

THE ASSESSMENT OF HEAVY METAL CONCENTRATION IN RIVER BANK SOIL UNDER THE EFFECT OF ELECTROKINETIC-ASSISTED PHYTOREMEDIATION USING XRF AND EDX ANALYSIS

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Graphical abstract



Abstract

River pollution may lead to the cause of death and diseases. The cause of its pollution could due to the mobility of the hazardous or toxic element from the human activities point sources through the groundwater system, and may resulting to a heavy metal migration into the river stream system. Therefore, an agro-based remediation methods known as Electrokinetic (EK)-assisted phytoremediation was implemented in this research. This technique is versatile and economical in decontaminating heavy metal at the river bank soil area. Hence, this research was focused on investigating the difference in trace elemental concentration in riverbank soil sample between pre- and post-phytoremediation under the electrokinetic influence. The riverbank soil sample was divided into two conditions which are: 1) control (as-received) and 2) EK-assisted phytoremediation by using a tropical plant species known as *Dieffenbachia* spp. In this study, two stainless steel electrodes were slot in at 5.0 cm depth on both side of this particular plant. A direct current (DC) voltage of 60 V was applied on both cathode and anode electrodes to form a uniform electric field with a magnitude of $6\text{V}/\text{cm}^{-1}$ around the plant root area. This electric field was applied consistently for 4 hours per day. Within a month, the reduction of trace element composition in the riverbank soil sample for pre and post experiment were determined using a non-destructive analytical technique, X-ray Fluorescence Spectroscopy (XRF) and Energy Dispersive X-ray Spectroscopy (EDX) analysis. The analysis show a significant correlation of elemental concentration between pre and post experiment for the soil sample where the soil concentration tend to reduce due to the EK assisted phytoremediation effect.

Keyword: XRF, EDX, Electrokinetic-assisted phytoremediation, trace element analysis, river bank soil, *Dieffenbachia* spp.

1.0 INTRODUCTION

Environment could be contaminated by heavy metals either naturally or by anthropogenic activities [2] such as agriculture, mining, smelting, electroplating and other industrial activities. Heavy metals originating from anthropogenic activities are frequently detected in sediments and water columns of river/lake, generating a substantial number of the world's rivers/lakes severely contaminated [7, 8, 12, 16, 17]. Intensive industrial development has led to worldwide concern on environmental and health impacts following decades of contaminated effluent discharge [14].

There are various methods that could be implemented to recover or remediate the contaminated soil and sediment such as amendments, sand cap, washing, electrochemical remediation, phytoremediation and etc. [10]. Among all these methods, phytoremediation appears to be a green solution to the problems of heavy metals contamination in soil, rivers and sediments. Phytoremediation is defined as clean up of pollutants primarily mediated by photosynthetic plants by destructing, inactivating or immobilizing the pollutant in a harmless form [13]. The process may be divided into several heads based on the nature of their remediation process which are phytoextraction, phytostabilization, phytodegradation, rhizofiltration, phytovolatilization and etc. [3]. Phytoextraction utilizes the roots of the plants to absorb, translocate and concentrate heavy metals from the contaminated soil to the above ground harvestable plant tissues [13].

Although this method is a promising approach in heavy metals decontamination due to its cost effectiveness, time would be its greatest limitation for it has to face with a slow rate of plant growth and a longer time required for soil clean up (Ali, *et al.*, 2013; Anjum, *et al.*, 2013). However, number of research has been done and electrokinetic remediation has been listed as one of the combined methods that could enhance the potential of heavy metal uptake by the phytoremediation plants [15]. Lim *et al.* [9] demonstrate the effectiveness of Indian mustard (*Brassica juncea*) in accumulating high tissue concentration of Pb, with the addition of ethylenediaminetetraacetic acid (EDTA) in the soil and the application of a DC electric field around the plant. They reported that the accumulation of Pb in the shoots using EDTA and a DC electric field was increase two to four times compared to using EDTA only. In 2008, Aboughalma *et al.* [1] studied the use of potato tubers to decontaminate soil polluted with Zn, Pb, Cu and Cd and the result reveal that the plant roots' heavy metals uptake under the influence of electric fields was generally higher than the control. A study by Cang *et al.* [5] on the effect of DC electric field current towards the growth of Indian mustard (*Brassica juncea*) in soil heavy metals proved that plant uptake of metal was increased by the electrokinetic-assisted phytoremediation. Thus this

research was conducted in order to investigate the effectiveness of the EK-assisted phytoremediation method in remediating a contaminated riverbank soil.

2.0 MATERIALS AND METHODS

2.1 Soil Sampling

The riverbank soil samples were acquired 2 m from the river stream of the interested area; Sedi River, Yong Peng, Johor as illustrated in Figure 1. The measurement of natural radioactivity dose-rate was performed using handheld Ludlum Micro R Meter (Model 19) prior to soil sampling. Besides that, the riverbank soil pH, the humidity percentage and coordinate location readings were also recorded by using Soil pH and Moisture Tester (DM-15) Takemura Japan and Global Positioning System (GPS), Garmin GPSmap Model 62s and tabulated in Table 1.



Figure 1 The location of sampling sites; (i) Sedi river

Table 1 Soil pH, Coordinate and Environmental Radiation Dose at the sampling site

Site	pH	Coordinate	Survey Meter Reading ($\mu\text{R/hr}$)
Sedi River	4.9 ± 0.1	N $01^{\circ} 59.918'$ E $103^{\circ} 04.832'$	13.7 ± 0.6

The collected riverbank soil samples were distributed into a phytoremediation reactor which consists of two clay pots designated as 'control' and 'EK' which stands for electrokinetic-assisted phytoremediation. The 'EK' clay pot was planted with the phytoremediation plant and installed with EK system while the 'control' clay pot was not disturbed.

2.2 Phytoremediation Plant Candidate

The chosen phytoremediation plant (phytoextractor candidate) was Dumb cane (*Dieffenbachia* spp) plant which was named after the German physician and botanist J. D. Dieffenbach (1794 – 1847) [6]. Representing a large group of tropical plants in the Araceae family, *Dieffenbachiaspp* contains raphides

(needle-like crystals) of calcium oxalate contained in idioblasts (cells) which could create severe irritation of skin and mucous membranes and inflammation when having direct contacts with the plant discharge [4]. Due to its natural habitat at humid and heavy watering such as a riverbank area, this plant was chosen to be the phytoextractor candidate in this research. The photo of the phytoremediation plant *Dieffenbachia* spp is shown in Figure 2.



Figure 2 A photo of the phytoremediation plant: *Dieffenbachia* spp

2.3 Electrokinetic (EK) Setup

The EK system which was installed in the “EK” clay pot consists of a pair of identical stainless steel plate electrode with a dimension of 17.5 cm x 2.5 cm and a DC power supply (0-110 V; 0-3 A) as illustrated in Figure 3. With a distance of 10 cm between each electrode, they were inserted vertically into the riverbank soil sample and the phyto-extractor candidate Dumb cane (*Dieffenbachia* spp) plant was positioned in between of it. 2.5 cm length of each electrode was left above the soil surface for DC power supply connection and 60 V of DC voltage was applied continuously for 4 hours per day within a month.

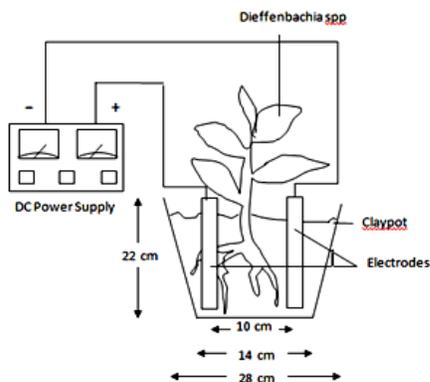


Figure 3 A photo of EK system arrangement

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electrode with a dimension of 17.5 cm x 2.5 cm and a DC power supply (0-110 V; 0-3 A). With a distance of 10 cm between each electrode, they were inserted vertically into the riverbank soil sample and the phytoextractor candidate Dumb cane (*Dieffenbachia* spp) plant was positioned in between of it. 2.5 cm length of each electrode was left above the soil surface for DC power supply connection and 60 V of DC voltage was applied continuously for 4 hours per day within a month.

2.4 Sample Preparation

The harvested riverbank soil sample from ‘control’ and ‘EK’ clay pots were dried in a furnace (Model Memmert) at 105°C for 24 hours after a period of one month. The ‘EK’ clay pot riverbank soil sample were partitioned into three sections according to its region; anode, middle and cathode region prior to the drying session. Subsequent to moisture removal process, the soil underwent the particle size reduction process (grinding) using a grinder model Planetary Mono Mill Pulverisette 6 and sieved with 50 µm Laboratory Test Sieve to achieve fine and homogeneous powder form samples.

2.5 Elemental Composition Analysis

The ground soil samples were analysed by two elemental composition analysis techniques which are X-ray Fluorescence Spectroscopy (XRF) and Energy Dispersive X-ray Spectroscopy (EDX). Hence, the ground soil samples were divided into two parts; one for XRF analysis and the other part was for EDX analysis. XRF analysis requires the sample to be in a pellet form. 7 g of powder form soil sample was mixed with 3 g of wax homogeneously and compressed with 8 N forces by PE-MAN compressor to become a 4 cm diameter and 5mm thick pellet. The pellets were sent for XRF elemental composition analysis afterward. The non-destructive x-ray analysis by XRF is suitable for rocks, minerals, sediments and fluids. The interaction of radiation with atoms generates X-ray fluorescence emission that could be utilised to analysed major and trace elements in material. When materials are excited with high-energy, short wavelength radiation like X-rays, they can become ionized. The atom becomes unstable and an outer electron replaces the ejected inner electron. The emitted radiation is of lower energy than the primary incident X-rays and is termed fluorescent radiation. Because the energy of the emitted photon is characteristic of a transition between specific electron orbital in a particular element, the resulting fluorescent X-rays can be used to detect the abundances of elements that are present in the soil sample. XRF can provide the information of ppm level for soils sample.

The EDX analysis was implemented by means of EDX spectrometer model JEOL JSM-6380-LA. Operating at a 15 kV voltage, it was set to 500x magnification power for images purposes. The

powder form soil samples were mounted on a stub with conductive carbon tape prior to analysis. The EDX spectrometer is coupled with Scanning Electron Microscopy (SEM) system. The electron gun from the system produces an electron beam that being scanned across the sample's surface. A variety of signals are generated and the detection of specific signals produces an image or a sample's elemental composition. Secondary electrons emitted from the atoms on the top surface producing an interpretable image of the surface. EDX is an x-ray technique used to identify the elemental composition of a sample. Attached to SEM instruments, the imaging capability of the microscope is used to identify the specimen of interest. Three fine spot areas are selected and the determination of elemental percentages is based on the average scanning. In this case, the elements of interest are consisting of Ni, Cu and Zn.

3.0 RESULTS AND DISCUSSION

3.1 Strength Development of Cement-SCB

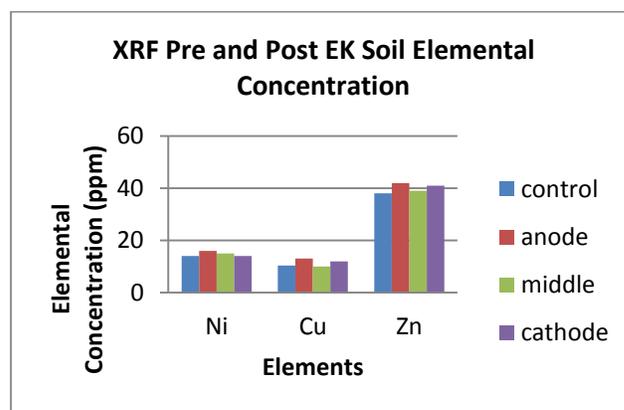
In this research, the soil sample were analysed by XRF and EDX analysis involving two types of soil; 'control' and 'EK' soil sample which have already being divided into three regions (anode, middle and cathode regions). The data acquired from the analysis was distributed in the Table 2. It is revealed that the highest preliminary elemental concentration by XRF analysis on 'control' or pre EK assisted phytoremediation soil sample is Zn with (38 ± 0) ppm while Ni and Cu concentrations are (14 ± 1) ppm and (10 ± 1) ppm respectively. The post EK assisted phytoremediation elemental concentration analysis in soil which executed in three regions of EK clay pot demonstrates a similar pattern obtained by Cang *et al.* [5] in their previous research which is the elemental concentrations in anode region are always higher than cathode and middle region.

Table 2 Soil Elemental Composition Analysis for Ni, Cu and Zn for pre and post EK assisted Phytoremediation by a) XRF analysis, and b) EDX analysis

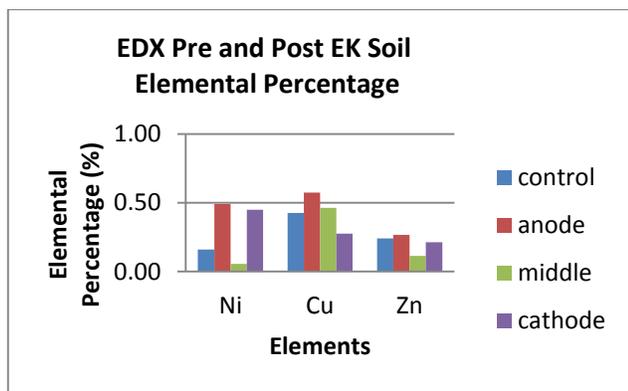
Element	XRF Analysis			
	Control (ppm)	Anode (ppm)	Middle (ppm)	Cathode (ppm)
Ni	14 ± 1	16 ± 0	15 ± 1	14 ± 0
Cu	10 ± 1	13 ± 1	10 ± 1	12 ± 0
Zn	38 ± 0	42 ± 1	39 ± 1	41 ± 0
Element	EDX Analysis			
	Control (%)	Anode (%)	Middle (%)	Cathode (%)
Ni	0.16 ± 0.09	0.49 ± 0.20	0.06 ± 0.04	0.45 ± 0.26
Cu	0.43 ± 0.05	0.57 ± 0.07	0.46 ± 0.20	0.28 ± 0.12
Zn	0.24 ± 0.02	$0.27 \pm .19$	0.11 ± 0.04	0.21 ± 0.06

The EDX analysis on the other hand demonstrate that Cu element gives the highest elemental percentages compared to Ni and Zn for the pre EK assisted phytoremediation soil sample. The range of elemental percentages of Ni, Cu and Zn is (0.16 ± 0.09) %, (0.43 ± 0.05) % and (0.24 ± 0.02) % respectively. The semi quantification of the post EK treatment soil sample at anode, cathode and middle area demonstrate a fluctuation in the elemental percentages measurement for each element. However, it is clearly noted that the count rate at the anode is slightly higher than cathode area, where the same result obtained from the XRF analysis above and also reported by Cang *et al.* [5]. This phenomenon occurs due to the process of plant roots' absorption and ion mobility under electrical influence.

The heavy metals ions which close to the root of the plant were originally being absorbed by root under the process of phytoremediation. The provision of electricity and presence of soil moisture during EK treatment has initiated the mobility of ions towards their opposite charged electrodes [11]. The mobility of these ions makes the process of heavy metals' absorption easier because the ions were nearer to the root thus creating a depletion of ion concentration in the middle region. The ions that were managed to pass through the root continue to move towards the electrodes and increasing the concentration of elements near the anode and cathode regions. The correlation between the elemental concentration of Ni, Cu and Zn and the soil sample section (control, cathode, anode and middle area) from XRF and EDX analysis is illustrated in Figure 4.



(a)



(b)

Figure 4 Soil Elemental Composition Analysis for Ni, Cu and Zn for pre and post EK assisted Phytoremediation by (a) XRF analysis, and (b) EDX analysis.

4.0 CONCLUSION

The elemental composition concentration of the trace elements (Ni, Cu and Zn) between pre- and post- EK assisted phytoremediation is successfully investigated in this research. There is a significant correlation between XRF and EDX analysis. XRF and EDX measurement proportional to the soil elemental concentration, therefore both methods agreed with each other. The trace element remediation process in soil involved two important mechanisms, which are ion absorption by the plant root and the ion mobility under the effect of uniform electric field which has lead to an increment in soil elemental concentration from cathode to anode. The depletion of the trace element metals at the middle of area of cathode and anode revealed that the riverbank soil is successfully remediated.

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References

[1] Aboughalma, H., Bi, R., & Schlaak, M. 2008. Electrokinetic Enhancement on Phytoremediation in Zn, Pb, Cu and Cd

Contaminated Soil Using Potato Plants. *Journal of Environmental Science and Health-Part A Toxic/Hazardous Substances and Environmental Engineering*. 43(8): 926-933.

[2] Ali, H., Khan, E., & Sajad, M. A. 2013. Phytoremediation of Heavy Metals—Concepts and Applications. *Chemosphere*. 91(7): 869-881.

[3] Anjum, N. A., Pereira, M. E., Ahmad, I., Duarte, A. C., Umar, S., & Khan, N. A. (Eds.). 2013. *Phytotechnologies; Remediation of Environmental Contaminants*. Boca Raton, FL: CRC Press.

[4] Barr, A. C. 2006. *Chapter 19-Household and Garden Plants Small Animal Toxicology*. Second Edition. Saint Louis: W.B. Saunders. 345-410.

[5] 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 Aand Uptake By Indian Mustard. *Separation and Purification Technology*. 79(2): 246-253.

[6] Cumpston, K. L., Vogel, S. N., Leikin, J. B., & Erickson, T. B. 2003. Acute Airway Compromise After Brief Exposure to a Dieffenbachia Plant. *The Journal of Emergency Medicine*. 25(4): 391-397.

[7] Duan, X., Wang, Z., Xu, M., & Zhang, K. 2009. Effect of Streambed Sediment on Benthic Ecology. *International Journal of Sediment Research*. 24(3): 325-338.

[8] Ezemonye, L. I. N., Ogeleka, D. F., & Okieimen, F. E. 2009. Lethal Toxicity of Industrial Detergent on Bottom Dwelling Sentinels. *International Journal of Sediment Research*. 24(4): 479-483.

[9] Lim, J.-M., Salido, A. L., & J. Butcher, D. 2004. Phytoremediation of Lead Using Indian Mustard (*Brassica Juncea*) with EDTA and Electrodicts. *Microchemical Journal*. 76(1-2): 3-9.

[10] Peng, J.-f., Song, Y.-h., Yuan, P., Cui, X.-y., & Qiu, G.-l. 2008. The Remediation of Heavy Metals Contaminated Sediment. *Journal of Hazardous Materials*. 161(2009): 633-640.

[11] Reddy, K. R., & Cameselle, C. (Eds.). 2009. *Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater*. Canada: John Wiley & Sons, Inc.

[12] Sin, S. N., Chua, H., Lo, W., & Ng, L. M. 2001. Assessment of Heavy Metal Cations in Sediments of Shing Mun River, Hong Kong. *Environment International*. 26(5-6): 297-301.

[13] Terry, N., & Banuelos, G. (Eds.). 2000. *Phytoremediation of Contaminated Soil and Water*. Boca Raton, Florida: CRC Press.

[14] Vernet, J.-P. 1991. *Heavy Metals in the Environment*. Elsevier, Amsterdam, 405.

[15] Yeung, A. T., & Gu, Y.-Y. 2011. A Review on Techniques to Enhance Electrochemical Remediation of Contaminated Soils. *Journal of Hazardous Materials*. 195(0): 11-29.

[16] Yi, Y., Wang, Z., Zhang, K., Yu, G., & Duan, X. 2008. Sediment Pollution and Its Effect on Fish Through Food Chain in the Yangtze River. *International Journal of Sediment Research*. 23(4): 338-347.

[17] Yunus, K., Yusuf, N. M., Shazili, N. A. M., Chuan, O. M., Saad, S., Chowdhury, A. J. K., et al. 2011. Heavy Metal Concentration in the Surface Sediment of Tanjung Lumpur Mangrove Forest, Kuantan, Malaysia. *Sains Malaysiana*. 40(2)(2011): 89-92.