UNIVERSITI PUTRA MALAYSIA

STABILISATION AND REMEDIATION OF HEAVY METALS IN MINE TAILINGS USING Vetiveria zizanioides (L.) NASH AMENDED WITH IRONCOATED AND UNCOATED RICE HUSK ASH

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By

TARIQ FARUQ SADIQ

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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DEDICATION

I would like to dedicate this work to those who taught, motivated and helped me throughout my study.

To my in memory of late father and martyred brother; my father’s dream was seeing me going abroad for education and my dream is seeing my sweet daughter Ronya doing the same.

This work is also dedicated to my dearest wife, Fatimah Jalal and my family with love and respect.
Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor of Philosophy

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By

TARIQ FARUQ SADIQ

June 2016

Chairman : Samsuri Abd. Wahid, PhD
Faculty : Agriculture

Mine tailings are regarded as a major source of environmental pollution due to the presence of high concentration of heavy metals, which can cause various health hazards. Decontamination of the mine tailings is necessary to reduce the concentration and the bioavailability of heavy metals. In recent years, phytoremediation technique has gained increasing attention for extraction and/or stabilisation of heavy metals from solid substrate such as mine tailings since the technique is efficient, simple, cost-effective and environmentally friendly. This study was undertaken to evaluate the potential of rice husk ash (RHA) or iron coated rice husk ash (Fe-RHA) as amendments for stabilisation and remediation of heavy metals in Penjom gold mine tailings using vetiver grass (*Vetiveria zizanioides* (L.) Nash). At the beginning of the study, the physicochemical properties of mine tailing and RH ashes were analysed. The metals in the tailings were extracted using a microwave-digestion method and analyzed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Fourier Transformed Infrared Spectroscopy (FTIR), multipoint Brunauer-Emmett-Teller (BET) and Scanning Electron Microscope-Electron Dispersive Spectroscopy (SEM-EDS) were used for the characterisation of (RHA) or (Fe-RHA). In this study, a series of experiments were conducted under laboratory and glasshouse conditions. The first study was conducted to determine the effects of RHA and Fe-RHA on the distribution of heavy metals fractions in the mine tailings. In the second study, an experiment was carried out to determine the effects of different rates of RHA and Fe-RHA on heavy metals availability and mobility in mine tailings. The third study was conducted in a glass house to evaluate the ability of vetiver grass to phytoremediate heavy metals in mine tailings amended with either RHA or Fe-RHA. In the fourth study, the effects of nitrogen, phosphorus and potassium (NPK) fertiliser on phytoremediation were determined. In the final study, a pot experiment was conducted to determine the role of dissolved organic carbon (DOC) on the heavy metals availability and uptake by vetiver grass. For the first 3 studies the tailings were treated with 0, 5, 10 or 20% (w/w) of either RHA or Fe-RHA. For the 4th experiment tailings were amended with 10% (w/w) of either RHA or Fe-RHA and three rates (0, 50 and 100 kg ha\(^{-1}\)) of NPK fertiliser. For the last experiment, the tailings amended with 10% (w/w) of RHA, Fe-RHA and W-RHA and 50 kg ha\(^{-1}\) of NPK
fertiliser. The physicochemical analysis data show that the Penjom gold mine tailings had a slightly alkaline pH (7.90) and the texture was silty loam. In addition, the mine tailings contained a significant amount As (1625.25 mg kg$^{-1}$), Cd (57.00 mg kg$^{-1}$), Cr (31.44 mg kg$^{-1}$), Cu (75.60 mg kg$^{-1}$), Mn (790.03 mg kg$^{-1}$), Pb (81.80 mg kg$^{-1}$) and Zn (174.80 mg kg$^{-1}$). The results also show increasing total surface area, pore surface area, pore volume and pore radius of Fe-RHA and W-RHA when compared to the RHA. The higher proportion of meso- and macropores than the micropores can be observed in all three ashes RHA, Fe-RHA and W-RHA SEM micrographs. Sequential extraction results show that addition of RHA and Fe-RHA significantly (P≤0.05) increased the easily exchangeable fraction and reduced carbonate and organic bound fraction of As. However the effects were the opposites for cationic metals. Both RHA and Fe-RHA applications reduced the easily exchangeable fraction and increased carbonate and organic bound fraction of Cd, Cr, Cu, Mn, Pb and Zn. In general, in the second study CaCl$_2$-extractable Cr, Cu, Pb and Zn were not detected in both control and amended samples, probably due to their low bioavailability and mobility. In the untreated mine tailings, there was a significant (P≤0.05) increase in the extractable and mobility of As, Cd and Mn from the tailings with incubation time. On other hand, the addition of RHA or Fe-RHA at all rates significantly (P≤0.05) increased the CaCl$_2$-extractable As and its mobility, compared to the controls over the incubation time. In contrast, the application of RHA and Fe-RHA reduced CaCl$_2$-extractable and mobility of Cd and Mn. The addition of RHA and Fe-RHA had significant (P≤0.05) effects on the chemical properties of the tailings, total dry biomass and heavy metals uptake. Moreover, the results were dependent on the type of ash used and heavy metals. The application of RHA significantly (P≤0.05) increased the pH, whereas Fe-RHA addition decreased the pH of the tailings. Vetiver grass grown in all Fe-RHA and RHA amended tailings had lower root, shoot and total biomass production compared with the vetiver grass grown in the controls. There was a significant difference (P≤0.05) in total metals among vetiver grass grown under different types and rates of ashes. For example, the uptake of As was significantly increased at all application rates of RHA or Fe-RHA, while the uptake of cationic metals was decreased as the result of RHA and Fe-RHA application. Biological accumulation coefficient (BAC), biological transfer coefficient (BTC) and bioconcentration factor (BCF) of vetiver grass were significantly affected by the types and rates of ashes used. The BAC and BCF values of the vetiver grass for As and Zn increased with RHA application rate but the BTC values of As and Zn were decreased. In Fe-RHA amended samples, As concentration in the shoot, and root concentrations of Cd and Zn were significantly higher compared to the control. The Fe-RHA treated samples also had lower BAC and BTC values for As and Zn than the control. However, the BCF values for those elements were higher than the control. This observation is in good agreement with the results obtained from the fractionation and incubation studies. In addition, the results show that NPK fertiliser application to the tailings amended with RHA or Fe-RHA enhanced phytoremediation of metals. The addition of NPK fertiliser to the unamended tailings (controls) increased vetiver root, shoot and total dry biomass production. In contrast, application NPK fertiliser to RHA treated samples reduced the root, shoot and total plant biomass production. Additionally, there were no significantly (P>0.05) changes in roots, shoots and total dry biomass of vetiver grass due to increase NPK fertiliser to tailings amended with Fe-RHA. Addition NPK fertiliser to un-amended tailings reduced As uptake by vetiver grass but increased the uptakes of Cr, Mn and Zn. In NPK plus RHA amended samples, the plant uptakes of As, Zn, Cd, Cu and Zn were increased. In addition, In Fe-RHA amended samples plus NPK fertiliser the total plant uptake of As and Zn increased but Cr and Cu reduced. It was observed that the DOC
could be one of the reasons for increasing As uptake in vetiver grass grown in tailings amended with RHA. The uptake of As, Cd, Cu and Mn in samples without DOC, i.e. the W-RHA treated samples, was significantly (P≤0.05) reduced by 30, 1.2, 8 and 5 %, respectively, compared to their uptakes in RHA treated samples. It can be concluded from this study that vetiver grass had tolerance to high concentrations of heavy metals. Overall, the results suggest that phytoremediation process using vetiver grass was effective for remediation of heavy metals in mine tailings. Therefore, RHA and Fe-RHA can be used as amendments to reduce the toxicity of cationic elements in highly contaminated tailings or they can also be used to enhance the uptake of As by plants.
Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

PENSTABILAN DAN PEMULIHAN LOGAM BERAT DALAM AMANG LOMBONG EMAS MENGGUNAKAN *Vetiveria zizanioides* (L.) Nash DIBANTU ABU SEKAM PADI DAN ABU SEKAM PADI BERSALUT BESI

Oleh

TARIQ FARUQ SADIQ

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Bagi eksperimen terakhir, amang lombong ditambah dengan 10% (b / b) samada RHA, Fe-RHA atau W-RHA dengan 50 kg ha⁻¹ baja NPK. Data analisis fizikokimia menunjukkan bahawa amang lombong emas Penjom adalah sedikit beralkali (pH 7.90), CEC adalah 10.75 cmol (+) kg⁻¹ dan EC (1.48 ds m⁻¹) dan tekstur adalah lempung berkelodak. Di samping itu, amang lombong mengandungi As (1625.251 mg kg⁻¹), Cd (57 mg kg⁻¹), Cr (31.44 mg kg⁻¹), Cu (75.6 mg kg⁻¹), Mn (790.03 mg kg⁻¹), Pb (81.8 mg kg⁻¹) dan Zn (174.8 mg kg⁻¹) tetapi rendah dalam nutrien makro penting; N (0.036%), P (0.076%) dan K (0.196%). Keputusan juga menunjukkan peningkatan jumlah luas permukaan, liang kawasan permukaan, isipadu liang dan liang jejeri Fe-RHA jika dibandingkan dengan RHA. Peratusan yang lebih tinggi liang meso- dan makro daripada liang mikro boleh diperhatikan dalam kedua-dua RHA dan Fe-RHA SEM mikrograf. Helaian selulosa dan lignin yang utuh dan cacat juga boleh dilihat dalam imej mikrograf SEM. Keputusan pengekstrakan berurutan menunjukkan bahawa penambahan RHA dan Fe-RHA meningkatkan (P<0.05) fraksi As mudah tukar dan mengurangkan fraksi terikat kepada karbonat dan organik. Namun, kesan penambahan RHA dan Fe-RHA adalah bertentangan bagi logam kationik. Kedua-dua penambahan RHA dan Fe-RHA mengurangkan fraksi mudah tukar dan meningkatkan fraksi terikat pada karbonat dan organik bagi Cd, Cr, Cu, Mn, Pb dan Zn. Secara umum, hasil kajian kedua menunjukkan bahawa kedapatan dan mobiliti As, Cd dan Mn telah dipengaruhi oleh tempoh eraman. Walau bagaimanapun, Cr, Cu, Pb dan Zn boleh ekstrak oleh CaCl₂ tidak dapat dikesan dalam kedua-dua sampel kawalan dan sampel yang dirawat, mungkin kerana kedapatan dan mobiliti logam tersebut adalah rendah. Dalam amang lombong tidak dirawat, terdapat peningkatan yang ketara dalam (P<0.05) ekstrak dan mobiliti As dan Mn berbanding amang terawat dengan masa pengeraman. Pada sudut yang lain, penambahan RHA atau Fe-RHA pada setiap kadar meningkat (P<0.05) meningkatkan CaCl₂ boleh ekstrak dan mobiliti As, Cd dan Mn berbanding amang terawat dengan masa pengeraman. Sebaliknya, penggunaan RHA dan Fe-RHA mengurangkan (P<0.05) CaCl₂ boleh ekstrak dan mobiliti Cd dan Mn. Pemerhatian ini adalah selari dengan keputusan yang diperolehi daripada kajian pemeringkatan. Penambahan RHA dan Fe-RHA mempunyai kesan yang besar (P<0.05) ke atas sifat-sifat kimia amang, jumlah bahan kering dan pengambilan logam berat. Selain itu, keputusan adalah bergantung kepada jenis abu digunakan dan logam berat. Penggunaan RHA meningkatkan dengan (P<0.05) ketara pH, manakala Fe-RHA menurunkan pH amang. Rumpun vetiver ditanam dalam sampel amang yang dirawat dengan Fe-RHA atau RHA mempunyai produksi akar, pucuk dan pengeluaran biojisim yang lebih rendah, berbanding rumpun vetiver yang ditanam di sampel kawalan. Terdapat perbezaan yang signifikan (P<0.05) dalam jumlah logam antara rumpun vetiver yang ditanam di bawah jenis dan kadar abu yang bebas. Sebagai contoh, pengambilan As meningkat dengan ketara dengan kadar pengekstrakan RHA atau Fe-RHA, manakala pengambilan logam kationik telah menurun dengan rawatan RHA dan Fe-RHA. Pekali Pengumpulan Biologi (BAC), Pekali Pemindahan Biologi (BTC) dan Faktor Biopemekatan (BCF) rumpun vetiver terjejas dengan (P<0.05) ketara oleh jenis dan kadar abu digunakan. Nilai BAC dan BCF rumpun vetiver untuk As dan Zn meningkat dengan kadar rawatan RHA tetapi nilai BTC As dan Zn telah berkurangan. Dalam sampel yang dirawat dengan Fe-RHA, kepekatan As dalam pucuk, dan kepekatan Cd dan Zn dalam akar jauh lebih tinggi berbanding dengan kawalan. Sampel yang dirawat dengan Fe-RHA juga mempunyai nilai BAC dan BTC lebih rendah untuk As dan Zn berbanding kawalan. Walaubagaimanapun, nilai BCF untuk unsur-unsur tersebut adalah lebih tinggi daripada kawalan. Pemerhatian ini adalah selari dengan keputusan yang diperolehi daripada kajian pemeringkatan dan pengeraman. Di samping itu, keputusan menunjukkan bahawa penambahan baja NPK kepada amang yang dirawat
dengan RHA atau Fe-RHA meningkatkan pemulihan fito logam. Penambahan baja NPK kepada amang yang tidak dirawat (kawalan) meningkatkan produksi akar, pucuk dan pengeluaran biojisim kering rumput vetiver. Sebaliknya, penambahan baja NPK ke atas sampel yang dirawat dengan RHA mengurangkan produksi akar, pucuk dan jumlah pengeluaran biojisim rumput vetiver. Selain itu, tidak ada perubahan ketara (P>0.05) pada akar, pucuk dan jumlah biojisim kering rumput vetiver dengan baja NPK untuk amang yang dirawat dengan Fe-RHA. Penambahan baja NPK kepada amang yang tidak dirawat mengurangkan pengambilan As oleh rumput vetiver tetapi meningkatkan pengambilan Cr, Mn dan Zn. Dalam sampel NPK bersama rawatan RHA, pengambilan As, Zn, Cd, Cu dan Zn telah meningkat. Tetapi, dalam sampel yang dirawat dengan Fe-RHA dan baja NPK, jumlah pengambilan As dan Zn meningkat tetapi Cr dan Cu dikurangkan dalam rumput vetiver. Adalah diperhatikan bahawa DOC boleh menjadi salah satu daripada sebab meningkatkan pengambilan As oleh rumput vetiver yang ditanam dalam amang yang dirawat dengan RHA. Pengambilan As, Cd, Cu dan Mn dalam sampel tanpa DOC, iaitu sampel yang dirawat dengan W-RHA, telah berkurang (P≤0.05) sebanyak 30, 1, 8 and 5 %, masing-masing, berbanding pengambilan logam tersebut dalam sampel yang dirawat dengan RHA. Dapat disimpulkan daripada kajian ini bahawa rumput vetiver mempunyai toleransi kepada kepekatan logam beruk yang tinggi. Penambahan RHA dan Fe-RHA adalah kaedah yang paling berkesan untuk mengurangkan ketersediaan dan mobiliti Cd, Cr, Cu, Mn, Pb dan Zn dalam amang lombong kecuali As. Penambahan baja NPK boleh meningkatkan pemulihan fito rumput vetiver. RHA mempunyai kecepatan yang lebih tinggi dalam mengurangkan logam kationik berbanding Fe-RHA manakala Fe-RHA mempunyai kecepatan yang lebih tinggi dalam mengurangkan ketersediaan As. Secara keseluruhan, keputusan menunjukkan bahawa proses pemulihan fito menggunakan rumput vetiver berkesan untuk pemulihan logam berat di dalam amang lombong. Oleh itu, RHA dan Fe-RHA boleh digunakan sebagai rawatan untuk mengurangkan ketoksikan elemen kationik dalam amang yang sangat tercemar atau bahan tersebut juga boleh digunakan.
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I certify that a Thesis Examination Committee has met on 03 June 2016 to conduct the final examination of Tariq Faruq Sadiq on his thesis entitled "Stabilisation and Remediation of Heavy Metals in Mine Tailings Using Vetiveria zizanoides (L.) Nash Amended with Iron-Coated and Uncoated Rice Husk Ash" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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7.2 Concentration (mg kg$^{-1}$) of metals in root of vetiver grass grown in (A) tailings, (B) 10% of RHA and (C) 10% of Fe-RHA amended with different levels of NPK fertiliser

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7.4 The uptake (µg plant$^{-1}$) of metals by the shoot of vetiver grass grown in (A) tailings, (B) 10% of RHA and (C) 10% of Fe-RHA amended with different levels of NPK fertiliser

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<td>T</td>
<td>Tailings</td>
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<tr>
<td>V.</td>
<td>Vetiver grass</td>
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<tr>
<td>RHA</td>
<td>Rice husk ash</td>
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<tr>
<td>Fe-RHA</td>
<td>Iron coated rice husk ash</td>
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<tr>
<td>W-RHA</td>
<td>Washed rice husk ash</td>
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<tr>
<td>BAC</td>
<td>Bioaccumulation coefficient</td>
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<td>BTC</td>
<td>Bio translocation coefficient</td>
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<tr>
<td>BCF</td>
<td>Bio concentration factor</td>
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<tr>
<td>TF</td>
<td>Translocation factor</td>
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<tr>
<td>As</td>
<td>Arsenic</td>
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<tr>
<td>Cd</td>
<td>Cadmium</td>
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<tr>
<td>Cr</td>
<td>Chromium</td>
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<tr>
<td>Cu</td>
<td>Copper</td>
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<td>Mn</td>
<td>Manganese</td>
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<td>Pb</td>
<td>Lead</td>
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<td>Zn</td>
<td>Zinc</td>
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<td>Fe</td>
<td>Iron</td>
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<tr>
<td>P</td>
<td>Phosphorus</td>
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<td>N</td>
<td>Nitrogen</td>
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<tr>
<td>K</td>
<td>Potassium</td>
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<tr>
<td>S</td>
<td>Sulfur</td>
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<tr>
<td>TC</td>
<td>Total carbon</td>
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<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
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<tr>
<td>EC</td>
<td>Electrical conductivity</td>
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<tr>
<td>CEC</td>
<td>Cation exchange capacity</td>
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<tr>
<td>mg</td>
<td>milligram</td>
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<tr>
<td>kg</td>
<td>kilogram</td>
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<tr>
<td>µg</td>
<td>microgram</td>
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<tr>
<td>SPE</td>
<td>Sequential extraction procedure</td>
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<tr>
<td>NH₄OAC</td>
<td>Ammonium acetate</td>
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<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
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<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
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<tr>
<td>HNO₃</td>
<td>Nitric acid</td>
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<tr>
<td>H₂O₂</td>
<td>Hydrogen peroxide</td>
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<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
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<tr>
<td>CaCl₂</td>
<td>Calcium chloride</td>
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<tr>
<td>FeCl₃</td>
<td>Iron(III) chloride</td>
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<tr>
<td>HF</td>
<td>Hydrofluoric acid</td>
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<tr>
<td>ANC</td>
<td>Acid neutralization capacity</td>
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<tr>
<td>ICP-OES</td>
<td>Inductively Coupled Plasma Optical Emission Spectrometry</td>
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<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscope-</td>
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<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
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<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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CHAPTER ONE

INTRODUCTION

1.1 General background

The mining industry, especially gold mining, is a significant contributor to Malaysia’s economy, but it is also a source of severe contamination to the environment. Mining activities and their resulting wastes (e.g. mine tailings) have created widespread pollution in many locations around the world. The Penjom gold mine launched production in December 1996 as an open pit mine with a mill capacity of about 500,000 tons per year and it is currently producing between 1.7 and 2.8 tons of gold per year (DOWEX, 2003). Also, according to the Avocet (2010) statistic report, each tonne of gold produced in Penjom gold mine leads to more than 9 million tons of mine wastes approximately. These wastes will be disposed of as tailing, which is regarded as the primary source of release of various heavy metals into the environment, especially As (Arsenic), as a result of arsenopyrite oxidation (USEPA, 1994). Tailings are the portion of the original mineral-bearing rock left after extraction of wanted minerals. The separation of these metals involves crushing and grinding the rock into a fine sand material and separation of ore minerals by many methods. Mine tailings contain a considerable amount of metals and sulphides such as pyrite (FeS2), arsenopyrite (FeAsS), galena (PbS), and sphalerite ([Fe, Zn]S). Oxidations, precipitation, dissolution, desorption, and adsorption mainly occurs when mine tailings are exposed to the air. The surrounding soil and groundwater will be contaminated by the oxidation of sulphide minerals when As and heavy metals in sulphide-bearing minerals are released (Kim and Jung, 2004).

Earlier studies showed that the tailings from Penjom gold mine contained high concentrations of heavy metals. For example, Seh-Bardan et al. (2012a, b) measured As (2030.000 mg kg⁻¹), Fe (10300.000 mg kg⁻¹), Mn (672.430 mg kg⁻¹), Zn (134.830 mg kg⁻¹) and Pb (90.060 mg kg⁻¹) in mine tailings from Penjom gold mine in Malaysia. Claoston (2015) also found high concentrations of As (2080.000 mg kg⁻¹), Mn (700.000 mg kg⁻¹), Pb (95.000 mg kg⁻¹) and Cu (78.000 mg kg⁻¹). Arsenic and heavy metals may be released from the mine wastes to the ground and surface water systems, as well as the geological environment due to their solubility and mobility (Jang et al., 2005). Mining waste can spread to the surrounding and lowland areas by erosion caused by rain and the wind. Therefore, mine tailings can raise the level of heavy metals in the environment through wind blow and acid mine drainage, consequently affecting the quality of the surrounding water, land and air. Remediation of the mine tailings is deemed necessary to protect the environment and public health.

Health authorities in many parts of the world are becoming increasingly concerned about the effects of heavy metals and metalloids on the environment and human health. Because of their persistence, toxicity, non-degradability and bio-accumulative behaviours, heavy metals are always regarded as the most serious pollutants in the
Heavy metals are harmful to the environment and living organisms, i.e., plants, animals and microorganisms. The Agency for Toxic Substances and Disease Registry (ATSDR, 1999) enlisted the top 20 hazardous substances which include heavy metals such as As, Pb, Hg, and Cd. These heavy metals can enter the human body through food, water, air, and contact with the skin (Wuana and Okieimen, 2011). Significant health risks associated with heavy metals include cardiovascular disease, chronic anaemia, cognitive impairment, cancer, damage to the kidneys, nervous system, brain, skin, teeth, and bones (Chen et al., 2014), and much more. Therefore, it is crucial to lowering these health risks through the exclusion of heavy metals from the environment. In this regard, this study discusses the safest way of heavy metals remediation, which is phytoremediation.

There are several methods to remove the soil pollutants, which can be categorised into chemical, physical and biological methods. The conventional methods of soil cleanup (including solidification, vitrification, electrokinesis, excavation, soil washing and flushing, oxidation and reduction) have been shown to be effective in small areas, they need special equipment and are labour intensive (Ullah et al., 2015). Due to the side effects and high costs of physical and chemical techniques, the biological methods especially phytoremediation, seem to be promising remedial strategies and so are highlighted as alternative techniques to traditional methods (Soleimani et al., 2011).

Phytoremediation is an emerging technology that uses various plants to degrade, extract, or immobilise contaminants from soil and water. This technology has been receiving attention lately as an innovative and cost-effective alternative to the more established treatment methods used at hazardous waste sites. Phytoremediation is non-disruptive to the environment compared to operations that require excavation of soil. The use of plants for purifying contaminated soils and water has been developed much more recently. In the 1970s, reclamation initiatives of mining sites developed technologies for covering the soil with vegetation for stabilisation purposes and reduction of visual impact (Williamson and Johnson, 1981). Phytoremediation technology can be classified, depending upon the process by which plants are removing or reducing the toxic effect of contaminants from the soil as follows (i) phytoextraction (ii) phytotransformation (iii) phytostimulation (iv) phytostabilisation (v) phytovolatilisation (vi) rhizo-filtration (vii) pump and treat and (viii) hydraulic control (USEPA, 2001a).

When designing an appropriate system of phytoremediation, different aspects of certain parameters must be thoroughly considered. These parameters include the types and concentrations of contaminants to be treated, the selection of plant species and land type and other biotic and abiotic conditions affecting the process of phytoremediation (Mudgal et al., 2010). The efficiency of phytoextraction depends on many factors such as bioavailability of the heavy metals in soil, soil properties, speciation of the heavy metals and plant species concerned.

Plants suitable for phytoextraction should ideally have the following characteristics: (i) high growth rate (ii) production of more above-ground biomass (iii) widely distributed and highly branched root system (iv) more accumulation of the target heavy metals from
soil (v) translocation of the accumulated heavy metals from roots to shoots (vi) tolerance to the toxic effects of the target heavy metals (vii) good adaptation to prevailing environmental and climatic conditions, (viii) resistance to pathogens and pests (ix) easy cultivation and harvest and (x) repulsion to herbivores to avoid food chain contamination (Pilon-Smits 2005; Memon and Schröder, 2009; Sood et al., 2012; Ali et al., 2013; Cook and Hesterberg, 2013).

Different plants have different phytoextraction potentials, depending upon the environments and their genetic variability. It is essential to select indigenous plant species for phytoremediation processes because these plants are often better suited to survival, growth, and reproduction under environmental extremes than plants introduced from other environments. Vetiver grass (*Vetiveria zizanioides* (L.) Nash) is a fast growing, tall (1–2 m), high biomass, xerophytic as well as hydrophytic grass with a long (3–4 m) and massive root system (Dalton et al., 1996; Truong, 2000; Pichai et al., 2001). It is resistant to a broad range of climatic conditions. Vetiver showed promise in removing various environmental contaminants from both aqueous media and soil. The vetiver grass has been successfully used to stabilise mining overburden and highly saline, sodic, and alkaline tailing of gold mines (Radloff et al., 1995).

Growing plants in mine tailings is a difficult task due to heavy metals toxicity, the lack of oxygen supply to the roots, the poor physicochemical characteristics of the gangues, and the lack of key plant nutrients (Wong, 2003). There has been considerable work showing that tailings can be improved if blended with other substrates (Madejón et al., 2010). The use of soil amendments like composts, sewage sludge, manures and plant cover is the basis of cost-effective and environmentally sustainable methods to manage landscapes in mined areas. Increasing the availability of metals for uptake by plant roots and their transportation to the shoot system plays a significant role in phytoremediation. Phytoremediation can be considerably advantageous when the metals are in the soil solution rather than held by soil constituents, and this can be achieved by using different techniques such as adding soil acidifiers, organic and inorganic compounds, as well as chelates (Akcil et al., 2015). Many factors influence the metal uptake by plants such as organic matter, and cation exchange capacity, pH, Fe and Al oxides, soil redox potential, plant species, age, and cultivars (Zeng et al., 2011; Ye et al., 2014).

Rice husk ash (RHA) is a byproduct produced by rice mills, where rice husk is used as a fuel. The worldwide annual rice husk output is about 80 million tonnes and over 97% of the rice husk is generated in the developing countries, including Malaysia. It is estimated that 408,000 metric tonnes of rice husk are produced in Malaysia each year (Noor Syuhadah and Rohasliney, 2012). In many countries, rice husk is burned in the open air, and their ashes are scattered back to the rice field as fertilisers. In Malaysia, approximately 1,200 metric tonnes of rice husk is burnt per mill per year as renewable fuel to operate rice dryers installed at the mills (Theeba et al., 2012). The rice husk and its ash may be used as a natural, low-cost adsorbent to remove toxic metals since the ash derived from rice husk has an excellent adsorptive ability. Some characteristics of rice husk that make it a suitable adsorbent material for treating heavy metals from wastewater include its insolubility in water, high mechanical strength, good chemical stability, and possesses a granular structure (Srinivas and Naidu, 2013). Many studies have reported
the ability of RHA to remove heavy metals such as Cd, Pb, Zn, Cu, Mn and Hg from aquatic solution (Feng et al., 2004; Yin et al., 2006; Mane et al., 2007). The use of waste-based materials for environmental conservation has been stressed on under Malaysia’s Green Strategies of the National Policy on the Environment (DOE, 1998). Rice husk waste-based material, has received much attention from local researchers in this context. To date, no specific study has been reported on the efficacy of rice husk, its derivatives, or both as amendment agents to enhance phytoremediation of heavy metals in contaminated soil or tailings. Therefore, this research was undertaken to evaluate the potential of RHA and iron coated rice husk ash (Fe-RHA) as soil amendments for enhancing the ability of vetiver grass to phytoremediate mine tailings contaminated with As, Cd, Cr, Cu, Mn, Pb and Zn.

1.2 Problem statement

The Penjom gold mine generates a lot of waste (mine tailings) and they contain higher concentrations of heavy metals as well as hydrocarbon. Unfortunately, heavy metals do not degrade by microbes or chemicals and, therefore, they remain in the environment, leading to bioaccumulation of metals in the food chain, and then thus proving risk to the biological system. The heavy metals in mine tailings are quickly discharged and distributed into the ground water causing serious environmental and health problems in the vicinity of the mine area. Earlier studies have indicated that the concentration of Fe, As, Mn, Zn and Pb was high in the Penjom gold mine tailings (Seh-Bardan et al., 2012a, b). At the moment, the concentration of water-soluble fraction of the metals is low due to the high pH of the tailings. However, with time, the pH of the residue will become low, and the concentration of water-soluble fraction will increase to alarming levels. Therefore, the tailings may pose environmental hazards if not properly treated.

Phytoremediation process has gained increasing attention for extraction or stabilisation of metals from solid substrate since it is an efficient, simple, cost-effective and environmentally friendly process. Most of the suitable plants used in phytoremediation have slow growth rates and low annual biomass production, which directly reduces their efficiency to remove heavy metals from contaminated sites (Zhuang et al., 2007). Increasing the availability of metals for uptake by plant roots and their transportation to the shoot system plays a significant role in phytoremediation (Ernst, 1996). Adding RHA to the tailings may enhance phytoremediation Therefore, the potential risk of surface and groundwater contamination from the tailing area will be reduced.

1.3 Aim and objectives of the study

This study was carried out with the aim of evaluating the potential of RHA and Fe-RHA as amendments for stabilisation and remediation of heavy metals in Penjom gold mine tailings using vetiver grass (Vetiveria zizanioides (L.) Nash). The specific objectives of this study were

1- To study the effect of RHA or Fe-RHA on heavy metals fractionation in mine tailings.
2- To study the effect of RHA or Fe-RHA on the availability and mobility of heavy metals in mine tailings.

3- To study the effect of RHA or Fe-RHA on heavy metals uptake by vetiver grass (*Vetiveria zizanioides* (L.) Nash) and to find out the distribution of heavy metals in different parts of plant.

4- To determine the effects of inorganic fertiliser on the phytoremediation of metals by vetiver grass.

5- To evaluate the role of dissolved organic carbon on metals availability and uptake by vetiver grass.
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