

# In-situ Immobilization of Selected Heavy Metals in Soils using Agricultural Wastes and Industrial By-products

Che Fauziah Ishak<sup>1</sup> and Rosazlin Abdullah<sup>2</sup>

<sup>1</sup>Department of Land Management, Faculty of Agriculture, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

<sup>2</sup>Institute of Biological Sciences, Faculty of Science, University of Malaya, 50603, Kuala Lumpur, Malaysia.

Corresponding author (E-mail: cfauziah@upm.edu.my)

**Abstract:** Malaysian soils dominantly fall (about 75%) into the Ultisol and Oxisol Orders in Soil Taxonomy. These soils are generally acidic, pH of 4.0-5.0 and contain essentially of variable charge minerals, namely sesquioxides and kaolinite, thus, have low cation exchange capacity or cations retention capacity. Factors controlling heavy metals reactions and mobility in the soil system are pH, CEC, redox potential, etc. and these parameters will be exploited in the management of heavy metals contaminated soils. Amongst the remediation techniques opted are liming, in-situ chemical stabilization using agricultural wastes converted to biochars, such as oil palm empty fruit bunch and rice husk biochars, and industrial by-products such as red gypsum, coal fly ash and water treatment residue, to be applied as soil amendments.

**Key words:** Acidic soil, liming, biochar, red gypsum, coal fly ash, drinking-water treatment residue

## 1. Introduction

From our earlier work undertaken to study the heavy metals distribution in agricultural soils of Malaysia (Zarcinas et al., 2004), concentrations of Co, Ni, Pb and Zn in the soils were strongly correlated with soils concentrations of Al and Fe, which suggest evidence of background variations due to changes in soil mineralogy. Chromium was correlated with pH and EC, Na, S and Ca suggesting association with acid sulphate soil and soil salinity components, while Hg was not suggesting association with acid sulphate soil and soil salinity components, while Hg was not suggesting association with acid sulphate soil and soil salinity components, suggesting diffuse pollution by aerial deposition. Arsenic, Cd, Cu were strongly associated with aqua-regia soluble and available P, and organic matter suggesting these metals are associated with agricultural inputs in agricultural fertilisers and soil organic amendments. This indicates heavy metal contamination to the majority of agricultural soils in Peninsular Malaysia is due to anthropogenic activity (possibly added in fertilizers, wastes, pesticides, effluents or atmospheric sources) that may pose a risk to the environment or human health.

The application of biochar to soil may also improve the sorption capacity of trace elements or heavy metals in soil. This carbonaceous product was reported to have many functional groups with high surface areas, which are likely related to its potential to act as an adsorbent. Heavy metal incorporation in the soil is controlled by adsorption processes, such as surface complexation and ionic exchange, but other mechanisms such as precipitation are likely to contribute to metal retention in the soil (Sastre et al., 2006). Adsorption is defined as the accumulation of ions at the interface between a solid phase and an aqueous phase. Adsorption isotherms have been widely used in studies on adsorption phenomena, supplying numerical parameters that provide information on the retention capacity and intensity of the metal by the soil (Casagrande et al., 2008). The advantage of these equations is that they can be applied to adsorption of any ions and gives straightforward parameters which can be related to soil properties. A number of studies have also demonstrated that biochar has a high capacity to adsorb pollutants in contaminated soils (Beesley et al. 2011; Yuan and Xu, 2011). Biochar can stabilize the heavy metals in the contaminated soils, improve the quality of the contaminated soil and has a significant reduction in crop uptake of heavy metals.

In many cases, a byproduct may not be ideal by itself for land application. Through co-utilization of byproducts, more products that are agronomically useful may result. The benefits of co-utilization may include nutrient balance, reduction of toxins or contaminants, improved moisture content, improved economic value, and improved soil conditioning effects. In-situ immobilization is a cost-effective approach where land-applied amendments are used to stabilize contaminants via adsorption and/or precipitation reactions that render the contaminant immobile (Adriano, 1986). Numerous inorganic amendments such as clays, Al/Fe/Mn oxides and hydroxides may be land applied to metal contaminated soils as means of reducing metal mobility. Nowadays, there is pressure on waste

management managers to find ways to convert wastes into resources instead of sending them to the landfill. Amongst the mineral wastes recommended for in-situ immobilization of heavy metals are red gypsum, coal fly ash and drinking water treatment residues. There has also been report that combination of mineral byproducts with biosolids or organic materials is in fact a more viable option than applying the byproducts singly for soil fertility improvement for crop production.

## 2. Liming

In Malaysia, liming is the most common management practice used to overcome the problems associated with soil acidification. Most plants grow well at a pH range of 5.5–6.5 and liming is aimed to maintain the pH at this range. The main purpose of liming is to reduce aluminium toxicity in highly weathered acidic tropical soil, but at the same time, this practice can help reduce heavy metals availability to plants via precipitation process. In a study on an Oxisol grown with cocoa, the application of lime at 2 t ha<sup>-1</sup> reduced soil solution Mn concentration in the 0-15 cm layer from 27 to 12 µM after 3 months (Shamshuddin et al., 1991).

## 3. Biochar

In term of remediation of heavy metal contaminated soils through their retention in the soil system, biochar has been considered to be potentially effective. Biochar is a fine-grained charcoal-like material produced through pyrolysis, which is heating of biomass to temperature of 300-600 °C under air deprived conditions. Through pyrolysis, the feedstock changes chemically to form structures that are more resistant to microbial degradation than the original material.

Utilization of biochar as a soil amendment has attracted great interest globally due to the apparent benefits to soil fertility and plant growth as well as the potential to store or sequester C in the soil system. It has been reported that activated carbon, which is a subset of biochar, had been used as a substrate to improve the adsorption of heavy metals such as mercury, a process which is termed as chemisorption. The mechanism of heavy metal retention in soil by biochar can be categorized as physical or chemical in nature. The physical aspects deal more with filtering mechanism of the heavy metal due to its structure or size by the pore size of the biochar. It is important to characterize the pore size distribution of biochar, the percentage of macropore, mesopore, nanopore, because the type of pores dictate the extent of liquid-solid adsorption processes.

In Malaysia, a pilot scale biochar manufacturing plant using a modern engineering system has been built by Universiti Putra Malaysia (UPM), in collaboration with a private company (Nasmech Technology Sdn. Bhd.). The plant was built to produce biochar from oil palm empty fruit bunches (EFB) and is capable of producing 20 t of biochar daily. Additionally, biochar derived from rice husks has been produced commercially in Malaysia to avert wastage of large quantities of rice husks (RH). It is reported that 97,980 million tonnes of rice husk was produced annually during the processing in the mills (Bernas Sdn. Bhd.).

The surface morphology of biochar samples was observed under Jeol JSM-6400 scanning electron microscope. Figure 1 shows that EFB biochar possesses uniform pores and smooth wall surfaces with maximal 20 µm in diameter. Small particle-like ashes were found scattered on the surface area of EFB biochar as observed in Figure 1a. In comparison, the pores on rice husk biochar are not well-shaped with diminished structure of pores (Figure 1b). Small pores on the rough rice husk biochar surface was observed as shown in Figure 2. Pyrolysis temperature can attribute to the pores formation and destruction on biochar. When low temperature was applied, the biochar cell structure and arrangement was found similar to the cell structure and arrangement of the original biomass (Pavithra, 2011). The stack of biochar cells and pores were arranged accordingly and well-shaped as found in the SEM image of EFB biochar. However, as the temperature increase, the pore size become enlarged and the walls between adjacent pores were destroyed (Zhang et al., 2004), which explained the diminish pores

on rice husk biochar. The lack of biochar structure also might be due to the volatilization process during the biochar production.

From the observation on the SEM images, both biochar generally exhibit macropores with internal diameter size of 10  $\mu\text{m}$ . The macroporosity ( $>50\text{ nm}$ ) of biochars are relevant for soil aeration and water movement (Troeh and Thompson, 2005). Macropores also facilitate the root movement through the soil and act as habitats for the soil microbes (Saito and Muramoto, 2002). Hence, biochar has the potential to improve soil physical properties such as soil water retention and porosity. Basso et al., (2013) reported the addition of biochar on sandy loam soil increased the water- holding capacity by 23% compared to the non-amended soil. Glaser et al. (2002) also found the increase of soil field capacity with the increase of char surface area and porous structure. The macropores are also important as feeder pores to transport adsorbate molecules to the meso- and micropores.

A mixture of meso- and micropores were also present on EFB and rice husk biochar surface. The micropores of biochar make the greatest contribution to total surface area, hence responsible for the high adsorption capacities of molecules (Rouquerol et al., 1999). Mesopores are also of importance for many liquid-solid adsorption processes, as reported by Lua et al., (2004), on pistachio-nut shells. Thus, based on the EFB and rice husk biochar structural surface, they have the potential to sorb metal and metalloid to reduce the mobility of these trace elements in soil.

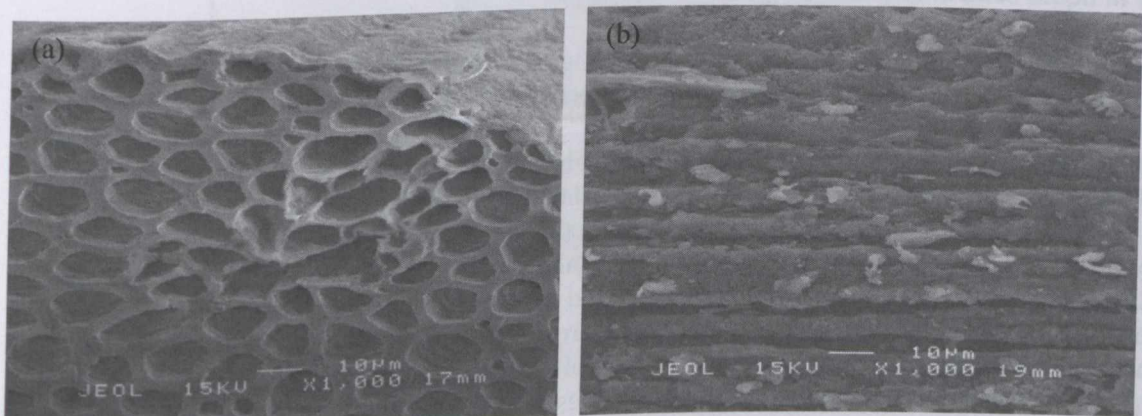


Figure 1. SEM image of EFB biochar at 1000 x magnification

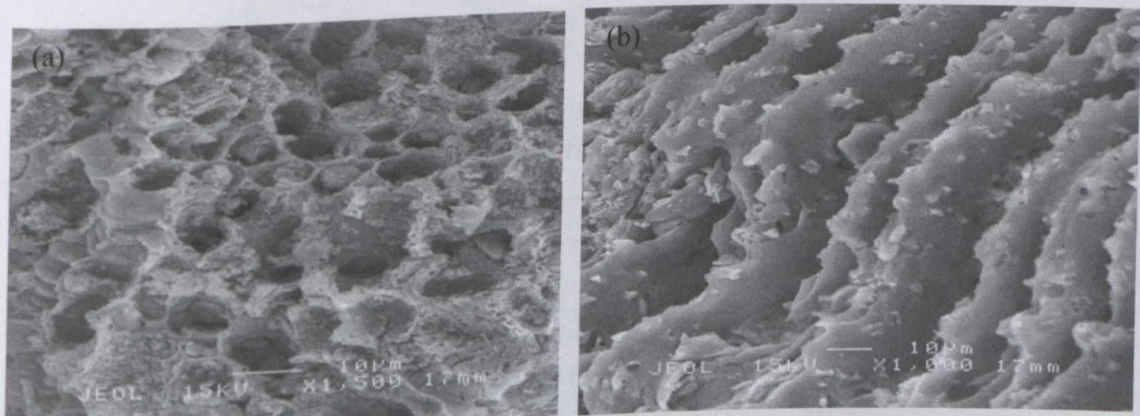


Figure 2. SEM image of rice husk biochar at (a)1500 and (b)1000 x magnification

The Brunauer, Emmett and teller (BET) surface area of biochar indicates the physical changes of biomass during the pyrolysis process. The surface area depends largely upon the carbon (C) mass removed during the processing, creating pores in the materials (Zabaniotou et al., 2008). The sorption ability of biochar can be determined from its surface area, where high surface area will increase the sorption capacity. Surface area and porosity of EFB and rice husk biochar are presented in Table 1.

Table 1: BET surface area and porosity of biochars

Biochar	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore surface area (m <sup>2</sup> /g)	Average pore diameter (nm)
EFB	46.32	0.01	0.61	3.85
Rice husk	23.22	0.01	1.41	4.34

Biochar produced from EFB had a larger surface area than RH biochar. The higher surfaces area of EFB biochar may indicate the adsorption capacity of heavy metals compared to RH biochar. In general, biochar surface areas can be influenced by biochar’s micropore volume, choice of feedstock and pyrolysis processing condition (Boateng et al., 2007). The micropore volume of EFB biochar was found to be same as RH biochar (~0.01 cm<sup>3</sup>/g). Internal surface area of biochar which represent pore on the inner wall resulted from interior crack was referred to as micropore area. Meanwhile, the average pore diameter for both biochar are in the range of mesopores diameters, with the internal pore width between 2 to 50 nm. This indicates the potential of adsorption capacity EFB biochar and RH biochar in liquid-solid adsorption (Bagreev et al., 2001).

The adsorption isotherm data were fitted to the Langmuir’s adsorption model. Table 2 shows the values of adsorption isotherm parameters for EFB biochar and RH biochar. The maximum adsorption capacity ( $q_{max}$ ) of EFB biochar for As was 0.424 mg g<sup>-1</sup>, which is higher than RH biochar (0.352 mg g<sup>-1</sup>). Similar trend was found on  $q_{max}$  of Cd with the values of 15.15 and 3.19 mg g<sup>-1</sup>, for EFB biochar and RH biochar, respectively. The parameter b is related to the affinity of the binding sites, which allows comparisons of the affinity of biochar toward the metal(loid) ions. EFB biochar had a higher affinity for As than did RH biochar. In contrast, the binding affinity (b) of Cd for RH biochar is higher than EFB biochar. There are several factors attributed to sorption mechanism of trace elements with addition of biochar, of which the most important are pH and CEC (Kumpiene et al., 2008). The alkaline properties of biochars increased the solution pH, which induced metal immobilization through metal precipitation and decreases metal solubility (Rees et al., 2013). Value of R<sup>2</sup> shows correlation or linear relationship, whereas the relationship become more linear when the value is closer to 1. The high correlation coefficient values (R<sup>2</sup>) which ranged from 0.98 to 0.99 indicate that the Langmuir isotherm best fitted the experimental data.

Table 2: Sorption isotherm obtained by fitting the data with the Langmuir isotherms for the EFB biochar and RH biochar

Biochar	Heavy metal	Langmuir model		
		$q_{max}$ (mg g <sup>-1</sup> )	b (L mg <sup>-1</sup> )	R <sup>2</sup>
EFB	As	0.4240	0.7299	0.9890
	Cd	15.1515	0.1142	0.9921
RH	As	0.3522	0.0248	0.9823
	Cd	3.1908	0.6920	0.9984

Samsuri et al. (2013) reported coating the biochars with Fe (III) greatly increased their adsorption capacities for both As (III) and As (V). The results indicate that the commercially produced EFB and RH from Malaysia have good potentials to be used as adsorbents for As (III) from aqueous solutions. Furthermore, coating the EFB and RH with Fe (III) increased their adsorption capacities for both As (III) and As (V) making the biochars more effective as adsorbents for both As (III) and As (V).

Soil solution study of incubated arsenic-rich Histosol amended with biochar was conducted to evaluate the effects of EFB biochar and RH biochar on water-soluble As naturally present in Histosol (Figure 3). Empty fruit bunch and RH biochars exhibit important feature as adsorbent with the porous structure and alkaline properties. The sorption experiment has shown the potential of these biochars to immobilize As in the soil system. The decreased of As concentration and increased of soil pH in soil solution study indicate the ability of biochar to reduce the phytoavailable As in contaminated soil (Figure 4).

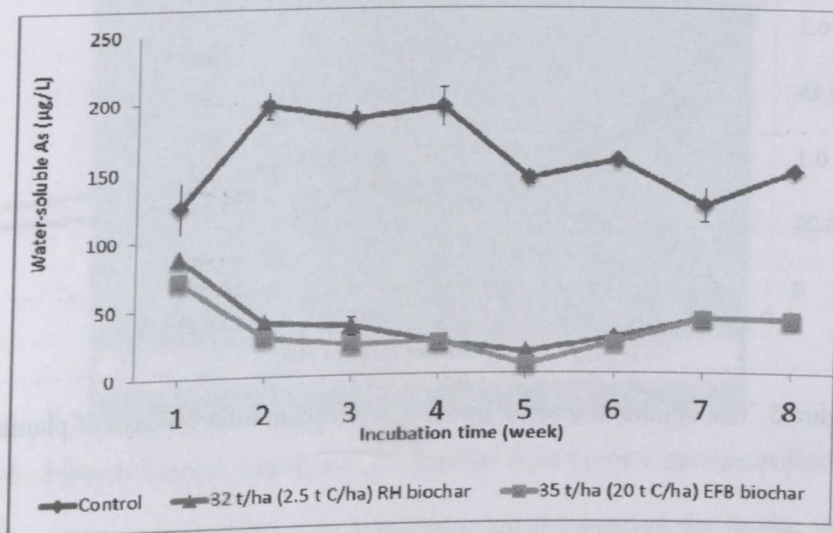


Figure 3: Effects of biochar on water-soluble arsenic in pore water

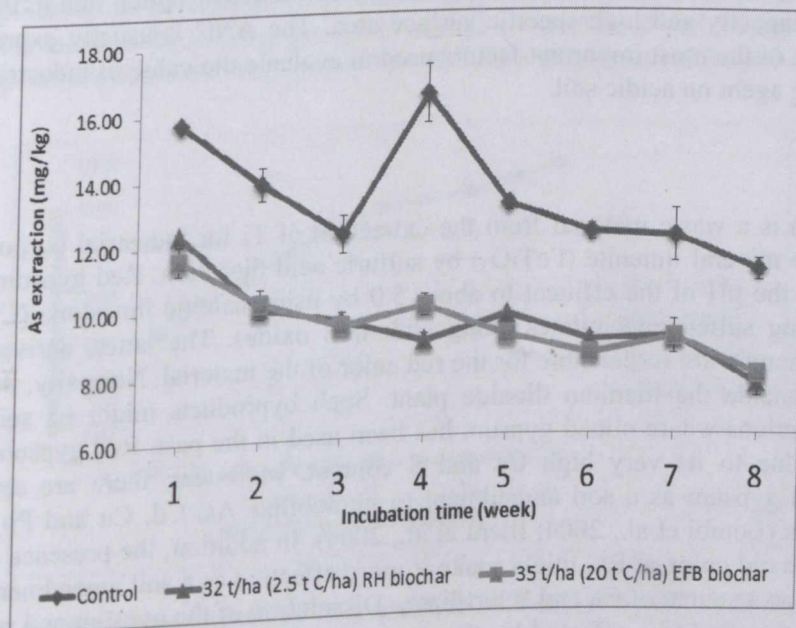


Figure 4: Effects of biochar on extractable arsenic in soil

The pot experiment was conducted to determine the optimum rates of biochars to reduce arsenic (As) uptake by sweet corn (Figure 5). Two types of biochars, EFB and RH with 5 rates (0, 2.5, 5, 10, 20 t C/ha) application were applied to 15 kg naturally contaminated soil in polybag. After 56 days of growth, biochar reduced the concentration of As in foliar tissue by 58% and 61% with the highest application of EFB and RH biochars at 20 t/ha C compared to the non-amended soil. The study shows the effectiveness of biochar in reducing the availability of As uptake by sweet corn as trace elements concentration decreased with increasing rate of biochar.

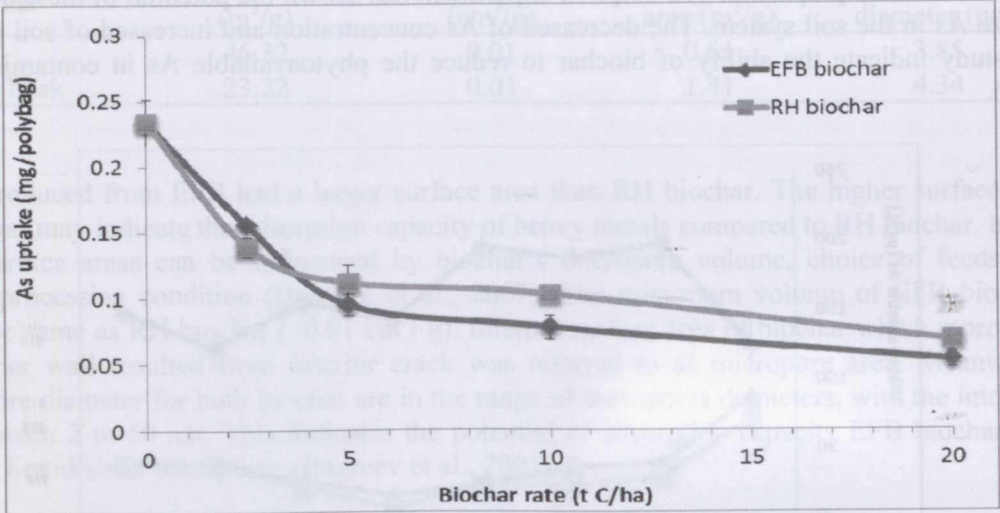


Figure 5. The uptake of arsenic by sweet corn plant after 56 days of planting

4. Industrial by-Products

Addition of industrial by-products to soil has gained importance recently as an alternative to remediate heavy metal contaminated soil. For example, byproducts from steel (iron oxides) and energy industries (ashes) will be assessed as an environmentally and resource-efficient option due to their alkalinity or acid neutralizing capacity and high specific surface area. The ANC is usually expressed as  $\text{CaCO}_3$  equivalent and one of the most important factors used to evaluate the value of industrial byproducts to be used as a liming agent on acidic soil.

4.1 Red Gypsum

Red gypsum (RG) is a waste material from the extraction of Ti for industrial purposes. Titanium is extracted from the mineral ilmenite ( $\text{FeTiO}_3$ ) by sulfuric acid digestion. Red gypsum is produced by further increasing the pH of the effluent to about 5.0 by using calcitic limestone ( $\text{CaCO}_3$ ), at which point the remaining sulfate precipitates along with iron oxides. The latter, derived from the iron contents of the ilmenite, are responsible for the red color of the material. Normally, this waste product is disposed off outside the titanium dioxide plant. Such byproducts might be suitable for use in agriculture in situations where mined gypsum has been used in the past. Red gypsum can be of great economic value due to its very high Ca and S content. Moreover, there are several reports on application of red gypsum as a soil amendment to immobilize As, Cd, Cu and Pb in heavy metal-contaminated soils (Lombi et al., 2004; Illera et al., 2004). In addition, the presence of the iron oxide responsible for the red color of RG might make it more effective as a soil amendment (Fauziah et al., 1996) rather than as a source of Ca and S fertilizer. Dissolution of the gypsum and subsequent supply of sulfate S to crops might be affected by the presence of the oxides, which have the possibility to adsorb sulfate.

The RG was alkaline in nature, with a pH of 7.98 due to the presence of residual  $\text{CaCO}_3$  in RG (Fauziah et al., 1996). This property can be exploited to reduce the solubility and hence, phyto-availability, of some heavy metals in the soil system. The acid neutralizing capacity is the most important characteristic in evaluation of the value of the material as a liming agent. Red gypsum is not a good liming agent, with only 1.79% calcium carbonate equivalence. However, high rates of application ( $> 2.5\%$ ) can have significant influence on the pH of the soil system (Nur Hanani et al., 2009). Iron oxide-rich gypsum by-products, including red gypsum ( $119 \text{ m}^2 \text{ g}^{-1}$ ), have very large surface areas (Peacock and David, 2000). The surface area for the red gypsum (pulverized and sieved through 2.0 mm sieve size) was  $39.8 \text{ m}^2 \text{ g}^{-1}$ . The high surface area plays a central role for adsorption behavior. Furthermore, the presence of Fe oxide can contribute to the co-existence of positive and negative charges on the variable charge oxide surface (Figure 6).

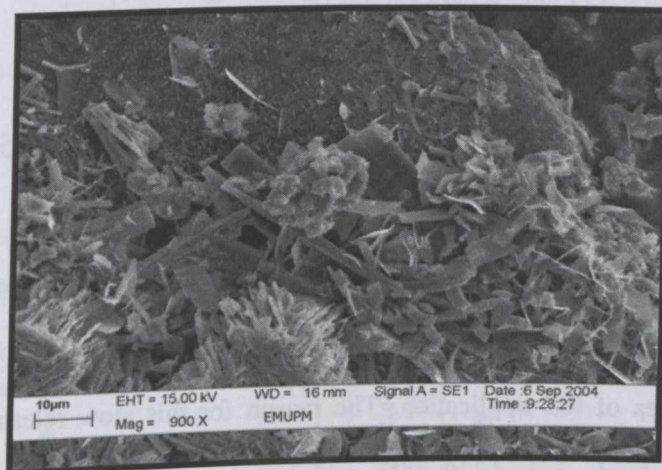


Figure 6 : Fibrous Crystal Aggregates of Gypsum with Some Coatings of Iron Oxides

A column leaching study was conducted to investigate the red gypsum for in-situ immobilization of arsenic in the soil system. In this experiment, the treatment used was the different rates of red gypsum. The treatments were: T1 : no red gypsum (control), T2 : 25 t/ha red gypsum, T3 : 50 t/ha red gypsum, T4 : 100 t/ha red gypsum. From this study, red gypsum application has the potential to immobilize arsenic in the soil system and thus prevent arsenic from being taken up by the crop grown on arsenic contaminated soil. The presence of Fe in red gypsum can help surface adsorbed or co-precipitate As in the soil system (Figure 7 and 8).

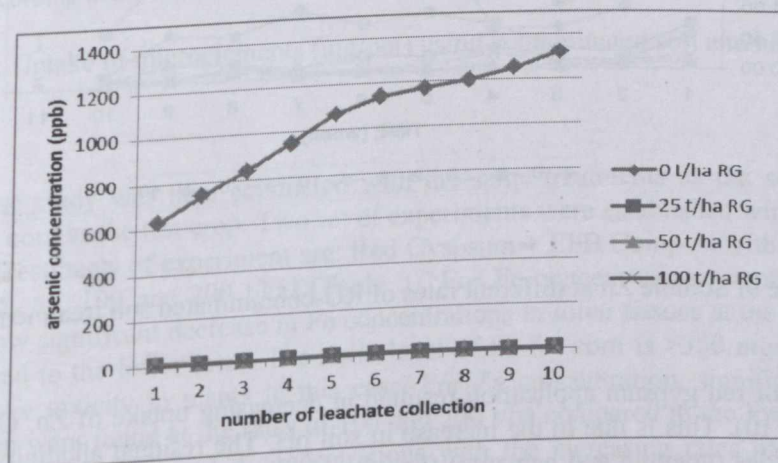


Figure 7: Arsenic concentration in each of the leachate collection (50 ml) up to one pore volume for each treatment.

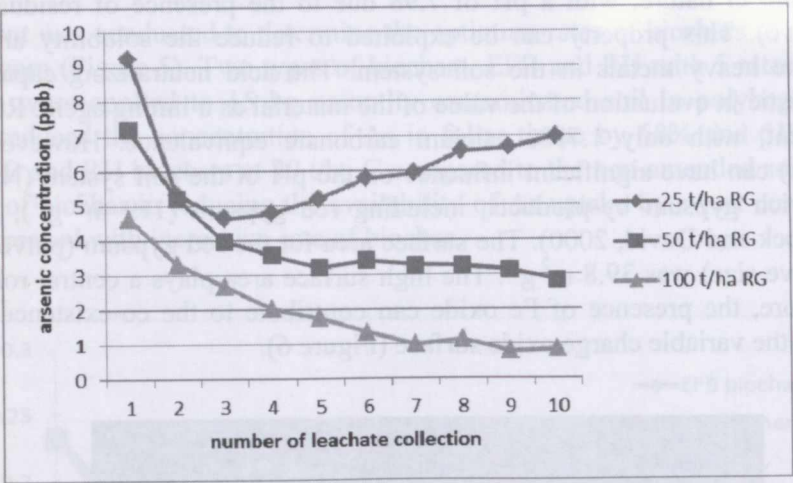


Figure 8: Arsenic concentration in each of the leachate collection (50 ml) for 25 t/ha, 50 t/ha and 100 t/ha red gypsum

In a soil incubation study, RG was applied to sewage sludge treated soil. Sewage sludge tend to have high concentrations of Cu and Zn and its application to soil increase these metals content. There seemed to be a lag-phase in the release of Zn from the RG minerals into the soil solution (Figure 9). The Zn concentrations in the soil solution started to increase only after 5 weeks of incubation for the treatments with low rates of RG application. The reason for this slow release of Zn into the soil solution is not known. However, this study demonstrated that increasing the RG amendment rates (5%, 10%, 20% and 40%) clearly reduced the Zn concentrations in soil solution after ten weeks of incubation. Thus, RG has the potential to fix Zn in the soil system and make it less phyto-available.

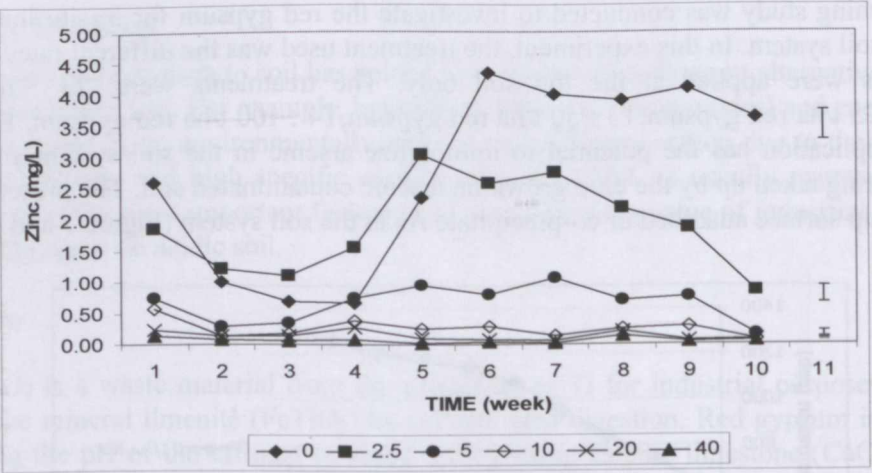
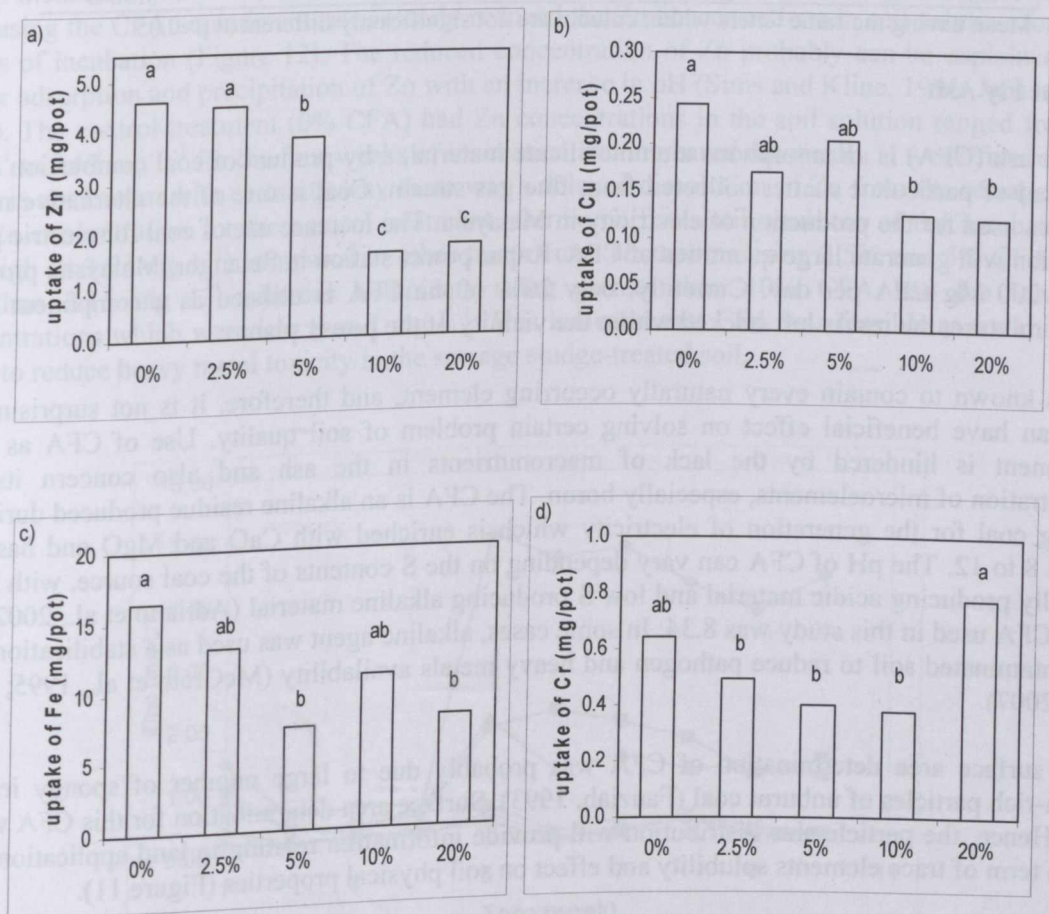


Figure 9. Soluble Zn at different rates of RG-contaminated soil treatments

Increasing the rate of red gypsum application resulted in decreasing uptake of Zn, Cu and Fe by the corn plants (Figure 10). This is due to the increase in soil pH. The residual alkalinity plus the buffer capacity of iron oxides (goethite and hematite) (Fauziah et al., 1996), allow red gypsum to consume protons from an acid soil. However, the results for Cr seemed to be rather varied. The grasses grown on heavy metals contaminated soil remediated with red mud (a by-product of the bauxite industry) had high Cr concentrations (Zhao et al., 2005; Snars et al., 2004). Thus, there may be room for speculation that RG also contain high levels of Cr. However, the levels of Cr in red gypsum were found to be low.

This study did not ascertain whether the organic matter in sludge alleviates the effect of excess Ca and Fe in the mixed soil system. This needs to be investigated. Furthermore, co-mixing two products such as RG and compost can turn the by-products into a more useful soil amendment as the amending capability of the by-product can be complemented and further enhanced by the co-mixed by-products (Fauziah et al., 2011).



Similar letters above bars indicate that the values represented by the bars are not significantly different at the 1% level, according to the Duncan New Multiple Range Test (DMRT)

Figure 10: Uptake of microelements (mg/pot) using contaminated soil amended with red gypsum

A glasshouse study was then conducted with the same treatments as the soil incubation study using sweet corn as the test crop. Two set of experiments were established with 4 treatments and 4 replicates. Treatments of experiment are: Red Gypsum + EFB Compost with different rate of red gypsum (2.5, 50, 100 and 200 t/ha) (Table 3). For Fe concentrations, application of RG+EFB compost show significant decrease in Fe concentrations in foliar tissues at the rate of 100 and 200 t/ha compared to the lower rates. The toxic level of Fe for corn is >350 mg/kg, thus there is no problem of Fe toxicity to plants in this case. For Zn concentration, significant decrease in Zn concentration were found at the rates of 100 and 200 t/ha compared to the lowest rate of RG. For Cd, significant decreased in Cd concentrations with the increasing rates of RG+EFB compost found at the rates of 100 t/ha and 200 t/ha compared to the lowest rate of RG+EFB compost used.

Table 3: Effects of treatments on heavy metals in foliar tissues

Treatment	mg/kg			
	Fe	Zn	Cd	Cr
RG 2.5t/ha + EFB Compost	305 ab	83.75 a	0.16 ab	0.98 ab
RG 50t/ha + EFB Compost	477 ab	75.65 a	0.08 ab	0.07 b
RG 100t/ha + EFB Compost	237 bc	39.20 b	0.03 b	0.14 ab
RG 200t/ha + EFB Compost	94 bc	9.63 b	0.05 b	0.06 b

Mean having the same letters within column are not significantly different at  $p>0.05$

4.2 Coal Fly Ash

Coal fly ash (CFA) is an amorphous aluminosilicate material, a by-product of coal combustion and is composed of particulate matter collected from flue gas stream. Coal is one of the alternative natural resources used for the production of electricity in Malaysia. The increase use of coal for electric power generation will generate large quantities of CFA. Kapar power station in Selangor, Malaysia, produced around 200 Mg CFA per day. Currently, only 20% of the CFA is utilized as a component in the cement mixture, the rest is left stacked within the vicinity of the power plant.

Coal is known to contain every naturally occurring element, and therefore, it is not surprising that CFA can have beneficial effect on solving certain problem of soil quality. Use of CFA as a soil amendment is hindered by the lack of macronutrients in the ash and also concern its high concentration of microelements, especially boron. The CFA is an alkaline residue produced during the burning coal for the generation of electricity which is enriched with CaO and MgO and has a pH around 8 to 12. The pH of CFA can vary depending on the S contents of the coal source, with high S generally producing acidic material and low S producing alkaline material (Adriano et al., 2002). The pH of CFA used in this study was 8.34. In some cases, alkaline agent was used as a stabilization agent for contaminated soil to reduce pathogen and heavy metals availability (McGrath et al., 1995; Zhang et al., 2007).

Large surface area determination of CFA was probably due to large number of spongy irregular carbon-rich particles of unburnt coal (Fauziah, 1993). Surface area determination for this CFA was 7.5 m<sup>2</sup>/g. Hence, the particle size distribution will provide information relating to land application of the ash, in term of trace elements solubility and effect on soil physical properties (Figure 11).

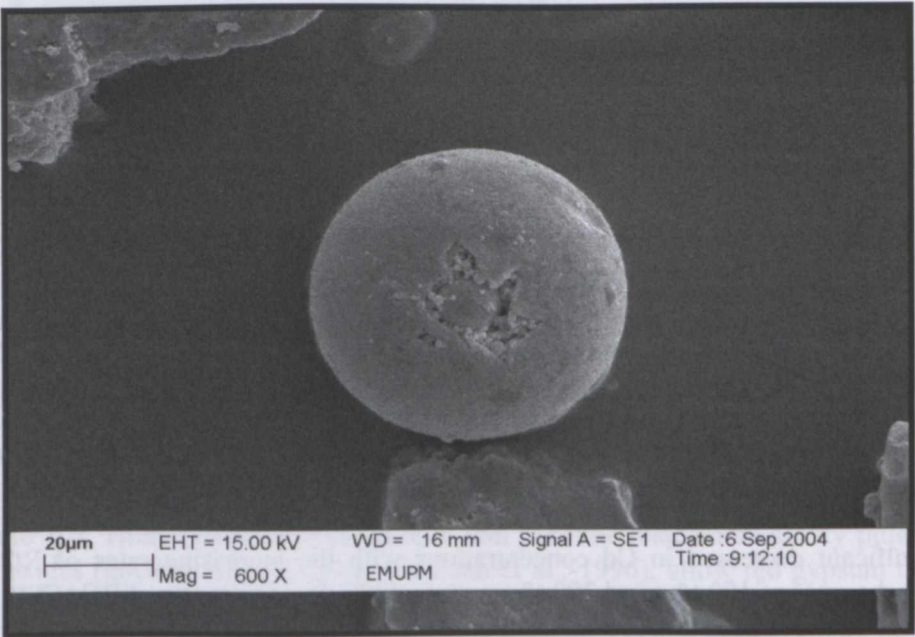


Figure 11 : Cenosphere Shape of Coal Fly Ash

The neutralization of acid by CFA is a relatively slow process that mainly involves the particle surfaces (Wong et al., 2002). The CFA was not a good liming agent, with only 0.504%  $\text{CaCO}_3$  equivalent (CCE). Based on the low level of Ca this CFA, it is considered only as a Class F fly ash (Bilski et al., 1995). Therefore, considerably large quantities of this CFA compared to lime will be required to raise the pH of soil to some target level.

A soil incubation study was also conducted whereby, CFA was applied on sewage sludge treated soil. Increasing the CFA amendment rates clearly reduced the Zn concentrations in soil solution for the ten weeks of incubation (Figure 12). The reduced concentration of Zn probably can be explained by the higher adsorption and precipitation of Zn with an increase in pH (Sims and Kline, 1991; Jackson et al., 1999). The control treatment (0% CFA) had Zn concentrations in the soil solution ranged from 1.47  $\text{mg L}^{-1}$  to 0.67  $\text{mg L}^{-1}$  for the four weeks of incubation and increased drastically at week five to 5.0  $\text{mg L}^{-1}$ . It is not known with certainty why there was a delayed dissolution of Zn from the sewage sludge. The Zn concentration for the control treatment after week five until week ten of the incubation was still high ( $> 3.73 \text{ mg L}^{-1}$ ) compared to other treatments. Treatments using 2.5% and 5% CFA ranged less than 2.15  $\text{mg L}^{-1}$  whereas treatments using greater than 10% CFA had the lowest Zn concentrations which were less than 1  $\text{mg L}^{-1}$ . This indicates that CFA was feasible as a stabilization agent to reduce heavy metal toxicity in the sewage sludge-treated soil.

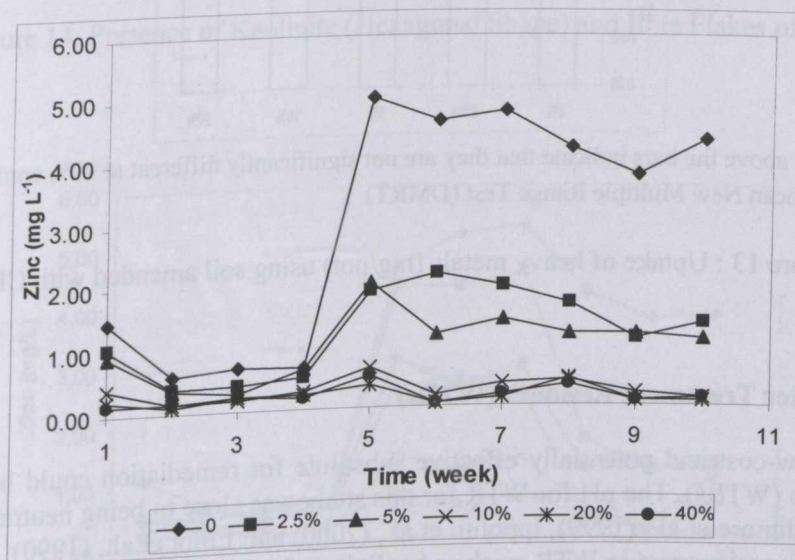
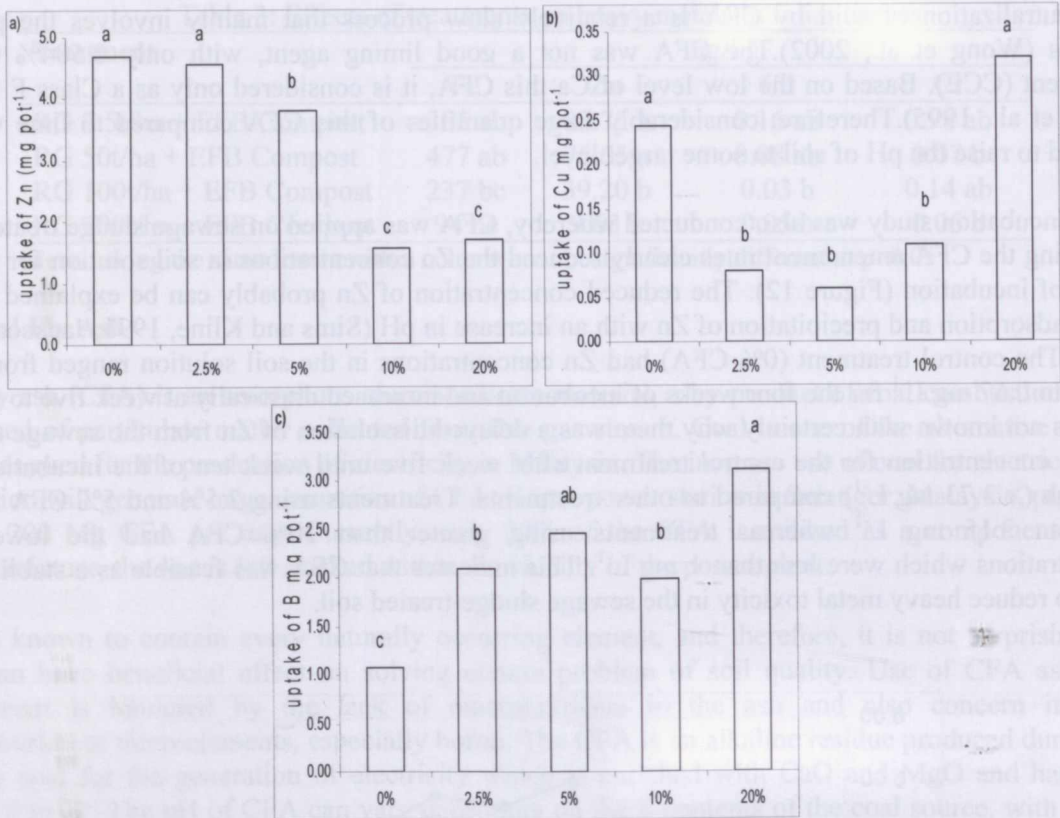


Figure 12: Soluble Zn at different rates of CFA-contaminated soil treatments

The Zn uptake by maize for treatment using CFA is shown in Figure. Overall, the concentration of Zn uptake by maize significantly decreased at higher rates of CFA treatments. Usage of 2.5% CFA did not show any significant result as compared to the control treatment. However, addition of more than 5% CFA significantly reduced Zn concentration in maize. This showed that the CFA was useful as a soil amendment to fix Zn in the contaminated soil.

The results showed application of CFA up to 10% reduced Cu uptake by the maize plants compared to the control (Figure 13). However, there was no significant difference in Cu uptake by maize between the control and the 20% CFA treatment indicating that CFA can be beneficial as a soil amendment to reduce Cu uptake by plant but, the amount of CFA should be applied at a proper rate to avoid Cu toxicity (Nur Hanani et al., 2010).



Note: Similar letters above the bars indicate that they are not significantly different at 99% confidence level, according to the Duncan New Multiple Range Test (DMRT)

Figure 13 : Uptake of heavy metals (mg/pot) using soil amended with CFA

4.3 Drinking-water Treatment Residues (WTRs)

In Malaysia, a low-cost and potentially effective substitute for remediation could be drinking-water treatment residues (WTRs). The pH for WTR for this study was close to being neutral just as stated in the reports of Gallimore et al., (1999), Ippolito et al., (2000) and Elliot et al., (1990) . The WTR has a pH of 7.07, the mineral present in WTR, such as kaolinite, gibbsite and Fe-oxides, provide surfaces for the adsorption of heavy metals. Value for WTR surface area was 28.3 m<sup>2</sup>/g and this value was largely dependent on the size of the sample which was less than 2 mm due to the grinding process. Surface area determination can be used to estimate the amount of surface sites available for surface complexation reaction (Figure 14). Butkus (1998) reported a surface area of WTR was 10 m<sup>2</sup>/g. Dzombak and Morel (1990) estimated that WTR can bind with protons, cations and anions based on the range of sorption maxima reported from 160 m<sup>2</sup>/g to 600 m<sup>2</sup>/g. The ANC of WTR was 0.504% CCE. Thus, WTR cannot be considered a good liming material compared to the pure CaCO<sub>3</sub>, but perhaps usage at high rates of this material can still increase the pH of acidic soil.

Also, in an incubation study of sewage sludge treated soil, treatment using the highest rates of WTR (40%) gave the lowest Zn concentration in the soil solution (Figure 15). Perhaps, the high Zn concentrations and high pHs at the higher WTR rates led to low solubility of Zn due to the pH effect and also the phenomenon call ageing (Lock and Janssen, 2003). The trend of Zn solubility indicates slow dissolution of Zn minerals at the initial stage, and then the concentration dropped again due to the precipitation or ageing affect. Zinc concentrations were found to be low in all treatments using different rates of WTR (2.5, 5, 10, 20, and 40%) compared to the control (0% WTR). Addition of WTR did reduce the release of Zn from the sewage sludge. Therefore, WTR can be considered to be a potential soil amendment to fix Zn in contaminated soils.

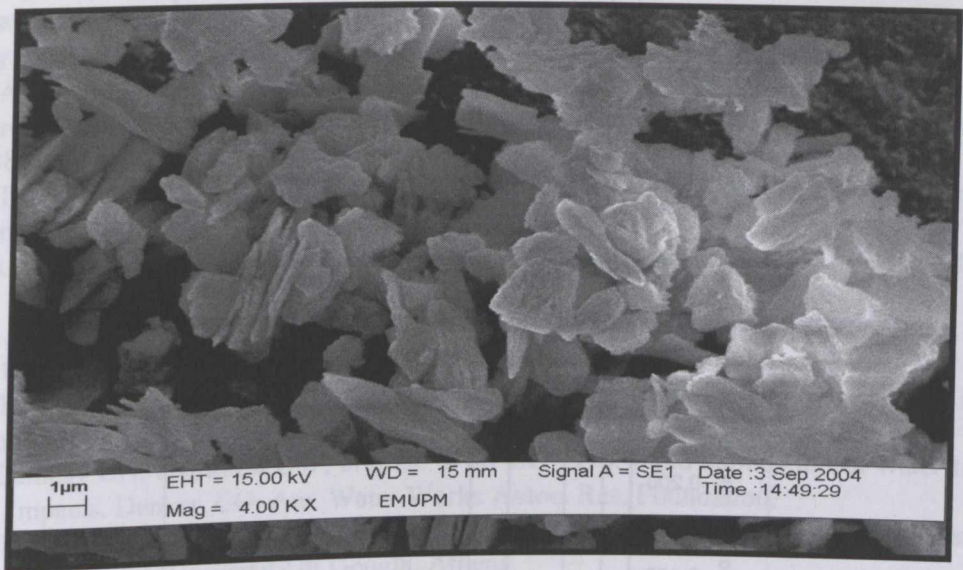


Figure 14: Presence of Kaolinite (Hexagonal Shape) and Illite Flakes of WTR

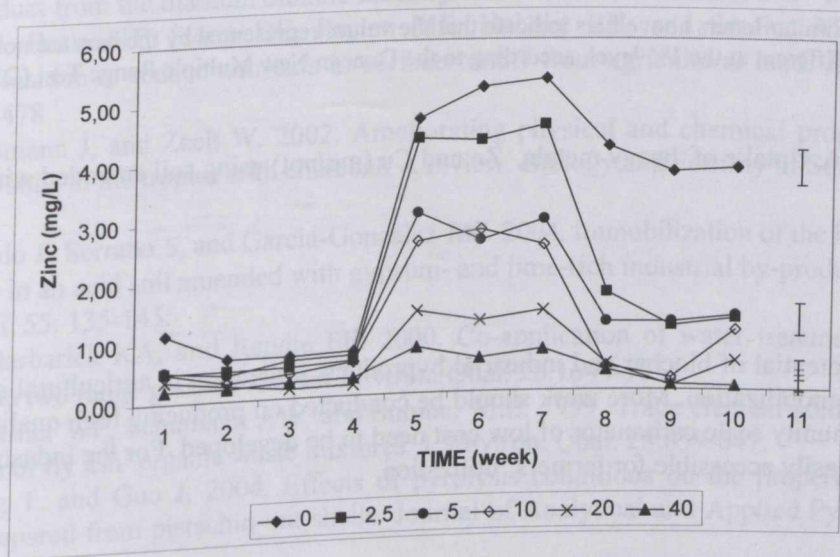
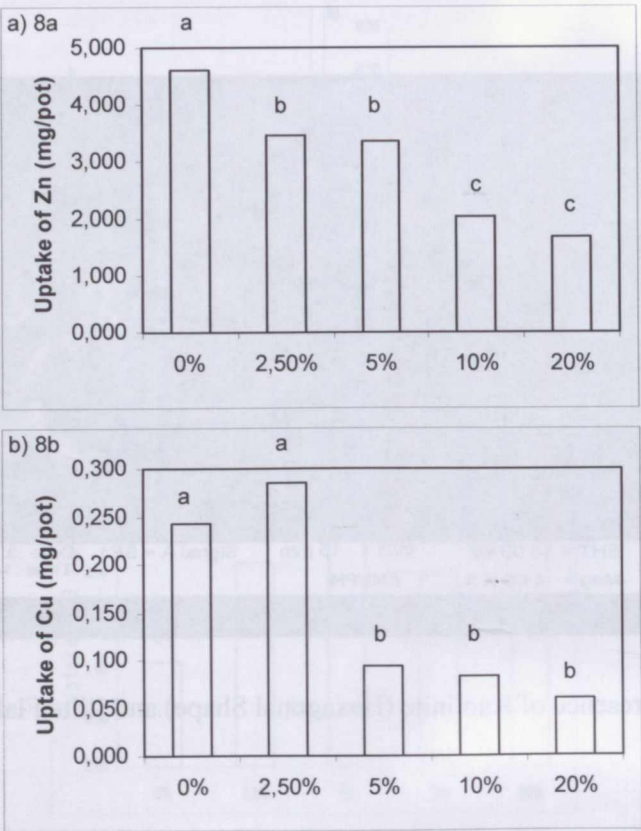


Figure15: Soluble Zn at different rates of WTR-contaminated soil treatments

Addition of WTR significantly reduced Zn uptake by corn plants compared to the control (Figure 16). This results show that the usage of WTR mixed with sewage sludge can significantly reduce the Zn uptake by corn. The major effect of high pH was to reduce the solubility of all micronutrients, especially Zn. Meanwhile, addition of more than 5% WTR, significantly reduced Cu uptake compared to the control. This results show that the usage of more than 5% WTR in sewage-sludge-amended soil can significantly reduce the Cu uptake by corn (Nur Hanani et al., 2008).



Similar letters above bars indicate that the values represented by the bars are not significantly different at the 1% level, according to the Duncan New Multiple Range Test (DMRT)

Figure 16. Uptake of heavy metals, Zn and Cu (mg/pot) using soil amended with WTR

### 5. Conclusion

There is great potential of biochar and industrial byproducts utilization in agricultural soils in term of heavy metals immobilization. More work should be conducted on producing high quality biochar. For biochar, a community scale carbonator of low cost need to be developed. For the industrial byproducts, they should be easily accessible for farmers' utilization.

### 6. Acknowledgement

We would like to thank UPM for giving us the permission to carry out this project under the Fundamental Research Grant Scheme and also to publish this research work.

### 7. References

Adriano DC. 1986. Trace elements in the terrestrial environment. New York: Springer-Verlag.

Adriano DC, Weber J, Bolan NS, Paramasivam S, Bon-Jun Koo, and Sajwan KS. 2002. Effects of high rates of coal fly ash on soil, turfgrass and groundwater quality. Water, Air and Soil Pollution 139: 365-385.

Bagreev A, Bandosz TJ, and Locke DC. 2001. Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage-derived fertilizer. Carbon 39: 1971-1979.

- Basso AS, Miguez FE, Laird DA, Horton R, and Westgate M. 2013. Assessing potential of biochar for increasing water-holding capacity of sandy soils. *GCB Bioenergy* 5: 132-143.
- Beesley L, and Marmiroli M. 2011. The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. *Environ. Pollution* 159:474-480.
- Boateng A.A. 2007. Characterization and thermal conversion of charcoal derived from fluidized-bed fast pyrolysis oil production of switch grass. *Industrial Engineering and Chemical Research* 46: 8857-8862.
- Bilski JJ, Alva K, and Sajwan K.S. 1995. Fly Ash. In: Rechcigl, J.E. (Editor). *Soil amendments and environmental quality*. Boca Raton, Florida: Lewis Publisher.
- Butkus MA. 1998. Surface complexation modeling on phosphate adsorption by water treatment residue. *Journal of Environ. Qual.* 27:1055-1063.
- Casagrande JC., Soares MR, and Mouta ER. 2008. Zinc adsorption in highly weathered soils. *Brasilia*. 43:131-139.
- Dzombak, D.A., & Morel, F.M.M. (1990). *Surface complexation modelling. Hydrous ferric oxide*. New York: John Wiley and Sons.
- Elliot HA, Dempsey BA, Hamilton DW, and De Wolf JR. 1990. Land application of water treatment sludges: Impacts. Denver, CO: Am. Water Works Assoc. Res. Foundation.
- Fauziah, C.I. (1993). Characterization and trace contaminant chemistry of coal combustion by-products. PhD Thesis, University of Georgia, Athens.
- Fauziah CI., Nur Hanani M, Zauyah S, Samsuri AW, and Rosazlin A. 2011. Co-application of red gypsum and sewage sludge on acidic tropical soils. *Communications in Soil Science and Plant Analysis* 42(21): 2561-2571.
- Fauziah CI, Zauyah S, and Jamal T. 1996. Characterization and land application of red gypsum: A waste product from the titanium dioxide industry. *Sci.Total Environ.* 188: 243 –251.
- Gallimore LE, Basta NT, Storm DE, Payton ME, Huhnke RH, and Smolen MD. 1999. Water treatment residue to reduce nutrients in surface runoff from agricultural land. *J. Environ. Qual.*, 28:1474-1478.
- Glaser B, Lehmann J, and Zech W. 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal: A review. *Biology and Fertility of Soils* 35: 219-230.
- Illera V, Garrido F, Serrano S, and Garcia-Gonzalez MT. 2004. Immobilization of the heavy metals Cd, Cu and Pb in an acid soil amended with gypsum- and lime-rich industrial by-products. *European J. of Soil Sci.* 55: 135-145.
- Ippolito JA, Barbarick KA, and Rendte EF. 2000. Co-application of water treatment residues and biosolids on two range grasses. *Journal Environ. Qual.* 28:1644-1650.
- Jackson BP, Miller WP, Schumann AW, and Sumner M.E. 1999. Trace element solubility from land application of fly ash/ organic waste mixtures. *J. Environ. Qual.* 28:639-647.
- Lua AC, Yang T. and Guo J. 2004. Effects of pyrolysis conditions on the properties of activated carbons prepared from pistachio-nut shells. *Journal of Analytical and Applied Pyrolysis* 72: 279-287.
- Luizão FJ, Petersen J, Neves EG. 2006. Black carbon increases cation exchange capacity in soils. *Soil Science Society of America Journal.* 70: 1719-1730.
- Kumpiene J., Lagerkvist A, and Maurice C. 2008. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments: A review. *Waste Management* 28: 215-225.
- Lock K, and Janssen CR. 2003. Influence of ageing on zinc bioavailability in soils. *Environ Pollution* 126: 371-374.
- Lombi E. Hamom RE. Wieshammer G, McLaughlin MJ, and McGrath SP. 2004. Assessment of the use of industrial by-products to remediate a copper- and arsenic-contaminated soil. *J. Environ. Qual.* 33: 902-910.
- McGrath SP, Chaudri AM, and Giller KE. 1995. Long-term effects of metals in sewage sludge on soils, microorganisms and plants. *Journal of Industrial Microbiology* 14: 94--104.
- Nur Hanani M, Che Fauziah I, Samsuri AW, and Zauyah S. 2010. Formulation of coal fly ash and sewage sludge mixtures to reduce impacts on the environment when used as soil ameliorant for acidic tropical soils. *Malaysian Journal of Soil Science* 14(1): 53-70.

- Nur Hanani M, Che Fauziah I, Samsuri AW, and Zaayah S. 2008. Utilization of drinking-water treatment residue to immobilize copper and zinc in sewage-sludge-amended soils. *Land Contamination and Reclamation* 16(4): 319-332.
- Pavithra S. 2011. Evaluation of Thermochemical Decomposition of Various Lignocellulosic Biomasses for Biochar Production, Master Thesis. McGill University, Ste Anne De Bellevue, Quebec, Canada.
- Peacock S, and David RL. 2000. The suitability of an iron oxide- rich gypsum byproduct as a soil amendment. *J. Environ. Qual.* 29: 1969-1975.
- Rees F, Simonnot MO, and Morel JL. 2013. Short-term effects of biochar on soil heavy metal mobility are controlled by intra-particle diffusion and soil pH increase. *European journal of Soil Science* 65 (1): 149-161
- Rouquerol F, Rouquerol I, and Sing K. 1999. Adsorption by Powders and Porous Solids. London, UK: Academic Press.
- Saito M. and Marumoto T. 2002. Inoculation with arbuscular mycorrhizal fungi: The status quo in Japan and the future prospects. *Plant and Soil* 244: 273-279.
- Samsuri AW, Sadegh-Zadeh F. and She-Bardan BJ. 2013. Adsorption of As(III) and As(V) by Fe coated biochars and biochars produced from empty fruit bunch and rice husk. *Journal of Environmental Chemical Engineering* 1 (4): 981-988.
- Sastre J, Rauret G. and Vidal M. 2006. Effect of the cationic composition of sorption solution on the quantification of sorption-desorption parameters of heavy metals in soils. *Environmental Pollution*. 140: 322-339.
- Shamshuddin J, Che Fauziah I, and Sharifuddin HAH. 1991. Effects of limestone and gypsum application to a Malaysian ultisol on soil solution composition and yields of maize and groundnut. *Plant and Soil*. 134: 45-52
- Sims JT, and Kline JS. 1991. Chemical fractionation and plant uptake of heavy metals in soil amended with composed sewage sludge. *J. Environ. Qual.* 13:344-349.
- Snars KE, Gilkes RJ, and Wong MTF. 2004. Use of red mud residue from bauxite processing to ameliorate soil acidity. In *Proc. the 6<sup>th</sup> International Symposium on Plant-Soil Interactions at Low pH*, Aug. 1-5, Sendai, Japan.
- Troeh FR. and Thompson LM. 2005. *Soils and Soil Fertility*. Iowa, USA: Blackwell Publishing.
- Wong SC, Li XD, Zhang G, Qi SH, and Min Y.S. 2002. Heavy metals in agricultural soils of the Pearl River Delta, South China. *Environ. Pollut.* 119:33-44.
- Yuan JH and Xu RK. 2011 Progress of the research on the properties of biochars and their influence on soil environmental functions. *Ecological and Environmental Science*. 20:779-785.
- Zabaniotou A, Stavropoulos G. and Skoulou V. 2008. Activated carbon from olive kernels in a two-stage process: Industrial improvement. *Bioresource Technology* 99: 320-326.
- Zarcinas AB, Fauziah CI, McLaughlin MJ, and Gill C. 2004. Heavy metals in soils and crops in Southeast Asia. 1. Peninsular Malaysia. *Environmental Geochemistry and Health* 26(4): 343-357.
- Zhang T, Walawender WP, Fan LT, Fan M, Daugaard D. and Brown R.C. 2004. Preparation of activated carbon from forest and agricultural residues through CO<sub>2</sub> activation. *Chemical Engineering Journal* 105: 53-59.
- Zhang H, Sun L, and Sun T. 2007. Solubility of ion and trace metals from stabilized sewage sludge by fly ash and alkaline mine tailing. *Journal of Environmental Science* 20: 710--716.
- Zhao FJ, McGrath SP, Dennis PG, Dunham SJ, and Gray CW. 2005. In-situ remediation of a heavy metal polluted soil using red mud. In *Proc. 8<sup>th</sup> International Conference on the Biogeochemistry of Trace Elements*, April 3-7, Adelaide, Australia.