ELECTROKINETIC-ASSISTED PHYTOREMEDIATION OF HEAVY METAL IN RIVERBANK SOIL

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For my beloved family

Muhammad Syazwan bin Shariffudin Sasidharan
Muhammad Zhariff Zhakwan bin Muhammad Syazwan
Muhammad Zhariff Zhafran bin Muhammad Syazwan
Saodah binti Sapuan
Shariffudin Sasidharan bin Abdullah
Rohana binti Haron

And all my family members

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The whole journey of this study was conducted to prove that EK technique does contribute to the improvement of phytoremediation method. In 2012, the study was started by selecting the suitable sampling site and collecting soil samples at the Sedi River with the endless support of my supervisor; Associate Professor Dr. Zaidi bin Embong, and fieldwork assistant; Mr. Mohd. Hanafi bin Mokhtar. Despite of his disability, Associate Professor Dr. Zaidi bin Embong tirelessly taught and guided me on how the study should be done.

The whole year of 2013 was spent on conducting the EK assisted phytoremedition study and in year 2014, the treated soil and plant samples were completely analyzed. The challenges in sample analysis process were to meticulously prepare the samples prior to analysis which sometimes took almost ten times of repetitions. The limited number of analyses equipments versus high number of students using it was also delaying the lab work. There was one time where the sample analysis process was delayed for almost two months due to equipment malfunction. Year 2015 was spent on analyzing the data and results obtained from the sample analysis processes. After all blood, sweat and tears, the findings of this study were compiled in this thesis. Therefore, I would like to express my earnest gratitude to my supervisor, Assoc. Prof. Dr. Zaidi bin Embong for his way of guidance, supervision and support throughout my research. My appreciation also goes to Mr. Mohd. Hanafi bin Mokhtar for assisting me in fieldwork tasks. I would also like to extend my appreciation to:

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ABSTRACT

Electrokinetic (EK)-assisted phytoremediation is one of the environmental remediation methods that have a big potential in enhancing the ability of plant heavy metal uptake in soils. This study was conducted to investigate the difference in heavy metal composition concentration of riverbank soil and the change of soil pH between pre and post phytoremediation and EK assisted phytoremediation treatment. The selected phytoremediation plant is *Dieffenbachia* 'Tropic Rain". The phytoremediation plant treatment was fertilized with organic and chemical fertilizer while the EK phytoremediation plant was induced with EK system (a pair of EK electrodes connected to a direct current (DC) power supply with a magnitude of 6 V/cm^{-1} electric field) for 4 hours/day. The soil and plant samples from pre and post treatments were analyzed using and X-ray Fluorescence Spectrometer (XRF), Scanning Electron Microscope / Energy Dispersive X-ray Spectroscopy (SEM/EDX) and Inductively Coupled Plasma Mass Spectrometer (ICP-MS). After 12 months of EK assisted phytoremediation treatment, the soil pH near the cathode increase 48.8% from pH 4.32 to pH 6.43 while in anode region the pH decrease 28% from pH 4.32 to pH 3.11. The element concentrations in cathode region for most elements of interest (Ni, Cu, Zn, As and Pb) were higher than anode and middle region with the highest is (47.3 ± 0.6) ppm Pb. The elemental concentration of Ni, Cu, Zn, As and Pb by EK assisted phytoremediation plants were slightly higher than the elements absorbed by the phytoremediation treated plants alone in the "chemical" and "organic" slots with the highest is (7.98 ± 0.68) ppb Zn. This showed that the EK assisted remediation treatment has increased the plant's absorption during the phytoremediation process.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABREVIATIONS

EK	electrokinetics
XRF	X-ray Fluorescence
SEM/EDX	Scanning Electron Microscopy / Energy Dispersive X-ray
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
Ni	Nickel
Cu	Copper
Zn	Zinc
As	Arsenic
Pb	Plumbum/lead
Z	Atomic number
EDTA	ethylenediamine tetracetic acid
EGTA	ethylene glycol-bis-[2-aminoethylether]-N,N,N,N, tetracetic acid
EDDS	SS-ethylene diaminedisuccinic acid
C	carbon
H	hydrogen
O	oxygen
RECESS, UTHM	Research Centre for Soft Soil, Universiti Tun Hussein Onn Malaysia
FKAAS, UTHM	Faculty of Civil and Environmental Engineering, Universiti Tun Hussein Onn Malaysia
HNO_3	nitric acid
H_2SO_4	sulphuric acid
$HClO_4$	perchloric acid
H_2O_2	hydrogen peroxide

Si	Silicon
Hg	Mercury
Se	Selenium
ppm	parts per million
ppb	parts per billion

LIST OF EQUATIONS

LIST OF APPENDIXES

ABSTRAK

Pemulihan fito berelektrokinetik (pemuliharaan fito EK) adalah salah satu langkah pemulihan alam sekitar yang mempunyai potensi yang besar untuk meningkatkan keupayaan penyerapan logam berat oleh pokok dalam proses pemuliharaan tanah. Kajian ini dijalankan untuk mengkaji kepekatan komposisi logam berat di dalam tanah tebing sungai dan perubahan dalam pH tanah menggunakan teknik pemuliharaan fito dan teknik pemulihan fito EK. Pokok yang dipilih untuk kajian ini adalah *Dieffenbachia* 'Tropic Rain". Untuk teknik pemulihan fito, pokok dibajai dengan baja organik dan kimia manakala teknik pemulihan fito EK dibekalkan dengan sistem EK yang mengandungi sepasang elektrod yang disambung kepada punca kuasa arus terus (DC) dengan medan elektrik sebanyak 6 V/cm^{-1} selama 4 jam sehari. Sampel tanah dan pokok dianalisa menggunakan Spektrometer Pendafluor Sinar-X (XRF), Mikroskop Imbasan Elektron / Spektrometer Sinar-X Sebaran Tenaga (SEM/EDX) dan Spektrometer Jisim Terganding Plasma Beraruh (ICP-MS). Selepas 12 bulan rawatan pemulihan fito EK, pH tanah kawasan katod meningkat 48.8% daripada pH 4.32 ke pH 6.43. pH tanah di kawasan anod menurun 28% daripada pH 4.32 ke pH 3.11. Kepekatan unsur Ni, Cu, Zn, As dan Pb di katod lebih tinggi berbanding anod dan kawasan tengah dengan kepekatan tertinggi ialah (47.3 ± 0.6) ppm Pb. Kepekatan unsur Ni, Cu, Zn, As dan Pb yang terserap di dalam pokok yang di rawat dengan teknik pemulihan fito EK didapati lebih tinggi daripada unsur di pokok dengan rawatan teknik pemulihan fito sahaja (di dalam slot "kimia" dan "organik") dengan nilai paling tinggi adalah (7.98 ± 0.68) ppb Zn. Hal ini menunjukkan bahawa teknik pemulihan fito EK berjaya membantu penyerapan unsur oleh pokok semasa proses pemulihan fito.

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Nowadays, heavy metals originating from anthropogenic activities are frequently detected in sediments and water columns of river/lake, which cause a considerable number of the world's rivers/lakes severely contaminated. There are two classifications of heavy metal which are essential and non-essential to the biological systems of living organism. Essential heavy metals are necessary biological function of living organism while non-essential heavy metals have no importance in living organisms (Ali, Khan &Sajad, 2013).

Anthropogenic activities are including mining, smelting, electroplating, agriculture and etc. The contaminationcaused by the industrial and agricultural activities has been emphasized in studies around the world due to the adverse biological effects on the health of the aquatic environment. The effects are including aquatic life mortality and immobilization.Figure 1.1 shows the heavy metal contamination in the river due to anthropogenic activities. The fishes are dead due to high concentration of heavy metals in the river water. Clearly, with this condition of river, it could be concluded that it is not safe for human consumption.

The buildup of potentially toxic metals carries a huge risk to the beneficial uses and sustainability of the natural resources such as water, plants and aquatic animals (Duan et al.,2009; Ezemonye, Ogeleka, &Okieimen, 2009; Sultan &Shazili, 2010) and furthermore could risk the life of human being. The migration of particle-reactive heavy metals from riverbank sediment into bottom sediment through water diffusion may quickly adsorb onto suspended matter and ultimately move to bottom sediment. In aquatic environment, heavy metal is usually distributed as follows: water-soluble species, colloids, suspended forms and sedimentary phases. However, heavy metals could not be removed by natural processes of decomposition like organic pollutants does (Penget al., 2008).

Figure 1.1: Heavy metal contamination in river system(Glennie& Cox, 2014)

As heavy metals usually possess significant toxicity to aquatic organisms and affect human health through food chain, therefore, riverbank soil /riverbank sediment remediation need to be considered as the priority in order to reduce or prevent the heavy metal migration into the river stream system.To clean up the heavy metal contamination in riverbank sediment system, various techniques of remediation are able to be applied on the sites depending on the condition and severity of the contamination level.

Some of the techniques are sand cap remediation technique, electrochemical technique, excavation and bioremediation technique, just to name a few. However, an extensive eco-technological technique such as phytoremediation can be a potential remediation options for the existing areas of land disposed dredged sediments and for the future treatment of the large volumes of contaminated dredged sediments. Figure 1.2 shows the transport mechanism of heavy metal in the environment.

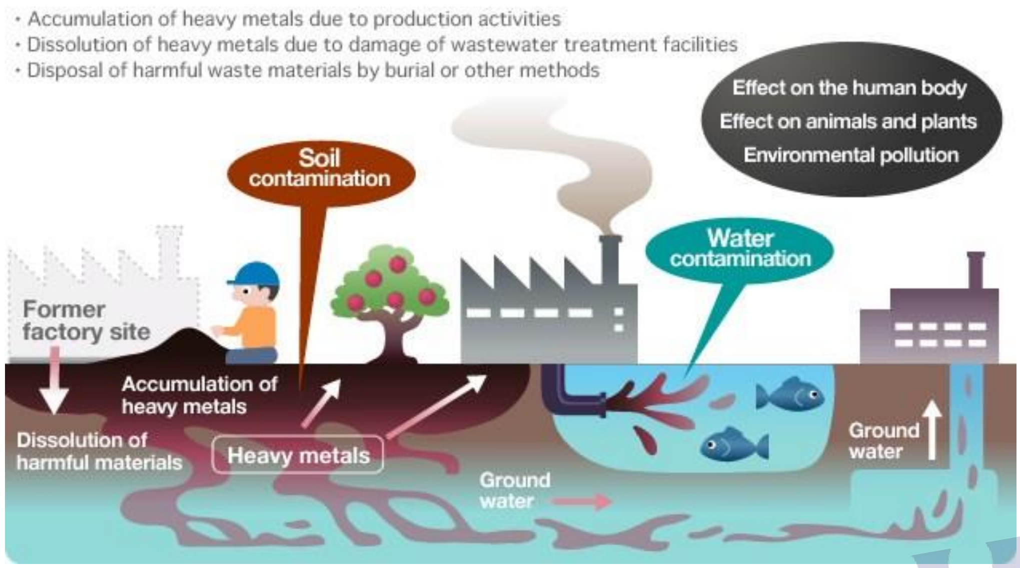

Figure 1.2: The transport mechanism of heavy metal in the environment(Sagasiki Environmental Developments Co.,Ltd, 2002)

1.2 Problems Statement

Contamination of inorganic metal in river, estuarine and marine sediment by anthropogenic activities are frequently detected and risking the aquatic life. This irresponsibility act could also threaten the life of human being. Besides mortality, heavy metal contamination could let human being end up with various health problems such as dysfunctional of physical abilities, mental problem and permanent handicap.Salem, Eweida, and Farag (2000) found the relationship between high heavy metals concentration in drinking water and health problem in human being in their study in Great Cairo Cities. The consumed heavy metals contaminated drinking water lead to renal failure, hair loss, liver cirrhosis, and chronic anemia.

Realized with the seriousness of these issues, researchers all over the world has conducted experiments and studies on how to restore or remediate the contaminated site to its original condition, or at least to reduce the dreadful condition to a better state. The types of remediation techniques were implemented depends on many factors such as the suitability of the technique with the contaminated site, the types of heavy metal to be remediate, the cost

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