguema, G., Brest, J., 2016. Arsenate and arsenite adsorption onto Al-containing ferrihydrites. Implications for arsenic immobilization after neutralization of acid mine drainage. Appl. Geochem. 64, 2–9.

Aida, S., Matsuno, T., Hasegawa, T., Tsuji, K., 2017. Application of principal component analysis for improvement of X-ray fluorescence images obtained by polycapillary-based micro-XRF technique. Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms 402, 267–273.

Alfeld, M., Janssens, K., 2015. Strategies for processing mega-pixel X-ray fluorescence hyperspectral data: a case study on a version of Caravaggio's painting Supper at Emmaus. J. Anal. Atomic Spectrom. 30 (3), 777–789.

Awasthi, S., Chauhan, R., Srivastava, S., Tripathi, R.D., 2017. The journey of arsenic from soil to grain in rice. Front. Plant Sci. 8, 1007.

Babel, S., Chauhan, R., Ali, N., Yadav, V., 2016. Preparation of Phosphate Mine Tailings and Low Grade Rock Phosphate Enriched Bio-Fertilizer. http://nopr.niscair.res.in/bitstream/123456789/33737/1/JSIR%2075%282%29%20120-123.pdf.

Baek, K., Kim, D.H., Park, S.W., Ryu, B.G., Bajargal, T., Yang, J.S., 2009. Electrolyte conditioning-enhanced electrokinetic remediation of arsenic-contaminated mine tailing. J. Hazard Mater. 161 (1), 457–462.

Cameselle, C., Chirakkara, R.A., Reddy, K.R., 2013. Electrokinetic-enhanced phytoremediation of soils: status and opportunities. Chemosphere 93 (4), 626–636.

Cang, L., Wang, Q.Y., Zhou, D.M., Xu, H., 2011. Effects of electrokinetic-assisted phytoremediation of a multiple-metal contaminated soil on soil metal bioavailability and uptake by Indian mustard. Separ. Purif. Technol. 79 (2), 246–253.

Cang, L., Zhou, D.-M., Wang, Q.-Y., Fan, G.-P., 2012. Impact of electrokinetic-assisted phytoremediation of heavy metal contaminated soil on its physicochemical properties, enzymatic and microbial activities. Electrochim. Acta 86, 41–48.

Chung, J.Y., Yu, S.D., Hong, Y.S., 2014. Environmental source of arsenic exposure. J. Prev. Med. Publ. Health 47 (5), 253–257.

Datta, R., Das, P., Tappero, R., Punamiya, P., Elzinga, E., Sahi, S., et al., 2017. Evidence for exocellular arsenic in fronds of pteris vittata. Sci. Rep. 7 (1), 2839.

Haider, S., Kueffer, C., Edwards, P.J., Alexander, J.M., 2012. Genetically based differentiation in growth of multiple non-native plant species along a steep environmental gradient. Oecologia 170 (1), 89–99.

Han, F.X., Kingery, W.L., Selim, H.M., Gerard, P.D., Cox, M.S., Oldham, J.L., 2004. Arsenic solubility and distribution in poultry waste and long-term amended soil. Sci. Total Environ. 320, 51–61.

Jadia, C.D., Fulekar, M., 2009. Phytoremediation of heavy metals: recent techniques. Afr. J. Biotechnol. 8. https://www.researchgate.net/publication/228614589_Phytoremediation_of_Heavy_Metals_Recent_Techniques.

Lageman, R., Clarke, R.L., Pool, W., 2005. Electro-reclamation, a versatile soil remediation solution. Eng. Geol. 77 (3-4), 191–201.

Mao, X., Han, F.X., Shao, X., Guo, K., McComb, J., Arslan, Z., et al., 2016. Electro-kinetic remediation coupled with phytoremediation to remove lead, arsenic and cesium from contaminated paddy soil. Ecotoxicol. Environ. Saf. 125, 16–24.

Moreno-Jimenez, E., Clemente, R., Mestrot, A., Meharg, A.A., 2013. Arsenic and selenium mobilisation from organic matter treated mine spoil with and without inorganic fertilisation. Environ. Pollut. 173, 238–244.

Paz-Garcia, J.M., Baek, K., Alshawabkeh, I.D., Alshawabkeh, A.N., 2012. A generalized model for transport of contaminants in soil by electric fields. J. Environ. Sci. Health A Tox. Hazard Subst. Environ. Eng. 47 (2), 308–318.

Peng, C., Almeira, J.O., Gu, Q., 2012. Effect of electrode configuration on pH distribution and heavy metal ions migration during soil electrokinetic remediation. Environ. Earth Sci. 69 (1), 257–265.

Read, J., Fletcher, T.D., Wevill, T., Deletic, A., 2009. Plant traits that enhance pollutant removal from stormwater in biofiltration systems. Int. J. Phytoremediation 12 (1), 34–53.

Reddy, K.R., Darko-Kagya, K., Al-Hamdan, A.Z., 2011. Electrokinetic remediation of chlorinated aromatic and nitroaromatic organic contaminants in clay soil. Environ. Eng. Sci. 28 (6), 405–413.

Rosas-Castor, J.M., Guzman-Mar, J.L., Hernandez-Ramirez, A., Garza-Gonzalez, M.T., Hinojosa-Reyes, L., 2014. Arsenic accumulation in maize crop (Zea mays): a review. Sci. Total Environ. 488–489, 176–187.

Sanchez-Lopez, A.S., Carrillo-Gonzalez, R., Gonzalez-Chavez, M.D.C.A., Rosas-Saito, G.H., Vangronsveld, J., 2015. Phytobarriers: plants capture particles containing potentially toxic elements originating from mine tailings in semiarid regions. Environ. Pollut. 205, 33e42.

Sanchez, V., Lopez-Bellido, F.J., Canizares, P., Rodriguez, L., 2018. Can electrochemistry enhance the removal of organic pollutants by phytoremediation? J. Environ. Manag. 225, 280–287.

Sánchez, V., López-Bellido, F.J., Rodrigo, M.A., Rodríguez, L., 2019. Electrokinetic-assisted phytoremediation of atrazine: differences between electrode and interelectrode soil sections. Separ. Purif. Technol. 211, 19–27.

Santibanez, C., de la Fuente, L.M., Bustamante, E., Silva, S., Leon-Lobos, P., Ginocchio, R., 2011. Potential use of organic-and hard-rock mine wastes on aided phytostabilization of large-scale mine tailings under semiarid Mediterranean climatic conditions: short-term field study. Appl. Environ. Soil Sci. 2012.

Seyfferth, A., Ross, J., Webb, S., 2017. Evidence for the root-uptake of arsenite at lateral root junctions and root apices in rice (Oryza sativa L.). Soils 1 (1).

Signes-Pastor, A., Burló, F., Mitra, K., Carbonell-Barrachina, A.A., 2007. Arsenic biogeochemistry as affected by phosphorus fertilizer addition, redox potential and pH in a West Bengal (India) soil. Geoderma 137 (3-4), 504–510.

Solé, V.A., Papillon, E., Cotte, M., Walter, P., Susini, J., 2007. A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra. Spectrochim. Acta B Atom Spectrosc. 62 (1), 63–68.

Suied, A.A., Ahmad Tajudin, S.A., Zakaria, M.N., Madun, A., 2018. Potential electrokinetic remediation technologies of laboratory scale into field application-methodology overview. J. Phys. Conf. 995.

Tang, X., Li, Q., Wang, Z., Hu, Y., Hu, Y., Li, R., 2018. In situ electrokinetic isolation of cadmium from paddy soil through pore water drainage: effects of voltage gradient and soil moisture. Chem. Eng. J. 337, 210–219.

USEPA, 1996. Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices. Method. 3052. Washington D. C., USA. https://www.epa.gov/sites/production/files/2015-12/documents/3052.pdf.

USEPA, 2007. Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils. Method. 3051A. Washington D. C., USA. https://www.epa.gov/sites/production/files/2015-12/documents/3051a.pdf.

Wawrecki, W., Zagorska-Marek, B., 2007. Influence of a weak DC electric field on root meristem architecture. Ann. Bot. 100 (4), 791–796.

Yang, D., Zeng, D.H., Zhang, J., Li, L.J., Mao, R., 2012. Chemical and microbial properties in contaminated soils around a magnesite mine in northeast China. Land Degrad. Dev. 23, 256e262.

Zhao, F.J., Ma, J.F., Meharg, A.A., McGrath, S.P., 2009. Arsenic uptake and metabolism in plants. New Phytol. 181 (4), 777–794.