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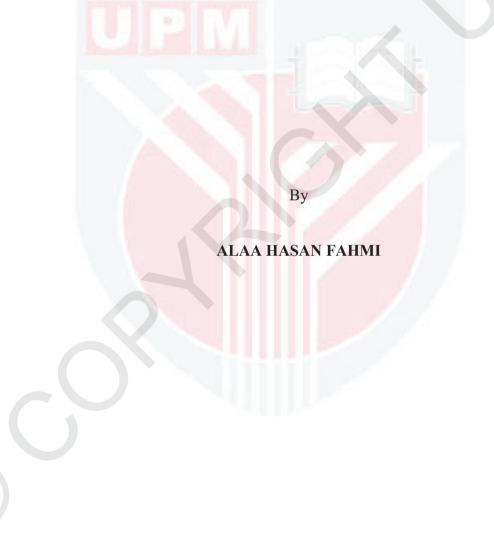
ADSORPTION, LEACHING AND BIOAVAILABILITY OF CADIMUM AND LEAD IN AQUEOUS SOLUTION AND CONTAMINATED SOILS AMENDED WITH MODIFIED BIOCHAR

ALAA HASAN FAHMI

FP 2019 14



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

November 2018

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DEDICATION

I dedicate this work to those who taught, motivated, and helped me throughout my study; to my parents;

Hasan Fhmi and Nahyia Salman, brothers & sisters.

It is also dedicated to my dearest wife; Hiba Abbas and my kids; Ban, Bashar, Mayar, & Baneen for their encouragements and patience toward achieving this goal.



Also, finally to my country Iraq

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

ADSORPTION, LEACHING AND BIOAVAILABILITY OF CADIMUM AND LEAD IN AQUEOUS SOLUTION AND CONTAMINATED SOILS AMENDED WITH MODIFIED BIOCHAR

By

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November 2018

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Cadmium (Cd) and lead (Pb) are among the global priority pollutants and contaminations of these heavy metals cover a wide range of soils. Biochar has been proven to be a very good adsorbent of heavy metals. Reduction of its particle size may increase the sorption and removal of heavy metals from soils or aqueous solution. The present study investigated the effects of crushing oil palm empty fruit bunch biochar (EFBB) to different particle sizes on the adsorptive removal of Cd and Pb from aqueous solution, extractable, leaching and phytoavailability of Cd and Pb in contaminated soil. Three different particle sizes of EFBB were used in this study; coarse (C-EFBB) (>2 mm), medium (M-EFBB) – (0.25 – 0.5 mm) and fine (F-EFBB) (< 0.05 mm). The F-EFBB was also coated with Fe to produce an iron coated F-EFBB (ICF-EFBB). A commercially available activated carbon (AC) was also included in the study as a benchmark for the sorption properties of the modified biochars. All the adsorbents were characterized for their physico-chemical and morphological properties using standard methods. A batch equilibrium study was performed using 0.1 g of each adsorbent with 40 mL of solution containing 0-500 mg L⁻¹ Cd and/or Pb. The isotherm data was fitted to Freundlich and Langmuir's sorption isotherm models. The C-EFBB and F-EFBB at three different rates (0%, 0.5% and 1%) were added to soils contaminated with Cd and/or Pb and the extractable, leaching and phytoavailability of these two metals were studied.

The results indicated that F-EFBB had the highest CEC, pH, and acidic functional groups among the adsorbents but the AC had the highest BET surface area. The scanning electron micrographs suggested that crushing the biochar exposed the micropores which were otherwise hidden in the inner structure of the larger particle size biochar. There was no evidence of macropores presence in the AC. Sorption

isotherm data of the all adsorbents for Cd in the single system were better fitted to the Langmuir than the Freundlich model, except for AC. However, the bisorbate system were better fitted to the Freundlich than the Langmuir model, except for ICF-EFBB. The sorption isotherms of all the adsorbents for Pb in the single and bisorbate system were better fitted to the Langmuir than the Freundlich model, except for AC in the bisorbate system. The Q_{max} values for Cd and Pb adsorption follow the order of ICF-EFBB > F-EFBB > M-EFBB > C-EFBB> AC in the single systems (55.87, 40.32, 19.34, 17.79 and 14.31 mg g⁻¹ for Cd and 142.86, 103.09, 58.14, 54.95 and 50.51 mg g⁻¹ for Pb, respectively). The same order was observed for Pb adsorption in bisorbate systems (126.58, 98.04, 51.02, 45.25 and 43.86 mg g⁻¹, respectively). The order of Q_{max} values for Cd adsorption in bisorbate systems exhibited the following order: F-EFBB > ICF-EFBB > M-EFBB > AC > C-EFBB (20.79, 17.86, 12.87, 6.25 and 5.59 mg g⁻¹, respectively). The adsorption of Pb was more preferable than Cd by all the adsorbents.

Application of EFBB to the soils contaminated with Cd and/or Pb significantly reduced the synthetic rainwater (SRW) extractable Cd and Pb. The lowest SRW extractable Cd and Pb was recorded by the contaminated soils applied with 1% F-EFBB. The lowest extractable values of Cd from Cd-soil and Cd+Pb-soil were 0 and 10.786 µg kg⁻¹ in week 8, respectively. The lowest extractable values of Pb from Pbsoil and Cd+Pb-soil were 4.180 and 9.770 µg kg⁻¹ in week 8, respectively. Similar results were obtained from the leaching study, which showed the effectiveness of the F-EFBB in reducing the leaching of Cd and Pb from the soils compared to the other adsorbents. The growth parameters of mustard plants grown in Cd- and Cd+Pb-soil treated with EFBBs were significantly better compared to the untreated soil (control). However, there was no significant difference in the growth parameters of mustard plants grown in Pb-soil treated with EFBBs compared to the control soil. There was also no significant effect of EFBB particle size on the growth parameters of the mustard plants grown on the contaminated soils. However, the application of 1% F-EFBB to the contaminated soils showed significantly lower Cd and Pb concentrations in the roots and shoots of the mustard plants as compared to the mustard plants grown on the untreated contaminated soil. The lower values of Cd in roots were 448.6 and 346 mg kg⁻¹, while, the lower values in shoots were 115.200 and 99 mgkg⁻¹ in contaminated soils Cd-soil and Cd+Pb-soil, respectively. For the lower Pb values in roots were 4196 and 1529.5 mg kg⁻¹, while, in shoots were 78.467 and 35.733 mg kg⁻¹ ¹, in contaminated soils Pb-soil and Cd+Pb-soil, respectively. This may be attributed to the reduction in bioavailable Cd and Pb in soils treated with F-EFBB. It can be concluded from this study that all the EFBBs, regardless of their particle size adsorbed Cd and Pb better than the commercial AC. Reducing the EFBB particle size improved its adsorption capacity as well as reduce the extractable and leaching of Cd and Pb from contaminated soils. Therefore, the EFBB can be an alternative to the much costlier AC as an adsorbent for Cd and Pb.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

JERAPAN, LARUTLESAP DAN KEDAPATANBIO Cd DAN Pb DALAM LARUTAN AKUEUS DAN TANAH TERCEMAR MENGGUNAKAN BIOCHAR YANG DIUBAH MENGGUNAKAN KAEDAH FIZIK DAN KIMIA

Oleh

ALAA HASAN FAHMI November 2018 Pengerusi : Samsuri Abd Wahid, PhD Fakulti : Pertanian

Kadmium (Cd) dan plumbum (Pb) adalah antara bahan cemar utama dunia dan pencemaran logam berat ini merangkumi pelbagai jenis tanah. Biochar telah dibuktikan sebagai penjerap logam berat yang sangat baik. Pengurangan saiz zarah biochar meningkatkan penjerapan dan penyingkiran logam berat dari tanah atau larutan berair. Kajian ini menyiasat kesan saiz zarah yang berbeza terhadap biochar dari tandan kosong kelapa sawit (EFBB) hancur dalam menyingkirkan Cd dan Pb dari larutan berair, boleh diekstrak, larutlesap dan kedapatan fito Cd dan Pb dalam tanah yang tercemar. Tiga saiz zarah EFBB digunakan dalam kajian ini; kasar (C-EFBB) (> 2 mm), sederhana (M-EFBB) - (0.25 - 0.5 mm) dan halus (F-EFBB) (<50 µm). EFBB juga disalut dengan Fe untuk menghasilkan F-EFBB bersalut ferum (ICF-EFBB). Karbon aktif komersial (AC) juga dimasukkan dalam kajian ini sebagai penanda aras bagi sifat-sifat penyerapan biochar yang telah diubahsuai. Sifat fizik-kimia dan morfologi semua penjerap dianalisis menggunakan kaedah piawai. Kajian keseimbangan berkumpulan dijalankan menggunakan 0.1 g setiap penjerap dengan larutan 40 mL yang mengandungi 0 - 500 mg L-1 Cd dan/atau Pb. Data isoterma dipadankan pada model isoterma jerapan Freundlich dan Langmuir. C-EFBB dan F-EFBB pada tiga kadar berbeza (0%, 0.5% dan 1%) telah ditambahkan pada tanah yang tercemar dengan Cd dan/atau Pb dan keboleh ekstrak, larutlesap dan kedapatan fito kedua-dua logam ini juga dikaji.

Keputusan menunjukkan bahawa F-EFBB mempunyai KPK, pH, dan kumpulan keasidan tertinggi di kalangan penjerap tetapi AC mempunyai keluasan permukaan BET tertinggi. Imbasan mikroskop elektron menunjukkan bahawa biochar yang dihancurkan membuka banyak liang-liang mikro yang tersembunyi di dalam struktur

dalaman biochar. Tiada bukti kehadiran liang makro pada AC ditemui. Data penjerapan isotermik semua penjerap untuk Cd dalam sistem logam tunggal lebih padan kepada model Langmuir berbanding model Freundlich, kecuali untuk AC. Walau bagaimanapun, sistem dwilogam lebih sepadan dengan model Freundlich daripada model Langmuir, kecuali untuk ICF-EFBB. Jerapan isoterma semua penjerap untuk Pb dalam sistem logam tunggal dan dwilogam lebih padan dengan model Langmuir daripada Freundlich, kecuali AC dalam dwilogam. Nilai Qmax untuk penjerapan Cd dan Pb mengikuti turutan ICF-EFBB > F-EFBB > M-EFBB > C-EFBB > AC (masing-masing sebanyak 55.87, 40.32, 19.34, 17.79 dan 14.31 mg g-1 bagi Cd dan 142.86, 103.09, 58.14, 54.95 dan 50.51 mg g-1 bagi Pb) dalam satu logam tunggal dan turutan yang yang sama diperhatikan untuk penjerapan Pb dalam sistem dwilogam. Turutan nilai Qmax untuk penjerapan Cd dalam sistem dwilogam menunjukkan urutan berikut: F-EFBB > ICF-EFBB > M-EFBB > AC > C-EFBB, iaitu masing-masing dijerap sebanyak 20.79, 17.86, 12.87, 6.25, dan 5.59 mg g-1. Penjerapan Pb lebih tinggi daripada penjerapan Cd.

Penambahan EFBB kepada tanah yang tercemar dengan Cd dan/atau Pb membantu mengurangkan Cd dan Pb yang boleh diekstrak oleh air hujan sintetik (AHS). Cadmium dan Pb yang diekstrak adalah terendah dalam tanah yang tercemar yang ditambah dengan 1% F-EFBB. Nilai Cd terendah bagi tanah Cd dan tanah Cd+Pb, masing-masing adalah 0 dan 10.786 µg kg-1 dalam minggu kelapan. Keputusan yang sama diperoleh daripada kajian larutlesap, yang menunjukkan keberkesanan F-EFBB dalam mengurangkan larutlesap Cd dan Pb dalam tanah berbanding dengan penjerap yang lain. Parameter tumbuhan sawi yang ditanam di tanah yang dicemari Cd- dan Cd+ Pb yang dirawat dengan EFBBs adalah jauh lebih baik berbanding dengan tanah kawalan yang tidak dirawat. Walau bagaimanapun, tidak perbezaan ketara yang ditemui pada tumbuhan sawi yang ditanam pada tanah yang dicemari Pb yang telah dirawat menggunakan EFBBs berbanding dengan tanah kawalan. Tidak ada kesan yang signifikan terhadap saiz zarah EFBBs pada parameter pertumbuhan pokok sawi yang ditanam di tanah yang tercemar. Walau bagaimanapun, penambahan 1% F-EFBB pada tanah yang tercemar menunjukkan kepekatan Cd dan Pb yang lebih rendah dalam akar, pucuk dan keseluruhan tumbuhan sawi berbanding tumbuhan sawi yang ditanam di atas tanah tercemar yang tidak dirawat. Nilai Cd dalam akar adalah 448.6 dan 346 mg kg-1 manakala terdapat 115.200 dan 99 mg kg-1 Cd dalam pucuk tumbuhan yang ditanam pada tanah tercemar dengan Cd dan Cd+Pb. Jumlah nilai Pb yang terendah dikenalpasti pada paras 4196 dan 1629.5 mg kg-1 dalam akar serta 78.467 dan 35.733 mg kg-1 dalam pucuk yang ditanam pada tanah tercemar dengan Pb dan Cd+Pb. Ini mungkin disebabkan pengurangan kedapatan bio Cd dan Pb dalam tanah yang dirawat dengan F-EFBB. Dapat disimpulkan daripada kajian ini bahawa semua EFBB, tanpa mengira saiz zarah boleh menjerap Cd dan Pb lebih baik daripada AC komersil. Pengurangan saiz zarah EFBB meningkatkan kapasiti penjerapan serta mengurangkan keboleh ekstrak dan larutlesap Cd dan Pb dari tanah yang tercemar. Oleh itu, EFBB boleh menjadi alternatif kepada AC yang jauh lebih mahal sebagai penjerap untuk Cd dan Pb.



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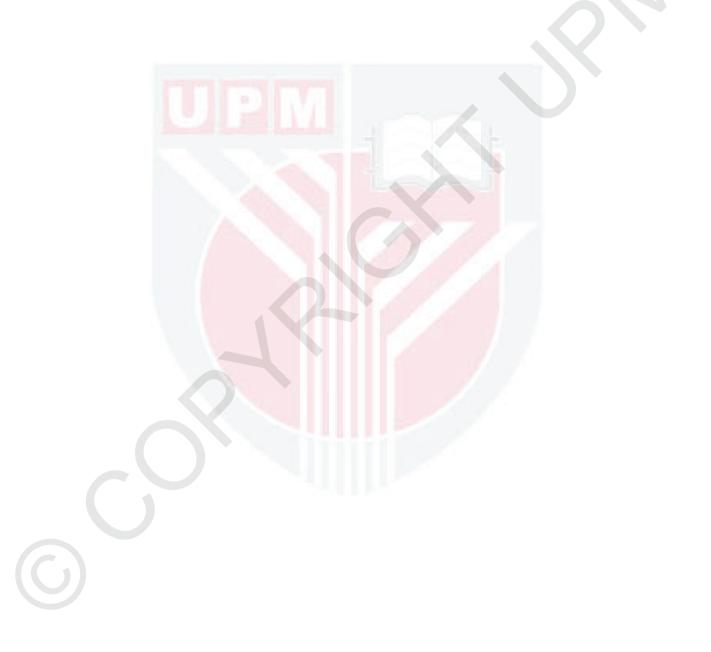
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LIST OF ABBREVIATIONS

	ANOVA	Analysis of Variance
	RCBD	Randomized Complete Block Design
	SAS	Statistical Analysis System
	SE	Standard Error
	rpm	Round Per Minute
	ASTM	American Society for Testing and Materials
	EFB	Empty Fruit Bunch
	EFBB	Empty Fruit Bunch Biochar
	F-EFBB	Fine Empty Fruit Bunch Biochar
	M-EFBB	Medium Empty Fruit Bunch Biochar
	C-EFBB	Coarse Empty Fruit Bunch Biochar
	ICF-EFBB	Iron Coated Fine Empty Fruit Bunch Biochar
	AC	Activated Carbon
	EC	Electrical Conductivity
	CEC	Cation Exchange Capacity
	FTIR	Fourier Transform Infrared Spectroscopy
	BET	Brunauer-Emmett-Teller
	FESEM	Field Emission Scanning Electron Microscope
	EDS	Electron Dispersive Spectroscopy
	SRW	Synthetic Rainwater
	TC	Total Carbon
	EDTA	Ethylenediaminetetraacetic acid
	ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
	AAS	Atomic Adsorption Spectrometer

b	Langmuir constant
Q _{max}	Langmuir maximum adsorption
K _F	Freundlich constant
1/n	The affinity of sorbate to the sorbent
Cd-soil	Contaminated soil with Cd 12 mg kg ⁻¹
Pb-soil	Contaminated soil with Pb 500 mg kg ⁻¹
Cd+Pb-soil	Contaminated soil with Cd $(12 \text{ mg kg}^{-1}) + \text{Pb} (500 \text{ mg kg}^{-1})$
PZC	Point of Zero Charge
WHO	World Health Organization
MPOB	Malaysian Palm Oil Board
USEPA	United States Environmental Protection Agency

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CHAPTER 1

INTRODUCTION

1.1 General Background

Cadmium (Cd) and lead (Pb) are significant pollutants found globally, causing contamination in many urban cities and related industrial sites (Mohan and Singh, 2002; Mohan et al., 2006; Thinakaran et al., 2017). Cadmium is toxic and can accumulate in bones and cause kidney damage in humans (Mohan and Singh, 2002; Yamkate et al., 2017). It is also a major cause of *itai-itai* disease (Mohan and Singh, 2002; Sharma et al., 2017). The major sources of Cd in the soils are by emission from alloy, pigments, battery, and from plastic manufacturing industries (Mohan and Singh, 2002; Peng et al., 2016) as well as from the application of phosphate fertilizers (Tianlik et al., 2016). Similarly, lead is released into the atmosphere or deposited in the soils or sediments through incomplete combustion of petroleum hydrocarbons and sulfide ore smelting (Mohan et al., 2014; Jiang and Zhou, 2018). In the case of water bodies, Pb is deposited on surface water resources via acid mine drainage (Mohan et al., 2014). Moreover, both Cd and Pb cannot be biodegraded (Inyang et al., 2012).

Heavy metals such as Cd and Pb can be removed from wastewater and soil using different technologies (Bolan et al., 2014). Some of the technologies used for wastewater heavy metals removal include precipitation, membrane filtration, electrocoagulation, ion exchange and packed-bed filtration (Inyang et al., 2012; Kim et al., 2013). Unfortunately, these technologies are costly and the pose disposal problems arising from the cumulation of sludge (Sud et al., 2008). Recently, the use of biosorbents has been reported to be a better alternative to the previously mentioned methods (Demirbas, 2009). Activated carbon (AC) is widely used in the decontamination of Cd and Pb from soils. However, as a result of biochar discovery, studies have indicated that AC is becoming less important in decontamination of heavy metals in soils because it is expensive to produce while biochar is cheaper and more environmentally friendly (Cornelissen et al., 2005; Kołtowski et al., 2017). Several investigators have proposed the use of biochar to replace AC as a biosorbent for largescale soil remediation of heavy metals (Babel and Kurniawan, 2003; Liang et al., 2010; Fu and Wang, 2011). Moreover, Cao et al. (2009) revealed that using different sorbents for heavy metals removal in wastewater only result in the binding of only one metal ion contaminant and the method is expensive.

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Biochar is defined as an organic material produced by heating biomass residues in the absence of oxygen (Sohi, 2012). Biochar has a capacity to sorb contaminants and heavy metals in soils (Beesley et al., 2011). Not only that, the addition of biochar to soil does serve various other functions such as increasing soil fertility and sequester carbon by storing carbon biomass which is more resistant to biodegradation (Sohi, 2012). Shen et al. (2015) showed that prior to a large-scale field application of biochar,

there is a need to rely on commercially available and renewable feedstock that proved to have the potential for soil decontamination. Oil palm empty fruit bunch (EFB) is abundantly produced in Malaysia and about 23 million tons are generated yearly (Vijaya et al., 2008). The EFB is usually disposed off in landfills and this can result in gas emission leading to pollution problems (Kong et al., 2014a). The Malaysian Palm Oil Board (MPOB), which is under the Ministry of Plantation Industry and Commodities, commercially produces biochar from EFB at its factory located in Bangi Lama, Selangor. The EFB biochar is produced at a temperature of 250 °C using a horizontal rotary kiln. The rotating motion of the kiln moves the EFB biomass along the kiln and the speed is controlled based on the period of the heating required.

The biochar produced at low temperature (<500 °C) has advantages and disadvantages. The advantages of biochar produced at low temperature include greater CEC (Kołodyńska et al., 2012) high nitrogen content (Chan and Xu, 2009) high exchangeable bases (Anyika et al., 2015) higher amounts of functional groups (Rutherford et al., 2008; Xie et al., 2015) high yield (Kong et al., 2014a) and the process consumes less energy (Cao et al., 2009). However, the biochar produced at low temperature has low pH, low surface area, and unexposed functional groups (Chen and Chen, 2009) which will result in low adsorption capacity of heavy metals and organic pollutants (Goswami et al., 2016). The resulting low surface area and unexposed functional groups of biochar produced at low temperature are due to pore closing and/or blockage by volatile material (Uchimiya et al., 2011a) or as a result of bottleneck phenomena (Dieguez-Alonso, 2015). The micropores are of considerable importance in adsorption process and the pore size can be widened with hightemperature pyrolysis due to the destruction of walls between the pores (Downie et al., 2009). On the other hand, high-temperature pyrolysis may lead to the loss of functional groups, which are also important in adsorption (Ding et al., 2014; Jindo et al., 2014). Biochar produced at low temperature can be a potential biosorbent to be used for soil amendment and environmental remediation purposes especially if its surface area can be increased and its inner pores and functional groups can be exposed by physical methods such as crushing.

1.2 Problem Statement

Previous studies have established that physical enhancing biochar properties may result in greater sorption of metals (Yargicoglu et al., 2015; Lu et al., 2017). The important the physical properties of biochar affecting sorption of metals include particle size, surface area (Shen et al., 2015; Shen et al., 2016; Lu et al., 2017) and pore volume (Kołodyńska et al., 2012). According to the terminology used by the International Union of Pure and Applied Chemistry (IUPAC), pores can be divided into three sizes: micropores (< 2 nm), mesopores (2 – 50 nm), and macropores (> 50 nm) (Thommes et al., 2015). The micropores and mesopores are the most important pore size in the adsorption of heavy metals (Mohan and Pittman, 2006; Ishak and Abdullah, 2014; Kunhikrishnan et al., 2015). Blockage of the inner pores either by ash content or volatile materials such as tars and bio-oil will cause the inner pores to become inaccessible surfaces for adsorption (Downie et al., 2009; Lee et al., 2010;

Gupta et al., 2013; Ahmad et al., 2014; Jindo et al., 2014). Therefore, exposing these inner pores will increase the effective adsorption capacity of biochar for heavy metals. According to Dieguez-Alonso (2015), to avoid bottlenecks phenomenon and pore blockage the biochar should be crushed to smaller particle size. However, for production pore of sizes up to 100 nm, the particle size should not be crushed less than $10 \,\mu\text{m}$. Therefore, in order to obtain biochar with pores up to 100 nm, the biochar has to be crushed to particle size near to $10 \,\mu\text{m}$. Previous studies have attempted to exploit the inner pores of biochar via particle size reduction (Mohanty and Boehm, 2014; Jaafar et al., 2015). However, the particle size that researchers used was much larger than 0.05 mm, which was not capable of exposing the occluded inner pores.

Shen et al. (2015) have reported the effect of particle size on metal sorption. They compared the sorption of Pb by Salisbury wood biochar of < 0.15 mm and 2 mm particles sizes and they found that the < 0.15 mm biochar adsorbed greater Pb relative to those of the 2 mm biochar. They attributed the higher sorption capacity of the fine particle size biochar for Pb to the CEC and a functional group, not the surface area. This because the sorption capacity of the Salisbury wood biochar was higher than that of sugarcane biochar reported by Inyang et al. (2011) even though the surface area of the former was higher. Shen et al. (2015) also concluded that the adsorption of Pb on the Salisbury wood biochar was not controlled by physical sorption but rather by chemisorption.

Meanwhile, the use of biochars with small particle sizes will require more specific and expensive filter paper to separate the biochar particles from the treated wastewater (Wang et al., 2014; Han et al., 2015). Consequently, it is assumed that magnetizing the biochar will ease its separation from the wastewater by using a magnet (Baig et al., 2014; Wang et al., 2015a; Tan et al., 2016). The smaller the size of the magnetic biochar, the better the separation from aqueous solution because of the higher adsorptive area. However, if the size of the magnetic biochar is too small, the magnetic tractive force will not be strong enough to overcome the Brownian motion, and therefore, the separation from the aqueous solution will be difficult (Cotten and Eldredge, 2002; Yavuz et al., 2006).

Studies have reported that impregnation of biochar with iron oxide increased the surface area and oxygen-containing functional groups of the biochar, hence increasing its adsorption capacity for heavy metals (Song et al., 2014; Wang et al., 2015b; Tan et al., 2016). However, other studies revealed that iron oxide could block the pores and reduce the pore volume and surface area of biochar (Wang et al., 2011; Hu et al., 2015).

According to Kołodyńska et al. (2012), 3 mechanisms exists for metal adsorption on biochar surfaces: (1) migration of the metal ions from the bulk solution to the external surfaces of the biochar (film diffusion), (2) migration of the metal ions into the biochar interior surfaces by either pore diffusion or surface diffusion, and (3) adsorption of metal ions on biochar surfaces. It is important to note that most of the reported

mechanisms involved the surface functional groups of the biochar. However, metal retention by the surface functional groups of the biochars inner pores has not been completely verified. Amonette and Joseph, (2009) and Mohan et al. (2015) reported that both acidic and basic functional groups do exist in the inner pores of the biochar and in biochars matrix.

As far as I know, very rare literature can be found on the influence of the inner pores functional groups to increase the sorption capacity of metals by exposing the inner pores via particle size reduction. In this study, the inner pores of biochar were exposed by crushing the biochar to a particle size of < 0.05 mm. It is hypothesized that this will expose the inner pores of the biochar, which may increase its adsorption capacity for heavy metals. It is also hypothesized that magnetizing the biochar separation from aqueous solution. Apart from studying the effect of particle sizes on the sorption characteristics, extractable, leaching and phytoavailability characteristics of Cd and Pb were also investigated.

1.3 Research Objectives

The general objective of this research was to study the effects of biochar particle size in increasing its adsorption capacity for Cd and Pb. Consequently, reducing the leaching and phytoavailability of the metals. The specific objectives are listed below:

- 1. To determine the physico-chemical, mineralogical and morphological characteristics of different sizes of biochar (C-EFBB, M-EFBB, and F-EFBB), magnetic biochar (ICF-EFBB) and activated carbon (AC).
- 2. To study the sorption capacity of Cd and Pb in the single and bisorbate system by different sizes biochars (C-EFBB, M-EFBB, F-EFBB, ICF-EFBB, and AC).
- 3. To investigate extractable and leaching of Cd and Pb in contaminated soil (Cd, Pb, Cd+Pb) amended with different particle sizes (C-EFBB and F-EFBB) and rates of biochar (0%, 0.5%, 1%).
- 4. To determine phytovailability of Cd and Pb in contaminated soil (Cd, Pb, Cd+Cd) amended with different particle sizes (C-EFBB and F-EFBB) and rates of biochar (0%, 0.5%, 1%) by the mustard plant.

REFERENCES

- Ab Aziz, N. S., bin Mohd Nor, M. A., & Hamzah, F. (2015). Suitability of biochar produced from biomass waste as soil amendment. *Procedia-Social and Behavioral Sciences*, 195, 2457-2465.
- Abbas, A., Al-Amer, A. M., Laoui, T., Al-Marri, M. J., Nasser, M. S., Khraisheh, M., & Atieh, M. A. (2016). Heavy metal removal from aqueous solution by advanced carbon nanotubes: Critical review of adsorption applications. *Separation and Purification Technology*, 157, 141-161.
- Abbas, T., Rizwan, M., Ali, S., Adrees, M., Mahmood, A., Zia-ur-Rehman, M., & Qayyum, M. F. (2018). Biochar application increased the growth and yield and reduced cadmium in drought stressed wheat grown in an aged contaminated soil. *Ecotoxicology and Environmental Safety*, 148, 825-833.
- Abdelhadi, S. O., Dosoretz, C. G., Rytwo, G., Gerchman, Y., & Azaizeh, H. (2017). Production of biochar from olive mill solid waste for heavy metal removal. *Bioresource Technology*, 244, 759-767.
- Abdelhafez, A. A., & Li, J. (2016). Removal of Pb (II) from aqueous solution by using biochars derived from sugar cane bagasse and orange peel. *Journal of the Taiwan Institute of Chemical Engineers*, *61*, 367-375.
- Abdelhafez, A. A., Li, J., & Abbas, M. H. (2014). Feasibility of biochar manufactured from organic wastes on the stabilization of heavy metals in a metal smelter contaminated soil. *Chemosphere*, 117, 66-71.
- Ahmad, M., Lee, S. S., Yang, J. E., Ro, H. M., Lee, Y. H., & Ok, Y. S. (2012). Effects of soil dilution and amendments (mussel shell, cow bone, and biochar) on Pb availability and phytotoxicity in military shooting range soil. *Ecotoxicology and Environmental Safety*, 79, 225-231.
- Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D., & Ok, Y. S. (2014). Biochar as a sorbent for contaminant management in soil and water:
 A review. *Chemosphere*, 99, 19-33.
- Ahmed, M. B., Zhou, J. L., Ngo, H. H., Guo, W., & Chen, M. (2016). Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. *Bioresource Technology*, *214*, 836-851.
- Al-Wabel, M. I., Al-Omran, A., El-Naggar, A. H., Nadeem, M., & Usman, A. R. (2013). Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes. *Bioresource Technology*, 131, 374-379.

- Al-Wabel, M. I., Usman, A. R. A., Al-Farraj, A. S., Ok, Y. S., Abduljabbar, A., Al-Faraj, A. I., & Sallam, A. S. (2017). Date palm waste biochars alter a soil respiration, microbial biomass carbon, and heavy metal mobility in contaminated mined soil. *Environmental Geochemistry and Health*, 1-18. DOI 10.1007/s10653-017-9955-0.
- Al-Wabel, M. I., Usman, A. R., El-Naggar, A. H., Aly, A. A., Ibrahim, H. M., Elmaghraby, S., & Al-Omran, A. (2015). Conocarpus biochar as a soil amendment for reducing heavy metal availability and uptake by maize plants. *Saudi journal of Biological Sciences*, 22, 503-511.
- Amonette, J. E., & Joseph, S. (2009). Characteristics of biochar: microchemical properties. In *Biochar for Environmental Management: Science and Technology* (pp. 33–52). London, UK: Earthscan.
- Anyika, C., Asri, N. A. M., Majid, Z. A., Jaafar, J., & Yahya, A. (2017). Batch sorption–desorption of As (III) from waste water by magnetic palm kernel shell activated carbon using optimized Box–Behnken design. *Applied Water Science*, 7, 4573-4591.
- Anyika, C., Majid, Z. A., Ibrahim, Z., Zakaria, M. P., & Yahya, A. (2015). The impact of biochars on sorption and biodegradation of polycyclic aromatic hydrocarbons in soils—a review. *Environmental Science and Pollution Research*, 22, 3314-3341.
- Anyika, C., Majid, Z. A., Isa, A. B., Ismail, N., Zakaria, M. P., & Yahya, A. (2016). Toxic and nontoxic elemental enrichment in biochar at different production temperatures. *Journal of Cleaner Production*, 131, 810-821.
- Asami, T. (1984). Pollution of soils by cadmium. In *Changing metal cycles and human health* (pp. 95–111). Springer, Berlin: Heidelberg.
- Azeez, J. O., Obanla, S. O., Ojo, A. O., & Shokalu, A. O. (2010). Cadmium sorption and desorption characteristics of tropical alfisols from different land uses. *Communications in Soil Science and Plant Analysis*, 41, 108-121.
- Babel, S., & Kurniawan, T. A. (2003). Low-cost adsorbents for heavy metals uptake from contaminated water: A review. *Journal of Hazardous Materials*, 97, 219-243.
- Baig, S. A., Zhu, J., Muhammad, N., Sheng, T., & Xu, X. (2014). Effect of synthesis methods on magnetic Kans grass biochar for enhanced As (III, V) adsorption from aqueous solutions. *Biomass and Bioenergy*, 71, 299-310.
- Bansal, R. C., & Goyal, M. (2005). Activated carbon adsorption. Florida. CRC press.
- Bansode, R. R., Losso, J. N., Marshall, W. E., Rao, R. M., & Portier, R. J. (2003). Adsorption of metal ions by pecan shell-based granular activated carbons. *Bioresource Technology*, 89, 115-119.

- Bashir, S., Zhu, J., Fu, Q., & Hu, H. (2018). Cadmium mobility, uptake and antioxidative response of water spinach (Ipomoea aquatic) under rice straw biochar, zeolite and rock phosphate as amendments. *Chemosphere*, *194*, 579-587.
- Beesley, L., & Marmiroli, M. (2011). The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. *Environmental Pollution*, 159, 474-480.
- Beesley, L., Moreno-Jiménez, E., & Gomez-Eyles, J. L. (2010). Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. *Environmental Pollution*, 158, 2282-2287.
- Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J. L., Harris, E., Robinson, B., & Sizmur, T. (2011). A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. *Environmental Pollution*, 159, 3269-3282.
- Beiyuan, J., Awad, Y. M., Beckers, F., Tsang, D. C., Ok, Y. S., & Rinklebe, J. (2017). Mobility and phytoavailability of As and Pb in a contaminated soil using pine sawdust biochar under systematic change of redox conditions. *Chemosphere*, 178, 110-118.
- Berti, W. R., & Jacobs, L. W. (1996). Chemistry and phytotoxicity of soil trace elements from repeated sewage sludge applications. *Journal of Environmental Quality, 25*, 1025-1032.
- Boehm, H. P., Diehl, E., Heck, W., & Sappok, R. (1964). Surface oxides of carbon. Angewandte Chemie International Edition in English, 3, 669-677.
- Bolan, N. S., Adriano, D. C., & Naidu, R. (2003). Role of phosphorus in (im) mobilization and bioavailability of heavy metals in the soil-plant system. In *Reviews of environmental contamination and toxicology* (pp. 1–44). Springer, New York, NY.
- Bolan, N., Kunhikrishnan, A., Thangarajan, R., Kumpiene, J., Park, J., Makino, T., & Scheckel, K. (2014). Remediation of heavy metal (loid) s contaminated soils-to mobilize or to immobilize. *Journal of Hazardous Materials*, 266, 141-166.
- Borchard, N., Wolf, A., Laabs, V., Aeckersberg, R., Scherer, H. W., Moeller, A., & Amelung, W. (2012). Physical activation of biochar and its meaning for soil fertility and nutrient leaching–a greenhouse experiment. *Soil Use and Management, 28*, 177-184.
- Campbell, P. G. (2007). Cadmium—a priority pollutant. *Environmental Chemistry*, *3*, 387-388.
- Cantrell, K. B., Hunt, P. G., Uchimiya, M., Novak, J. M., & Ro, K. S. (2012). Impact of pyrolysis temperature and manure source on physico-chemical characteristics of biochar. *Bioresource Technology*, *107*, 419-428.

- Cao, X., & Harris, W. (2010). Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Bioresource Technology*, 101, 5222-5228.
- Cao, X., Ma, L., Gao, B., & Harris, W. (2009). Dairy-manure derived biochar effectively sorbs lead and atrazine. *Environmental Science & Technology*, 43, 3285-3291.
- Cao, X., Ma, L., Liang, Y., Gao, B., & Harris, W. (2011). Simultaneous immobilization of lead and atrazine in contaminated soils using dairy-manure biochar. *Environmental Science & Technology*, 45, 4884-4889.
- Chan, K. Y., & Xu, Z. (2009). Biochar: nutrient properties and their enhancement. In *Biochar for environmental management* (pp. 67-84). London, UK: Earthscan.
- Chen, B., & Chen, Z. (2009). Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. *Chemosphere*, *76*, 127-133.
- Chen, B., Chen, Z., & Lv, S. (2011a). A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. *Bioresource Technology*, 102, 716-723.
- Chen, B., Zhou, D., and Zhu, L. (2008). Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environmental Science & Technology*, *42*, 5137-5143.
- Chen, D., Xie, S., Chen, C., Quan, H., Hua, L., Luo, X., & Guo, L. (2017). Activated biochar derived from pomelo peel as a high-capacity sorbent for removal of carbamazepine from aqueous solution. *RSC Advances*, *7*, 54969-54979.
- Chen, G. C., Shan, X. Q., Wang, Y. S., Pei, Z. G., Shen, X. E., Wen, B., & Owens, G. (2008). Effects of copper, lead, and cadmium on the sorption and desorption of atrazine onto and from carbon nanotubes. *Environmental Science & Technology*, 42, 8297-8302.
- Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M. B., & Hay, A. G. (2011b). Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. *Bioresource Technology*, 102, 8877-8884.
- Cheng, C. H., & Lehmann, J. (2009). Ageing of black carbon along a temperature gradient. *Chemosphere*, 75, 1021-1027.
- Cheng, C. H., Lehmann, J., Thies, J. E., Burton, S. D., & Engelhard, M. H. (2006). Oxidation of black carbon by biotic and abiotic processes. *Organic Geochemistry*, *37*, 1477-1488.
- Cheng, H., & Hu, Y. (2010). Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: a review. *Environmental Pollution*, 158, 1134-1146.

- Cheng, T. W., Lee, M. L., Ko, M. S., Ueng, T. H., & Yang, S. F. (2012). The heavy metal adsorption characteristics on metakaolin-based geopolymer. *Applied Clay Science*, *56*, 90-96.
- Cheung, C. W., Porter, J. F., & McKay, G. (2000). Elovich equation and modified second- order equation for sorption of cadmium ions onto bone char. *Journal of Chemical Technology and Biotechnology*, *75*, 963-970.
- Chingombe, P., Saha, B., & Wakeman, R. J. (2005). Surface modification and characterisation of a coal-based activated carbon. *Carbon*, 43, 3132-3143.
- Chlopecka, A., Bacon, J. R., Wilson, M. J., & Kay, J. (1996). Forms of cadmium, lead, and zinc in contaminated soils from southwest Poland. *Journal of Environmental Quality*, 25, 69-79.
- Chun, Y., Sheng, G., Chiou, C. T., & Xing, B. (2004). Compositions and sorptive properties of crop residue-derived chars. *Environmental Science & Technology*, 38, 4649-4655.
- Claoston, N. (2015). Immobilisation of arsenic, copper, manganese and lead in gold mine tailings by oil palm empty fruit bunch and rice husk biochars pyrolysed at different temperatures (MSc thesis). Universiti Putra Malaysia.
- Claoston, N., Samsuri, A. W., Ahmad Husni, M. H., & Mohd Amran, M. S. (2014). Effects of pyrolysis temperature on the physico-chemical properties of empty fruit bunch and rice husk biochars. *Waste Management & Research*, 32, 331-339.
- Coelho, G. F., GonÇalves Jr, A. C., Nóvoa-Muñoz, J. C., Fernández-Calviño, D., Arias-Estévez, M., Fernández-Sanjurjo, M. J.,& Núñez-Delgado, A. (2016). Competitive and non-competitive cadmium, copper and lead sorption/desorption on wheat straw affecting sustainability in vineyards. *Journal of Cleaner Production*, 139, 1496-1503.
- Cornelissen, G., Gustafsson, Ö., Bucheli, T. D., Jonker, M. T., Koelmans, A. A., & van Noort, P. C. (2005). Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environmental Science & Technology*, *39*, 6881-6895.
- Cotten, G. B., & Eldredge, H. B. (2002). Nanolevel magnetic separation model considering flow limitations. *Separation Science and Technology*, *37*, 3755-3779.
- Cui, X., Fang, S., Yao, Y., Li, T., Ni, Q., Yang, X., & He, Z. (2016). Potential mechanisms of cadmium removal from aqueous solution by Canna indica derived biochar. *Science of the Total Environment*, 562, 517-525.
- Dabrowski, A. (2001). Adsorption—from theory to practice. *Advances in Colloid and Interface Science*, *93*, 135-224.

- Dahlawi, S., Naeem, A., Rengel, Z., & Naidu, R. (2018). Biochar application for the remediation of salt-affected soils: Challenges and opportunities. *Science of The Total Environment*, 625, 320-335.
- De Matos, A. T., Fontes, M. P. F., Da Costa, L. M., & Martinez, M. A. (2001). Mobility of heavy metals as related to soil chemical and mineralogical characteristics of Brazilian soils. *Environmental Pollution*, 111, 429-435.
- De Matos, A. T., Fontes, M. P. F., Jordão, C. P., & Da Costa, L. M. (1996). Heavy metals mobility and retention forms in a Brazilian Oxisol. *Revista Brasileira de Ciencia do Solo (Brazil)*.
- Demirbas, A. (2008). Heavy metal adsorption onto agro-based waste materials: a review. *Journal of Hazardous Materials*, 157, 220-229.
- Demirbas, A. (2009). Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review. *Journal of Hazardous Materials*, 167, 1-9.
- Dieguez Alonso, A. (2015). Fixed-bed biomass pyrolysis: mechanisms and biochar production. Univ. Berlin Dissertati.
- Ding, W., Dong, X., Ime, I. M., Gao, B., & Ma, L. Q. (2014). Pyrolytic temperatures impact lead sorption mechanisms by bagasse biochars. *Chemosphere*, 105, 68-74.
- Dong, X., Ma, L. Q., & Li, Y. (2011). Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing. *Journal of Hazardous Materials*, 190, 909-915.
- Doumer, M. E., Rigol, A., Vidal, M., & Mangrich, A. S. (2016). Removal of Cd, Cu, Pb, and Zn from aqueous solutions by biochars. *Environmental Science and Pollution Research*, 23, 2684-2692.
- Downie, A., Crosky, A., & Munroe, P. (2009). Physical properties of biochar. In *Biochar for environmental management: science and technology* (pp. 13–32). London, UK: Earthscan.
- Doyle, J. J. (1977). Effects of low levels of dietary cadmium in animals—A review. Journal of Environmental Quality, 6, 111-116.
- Du, Y., Lian, F., & Zhu, L. (2011). Biosorption of divalent Pb, Cd and Zn on aragonite and calcite mollusk shells. *Environmental Pollution*, 159, 1763-1768.
- Duku, M. H., Gu, S., & Hagan, E. B. (2011). Biochar production potential in Ghana— A review. *Renewable and Sustainable Energy Reviews*, 15, 3539-3551.
- Echeverria, J. C., Morera, M. T., Mazkiaran, C., & Garrido, J. J. (1998). Competitive sorption of heavy metal by soils. Isotherms and fractional factorial experiments. *Environmental Pollution*, *101*, 275-284.

- Ferreira Fontes, M. P., de Matos, A. T., da Costa, L. M., & Lima Neves, J. C. (2000). Competitive adsorption of zinc, cadmium, copper, and lead in three highlyweathered Brazilian soils. *Communications in Soil Science and Plant Analysis*, 31, 2939-2958.
- Foo, K. Y., & Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal, 156*, 2-10.
- Fu, F., & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: a review. Journal of Environmental Management, 92, 407-418.
- Ghorbel-Abid, I., & Trabelsi-Ayadi, M. (2015). Competitive adsorption of heavy metals on local landfill clay. *Arabian Journal of Chemistry*, 8, 25-31.
- Giles, C. H., Smith, D., & Huitson, A. (1974). A general treatment and classification of the solute adsorption isotherm. I. Theoretical. *Journal of Colloid and Interface Science*, 47, 755-765.
- Gillman, G. P., & Sumpter, E. A. (1986). Modification to the compulsive exchange method for measuring exchange characteristics of soils. *Soil Research*, 24, 61-66.
- Godwin, H. A. (2001). The biological chemistry of lead. *Current Opinion in Chemical Biology*, 5, 223-227.
- Goertzen, S. L., Thériault, K. D., Oickle, A. M., Tarasuk, A. C., & Andreas, H. A. (2010). Standardization of the Boehm titration. Part I. CO2 expulsion and endpoint determination. *Carbon*, 48, 1252-1261.
- Goswami, R., Shim, J., Deka, S., Kumari, D., Kataki, R., & Kumar, M. (2016). Characterization of cadmium removal from aqueous solution by biochar produced from Ipomoea fistulosa at different pyrolytic temperatures. *Ecological Engineering*, 97, 444-451.
- Gray, C. W., Dunham, S. J., Dennis, P. G., Zhao, F. J., & McGrath, S. P. (2006). Field evaluation of in situ remediation of a heavy metal contaminated soil using lime and red-mud. *Environmental Pollution*, 142, 530-539.
- Guo, Y., & Rockstraw, D. A. (2007). Activated carbons prepared from rice hull by one-step phosphoric acid activation. *Microporous and Mesoporous Materials*, *100*, 12-19.
- Gupta, V. K., Jain, C. K., Ali, I., Sharma, M., & Saini, V. K. (2003). Removal of cadmium and nickel from wastewater using bagasse fly ash—a sugar industry waste. *Water research*, *37*, 4038-4044.
- Gupta, V. K., Kumar, R., Nayak, A., Saleh, T. A., & Barakat, M. A. (2013). Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review. *Advances in Colloid and Interface Science*, 193, 24-34.

- Gwenzi, W., Chaukura, N., Mukome, F. N., Machado, S., & Nyamasoka, B. (2015). Biochar production and applications in sub-Saharan Africa: Opportunities, constraints, risks and uncertainties. *Journal of Environmental Management*, 150, 250-261.
- Hale, S., Hanley, K., Lehmann, J., Zimmerman, A., & Cornelissen, G. (2011). Effects of chemical, biological, and physical aging as well as soil addition on the sorption of pyrene to activated carbon and biochar. *Environmental Science & Technology*, 45, 10445-10453.
- Hale, S., Hanley, K., Lehmann, J., Zimmerman, A., & Cornelissen, G. (2011). Effects of chemical, biological, and physical aging as well as soil addition on the sorption of pyrene to activated carbon and biochar. *Environmental Science & Technology*, 45, 10445-10453.
- Hammes, K., & Schmidt, M. W. (2009). Changes of Biochar in Soil. In *Biochar for Environmental Management* (pp. 169-182). London, UK: Earthscan.
- Han, Y., Cao, X., Ouyang, X., Sohi, S. P., & Chen, J. (2016). Adsorption kinetics of magnetic biochar derived from peanut hull on removal of Cr (VI) from aqueous solution: effects of production conditions and particle size. *Chemosphere*, 145, 336-341.
- Han, Z., Sani, B., Mrozik, W., Obst, M., Beckingham, B., Karapanagioti, H. K., & Werner, D. (2015). Magnetite impregnation effects on the sorbent properties of activated carbons and biochars. *Water Research*, 70, 394-403.
- Harikishore, D., K. Reddy, & S.-M. Lee. 2014. Magnetic biochar composite: Facile synthesis, characterization, and application for heavy metal removal. *Colloids and Surfaces A: Physicochem. Engineering Aspects*, 454, 96–103.
- Harvey, O. R., Herbert, B. E., Rhue, R. D., & Kuo, L. J. (2011). Metal interactions at the biochar-water interface: energetics and structure-sorption relationships elucidated by flow adsorption microcalorimetry. *Environmental Science & Technology*, 45, 5550-5556.
- He, K., Wang, S., & Zhang, J. (2009). Blood lead levels of children and its trend in China. *Science of the Total Environment*, 407, 3986-3993.
- Herath, I., Kumarathilaka, P., Navaratne, A., Rajakaruna, N., & Vithanage, M. (2015). Immobilization and phytotoxicity reduction of heavy metals in serpentine soil using biochar. *Journal of Soils and Sediments*, *15*, 126-138.
- Ho, S. H., Yang, Z. K., Nagarajan, D., Chang, J. S., & Ren, N. Q. (2017). Highefficiency removal of lead from wastewater by biochar derived from anaerobic digestion sludge. *Bioresource Technology*, 246, 142-149.

- Hooper, K., Iskander, M., Sivia, G., Hussein, F., Hsu, J., DeGuzman, M., & Simmons, B. (1998). Toxicity characteristic leaching procedure fails to extract oxoanion-forming elements that are extracted by municipal solid waste leachates. *Environmental Science & Technology*, 32, 3825-3830.
- Houben, D., Evrard, L., & Sonnet, P. (2013a). Mobility, bioavailability and pHdependent leaching of cadmium, zinc and lead in a contaminated soil amended with biochar. *Chemosphere*, *92*, 1450-1457.
- Houben, D., Evrard, L., & Sonnet, P. (2013b). Beneficial effects of biochar application to contaminated soils on the bioavailability of Cd, Pb and Zn and the biomass production of rapeseed (Brassica napus L.). *Biomass and Bioenergy*, 57, 196-204.
- Hu, X., Ding, Z., Zimmerman, A. R., Wang, S., & Gao, B. (2015). Batch and column sorption of arsenic onto iron-impregnated biochar synthesized through hydrolysis. *Water Research*, 68, 206-216.
- Hussain, M., Farooq, M., Nawaz, A., Al-Sadi, A. M., Solaiman, Z. M., Alghamdi, S. S., & Siddique, K. H. (2017). Biochar for crop production: potential benefits and risks. *Journal of Soils and Sediments*, 17, 685-716.
- IBI. 2015. Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil. International biochar initiative (November): 1–61.
- Ifthikar, J., Wang, J., Wang, Q., Wang, T., Wang, H., Khan, A., & Chen, Z. (2017). Highly efficient lead distribution by magnetic sewage sludge biochar: sorption mechanisms and bench applications. *Bioresource Technology*, 238, 399-406.
- Igalavithana, A. D., Lee, S. E., Lee, Y. H., Tsang, D. C., Rinklebe, J., Kwon, E. E., & Ok, Y. S. (2017). Heavy metal immobilization and microbial community abundance by vegetable waste and pine cone biochar of agricultural soils. *Chemosphere*, 174, 593-603.
- Inyang, M. I., Gao, B., Yao, Y., Xue, Y., Zimmerman, A., Mosa, A., & Cao, X. (2016). A review of biochar as a low-cost adsorbent for aqueous heavy metal removal. *Critical Reviews in Environmental Science and Technology*, *46*, 406-433.
- Inyang, M., Gao, B., Ding, W., Pullammanappallil, P., Zimmerman, A. R., & Cao, X. (2011). Enhanced lead sorption by biochar derived from anaerobically digested sugarcane bagasse. *Separation Science and Technology*, 46, 1950-1956.

Inyang, M., Gao, B., Yao, Y., Xue, Y., Zimmerman, A. R., Pullammanappallil, P., & Cao, X. (2012). Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass. *Bioresource Technology*, 110, 50-56.

- Ippolito, J. A., Strawn, D. G., Scheckel, K. G., Novak, J. M., Ahmedna, M., & Niandou, M. A. S. (2012). Macroscopic and molecular investigations of copper sorption by a steam-activated biochar. *Journal of Environmental Quality*, 41, 1150-1156.
- Ishak, C. F., & Abdullah, R. (2014). In-situ immobilization of selected heavy metals in soil using agricultural wastes and industrial by-products. *In* Proc. of MARCO-FFTC Joint International Seminar on Management and Remediation Technologies of Rural Soils Contaminated by Heavy Metals and Radioactive Materials. Taichung, Taiwan, 22-26.
- Jaafar, N. M., Clode, P. L., & Abbott, L. K. (2015). Soil microbial responses to biochars varying in particle size, surface and pore properties. *Pedosphere*, 25, 770-780.
- Jaafar, S. K., & Boehm, A. B. (2014). Escherichia coli removal in biochar-augmented biofilter: Effect of infiltration rate, initial bacterial concentration, biochar particle size, and presence of compost. *Environmental Science & Technology*, 48, 11535-11542.
- Jayaweera, P., Hettiarachchi, S., & Ocken, H. (1994). Determination of the high temperature zeta potential and pH of zero charge of some transition metal oxides. *Colloids and Surfaces A: Physico-chemical and Engineering Aspects*, 85, 19-27.
- Jennings, A. A. (2013). Analysis of worldwide regulatory guidance values for the most commonly regulated elemental surface soil contamination. *Journal of Environmental Management, 118*, 72-95.
- Jiang, J., & Xu, R. K. (2013). Application of crop straw derived biochars to Cu (II) contaminated Ultisol: evaluating role of alkali and organic functional groups in Cu (II) immobilization. *Bioresource Technology*, 133, 537-545.
- Jiang, K., & Zhou, K. (2018). Chemical immobilization of lead, cadmium, and arsenic in a smelter-contaminated soil using 2, 4, 6-trimercaptotriazine, trisodium salt, nonahydrate and ferric sulfate. *Journal of Soils and Sediments*, 18, 1060-1065.
- Jiang, T. Y., Jiang, J., Xu, R. K., & Li, Z. (2012). Adsorption of Pb (II) on variable charge soils amended with rice-straw derived biochar. *Chemosphere*, 89, 249-256.
- Jiang, X. J., Luo, Y. M., Liu, Q., Liu, S. L., & Zhao, Q. G. (2004). Effects of cadmium on nutrient uptake and translocation by Indian Mustard. *Environmental Geochemistry and Health*, 26, 319-324.
- Jien, S. H., & Wang, C. S. (2013). Effects of biochar on soil properties and erosion potential in a highly weathered soil. *Catena*, 110, 225-233.

- Jindo, K., Mizumoto, H., Sawada, Y., Sanchez-Monedero, M. A., & Sonoki, T. (2014). Physical and chemical characterization of biochars derived from different agricultural residues. *Biogeosciences*, 11, 6613-6621.
- Johns, M. M., Marshall, W. E., & Toles, C. A. (1998). Agricultural by- products as granular activated carbons for adsorbing dissolved metals and organics. Journal of Chemical Technology & Biotechnology: International Research in Process, *Environmental and Clean Technology*, 71, 131-140.
- Jones, D. R., Jarrett, J. M., Tevis, D. S., Franklin, M., Mullinix, N. J., Wallon, K. L., & Jones, R. L. (2017). Analysis of whole human blood for Pb, Cd, Hg, Se, and Mn by ICP-DRC-MS for biomonitoring and acute exposures. *Talanta*, 162, 114-122.
- Joseph, S. D., Camps-Arbestain, M., Lin, Y., Munroe, P., Chia, C. H., Hook, J., & Lehmann, J. (2010). An investigation into the reactions of biochar in soil. *Soil Research*, 48, 501-515.
- Joseph, S., Peacocke, C., Lehmann, J., & Munroe, P. (2009). Developing a biochar classification and test methods. In *Biochar for environmental management: Science and Technology* (pp. 107-126). London, UK: Earthscan.
- Jung, K. W., Hwang, M. J., Jeong, T. U., & Ahn, K. H. (2015). A novel approach for preparation of modified-biochar derived from marine macroalgae: dual purpose electro-modification for improvement of surface area and metal impregnation. *Bioresource Technology*, 191, 342-345.
- Kalijadis, A. M., Vukčević, M. M., Jovanović, Z. M., Laušević, Z. V., & Laušević, M. D. (2011). Characterization of surface oxygen groups on different carbon materials by the Boehm method and temperature programmed desorption. *Journal of the Serbian Chemical Society*, 76, 757-768.
- Kalra, Y. (Ed.). (1997). Handbook of reference methods for plant analysis. Florida. CRC press.
- Karami, N., Clemente, R., Moreno-Jiménez, E., Lepp, N. W., & Beesley, L. (2011).
 Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass. *Journal of Hazardous Materials*, 191, 41-48.
- Karunanayake, A. G., Todd, O. A., Crowley, M., Ricchetti, L., Pittman Jr, C. U., Anderson, R., & Mlsna, T. (2018). Lead and cadmium remediation using magnetized and nonmagnetized biochar from Douglas fir. *Chemical Engineering Journal*, 331, 480-491.
- Kasuya, M. (2000). Recent epidemiological studies on itai-itai disease as a chronic cadmium poisoning in Japan. *Water Science and Technology*, 42, 147-154.

- Khairy, M., El-Safty, S. A., & Shenashen, M. A. (2014). Environmental remediation and monitoring of cadmium. *TrAC Trends in Analytical Chemistry*, 62, 56-68.
- Kikuchi, Y., Qian, Q., Machida, M., & Tatsumoto, H. (2006). Effect of ZnO loading to activated carbon on Pb (II) adsorption from aqueous solution. *Carbon, 44*, 195-202.
- Kim, W. K., Shim, T., Kim, Y. S., Hyun, S., Ryu, C., Park, Y. K., & Jung, J. (2013). Characterization of cadmium removal from aqueous solution by biochar produced from a giant Miscanthus at different pyrolytic temperatures. *Bioresource Technology*, 138, 266-270.
- Kistler, R. C., Widmer, F., & Brunner, P. H. (1987). Behavior of chromium, nickel, copper, zinc, cadmium, mercury, and lead during the pyrolysis of sewage sludge. *Environmental Science & Technology*, 21, 704-708.
- Kobya, M., Demirbas, E., Senturk, E., & Ince, M. (2005). Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. *Bioresource Technology*, 96, 1518-1521.
- Kołodyńska, D., Krukowska, J., & Thomas, P. (2017). Comparison of sorption and desorption studies of heavy metal ions from biochar and commercial active carbon. *Chemical Engineering Journal*, 307, 353-363.
- Kołodyńska, D., Wnętrzak, R., Leahy, J. J., Hayes, M. H. B., Kwapiński, W., & Hubicki, Z. (2012). Kinetic and adsorptive characterization of biochar in metal ions removal. *Chemical Engineering Journal*, 197, 295-305.
- Kołtowski, M., Charmas, B., Skubiszewska-Zięba, J., & Oleszczuk, P. (2017). Effect of biochar activation by different methods on toxicity of soil contaminated by industrial activity. *Ecotoxicology and Environmental Safety*, 136, 119-125.
- Kong, L., Xiong, Y., Sun, L., Tian, S., Xu, X., Zhao, C., & Liu, H. (2014b). Sorption performance and mechanism of a sludge-derived char as porous carbon-based hybrid adsorbent for benzene derivatives in aqueous solution. *Journal of Hazardous Materials*, 274, 205-211.
- Kong, S. H., Loh, S. K., Bachmann, R. T., Rahim, S. A., & Salimon, J. (2014 a). Biochar from oil palm biomass: a review of its potential and challenges. *Renewable and Sustainable Energy Reviews*, 39, 729-739.
- Kopittke, P. M., Asher, C. J., & Menzies, N. W. (2008). Prediction of Pb speciation in concentrated and dilute nutrient solutions. *Environmental Pollution*, 153, 548-554.
- Kumar, A. S. K., Gupta, T., Kakan, S. S., Kalidhasan, S., Rajesh, V., & Rajesh, N. (2012). Effective adsorption of hexavalent chromium through a three center (3c) co-operative interaction with an ionic liquid and biopolymer. *Journal of Hazardous Materials, 239*, 213-224.

- Kunhikrishnan, A. Bibi, I., Bolan, N., Seshadri, B., Choppala, G., Niazi, N. K., Kim, W., and Ok, Y. S. (2015). Biochar for Inorganic Contaminant Management in Waste and Wastewater. In *Biochar: Production, Characterization, and Applications* (pp. 167-219). Taylor & Francis Group. CRC Press.
- Laidler, K. J., & Meiser, J. H. (1999). *Physical Chemistry*. 3rd ed. Houghton Mifflin. Boston.
- Laird, D., Fleming, P., Wang, B., Horton, R., & Karlen, D. (2010). Biochar impact on nutrient leaching from a Midwestern agricultural soil. *Geoderma*, 158, 436-442.
- Lao, C., Zeledón, Z., Gamisans, X., & Solé, M. (2005). Sorption of Cd (II) and Pb (II) from aqueous solutions by a low-rank coal (leonardite). Separation and Purification Technology, 45, 79-85.
- Lee, J. W., Kidder, M., Evans, B. R., Paik, S., Buchanan Iii, A. C., Garten, C. T., & Brown, R. C. (2010). Characterization of biochars produced from cornstovers for soil amendment. *Environmental Science & Technology*, 44, 7970-7974.

Lehmann, J. (2007). A handful of carbon. Nature, 447, 143-144.

- Lehmann, J., & Joseph, S. (2009). Biochar for environmental management: an introduction. In *Biochar for Environmental Management* (pp. 1-12). London, UK: Earthscan.
- Levy, D. B., Barbarick, K. A., Siemer, E. G., & Sommers, L. E. (1992). Distribution and partitioning of trace metals in contaminated soils near Leadville, Colorado. *Journal of Environmental Quality*, 21, 185-195.
- Li, H., Dong, X., da Silva, E. B., de Oliveira, L. M., Chen, Y., & Ma, L. Q. (2017). Mechanisms of metal sorption by biochars: biochar characteristics and modifications. *Chemosphere*, 178, 466-478.
- Li, J. H., Lv, G. H., Bai, W. B., Liu, Q., Zhang, Y. C., & Song, J. Q. (2016). Modification and use of biochar from wheat straw (*Triticum aestivum* L.) for nitrate and phosphate removal from water. *Desalination and Water Treatment*, 57, 4681-4693.
- Li, L., Zheng, C., Fu, Y., Wu, D., Yang, X., & Shen, H. (2012). Silicate-mediated alleviation of Pb toxicity in banana grown in Pb-contaminated soil. *Biological Trace Element Research*, 145, 101-108.
- Li, Y., Shao, J., Wang, X., Deng, Y., Yang, H., & Chen, H. (2014). Characterization of modified biochars derived from bamboo pyrolysis and their utilization for target component (furfural) adsorption. *Energy & Fuels, 28*, 5119-5127.
- Lian, F., Sun, B., Song, Z., Zhu, L., Qi, X., & Xing, B. (2014). Physico-chemical properties of herb-residue biochar and its sorption to ionizable antibiotic sulfamethoxazole. *Chemical Engineering Journal*, 248, 128-134.

- Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'neill, B., & Neves, E. G. (2006). Black carbon increases cation exchange capacity in soils. *Soil Science Society of America Journal*, 70, 1719-1730.
- Liang, S., Guo, X. Y., Feng, N. C., & Tian, Q. H. (2010). Effective removal of heavy metals from aqueous solutions by orange peel xanthate. *Transactions of Nonferrous Metals Society of China*, 20, s187-s191.
- Liu, W. J., Jiang, H., & Yu, H. Q. (2015). Development of biochar-based functional materials: toward a sustainable platform carbon material. *Chemical Reviews*, 115, 12251-12285.
- Lomaglio, T., Hattab-Hambli, N., Miard, F., Lebrun, M., Nandillon, R., Trupiano, D., & Morabito, D. (2017). Cd, Pb, and Zn mobility and (bio) availability in contaminated soils from a former smelting site amended with biochar. *Environmental Science and Pollution Research*, 1-13.
- Lu, H., Zhang, W., Yang, Y., Huang, X., Wang, S., & Qiu, R. (2012). Relative distribution of Pb²⁺ sorption mechanisms by sludge-derived biochar. *Water Research*, 46, 854-862.
- Lu, K., Yang, X., Gielen, G., Bolan, N., Ok, Y. S., Niazi, N. K., & Liu, D. (2017). Effect of bamboo and rice straw biochars on the mobility and redistribution of heavy metals (Cd, Cu, Pb and Zn) in contaminated soil. *Journal of Environmental Management, 186*, 285-292.
- Lu, K., Yang, X., Shen, J., Robinson, B., Huang, H., Liu, D., & Wang, H. (2014). Effect of bamboo and rice straw biochars on the bioavailability of Cd, Cu, Pb and Zn to Sedum plumbizincicola. Agriculture, Ecosystems & Environment, 191, 124-132.
- Ma, L., Xu, R., & Jiang, J. (2010). Adsorption and desorption of Cu (II) and Pb (II) in paddy soils cultivated for various years in the subtropical China. *Journal of Environmental Sciences*, 22, 689-695.
- Mahar, A., Ping, W. A. N. G., Ronghua, L. I., & Zhang, Z. (2015). Immobilization of lead and cadmium in contaminated soil using amendments: a review. *Pedosphere*, 25, 555-568.
- Mahmood, Q., Rashid, A., Ahmad, S. S., Azim, M. R., & Bilal, M. (2012). Current status of toxic metals addition to environment and its consequences. In *The Plant Family Brassicaceae* (pp. 35-69). Dordrecht, Springer.
- Malaysian Palm Oil Board (2012). Malaysian Oil Palm Statistics, 2011. Malaysian Palm Oil Board (MPOB), Malaysia
- McBeath, A. V., & Smernik, R. J. (2009). Variation in the degree of aromatic condensation of chars. *Organic Geochemistry*, 40, 1161-1168.

- McBride, M., Sauve, S., & Hendershot, W. (1997). Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *European Journal of Soil Science*, 48, 337-346.
- McBride, M.B. 1994. Environmental Chemistry of Soils. Oxford Univ. NY, Press.
- McGrath, S. P., & Cunliffe, C. H. (1985). A simplified method for the extraction of the metals Fe, Zn, Cu, Ni, Cd, Pb, Cr, Co and Mn from soils and sewage sludges. *Journal of the Science of Food and Agriculture, 36*, 794-798.
- McGuinness, M., & Dowling, D. (2009). Plant-associated bacterial degradation of toxic organic compounds in soil. *International journal of Environmental and Public Health*, 6, 2226-2247.
- McLean, J. E., Bledsoe, B. E., & Sourcebook, E. E. A. (1996). Behavior of metals in soils. EPA Environmental Assessment Sourcebook, 19.
- McLean, J.E., and B.E. Bledsoe. 1992. Behavior of Metals in Soils. EPA Ground Water Issue. Environmental Protection Agency, Washington.EPA 540-S-92-018:25PP.
- Meers, E., Van Slycken, S., Adriaensen, K., Ruttens, A., Vangronsveld, J., Du Laing, G., & Tack, F. M. G. (2010). The use of bio-energy crops (*Zea mays*) for 'phytoattenuation'of heavy metals on moderately contaminated soils: a field experiment. *Chemosphere*, 78, 35-41.
- Melo, L. C., Puga, A. P., Coscione, A. R., Beesley, L., Abreu, C. A., & Camargo, O. A. (2016). Sorption and desorption of cadmium and zinc in two tropical soils amended with sugarcane-straw-derived biochar. *Journal of Soils and Sediments*, 16, 226-234.
- Mohamed, I., Zhang, G. S., Li, Z. G., Liu, Y., Chen, F., & Dai, K. (2015). Ecological restoration of an acidic Cd contaminated soil using bamboo biochar application. *Ecological Engineering*, 84, 67-76.
- Mohan, D., & Pittman Jr, C. U. (2006). Activated carbons and low cost adsorbents for remediation of tri-and hexavalent chromium from water. *Journal of Hazardous Materials*, 137, 762-811.
- Mohan, D., & Singh, K. P. (2002). Single-and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste. *Water Research*, *36*, 2304-2318.
- Mohan, D., Kumar, H., Sarswat, A., Alexandre-Franco, M., & Pittman Jr, C. U. (2014). Cadmium and lead remediation using magnetic oak wood and oak bark fast pyrolysis bio-chars. *Chemical Engineering Journal, 236*, 513-528.
- Mohan, D., Pittman Jr, C. U., & Steele, P. H. (2006). Single, binary and multicomponent adsorption of copper and cadmium from aqueous solutions on Kraft lignin—a biosorbent. *Journal of Colloid and Interface Science*, 297, 489-504.

- Mohan, D., Pittman Jr, C. U., Bricka, M., Smith, F., Yancey, B., Mohammad, J., & Gong, H. (2007). Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. *Journal of Colloid and Interface Science*, 310, 57-73.
- Mohan, D., Singh, P., Sarswat, A., Steele, P. H., & Pittman Jr, C. U. (2015). Lead sorptive removal using magnetic and nonmagnetic fast pyrolysis energy cane biochars. *Journal of Colloid and Interface Science*, 448, 238-250.
- Mohanty, S. K., & Boehm, A. B. (2014). Escherichia coli removal in biocharaugmented biofilter: Effect of infiltration rate, initial bacterial concentration, biochar particle size, and presence of compost. *Environmental science & technology*, 48, 11535-11542.
- Mondal, M. K. (2009). Removal of Pb (II) ions from aqueous solution using activated tea waste: Adsorption on a fixed-bed column. *Journal of Environmental Management*, 90, 3266-3271.
- Mousavi, H. Z., Hosseinifar, A., & Jahed, V. (2010). Removal of Cu (II) from wastewater by waste tire rubber ash. *Journal of the Serbian Chemical Society*, 75, 845-853.
- Mukherjee, A., Zimmerman, A. R., & Harris, W. (2011). Surface chemistry variations among a series of laboratory-produced biochars. *Geoderma*, 163, 247-255.
- Nagodavithane, C. L., Singh, B., & Fang, Y. (2014). Effect of ageing on surface charge characteristics and adsorption behaviour of cadmium and arsenate in two contrasting soils amended with biochar. *Soil Research*, *52*, 155-163.
- Naidu, R., Bolan, N. S., Kookana, R. S., & Tiller, K. G. (1994). Ionic- strength and pH effects on the sorption of cadmium and the surface charge of soils. *European Journal of Soil Science*, *45*, 419-429.
- Namgay, T., Singh, B., & Singh, B. P. (2010). Influence of biochar application to soil on the availability of As, Cd, Cu, Pb, and Zn to maize (Zea mays L.). Soil Research, 48, 638-647.

Needleman, H. (2004). Lead poisoning. Annu. Rev. Med., 55, 209-222.

- Norazlina, A. S., Che, F. I., & Rosenani, A. B. (2014). Characterization of oil palm empty fruit bunch and rice husk biochars and their potential to adsorb arsenic and cadmium. *American Journal of Agricultural and Biological Sciences*, *9*, 450-456.
- Nordberg, G. F., Fowler, B. A., & Nordberg, M. (2015). Toxicology of metals: overview, definitions, concepts, and trends. In *Handbook on the Toxicology of Metals* (Fourth Edition) (pp. 1-12). San Diego, Academic Press.

- Novak, J. M., Busscher, W. J., Laird, D. L., Ahmedna, M., Watts, D. W., & Niandou, M. A. (2009). Impact of biochar amendment on fertility of a southeastern coastal plain soil. *Soil Science*, 174, 105-112.
- Ok, Y. S., Uchimiya, S. M., Chang, S. X., and Bolan, N. (Eds.). (2015). *Biochar: Production, Characterization, and Applications*. Taylor & Francis Group. CRC Press.
- Omer, S. A., Elobeid, M. A., Fouad, D., Daghestani, M. H., Al-Olayan, E. M., Elamin, M. H., & El-Mahassna, A. (2012). Cadmium bioaccumulation and toxicity in tilapia fish (Oreochromis niloticus). *Journal of Animal and Veterinary Advances*, 11, 1601-1606.
- Padmavathiamma, P. K., & Li, L. Y. (2007). Phytoremediation technology: hyperaccumulation metals in plants. *Water, Air, and Soil Pollution, 184*, 105-126.
- Park, J. H., Choppala, G. K., Bolan, N. S., Chung, J. W., & Chuasavathi, T. (2011). Biochar reduces the bioavailability and phytotoxicity of heavy metals. *Plant and Soil*, 348, 439-451.
- Park, J. H., Choppala, G., Lee, S. J., Bolan, N., Chung, J. W., & Edraki, M. (2013). Comparative sorption of Pb and Cd by biochars and its implication for metal immobilization in soils. *Water, Air, & Soil Pollution, 224*, 1711.
- Park, J. H., Ok, Y. S., Kim, S. H., Cho, J. S., Heo, J. S., Delaune, R. D., & Seo, D. C. (2015). Competitive adsorption of heavy metals onto sesame straw biochar in aqueous solutions. *Chemosphere*, 142, 77-83.
- Peng, Q., Liu, L., Luo, Y., Zhang, Y., Tan, W., Liu, F., & Qiu, G. (2016). Cadmium removal from aqueous solution by a deionization supercapacitor with a birnessite electrode. ACS Applied Materials & Interfaces, 8, 34405-34413.
- Puga, A. P., Abreu, C. A., Melo, L. C. A., & Beesley, L. (2015). Biochar application to a contaminated soil reduces the availability and plant uptake of zinc, lead and cadmium. *Journal of Environmental Management*, 159, 86-93.
- Qian, L., & Chen, B. (2014). Interactions of aluminum with biochars and oxidized biochars: Implications for the biochar aging process. *Journal of agricultural and food chemistry*, 62, 373-380.
- Rabileh, M. A., Shamshuddin, J., Panhwar, Q. A., Rosenani, A. B., & Anuar, A. R. (2015). Effects of biochar and/or dolomitic limestone application on the properties of Ultisol cropped to maize under glasshouse conditions. *Canadian Journal of Soil Science*, 95, 37-47.
- Raikwar, M. K., Kumar, P., Singh, M., & Singh, A. (2008). Toxic effect of heavy metals in livestock health. *Veterinary World*, 1, 28-30.

- Rajapaksha, A. U., Chen, S. S., Tsang, D. C., Zhang, M., Vithanage, M., Mandal, S., & Ok, Y. S. (2016). Engineered/designer biochar for contaminant removal/immobilization from soil and water: potential and implication of biochar modification. *Chemosphere*, 148, 276-291.
- Reddy, D. H. K., & Lee, S. M. (2014). Magnetic biochar composite: facile synthesis, characterization, and application for heavy metal removal. *Colloids and Surfaces A: Physico-chemical and Engineering Aspects, 454*, 96-103.
- Rengasamy, P., & Churchman, G. J. (1999). Cation exchange capacity, exchangeable cations and sodicity. In *Soil Analysis: an Interpretation Manual* (pp. 147–157). Melbourne, CSIRO.
- Renner, R. (2004). Plumbing the depths of DC's drinking water crisis. *Environmental Science & Technology*. 2004, 225A–227A.
- Ricordel, S., Taha, S., Cisse, I., & Dorange, G. (2001). Heavy metals removal by adsorption onto peanut husks carbon: characterization, kinetic study and modeling. *Separation and Purification Technology*, 24, 389-401.
- Rieuwerts, J. S. (2007). The mobility and bioavailability of trace metals in tropical soils: a review. *Chemical Speciation & Bioavailability*, 19, 75-85.
- Ritter, J. A., Bhadra, S. J., & Ebner, A. D. (2011). On the use of the dual-process Langmuir model for correlating unary equilibria and predicting mixed-gas adsorption equilibria. *Langmuir*, 27, 4700-4712.
- Rodríguez-Vila, A., Covelo, E. F., Forján, R., & Asensio, V. (2014). Phytoremediating a copper mine soil with Brassica juncea L., compost and biochar. *Environmental Science and Pollution Research*, 21, 11293-11304.
- Rutherford, D.W., Wershaw, R.L., & Reeves III, J.B., 2008, Development of acid functional groups and lactones during the thermal degradation of wood and wood components: U.S. Geological Survey Scientific Investigations Report 2007–5013, 43 p.
- Samsuri, A. W., Sadegh-Zadeh, F., & Seh-Bardan, B. J. (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*, 981-988.
- Samsuri, A. W., Sadegh-Zadeh, F., & Seh-Bardan, B. J. (2014). Characterization of biochars produced from oil palm and rice husks and their adsorption capacities for heavy metals. *International Journal of Environmental Science and Technology*, 11, 967-976.

- Santos-Francés, F., Martínez-Graña, A., Alonso Rojo, P., & García Sánchez, A. (2017). Geochemical background and baseline values determination and spatial distribution of heavy metal pollution in soils of the Andes Mountain range (Cajamarca-Huancavelica, Peru). *International journal of Environmental Research and Public Health*, 14, 1-22.
- Sarwar, N., Imran, M., Shaheen, M. R., Ishaque, W., Kamran, M. A., Matloob, A., & Hussain, S. (2017). Phytoremediation strategies for soils contaminated with heavy metals: Modifications and future perspectives. *Chemosphere*, 171, 710-721.
- Savova, D., Apak, E., Ekinci, E., Yardim, F., Petrov, N., Budinova, T., & Minkova, V. (2001). Biomass conversion to carbon adsorbents and gas. *Biomass and Bioenergy*, 21(2), 133-142.
- Selatnia, A., Bakhti, M. Z., Madani, A., Kertous, L., & Mansouri, Y. (2004). Biosorption of Cd from aqueous solution by a NaOH-treated bacterial dead Streptomyces rimosus biomass. *Hydrometallurgy*, 75, 11-24.
- Selim, H. M. (Ed.). (2012). Competitive sorption and transport of heavy metals in soils and geological media. Taylor & Francis Group. CRC Press.
- Semenzin, E., Critto, A., Carlon, C., Rutgers, M., & Marcomini, A. (2007). Development of a site-specific ecological risk assessment for contaminated sites: part II. A multi-criteria based system for the selection of bioavailability assessment tools. *Science of the Total Environment*, 379, 34-45.
- Shamshuddin, J. & Fauziah, C. I. (2010). Weathered tropical soils: the ultisols and oxisols (Vol. 134). Serdang, UPM Press.

Shamshuddin, J. (2011). Methods in Soil Mineralogy. Universiti Putra Malaysia Press.

- Sharma, R., Sarswat, A., Pittman, C. U., & Mohan, D. (2017). Cadmium and lead remediation using magnetic and non-magnetic sustainable biosorbents derived from Bauhinia purpurea pods. *RSC Advances*, 7, 8606-8624.
- Shen, H., Zhang, W., Yang, Y., Huang, X., Wang, S., & Qiu, R. (2012). Relative distribution of Pb sorption mechanisms by sludge-derived biochar. *Water Research*, *46*, 854-862.
- Shen, Z., Jin, F., Wang, F., McMillan, O., & Al-Tabbaa, A. (2015). Sorption of lead by Salisbury biochar produced from British broadleaf hardwood. *Bioresource Technology*, 193, 553-556.
- Shen, Z., McMillan, O., Jin, F., & Al-Tabbaa, A. (2016). Salisbury biochar did not affect the mobility or speciation of lead in kaolin in a short-term laboratory study. *Journal of Hazardous Materials, 316*, 214-220.

- Shi, T., Jia, S., Chen, Y., Wen, Y., Du, C., Guo, H., & Wang, Z. (2009). Adsorption of Pb (II), Cr (III), Cu (II), Cd (II) and Ni (II) onto a vanadium mine tailing from aqueous solution. *Journal of Hazardous Materials*, *169*, 838-846.
- Singh, B. (2001). Heavy metals in soils: sources, chemical reactions and forms. In: Proceeding of 2nd Australia and New Zealand Conference on Environmental Geotechnics-Geo Environment 2001. Environmental Geotechnics.
- Singh, B., Camps-Arbestain, M., & Lehmann, J. (Eds.). (2017). *Biochar: a guide to analytical methods*. Csiro Publishing.
- Singh, B., Singh, B. P., & Cowie, A. L. (2010). Characterisation and evaluation of biochars for their application as a soil amendment. *Soil Research*, 48, 516-525.
- Singh, B., Singh, B. P., & Cowie, A. L. (2010). Characterisation and evaluation of biochars for their application as a soil amendment. *Soil Research*, 48, 516-525.
- Singh, R., Gautam, N., Mishra, A., & Gupta, R. (2011). Heavy metals and living systems: An overview. *Indian Journal of Pharmacology*, 43, 246-253.
- Singh, U. K., & Kumar, B. (2017). Pathways of heavy metals contamination and associated human health risk in Ajay River basin, India. *Chemosphere*, 174, 183-199.
- Sizmur, T., Fresno, T., Akgül, G., Frost, H., & Moreno-Jiménez, E. (2017). Biochar modification to enhance sorption of inorganics from water. *Bioresource Technology*, 246, 34-47.
- Smolders, E., & Mertens, J. (1995). Cadmium. In *Heavy Metals in Soils* (pp. 283–311): Springer, Netherlands.
- Sohi, S. P. (2012). Carbon storage with benefits. Science, 338, 1034-1035.
- Solaiman, Z. M., & Anawar, H. M. (2015). Application of biochars for soil constraints: challenges and solutions. *Pedosphere*, 105, 47-82.
- Son, E. B., Poo, K. M., Chang, J. S., & Chae, K. J. (2018). Heavy metal removal from aqueous solutions using engineered magnetic biochars derived from waste marine macro-algal biomass. *Science of the Total Environment*, 615, 161-168.
- Song, W., and Guo, M. (2012). Quality variations of poultry litter biochar generated at different pyrolysis temperatures. *Journal of Analytical and Applied Pyrolysis*, *94*, 138-145.
- Song, Z., Lian, F., Yu, Z., Zhu, L., Xing, B., & Qiu, W. (2014). Synthesis and characterization of a novel MnOx-loaded biochar and its adsorption properties for Cu²⁺ in aqueous solution. *Chemical Engineering Journal*, *242*, 36-42.
- Sposito, G. (2008). The chemistry of soils. Madison Avenue, NY, Oxford University Press.

- Srivastava, P., Singh, B., & Angove, M. (2005). Competitive adsorption behavior of heavy metals on kaolinite. *Journal of Colloid and Interface Science*, 290, 28-38.
- Stewart, K. J., & Janin, A. (2014). Leonardite and biochar for mine impacted water and soils. Technical Report prepared for Wapaw Bay Resources (No.1-25). Whitehorse: Yukon Research Centre, Yukon College.
- Stumm, W., and J.J. Morgan. 1996. Aquatic Chemistry, John Wiley & Sons. Inc., New York.
- Sud, D., Mahajan, G., & Kaur, M. P. (2008). Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions–A review. *Bioresource Technology*, 99, 6017-6027.
- Tan, K. H. (2010). Principles of soil chemistry. Boca Raton London, NY. CRC press.
- Tan, X. F., Liu, Y. G., Gu, Y. L., Xu, Y., Zeng, G. M., Hu, X. J. & Li, J. (2016). Biochar-based nano-composites for the decontamination of wastewater: a review. *Bioresource Technology*, 212, 318-333.
- Teh, C. B. S. and Talib, J. (2006). *Soil physics analyses: volume 1* (pp. 1-6). Universiti Putra Malaysia Press.
- Thinakaran, N., Subramani, S. E., Priya, T., Dhanalakshmi, N., Vineesh, T. V., & Kathikeyan, V. (2017). Electrochemical determination of Cd and Pb using NSAID- mefenamic acid functionalized mesoporous carbon microspheres modified glassy carbon electrode. *Electroanalysis*, 29, 1903-1910.
- Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J. P., Rodriguez-Reinoso, F., Rouquerol, J., & Sing, K. S. (2015). Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure and Applied Chemistry*, 87, 1051-1069.
- Tianlik, T. E. H., Norulaini, N. A. R. N., Shahadat, M., Yoonsing, W. O. N. G., & Omar, A. K. M. (2016). Risk assessment of metal contamination in soil and groundwater in Asia: a review of recent trends as well as existing environmental laws and regulations. *Pedosphere*, 26, 431-450.
- Tomaszewski, J. E., Werner, D., & Luthy, R. G. (2007). Activated carbon amendment as a treatment for residual DDT in sediment from a superfund site in San Francisco Bay, Richmond, California, USA. *Environmental Toxicology and Chemistry*, 26, 2143-2150.
- Tong, X. J., Li, J. Y., Yuan, J. H., & Xu, R. K. (2011). Adsorption of Cu (II) by biochars generated from three crop straws. *Chemical Engineering Journal*, 172, 828-834.

- Trakal, L., Bingöl, D., Pohořelý, M., Hruška, M., & Komárek, M. (2014). Geochemical and spectroscopic investigations of Cd and Pb sorption mechanisms on contrasting biochars: engineering implications. *Bioresource Technology*, 171, 442-451.
- Trakal, L., Veselská, V., Šafařík, I., Vítková, M., Číhalová, S., & Komárek, M. (2016). Lead and cadmium sorption mechanisms on magnetically modified biochars. *Bioresource Technology*, 203, 318-324.
- Tsai, W. T., Liu, S. C., Chen, H. R., Chang, Y. M., & Tsai, Y. L. (2012). Textural and chemical properties of swine-manure-derived biochar pertinent to its potential use as a soil amendment. *Chemosphere*, *89*, 198-203.
- Uchimiya, M. (2014). Influence of pH, ionic strength, and multidentate ligand on the interaction of CdII with biochars. *ACS Sustainable Chemistry & Engineering*, 2, 2019-2027.
- Uchimiya, M., Lima, I. M., Klasson, K. T., & Wartelle, L. H. (2010a). Contaminant immobilization and nutrient release by biochar soil amendment: roles of natural organic matter. *Chemosphere*, *80*, 935-940.
- Uchimiya, M., Lima, I. M., Thomas Klasson, K., Chang, S., Wartelle, L. H., & Rodgers, J. E. (2010b). Immobilization of heavy metal ions (CuII, CdII, NiII, and PbII) by broiler litter-derived biochars in water and soil. *Journal of Agricultural* and Food Chemistry, 58, 5538-5544.
- Uchimiya, M., S. Chang, & K.T. Klasson. (2011b). Screening biochars for heavy metal retention in soil: role of oxygen functional groups. *Journal Hazard. Materials* 190: 432–441.
- Uchimiya, M., Wartelle, L. H., Klasson, K. T., Fortier, C. A., & Lima, I. M. (2011a). Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil. *Journal of Agricultural and Food Chemistry*, 59, 2501-2510.
- Ugochukwu, N., Mohamed, I., Ali, M., Iqbal, J., Fu, Q., Zhu, J., & Hu, H. (2013). Impacts of inorganic ions and temperature on lead adsorption onto variable charge soils. *Catena*, 109, 103-109.
- USEPA (1997). Exposure factors handbook. Office of Research and Development, Washington. US Environmental Protect Agency.
- Van Poucke, R., Ainsworth, J., Maeseele, M., Ok, Y. S., Meers, E., & Tack, F. M. G. (2018). Chemical stabilization of Cd-contaminated soil using biochar. *Applied Geochemistry*, 88, 122-130.
- Van Zwieten, L., Kimber, S., Morris, S., Chan, K. Y., Downie, A., Rust, J., & Cowie, A. (2010). Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant and Soil*, 327, 235-246.

- Vareda, J. P., Valente, A. J., & Durães, L. (2016). Heavy metals in Iberian soils: Removal by current adsorbents/amendments and prospective for aerogels. Advances in Colloid and Interface Science, 237, 28-42.
- Vijaya, S., Ma, A. N., Choo, Y. M., & Nik Meriam, N. S. (2008). Life cycle inventory of the production of crude palm oil—A gate to gate case study of 12 palm oil mills. *Journal of Oil Palm Research, 20*, 484-494.
- Vodyanitskii, Y. N. (2016). Standards for the contents of heavy metals in soils of some states. *Annals of Agrarian Science*, 14, 257-263.
- Wang, H., Gao, B., Wang, S., Fang, J., Xue, Y., & Yang, K. (2015b). Removal of Pb (II), Cu (II), and Cd (II) from aqueous solutions by biochar derived from KMnO₄ treated hickory wood. *Bioresource Technology*, 197, 356-362.
- Wang, S. Y., Tang, Y. K., Li, K., Mo, Y. Y., Li, H. F., & Gu, Z. Q. (2014). Combined performance of biochar sorption and magnetic separation processes for treatment of chromium-contained electroplating wastewater. *Bioresource Technology*, 174, 67-73.
- Wang, S., Gao, B., Zimmerman, A. R., Li, Y., Ma, L., Harris, W. G., & Migliaccio, K. W. (2015a). Removal of arsenic by magnetic biochar prepared from pinewood and natural hematite. *Bioresource Technology*, 175, 391-395.
- Wang, X. J., Wang, Y., Wang, X., Liu, M., Xia, S. Q., Yin, D. Q., & Zhao, J. F. (2011). Microwave-assisted preparation of bamboo charcoal-based iron-containing adsorbents for Cr (VI) removal. *Chemical Engineering Journal*, 174, 326-332.
- Wang, Y., & Liu, R. (2017). Comparison of characteristics of twenty-one types of biochar and their ability to remove multi-heavy metals and methylene blue in solution. *Fuel Processing Technology*, 160, 55-63.
- Woldetsadik, D., Drechsel, P., Keraita, B., Marschner, B., Itanna, F., & Gebrekidan, H. (2016). Effects of biochar and alkaline amendments on cadmium immobilization, selected nutrient and cadmium concentrations of lettuce (*Lactuca sativa*) in two contrasting soils. *SpringerPlus*, 5, 1-16.
- World Health Organization (WHO). (2011). Guidelines for drinking-water quality. Geneva, WHO, 38, 104-8.
- Wu, H., Che, X., Ding, Z., Hu, X., Creamer, A. E., Chen, H., & Gao, B. (2016). Release of soluble elements from biochars derived from various biomass feedstocks. *Environmental Science and Pollution Research*, 23, 1905-1915.
- Wuana, R. A., & Okieimen, F. E. (2011). Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. *Isrn Ecology*, 2011.

- Xie, T., Reddy, K. R., Wang, C., Yargicoglu, E., & Spokas, K. (2015). Characteristics and applications of biochar for environmental remediation: a review. *Critical Reviews in Environmental Science and Technology*, 45, 939-969.
- Xiong, Z., Shihong, Z., Haiping, Y., Tao, S., Yingquan, C., & Hanping, C. (2013). Influence of NH 3/CO 2 modification on the characteristic of biochar and the CO 2 capture. *BioEnergy Research*, *6*, 1147-1153.
- Xu, P., Sun, C. X., Ye, X. Z., Xiao, W. D., Zhang, Q., & Wang, Q. (2016). The effect of biochar and crop straws on heavy metal bioavailability and plant accumulation in a Cd and Pb polluted soil. *Ecotoxicology and Environmental Safety*, 132, 94-100.
- Xu, X., Cao, X., & Zhao, L. (2013b). Comparison of rice husk-and dairy manurederived biochars for simultaneously removing heavy metals from aqueous solutions: role of mineral components in biochars. *Chemosphere*, 92, 955-961.
- Xu, X., Cao, X., Zhao, L., Wang, H., Yu, H., & Gao, B. (2013a). Removal of Cu, Zn, and Cd from aqueous solutions by the dairy manure-derived biochar. *Environmental Science and Pollution Research*, 20, 358-368.
- Xu, X., Cao, X., Zhao, L., Zhou, H., & Luo, Q. (2014). Interaction of organic and inorganic fractions of biochar with Pb (II) ion: further elucidation of mechanisms for Pb (II) removal by biochar. *RSC Advances*, 4, 44930-44937.
- Yakout, S. M., Daifullah, A. E. H. M., & El-Reefy, S. A. (2015). Pore structure characterization of chemically modified biochar derived from rice straw. *Environmental Engineering & Management Journal (EEMJ)*, 14, 473-480.
- Yamkate, N., Chotpantarat, S., & Sutthirat, C. (2017). Removal of Cd, Pb, and Zn²⁺ from contaminated water using dolomite powder. Human and Ecological Risk Assessment: *An International Journal*, 23, 1178-1192.
- Yang, J. Y., Yang, X. E., He, Z. L., Li, T. Q., Shentu, J. L., & Stoffella, P. J. (2006). Effects of pH, organic acids, and inorganic ions on lead desorption from soils. *Environmental Pollution*, 143, 9-15.
- Yang, X., Liu, J., McGrouther, K., Huang, H., Lu, K., Guo, X., & Wang, H. (2016a). Effect of biochar on the extractability of heavy metals (Cd, Cu, Pb, and Zn) and enzyme activity in soil. *Environmental Science and Pollution Research*, 23, 974-984.
- Yang, Y., Wei, Z., Zhang, X., Chen, X., Yue, D., Yin, Q., & Yang, L. (2014). Biochar from Alternanthera philoxeroides could remove Pb (II) efficiently. *Bioresource Technology*, 171, 227-232.
- Yang, Z., Fang, Z., Zheng, L., Cheng, W., Tsang, P. E., Fang, J., & Zhao, D. (2016b). Remediation of lead contaminated soil by biochar-supported nanohydroxyapatite. *Ecotoxicology and Environmental Safety*, 132, 224-230.

- Yap, M. W., Mubarak, N. M., Sahu, J. N., & Abdullah, E. C. (2017). Microwave induced synthesis of magnetic biochar from agricultural biomass for removal of lead and cadmium from wastewater. *Journal of Industrial and Engineering Chemistry*, 45, 287-295.
- Yargicoglu, E. N., Sadasivam, B. Y., Reddy, K. R., & Spokas, K. (2015). Physical and chemical characterization of waste wood derived biochars. *Waste Management*, 36, 256-268.
- Yavuz, C. T., Mayo, J. T., William, W. Y., Prakash, A., Falkner, J. C., Yean, S., & Natelson, D. (2006). Low-field magnetic separation of monodisperse Fe₃O₄ nanocrystals. *Science*, 314, 964-967.
- Yi, X. U., Liang, X., Yingming, X. U., Xu, Q. I. N., Huang, Q., Lin, W. A. N. G., & Yuebing, S. U. N. (2017). Remediation of heavy metal-polluted agricultural soils using clay minerals: A review. *Pedosphere*, 27, 193-204.
- Yi, X. U., Liang, X., Yingming, X. U., Xu, Q. I. N., Huang, Q., Lin, W. A. N. G., & Yuebing, S. U. N. (2017). Remediation of heavy metal-polluted agricultural soils using clay minerals: A review. *Pedosphere*, 27, 193-204.
- Yoon, R. H., & Yordan, J. L. (1986). Zeta-potential measurements on microbubbles generated using various surfactants. *Journal of Colloid and Interface Science*, 113, 430-438.
- Younis, U., Qayyum, M. F., Shah, M. H. R., Danish, S., Shahzad, A. N., Malik, S. A., & Mahmood, S. (2015). Growth, survival, and heavy metal (Cd and Ni) uptake of spinach (Spinacia oleracea) and fenugreek (*Trigonella corniculata*) in a biocharamended sewage- irrigated contaminated soil. *Journal of Plant Nutrition and Soil Science*, 178, 209-217.
- Yousaf, B., Liu, G., Wang, R., Zia-ur-Rehman, M., Rizwan, M. S., Imtiaz, M., & Shakoor, A. (2016). Investigating the potential influence of biochar and traditional organic amendments on the bioavailability and transfer of Cd in the soil-plant system. *Environmental Earth Sciences*, 75, 374.
- Yu, W., Lian, F., Cui, G., & Liu, Z. (2018). N-doping effectively enhances the adsorption capacity of biochar for heavy metal ions from aqueous solution. *Chemosphere*, 193, 8-16.
- Zenteno, M. C., de Freitas, R. C. A., Fernandes, R. B. A., Fontes, M. P. F., & Jordão, C. P. (2013). Sorption of cadmium in some soil amendments for in situ recovery of contaminated soils. *Water, Air, & Soil Pollution, 224*, 1418.
- Zhang, F., Wang, X., Yin, D., Peng, B., Tan, C., Liu, Y., & Wu, S. (2015). Efficiency and mechanisms of Cd removal from aqueous solution by biochar derived from water hyacinth (Eichornia crassipes). *Journal of Environmental Management*, 153, 68-73.

- Zhang, M., Gao, B., Varnoosfaderani, S., Hebard, A., Yao, Y., & Inyang, M. (2013a). Preparation and characterization of a novel magnetic biochar for arsenic removal. *Bioresource Technology*, 130, 457-462.
- Zhang, R. H., Li, Z. G., Liu, X. D., Wang, B. C., Zhou, G. L., Huang, X. X., & Brooks, M. (2017). Immobilization and bioavailability of heavy metals in greenhouse soils amended with rice straw-derived biochar. *Ecological Engineering*, 98, 183-188.
- Zhang, X., Wang, H., He, L., Lu, K., Sarmah, A., Li, J., & Huang, H. (2013c). Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. *Environmental Science and Pollution Research*, 20, 8472-8483.
- Zhang, Y., Chen, T., Liao, Y., Reid, B. J., Chi, H., Hou, Y., & Cai, C. (2016). Modest amendment of sewage sludge biochar to reduce the accumulation of cadmium into rice (Oryza sativa L.): a field study. *Environmental Pollution*, 216, 819-825.
- Zhang, Z., Solaiman, Z. M., Meney, K., Murphy, D. V., & Rengel, Z. (2013b). Biochars immobilize soil cadmium, but do not improve growth of emergent wetland species Juncus subsecundus in cadmium-contaminated soil. *Journal of Soils and Sediments*, 13, 140-151.
- Zhao, B., Xu, R., Ma, F., Li, Y., & Wang, L. (2016). Effects of biochars derived from chicken manure and rape straw on speciation and phytoavailability of Cd to maize in artificially contaminated loess soil. *Journal of Environmental Management*, 184, 569-574.
- Zheng, R., Li, C., Sun, G., Xie, Z., Chen, J., Wu, J., & Wang, Q. (2017). The influence of particle size and feedstock of biochar on the accumulation of Cd, Zn, Pb, and As by Brassica chinensis L. *Environmental Science and Pollution Research*, 24, 22340-22352.
- Zhou, Y., Gao, B., Zimmerman, A. R., Chen, H., Zhang, M., & Cao, X. (2014). Biochar-supported zerovalent iron for removal of various contaminants from aqueous solutions. *Bioresource Technology*, 152, 538-542.
- Zimmerman, A. R. (2010). Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). *Environmental Science & Technology*, 44, 1295-1301.

BIODATA OF STUDENT

Alaa Hasan Fahmi was born on 1 September 1977 in Baqubah city located in Diyala Province - Iraq. He finished his primary and secondary school in (Al-Wa'am and Al-Adalah school, respectively) located in Hdmixer village, Baqubah city and finished his high school in Al-Markazia school located in Baqubah city. He obtained B.Sc. degree in soil and water science (honor study) from the College of Agriculture, Baghdad University in 1999. Then, he assigned to College of Agriculture, Diyala University. He obtained M.Sc. degree in soil chemistry and organic matter from the College of Agriculture, Tikrit University in 2011. After that, he worked as an assistant lecturer and decider of the Soil and Water Science Department in College of Agriculture, Diyala University, where he was offered a scholarship award from Diyala University- Ministry of Higher Education and Scientific Research-Iraq to study his Ph.D. at University Putra Malaysia in 2014.



LIST OF PUBLICATIONS

- Fahmi, A. H., Samsuri A. W., Hamdan J. and Daljit S. 2018. "Physical Modification of Biochar to Expose the Inner pores and Their Functional Groups" has been accepted by the Royal Society of Chemistry, (RSC Advances).
- Fahmi, A. H., Samsuri A. W., Hamdan J. and Daljit S. 2018. "Bioavailability and Leaching of Cd and Pb from Contaminated Soil Amended With Different Sizes of Biochar" has been accepted by the Royal Society Open Science journal.
- Fahmi, A. H., Samsuri A. W., Hamdan J. and Daljit S. 2018. "Magnetization Improved Lead Adsorption of Fine Particle Biochar" has been submitted to Journal.
- Fahmi, A. H., Samsuri A. W., Hamdan J. and Daljit S. 2018. "Effects of Particle Size and Rate of Biochar on the Phytoavailability of Cd and Pb by Mustard Plants Grown in Contaminated Soils" has been submitted journal.