UNIVERSITY FOR DEVELOPMENT STUDIES, TAMALE

ECO-FRIENDLY BIOCHARS FOR THE ADSORPTION OF HEAVY METALS FROM AQUEOUS PHASE

ABUDU BALLU DUWIEJUAH

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BY

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THESIS SUBMITTED TO THE DEPARTMENT OF BIOTECHNOLOGY, FACULTY OF AGRICULTURE, UNIVERSITY FOR DEVELOPMENT STUDIES, IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE MASTER OF PHILOSOPHY DEGREE IN BIOTECHNOLOGY

DECEMBER, 2017

DECLARATION

I hereby declare that this thesis is the result of my own original research work except for citations and quotations which have been duly acknowledged. I also declare that no part of it has been previously and concurrently presented for another degree in this University or elsewhere.

Candidate's Signature ……………..…………….. Date …………..………………

Abudu Ballu Duwiejuah

I hereby declare that the preparation and presentation of the thesis was supervised in accordance with the guidelines on supervision of thesis laid down by the University for Development Studies.

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Prof. Albert Kojo Quainoo

ABSTRACT

Adsorption is a unique and promising method for the removal of heavy metals from aqueous environment using cost-effective and readily available materials. This study examined mono and simultaneous adsorption of cadmium (Cd), mercury (Hg) and lead (Pb) onto biochars produced from groundnut and shea nut shell biomass feed stocks at pyrolysis temperatures of 350 ± 5 ºC and 700 ± 5 ºC. Fifty mg/l of heavy metal ion with 2 g/ 50 ml of adsorbent dosage were leached at constant room temperature of 24 ± 0.5 ºC in laboratory and constant contact time of 72 min. A total of 126 elutes (consisting of 54 mono, 54 binary and 18 ternary samples) were obtained from the batch experiments and conveyed to the Ecological Laboratory of University of Ghana, for the analysis. The removal efficiency of Hg was almost 100%, Cd and Pb were higher than 99.50% and 99.10%, respectively in mono-component system by groundnut and shea nut shell biochars. The experiment showed that shea nut shell biochars had the strongest affinity for heavy metal ions in the mono aqueous phase. In the binary system of Cd and Hg the removal efficiency were above 99.70% and 100%, respectively. The ternary experiment showed the order of adsorption of $Pb^{2+} > Hg^{2+} > Cd^{2+}$ for Cd, Hg and Pb ions onto groundnut and shea nut shells biochars. The fast pyrolysis temperature and type of biochar showed a slight increase in the adsorption efficiency of metal ions but the increase was not statistically significant ($p > 0.05$). The study revealed that Langmuir adsorption isotherm was the best fit model for heavy metal ion adsorption onto biochars in the batch experiment. The interactive effects of binary and ternary metal systems onto biochars were either antagonistic or synergistic in nature. Based on these results, it is therefore recommended that further competitive adsorption study on these biochars should be undertaken for accurate estimation of adsorption in natural environments.

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DEDICATION

To my entire family, the poor and vulnerable in society.

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CHAPTER ONE

INTRODUCTION

1.1 Background

Biochar is a carbon-rich product produced from biomass that include wood, manure, seeds, or leaves that are often heated in a barred vessel with little or no air. Biochar therefore refer to a heterogeneous substance that is rich in minerals and aromatic carbon (Schmidt *et al.*, 2014). Biochar is usually produced by thermal decomposition of organic material under restricted supply of oxygen (O_2) and at relatively low temperatures (Lehmann, 2009). It is a relatively modern development, evolving in coincidence with soil management, carbon sequestration issues, and control of pollutants (Kajitani *et al.*, 2013).

The awareness of current and past environmental issues and the various ways they change are required for environmental restoration, remediation and sustainability. It is obvious that deterioration owing to industrial and human activities and change in the environments are the prime topics for monitoring studies (Dobaradaran *et al.*, 2010). Many anthropogenic activities lately has major influence on the aquatic environment in the form of sub-lethal pollution that usually results in chronic stress conditions that have negative influence on aquatic life, human and other animals (Palanisamy *et al.*, 2011).

Freshwaters are highly vulnerable to pollution since they act as immediate sinks for pollutants resulting from human activities (Sachar and Raina, 2014). Due to the discharge of elevated concentrations of heavy metals such as arsenic (As), cadmium

(Cd), mercury (Hg) and lead (Pb) through mining, urbanisation, land field wastewater among others, most essential and mostly used aqueous environment are polluted. Trace metals are introduced into aqueous environment from numerous domestic and industrial sources (Gautam *et al.*, 2015). Heavy metals have become a global issue of environment and public health concern due to their toxicities, bioaccumulation in the human body and food chain, carcinogenicities, and mutagenesis in various living organisms (Wang *et al.*, 2013a; Sarkar *et al.*, 2014; Chowdhury *et al.*, 2015).

Toxicity of heavy metals in aquatic organisms, their long residence time within the trophic chains, in addition to the possible risk of human exposure to trace metals, makes it vital to evaluate their concentrations on the aquatic environment and living organisms (Giarratano and Amin, 2010). Trace metals can also induce sub-lethal effects such as impairment at cellular and molecular levels, and disruption of homeostasis in aquatic organisms (Tsangaris *et al.*, 2010). These aquatic organisms contribute immensely to human health and food security aside their economic importance. These heavy metals, may also negatively impact by seriously decreasing the tenacity of the organism by enhancing susceptibility to impairment and diseases (Chandurvelan *et al.*, 2015).

These necessitated the treatment of metal-contaminated aqueous environment through low cost means. There is currently a continuous call for more novel remediation measures to address environmental concerns, which will guarantee the safety of humans and their environment. Conventional treatment processes which include chemical precipitation, ion exchange and electrochemical can be used to remove heavy metal from inorganic effluent. However, these processes have significant demerits such as incomplete removal, high requirements of energy, and production of toxic sludge (Eccles, 1999). This suggests that, it is not practically and economically viable for the removal of heavy metals in aqueous phase unlike biochar.

Biochar has been proven to be the most efficient and effective method for heavy metal or trace metals removal from aqueous environment (Cao *et al.*, 2009; Liu and Zhang, 2009; Liu *et al.*, 2012; Kołodyńska *et al.*, 2012; Regmi *et al.*, 2012). This makes it highly suitable for the purpose of remediating contaminated aqueous environment. The adsorption mechanisms mainly involve chemical precipitation, electrostatic interaction, ionic exchange and complexion with functional groups on biochar surface (Cao *et al.*, 2009; Liu and Zhang, 2009; Regmi *et al.*, 2012; Zhang *et al.*, 2013a).

Previous researches have proven boichar's capability of adsorbing heavy metals such as cadmium, copper, mercury, lead and some organic pollutants found in aqueous environment that are harmful to animals, human and plants (Ameloot *et al.*, 2013). Cost-effective biochars can meritoriously normalise organic pollutants in aqueous environment and decrease their bioavailability to carbonaceous adsorbents that could easily be managed. The application of biochar to treat surface water and land field wastewater contaminated by heavy metals involves replacing already existing ions that may be present on biochar with metal ion in solution system, signifying a potential correlation between content of biochar and its remediation potential for metals (Chen *et al.*, 2013). This study sought to generate biochars for adsorption of heavy metals in aqueous phase for proper application to benefit environmental concerns in Ghana and less developed countries.

1.2 Problem Statement and Justification

Water is required by every living organism to function. This place more pressure on the already scarce and now most quality compromised commodity in many countries around the world. The persistent deterioration of groundwater and surface water bodies' can be attributed to the anthropogenic introduction of heavy metals and other pollutants. This has attracted worldwide attention as the main sources of these metals locally and internationally is human based activities that can be properly managed to avoid environmental pollution and contamination as it constitutes a risk to the health of humans and animals.

Mixtures of metal adsorption studies are also very relevant to evaluate the interference nature of the co-ions and absorbents efficiency to remove the metal ions from wastewaters (Srivastava *et al.*, 2006). There are few or limited multi-metal system studies that have been conducted to assess the competitive or simultaneous adsorption of different trace metals. It is therefore very important to utilise eco-friendly biochar for adsorption of heavy metals and to enhance the understanding of their competition and interference during adsorption in contaminated aqueous environments.

It is believed that remediation methods that cost-effective are preferred and have been used particularly as an alternative option to remove heavy metals from aqueous environments. However, there is still the need to undertake novel research with the aim of coming out with cost-effective eco-friendly techniques and biomass feed stock for heavy metals removal from aqueous contaminated environments. The elevated levels of heavy metals in surface water in mining areas and wastewater is a major concern to public health in Ghana to which Tamale Metropolis is not an exception.

The removal and recovery of trace metals from contaminated aqueous environments is possible through the use of conventional technologies such as adsorption by activated carbon, chemical precipitation, electrochemistry removal, ion exchange, membrane and microbe separations just to mention a few (Srivastava and Majumder, 2008). It is indisputable that majority of these methods have their limitations that include high capital, operational cost, and problem of resulting from sludge disposal. Activated carbon for instance is more expensive than biochar which makes its utilisation in a large scale a major limitation. Estimated cost of biochar is US$ 246 per tonne, which is about one-sixth of the cost of commercially available activated carbon that cost approximately US$ 1500 per tonne (Ahmad *et al.*, 2014). Aside this cost-effectiveness, biochar needs less energy than activated carbon and can easily be used without further modification or activation. Consequently, there is the urgent need to develop a novel method that will not only be cost-effective but practically workable. Adsorption onto low-cost adsorbent will be a better choice to overcome limitations of other methods. The removal of heavy metals from aqueous environment by means of adsorption has been an efficient method due to its effectiveness at concentration that is low (Liang *et al.*, 2009; Amuda and Edewor, 2013).

The use of activated carbon as an adsorbent has gone out of the reach of the poor and developing countries that are confronted with economic challenges because of its relative cost. Biochar can be obtained from the direct burning of precursors, due to the wide availability of its feed stocks. This makes the production of biochar much less expensive when compared to activated carbon (Qiu *et al.*, 2009).

Biochar product characteristics are heavily influenced by the extent of pyrolysis (pyrolytic temperature and residence pressure) and exclusively by biomass size and kiln or furnace residence time (Asensio *et al.*, 2013). Pyrolytic temperature has significant influence on the elemental, morphological, structural and the properties of biochars (Kołodyńska *et al.*, 2012). The most common technology used is the slow pyrolysis for heavy metals removal in aqueous environment. Biochar produced by low pyrolysis processes has proven effective in the removal of contaminants (15% to 89%) within a few minutes to days of residence time (Tong *et al.*, 2011; Yao *et al.*, 2011; Chen *et al.*, 2012).

Some adsorbents are broad ranged, bind and collect most trace metals without specificity, whereas others are specific for certain heavy metals. Biochar possess a carbon matrix structure with high degree of porosity and extensive surface area, suggesting that it may act as adsorbent that is similar in some aspects to activated carbon. Hence, play a crucial role in controlling pollutants in the environment (Chen *et al.*, 2011). In spite these advantages, the production cost of biochar, all year round availability of feedstock, and patronage and availability of biochar is characterised with uncertainties. Also, the main limitations in large-scale and long-term utilisation of biochar in agricultural and environmental management are concern with the loss of indigenous feed stock and introduction of xenobiotic such as dioxins and polycyclic aromatic hydrocarbons (PAHs) (Wardle *et al.*, 2008).

Agricultural by waste can be used as biochar for adsorption of contaminants from aqueous environment. The use of agricultural wastes as adsorbents for the removal of trace metals has some advantages that include available in large quantities, eco-friendly, cost-effectiveness and renewable in nature (Choi *et al.*, 2011; Singha and Das, 2013). Many researchers have tried to come out with economically efficient and unconventional adsorbents produced from agricultural/ plant wastes (Apaydin-Varol *et al.*, 2007). For instance, grinded shea nut shells have proven effective in the removal of heavy metals particularly Mn, Fe, Zn and Cu in soils using lettuce as test crop (Quainoo *et al.*, 2015). Shea nut shells are readily available as it is agricultural residues that are predominant in Northern Ghana. In addition, it is said to be very economical and eco-friendly for the remediation of polluted environments (Quainoo *et al.*, 2015).

There is gradual increase in the utilisation of agricultural waste as biochar feed stock as part of waste management strategy and mainly due to their relative cost and availability. The operational cost of managing the abundant agricultural waste is save or reduce by the conversion of agricultural waste biomass to eco-friendly biochar products. The annual production of agricultural wastes was estimated to be 500 million tonnes worldwide (Duku *et al.*, 2011). In Ghana, majority of agricultural residues generated are mainly waste or by-products generated during processing and harvesting of crops such as cereals and legumes.

Reasons for selection of the groundnut and shea nut shells as feed stocks for this study was due to availability, cost-effectiveness, and as a way of waste utilisation and perhaps the presence of lignocellulosic biomass (cellulose, hemicellulose and lignin) which is a characteristic for successful heavy-metal adsorption. As agricultural products contain acidic groups such as carboxylic and phenolic groups, which are characteristics for successful heavy-metal adsorption products (Castro *et al.*, 2011).

Some have proven useful and effective for adsorbing various heavy metals that include cadmium, copper, lead, mercury and nickel. However, the spatial distribution and availability of the agricultural wastes stimulate further research in some localities. Also, the removal efficiencies of heavy metals of the various adsorbents are different. Hence, research is continuously conducted to develop and evaluate new promising adsorbents (Ayala *et al.*, 1998). Hence, the need to generate biochar for adsorption of heavy metals in aqueous phase for proper application to benefit environmental concerns.

1.3 Main Objective of the Study

The main objective of the study was to generate biochars for adsorption of heavy metals from aqueous phase.

1.3.1 Specific Objectives

- To determine the adsorption capacity of biochars in maximum contamination limits (one fold, two fold and five fold) of 0.04 mg/l for Cd, 0.10 mg/l for Hg, and 0.10 mg/l for Pb (one fold), 0.08 mg/l for Cd, 0.20 mg/l for Hg, and 0.50 mg/l for Pb (two fold), and 0.20 mg/l for Cd, 0.50 mg/l for Hg, and 0.50 mg/l for Pb (five fold) from the aqueous phase.

- To measure the simultaneous adsorption of two or more heavy metals (binary and ternary of Cd, Hg and Pb) in the prepared aqueous phase by the various biochars.
- To compare the adsorption capacity of biochars produced at conditions of slow and fast pyrolysis.
- To assess the effect of solution pH on adsorption of Cd, Hg and Pb onto biochars.
- To examine Cd, Hg and Pb adsorption isotherms onto biochars.
- To evaluate the interactive behaviour of heavy metals ions in both binary and ternary mixtures.

CHAPTER TWO

LITERATURE REVIEW

2.1 Biochar, Adsorption and Heavy Metals

2.1.1 Biochar

Biochar is produced from biomass or feed stock pyrolysis which is a process that involves breaking down of organic substances at temperatures that ranged from 350 °C to 1000 °C in a low-oxygen thermal process (European Biochar Certificate (EBC), 2012). The pyrolysis of biomass or feed stock is done under controlled conditions with clean technology and can be used for environmental restoration purposes. This makes specific pyrolysis of biochar to be characterised by their superfluous environmentally sustainable production, quality and usage features (EBC, 2012).

Biochar is a relatively modern development, evolving in coincidence with soil management, carbon sequestration issues, and control of pollutants (Kajitani *et al.*, 2013). Basically, guidelines are applied to differentiate between two different biochar grades thus its own threshold values ('basic') and environmental requirements ('premium'). In order, to obtain European biochar certificate these criteria concerning biomass feed stock, production method, properties of the biochar and the mode of application have to be met (EBC, 2012).

2.1.2 Adsorption

Lately, the adsorption process is one of the most efficient and attractive methods for removal of aqueous contaminants, due to its characteristics such as easy process control, cost-effective and efficient energy requirements (Chen *et al.*, 2010; Mittal *et* *al.*, 2012). The cost involved in the use of adsorption technology can be reduced provided the adsorbent is cheap (Onundi *et al.*, 2010). Adsorption capacity of any adsorbent is influenced by its pore size, chemical structure (that stimulate its interaction with polar and non-polar adsorbates) and active sites (which influences the type of chemical reactions with other molecules) (Onundi *et al.*, 2010).

2.1.3 Heavy Metals

Heavy metals are those with density that generally exceed 5 g/ cm^3 (Barakat, 2011). Heavy metals have been the main environmental contaminants that usually pose a serious threat to human well being and animal health by their continuous existence in the environment (Subhashini and Swamy, 2013). The earth's crust is a natural source of heavy metals (Ismail *et al.*, 2013). In developed and developing countries the most common aqueous contaminated heavy metals are Cd, Cr, Cu, Hg, Pb, and Zn.

Basically, the occurrence of heavy metals in aqueous phase can result from two main sources. Naturally heavy metals occurs and can be found in aqueous environment from a pedogenetic processes that involves weathering of parent materials at levels that can be regarded as trace (less than 1000 mg/ kg) and rarely toxic (Parizanganeh *et al.*, 2012). Anthropogenic sources include activities such as electroplating, energy and fuel production, mining, melting operations, intensive agriculture, smelting, sludge dumping, and power transmission, are the major contributor to heavy metals contamination (Ismail *et al.*, 2013). The mining sector and waste land field sites are major contributing sources of heavy metals contamination in aqueous environment.

2.2 Overview of Biomass Feed Stocks

Feed stock is a conventional term that often refers to the type of biomass that is pyrolysed in order to obtain a biochar (Verheijen *et al.*, 2010). Feed stock and conditions of pyrolysis are crucial factors that depend on the various properties of any biochar produced. Biochars can be produced from various biomass feed stocks with varied physical and chemical properties. These properties possessed by biomass feed stock are crucial for the thermal conversion processes, caloric value, principally the proximate analysis (ash and moisture content), fractions of fixed carbon, and volatile components (Angin, 2013), proportion of cellulose, hemicellulose and lignin (Shivaram *et al.*, 2013), percentage and composition of inorganic substance, bulk, moisture content, true density and particle size.

Cellulose and lignin of a feed stock endure thermal degradation at temperatures range of 240 ºC to 350 ºC and 280 ºC to 500 ºC, respectively (Demirbas, 2004). Hence, the fractional proportions of each component on biomass feed stock determine the biomass structure that will remain of pyrolysis process at any given temperature. This was proven by Winsley (2007) where a pyrolysis of a feed stock from wood-based generated coarser and added resistant biochars with carbon contents of 80% as the unbending ligninolytic nature of the raw material remains in biochar residue. Biomass feed stock composes of high lignin contents for instance olive husks have highest yields of biochar due to the stability of lignin in thermal degradation (Demirbas, 2004). Consequently, lignin loss is typically less than half of cellulose loss in terms of comparable temperatures and residence times (Demirbas, 2004). Biochars produced at higher temperatures (lower oxygen to carbon ratio) are usually expected to be donors, whilst biochars produced at lower temperatures are anticipated to be π-acceptors

(Yang *et al.*, 2013). Lignocellulosic biomass is one of the most abundant naturally occurring available raw materials, which is a preferred feed stock choice (Amonette and Joseph, 2009). The ready availability of specific biochars and their economic value is influenced by spatial and temporal occurrence of biomass feed stock (Verheijen *et al.*, 2010).

Wide-ranged of feed stock biomasses have recently been used in the production of biochar (Angin, 2013) such as agricultural waste (Liu and Zhang, 2009; Tsai *et al.*, 2012; Wang *et al.*, 2012), bioenergy crops (willows, miscanthus and switch grass) (Zimmerman *et al.*, 2010; Beeseley and Marmiroli, 2011), forest residues (sawdust, grain crops, and nut shells) (Xu *et al.*, 2012), organic waste (green yard waste and animal manure) (Cao and Harris, 2010; Song and Guo, 2012), kitchen waste, and sewage sludge (Lu *et al.*, 2012).

Many biomass feed stocks have been used for the production of biochar. These include grain husks, nut shells, manure, crop residues and wood, whilst those with the highest carbon contents (for example nut shell and wood), abundance and cost-effectiveness are currently used for activated carbon production (Martínez *et al.*, 2006). Biochar produced using agricultural waste biomasses feed stocks does not cause any notable life cycle based greenhouse gas (GHG) emissions (De *et al.*, 2013). However, not much have been done about the uses of readily available, eco-friendly and cost-effective biomass feed stocks (such as groundnut and shea nuts shells) that have the potency for effective removal of heavy metals from aqueous environment.

Furthermore, the moisture content, volatile component, and particle size and shape of biomass have effect on the property of biochar obtained. Collison and his associates (2009) established that within a biomass feed stock type, different composition could arise based on its growing environmental conditions that include moisture content, temperature, soil type and those relating to harvesting time with regard to the characteristics of some plant feed stocks. It is obvious that compositional heterogeneity is common within the same plant material. The suitability of each biomass feed stock type for biochar is largely dependent on a number of chemical, environmental, physical as well as economic and logistical factors (Collison *et al.*, 2009). Thus, biochar produced from cost-effective and readily available groundnut and shea nut shells are likely to pose no threat on the aqueous phase, other environmental media, human health and emission of greenhouse gases to the atmosphere.

Feed stocks utilised for biochar production include crop residues, grasses, and manures and woody biomass that influence biochar characteristics such as concentrations of elemental constituents, density, hardness and porosity (Spokas *et al.*, 2012). Optimising biochar for an intended application could require careful selection of a biomass feed stock as well as pyrolysis technique of production and conditions to produce biochars with specific characteristics. Studies have explored the relationships between biochar production conditions, biochar characteristics, and possible end-uses of biochar.

2.3 Production of Biochar for Adsorption

Activated carbon usually has different physical and chemical properties dependent on the technology employed for its production (Zhang *et al.*, 2013a). Pyrolysis is based on the principle of heating in an oxygen-depleted environment. The absence of oxygen prevents combustion from occurring, hence yields carbon-based end products that are different from those produced during incineration. This has already been used to produce biochars for immobilisation of both inorganic and organic pollutants in aqueous phase.

The traditional earthen charcoal kilns are usually used to produce biochar, where combustion, gasification and pyrolysis process are deployed in parallel below the earthen kiln layer. Whilst in modern biochar retorts, where pyrolysis and combustion processes are physically detached by a metal barrier (Asensio *et al.*, 2013).

Pyrolysis technology is eminent by the residence time, pyrolytic temperature of the pyrolysis material (for example slow and fast pyrolysis process), pressure, size of adsorbent, and the heating rate and method (for example pyrolysis started by the burning of fuels, by electrical heating, or by microwaves) (Obemah and Baowei, 2014). Pyrolysis technology is differentiated based on the pyrolytic temperature and the residence time of the pyrolysis or carbonisation process (Asensio *et al.*, 2013). Pyrolysis should be done by constantly given much consideration to biochar yield, energy efficiency, heavy metal stability and structure (Agrafioti *et al.*, 2013).

Slow pyrolysis is often referred as a continuous process that purged (oxygen-free) feed stock biomass by transferring into an external heated kiln or furnace (gas flow removing volatile biochar emerging at the other end). Whilst fast pyrolysis usually depends on very quick heat transfer, normally to fine biomass particles at less than 650 °C with rapid heating rate (Meyer *et al.*, 2011). The most common technology used is the slow pyrolysis for heavy metals removal in aqueous environment. Biochar produced by low pyrolysis processes has proven effective in the removal of contaminants (15% to 89%) within a few minutes to days of residence time (Tong *et al.*, 2011; Yao *et al.*, 2011; Ahmad *et al.*, 2012a; Chen *et al.*, 2012). The weight loss at low temperature during the drying process is attributable to evaporation of water.

Subsequently, the major decomposition processes usually occurred between 200 °C and 500 °C (Chen and Chen, 2009; Chen *et al.*, 2012; Shen *et al.*, 2012), and sequentially follow four steps that include the partial hemicellulose decomposition; the complete hemicellulose decomposition to partial cellulose decomposition; the whole cellulose and unfinished lignin decomposition; and the successive decomposition and increasing degree of carbonisation (Kumar *et al.*, 2011a; Chen *et al.*, 2012; Rutherford *et al.*, 2012; Shen *et al.*, 2012). This was followed by gradual loss in weight of biochar when the temperature was up to 700 °C. The yields of biochar were about 15% to 90% by different biomass feed stocks and decomposition processes, and reduced with the increase in temperature. Whilst, approximately 15% to 25% of biochar still remained even with temperature up to 700 °C (Chen *et al.*, 2012; Oh *et al.*, 2012; Ahmad *et al.*, 2013; Qian and Chen, 2013), indicating the thermal stability of biochar as an adsorbent.

Biochar product characteristics are heavily influenced by the extent of pyrolysis (pyrolytic temperature and residence pressure) and exclusively by biomass size and kiln or furnace residence time (Asensio *et al.*, 2013). The vapour residence time is determined by the rate at which volatile and gases are removed in a kiln or furnace (Meyer *et al.*, 2011).

Prolonged residence time has secondary reactions thus the reactions of tar on biochar surfaces and charring of the tar instead of additional combustion or processing outside the kiln or furnace (Oliver *et al.*, 2013). It is obvious that typical solid product yields produced from gasification and fast pyrolysis process are considerably lower when compared with the solid product yields of flash carbonisation, hydrothermal carbonisation, slow pyrolysis, and torrefaction (Meyer *et al.*, 2011). Dowie *et al.* (2009) reported that yields of biochar products that ranged from 25 to 40 wt% and observed slightly decrease at higher pyrolysis temperature that was attributed to the volatilisation of other volatile products from the component of the biomass. The experimental pyrolysis was conducted at the heating rate of about 10 k/ min up to the press cubed pyrolytic temperature ranging from 400 °C to 700 °C (Dowie *et al.*, 2009). Pellera *et al.* (2012) also reported biochar yields of rice husk and compost derived after hydrothermal pyrolysis of about 62.5%, and olive pomace and organic waste at a quite lower of 37.5%. This revealed that increase in pyrolytic temperature led to a decrease in the yield for all produced materials through the pyrolysis. To be precise, the yields of biochar at 300 °C and 600 °C were 32.8% and 31.9% for rice husks, 39.6% and 32.8% for orange waste, 39.3% and 26.7% for olive pomace, and 78.7% and 46% for compost, respectively (Pellera *et al.*, 2012).

Producing biochar at higher efficiency rate via slow pyrolysis by developing integrated systems is still at juvenile stage. Hence, the exploitation of the technology by researchers and other research centres and institutions is very minimal.

2.4 Physico-Chemical Characterisation of Biochar

Generally, both biomass feed stock and biochar produced can be subjected to physico-chemical analysis to come out with the basic characteristics of each raw and pyrolysed material. The biochars produced at different pyrolytic temperature usually will have discrete honey-comb-like structure because of tubular structures presence emanating from the plant cells. The well-built pores of biochars aid its high Brunauer Emmett Teller (BET) surface area. The significance of pyrolytic temperature leads to the suggestion that biochar produced at high temperatures would lead to a material analogous to activated carbon in environmental remediation (Gao *et al.*, 2013).

It was deduced that the surfaces of low temperatures biochar can be hydrophobic, and this may reduce its capacity to adsorb pollutants. The characteristics, nature, quality, and potential use of biochar are affected by the form, type, preliminary preparation steps and biomass feed stock size and type of pyrolysis product (Harmsen and Naidu, 2013). The initial ratio of exposure to total surface area of biochar could be affected by its size. Also, low pyrolytic temperature biochar is stronger than high temperature products, as it is brittle and pores can easily be abraded into fine fractions. The relationship between the mechanism of heavy metal adsorption and scanning electron microscopy (SEM) has been explained by Qiu *et al.* (2012) that proposed a vivid explanation. In it, they observed bright zones on the pores surface of Pb-loaded biochar at pH of 5 in the SEM photography. Its energy dispersive X-ray (EDX) spectrum signifies the red surface and also established the occurrence of silicon and phosphorus, which perhaps existed in the form of 5 $PbO{\cdot}P_2O_5{\cdot}SiO_2$ (lead phosphate silicate) precipitates that was again identified by X-ray diffraction (XRD) spectra (Qiu *et al.*, 2012). It was then concluded that the precipitates can be an important means of modelling the mechanism for Pb^{2+} removal from soil system that can be related to solution system (Qiu *et al.*, 2012).

The chemical characteristics of individual feed stock species and its biochar are always at significantly varying rate, both spatially and temporarily (Zhang *et al.*, 2013a). It is indisputable that fixed carbon is the solid combustible residue that usually remains after a particle sample is carbonised and volatile matter is expelled (Dong *et al.*, 2011). Elemental ratios of O/ C, O/ H, and C/ H have been established to be a reliable measure of both the extent of pyrolysis and oxidative adjustment level of biochar in the solution systems and can simply be determined (Haefele *et al.*, 2011).

Cationic exchange capacity (CEC) basically is the measure of the surface charge in biochar that increases as the biochar ages (Zhang *et al.*, 2013a) and has been recognised to increase in some oxygenated functional groups on the surface of the biochar (Qiu *et al.*, 2009). The most distinct change observed in biochar in cationic exchange capacity values is as a result of time where an increase from 278 $mmol_c\ kg^{-1}$ to 518 $mmol_c\ kg^{-1}$ was observed, due to oxidation process created by hydroxyl and carboxylic acid functional groups (Hale *et al.*, 2011). The nature of biomass feed stock mainly influences the physico-chemical properties; the most important process parameter is pyrolytic temperature; and biochar carbon content is not directly related to biochar yield.

2.5 Mechanism of Interaction between Biochar and Heavy Metals

The unique characteristics of a biochar are due to its functional factors which include the type and size of feed stock biomass, temperature and conditions of pyrolysis. The wide variant unique characteristics of biochar make some particular raw materials more suitable than others for adsorption of different heavy metals. The choice of biochar for adsorption purposes should not only be based on aqueous environmental nature, heavy metals concentrations, and multiple contaminations but also on physico-chemical properties of the biochar produced. The adsorption mechanism could be largely dependent on some properties of biochar that included mineral components, porous structure, surface functional groups and specific surface area.

In the utilisation of biochar, including other methods like complexation, electrostatic interaction (chemisorption), ion exchange, precipitation and physical sorption in the removal of heavy metals from aqueous solutions a lot of mechanisms are involved (Patra *et al.*, 2017). Unlike activated carbon, biochar is a modern technology that is evolving due to its eco-friendliness, cost-effectiveness and effective in adsorption. In the production of activated carbon higher temperature and additional activation process are required. The generation of biochar is less expensive with lesser energy requirements (Zheng *et al.*, 2010).

Some consideration that are crucial properties of biochar such as ash, carbon contents, pH and surface area can be affected by post-treatments and therefore enhance their ability to immobilise heavy metals (Lima *et al.*, 2014). Biochars act on bioavailable fraction of heavy metals and which can also reduce their leachability, hence it is necessary to reviewing the mechanisms pertaining to the interaction between biochar and heavy metal before application (Paz-Ferreiro *et al.*, 2014). Heavy metals have different and specific mechanisms of adsorption which is largely depended on the difference and the properties of biochars (Tan *et al.*, 2015).

The adsorption of trace metals by diffusional movement of the metal ions into sorbent pores devoid of formation of chemical bonds is defined by surface or physical sorption. For biochars produced from plant and animal biomass, the temperature increases of carbonisation (of 300 °C) will lead to high surface areas and pore volumes in the biochars (Patra *et al.*, 2017). Another mechanism involves heavy metals sorption via exchange of ionisable cations/ protons on the biochar surfaces with dissolved metal species. Also, electrostatic interaction among surface charged biochars and heavy metal ions lead immobilisation of heavy metals (Patra *et al.*, 2017).

Mechanism of biochar largely depends on the process of biochar-metal sorption which is usually dependent on biochar's point of zero charge (PZC) and pH solution (Liu and Zhang, 2009; Dong *et al.*, 2011). High temperatures of > 400 °C of carbonisation also help in the formation of graphene structures in the chars to favour the mechanisms of electrostatic attractions sorption (Kim *et al.*, 2013). Precipitation is the formation of solid(s) at the time of sorption process is either in solution or on a surface. It has often been mentioned as essential mechanism that influences the immobilisation of trace metals by means of biochar sorbents (Patra *et al.*, 2017). Owing to the optimisation of adsorption process, the pH of the solution is the most important parameter, as it influences degree of ionisation, charge surface area and speciation of adsorbent.

Biochar carried various surface functional groups (mainly oxygen containing groups thus AOH and carboxylate, hydroxyl and ACOOH) (Patra *et al.*, 2017). These functional groups change and acts with the upsurge of the pH solution. The functional groups on biochars at low pH are present in the form of positively charged. As it was proven that pyrolytic temperature have significant influence on the elemental, morphological, structural and the properties of biochars (Kołodyńska *et al.*, 2012; Zhang *et al.*, 2013b).

Biochars with pore volumes and high surface area have a more affinity for heavy metals since metallic ions can be substantially sorbed on top of the char surface and remains within the ores (Kumar *et al.*, 2011a). Most biochars surfaces with negative charges and can adsorb heavy metals that are positively charged through ligands specificity, electrostatic attractions and different functional groups on biochars can also interact with different trace metals by forming complexities (Dong *et al.*, 2011; Wang *et al.*, 2015) or precipitates of their solid mineral phase (Inyang *et al.*, 2012).

Many surface functional groups when exhibited on biochar's surface will likely influence its interactions with heavy metals thus electrostatic attraction, ion-exchange and surface complexation. These effects are demonstrated by the changes in functional groups of biochar before and after the metal ion adsorption (Khare *et al.*, 2013). The large surface area of biochar implies a high capacity for adsorption of complex heavy metals on their surface. Surface sorption of heavy metals on biochar has been proven on multiple studies using scanning electron microscopy (Beeseley and Marmiroli, 2011; Lu *et al.*, 2012). This sorption can be due to different functional groups present as result of complexation of heavy metals in the biochar, and the exchange of trace metals with cations associated with biochar thus Ca^{2+} and Mg^{2+} (Lu *et al.*, 2012), K^{+}, Na^{+} and S (Uchimiya *et al.*, 2011), or due to physical adsorption nature (Lu *et al.*, 2012). Lu *et al.* (2012) also suggested that functional groups played an important role in Pb adsorption on biochar produced from sludge. This include metal exchange with K^{+} and Na^{+} due to the electrostatic outer-sphere complexation, inner-sphere complexation with free hydroxyl groups and surface complexation with free carboxyl functional groups and free hydroxyl functional groups.

Similar mechanisms was observed in Hg (II) adsorption onto biochar produced from soybean stalk (Kong *et al.*, 2011) and Cd (II) adsorption onto biochar produced from corn straw (Sun *et al.*, 2014). Also oxygen functional groups are noted to have stabilised heavy metals in a surface of biochar, mostly for softer acids like Pb^{2+} and Cu^{2+} (Uchimiya *et al.*, 2011; Paz-Ferreiro *et al.*, 2014). Moreover, Cu^{2+} adsorption was reported to have related to the higher oxygenated surface groups and also with higher superficial charge density, high average pore diameter and Ca^{2+} and Mg^{2+} exchange of content with biochar (Méndez *et al.*, 2009). The adsorption mechanisms of biochar are largely dependent on aqueous phase and the presents of cations in the aqueous environment and biochar. Some other compounds present in the ash that include carbonates, phosphates or sulphates (Cao *et al.*, 2009; Karami *et al.*, 2011; Park *et al.*, 2013) can stabilise heavy metals by precipitation of these compounds with the contaminants.

Higher pH values after biochar addition can affect the rate and efficacy of adsorption of heavy metal in aqueous environments. The pyrolysis temperature of biochar can increase their pH values (Wu *et al.*, 2012), which is usually associated with a higher proportion of ash content (Cantrell *et al.*, 2012). Biochar can also lessen the mobility of heavy metals by altering their redox state (Choppala *et al.*, 2012). It is possible for addition of biochar in aqueous environment to the transform Cr^{6+} to a less mobile Cr^{3+} (Choppala *et al.*, 2012). In spite of Houben *et al.* (2013) suggestion that mechanism of heavy metal immobilisation by different biochars is mostly affected by pH, there a lot of unknown factors largely contribute to heavy metal immobilisation by different biochars.

Additionally, the mineral components of the biochar played a great role in the adsorption process of the leaching solution. It was demonstrated by Xu *et al.* (2013a) that compared the concurrent removal effect of heavy metals (Cd, Cu, Pb and Zn) from aqueous solutions using biochar produced from rice husk and dairy manure. In the study, the removal ability shows variation with different biochar feed stock sources and the mineral components thus CO_3^{2-} and PO_4^{3-} originating from the feed stock play an important role in the biochar adsorption ability. In one of their studies that involve Cu, Cd and Zn removal using biochar produced from dairy manure, show the biochar were rich in CO_3^{2-} and PO_4^{3}. These serve as supplementary sites for adsorption leading to high adsorption capacity of biochar for heavy metals (Xu *et al.*, 2013b).

However, biochar surface area and porous structure seem to have little effect on heavy metal adsorption ability than oxygen-containing functional groups (Tan *et al.*, 2015). Ding *et al.* (2014) demonstrated that oxygen functional groups were perhaps responsible for the high Pb adsorption onto biochars produced at low temperature (250 °C and 400 °C). Whilst intraparticle diffusion was mainly responsible for the low Pb adsorption onto biochars produced at high temperature (500 °C and 600°C).

Samsuri *et al.* (2014) used biochar produced from oil palm and rice husk for adsorption of different heavy metals. The study revealed that biochar produced from oil palm with lower surface area shows a higher adsorption capacity for heavy metals than the rice husk. This implied that the surface area was less important than oxygen-containing functional groups.

2.6 Adsorptive Properties of Biochar

Biochar is normally used for soil amendment but has proven effective and successful in removal of aqueous contaminants such as treatment of contaminated waste, contaminated water, among others unlike any other carbonaceous fuel. Its physico-chemical properties that include surface area, charged surface, and functional group vary significantly dependent on the biomass source and condition of pyrolysis, which influences the adsorptive capacity of biochar to heavy metals and organic pollutants or compounds.

2.6.1 Adsorption of Heavy Metals

In recent times, the most appropriate and cost-effective method for trace metal removal has been proven to be adsorption using biochar (Cao *et al.*, 2009; Lu *et al.*, 2012; Tsai *et al.*, 2012). However, the biochar nature, available and cost of production is crucial when remediating any aqueous phase such as land field waste water and polluted mining water. The adsorption mechanisms primarily involves chemical precipitation, electrostatic interaction, ionic exchange, and complexion with functional groups on biochar surface (Liu and Zhang, 2009; Zhang *et al.*, 2013a).

Mechanisms of heavy metal sorption in aqueous phase by biochar can be examined using different methods such as adsorption isotherms and kinetic models desorption studies, and industrial analysis that included X-ray diffraction (XRD), Fourier transform infra-red **(**FTIR) and scanning electron microscopy (SEM). These are used for the characterisation of the functional groups possessed by the biochar surfaces in both pre and post sorption.

Sorption may involve the electrostatic attraction and inner sphere complex with free and complexed carboxyl, alcoholic hydroxyl, or phenolic hydroxyl groups on biochar surface (thus R–COOH, –COOMe, –ROH, and –ROMe, note Me represents the central metal atoms) as well as superficial precipitation or coprecipitation (Qiu *et al.* 2012). Carboxyl (R–COOH) and alcoholic or phenolic hydroxyl groups (R–OH) have been recognised as the main groups contributing to coordination between heavy metals and sorbent surface (Wu *et al.*, 2013). There is inadequate information on the factors that regulate the immobilisation of inorganic pollutants on biochar and the impact of biochar on heavy metal retention in soils when compared with organic pollutants (Cao *et al.*, 2009).

Studies utilising activated carbons (ACs) was based on the solution composition and the carbon type. The following mechanism dominate: electrostatic interaction between metal cations and negatively charged carbon surfaces (above pH_{pze} of carbon); and ionic exchange between ionisable protons at the surface of the acidic carbonaceous adsorbent via proton exchange ($–C\pi–H_3O^+$) (Pellera *et al.*, 2012) or coordination of d-electrons (Cao and Harris, 2010). Impurities of mineral origin that include ash and basic nitrogen groups (for example pyridine) serve as added site of adsorption of the carbonaceous material. Sorption is an endothermic physical process as revealed by the analysis of the thermodynamic parameters of metal sorption to biochars and activated carbons (Liu and Zhang, 2009; Uchimiya *et al.*, 2010a; Harvey *et al.*, 2011). To be precise, an electrostatic interaction transpires between metal cations that are positively charged and that is π-electrons associated with either C=O ligands or (most likely) C=C of a pooled electron cloud on aromatic structures of biochar (Chen *et al.*, 2008; Cao *et al.*, 2009; Uchimiya *et al.*, 2010b). They researchers insinuated that biochar reduces Pb mobility as a result of the precipitation of insoluble Pb-phosphates. Biochars derived from manure have been reported to be rich in phosphate (Cao and Harris, 2010).

Solution pH affects both the surface charge density of the adsorbent and the metal ion speciation making it an important parameter (Chen *et al.*, 2011). Chen *et al.* (2011) also reported that pH effects on the adsorption of Cu (II) and Zn (II) onto biochar was highly significant and more pronounced for corn straw based biochar produced at 600 °C and hardwood based biochar produced at 450 °C (Zheng *et al.*, 2010). It was revealed that the adsorption capacities (mg/g) of these biochars increased with corresponded increase in pH values of the test solution until it reaches its maximum at pH 5. Change in solution measurement of pH after biochar application and adsorption equilibrium revealed that both biochars had a buffering capacity that was distinguished from that of the electrolyte.

2.6.2 Biochar Use for Removal of Inorganic and Organic Contaminants

Biochar has high affinity to adsorb molecular ions that is making it possible to be used for various toxicological mediation strategies. It has proven effective and useful for mitigating aqueous metals, organic compounds, suspended solids, and organic hydrocarbons in urban and residential storm water runoff, landfill leachates, industrial yard runoff, resource extraction runoff, and industrial wastewater filtration. A study has found raw biochar (sugar cane) to be effective as traditional activated carbon in toxicant immobilisation (Carrier *et al.*, 2012). This is applicable in either a water filtration strategy or a solid immobilisation strategy for amending biochar to contaminated media to prevent pollutant runoff and infiltration.

Charcoal has long history of being used for the removal of impurities from aqueous environment (Ippolito *et al.*, 2012). The use of biochar as a media for removal of heavy metals from aqueous environment is explored. According to Uchimiya *et al.* (2012) heavy metals need to interact with the biochar (media) through electrostatic interactions, ionic exchange, sorption through proton exchange, or specific ligand binding for stabilisation to occur. They studied sorption of Cd, Cu, Ni, and Pb to a South Carolina Ultisol amended with five types of manure biochars (dairy, poultry litter, paved feedlot, swine solids and turkey litter) pyrolysed at different 350 °C and 700 °C. Ippolito *et al.* (2012) reported biochar adsorption of aqueous solutions up to 42,000 mg/kg of Cu which was dependent on initial pH of the solution. Uchimiya *et al.* (2012) recounted similar finding on study using X-ray adsorption fine structure spectroscopy where Cu was sorbed as an organic phase at lower pH values.

However, at higher pH values, Cu remained binding to the organic ligands of the biochar surface and through precipitation it was separate as carbonate and oxide mineral phase. A study by Choppala *et al.* (2012) has proven to be effective for utilisation of biochar for the reduction of the bioavailable and toxic form of Cr (VI) to Cr (III) form that is strongly bound and nontoxic. Specifically designed biochars could be very effective in removal of heavy metals from aqueous environment that are contaminated. The multiple factors that determine the adsorption of heavy metals in aqueous environment or phase needs to be carefully examined. Cost-effectiveness of biomass feed stock and eco-friendliness of techniques need to also be given much consideration by way of making comparison with existing contaminant mitigation technologies.

Heavy metals are noted for their deleterious human health effects that include cancer, nervous system damage, reduced growth and development, organ damage, and sometimes it could be fatal. Cadmium and lead exposure can cause development of autoimmunity resulting in attacking of its own cells in a person’s immune system. This can result in diseases that include circulatory system, kidneys diseases, rheumatoid arthritis, nervous system, and fatal brain damage (Barakat, 2011). Elevated heavy metals concentrations can cause permanent brain damage (Barakat, 2011). Almost every country has wastewater regulations to help lessen human and environmental exposure to toxicants this includes limits on heavy metals concentrations and types found in the discharged wastewater (Babel and Kurniawan, 2003).

Recently, numerous approaches have been studied for the production of cheaper and relatively effective technologies, both to cut the amount of wastewater generated and to improve the quality of the treated effluent (Barakat, 2011). Adsorption has become one of the alternative treatments in recent times as the search for low-cost adsorbents that have metal-binding capacities has intensified (Leung *et al.*, 2000). This study presents an overview of using biochars for removal of heavy metals from aqueous contaminants such as land field wastewater and mining polluted water.

Landfill leachate and polluted mining water may contain various kinds of contaminants that may include dissolved metals, agrochemical pollutants, suspended solids and PAHs which often exceed recommended standard limits of Environmental Protection Agency of Ghana. A low-cost biochar looks very promising for bioretention and filtration. A recent study successfully tested a 30% of biochar (hardwood) to 70% of sand ratio as a filtration media for removal of point source and non-point-source of Zn, Cu, and solids suspended on log yard storm water effluent (Kennedy Jenks Consultants, 2014).

A column filtration tested with biochar such as digester waste, green waste, poultry litter and waste wood, led to reduction of toxic metal (Cd, Cr, Cu, Ni, Pb and Zn) that ranged from 17 to 75% dependent on the metal, nitrate decline of 86%, total suspended solid (TSS) reduction of around 86%, and up to 100% efficiency removal of some PAHs (Park and Choppala, 2011; Inyang *et al.*, 2012; Reddy *et al.*, 2014). The differences in pore size and other properties determine the adsorption ability and highly selective of metals of particular type of biochar (Caporale and Pigna, 2014).

The use of biochar for contaminant immobilisation has been successfully. It can be used as a medium in aqueous environment such as lakes, streams and aquifers buffers to mitigate or reduce the contamination potential from anthropogenic activities such as land filling, mining, agricultural activities that involves application of pesticide and fertilisers and industrial applications. Biochar produced from poultry litter has proven effective in immobilising toxic heavy metals that include As, Cu, Pb and Zn within contaminated soils (Oh and Yoon, 2013; Kim *et al.*, 2014) for amending historical mining drainage sites and other aqueous environment.

Some biochars by means of filtration method has proven effective and successful for fracking wastewater. Biochar produced from oak and pine have been used to remove about 95% of hydrocarbons residual and up to 46% of different organic salts commonly used in fracking operations (Cooks, 2014). The use of biochar by means of filtration methods can be explored to mitigate other aqueous contaminants for regulatory compliance.

2.6.3 Adsorption of Heavy Metals and other Ion Mixtures

The mixtures of heavy metals exert significant influence on the equilibrium adsorption capacity typically for the utilisation of biochar in the aqueous environment. This is due to the complex pollutants co-existing in environment, which has interaction effects on the adsorption efficiency. The co-existed heavy metals are studied for the better understanding of biochar adsorption mechanism on contaminants in the aqueous environment (Tan *et al.*, 2015). The effects of heavy metal ions on the adsorption of oxytetracycline by biochar produced from maize straw were studied by

Jia *et al.* (2013). It was reported that the existence of heavy metals showed different effects on oxytetracycline adsorption onto biochar: slight inhibition by Pb^{2+}, insignificant by Cd^{2+}, slight facilitation by Zn^{2+}, and Cu^{2+} facilitated the adsorption of oxytetracycline at all estimated pH values (Jia *et al.*, 2013). Similarly, phenanthrene (PHE) and Hg (II) co-existed in aqueous solution, resulted in direct competition in adsorption as each one suppressed another, leading to reduction in adsorption (Kong *et al.*, 2011). Nevertheless, Wang *et al.* (2013b) established that the co-existence of humic acid and metal cations increased the polychlorinated biphenyls adsorption on biochars. Besides, the particular mechanism that influences these still remains confusing. These inconsistencies shows further studies should be focused on analysing the effects of competitive adsorption and ionic strength of biochars (Tan *et al.*, 2015). For the purpose of consistency with the real situation and good understanding of the influence mechanism, the cations and anions with their concentrations (ionic strength) in aqueous solution need to be thoroughly evaluated on an individual basis (Tan *et al.*, 2015).

It is indisputable fact that most studies on adsorption of heavy metals using biochar were mostly artificial aqueous phase like simulated wastewater, but its application in remediating real environment remains a gap. The use of biochar for real aqueous environments treatment like landfill wastewater, polluted mining water, industrial sludge among others are still lacking. Besides, the influence of equilibrium adsorption capacity of complex pollutants and various ions co-existing in the aqueous environment is given little consideration.

2.6.4 Dosage of Adsorbent for Effective Removal

The efficiency of adsorption is usually influenced by the dosage of adsorbent. Hence, for effective and efficient removal of contaminants the optimum dosage of biochar needs to be carefully chosen and applied. Chen *et al.* (2011) reported that increase in the concentration of biochar decreased the adsorption efficiencies. The highest observed heavy metal adsorption efficiencies for biochar was that produced from hardwood and corn straw at 1 g/l (Chen *et al.*, 2011). Subsequently, increase in adsorbent concentration leads to the increase in total amount of active sites which improved the efficiency the removal of the total heavy metals. Similarly, Tsai and Chen (2013) reported that the number of adsorption sites increased in line with increase in dosage of adsorbents (that is 0.10 to 0.30 g/l). Nonetheless, biochar produced from agricultural waste and other feed stock can show adsorption efficiency that decreases as its mass increases.

2.7 Sources of Heavy Metals in Aqueous Environments

Basically, the sources of trace metals in aqueous environment are natural and anthropogenic activities. These heavy metals in aqueous environment have proven to have significantly deteriorated the quality of existing waters. Human exposure to heavy metals can occur in numerous ways that ranged from the direct consumption of polluted food, exposure to air contaminated particles, and direct contact or ingestion of polluted water which accumulate over a period of time (United Nations Environmental Protection/ Global Program of Action, 2004).

Naturally, rocks and volatiles of volcanic origins have contributed to increase in heavy metals concentration in soils and waters in developed countries however minimal in developing countries especially Ghana. Volcanoes activities release heavy metals that include aluminium, arsenic, copper, cadmium, mercury, magnesium, lead, zinc, rubidium among others. This is through diffusion of volcanic acidic gases via water penetrable rocks (Amaral *et al.*, 2006). Naturally, soil erosion has also in multiple ways contributed to heavy metal pollution in aqueous environment. The process via runoff release sediment-bound trace metals into aqueous environment. Water containing agrochemicals with toxic metals concentrations descent this sediment bound metal in the aqueous environment (Kaizer and Osakwe, 2010). Mostly during run-off, some heavy metal bound wastes are washed into poor drainage systems and subsequently into nearby aqueous environment (Taiwo *et al.*, 2011) such as rivers, stream, among other surface water bodies in both developed and developing nations especially Ghana. In addition, some aerosol particles naturally contain smoke cloud and heavy metals contaminants which usually accumulate on leaf surfaces via runoff they enter aqueous environment (Sardar *et al.*, 2013).

Major anthropogenic activities or source of heavy metals in aqueous environment especially land field waste water, water bodies among others in both developed and developing countries include domestic and industrial waste, textiles activities, mining and extraction operations, metal finishing and electroplating, landfill leachates and nuclear power (Akpor *et al.*, 2014; Eman *et al.*, 2015). Metal finishing and electroplating lead to release of toxic heavy metal into aqueous environment. Improper disposal of domestic and industries solid and liquid wastes have contributed to heavy metal contamination of aqueous phase in both developed and developing countries to which Ghana is no exception.

Basically, mining activities have been unpopular in countries endowed with minerals because it has demonstrated in multiple ways as source of toxic metals contributor in aqueous environment. Metal mining and smelting activities have contributed substantial amount of toxic metal contaminants in crops, vegetable, soil and water (Wei *et al.*, 2008). Additionally, textile industries have proven to be major sources of heavy metal pollutants in aqueous environment in both developed and developing countries to which Ghana is no exception.

Landfill leachate that is produced as a result of the waste mass degradation by the infiltrated water, in soluble form is organic and inorganic pollutants. The four major groups of pollutants in leachate include dissolve organics matter, heavy metals, inorganic macro component and xenobiotic organic compounds (Christensen *et al.*, 2001). Nuclear generating facilities mostly found in developing countries have proven to be a source of discharge of copper and zinc to aqueous environment. Due to the large amount of consumption of water during and after operation, the nuclear effluent that is not free from heavy metals are usually discharged into surface water and ground water bodies that pollute aqueous phase (Begum *et al.*, 2011).

2.7.1 Effect of Heavy Metal Pollution on Aqueous Environments

Heavy metals contamination is of great concern to human settings with high anthropogenic activities. They are injurious to humans due to their characteristics such as long biological half-lives, non-biodegradable nature and their ability to accumulate in different human body parts (Monu *et al.*, 2008). The continuous intake of heavy metals by human populations via food chain have been reported in many countries and has now received attention from the general public as well as governmental agencies in developing countries (Ejaz Ul *et al.*, 2007). Small-scale mining has enormously contributed to Ghanaian economy for some years now. However, it has also negatively affected the environment and human health as a result of the ever continuous introduction of harmful and toxic metals that includes arsenic (As), cadmium (Cd), mercury (Hg), lead (Pb) among others (Paruchuri *et al.*, 2010).

Untreated or inadequately waste found in land fields may contain heavy metal that usually leach into liquid ponds and leachates released into receiving aqueous environment that can caused environmental impacts and various human health problems (Akpor *et al.*, 2014). Heavy metal contaminants continue to serve as a major threat to aqueous environment and plants. The intake of toxic heavy metals in corn products and vegetables accumulate in the kidney causing its dysfunction. Studies have linked skeletal damage (osteoporosis) in humans to heavy metals (Abdullahi, 2013). Heavy metals polluted wastewater effluents on humans can include toxic (acute, chronic or sub-chronic), carcinogenic, mutagenic or teratogenic and neurotoxic (Duruibe *et al.*, 2007).

The heavy metals usually have their individual specific toxicity effects. Generally, the inhalation of vapours and ingestion of aluminium, arsenic, cadmium, copper, lead, mercury and zinc can result in poisoning, diarrhoea, gastrointestinal disorders, stomatitis, tremor, haemoglobinuria triggering a rust-red colour to human stool, ataxia, vomiting and convulsion, depression, pneumonia and paralysis (Duruibe *et al.*, 2007). Heavy metals become only toxic in human systems as results of failures to metabolise and synthesise and subsequently accumulate in the soft tissues of the human body (Akpor *et al.*, 2014).

Lead toxicity is as a result of accumulation that can cause decrease in haemoglobin production, joint, kidney, reproductive and cardiovascular systems conditions and long-term damage to the central and peripheral nervous systems (Galadima and Garba, 2012). Pb can exists in the Pb^0, Pb^{2+}, and Pb^{4+} oxidation states and can form compounds when combine with two or more elements (Agency for Toxic Substance and Disease Registry, 2007). Its level in the environment has increased over 1,000 times as of anthropogenic activities in the last three centuries, the highest increase occurred between 1950 and 2000 (Agency for Toxic Substance and Disease Registry, 2007).

Speciation of lead in aquatic environment is mainly influenced by chlorates, carbonates and organic natural ligands (Zuluaga-Rodríguez *et al.*, 2015). The proportion of lead in the inorganic complexes is mainly determined by the pH of the water. This complex gradually increase in concentration with increasing total lead (metal) loading in sediments which submit a potential threat to aquatic biota and benthic organisms in the aquatic system (Chakraborty *et al.*, 2012; Woosley and Millero, 2013). It is transported in the bloodstream to other tissues once it is absorbed, which accumulates in high concentrations in brain, bones, liver, lung, kidney, spleen and teeth, going through blood-brain and placental barrier (Tokar *et al.*, 2015). In the blood, lead has a probable average life of 35 days, in the soft tissue, of 40 days, and in bones, 20 to 30 years, the average Pb biological life can be substantial higher in the children than in the adults (Papanikolaou *et al.*, 2005).

The main pathway for the absorption of Pb excretion is the urinary tract, with the glomerular kidney filtration Pb is also excreted with the bile via the gastrointestinal tract (Tokar *et al.*, 2015). The cardiovascular, hematologic, nervous and renal are the most affected systems by exposure of Pb. The chronic toxicity of Pb in humans regularly produces apathy, convulsions, coma, constipation, epigastric pain, low attention capacity, irritability, vomit and death (Zuluaga-Rodríguez *et al.*, 2015).

In children, it can lead to encephalopathy with lethargy, anorexia, mental dullness, irritability, and vomit. Persistent Pb exposure can reduce the cognitive function and cause conduct disorders, particularly aggression, confusion, mental deficit and psychosis (Agency for Toxic Substance and Disease Registry, 2007). Pb has been categorised as carcinogenic for people with 2B Group whilst the inorganic lead compounds have been noted as carcinogenic for humans with 2A Group, mostly related to stomach cancer (International Agency for Research in Cancer, 2016).

Cadmium is highly toxic heavy metal regardless of its concentration levels in human beings. Human beings absorb cadmium ranged from 5% to 8% a factor that is favoured with low calcium, iron and protein diets. Cadmium is transported by the blood and distributed largely to the kidney and liver (Tokar *et al.*, 2015) wherever it is long-term deposited in the organism, taking an average biological life of 17 to 30 years in human beings (Zuluaga-Rodríguez *et al.*, 2015).

Cadmium exposure to humans at long term causes renal dysfunction whilst elevated concentrations of exposure cause bone defects, cadmium pneumonitis, increased blood pressure, obstructive lung disease, osteomalacia, osteoporosis and spontaneous fractures and myocardic dysfunctions (Duruibe *et al.*, 2007). Its exposure concentration determines the symptoms such as abdominal cramps, nausea, vomiting, dyspnea and muscular weakness and at severe exposure cause pulmonary odema and fatal (Duruibe *et al.*, 2007). Cd exposure negatively affects the kidney, inducing chronic kidney failure and tubular kidney failure, and in the lungs, it leads to fibrosis (Agency for Toxic Substance and Disease Registry, 2012).

Furthermore, Cd exposure also affects children central nervous system causing learning problems, hyperactivity and neurological disorders (Kim, 2012). Some previous studies on adults and children's exposure to cadmium have revealed abnormal behaviour and decreased intelligence due to the blood-barrier protection. The direct toxic effect to occur only with exposure of cadmium prior to the blood-brain barrier formation or with blood-brain barrier dysfunction (Tokar *et al.*, 2015). It has been noted as carcinogen for humans with group 1, and it has been mostly related to bladder, lung, kidney, prostate and pancreas cancer (International Agency for Research in Cancer, 2016).

Mercury is noted in its most common forms to be a toxic element thus inorganic mercury, elemental mercury and methyl mercury (Koch *et al.*, 2013). Owing to its presence in dental amalgams and to methyl mercury much consideration has been given to the poisonous effects of elemental mercury for of its ubiquity and propensity to bio concentrate (Quig, 1998). The health of top predators thus human and animals has been threatened for some decades now. Non-biodegradable mercury are in three forms of contaminants thus oxidised mercury (Hg^{2+}), elemental mercury (Hg^{0}), and particulate-bound mercury (HgP). Owing to the major harm it does to the human health and environment, mercury contamination is well-thought-out as the topmost environmental contaminants by the World Health Organisation (Wang *et al.*, 2013c).

Mercury in oxidised form is converted into its poisonous methylated species, transferred, and bioamplified by way of monomethyl mercury (MMHg) in the food chains (Trasande *et al.*, 2005). The main sources of mercury emission worldwide emanate from alluvial gold (Au) amalgamation and coal combustion (Jaffe and Strode, 2008). Alluvial gold mining activities, using elemental mercury for gold-mercury amalgamation establish biogeochemical reactors where suphate (SO_4), dissolved organic matter (OM) and iron (Fe) oxides favour bacterial activity (Muresan *et al.*, 2011). The introduction of mercury into water bodies is ever increasing and non-admissible level of more than 1 µg/l is established in the surface and groundwater (USEPA, 2001). Methyl mercury induced by the microbial bio methylation of mercuric ions (Hg^{2+}) can accumulate in the body and can cause brain damage and other chronic diseases (Qu *et al.*, 2010; Wang *et al.*, 2013c).

Organic mercury exposure has been linked to blindness, cerebral palsy, deafness and mental retardation especially in children exposed in utero (Golding *et al.*, 2013; Boucher *et al.*, 2014). Mercury is heavily use in industrial, as their demand peaked in 1964 and fell 74% between 1980 and 1993 and subsequently by 75% between 1988 and 1996. This was attributable to federal bans on mercury additives in paint, pesticides and the reduction of mercury in batteries (EPA, 1997).

The protection of human, animals and the environment required innovative methods and technologies that are cost-effective and efficient in removal of Hg from aqueous environment. Although some means of Hg removal from aqueous phase are becoming more apparent and useful, they still do not meet long-term performance criteria (Feeley *et al.*, 2003). Hence, testing the removal of mercury (Hg^{2+}) from in aqueous phase in the laboratory using biochar produced from agricultural waste, as a way of simulating its removal from real water bodies remains a current and important research topic. The adsorption of dissolved mercury ions can be hindered by the lack of reliable sorbents and solution chemistry. Besides, there are fewer and location specific technologies exist for heavy metals removal from landfill wastewater and mining polluted water.

The toxicological effect of Hg varies dependent on its form. The exposure to MeHg and Hg^0 produce signs in the central nervous system whilst Hg in mono and divalent forms acts mostly in the kidney. MeHg links to the most toxic organic form of Hg (Carocci *et al.*, 2014). It is neurotoxic owing to its accumulation in the central nervous system, worsening physiological functions via the interruption of the endocrine glands (Tan *et al.*, 2009). MeHg is noted as carcinogenic for humans with group 2B, mostly related to oesophagus and liver cancer (International Agency for Research in Cancer, 2016). Moreover, methylmercury can cross the placenta and trigger neurotoxic effects during human brain development that may probably be permanent (Debes *et al.*, 2015).

2.8 Adsorbents Produced from Agriculture Products

In recent times many researcher have shown a great deal of interest in removing heavy metals from industrial effluent and have focused on using indigenous agricultural by-products with novelty as adsorbents (Barakat, 2011). This is often referred to as bio-sorption in bioremediation of heavy metal ions. This utilises non-living (inactive) microbial biomass to bind and then concentrate trace metals from waste streams by purely physico-chemical pathways (mainly adsorption and chelation) of uptake (Igwe *et al.*, 2005).

Biomass feed stocks that include hazelnut shell, jackfruit, maize cob or husk, rice husk, groundnut shells, shea nut shells, moringa stem, coconut shells, dawadawa husks, pecan shells among others can potentially be used as an adsorbent for heavy metal removal after chemical modification or conversion by heating into activated carbon. Ajmal *et al.* (2000) used orange peel for Ni (II) removal from simulated wastewater and observed the maximum metal removal occurred at pH 6.0. The use of coconut shell charcoal modified with oxidising agents and/ or chitosan for Cr (VI) removal was reported by Babel and Kurniawan (2004). Cu (II) and Zn (II) removal from raw wastewater was studied using pecan shells-activated carbon (Bansode *et al.*, 2003) and potato peels charcoal (Amana *et al.*, 2008).

Bishnoi *et al.* (2003) studied Cr (VI) removal by rice husk-activated carbon from an aqueous solution and deduced that the maximum metal removal by rice husk took place at pH 2.0. Rice hull, containing cellulose, lignin, carbohydrate and silica, was studied for Cr (VI) removal from simulated solution (Tang *et al.*, 2003). To enhance its metal removal the adsorbent was reformed with ethylenediamine. The maximum Cr (VI) adsorption of 23.4 mg/g was observed at a pH of 2.

2.8.1 Natural Biosorbents Used for Adsorption

The major categories of adsorbents include agricultural wastes, carbon, clays, industrial wastes, and indigenous regenerative shrubs and tree extracts or products among others. Biochar's feed stocks (especially for plant biomass or agricultural waste) are composed basically of cellulose, hemicellulose and lignin (Rutherford *et al.*, 2012), which are gradually pyrolysed with the increase of temperature. In charring of the feed stock lignin have demonstrated to be much more recalcitrant than hemicellulose and cellulose (Rutherford *et al.*, 2012). These waste constituents and others such as ash, hemicelluloses, hydrocarbons, lipids, proteins, simple sugars, starches, water, among others compounds that usually contain a range of functional groups in their binding process like amino, alcohol, carboxyl and esters (Gupta and Ali, 2000). These groups have the ability to bind heavy metals by means of replacement of the hydrogen ions for metal ions in solution or by means of donation of an electron pair for the formation of complex with metal ion in the solution. This relation between the different functional groups and their complexation with trace metals in the course of biosorption process has been described by many researchers (Tarley and Arruda, 2004).

Some adsorbents that have proven effective and successful with high loading capacities of less than 90 mg/g include aliginate carriers, *Alcaligenes eutrophus*, baker's yeast, broad bean peel, fig leaves, modified sugarcane bagasse, modified wheat bran, medlar peel, kraft lignin, *Platanus orientalis*, peas peel and rice husk (Rao *et al.*, 2010). The capacity of four inexpensive materials agriculture waste such as broad bean, fig leaves, medlar and peels of peas have been used for the removal of cadmium from aqueous solutions (Benaissa, 2006). However, it was noted that biosorbents have shorter life time when matched with the conventional sorbents (Fu and Wang, 2011). The early saturation of biosorbent is as results of metal interactive sites are being occupied (Gadd, 2008). The recyclable and decomposable properties of biomass usually delay their long-term applications in adsorption processes (Sahmoune *et al.*, 2011). The broad bean peel has proven to possess the maximum adsorption capacity for Cd (II). Moreover, sisal fibre (*Agave sisalana*) was used as a biosorbent for removal of Pb (II) and Cd (II) ions from natural waters (dos Santos *et al.*, 2011). In addition, Ni (II) ion adsorption from water was studied employing two strains of *Yarrowia lipolytica* (Shinde *et al.*, 2012). A freshly developed deep-sea bacterium thus *Pseudo alteromonas* has proven effective as a biosorbent for removal of Cd (II) from water (Zhou *et al.*, 2013).

2.8.2 Shells and Husks Biosorbents Used for Adsorption

A study on coconut shell (*Cocos nucifera*) powder has proven as a potent and economical alternative for the biosorption removal of dissolved metals (Pino *et al.*, 2006). A study by Alves and Coelho (2013) using *Moringa oleifera* husks for adsorption removal of chromium in water has proven effective and successful. Black gram (*Cicer arientinum*) husk was also studied as a new biosorbent of Cd (II) from low concentration aqueous solutions (Saeed and Iqbal, 2003). Moreover, rice husk has been used for the removal and recovery of Cd (II) from waste waters by Ajmal *et al.* (2003). These give more room for more studies to be conducted using waste material such as groundnut shells and shea nut shells as biosorbents as only few are already used.

2.9 Adsorption Isotherm Models

2.9.1 Adsorption Isotherm

Adsorption isotherm is important in elevating the use of adsorbents since it vividly describes the interaction between adsorbates and with adsorbents (Goh *et al.*, 2008). Some mathematical models have been used to describe the adsorption equilibrium of heavy metals on biochars and examine experimental data. Langmuir, Freundlich, Langmuir–Freundlich and Temkin equations are the most popular and widely used.

The results using these models are largely dependent on biochar properties and the target contaminant. The Langmuir isotherm usually assumes monolayer adsorption of adsorbate on adsorbent with a homogeneous surface (Hu *et al.*, 2011). Chen *et al.* (2011) studied adsorption isotherms at different initial concentrations of Cu (II) and Zn (II) that ranged from 0.1 to 5.0 mM that has proven that the Langmuir model ($R^2 >$ 0.998) fit the data better than the Freundlich model (R^2 were 0.86 to 0.94).

Many researchers also reported that adsorption of heavy metals by biochar fits better to Freundlich than Langmuir isotherm in the experiment data (Lu *et al.*, 2012; Zhang *et al.*, 2013c; Agrafioti *et al.*, 2014; Yang *et al.*, 2014). The Freundlich isotherm discloses information on the heterogeneous adsorption and is not limited to the formation of a monolayer (Hu *et al.*, 2011; Kim *et al.*, 2013). The study of Cr (VI) and Pb (II) adsorption by biochar pyrolysed from the municipal wastewater sludge, adsorption isotherms on the biochar were simulated with Langmuir and Freundlich equations. The study revealed that Pb (II) adsorption behaviour fitted better with

Langmuir equation than Freundlich equation (Zhang *et al.*, 2013c). Biochar also showed high affinity for organic contaminants (Kumar *et al.*, 2011a).

In recent times, most laboratory experiments were performed to investigate the potential of biochar as an adsorbent for removal of organic pollutants from aqueous solution. Overall, the results from these studies demonstrated that the biomass resultant biochar can be used as a cost-effective adsorbent for removal of environmental organic pollutants from the water. The toxins include dyes, pesticides, herbicides, antibiotics, and other organic contaminants.

2.9.2 Langmuir Model

Undoubtedly, the best and most extensively used sorption isotherm is the Langmuir model (Gerente *et al.*, 2007). The mechanistic model is usually based on numerous assumptions including monolayer adsorption (adsorbed layer is one (1) molecule of thickness), in which sorption only happens at a finite number of indistinguishable active sites. Moreover, there are no steric hindrances or lateral interactions between adsorbed molecules and the adjacent sites (Vijayaraghavan *et al.*, 2006; Foo and Hameed, 2010). Furthermore, the model of Langmuir implicitly assumes that the binding to an adsorbent's (biochar) surface is single-minded by the physical forces and all sites are actively equivalent with affinity for the sorbate being equal (Vijayaraghavan *et al.*, 2006). The model has been extensively used to explain the sorption of heavy metals by biochar.

2.9.3 Freundlich Model

The Freundlich model is often used for non-ideal sorption on the heterogeneous surfaces in addition to multilayer sorption (Gerente *et al.*, 2007). Freundlich equation does not assume unlike the Langmuir model, the sorption sites are homogenous and actively equivalent. In contrast, the Freundlich model assumes that sorption sites of the biochar (adsorbent) are of diverse affinities, and stronger binding sites are engaged first in a way that the strength of binding decreases with increase in the degree of site occupation (Vijayaraghavan *et al.*, 2006). Therefore, the quantity adsorbed is a summation of all the sites of adsorption (each site taking its own bond energy) and exponentially the energy distribution of the sorption sites decays, until the completion of the process of adsorption (Gerente *et al.*, 2007; Foo and Hameed, 2010). The Freundlich model has been successfully used to explain the sorption isotherms of heavy metals on various biochars.

2.9.4 Temkin Model

Temkin model approves effect of particular indirect interactions amongst heavy metals ions or adsorbate particles and proposes linear decrease in adsorption of heat of all the molecules in the layer, owing to the interactions. Temkin adsorption isotherm has a factor that explicitly takes into the consideration of biochar (adsorbent) and metal ion (adsorbate) interactions. By way of ignoring extremely low and large value of concentrations, the model assumes that the fall in the heat of adsorption (function of temperature) of all molecules in the layer is linear rather than logarithmic with coverage (Temkin and Pyzhev, 1940).

2.10 Previous Batch Experiments

The study of systems with a mixture of contaminants is paramount particularly heavy metals as they usually coexist in the environment and undergo competitive sorption. Inyang *et al.* (2012) performed batch experiment by using dairy waste and sugar beet as feed stocks, where the residue materials were first dried at 80 ºC prior to the production of the biochar. Five hundred grams (500 g) of dried feed stock was heated at 600 ºC for 2 h in a furnace with N_2 environment. The concentration of each heavy metal in the solution was then adjusted to 0.10 mmol/l. After which 0.10 g of biochar was added into 68 ml digested vessels and then mixed with the 50 ml of heavy metal solution at room temperature of 22 ± 0.5 ºC (Inyang *et al.*, 2012). It was then shaken in a reciprocating shaker for 24 h. The adsorption efficiency of the four heavy metals (Pb^{2+}, Cu^{2+}, Cd^{2+} and Ni^{2+}) by digested whole sugar beet biochar was higher than 97%, indicating the biochar has a strong affinity for the four heavy metals tested. Digested dairy waste biochar also showed high adsorption efficiency for Pb^{2+} (99%) and Cu^{2+} (98%), but relatively low adsorption efficiency for Cd^{2+} (57%) and Ni^{2+} (26%) (Inyang *et al.*, 2012).

Regmi *et al.* (2012) conducted batch experiment, which they first made 50 ml aqueous cadmium or copper solution at temperature of 23 ± 1 ºC for 24 h. After contact time of 24 h the solutions were collected and filtered via a 0.45 mm nylon filter at consistent intervals in glass tubes. The batch experiments were done with an initial heavy metal concentration of 40 mg/l at pH 5.0 pH-units and contact time of 24 h occasioned in almost to 100% cadmium and copper removal by activated hydrothermal carbonisation biochar (HTCB) at 2 g/l, far greater than that of powdered activated carbon (PAC) (4% and 7.70%) and HTC biochar (16% and 5.60%).

Activated HTCB adsorption capacities for cadmium and copper removal were 34 mg/g and 31 mg/g, respectively. The activated HTCB showed a higher adsorption potential for cadmium and copper than HTC biochar and PAC (Regmi *et al.*, 2012).

Hegazi (2013) used agriculture waste and fly ash as the feed stock. Heavy metal concentration (Cu, Fe and Ni) of 10 mg/l at an agitation rate of 200 rpm with 20 min as the adsorbent time at room temperature of 25 ± 3 ºC. Langmuir isotherms were attained by equilibrating heavy metal ion solutions of different adsorbent doses (5–30 mg/l) with different contact times (20–150 min) at equilibrium pH and rpm with 10 mg/l as the initial metal concentration at room temperature. The adsorption efficiency of the Fe, Ni and Pb were 99.25%, 96.15% and 87.17%, respectively by the rice husk and Cu and Cd were 98.54% and 73.54%, respectively by fly ash. The rice husk was effective in the simultaneous adsorption of Fe, Pb and Ni whilst fly ash was also effective in the removal of Cd and Cu in in the real wastewater (Hegazi, 2013).

An experiment conducted in 60 ml polypropylene tubes that involve the mixture of 0.125 g biochar with 25 ml 0.01 M $NaNO_3$ solution containing 0, 1, 2, 3, 4 and 5 mM of Cu, Zn or Cd, respectively. The agitation of the mixture was done on a reciprocating shaker at 100 rpm for 10 h. Preliminary experiment shows the contact time was enough for sorption of all heavy metals to reach equilibrium. After the equilibrium, liquid and solid phase were then separated by centrifugation at 4000 rpm for 15 min, and the aqueous solution was filtered through a 0.22 µm Millipore filter. The heavy metal concentrations were determined using atomic adsorption spectroscopy (AAS). The maximum adsorption capacities of Cu, Cd and Zn by dairy manure at 200 °C were 48.40 mg/g, 31.90 mg/g and 31.60 mg/g, respectively and

54.40 mg/g, 51.40 mg/g and 32.80 mg/g by dairy manure at 350 °C (Xu *et al.*, 2013b). In a batch experiments was conducted with initial Cd and Pb concentration of 10 to 200 mg/l and 10 to 250 mg/l, respectively. The sorbent concentration was 2 g/l and the pH of the solutions was adjusted to 5.0 pH-units with 0.01 and 0.10 M of NaOH and HNO_3. The experiments were done in a rotary shaker set at 30 rpm with constant temperature of 25 °C and equilibrium time of 24 h. The heavy metal concentration of the solution was determined using AAS. The maximum adsorption affinity of rapeseed thus studied materials and its adsorption capacity was 83.50 mg/g and 31.60 mg/g for Pb and Cd (Štefušová *et al.*, 2012).

The batch adsorption experiment was also conducted by treating a prepared stock solutions with different ranges of carbon nanotubes (CNTs) dosage from 0.03 to 0.09 g, agitation speed from 100 to 150 rpm, pH of 4–6 for Pb^{2+} and 4–8 for Cr^{3+} with changing agitation time from 10 to 50 min and from 10 to 60 min, respectively. The pH value of the stock solution was adjusted using 0.50 M of the NaOH solution. The initial concentration of 2 mg/l recorded removal efficiency of 99.90% for Pb^{2+} ions and 95.50% for Cr^{3+} ions. The maximum adsorption capacities ions onto the carbon nanotubes were 15.34 mg/g for Pb^{2+} ions and 24.45 mg/g for Cr^{3+} ions (Mubarak *et al.*, 2016).

A batch experiment where seven columns were filled with different dose of biochars produced from scots pine and silver birch. Adsorption capacity of Pb (II) on biochars produced from silver birch and scots pine varied from 0.00129 to 0.00377 mg/g and 0.00237 to 0.00449 mg/g, respectively. The maximum adsorption capacity of Cu (II) on biochar produced from silver birch (*Betula pendula*) was 0.1287 mg/g and Zn (II) on biochar from scots pine (*Pinus sylvestris L.*) was 0.1070 mg/g (Komkiene and Baltrenaite, 2016).

In a study, where adsorbent were sunflower stem carbon (SSC) and sunflower head carbon (SHC). Same process optimised for mono-metal solutions were used for the binary and tertiary systems, thus pH 2.0 for Cr (VI) and 6.0 for both Ni (II) and Cd (II), volume of 50 ml, co-cation concentration varied between 0.5 mM and 2.0 mM for binary system and between 0.25 : 0.25 and 1.0 : 1.0 for tertiary system, adsorbent dose of 0.20 g/ 50 ml, contact time of 180 min, stirring speed of 180 rpm and temperature of 25 ± 1 °C. It was reported that adsorption capacity of Cd (II), Cr (VI) and Ni (II) by sunflower head carbon and sunflower stem carbon in mono-component system of metals was higher than combination of the metals systems. The sunflower stem carbon had higher adsorption capacity than sunflower head carbon for Cd (II), Cr (VI) and Ni (II) in mono-component system. It was 0.32 mM/g for Ni (II), 0.25 mM/g for Cd (II) and 0.20 mM/g for Cr (VI) by sunflower head carbon, whilst 0.45 mM/g for Ni (II), 0.32 mM/g for Cd (II) and 0.28 mM/g for Cr (VI) by sunflower stem carbon (Jain *et al.*, 2015).

Lastly, in a batch experiment where biochar and activated carbon were studied, it was reported that 96.88% of Cd (II), 96.23% of Zn (II), 95.96% of Co (II), 93.38% of Cu (II) and 88.79% of Pb (II), ions were removed by biochar in acidic solutions, whilst only 80.58% of Cu (II), 68.08% of Cd (II), 63.08% of Zn (II), 54.69% of Pb (II) and 36.70% of Co (II) ions were adsorbed by removed from activated carbon (Kołodyńska *et al.*, 2017). Chen and his associates have made impact in their contribution of literature in this field of adsorption of heavy metals using adsorbents.

2.11 Factors Affecting Adsorption of Heavy Metals

A variety of multiple operation factors effect adsorption of heavy metals. These include adsorbent dosage, agitation speed, initial concentration of heavy metal, temperature, particle size of adsorbent, effect of pH on the adsorption capacity and other factors (Chojnacka, 2010). It was reported by Chojnacka (2010) that the sorbent dosage decreases the quantity of biosorbed pollutant per unit weight of biosorbent which lead to increase in its removal efficiency whilst the initial contaminant concentration increases the quantity of biosorbed contaminant per unit weight of biosorbent which lead to decrease in its removal efficiency. It was also noted that pH of the solution could enhance biosorptive removal of cationic metals or basic dyes, nonetheless lessens that of anionic metals or acidic dyes.

Basically temperature could enhance adsorptive removal of contaminants by increasing surface activity and kinetic energy of the adsorbate. However, it can damage the physical structure of the adsorbent. Chojnacka (2010) also reported that agitation speed could also enhance biosorptive removal rate of adsorptive contaminant by minimising its mass transfer resistance, nonetheless could damage the physical structure of the biosorbent. It was noted that ionic strength can reduce biosorptive removal of adsorptive contaminant due to competition with the adsorbate for binding sites of adsorbent. The particle size of the biosorbent could also favour the batch process due to higher surface area of the adsorbent, but not for column process due to its low mechanical strength and clogging of the column. In multiple pollutants concentrations situation the coexisting of the pollutants competes with a target contaminant for binding sites or form any complex with it causing the higher concentration of other pollutants to reduce adsorptive removal of the target pollutant (Chojnacka, 2010).

2.12 Pre and Post Biochar Utilisation Challenges

Generally, biochar has proven to be technically effective and efficient as eco-friendly media for removal of organic and inorganic contaminants in aqueous environment such as polluted soil, water, waste effluents among others. It has also proven to have contained toxins in both organic and inorganic forms that are within acceptable limits and regulation standards after its production. However, like any other remediation innovation, biochars have their limitations that are not only about cost of production and technically in its utilisation but also post utilisation issues.

The source of raw material used for biochar has proven to be source of dangerous components such as organic pollutants and heavy metals that pose potential risk to human and their environment. Agricultural waste such as rice husk and rice straw utilised as biomass feed stocks for biochars generally contains elevated levels of silica, given their biochars ability to form crystalline silica. It has been established that biochars residues have the tendency to form poly aromatic hydrocarbons (PAHs) that are generally carcinogenic and can be injurious to human health. The residues are the ash containing those contaminants like heavy metals, which after their utilisation researchers face challenges of disposing. Biochar used for removal of aqueous phase may not leave the aqueous environment free from dangerous pathogens.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Production of Biochars

Biochars were produced from groundnut and shea nut shells (**Plate 1 and 2**) in the Agricultural Sub-sector Improvement Programme (AgSsIP) Laboratory of the University for Development Studies, Nyankpala Campus, Ghana. The agricultural wastes are often in abundance during the earlier and late part of the raining season in many parts of the Guinea savannah zone of Northern Ghana, West Africa. The groundnut and shea nut shells were collected from Phebsigu and Shishegu all in the Tamale Metropolis. Foreign biomass and other materials were then removed from the feed stocks.

Feed stocks were kept in small earthen pots and transferred into a muffle furnace and pyrolysis was done under limited oxygen (O_2) conditions at a temperature of 350 ± 5 °C (slow pyrolysis) for 60 min and 180 min for groundnut and shea nut shells, respectively. Biochar produced under fast pyrolysis was done at a temperature of 700 ± 5 °C for 45 min and 90 min for groundnut and shea nut shells, respectively. The process was separately carried out continuously under both pyrolysis to obtain a total of about 2 kg of the various biochars. The difference in residence time of pyrolysis of groundnut and shea nut shells are due to their difference in lignocellusosic biomass.

Plate 1: Groundnut shell biochar produced under limited O_2 conditions at a temperature of 350 ± 5 °C for 60 min

Plate 2: Shea nut shell biochar produced under limited O_2 conditions at a temperature of 700 ± 5 °C for 90 min

3.2 Preparation of Aqueous Phase and Adsorption Experiments

The experiment was carried out in the Spanish Laboratory at the Nyankpala Campus of the University for Development Studies, Ghana. Aqueous phase were prepared by dissolving accurately weighted 1.68 g of cadmium chloride ($CdCl_2$: grade; anhydrous, assay; 99.99%), 1.35 g of mercury chloride ($HgCl_2$: grade; ACS reagent, assay; $\geq$ 99.5%) and 1.60 g of lead nitrate ($Pb\ (NO_3)_2$: grade; GR, assay; 99.5%) in deionised water to prepare solutions of 1000 mg/l concentrations of the aqueous phase. Molecular weight of $CdCl_2$ (183.32), $HgCl_2$ (271.50) and $Pb(NO_3)_2$ (331.21) were calculated and divided by atomic weight of Cd (122.41), Hg (200.60) and Pb (207.20), respectively to obtain amount of compounds containing 1 mg each of the heavy metals. Heavy metal solution mixtures were prepared in a 1000 ml volumetric flask.

Serial dilutions were done to obtain maximum concentration limits of the leaching metals in the various folds. The leaching solutions were prepared by following the equation below:

$$\mathbf{M_1V_1 = M_2V_2}$$

Where, $\mathbf{M_1}$ = Concentration of leaching stock solution; $\mathbf{V_1}$= Volume of leaching stock solution needed; M_2 = Concentration of heavy metal needed; $\mathbf{V_2}$ **=** Volume of distilled water to which leaching stock solution is added. The leaching solutions were in composition of one fold, two folds, and five folds value of maximum contaminant level (MCL) for selected heavy metal ions in aqueous phase. Mixtures system experiments of the heavy metals were also performed to determine their adsorption capacity. The leaching solutions were simulated in accordance with the procedure proposed by Saveyn *et al*. (2014) for discharge into receiving water bodies (**Table 1**).

Table 1: Maximum contaminants limits (mg/l) of heavy metals in aqueous phase

Batch	Metal	One fold	Two fold	Five fold	N
Mono	Cd	0.04	0.08	0.20	18
	Hg	0.10	0.20	0.50	18
	Pb	0.10	0.20	0.50	18
Binary	Cd:Hg	0.04:0.10	0.08:0.20	0.20:0.50	18
	Cd:Pb	0.04:0.10	0.08:0.20	0.20:0.50	18
	Hg:Pb	0.10:0.10	0.20:0.20	0.50:0.50	18
Ternary	Cd:Hg:Pb	0.04:0.10:0.10	0.08:0:20:0.20	0.20:0.50:0.50	18

Note: Folds calculations were done in accordance with Saveyn *et al.* (2014).

3.3 Mono and Multi-components Studies

The adsorption was carried out in batch system of the trace metals by using the individual biochars and combination of the two to determine their mono-component adsorption capacity. Fifty mg/l of heavy metal ion with 2 g / 50 ml of adsorbent dosage was leached at constant room temperature of 24 ± 0.5 ºC in laboratory and constant contact time of 72 min. All the experiments were carried out at their respective pH that ranged from 3.25 – 4.63. The adsorption effect of the co-cations of the heavy metals on the individual biochar and combination of the two was also performed in both binary and ternary component systems. The experimental design used is shown in table 1. The batch system, trace metal and co-cation concentrations (mM) were maintained at their respective ratio of maximum contaminants limits (**Table 1**). Control samples were taken from the prepared aqueous phase and analysis to confirm the various initial concentrations in the mono, binary and ternary systems before carry out the leaching.

3.4 Retention Experiments

Six organic glass separatory funnels (Probel model, 100 ml capacity) with internal diameter of 38 mm and height of 294 mm were filled with cotton wool at the neck (**Plate 3**). The funnels were then filled with 2 g each of the different biochars (in the case of the combination of biochars it was 1 g each making up the 2 g) which had been crushed into particles size of 2 mm using a mortar and pestle made of clay (**Plate 4**). Test solutions were allowed to gravitationally leach from the top of experiment funnels at a constant room temperature of 24 ± 0.5 ºC in the laboratory, and constant contact time of 72 min under a constant flow rate. Elutes were then automatically sampled immediately after the whole retention test and elutes were then filtered using Whatman's qualitative filter paper with a particle retention size of 125 mm Ø. Screw cap plastic bottles with volume capacity of 35 ml were used to collect elute and conveyed to the laboratory. Elutes were kept in an ice chest and transported to the Ecological Laboratory of the University of Ghana, for prior analysis. The analysis of cadmium, mercury and lead was done using the Perkin Elmer PIN Accle 900T Graphite Atomic Absorption Spectrophotometer (AAS), (Waltham, United States of America).

Plate 3: Separatory funnels with cotton wool and biochar

Plate 4: Shea nut shell biochar crushed for sieving through 2 mm standard sieve

3.5 Quality Assurance and Quality Control

Strict quality assurance and quality control measures and standard were observed in the production of biochars and all laboratory procedures to ensure reliability of the results. Batch isotherm tests were replicated three times and blanks of the metals were run in parallel to establish accuracy, reproducibility and reliability. The reagents and chemicals used were of high purity. Glass wares used were cleaned thoroughly with detergent and rinsed using deionised water. A blank solution was read twenty five times for the purposes of detection and quantification limits of the Atomic Absorption Spectrophotometer (AAS), and the standard deviations were computed for the noise levels generated for each of the heavy metals.

The detection limit (LOD) for each metal was calculated as follows: LOD = $\frac{3 \, x \, S}{M}$ where **S** is the standard deviation of the blank readings and M refers to the gradient of the calibration curve for each metal. Quantification limit was computed using 10 s/m. The reproducibility and accuracy of the analytical procedure was done by spiking and homogenising three replicates of each of three elute (samples) selected at random. Triplicate of each sample was spiked with three different concentrations of the metal of interest and treated in a similar manner as the sample. The absorbances measured by the AAS were converted to concentrations using standard calibration curves. The detection limits of the metal ions were 0.0008 mg/l for Cd, 0.0001 mg/l for Hg and 0.003 mg/l for Pb.

3.6 Calculation of Adsorption Efficiency of Heavy Metals

The heavy metal uptake loading capacity Q_e (mg of metal per g of adsorbent) for each sorption system was determined using equation 1:

$$Q_e = \frac{C_o - C_e}{M} \text{ x V} \ldots\ldots(1)$$

and the adsorption efficiency of heavy metals (Cd, Hg and Pb), Q_e (mg/g) in percentage was calculated using the equation 2:

$$Q_e = \frac{(C_o - C_e)V}{M} \text{x } 100\% \ldots\ldots(2)$$

Where C_o and C_e are the initial and final concentrations (mg/l), respectively, M is the adsorbent dosage (g), and V is the volume of solution (l).

3.7 Data Modelling Using Langmuir, Freundlich and Temkin Equations

Adsorption isotherm models were deployed to elucidate the relationship that exists between the adsorbate loading on the adsorbent (Q) and aqueous phase concentration of adsorbate (C) at equilibrium conditions (Kumar *et al.*, 2011b). This study employed Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) models for fitting the equilibrium data.

Langmuir adsorption isotherm explains the quantitative formation of a monolayer heavy metal (adsorbate) on the outer surface of the biochar (adsorbent), and after that no further adsorption occurs. On a surface having a finite number of identical sites Langmuir isotherm is usually valid for monolayer adsorption. Langmuir model assumes uniform energies of adsorption on the surface and no transmigration of heavy metal (adsorbate) in the plane of the surface. Based on these assumptions, Langmuir exemplified the following equation 3:

$$Q_e = \frac{Q_{\max} K_l C_e}{1 + K_l C_e} \text{...(3)}$$

Parameters for Langmuir adsorption were determined by transforming the Langmuir equation 3 into a linear form.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_o K_l C_e} \quad \text{..(4)}$$

Where Q_{max} is the maximum adsorption capacity calculated by Langmuir model; Q_e = the amount of heavy metal adsorbed per gram of the biochar (adsorbent) at equilibrium (mg/g); Q_o = maximum monolayer coverage capacity (mg/g); K_l = Langmuir isotherm constant (l/mg); and C_e = the equilibrium concentration of heavy metal (adsorbate) (mg/l^{-1}). The values of Q_{max} and K_l were calculated from the intercept and slope of the Langmuir plot of Ce vrs ${}^{C_e}/{}_{Q_e}$ (Langmuir, 1918).

The important features of the Langmuir isotherm may be the expression of equilibrium parameter R_L, which is a dimensionless constant denoted as equilibrium parameter or separation factor (Webber and Chakravarti, 1974).

$$R_L = \frac{1}{1+(1+K_l C_0)} \text{...(5)}$$

Where: C_0 = initial concentration of absorbate, K_L = the constant that is related to the adsorption energy (Langmuir constant). R_L value designates the nature of adsorption to be either, linear if $R_L = 1$, favourable if $0 < R_L < 1$, unfavourable if $R_L > 1$ and irreversible if $R_L = 0$.

The Freundlich adsorption isotherm is often used to describe the characteristics of adsorption for heterogeneous surface (Hutson and Yang, 2000). Freundlich constants that signifies extent of the adsorption and the degree of nonlinearity between aqueous solution concentration and adsorption, respectively. These data often fit the empirical equation (6) proposed by Freundlich:

$$Q_e = K_f C_e^{1/n} \quad \text{......................................}(6)$$

Where Q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g); K_f = Freundlich isotherm constant (mg/g); C_e = the equilibrium concentration of adsorbate (mg/l); and n = adsorption intensity.

Linearising equation:

$$\log Q_e = \log K_f + {}^{1}\!/_{n} \log C_e \quad \text{......................................}(7)$$

The constant K_f is an approximate indicator of adsorption capacity, whilst ${}^{1}\!/_{n}$ is a function of the strength of adsorption in the adsorption process (Voudrias *et al.*, 2002). If n = 1 then the partition between the two phase are independent of the concentration. If value of ${}^{1}\!/_{n}$ is below one it shows a normal adsorption. On the other hand, ${}^{1}\!/_{n}$being above one shows co-operative adsorption (Mohan and Karthikeyan, 1997).

Temkin adsorption isotherm has a factor that explicitly takes into the consideration of biochar (adsorbent) and metal ion (adsorbate) interactions. By way of ignoring extremely low and large value of concentrations, the model assumes that the fall in the heat of adsorption (function of temperature) of all molecules in the layer is linear rather than logarithmic with coverage (Temkin and Pyzhev, 1940). Its derivation is characterised by a uniform distribution of binding energies (up to some maximum binding energy) as implied in the equation. The linear plots of Qe against *In Ce* and the slope and intercept of linear equation for Temkin model were used to calculate for the constants. The model is given by the following equation (Temkin and Pyzhev, 1940):

$$Qe = \frac{RT}{b} In(A_T C_e) \ldots\ldots (8)$$

$$Qe = \frac{RT}{b_T} InA_T + (\frac{RT}{b}) InC_e \ldots\ldots (9)$$

$$B = \frac{RT}{b_T} \ldots\ldots (10)$$

$$Qe = BInA_T + BInC_e \ldots\ldots (11)$$

A_T = Temkin isotherm equilibrium binding constant (L/g), b_T = Temkin adsorption isotherm constant, R = universal gas constant (8.314 J/mol/K), T = temperature at 297 K, and B = constant related to heat of sorption (J/mol).

3.8 Interactive Behaviour of Heavy Metals

The selectivity of adsorbents for Cd, Hg and Pb in both binary and tertiary mixture was determined in terms of relative metal *i* adsorption that is R_i (%) which is defined as in Chang and Chen (1998). The percentage R_i will determine whether the combinations in binary and tertiary system are antagonistic, synergistic or non-interactive in nature.

$$\mathrm{R}i = \frac{\text{Metal } i \text{ adsorption capacity with co−existence of metal } j \text{ and } k}{\text{Metal } i \text{ adsorption capacity without co−existence of metal } j \text{ and } k} x\ 100\% \ldots\ldots\ldots\ldots (12)$$

If Ri > 100 percent, it shows that the interactive effect of a mixture of metals (say, j and k) is synergistic, If Ri < 100% indicates antagonistic behaviour and $\mathrm{R_i}$ = 100% indicates non-interactive behaviour.

3.9 Statistical Analysis

The effects of pyrolysis temperature (slow vs fast), type of biochars (groundnut biochar vs shea nut shell biochar vs combination of the two biochars), pH of aqueous phase and the different maximum contamination limits (fold one vs fold two vs fold five) on the adsorption capacity of Cd, Hg and Pb ions onto biochar were statistically analysed using the Statistical Package for the Social Sciences (SPSS version 16). Differences were considered to be significant at $p < 0.05$.

CHAPTER FOUR

RESULTS

4.0 Adsorption Efficiency of Heavy Metals

The results of the batch experiment are presented below.

4.1 Adsorption Efficiency of Mono Metals onto Biochars Produced under Slow and Fast Pyrolysis

The removal efficiency of cadmium ions in the aqueous phase with a concentration of 0.04 mg/l (one fold) by groundnut shell, shea nut shell, and the combination of groundnut and shea nut shells biochars produced at pyrolysis temperature of 350 ± 5 °C was 100% (**Table 2**). Cadmium removal efficiency at a concentration of 0.08 mg/l (fold two) were 100%, 99.99% and 99.59% by shea nut shell, groundnut shell, and the combination of groundnut and shea nut shells biochars produced at pyrolysis temperature of 350 ± 5 °C, respectively (**Table 2**). The removal efficiency of cadmium ions at fold five (0.20 mg/l) by groundnut shell biochar, shea nut shell biochar and the combination of groundnut and shea nut shells biochars produced at pyrolysis temperature of 350 ± 5 °C were 100%, 99.98% and 99.92%, respectively (**Table 2**).

Also biochars produced at pyrolysis condition of 700 ± 5 °C were able to remove all cadmium ions in the aqueous phase at a concentration of 0.04 mg/l (**Table 2**). The cadmium removal efficiency at a concentration of 0.08 mg/l (fold two) and 0.20 mg/l were 99.67% and 99.93% for biochars produced from groundnut shell only at pyrolysis temperature of 700 ± 5 °C, respectively. Regarding fold two and fold five the removal efficiency for both shea nut shell biochar and the combination of groundnut and shea nut shells biochars was 100% (**Table 2**).

Table 2: Adsorption efficiency of mono metals by biochars

			Type of biochar		
Pyrolysis	Metal	Initial conc (mg/l)	Groundnut shell (%)	Shea nut shell (%)	Groundnut and shea nut shells (%)
Slow pyrolysis	Cd	0.04	100	100	100
		0.08	99.99	100	99.59
		0.20	100	99.98	99.92
Fast pyrolysis	Cd	0.04	100	100	100
		0.08	99.67	100	100
		0.20	99.93	100	100
Slow pyrolysis	Pb	0.10	99.12	100	99.47
		0.20	100	100	99.68
		0.50	100	100	99.84
Fast pyrolysis	Pb	0.10	100	100	100
		0.20	100	100	100
		0.50	100	100	100
Slow pyrolysis	Hg	0.10	99.99	100	100
		0.20	100	100	100
		0.50	100	100	100
Fast pyrolysis	Hg	0.10	100	100	100
		0.20	100	100	100
		0.50	100	100	100

The adsorption efficiency of lead ions at concentration of 0.10 mg/l (fold one) by groundnut shell, shea nut shell biochar and biochar from the combination of groundnut and shea nut shell produced under pyrolysis temperature of 350 ± 5 °C were 100%, 99.47% and 99.12%, respectively (**Table 2**). The removal efficiency of lead ions at a concentration of 0.20 mg/l (fold two) and 0.50 mg/ l (fold five) were 100% for both biochars produced from groundnut shell, and shea nut shell at pyrolysis temperature of 350 ± 5 °C, respectively (**Table 2**). Whilst the removal efficiency for biochar that involves the combination of groundnut and shea nut shells was 99.68% for fold two and 99.84% for fold five (**Table 2**).

The adsorption efficiency of lead ions in aqueous phase with concentrations of 0.10 mg/l, 0.20 mg/l and 0.50 mg/l (thus fold one, two and five) by biochars produced from groundnut shell, shea nut shell and the combination of groundnut and shea nut shells at pyrolysis temperature of 700 ± 5 °C was 100% (**Table 2**).

The removal efficiency of mercury ions in the prepared aqueous phase with a concentration of 0.10 mg/l (one fold) by biochars produced from groundnut shell, shea nut shell and the combination of groundnut and shea nut shells at pyrolysis temperature of 350 ± 5 °C were 99.99%, 100% and 100%, respectively (**Table 2**). The biochars produced from groundnut shell only, shea nut shell only and the combination of groundnut and shea nut shells at pyrolysis condition of 350 ± 5 °C were able to remove all mercury ions (100%) from the aqueous phase with concentrations of 0.20 mg/l and 0.50 mg/l (**Table 2**). The removal efficiency of biochars produced from groundnut shell only, shea nut shell only and the combination of groundnut and shea nut shell at temperature of 700 ± 5 °C regardless the fold of concentrations in the prepared aqueous phase was 100% (**Table 2**).

4.2 Adsorption Efficiency of Binary Metals onto Biochars Produced under Slow and Fast Pyrolysis

The adsorption efficiency of biochar produced from groundnut shell at pyrolysis temperature of 350 ± 5 °C for aqueous phase with concentrations of 0.04 : 0.10 mg/l (fold one), 0.08 : 0.20 mg/l and 0.20 : 0.50 mg/l were 99.67%, 99.98% and 99.96%, respectively for cadmium ions whilst mercury ions showed 100% removal in the binary mixture of cadmium and mercury (**Table 3**). The removal efficiency for shea nut shell biochar and biochar that involves the combination of groundnut and shea nut shells (produced at temperature of 350 ± 5 °C) ascertained 100% removal for both cadmium and mercury ions in binary mixture of the aqueous phase with concentrations of 0.04 : 0.10 mg/l (fold one), 0.08 : 0.20 mg/l (fold two) and 0.20 : 0.50 mg/l (fold five) (**Table 3**).

The biochars produced from groundnut shell, shea nut shell and the combination of the two at pyrolysis condition of 700 ± 5 °C showed 100% removal of cadmium and mercury ions from the prepared aqueous phase with concentrations of 0.04 : 0.10 mg/l (**Table 3**). The binary (0.08 : 0.20 mg/l) experiment showed adsorption efficiency of 99.99% for cadmium and 100% for mercury ions by groundnut shell biochar, 100% each for cadmium and mercury ions by shea nut shell biochar and 99.95% for cadmium and 100% for mercury by the combined biochars that were produced at pyrolysis temperature of 350 ± 5 °C (**Table 3**). The biochars produced from shea nut shell and the combination of groundnut and shea nut shells were able to remove all cadmium and mercury ions (100% each), and 99.95% for cadmium and 100% for mercury by groundnut shell biochar from the binary mixture with concentration of 0.20 : 0.50 mg/l at pyrolysis temperature of 700 ± 5 °C (**Table 3**).

Table 3: Removal efficiency of binary metals by biochars

Pyrolysis	Cd : Hg Conc (mg/l)	Groundnut shell		Shea nut shell		Groundnut and shea nut shells	
		Cd (%)	Hg (%)	Cd (%)	Hg (%)	Cd (%)	Hg (%)
Slow pyrolysis	0.04:0.10	99.67	100	100	100	100	100
	0.08:0.20	99.98	100	100	100	100	100
	0.20:0.50	99.96	100	100	100	100	100
Fast pyrolysis	0.04:0.10	100	100	100	100	100	100
	0.08:0.20	99.99	100	100	100	99.95	100
	0.20:0.50	99.98	100	100	100	100	100
Pyrolysis	Conc (mg/l)	Cd (%)	Pb (%)	Cd (%)	Pb (%)	Cd (%)	Pb (%)
Slow pyrolysis	0.04:0.10	99.7	100	100	100	100	100
	0.08:0.20	99.7	100	100	100	99.61	100
	0.20:0.50	100	100	100	100	99.9	100
Fast pyrolysis	0.04:0.10	100	100	100	99.04	100	98.2
	0.08:0.20	100	100	100	100	100	100
	0.20:0.50	100	100	100	100	100	100
Pyrolysis	Conc (mg/l)	Hg (%)	Pb (%)	Hg (%)	Pb (%)	Hg (%)	Pb (%)
Slow pyrolysis	0.10:0.10	99.99	100	100	99.14	100	98.84
	0.20:0.20	99.92	100	100	100	100	100
	0.50:0.50	99.84	100	100	100	100	100
Fast pyrolysis	0.10:0.10	100	100	100	98.72	99.99	100
	0.20:0.20	100	100	100	100	100	100
	0.50:0.50	100	100	100	100	100	100

The experiment showed 100% removal efficiency for binary mixtures made up of cadmium and lead ions with concentrations of 0.04 : 0.10 mg/l, 0.08 : 0.20 mg/l and 0.20 : 0.50 mg/l by biochars produced from groundnut shell, shea nut shell and the combination of groundnut and shea nut shells at pyrolysis condition of 350 ± 5 °C (**Table 3**). Except for groundnut shell biochar that recorded 99.70% removal efficiency for cadmium ions in binary mixtures with concentration of 0.04:0.10 mg/l and 0.08 : 0.20 mg/l and 99.61% and 99.69% in the mixtures with concentration of 0.08 : 0.20 mg/l and 0.20 : 0.50 mg/l, respectively (**Table 3**).

The biochars produced under a pyrolysis temperature of 700 ± 5 °C were able to ascertain 100% removal efficiency for binary mixtures of cadmium and lead ions at concentrations of 0.04 : 0.10 mg/l, 0.08 : 0.20 mg/l and 0.20 : 0.50 mg/l (**Table 3**). Except for groundnut shell biochar and combination of the two biochars that recorded 99.04% and 98.20% removal efficiency for lead ions, respectively in binary mixtures with concentration of 0.04 : 0.10 mg/l (**Table 3**).

The binary mixtures of mercury and lead ions at concentrations of 0.10 : 0.10 mg/l, 0.20 : 0.20 mg/l and 0.50 : 0.50 mg/l were effectively removed (100%) by groundnut shell, shea nut shell, and the combination of groundnut and shea nut shells biochars produced at a pyrolysis temperature of 350 ± 5 °C. Except for groundnut shell biochar that showed 99.99%, 99.92% and 99.84% removal efficiency for mercury ions in the concentrations of 0.10 : 0.10 mg/l, 0.20 : 0.20 mg/l and 0.50 : 0.50 mg/l, respectively and 99.14% and 98.84% for lead ions in the concentrations of 0.20 : 0.20 mg/l and 0.50 : 0.50 mg/l (**Table 3**).

The biochars produced at a pyrolysis temperature of 700 ± 5 °C were able to ascertain 100% removal efficiency for binary mixtures of mercury and lead ions with concentrations of 0.10 : 0.10 mg/l, 0.20 : 0.20 mg/l and 0.50 : 0.50 mg/l (**Table 3**). Except for shea nut shell biochar and combination of groundnut and shea nut shells biochars that had 98.72% and 99.99% removal efficiency for lead and mercury ions, respectively in binary mixtures with concentration of 0.10 : 0.10 mg/l (**Table 3**).

4.3 Adsorption Efficiency of Ternary Metals by Biochar Produced under Slow and Fast Pyrolysis

The removal efficiency of biochar produced from groundnut shell at pyrolysis condition of 350 ± 5 °C was 100% for lead and mercury except cadmium ion that showed 99.05%, 99.46% and 99.69% at fold one, two and five, respectively (**Table 4**). Also biochar produced from groundnut shell at pyrolysis condition of 700 ± 5 °C showed removal efficiency of 100% for lead and mercury ions except cadmium ion that showed 99.99% and 99.98% at fold two and five, respectively (**Table 4**).

The adsorption efficiency of cadmium, mercury and lead ions by shea nut shell biochar produced at pyrolysis condition of 350 ± 5 °C was higher than 97%. Whilst at condition of 700 ± 5 °C the removal efficiency was higher than 98% for the prepared aqueous phase with concentrations of 0.04 : 0.10 : 0.10 mg/l, 0.08 : 0:20 : 0.20 mg/l and 0.20 : 0.50 : 0.50 mg/l (**Table 4**).

The removal efficiency of cadmium, mercury and lead ions by combination of groundnut and shea nut shells biochars produced a temperatures of 350 ± 5 °C and 700 ± 5 °C was higher than 98% for the prepared aqueous phase with concentrations of 0.04 : 0.10 : 0.10 mg/l, 0.08 : 0:20 : 0.20 mg/l and 0.20 : 0.50 : 0.50 mg/l (**Table 4**).

Table 4: Removal efficiency of ternary metals by biochars

Slow pyrolysis		Initial conc (mg/l)		
Biochar	Ions	0.04:0.10:0.10	0.08:0:20:0.20	0.20:0.50:0.50
Groundnut shell	Cd (%)	99.05	99.46	99.69
	Hg (%)	99.98	100	100
	Pb (%)	100	100	99.9
Shea nut shell	Cd (%)	100	100	100
	Hg (%)	100	99.98	99.95
	Pb (%)	97.5	100	100
Groundnut and shea nut shells	Cd (%)	100	99.95	99.9
	Hg (%)	100	99.98	99.96
	Pb (%)	98.8	100	100

Fast pyrolysis		Initial conc (mg/l)		
Biochar	Ions	0.04:0.10:0.10	0.08:0:20:0.20	0.20:0.50:0.50
Groundnut shell	Cd (%)	100	99.99	99.98
	Hg (%)	99.96	100	100
	Pb (%)	100	100	100
Shea nut shell	Cd (%)	100	99.99	100
	Hg (%)	98.18	100	100
	Pb (%)	98.46	100	100
Groundnut and shea nut shells	Cd (%)	100	99.94	99.85
	Hg (%)	99.8	100	100
	Pb (%)	98.4	100	100

4.4 Solution pH in Mono, Binary and Ternary Systems

The pH values of the aqueous solution were in the acidic range for systems: mono system were 4.63, 3.91 and 3.58 for Cd, 3.42, 3.39 and 3.36 for Hg, 3.85, 3.39 and 3.36 for Pb; binary system were 3.32, 3.40 and 3.41 for Cd : Hg, 3.63, 3.25 and 3.31

for Hg : Pb and 3.39, 3.33 and 3.39 ; and ternary system were 3.39, 3.28 and 3.35 for Cd : Hg : Pb for fold one, two and five, respectively (**Table 5**). The adsorption of heavy metals was generally effective under the varied pH values.

Table 5: pH of mono, binary and ternary aqueous phase

Metal	pH for fold one	pH for fold two	pH for fold five
Cd	4.63	3.91	3.58
Hg	3.42	3.39	3.36
Pb	3.85	3.38	3.36
Cd : Hg	3.31	3.40	3.41
Cd : Pb	3.63	3.25	3.31
Hg : Pb	3.39	3.33	3.39
Cd : Hg : Pb	3.39	3.28	3.35

All measured in pH-units

4.5 Langmuir, Freundlich and Temkin Isotherms

Langmuir adsorption isotherm was used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the groundnut, shea nut shell and the combination of the groundnut and shea nuts shells biochar. The specific plots of sorption ($^{Ce}/_{Qe}$) against the equilibrium concentration (Ce) for heavy metals that did not ascertain total adsorption in batch experiment systems (mono, binary and ternary systems) are shown in **figures 1 to 26**. The linear isotherm values of Q_{max}, K_l were computed from the slope and intercept of the Langmuir graphs and the coefficient of determinations (R^2) obtained from the graphs are presented in **table 6**.

The correlation coefficient (R^2) values for Langmuir isotherm for mono-component system were in the range of 0.43 to 0.84 for biochars produced under slow pyrolysis temperature. For the fast pyrolysis, only Cd and Hg in mono system did not ascertain complete adsorption hence the plots showed R^2 of 0.89 and 0.94 onto groundnut shell, and the combination of groundnut and shea nut shells biochar, respectively (**Table 6**). Langmuir isotherm R^2 for binary system ranged from 0.28 to 1 for biochars produced under slow pyrolysis temperature and 0.90 to 0.99 for biochars produced under fast pyrolysis temperature (**Table 6**).

In ternary system the R^2 ranged from 0.89 to 1, for biochars produced under slow pyrolysis temperature whilst in the fast pyrolysis, only Cd and Hg in ternary system did not ascertain complete adsorption hence the plots showed R^2 of 0.87 and 97 by groundnut shell biochar, and the combination of groundnut and shea nut shells biochar, respectively (**Table 6**).

The maximum Langmuir capacity for mono-component system ranged from 0.14 to 0.87 mg/g for metals by biochars produced under slow pyrolysis temperature and 0.18 mg/g for Cd and 0.55 mg/g for Hg only by groundnut and shea nut shells biochars produced under fast pyrolysis temperature, respectively (**Table 6**). Whilst, it ranged from 0.04 to 0.89 mg/g and -0.08 to 0.22 mg/g for binary mixture by biochars produced under slow and fast pyrolysis temperatures, respectively and between 0.05 to 1.12 mg/g and 0.08 to 0.22 mg/g for ternary mixtures by biochars produced under slow and fast pyrolysis temperatures, respectively (**Table 6**). The R_L was found to be less than 1 for all metals in this study, biochar type and the pyrolysis temperature (**Table 6**).

Table 6: Adsorption isotherm parameters based on Langmuir models

Adsorbent	Pyrolysis	Absorbate	Estimate parameters of R^2 Langmuir Isotherm			
			Qmax (mg/g)	K$_L$ (l/ mg)	R$_L$	R^2
Mbiochar	Slow	**Cd**	0.22	45454.55	1x10^{-4}	0.89
Mbiochar	Slow	**Pb**	0.36	9259.26	2.2x10^{-4}	0.56
Gbiochar	Slow	**Hg**	0.14	-714286	-3 x10^{-6}	0.43
Sbiochar	Slow	**Hg**	0.87	115380	1x10^{-5}	0.75
Gbiochar	Slow	**Cd**+Pb	0.09	15873.01	3x10^{-4}	0.95
Mbiochar	Slow	**Cd**+Pb	0.08	0	0	1
Mbiochar	Slow	**Hg**+Cd	0.89	140449.40	1x10^{-5}	0.42
Sbiochar	Slow	**Hg**+Cd	0.56	598700	3x10^{-6}	0.91
Gbiochar	Slow	**Hg**+Cd	0.09	-555556	-4x10^{-6}	0.93
Gbiochar	slow	**Pb**+Hg	0.56	8928.57	2.2 x10^{-4}	0.89
Gbiochar	Slow	**Hg**+Pb	0.48	-694444	-3x10^{-6}	1
Sbiochar	Slow	**Hg**+Pb	0.04	0	0	0.28
Mbiochar	Slow	**Hg**+Pb	0.50	666666.70	3x10^{-6}	0.57
Mbiochar	Slow	**Hg**+Cd+Pb	0.09	-1851852	-1x10^{-6}	0.99
Sbiochar	Slow	**Hg**+Cd+Pb	1.12	148809.50	1.3x10^{-5}	0.99
Gbiochar	Slow	**Cd**+Hg+Pb	0.05	-38632	-1.3x10^{-4}	0.69
Mbiochar	Slow	**Cd**+Hg+Pb	0.22	45454.55	1.1x10^{-4}	0.89
Gbiochar	Slow	**Hg**+Cd+Pb	0.10	-2022600	-1x10^{-6}	1
Gbiochar	Fast	**Cd**	0.18	55555.56	9 x10^{-6}	0.89
Sbiochar	Fast	**Hg**	0.55	606060.60	3.3 x10^{-6}	0.94
Gbiochar	Fast	**Cd**+Hg	0.22	151515.20	3.3 x10^{-5}	0.90
Mbiochar	Fast	**Cd**+Hg	0.22	22727.27	2.2 x10^{-4}	0.90
Sbiochar	Fast	**Hg**+Pb	-0.17	-98039.20	-2 x10^{-5}	0.99
Mbiochar	fast	**Hg**+Pb	-0.08	-125000	-2 x10^{-5}	0.91
Gbiochar	fast	**Cd**+Hg+Pb	0.08	-125000	-4 x10^{-5}	0.87
Mbiochar	Fast	**Cd**+Hg+Pb	0.22	22727.27	2.2 x10^{-4}	0.93

Note: Gbiochar: Groundnut shells; Sbiochar: Shea nut shells; Mbiochar: Groundnut and shea nut shells; R$^{2:}$ Correlation coefficient

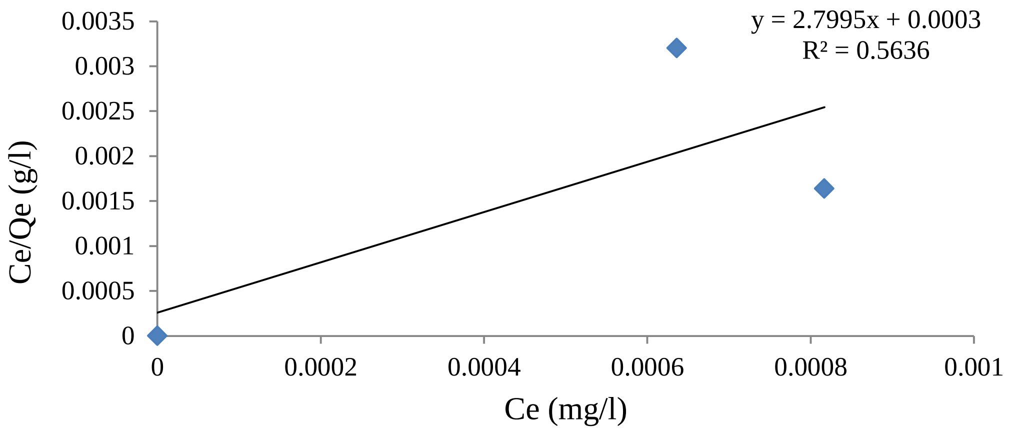

Figure 1: Langmuir isotherm for adsorption of Pb in mono aqueous phase onto combined groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

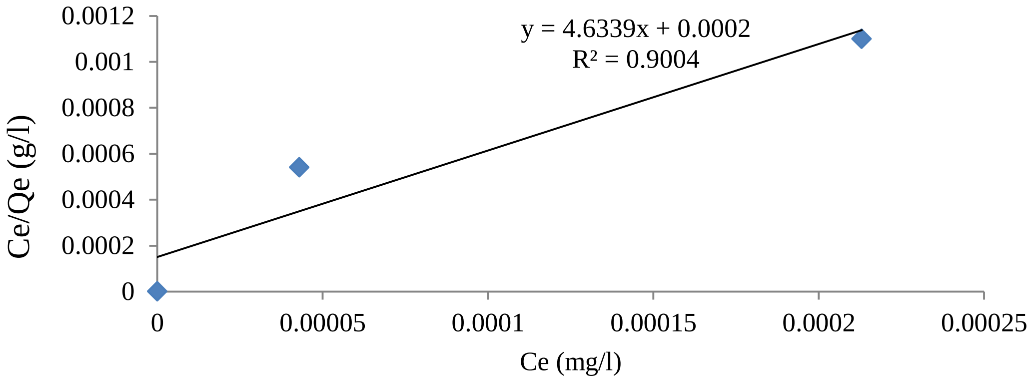

Figure 2: Langmuir isotherm for adsorption of Cd in binary aqueous phase (Cd vrs Hg) onto the combined groundnut and shea nut shells biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

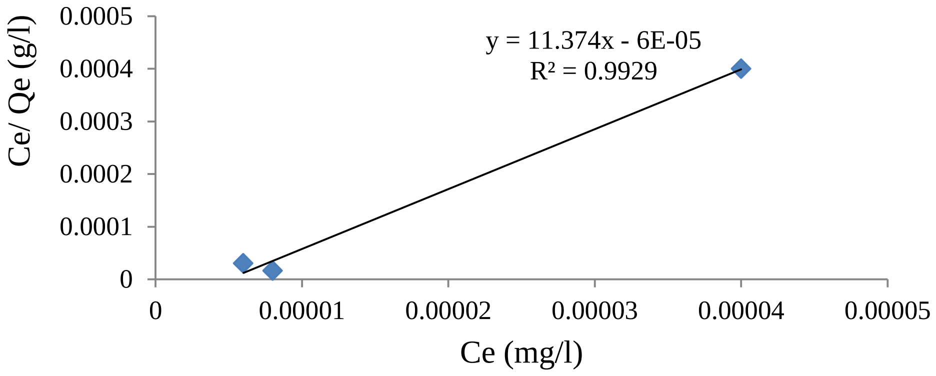

Figure 3: Langmuir isotherm for adsorption of Hg in ternary aqueous phase (Cd, Hg and Pb) onto the combined groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

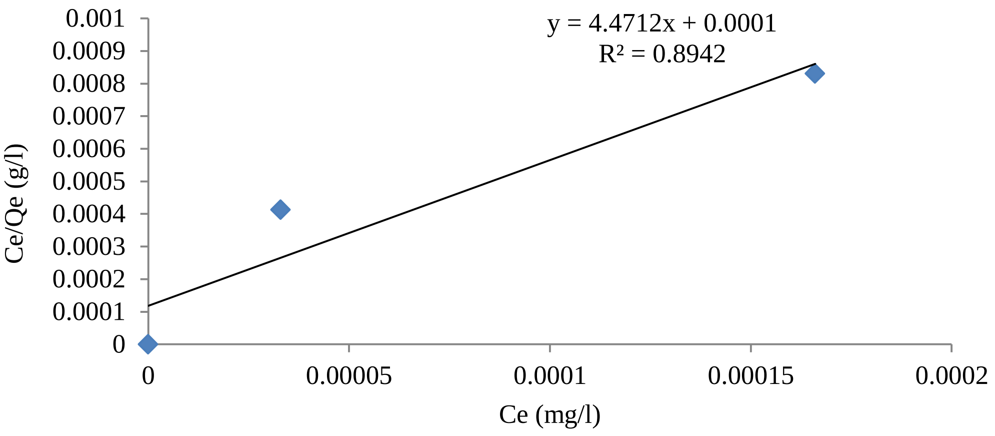

Figure 4: Langmuir isotherm for adsorption of Cd in mono aqueous phase on groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

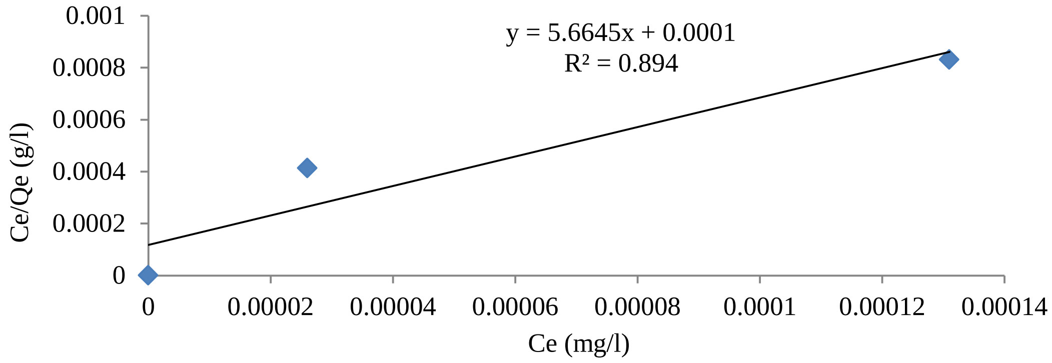

Figure 5: Langmuir isotherm for adsorption of Cd in mono aqueous phase on ground shell biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

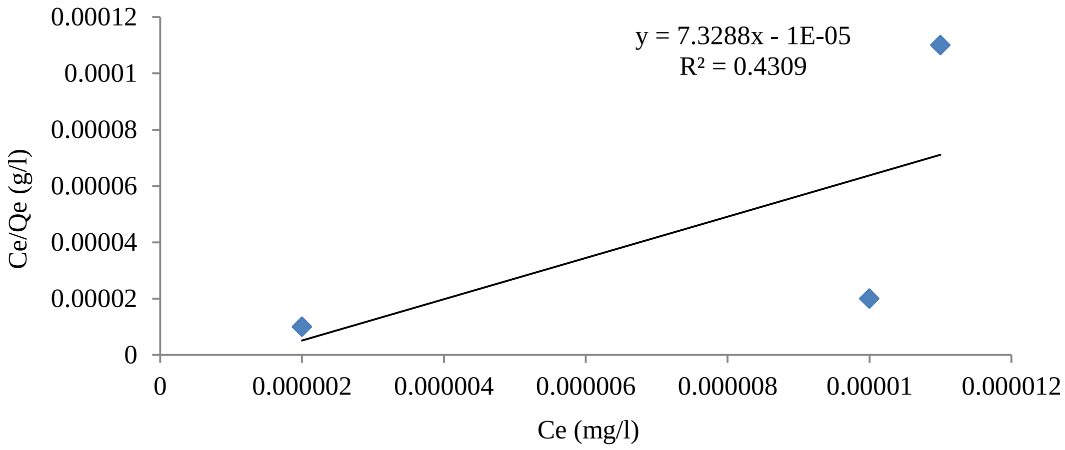

Figure 6: Langmuir isotherm for adsorption of Hg in mono aqueous phase on groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

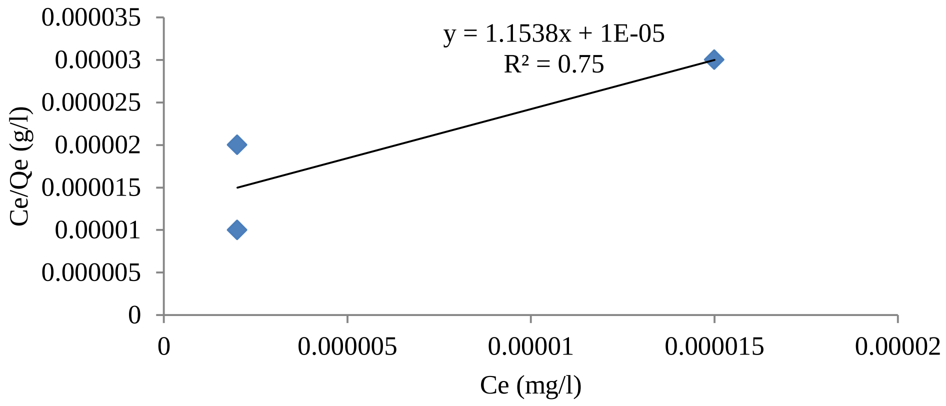

Figure 7: Langmuir isotherm for adsorption of Hg in mono aqueous phase on shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

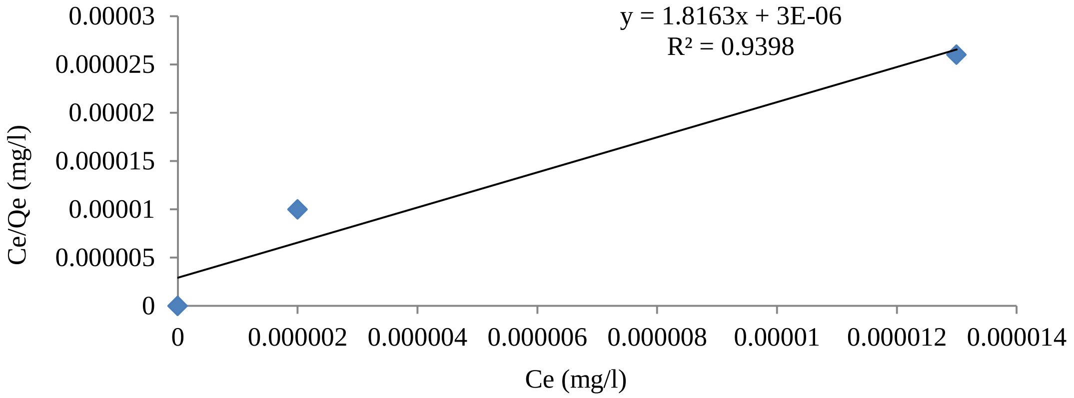

Figure 8: Langmuir isotherm for adsorption of Hg in mono aqueous phase onto shea nut shells biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

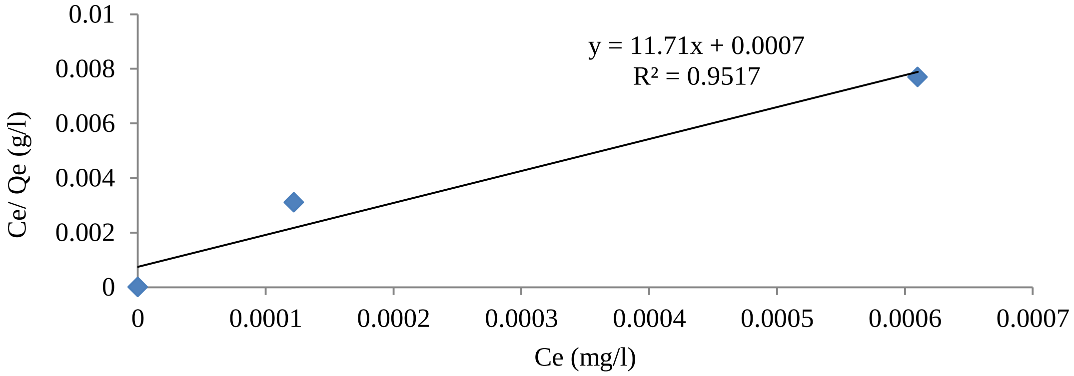

Figure 9: Langmuir isotherm for adsorption of Cd in binary aqueous phase (Cd vrs Pb) on groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

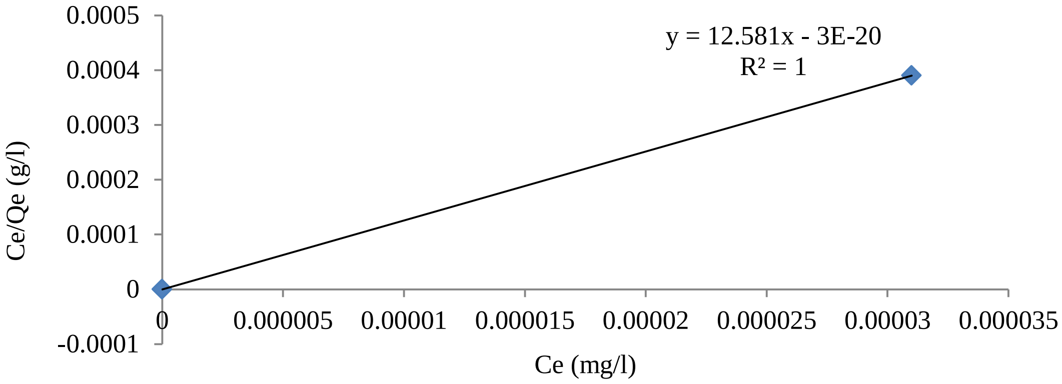

Figure 10: Langmuir isotherm for adsorption of Cd in binary aqueous phase (Cd vrs Pb) on groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

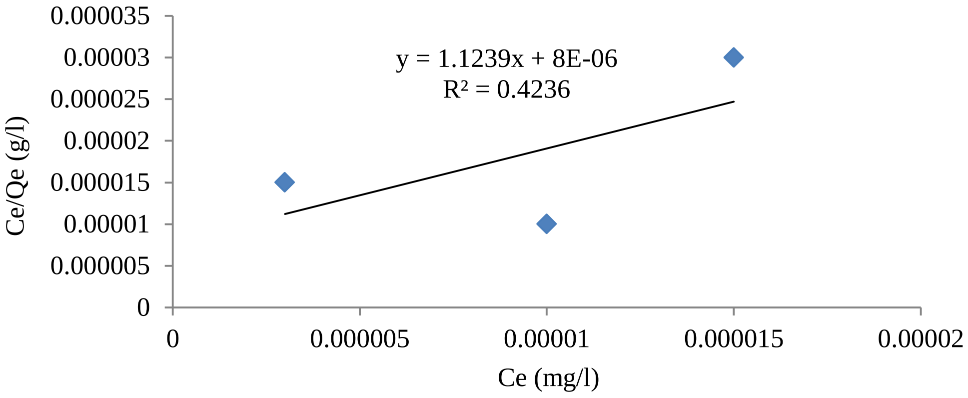

Figure 11: Langmuir isotherm for adsorption of Hg in binary aqueous phase (Cd vrs Hg) onto groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

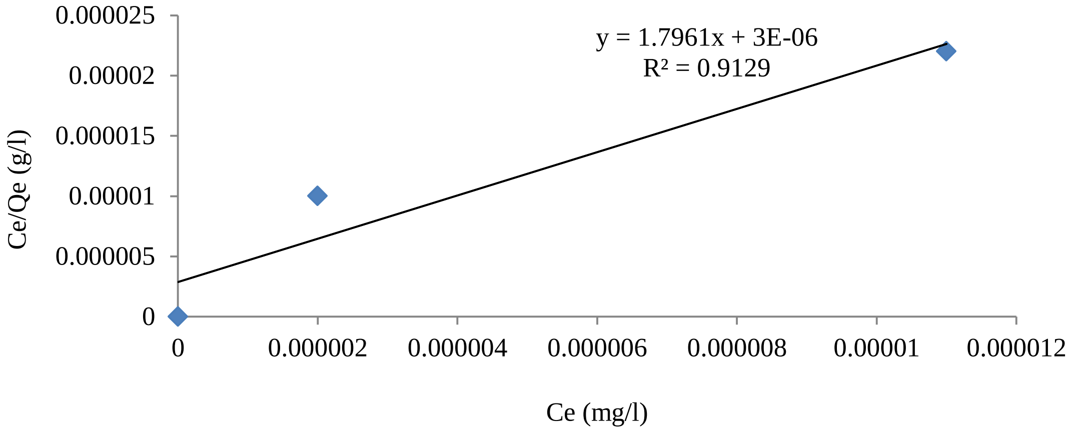

Figure 12: Langmuir isotherm for adsorption of Hg in binary aqueous phase (Cd vrs Hg) onto shea nut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

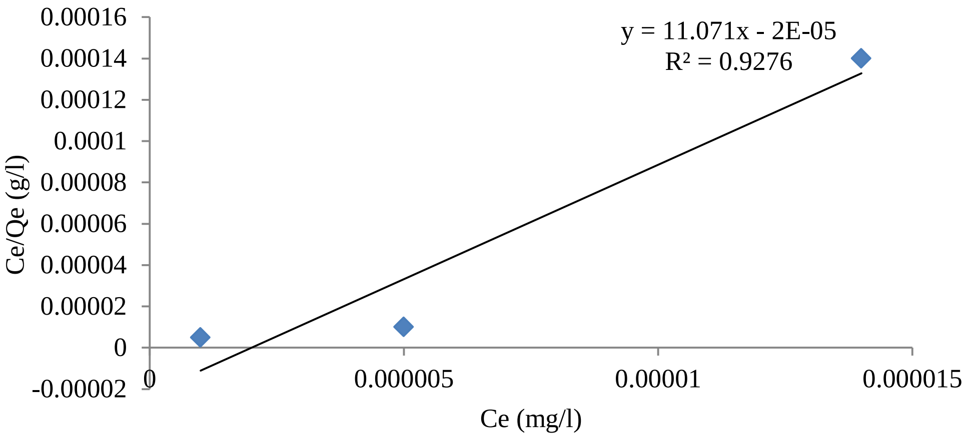

Figure 13: Langmuir isotherm for adsorption of Hg in binary aqueous phase (Cd vrs Hg) on groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

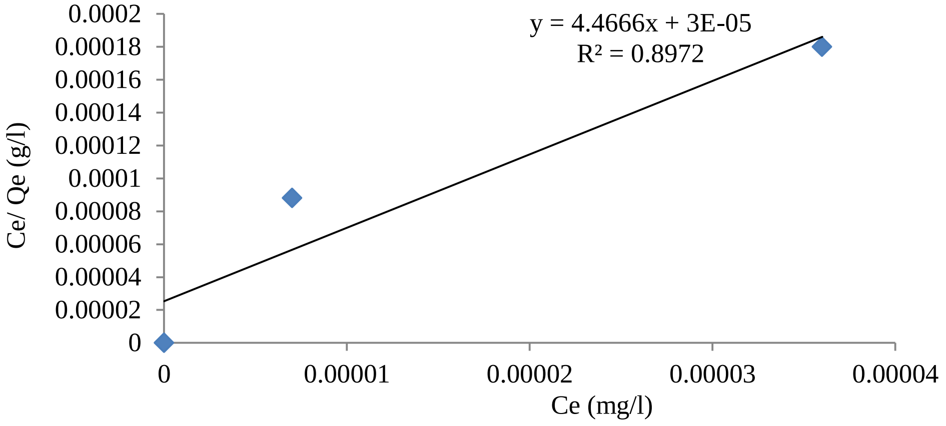

Figure 14: Langmuir isotherm for adsorption of Cd in binary aqueous phase (Cd vrs Hg) on groundnut shell biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

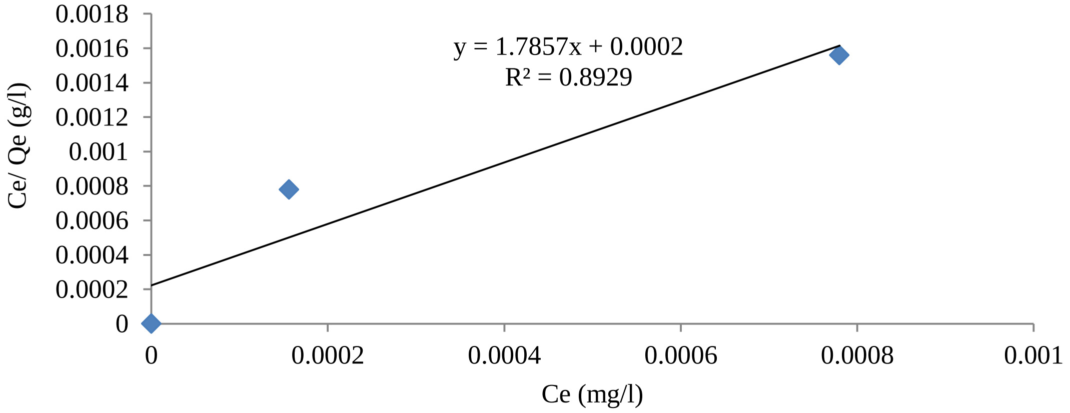

Figure 15: Langmuir isotherm for adsorption of Pb in Pb and Hg aqueous phase on groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

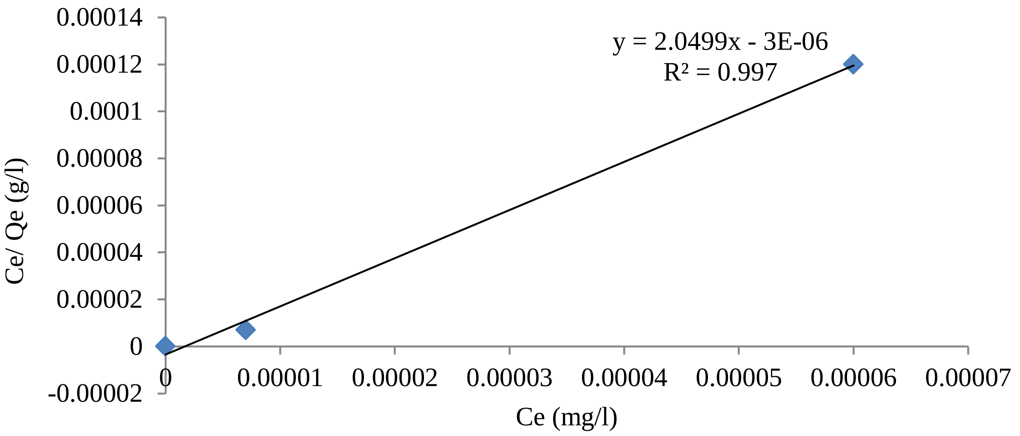

Figure 16: Langmuir isotherm for adsorption of Hg in Pb vrs Hg aqueous phase on groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

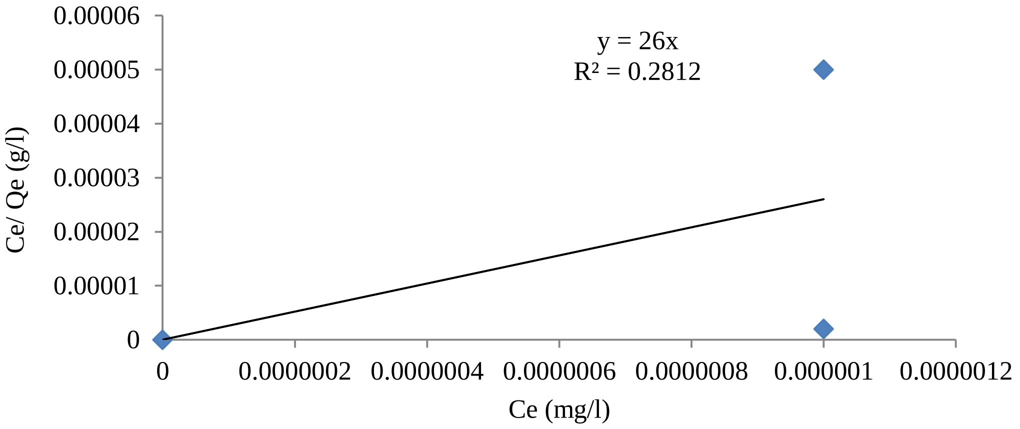

Figure 17: Langmuir isotherm for adsorption of Hg in Pb vrs Hg aqueous phase onto shea nut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

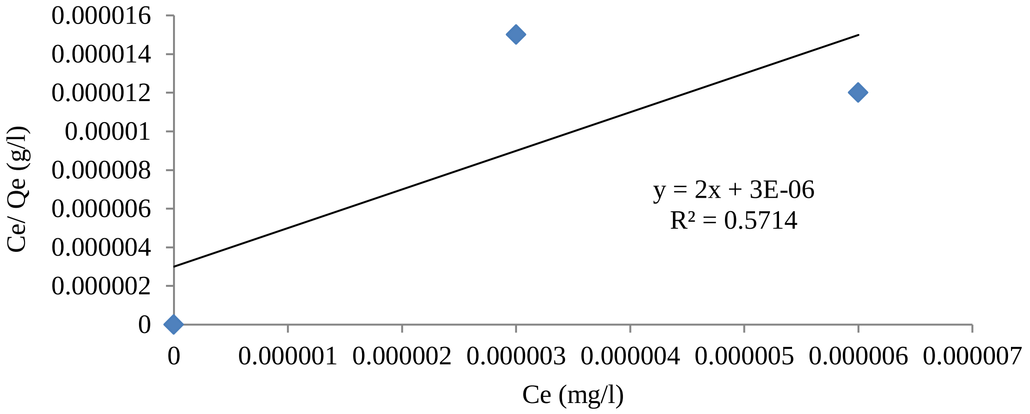

Figure 18: Langmuir isotherm for adsorption of Hg in Pb vrs Hg aqueous phase on groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

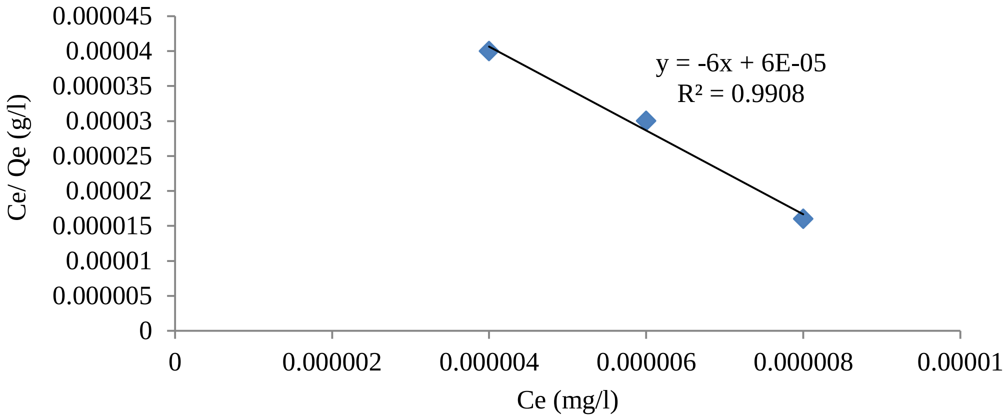

Figure 19: Langmuir isotherm for adsorption of Hg in Pb vrs Hg aqueous phase on shea nut shell biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

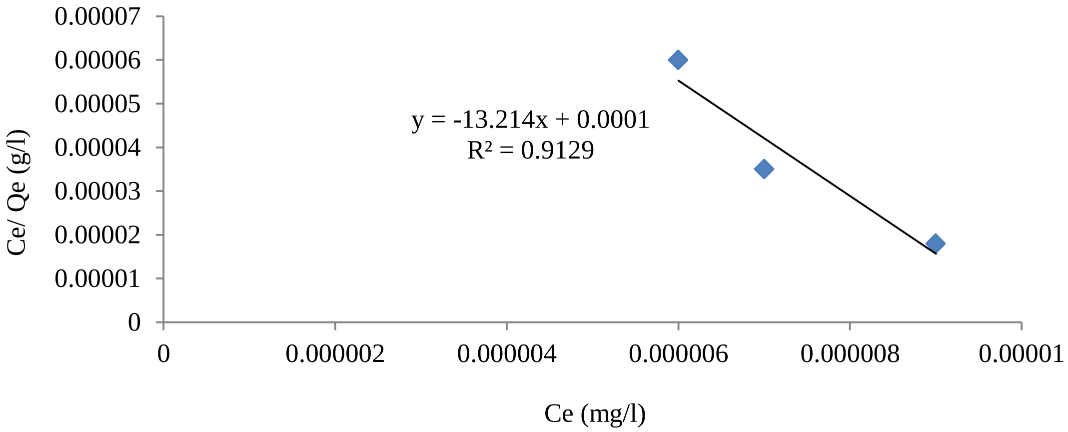

Figure 20: Langmuir isotherm for adsorption of Hg in Pb vrs Hg aqueous phase on groundnut and shea nut shells biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

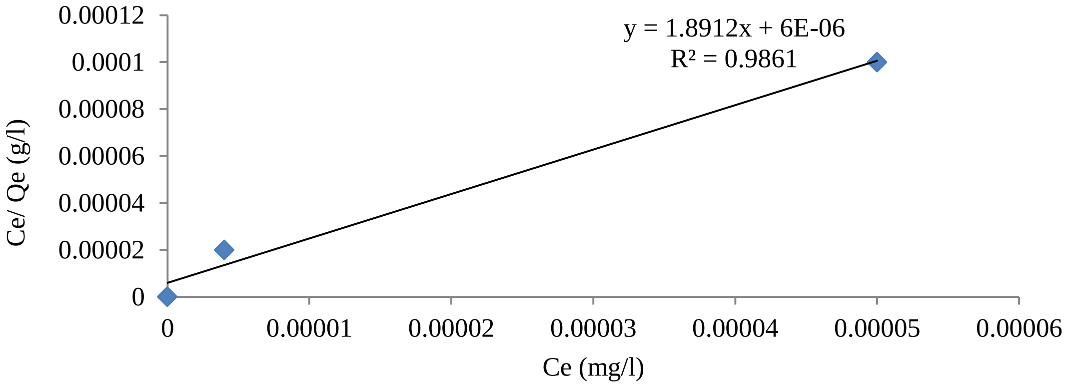

Figure 21: Langmuir isotherm for adsorption of Hg in ternary aqueous phase (Cd, Hg and Pb) onto shea nut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

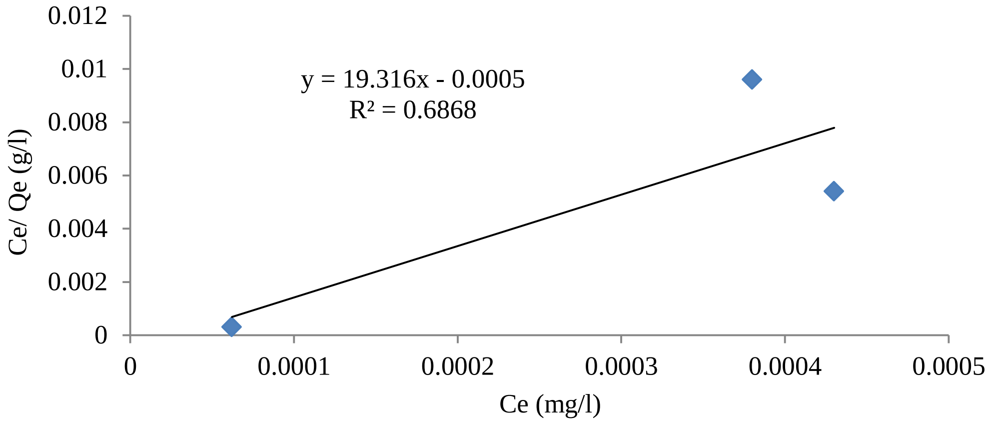

Figure 22: Langmuir isotherm for adsorption of Cd in ternary aqueous phase (Cd, Hg and Pb) onto groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

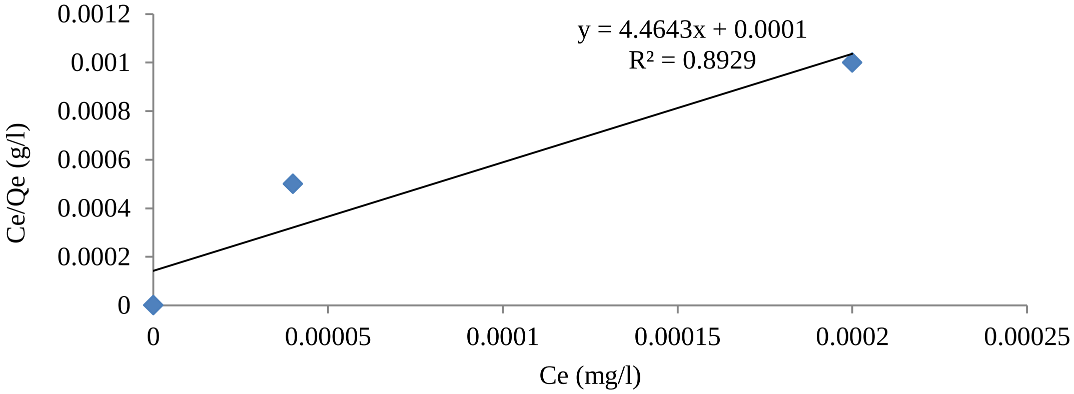

Figure 23: Langmuir isotherm for adsorption of Cd in ternary aqueous phase onto groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

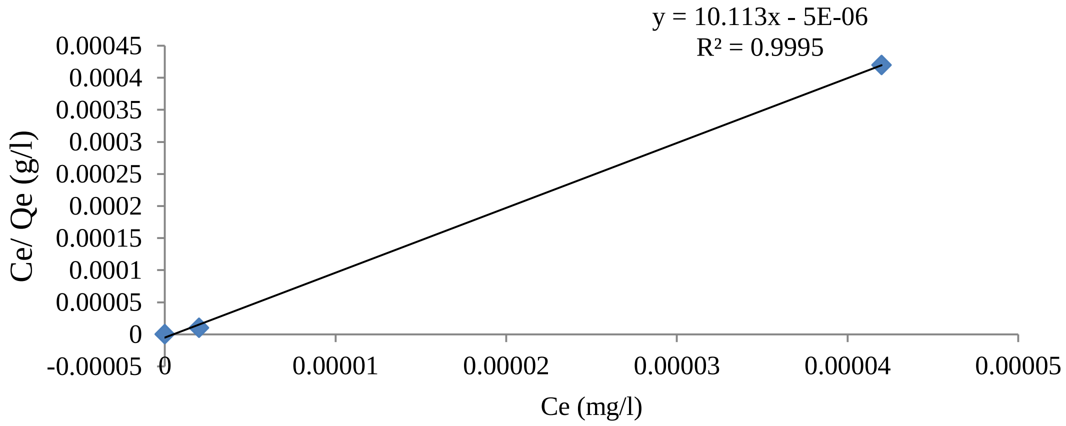

Figure 24: Langmuir isotherm for adsorption of Hg in ternary aqueous phase on groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

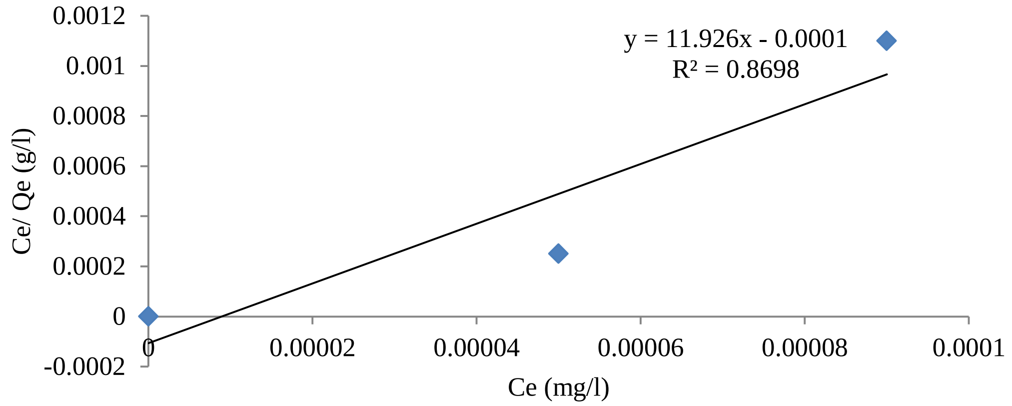

Figure 25: Langmuir isotherm for adsorption of Cd in ternary aqueous phase on groundnut shell biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

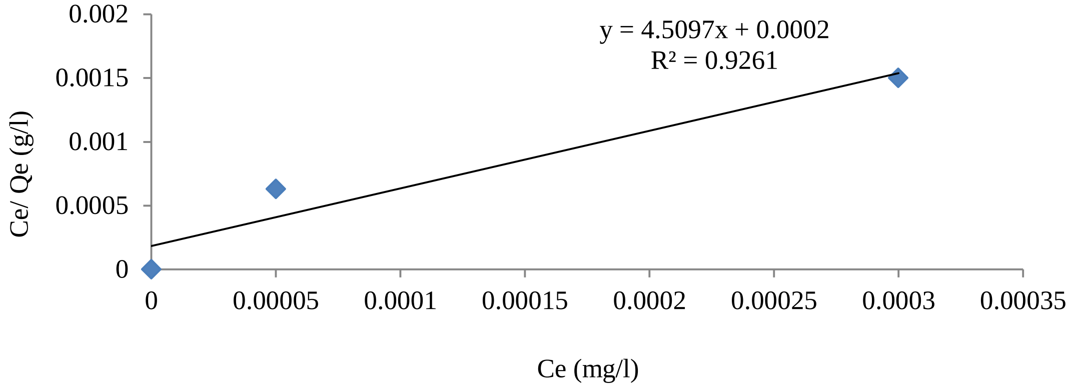

Figure 26: Langmuir isotherm for adsorption of Cd in ternary aqueous phase on groundnut and shea nut shells biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

Freundlich adsorption isotherm was used to study the fitness of the experimental data in terms of heterogeneous nature of the surface sites of biochars involved in heavy metal uptake. The specific plots of Log Q_e against Log C_e, gives a slope with the value of 1/n and an intercept magnitude of log K_F for heavy metals that did not obtain complete adsorption in the batch experiments system (mono, binary and ternary systems) and are shown in **figures 27 to 52**. The R^2 values for mono-component system ranged from 0.0 to 0.82 that of binary mixtures ranged from 0.01 to 1 whilst ternary mixtures ranged from 0.49 to 0.72 by biochars produced under both slow and fast pyrolysis temperatures (**Table 7**). The approximate indicators of the adsorption capacity (K_F) and the adsorption intensity (n) of all isotherm equations are shown in **table 7**. Generally, n values obtain for this study ranged from -47.85 to 90.02 (**Table 7**) and K_F values ranged from -0.0 to 515.82 (**Table 7**).

Table 7: Adsorption isotherm parameters based on Freundlich models

Adsorbent	Pyrolysis	Absorbate	Estimated parameters of R^2 Freundlich isotherm			
			1/n	N	K_F (mg/g)	R^2
Mbiochar	Slow	**Cd**	-0.11	-9.39	0.04	0.53
Mbiochar	Slow	**Pb**	-0.16	-6.43	0.10	0.65
Gbiochar	Slow	**Hg**	0.03	34.60	0.31	0
Sbiochar	Slow	**Hg**	0.63	1.60	515.82	0.82
Gbiochar	Slow	**Cd**+Pb	0.16	6.17	0.21	0.93
Mbiochar	Slow	**Cd**+Pb	0.01	90.01	0.09	0.01
Mbiochar	Slow	**Hg**+Cd	0.32	3.17	8.83	0.11
Sbiochar	Slow	**Hg**+Cd	-0.08	-12.27	0.11	0.49
Gbiochar	Slow	**Hg**+Cd	-0.19	-5.30	0.02	0.10
Gbiochar	Slow	**Pb**+Hg	-0.12	-8.12	0.11	0.51
Gbiochar	Slow	**Hg**+Pb	0.01	89.29	0.23	0.01
Sbiochar	Slow	**Hg**+Pb	-0.08	-12	0.10	0.68
Mbiochar	Slow	**Hg**+Pb	-0.09	-11.14	0.10	0.63
Mbiochar	Slow	**Hg**+Cd+Pb	-0.58	-1.71	-0.00	0.54
Sbiochar	Slow	**Hg**+Cd+Pb	-0.09	-11.66	0.11	0.49
Gbiochar	Slow	**Cd**+Hg+Pb	0.46	2.19	2.03	0.71
Mbiochar	Slow	**Cd**+Hg+Pb	0.19	5.25	0.05	0.56
Gbiochar	Slow	**Hg**+Cd+Pb	0.09	10.79	0.44	0.62
Gbiochar	Fast	**Cd**	-0.10	-9.62	0.04	0.55
Sbiochar	Fast	**Hg**	-0.08	-11.86	0.11	0.55
Gbiochar	Fast	**Cd**+Hg	-0.02	-47.85	0.04	0.05
Mbiochar	Fast	**Cd**+Hg	-0.11	-9.18	0.04	0.53
Sbiochar	Fast	**Hg**+Pb	2.28	0.44	1.92×10^{11}	0.96
Mbiochar	Fast	**Hg**+Pb	4.11	0.24	2.86×10^{20}	1
Gbiochar	Fast	**Cd**+Hg+Pb	-0.12	-8.08	0.04	0.72
Mbiochar	Fast	**Cd**+Hg+Pb	-0.11	-9.15	0.05	0.51

Note: Gbiochar: Groundnut shells; Sbiochar: Shea nut shells; Mbiochar: Groundnut and shea nut shells; R^2: Correlation coefficient

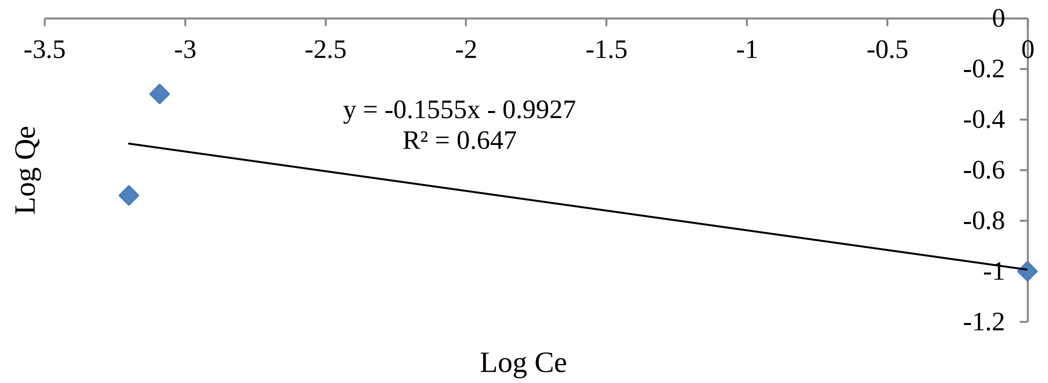

Figure 27: Freundlich isotherm for adsorption of Pb in mono aqueous phase onto the combined groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

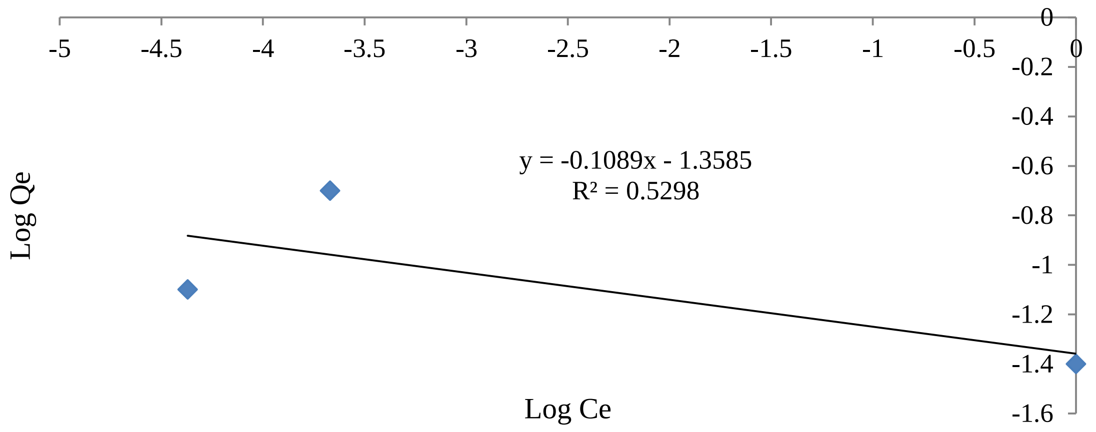

Figure 28: Freundlich isotherm for adsorption of Cd in binary aqueous phase (Cd vrs Hg) onto the combined groundnut and shea nut shells biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

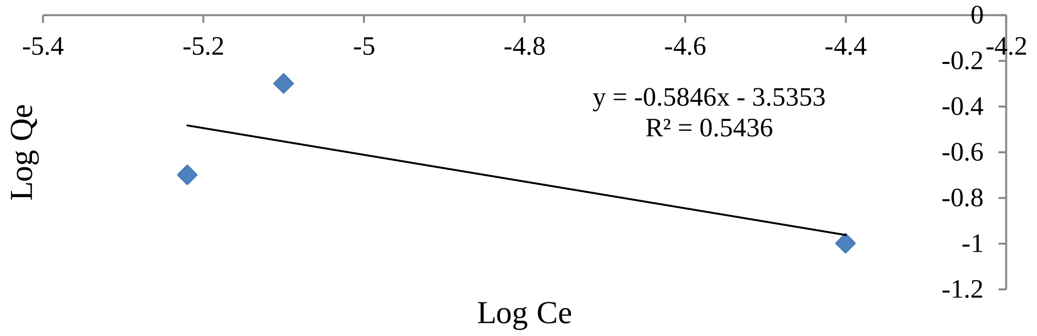

Figure 29: Freundlich isotherm for adsorption of Hg in ternary aqueous phase (Cd, Pb and Hg) onto the combined groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

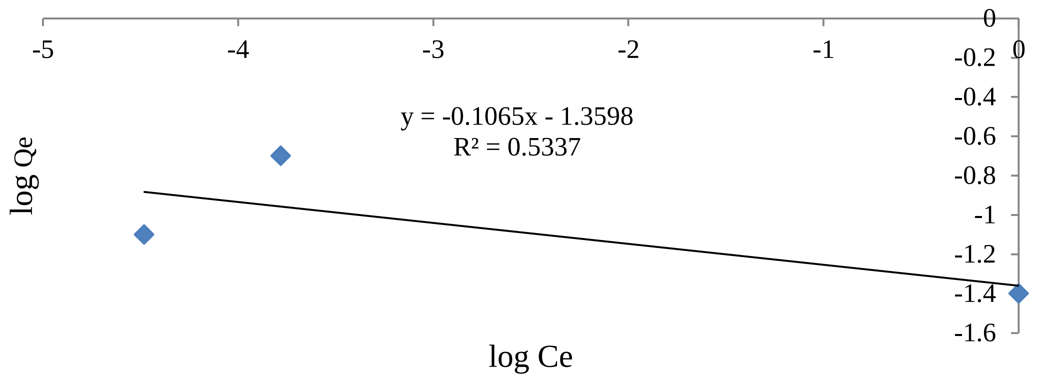

Figure 30: Freundlich isotherm for adsorption of Cd in mono aqueous phase on groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

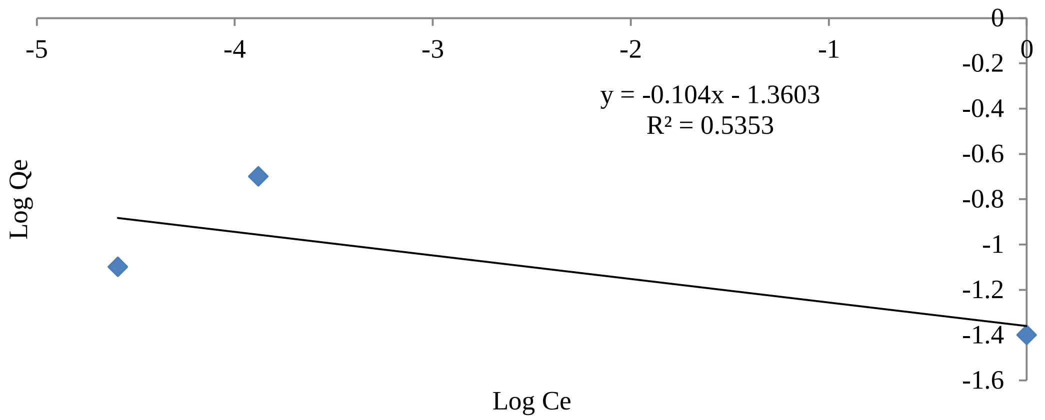

Figure 31: Freundlich isotherm for adsorption of Cd in mono aqueous phase on ground shell biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

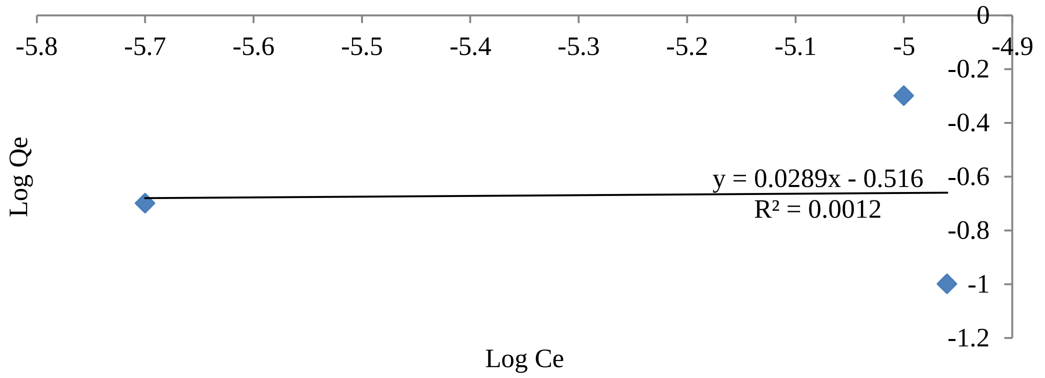

Figure 32: Freundlich isotherm for adsorption of Hg in mono aqueous phase on groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

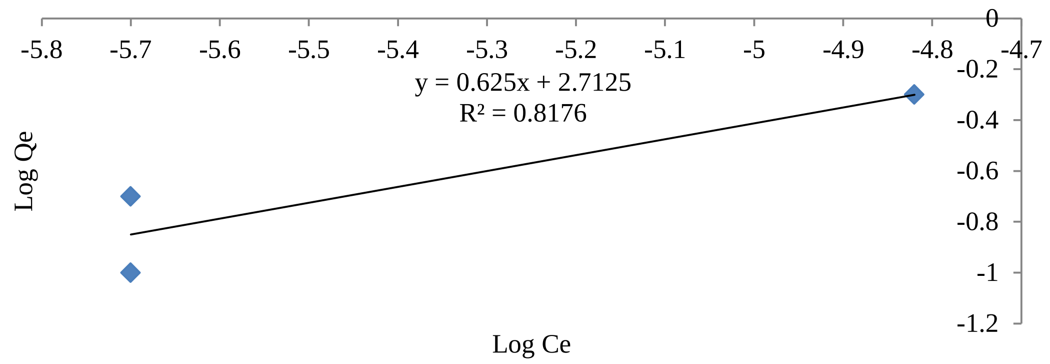

Figure 33: Freundlich isotherm for adsorption of Hg in mono aqueous phase onto shea nut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

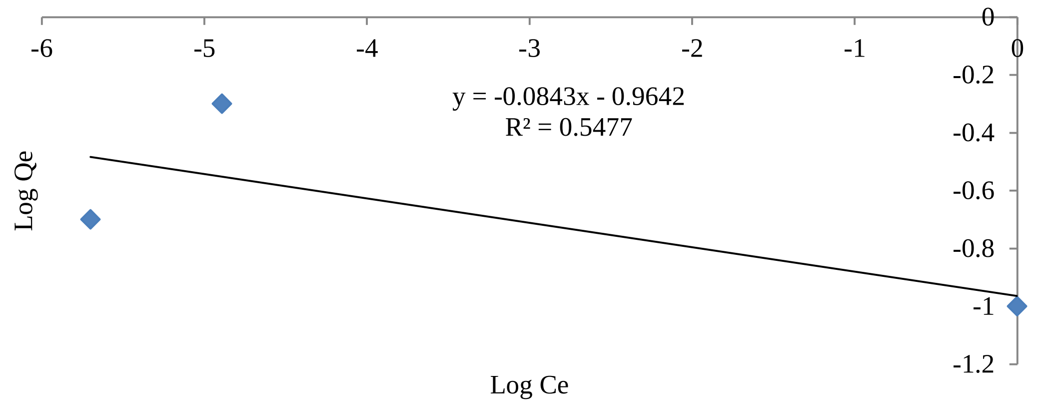

Figure 34: Freundlich isotherm for adsorption of Hg in mono aqueous phase on shea nut shell biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

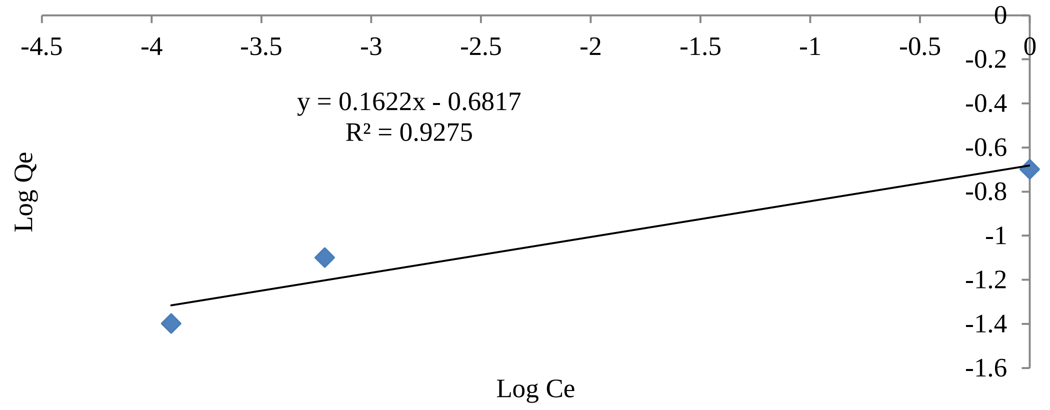

Figure 35: Freundlich isotherm for adsorption of Cd in binary aqueous phase (Cd vrs Pb) on groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

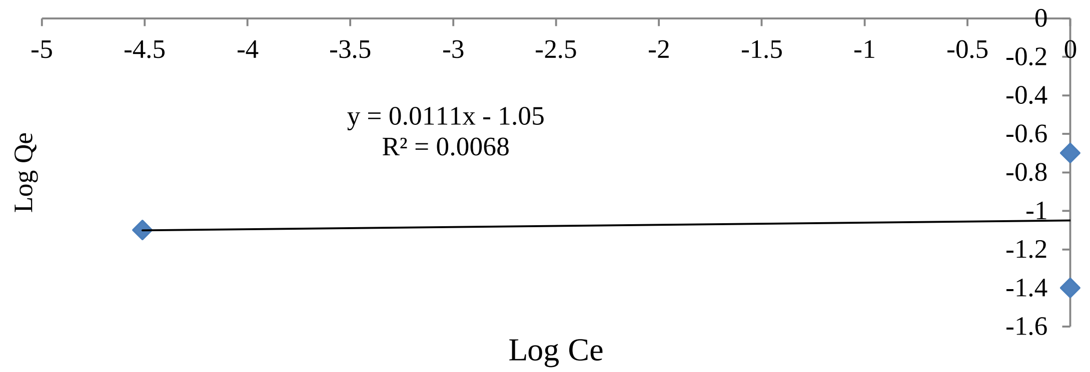

Figure 36: Freundlich isotherm for adsorption of Cd in binary aqueous phase (Cd vrs Pb) on groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

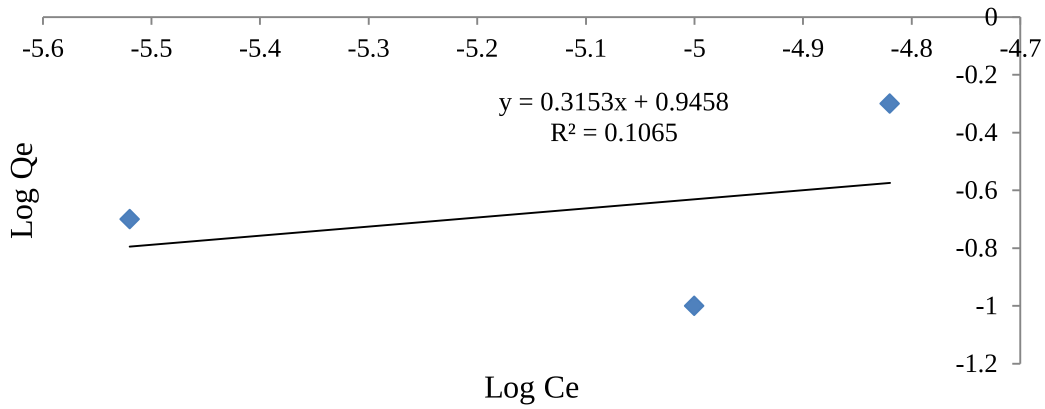

Figure 37: Freundlich isotherm for adsorption of Hg in binary aqueous phase (Cd vrs Hg) onto groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

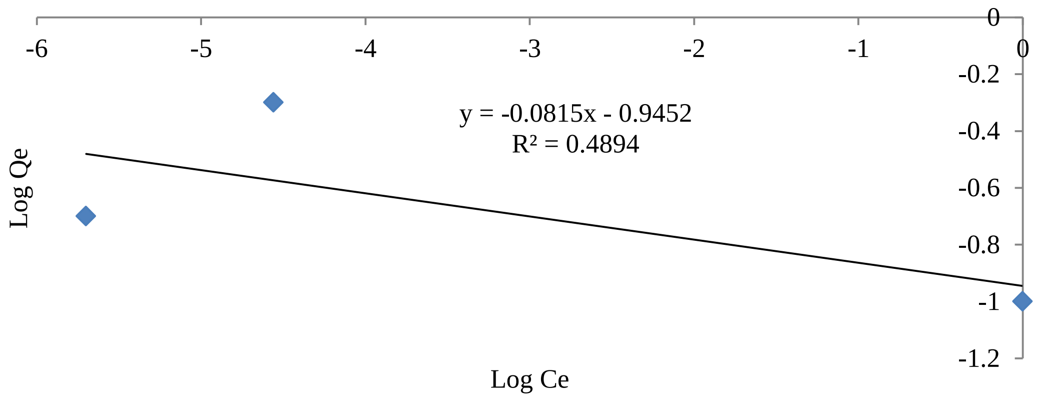

Figure 38: Freundlich isotherm for adsorption of Hg in binary aqueous phase (Cd vrs Hg) onto shea nut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

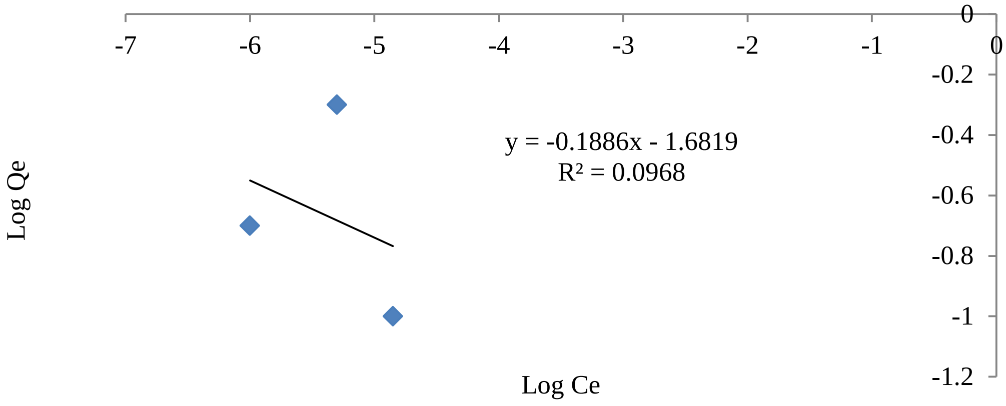

Figure 39: Freundlich isotherm for adsorption of Hg in binary aqueous phase (Cd vrs Hg) onto groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

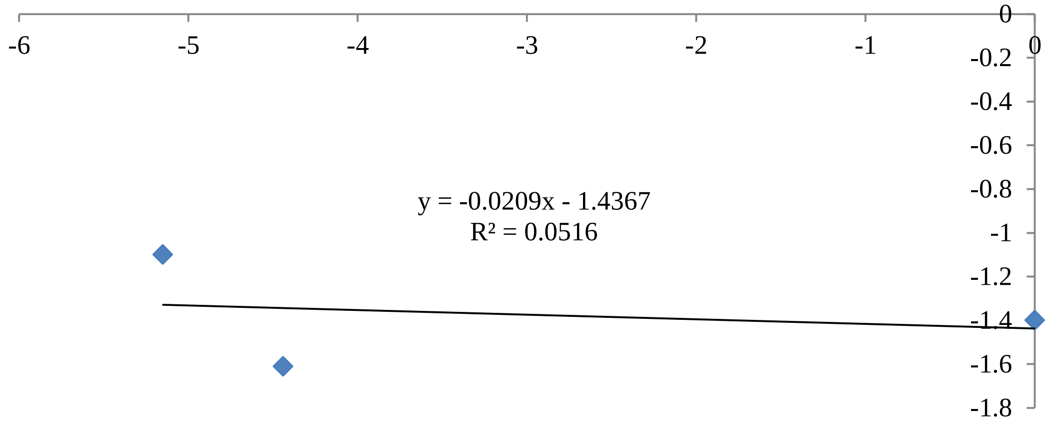

Figure 40: Freundlich isotherm for adsorption of Cd in binary aqueous phase (Cd vrs Hg) on groundnut shell biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

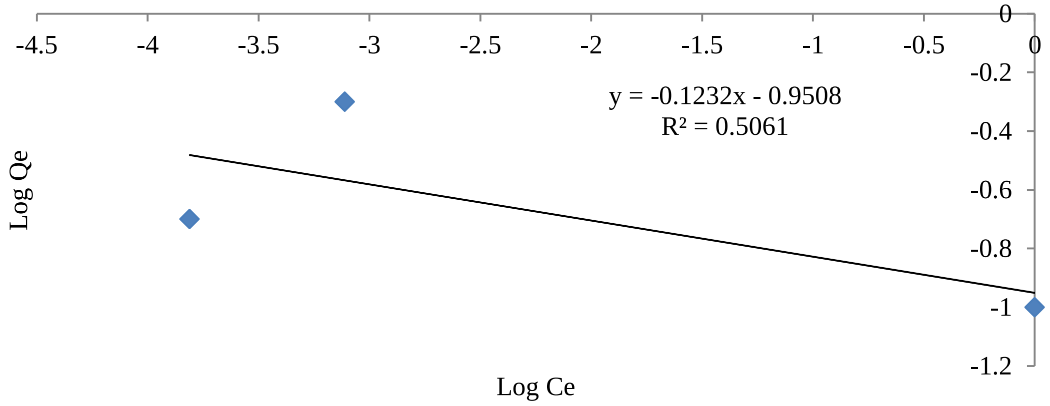

Figure 41: Freundlich isotherm for adsorption of Pb in Pb vrs Hg aqueous phase on groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

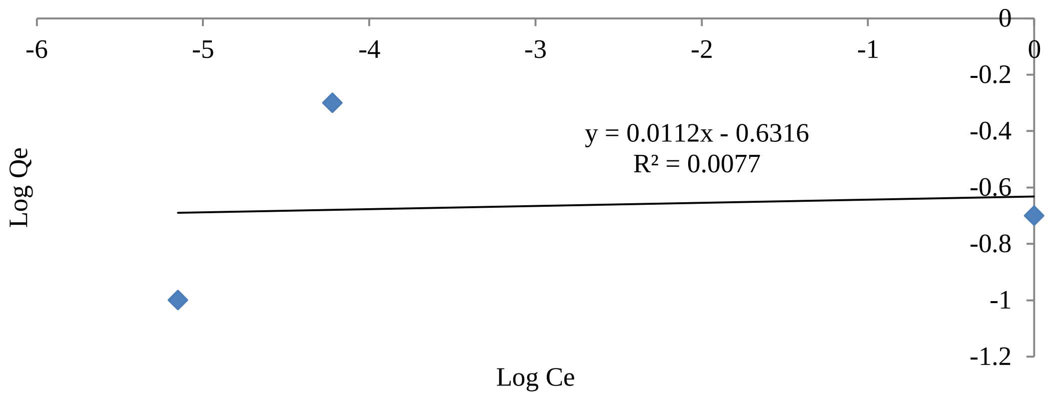

Figure 42: Freundlich isotherm for adsorption of Hg in Pb vrs Hg aqueous phase on groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

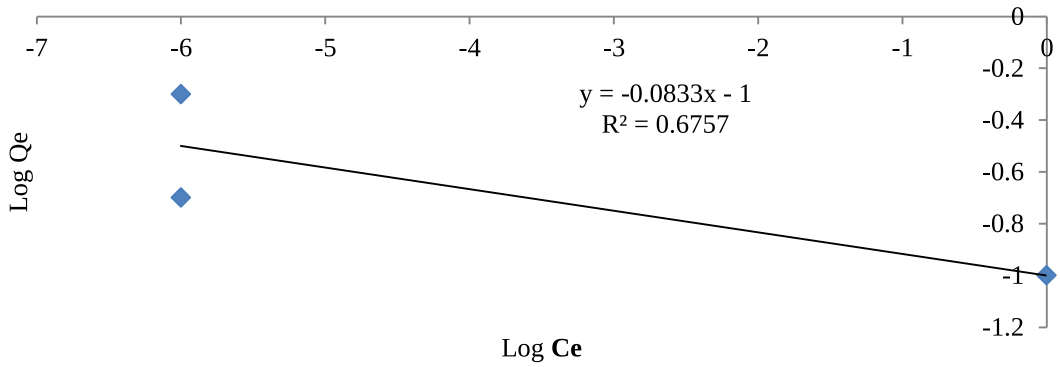

Figure 43: Freundlich isotherm for adsorption of Hg in Pb vrs Hg aqueous phase on shea nut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

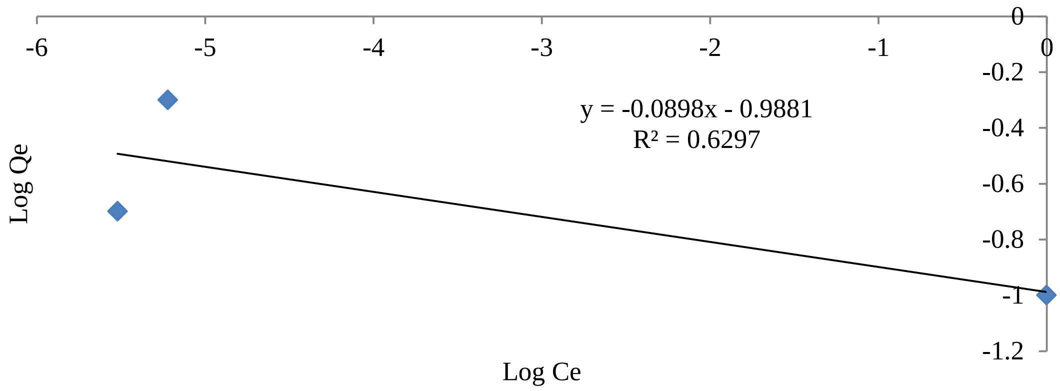

Figure 44: Freundlich isotherm for adsorption of Hg in Pb vrs Hg aqueous phase on groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

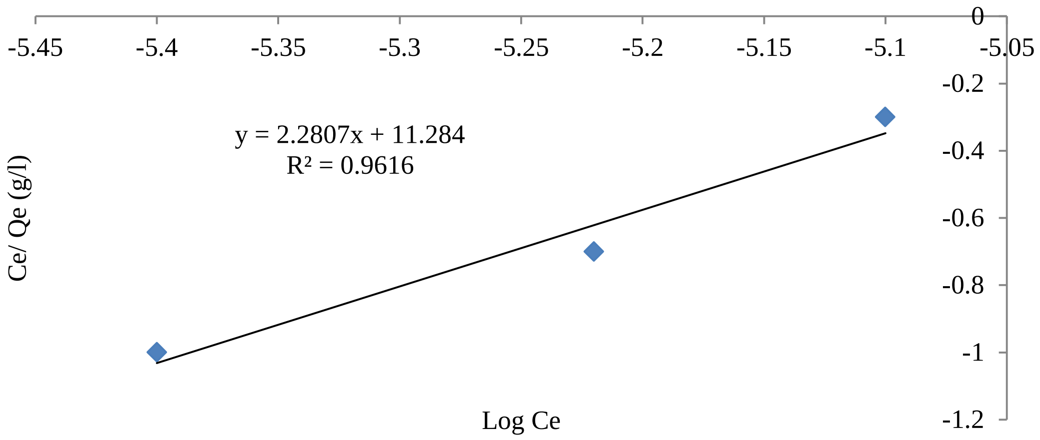

Figure 45: Freundlich isotherm for adsorption of Hg in Pb vrs Hg aqueous phase onto shea nut shell biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

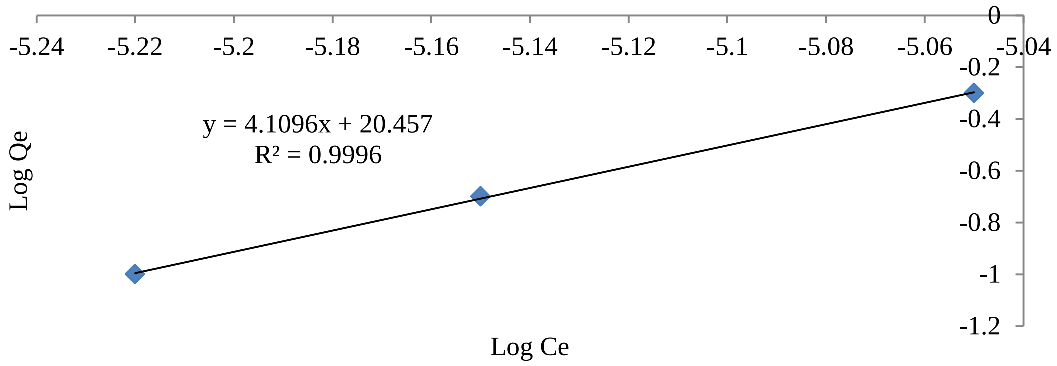

Figure 46: Freundlich isotherm for adsorption of Hg in Pb vrs Hg aqueous phase on groundnut and shea nut shells biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

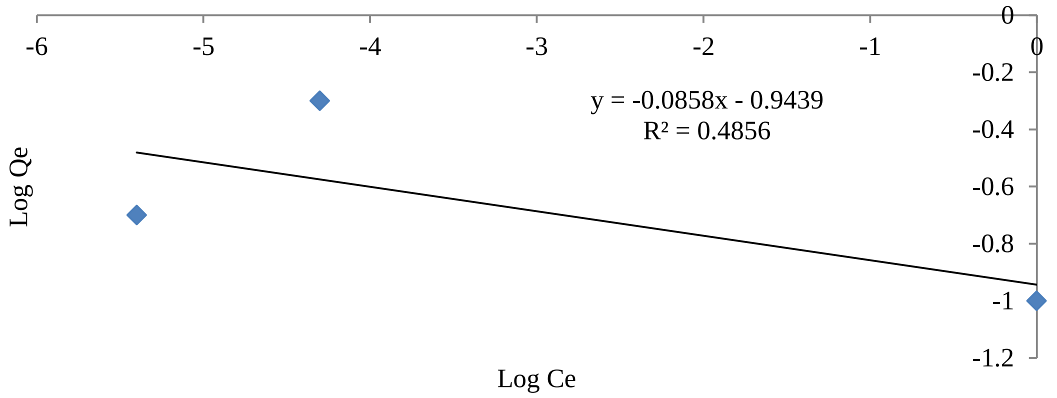

Figure 47: Freundlich isotherm for adsorption of Hg in ternary aqueous phase (Cd, Hg and Pb) onto shea nut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

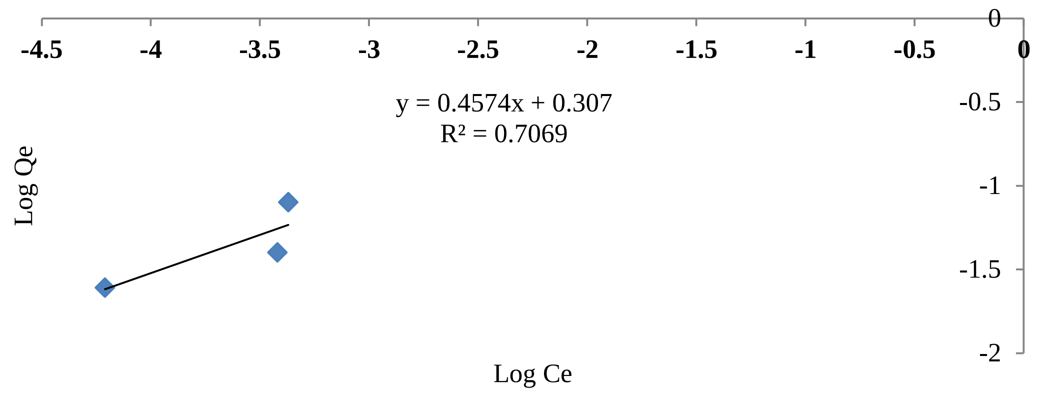

Figure 48: Freundlich isotherm for adsorption of Cd in ternary aqueous phase onto groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

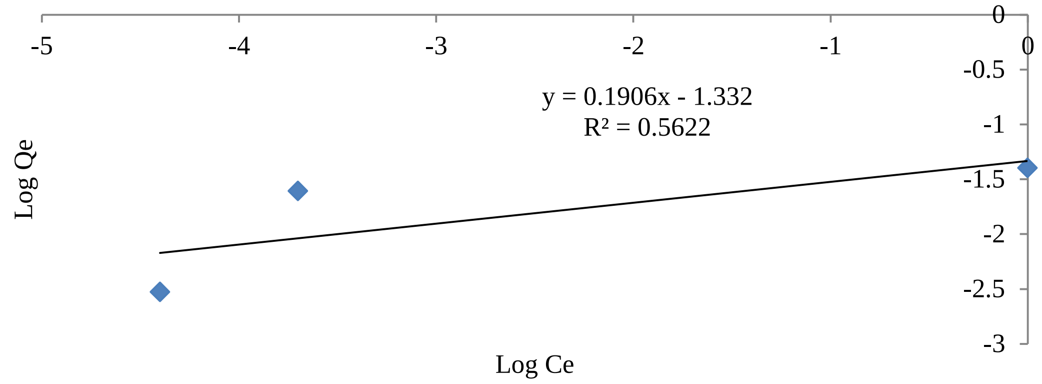

Figure 49: Freundlich isotherm for adsorption of Cd in ternary aqueous phase on groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

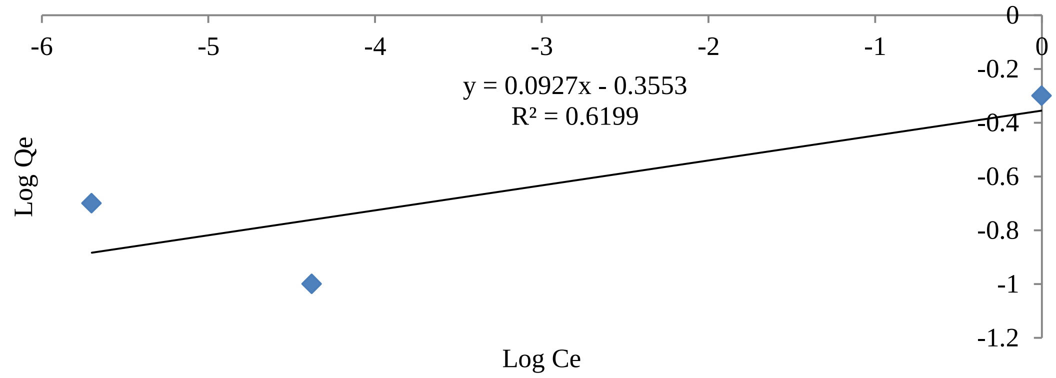

Figure 50: Freundlich isotherm for adsorption of Hg in ternary aqueous phase onto groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

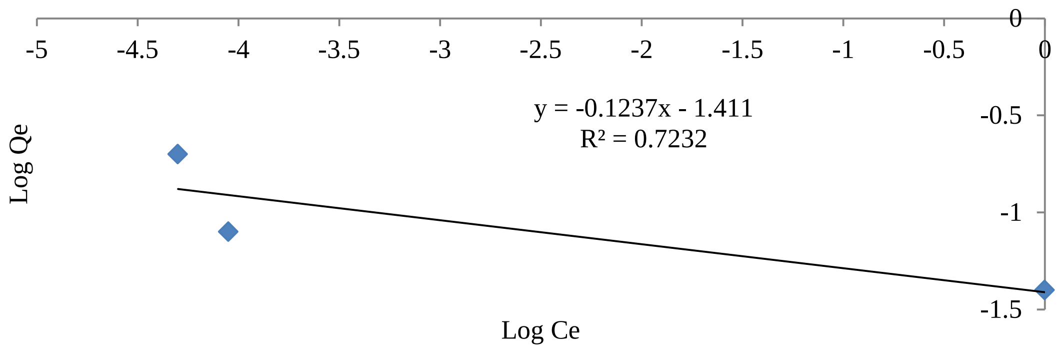

Figure 51: Freundlich isotherm for adsorption of Cd in ternary aqueous phase on groundnut shell biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

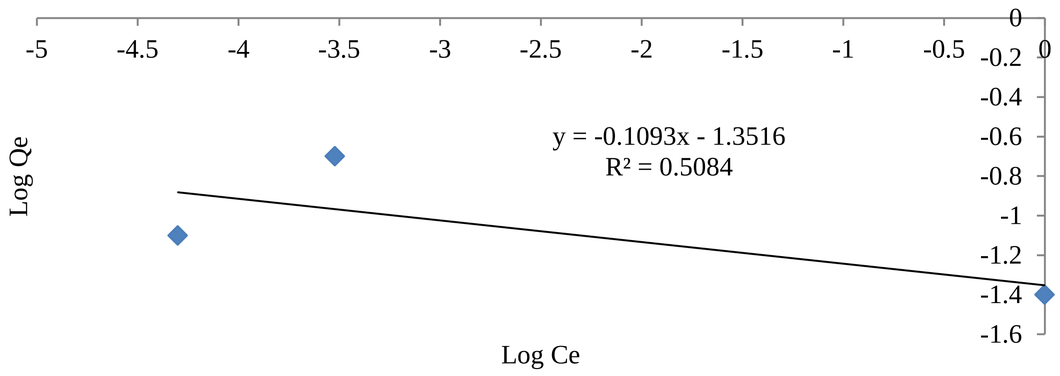

Figure 52: Freundlich isotherm for adsorption of Cd in ternary aqueous phase on groundnut and shea nut shells biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

Temkin isotherm has a factor that explicitly takes into the consideration of biochar (adsorbent) and metal ion (adsorbate) interactions. The regression co-efficient of Temkin model ranged from 0.01 to 1 and 0.32 to 0.98 for metal ions in mono, binary and ternary systems that were adsorbed by biochars produced under both slow and fast pyrolysis, respectively (**Table 8**). The B values ranged from -0.0 to 1.02 KJ/ mol for biochars produced under slow pyrolysis and adsorbate in mono, binary and ternary systems whilst biochars produced under fast pyrolysis and adsorbate recorded B values that ranged from -0.01 to 1.02 KJ/ mol (**Table 8**). The A_T values ranged from

2.23 to 3.19 L/mg for biochars produced under slow pyrolysis and adsorbate in mono, binary and ternary systems whilst biochars produced under fast pyrolysis and adsorbate recorded B values that ranged from 2.51 to 3.67 L/mg (**Table 8**). The specific plots of sorption Qe against the equilibrium concentration *In* Ce for heavy metals that did not ascertain total adsorption in batch experiment systems (mono, binary and ternary systems) are shown in **figures 53 to 78**.

Table 8: Temkin isotherm constants for adsorption of metal ions

Adsorbent	Pyrolysis	Absorbate	Estimate parameters of R^2 Temkin Isotherm			
			A_T (L/mg)	b_T	B	R^2
Mbiochar	Slow	**Cd**	3.16	-283822.76	-0.01	0.34
Mbiochar	Slow	**Pb**	2.46	-73929.88	-0.03	0.45
Gbiochar	Slow	**Hg**	2.69	48993.21	0.05	0.05
Sbiochar	Slow	**Hg**	2.66	14182.99	0.17	0.94
Gbiochar	Slow	**Cd**:Pb	3.19	142731.68	0.02	1
Mbiochar	Slow	**Cd**:Pb	2.80	633143.08	0.004	0.08
Mbiochar	Slow	**Hg**:Cd	2.64	20026.42	0.12	0.24
Sbiochar	Slow	**Hg**:Cd	3.13	-140298.75	-0.02	0.36
Gbiochar	Slow	**Hg**:Cd	3.0	-135673.52	-0.02	0.01
Gbiochar	slow	**Pb**:Hg	2.23	-99166.99	-0.02	0.31
Gbiochar	Slow	**Hg**:Pb	3.04	-685905	-0.004	0.01
Sbiochar	Slow	**Hg**:Pb	3.0	-136423.09	-0.02	0.48
Mbiochar	Slow	**Hg**:Pb	2.86	-129280.52	-0.02	0.43
Mbiochar	Slow	**Hg**:Cd:Pb	2.72	-20577.15	-0.12	0.35
Sbiochar	Slow	Hg:Cd:Pb	3.19	-143561.51	-0.02	0.29
Gbiochar	Slow	**Cd**:Hg:Pb	2.59	-33595.35	-0.07	0.91
Mbiochar	Slow	**Cd**:Hg:Pb	3.13	-280597.50	-0.01	0.34
Gbiochar	Slow	**Hg**:Cd:Pb	3.03	91116.53	0.03	0.80
Gbiochar	Fast	**Cd**	3.25	-290500	-0.01	0.34
Sbiochar	Fast	**Hg**	3.16	-141911.38	-0.02	0.35
Gbiochar	Fast	**Cd**:Hg	3.67	-320682.86	-0.01	0.36
Mbiochar	Fast	**Cd**:Hg	3.06	-277444.72	-0.01	0.34
Sbiochar	Fast	**Hg**:Pb	2.69	4449.92	0.55	0.86
Mbiochar	fast	**Hg**:Pb	2.72	2419.89	1.02	0.98
Gbiochar	fast	**Cd**:Hg:Pb	2.51	-226537.43	-0.01	0.53
Mbiochar	Fast	**Cd**:Hg:Pb	3.13	-280597.50	-0.01	0.32

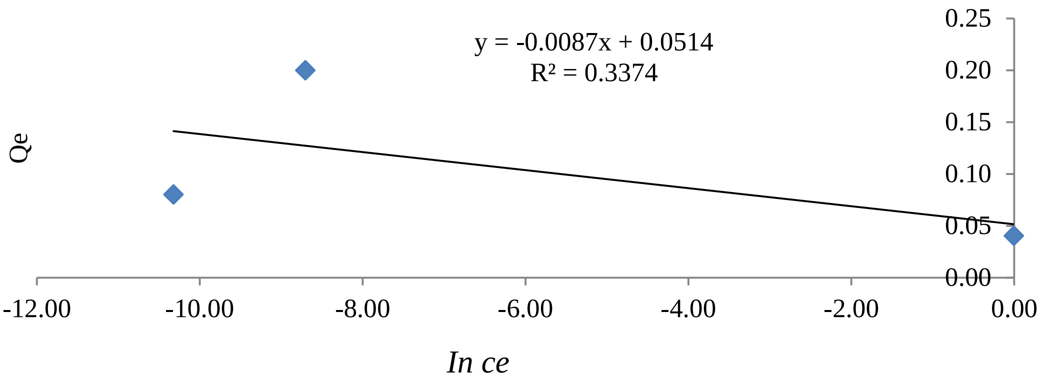

Figure 53: Temkin isotherm for adsorption of Cd in mono aqueous phase on groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

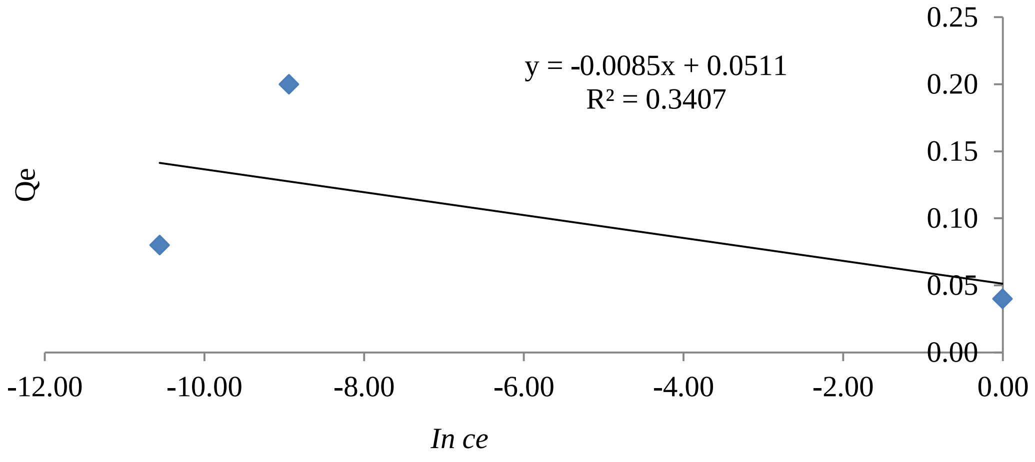

Figure 54: Temkin isotherm for adsorption of Cd in mono aqueous phase on ground shell biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

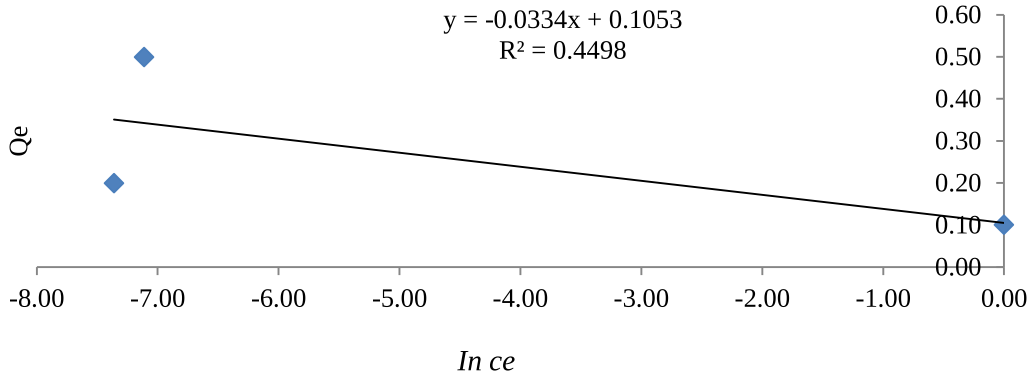

Figure 55: Temkin isotherm for adsorption of Pb in mono aqueous phase onto the combined groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

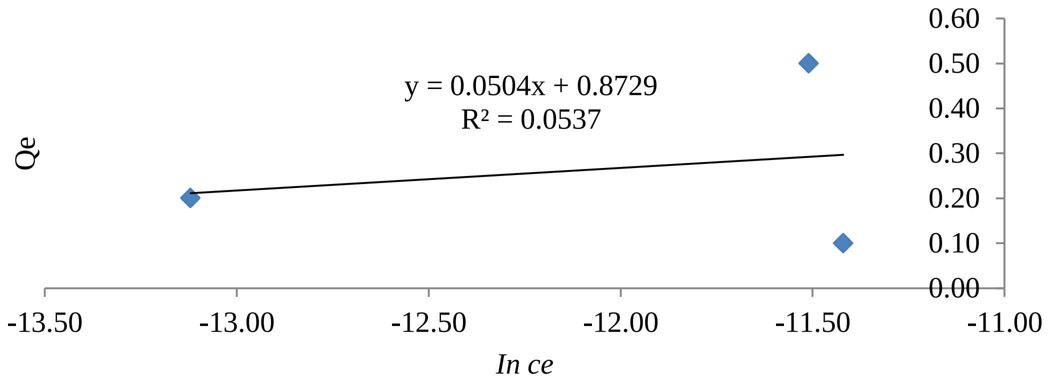

Figure 56: Temkin isotherm for adsorption of Hg in mono aqueous phase on groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

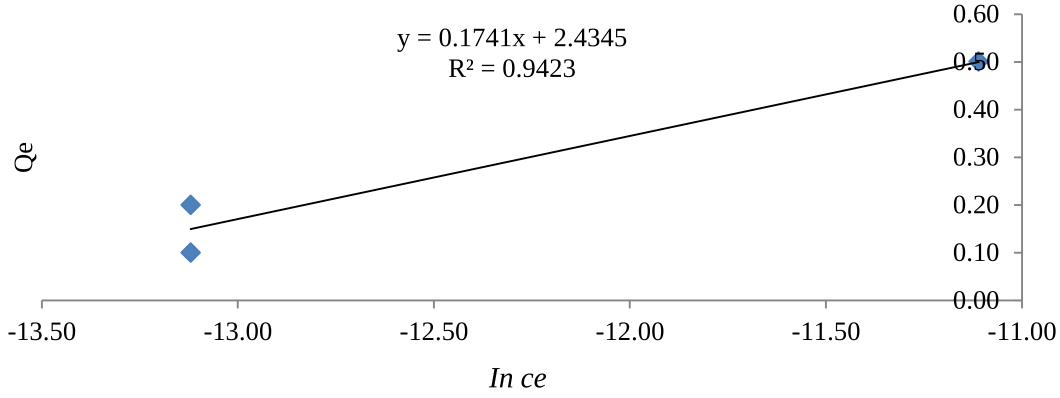

Figure 57: Temkin isotherm for adsorption of Hg in mono aqueous phase onto shea nut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

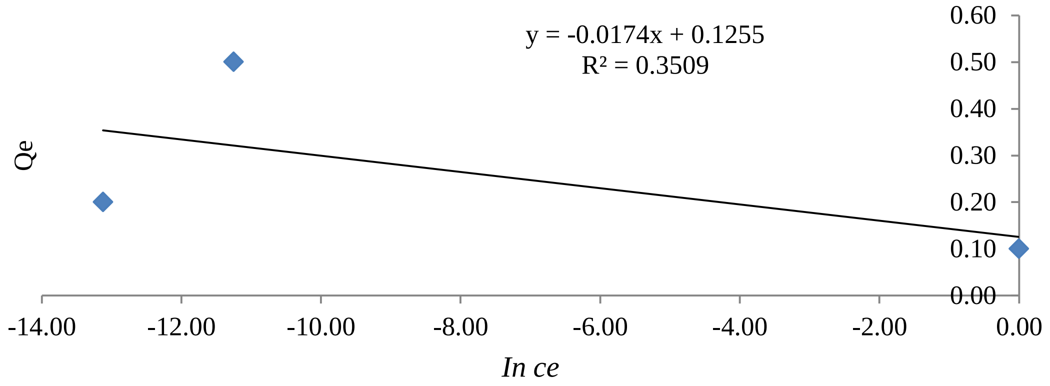

Figure 58: Temkin isotherm for the adsorption of Hg in mono aqueous phase on shea nut shell biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

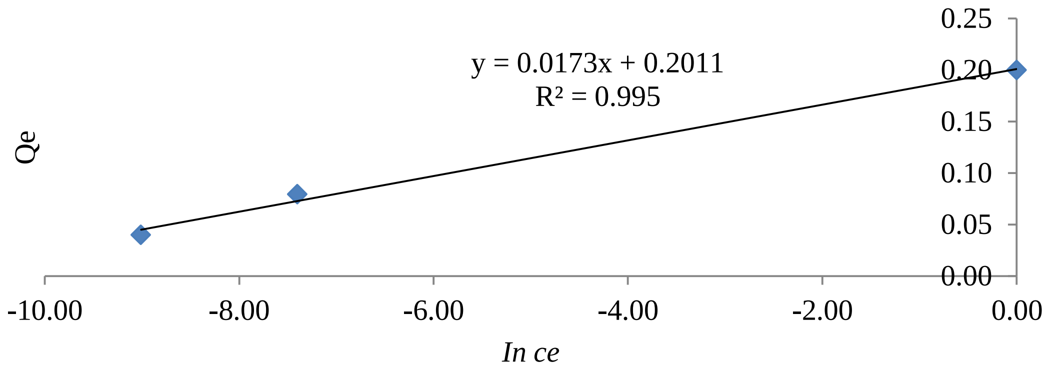

Figure 59: Temkin isotherm for adsorption of Cd in binary aqueous phase (Cd vrs Pb) on groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

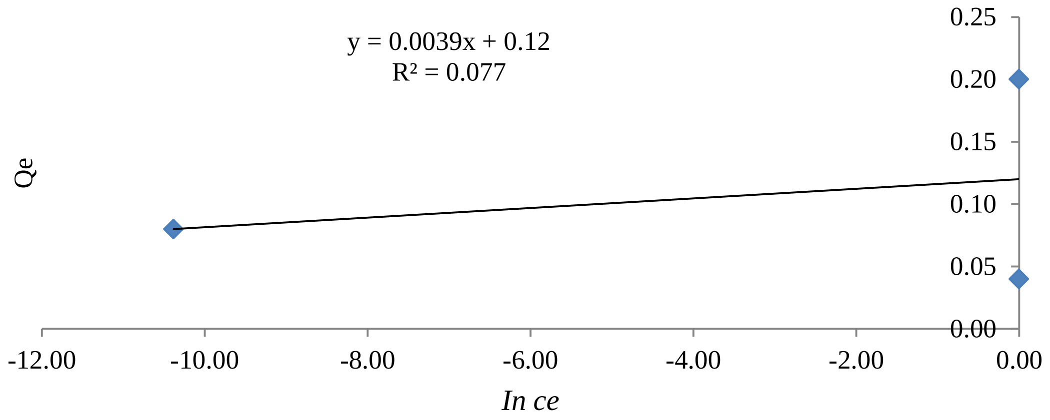

Figure 60: Temkin isotherm for adsorption of Cd in binary aqueous phase (Cd vrs Pb) on groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

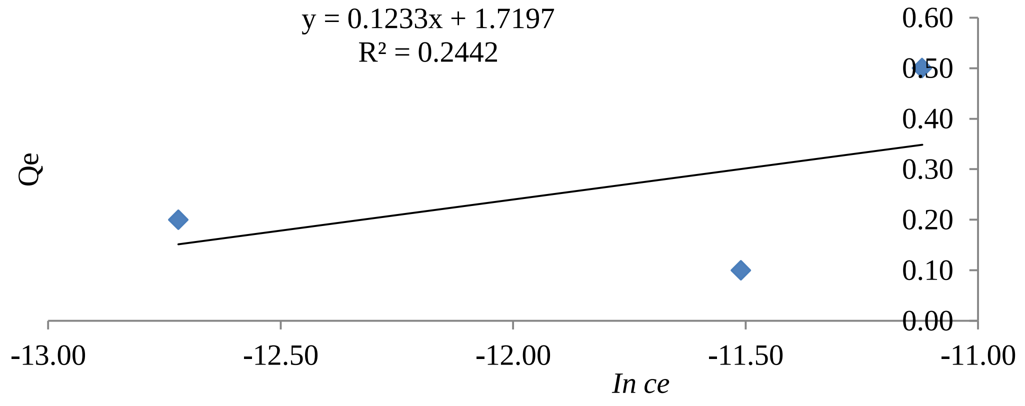

Figure 61: Temkin isotherm for adsorption of Hg in binary aqueous phase (Cd vrs Hg) onto groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

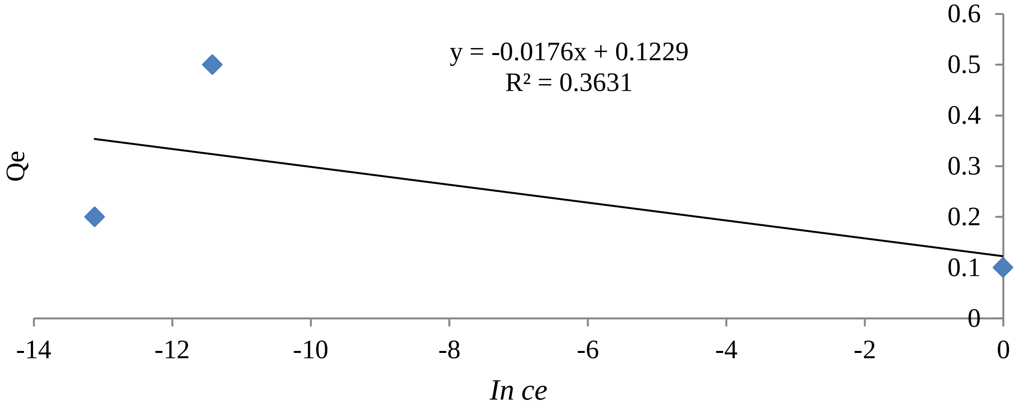

Figure 62: Temkin isotherm for adsorption of Hg in binary aqueous phase (Cd vrs Hg) onto shea nut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

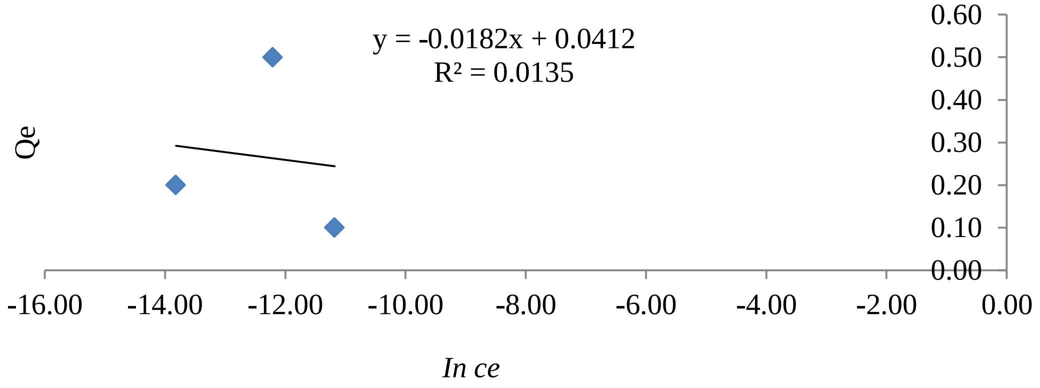

Figure 63: Temkin isotherm for adsorption of Hg in binary aqueous phase (Cd vrs Hg) onto groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

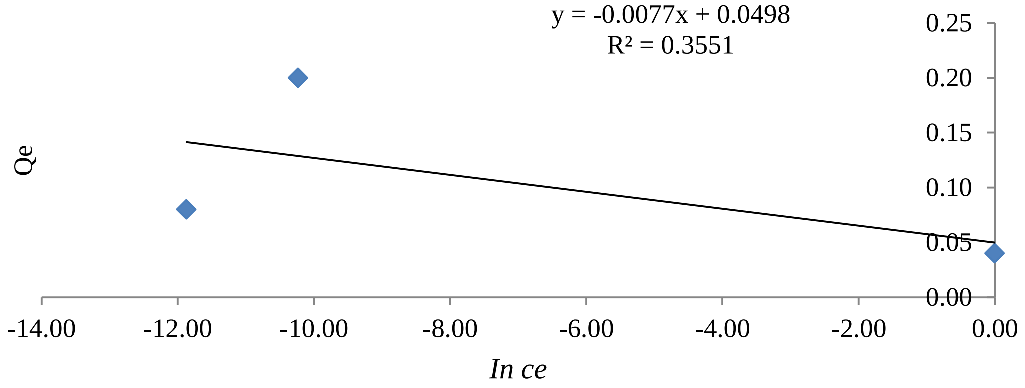

Figure 64: Temkin isotherm for adsorption of Cd in binary aqueous phase (Cd vrs Hg) on groundnut shell biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

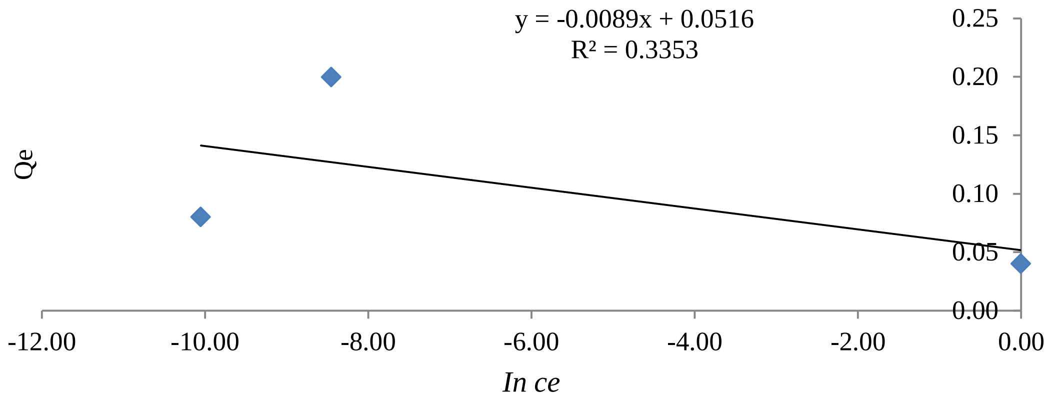

Figure 65: Temkin isotherm for adsorption of Cd in binary aqueous phase (Cd vrs Hg) onto the combined groundnut and shea nut shells biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

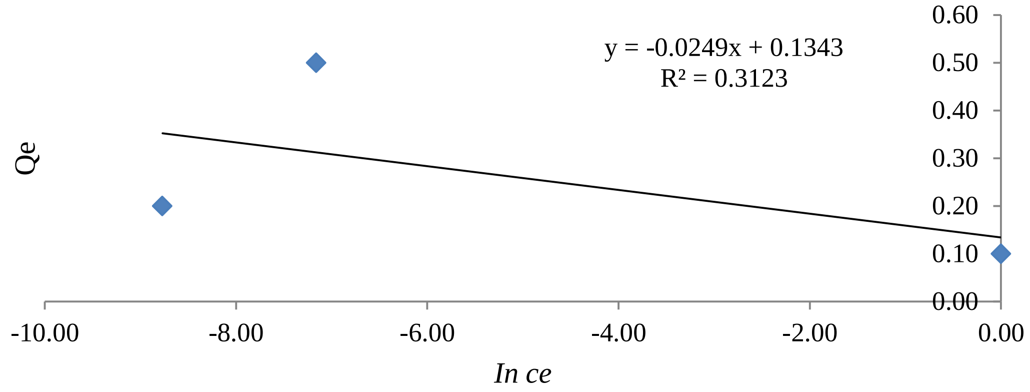

Figure 66: Temkin isotherm for adsorption of Pb in Pb vrs Hg aqueous phase on groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

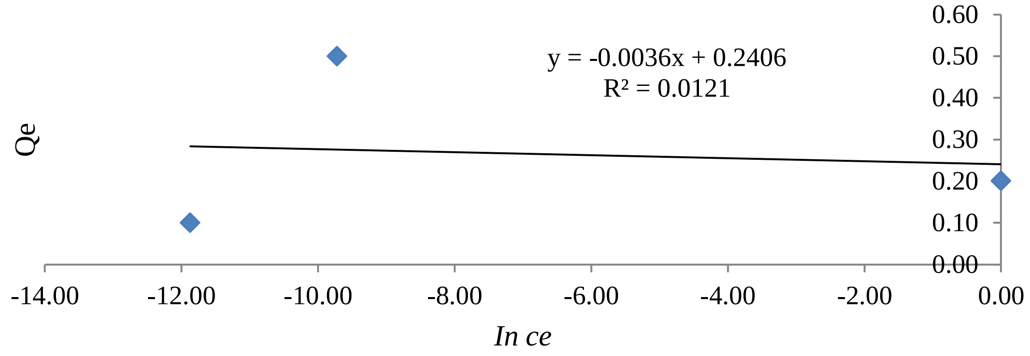

Figure 67: Temkin isotherm for adsorption of Hg in Pb vrs Hg aqueous phase on groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

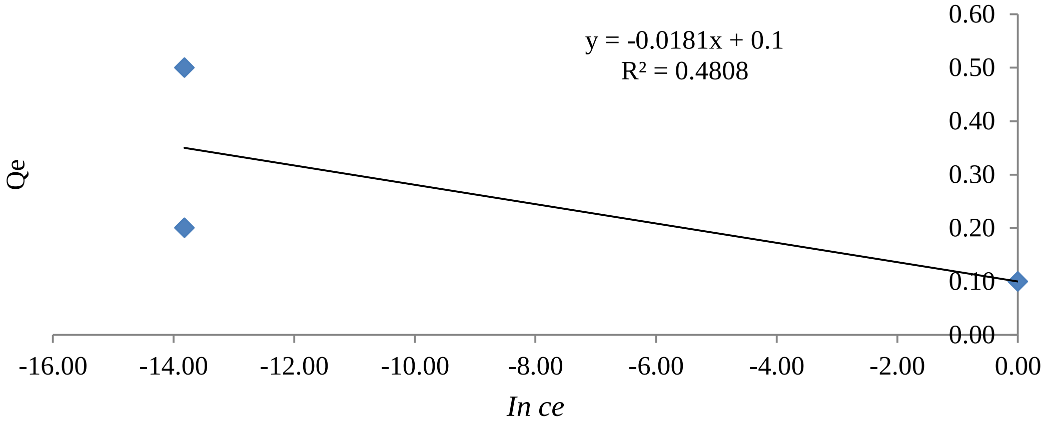

Figure 68: Temkin isotherm for adsorption of Hg in Pb vrs Hg aqueous phase on shea nut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

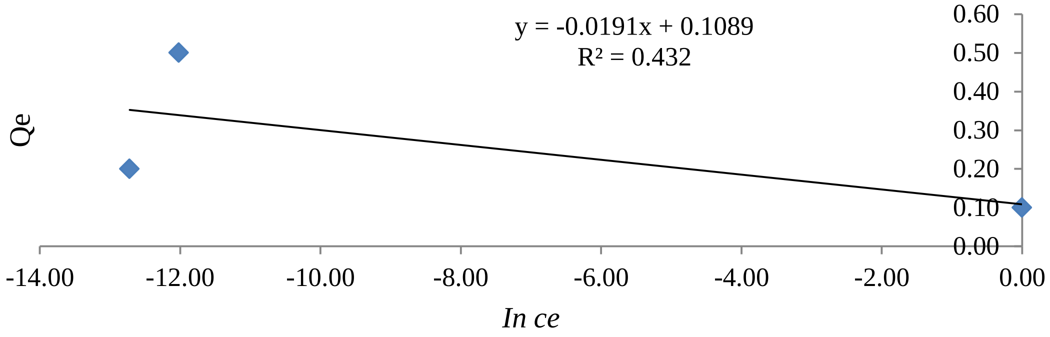

Figure 69: Temkin isotherm for adsorption of Hg in Pb vrs Hg aqueous phase on groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

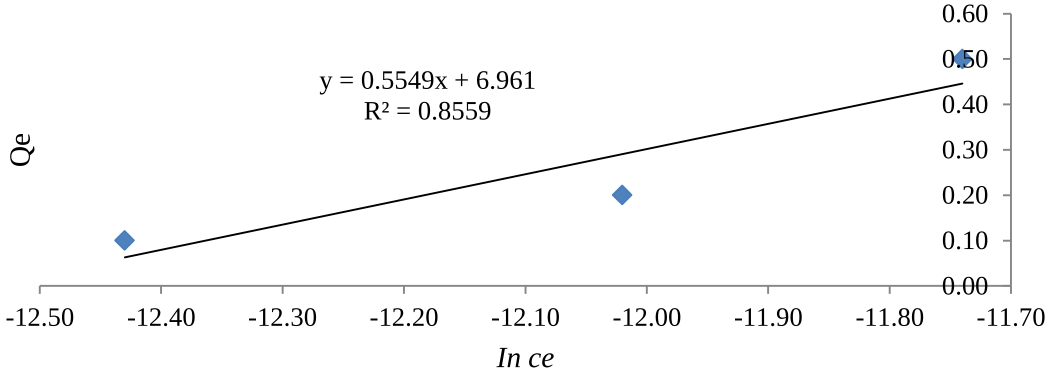

Figure 70: Temkin isotherm for adsorption of Hg in Pb vrs Hg aqueous phase onto shea nut shell biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

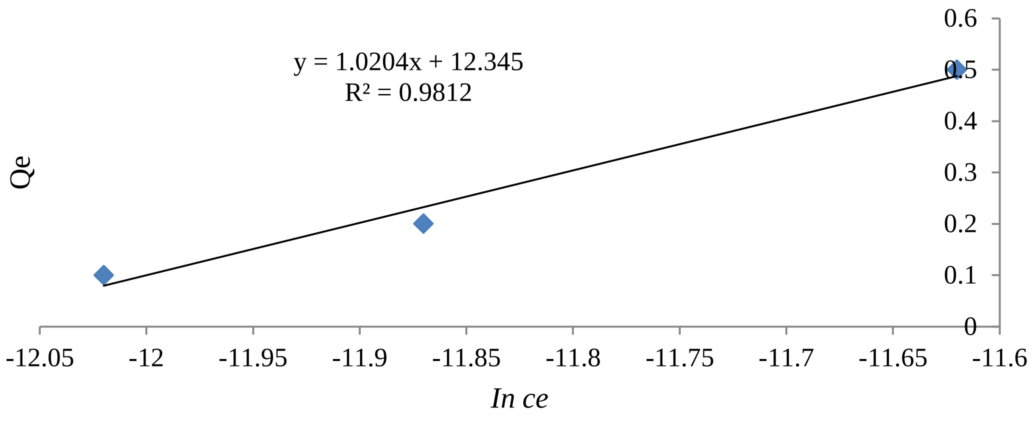

Figure 71: Temkin isotherm for adsorption of Hg in Pb vrs Hg aqueous phase on groundnut and shea nut shells biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

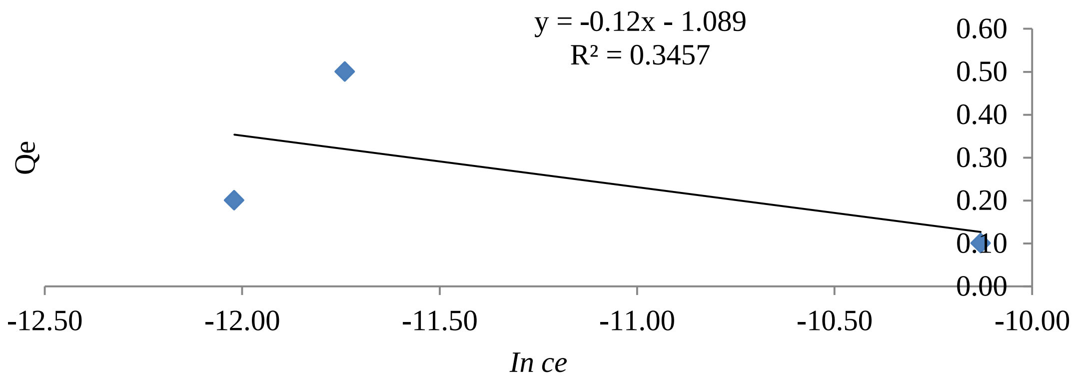

Figure 72: Temkin isotherm for adsorption of Hg in ternary aqueous phase (Cd, Pb and Hg) onto the combined groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

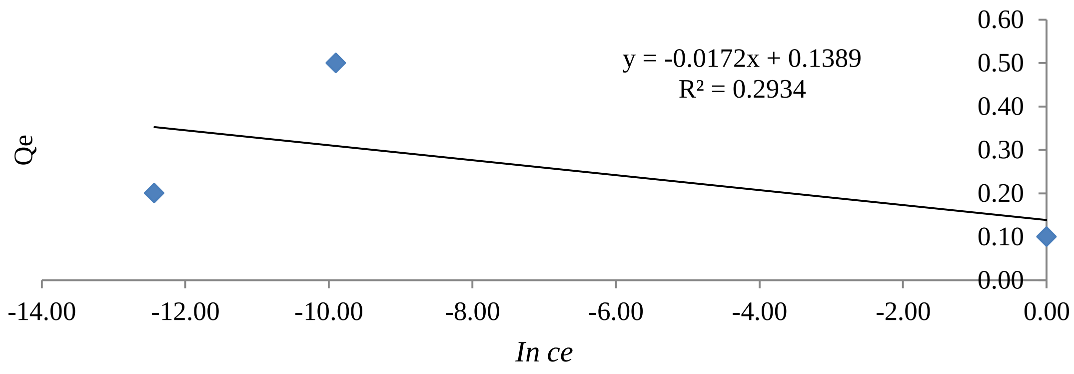

Figure 73: Temkin isotherm for adsorption of Hg in ternary aqueous phase (Cd, Hg and Pb) onto shea nut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

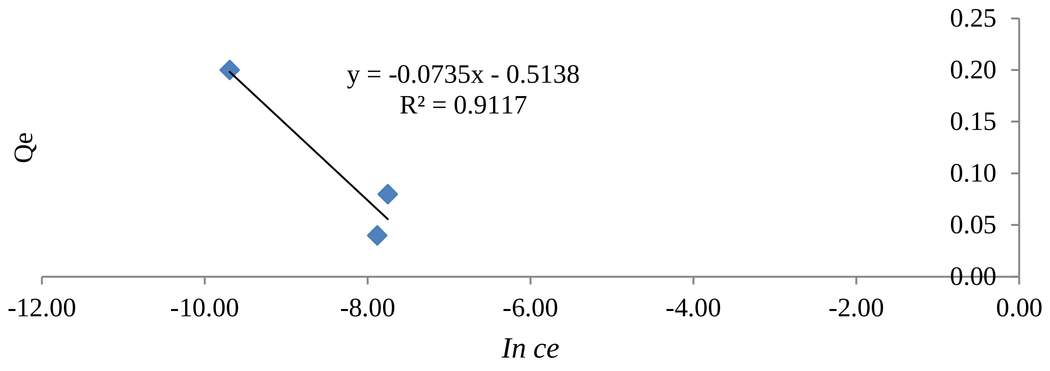

Figure 74: Temkin isotherm for adsorption of Cd in ternary aqueous phase onto groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

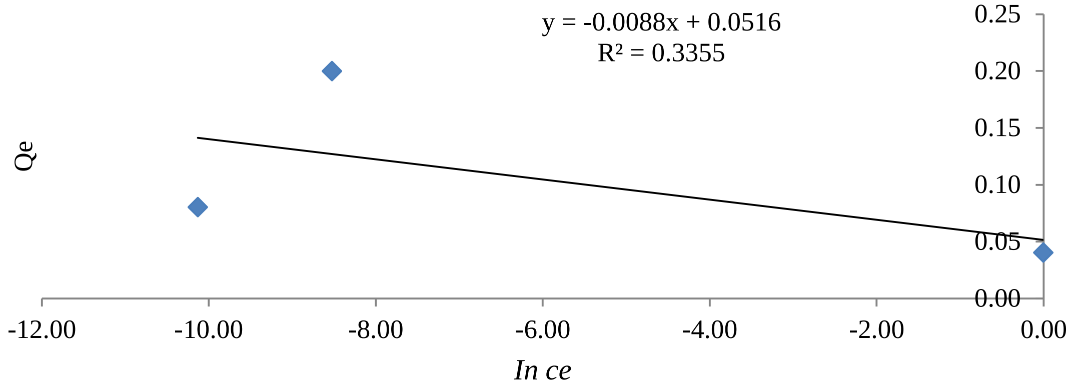

Figure 75: Temkin isotherm for adsorption of Cd in ternary aqueous phase on groundnut and shea nut shells biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

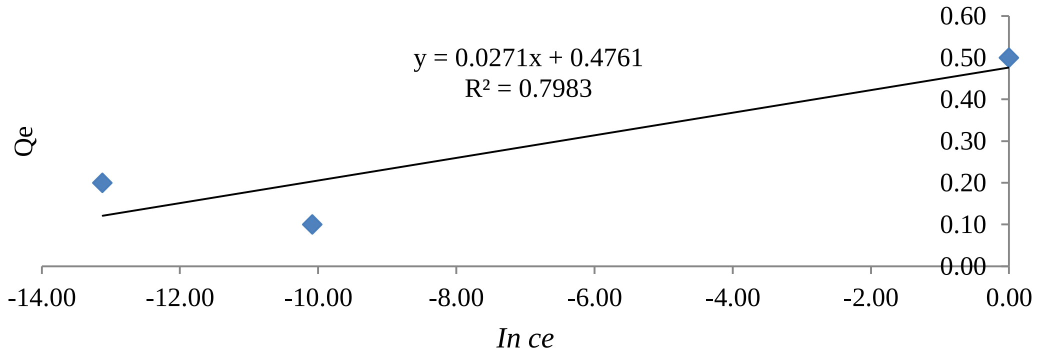

Figure 76: Temkin isotherm for adsorption of Hg in ternary aqueous phase onto groundnut shell biochar produced at a temperature of 350 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

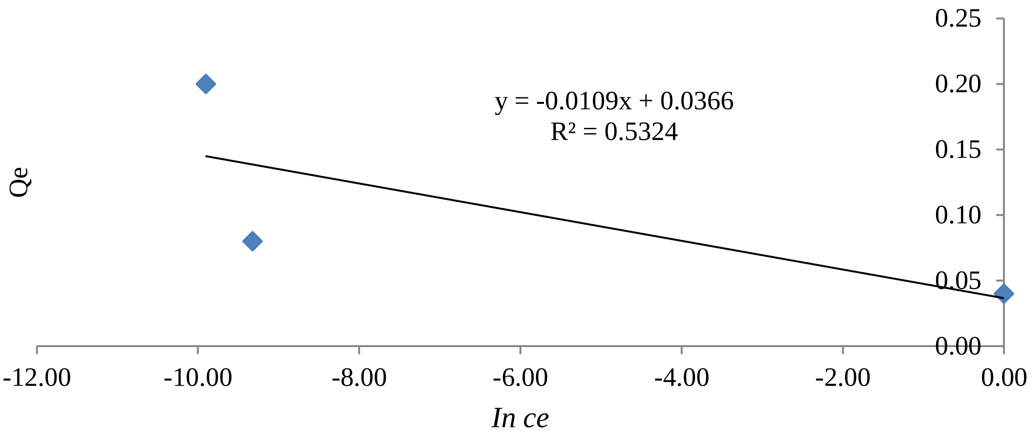

Figure 77: Temkin isotherm for adsorption of Cd in ternary aqueous phase on groundnut shell biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

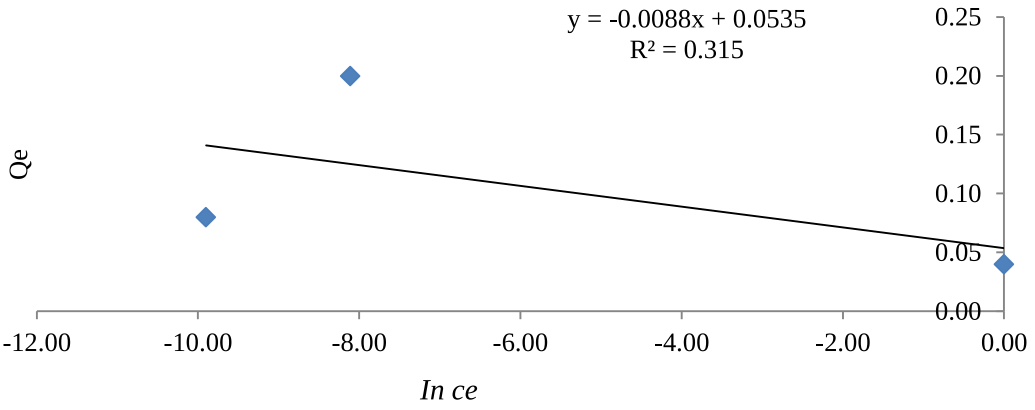

Figure 78: Temkin isotherm for adsorption of Cd in ternary aqueous phase on groundnut and shea nut shells biochar produced at a temperature of 700 °C (solution volume: 50 ml; adsorbent dose: 2 g; contact time: 72 min)

4.6 Interactive Behaviour of Cd, Hg and Pb ions in Binary and Ternary Systems

The interactive effects of mixtures in the aqueous phase onto biochars produced under slow and fast pyrolysis temperature are presented in **tables 9 and 10**. Some of the R_i values are less than 100% in binary and ternary metal systems and others are also greater than 100% especially for mercury ion in the mixtures that interacted with biochars produced under slow pyrolysis temperature (**Table 9**).

In binary system of cadmium and mercury both were antagonistic in their interaction in fold one and fold two of the aqueous phase, respectively with groundnut shell biochar produced under slow pyrolysis, at both fold two and fold five only mercury was antagonistic in nature in the aqueous phase with shea nut shell biochar produced under slow pyrolysis and mercury ion was also antagonistic in its interaction in fold two aqueous phase with the combined biochar produced under slow pyrolysis (**Table 9**). Whilst at fold five, cadmium and mercury in the mixture showed their interaction is synergistic in nature with the combined groundnut and shea nut shells biochar produced under slow pyrolysis (**Table 9**).

The binary system of cadmium and mercury aqueous phase with groundnut shell biochar produced under fast pyrolysis showed cadmium ion interaction was antagonistic in nature at fold one, and mercury was antagonistic at both fold two and fold five and synergistic in nature at fold one (**Table 10**).

The mixture of cadmium and lead aqueous with groundnut shell biochar produced under slow pyrolysis showed cadmium ion was synergistic in nature at fold two, same mixture with combined groundnut and shea nut shells biochar produced under slow pyrolysis cadmium ion was also synergistic in nature at both fold two and five (**Table 9**).

Table 9: Interactive effect of mixture of metal ions in the binary and ternary systems onto biochars produced under slow pyrolysis

Biochar at 350 °C		Groundnut shell		Shea nut shell		Groundnut and shea nut shells	
Mixture	Conc (mg/l)	R_i	Int. effect	R_i	Int. effect	Ri	Int. effect
Cd+Hg	0.08	80%	Ant	*	*	*	*
Cd+Hg	0.20	*	*	*	*	121%	Syn
Hg+Cd	0.20	80%	Ant	67%	Ant	9%	Ant
Hg+Cd	0.50	*	*	73%	Ant	214%	Syn
Cd+Pb	0.08	3050%	Syn	*	*	939%	Syn
Cd+Pb	0.20	*	*	*	*	117%	Syn
Hg+Pb	0.10	64%	Ant	*	*	*	*
Hg+Pb	0.20	*	*	33%	Ant	*	*
Hg+Pb	0.50	60%	Ant	7%	Ant	86%	Ant
Pb+Hg	0.10	*	*	*	*	216%	Syn
Cd+Hg+Pb	0.08	2150%	Syn	*	*	121%	Syn
Cd+Hg+Pb	0.20	*	*	*	*	120%	Syn
Hg+Cd+Pb	0.10	*	*	*	*	191%	Syn
Hg+Cd+Pb	0.20	*	*	1333%	Syn	*	*
Hg+Cd+Pb	0.50	*	*	3333%	Syn	1143%	Syn
Pb+Cd+Hg	0.20	*	*	*	*	224%	Syn

Note: * Denote adsorption was completely 100% and Ri values cannot be computed for interpretation; all concentration values are in mg/l; Int. effect: Interactive effect; Ant: Antagonistic; Syn: Synergistic; and R_i: Relative adsorption capacity.

The binary system of mercury and lead with groundnut shell biochar produced under slow pyrolysis showed mercury ion interaction was antagonistic in nature at both fold one and fold five. Mercury ions in same mixture with shea nut shell biochar produced under slow pyrolysis was also antagonistic in nature at fold two and fold five. Whilst the mixture with combined groundnut and shea nut shells biochar produced under slow pyrolysis also showed antagonistic interaction behaviour at fold five (**Table 9**). It was only at fold one of binary mixture of the mercury and lead that, lead ion showed synergistic interaction behaviour with the combined groundnut and shea nut shells biochar produced under slow pyrolysis (**Table 9**).

The mixture of mercury and lead aqueous phase with shea nut shell biochar, and the combined groundnut and shea nut shells biochar produced under fast pyrolysis showed mercury ion behaviour was antagonistic in nature at fold five, respectively. Whilst the mixture with shea nut shell biochar produced under fast pyrolysis showed mercury ion interaction behaviour was synergistic in nature at fold two (**Table 10**).

In ternary system of the aqueous phase with groundnut shell, and the combined groundnut and shea nut shells biochars produced under slow pyrolysis, cadmium showed synergistic interaction behaviour at fold one, and fold two and fold five, respectively. With same ternary mixture with shea nut shell biochar, and the combined groundnut and shea nut shells biochars produced under slow pyrolysis showed mercury ion was synergistic in nature at fold two and fold five, and fold one and fold five, respectively (**Table 9**).

In ternary system of the aqueous phase with groundnut shell biochar produced under fast pyrolysis showed cadmium was antagonistic in nature at both fold two and fold five (**Table 10**). The aqueous phase of the mixture with groundnut shell biochar produced under fast pyrolysis showed mercury ion was antagonistic in nature at only fold two and synergistic in nature at only fold one (**Table 10**). Mercury in the ternary mixture with shea nut shell, and the combined groundnut and shea nut shells biochar produced under fast pyrolysis showed interaction behaviour was synergistic in nature at fold two and fold five, respectively (**Table 10**).

Table 10: Interactive effect of mixture of metal ions in the binary and ternary systems onto biochars produced under fast pyrolysis

Biochar at 700 °C		Groundnut shell		Shea nut shell		Groundnut and shea nut shells	
Metal system	Conc (mg/l)	Ri	Int. effect	Ri	Int. effect	Ri	Int. effect
Cd+Hg	0.08	27%	Ant	*	*	*	*
Hg+Cd	0.10	350%	Syn	*	*	*	*
Hg+Cd	0.20	33%	Ant	*	*	*	*
Hg+Cd	0.50	27%	Ant	*	*	*	*
Hg+Pb	0.20	*	*	200%	Syn	*	*
Hg+Pb	0.50	*	*	62%	Ant	69%	Ant
Cd+Hg+Pb	0.08	35%	Ant	*	*	*	*
Cd+Hg+Pb	0.20	38%	Ant	*	*	*	*
Hg+Cd+Pb	0.10	1050%	Syn	*	*	*	*
Hg+Cd+Pb	0.20	67%	Ant	*	*	*	*
Hg+Cd+Pb	0.50	*	*	123%	Syn	154%	Syn

Note: * Denote adsorption was completely 100% and Ri values cannot be computed for interpretation; all concentration values are in mg/l; Int. effect: Interactive effect; Ant: Antagonistic; and Syn: Synergistic.

CHAPTER FIVE

DISCUSSION

5.0 Removal of Cd, Hg and Pb from Aqueous Phase

The agricultural wastes based biochars produced has a strong affinity for Cd, Hg and Pb ions in aqueous phase. The development of biochar technology gives opportunities to satisfy the need for cost-effective and eco-friendly adsorbents for removal of aqueous heavy metals.

5.1 Adsorption of Mono-component System onto Biochars Produced under Slow and Fast Pyrolysis Temperatures

Cadmium removal efficiency in mono-component system by biochars was higher than 99.50%. The experiment shows shea nut shell biochar produced under both slow and fast pyrolysis temperatures had the strongest affinity for cadmium in the mono aqueous phase, followed by biochar that involves the combination of groundnut and shea nut shells. Though, the removal rate was generally effective, the groundnut shell biochar produced under fast pyrolysis temperature and the combination of groundnut and shea nut shells produced under slow pyrolysis temperature seem to be less effective in removal of cadmium at different high maximum contamination limits of the aqueous phase. This may be due to the nature of feed stock. As shea nut shell biomass may be richer in lignocellulosic biomass (cellulose, hemicellulose and lignin) which is a good characteristic for effective adsorption of metal ions hence the difference in their performance. This finding learn support from Harmsen and Naidu (2013) that reported that the characteristics, nature, quality, and potential use of biochar are affected by the form, type, preliminary preparation steps and biomass feed stock size and type of pyrolysis product.

Similar mono-component system using *Eichornia crassipes* (agricultural waste) for removal of cadmium ion in aqueous phase with optimum pH value of 5.0 showed nearly 90% removals (Li *et al.*, 2016). Also, a study conducted to select the best absorbent produced from agricultural wastes (mushroom waste, wolffia, lemna, rice materials; straw, stubble, husk, and root), water hyacinth materials (stems, leaves, and roots), legume straw, oil-tea camellia seed cake, and peanut husks) for cadmium (Cd) ion in aqueous phase, found peanut husk biochar to be the best absorbent for Cd among the absorbents (n = 22), and its adsorption reached equilibrium within 12 hours (Cheng *et al.*, 2016). The optimum conditions for the experiment were a peanut husk biochar dosage of 40 g/l, an initial Cd concentration of 200 mg/l, pH 5.0 and room temperature. Under these conditions, the Cd removal efficiency of the biochar was 99.90% (Cheng *et al.*, 2016). Mushroom waste biochar exhibited the lowest efficiency (38.70%) among the biomasses, soyabean straw biochar also showed higher removal efficiency of 86.60%, peanut husk biochar recorded a highly significantly (P = 0.001) removal efficiency of 99.20% for the adsorption of Cd as compared to the other kinds of biochars (Cheng *et al.*, 2016). Corn straw biochar produced under pyrolysis temperature of 400 °C for 2 h reached removal efficiencies of 99.24% for Cd from water with biochar dosage of 20 g/l and initial concentration of 20 mg/l (Tong *et al.*, 2017).

Comparatively, biochars produced under both slow and fast pyrolysis temperatures for this study showed the highest removal efficiency of Cd in mono-component system thus without taken into consideration the different optimum conditions of the various experiments. The peanut husk contains many compounds such as cellulose, lignin, organic acids, pentosan and tannins that can bind heavy metal ions (Ding *et al.*,

2012) this will likely be the case for shea nuts shells and other agricultural waste. The surface of biochar from peanut husks contains different active functional groups (COOH and OH) (Ahmad *et al.*, 2014; Khan *et al.*, 2015). This may be similar for the shea nut shell biochar.

Mercury (Hg) removal efficiency by biochars in mono-component system with different maximum concentration limits was almost 100%. The experiment showed that groundnut and shea nut shells biochars produced under both slow and fast pyrolysis temperatures had a strong affinity for mercury in the mono aqueous phase. Similarly, soybean stalk biochar was able to remove mercury by 75% to 87% from a mono aqueous solution (Kong *et al.*, 2011). This experiment showed that high efficiency and cost-effective biochars can be derived from groundnut and shea nut shells as it required no such as pretreatment or modification of biochar surfaces for adsorption, and comparable with some commercial activated carbons in removing mercury in mono aqueous environment.

The removal efficiency of lead in mono-component system by biochars was higher than 99.10%. The experiment showed shea nut shell biochar produced under both slow and fast pyrolysis temperatures had the strongest affinity for lead in mono aqueous phase, followed by groundnut shell biochar and the least was combination of groundnut and shea nut shells biochar. At slow pyrolysis, the adsorption was not 100% for Pb at the different maximum concentration limits of the mono aqueous phase as compare to binary and ternary aqueous phase. The individual groundnut and shea nut shells biochars has high affinity for Pb in mono-component system.

Similar agricultural wastes used for mono-component system study on lead showed efficiencies of 85% for chalf, 86% for sun flower husk, 90% for rice husk, 98% for tea waste and 100% for sesame husk for Pb ion removal (Surchi, 2011). Cao *et al.* (2009) also reported precipitation account for 82% to 87% of Pb adsorption on a dairy manure derived biochar in a mono-component system. It was reported that adsorption of Pb onto biochar is often influenced by the coordination of the carbonyl and hydroxyl functional group that accounts for 32.80% to 42.30% (Lu *et al.*, 2012). Also complex or co-precipitation of Pb on the biochar minerals surface usually accounted for 58% to 62% of total Pb ions adsorption (Lu *et al.*, 2012). *Lemna perpusilla* Torr has proven to be a good adsorbent for Pb^{2+} as has been able to ascertain more than 95% adsorption efficiency after 210 min with a dose of 4 g/l and an initial Pb^{2+}concentration of 50 mg/l (Tang *et al.*, 2013).

Corn straw biochar produced under pyrolysis temperature of 400 °C for 2 h reached removal efficiencies of 98.62% for Pb from water with biochar dosage of 20 g/l and initial concentration of 20 mg/l (Tong *et al.*, 2017). Except, the sesame husk biochar, comparatively the individual groundnut and shea nut shells biochars have proven more effective, preferable, eco-friendly and attractive alternative adsorption materials than other agricultural wastes utilised for Pb ion removal in mono-component system. The experiment showed that mineral in the groundnut and shea nut shells biochars may have contributed to the effective removal of heavy metal ions from aqueous solutions. Also some of experimental factors such as contact time, dosage of biochar, pH and temperature considered by this study favoured the ions adsorption.

5.2 Adsorption of Binary-component System onto Biochars Produced under Slow and Fast Pyrolysis Temperatures

A polluted aqueous environment may contain more than one metal ion. Therefore, any remediation study needs to examine the multiple metal interactions simultaneously for accurate adsorption of contaminants.

In the binary system of Cd and Hg, Cd removal efficiency was higher than 99.70% whilst Hg was 100%. Shea nut shell biochar had the strongest affinity for Cd and Hg ions in the aqueous phase, followed by biochar that involves the combination of groundnut and shea nut shells biochar, and the least was groundnut shell biochar. The order of adsorption for Hg and Cd ions onto groundnut and shea nut shells biochars was therefore: Hg^{2+} > Cd^{2+}, when theoretically linked in same order of biosorption that is attributable to the size of the metal ions according to ionic radii (A°), Hg^{2+} = 1.02 and Cd^{2+} = 0.97. The strength of binding to biochars depends on metal chemistry (including parameters such as ionic radii (A°), charge, and Pauling electronegativity), the type of metal binding (electrostatic or covalent) and affinity for binding sites (Fourest and Roux, 1992; Veglio and Beolchini, 1997).

The removal efficiency of cadmium and lead in binary system by biochars was also effective. The experiment showed that shea nut shell biochar produced under both slow and fast pyrolysis temperatures had the strongest affinity for cadmium and lead ions in binary aqueous phase. There is no clear cut difference between groundnut shell biochar and the combination of groundnut and shea nut shells biochar in terms of their removal efficiency. Similar, binary study by Mohan *et al.* (2007) reported effective removal of cadmium and lead by oak bark biochar are comparable to that of commercial activated carbon (Calgon F-400). The experiment showed order of adsorption in binary component system of Pb and Cd ions onto groundnut and shea nut shells biochars to be $Pb^{2+} > Cd^{2+}$. This may be attributed to the fact that in the multi-metal adsorption isotherm, the hydrated radius of Pb^{2+} (4.01 A°) is smaller than that of Cd^{2+} (4.26 A°) and Pb has a greater affinity for most functional groups in organic matter, including phenolic and carboxylic groups. This may generally be attributed to the differences in chemical characteristics between Pb and Cd ions (Park *et al.*, 2016). Lead (Pb^{2+} is a hard Lewis acid whilst Cd^{2+} is a soft Lewis acid) has a higher electronegativity (2.33 for Pb and 1.69 for Cd) than Cd, also Pb (7.71) has a lower pKH than Cd (10.10). Pb is more favoured by these factors enabling it to adsorb through inner sphere surface complexation or sorption reactions than Cd (Park *et al.*, 2016).

In the binary system of Hg and Pb, Hg removal efficiency was almost 100% in the various maximum concentration limits. The shea nut shell biochar produced under both slow and fast pyrolysis temperatures showed the strongest affinity for Pb and Hg ions in the aqueous phase, the groundnut shell biochar produced under slow pyrolysis a slightly less affinity for mercury when compared to the others. Comparatively, the adsorption of two metals has not shown clear difference in adsorption in binary mixtures as the concentrations were low. However, based on the other binary experiments, the order of adsorption of Hg and Pb ions onto groundnut and shea nut shells biochars will likely be: $Pb^{2+} > Hg^{2+}$. Due to the fact that in the multi-metal adsorption isotherm, the hydrated radius of Pb^{2+} (4.01 A°) is smaller than that of Hg^{2+} (4.22 A°) and Pb had a greater affinity for most functional groups in the organic matter, including phenolic and carboxylic groups.

5.3 Adsorption of Ternary-component System onto Biochars Produced under Slow and Fast Pyrolysis Temperatures

The experiment showed the order of adsorption for Cd, Hg and Pb ions onto groundnut and shea nut shells biochars in ternary system was $Pb^{2+} > Hg^{2+} > Cd^{2+}$. An explanation for the trend in the ternary system is that the hydrated radius of Pb^{2+} (4.01 Å) is smaller than that of Hg^{2+} (4.22 A°) and Cd^{2+} (4.26 A°), and Pb has a greater affinity for most functional groups in organic matter. The ionic properties of the three metals make Pb more favourable in terms of adsorption through inner sphere surface complexation or sorption reactions than Hg and Cd. Since, high adsorption of Pb^{2+} from aqueous solutions onto adsorbents through surface electrostatic attraction is attributable to its high electronegativity constant of 2.33 which results in a high tendency for specific adsorption (Shi *et al.*, 2009). The electrochemical potential, ionic charge and ionic radius affect biosorbent adsorption capacity in the multi-metal system (Yakup-Arica *et al.*, 2004).

The adsorption capacity of biochars did not show any decrease or increase in any of the batch experiments probability due to high affinity of biochars for heavy metal ions that did not fully occupy the binding sites. As some of experimental factors such as contact time, dosage of biochar, pH and temperature considered by this study favoured the ions adsorption. Factors that affect adsorption preference of an adsorbent for heavy metal ions in multi-metal system are basically related to physico-chemical properties of aqueous solution such as temperature, surface properties of the adsorbent, pH and metals ionic properties (such as ionic radius, electronegativity and electronic configuration) (Srivastava *et al.*, 2006). The adsorption capacity of the multi-metal adsorption system will have decrease with respect to single metal adsorption capacity (Padilla-Ortega *et al.*, 2013) if the binding sites were fully occupied with remaining heavy metals ions in the aqueous phase.

Similar, multi-metals systems using agricultural wastes biochars showed adsorption efficiency of 99.25% for Fe, 96.15% for Ni and 87.17% for Pb by the rice husk and 98.54% for Cu and 73.54% for Cd by fly ash. The rice husk was effective in the simultaneous adsorption of Fe, Pb and Ni whilst fly ash was also effective in the removal of Cd and Cu in in the real wastewater (Hegazi, 2013). The adsorption efficiency of heavy metals by digested whole sugar beet biochar was higher than 97%, indicating the biochar has a strong affinity for the Pb^{2+}, Cu^{2+}, Cd^{2+} and Ni^{2+} ions tested. Digested dairy waste biochar also showed high adsorption efficiency for Pb^{2+} (99%) and Cu^{2+} (98%), but relatively low adsorption efficiency for Cd^{2+} (57%) and Ni^{2+} (26%) (Inyang *et al.*, 2012).

Lastly, in a batch experiment where biochar and activated carbon were studied, it was reported that 96.88% of Cd (II), 96.23% of Zn (II), 95.96% of Co (II) , 93.38% of Cu (II) and 88.79% of Pb (II), ions were removed by biochar in acidic solutions, whilst only 80.58% of Cu (II), 68.08% of Cd (II), 63.08% of Zn (II), 54.69% of Pb (II) and 36.70% of Co (II) ions were adsorbed by removed from activated carbon (Kołodyńska *et al.*, 2017). The present study showed higher adsorption efficiency than these previous studies.

5.4 Adsorption Performance of Biochars Produced under Slow and Fast Pyrolysis Temperatures

The present study shows that shea nut shells based biochar have had a greater affinity for the heavy metals in the mono, binary and ternary systems. The combined biochars seem to be also better than biochar produced from groundnut shells. The groundnut shell biochar will likely not be effective in the removal of mercury in higher concentrations in an aqueous environment. The study revealed biochars produced under fast pyrolysis temperature somehow seem to have more affinity for metals in the aqueous phase particularly in binary and ternary systems when compared to that of biochars produced under slow pyrolysis.

The fast pyrolysis temperatures and type of biochar showed a slight increase in the adsorption efficiency of metal ions but this increase is not statistically significant ($p > 0.05$). This implies that the increased in pyrolysis temperature did not significantly affect mono, binary and ternary aqueous phase of Cd, Hg, Pb ion adsorption onto biochar. This finding learn supported from Kim *et al.* (2013) and Tran *et al.* (2015) who demonstrated the influence of various pyrolytic temperatures of 300 °C, 400 °C, 500 °C and 600 °C, and 400 °C, 500 °C, 600 °C, 700 °C and 800 °C, respectively on the adsorption of Cd from an aqueous solution onto biochar produced from a giant miscanthus and orange peel derived biochar, respectively. It is obvious that the properties of biochars influencing their adsorption ability toward various pollutants are affected by the nature and type of feed stock and pyrolysis conditions. Therefore, it is critical to manage appropriate conditions in the production of biochar (Ahmad *et al.*, 2014). The influence of pyrolysis temperatures of 350 °C (slow pyrolysis) and

650 °C (fast pyrolysis) on lead (Pb) adsorption onto biochar produced from broiler litter was evaluated. The results demonstrated that biochar produced at 350 °C (low pyrolysis temperature) was favourable for the removal of Pb (Uchimiya *et al.*, 2012).

Also, the partition of organic pollutants into non-carbonised biochar fractions produced from pine needles was the main adsorption mechanism at low pyrolysis temperatures of 100 to 300 °C, whilst adsorption on porous carbonised fractions was dominant at high temperatures of 400 to 700 °C (Chen *et al.*, 2008). Aromaticity and surface polarity are essential characteristics of biochars, as they affect aqueous organic contaminant sorption (Chen *et al.*, 2008). Uchimiya *et al.* (2010b) stated an increase in the sorption capacity of the deisopropylatrazine with an increase in aromaticity carbons of biochar produced from broiler litter at 700 °C. Similar findings were observed for trichloroethylene adsorption onto biochars produced from soybean stover and peanut (groundnut) shells at 700 °C against at 300 °C (Ahmad *et al.*, 2012b).

5.5 Influence of Aqueous Phase pH on the Adsorption Capacity of Biochars

The influence of pH on adsorption largely depend on biochars' types and the target metal ion. pH affects not only the biochar surface charge, but also the degree of ionisation and speciation of the heavy metal (adsorbate) (Kołodyńska *et al.*, 2012; Regmi *et al.*, 2012; Li *et al.*, 2013; Zhang *et al.*, 2013d). Biochar contains different surface functional groups that mainly contain oxygen groups. An increase in pH of the aqueous phase leads to change in behaviour of these functional groups. Most functional groups possessed by biochars are protonated at low pH and presented in positively charged form (Tan *et al.*, 2015).

pH influences the adsorption of metal ions in aqueous solution. This is attributable to the counter reaction of the competing hydrogen ion in addition to chemistry of the active binding sites of the sorbent (Abdus-salam and Adekola, 2008). Increasing the pH leads to precipitation of insoluble hydrated oxide or hydroxide, in so doing lowers the heavy metal ion availability for sorption. Then again, a decrease in pH leads to increase in the hydrogen ion concentration and therefore probable competition for the binding sites (Kahraman *et al.*, 2008). Generally, sorption media pH is related to the metal adsorption mechanism of the surfaces from the water and revealed the nature of the physico-chemical interaction of metal ions in solution and nature of the sorption sites (Mahvi, 2008).

Generally, pH values of the aqueous solution were in the acidic range of less than 5 pH units for mono system, binary system and ternary system for fold one, two and five, respectively. The pH decreases in the prepared aqueous phase as the concentrations in folds in the order of fold > fold two > fold five for mono, binary and ternary systems. The adsorption of heavy metals was generally effective under the varied pH values of the aqueous phase. The adsorption was highly favoured by pH of the aqueous phase under the various maximum concentration limits hence the increase in Cd, Hg and Pb ions uptake. Generally, although the pH of the aqueous phase had proven effective in adsorption of metal ions regardless of the component system and fold of the contamination limits, there is no significant difference ($p > 0.05$).

A study reported pH of 4 for Cd^{2+}, 6 for Pb^{2+}, and 5 for Fe^{3+}, Cr^{3+}, and Zn^{2+} as the maximum sorption capacity of the metal ions (Osemeahon *et al.*, 2013) that also fall under the acidic range of less than 7. The present study suggests that the slight differences in the pH optimal for different metal ions in mono, binary and ternary systems could probably be due to the different solution chemistry of cadmium, mercury and lead ions (Abdus-salam and Adekola, 2008).

5.6 Langmuir, Freundlich and Temkin Isotherms

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The study results revealed that Langmuir adsorption isotherm was the best model for heavy metal ions adsorption onto biochars in batch experiments. The correlation coefficients (R^2) showed the order of mono < binary < ternary system. This shows that Langmuir model provides a reasonable fit to the multi-metals adsorption data.

The maximum sorption capacity corresponding to complete monolayer coverage showed that biochars produced under slow pyrolysis temperature had a mass capacity for Cd^{2+} (0.22 mg/g for combined groundnut and shea nut shells biochar), Pb^{2+} (0.35 mg/g for shea nut shell biochar), Hg^{2+} (0.14 mg/g for groundnut shell biochar) and Hg^{2+} (0.87 mg/g for shea nut shell biochar), whilst biochars produced under fast pyrolysis had a mass capacity for Cd^{2+} (0.18 mg/g for groundnut shell biochar) and Hg^{2+} (0.55 mg/g for shea nut shell biochar) in mono-component system. The study showed that Hg^{2+} had highest maximum uptake capacity onto shea nut shell biochar produced under both slow and fast pyrolysis, respectively.

Similar study conducted using agricultural wastes biochar reported maximum adsorption capacities of Cd to be 49.84 mg/g, 36.90 mg/g, and 25.83 mg/g based on the Langmuir isotherm calculation (Li *et al.*, 2016). Also some studies on cadmium adsorption onto biochars derived from different raw materials recorded a maximum sorption capacity of about 54.48 mg/g for orange peel (Tran *et al.*, 2015), 26.32 mg/g for corn straw (Liu *et al.*, 2012), 25 mg/g for straw (Remenarova *et al.*, 2012) and 6.22 mg/g for household biowaste (Qin *et al.*, 2012). This study found the order of maximum adsorption capacity to be mono > binary > ternary system. The R_L was found to be $0 < R_L < 1$ regardless of the heavy metal, biochar type and pyrolysis temperature implying that nature of adsorption was favourable. This indicates that the biosorption of the heavy metal ions under this study is a chemical process.

Freundlich isotherm was used to represent adsorption of Cd, Hg and Pb from the prepared aqueous phase onto biochars. It is a semi-empirical equation that is used to describe the multi-layer sorption and surface sorption under different non-ideal conditions (Ding *et al.*, 2012). The two isotherm models were fitted in the adsorption of Cd, Hg and Pb by biochars produced from groundnut and shea nut shells. The correlation coefficients (R^2) derived from the Freundlich equations ranged from 0 to 1, showed that some few data fit this model well. Similar study, used adsorption equilibrium data that was well correlated with Freundlich model with correlation coefficient (R^2) ranging from 0.95 to 0.99 (Surchi, 2011).

Generally, almost all values of $1/n$ were less than 1, signifying adsorption by heterogeneous media where high energy sites were occupied first, before sorption at lower energy sites (Peruchi *et al.*, 2015). However, $1/n$ values for some Hg and Cd were above 1 which indicates that a cooperative adsorption occurred.

Temkin Adsorption Isotherm was also used as the model assumes low interactions between the biochar (adsorbent) and heavy metal ion (adsorbate) and energy of adsorption of all the molecules in the surface layer decrease at the cover surface (Nechifor *et al.*, 2015). Generally, most of the co-efficient correlation values regardless of batch systems are below 0.5 that showed poor linearity regardless of the maximum capacity of adsorption used to the estimation of the coverage area. Whilst the few that are higher show a good linearity regardless of the maximum capacity of adsorption used to the estimation of the coverage area. It is obvious that most of the R^2 values were the poorest fit of experimental data. Low values of B (constant related to heat of sorption (J/mol)) in this study showed a weak interaction between biochars and metal ions supporting a mechanism of ion exchange. It also implies that the interaction between biochar and Cd, Hg and Pb ions in batch systems in the surface layer decrease at the cover surface.

5.7 Interactive Behaviour of Cd, Hg and Pb ions in Binary and Ternary Systems

The selectivity of biochars for Cd, Hg and Pb in both binary and tertiary mixture was determined in terms of relative metal *i* adsorption that is R*i* (%) as defined by Chang and Chen (1998). The R*i* percentage was used to determine whether the interaction among mixtures in binary and tertiary system were antagonistic, synergistic or non-interactive in nature. The study revealed that interactions behaviour between the Cd, Hg and Pb ions were both antagonistic and synergistic in nature. Those metal ions that are antagonistic in nature implies their effect in the mixture is less than the sum of individual effect of the constituents or is more likely that their individual effect on the substances added together is less than the expected response to multiple component. The antagonistic nature of some of the metals ions in the mixtures is attributable to the screening effect by the metals present in the solution (Sag and Kutsal, 1996). However, synergistic nature of some of the metal ions particularly mercury ions in this study implies their effect in the mixture is greater than the sum of their individual effect of the constituents or their individual effect on the substances added together is greater than the expected response to multiple component system. Similar, multi-metal study involving metals such as Ni (II), Cd (II) and Cr (VI) by Jain *et al.* (2015) reported R_i values that were all less than 100% in binary and ternary metal systems. Inferring that the interactions between different metal ions are antagonistic in nature.

CHAPTER SIX

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

This present study was to generate biochars for adsorption of heavy metals from aqueous phase. The mono, binary and ternary adsorption systems of cadmium, mercury and lead onto groundnut shell, shea nut shell and the combination of the two feed stocks biochars produced under slow and fast pyrolysis temperatures were performed in order to estimate the adsorption behaviour of heavy metals.

The experiment showed that shea nut shell biochar produced under both slow and fast pyrolysis temperatures had the strongest affinity for cadmium, mercury and lead in the mono aqueous phase. The fast pyrolysis temperature and type of biochar showed a slight increase in the adsorption efficiency of metal ions but this increase is not statistically significant ($p > 0.05$). Langmuir adsorption isotherm was the best model for the heavy metal ions adsorption onto biochars in the batch experiment. The Temkin model has proven to be the poorest fit of experimental data. The study revealed that the interaction behaviour of the metals was either antagonistic or synergistic in nature.

The present study showed that shea nut shell based biochar had a greater affinity for heavy metals in mono, binary and ternary systems. The combined biochars seem to be also better than biochar produced from groundnut shell only. The groundnut shell biochar will likely not be effective in the removal of mercury in higher concentrations in an aqueous environment. Based on these results, groundnut and shea nut shells based biochars have a strong affinity for Cd, Hg and Pb ions in the aqueous environment. The adsorption of heavy metals was generally favoured by various pH of the aqueous phase. The development of biochar technology using groundnut and shea nuts shells gives opportunities to satisfy the need for cost-effective and eco-friendly adsorbents for removal of aqueous heavy metals. This provide a great advantage in the remediation of contaminated wastewaters, mining sites, landfilling ponds, wastewater, untreated sludge from water treatment plants and other industries sources that potentially release substances in aggregates into groundwater, surface water and soil that may contain more than one metal ion.

6.2 Recommendations

- Based on the results, it is recommended that further competitive adsorption study for biochars should be conducted for accurate estimation of adsorption in natural environments.
- Further experiment should be carried out to examine adsorption of the heavy metal contaminants at higher concentrations or a reduced biochar dosage.
- Also, experimental study should be conducted at different contact time.
- Physical and chemical characterisation of biochars should be carried out to understand the mechanisms and assess the multiple utilisations of biochars.
- Further study is required to evaluate the feasibility of biochars for the removal of heavy metals from the real environment.

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APPENDICES

Appendix 1: Result of mono-component system

			Slow pyrolysis		
MONO CODE	ug/l Cd		ug/l Pb		ug/l Hg
Cd1FSG	BDL	Pb1FSG	0.884	Hg1FSG	0.011
Cd1FSS	BDL	Pb1FSS	BDL	Hg1FSS	0.002
Cd1FSM	BDL	Pb1FSM	0.535	Hg1FSM	BDL
Cd2FSG	0.02	Pb2FSG	BDL	Hg2FSG	0.002
Cd2FSS	BDL	Pb2FSS	BDL	Hg2FSS	0.003
Cd2FSM	0.033	Pb2FSM	0.636	Hg2FSM	BDL
Cd5FSG	BDL	Pb5FSG	BDL	Hg5FSG	0.01
Cd5FSS	0.04	Pb5FSS	BDL	Hg5FSS	0.015
Cd5FSM	0.166	Pb5FSM	0.817	Hg5FSM	0.007
			Fast pyrolysis		
MONO CODE	ug/l Cd		ug/l Pb		ug/l Hg
Cd1FFG	BDL	Pb1FFG	BDL	Hg1FFG	0.004
Cd1FFS	BDL	Pb1FFS	BDL	Hg1FFS	BDL
Cd1FFM	BDL	Pb1FFM	BDL	Hg1FFM	BDL
Cd2FFG	0.026	Pb2FFG	BDL	Hg2FFG	0.003
Cd2FFS	BDL	Pb2FFS	BDL	Hg2FFS	0.002
Cd2FFM	BDL	Pb2FFM	BDL	Hg2FFM	BDL
Cd5FFG	0.131	Pb5FFG	BDL	Hg5FFG	BDL
Cd5FFS	BDL	Pb5FFS	BDL	Hg5FFS	0.013
Cd5FFM	BDL	Pb5FFM	BDL	Hg5FFM	0.013

Appendix 2: Result of the binary system

BINARY		Slow pyrolysis						
CODE	Cd	Pb	CODE	Cd	Hg	CODE	Pb	Hg
CdvrPb1FSG	0.12	BDL	CdvrHg1FSG	0.131	BDL	PbvrHg1FSG	BDL	0.007
CdvrPb1FSS	BDL	BDL	CdvrHg1FSS	BDL	BDL	PbvrHg1FSS	0.861	BDL
CdvrPb1FSM	BDL	BDL	CdvrHg1FSM	BDL	0.01	PbvrHg1FSM	1.158	BDL
CdvrPb2FSG	0.61	BDL	CdvrHg2FSG	0.016	BDL	PbvrHg2FSG	0.156	BDL
CdvrPb2FSS	BDL	BDL	CdvrHg2FSS	BDL	0.002	PbvrHg2FSS	BDL	0.001
CdvrPb2FSM	0.31	BDL	CdvrHg2FSM	BDL	0.003	PbvrHg2FSM	BDL	0.003
CdvrPb5FSG	BDL	BDL	CdvrHg5FSG	0.081	BDL	PbvrHg5FSG	0.78	0.006
CdvrPb5FSS	BDL	BDL	CdvrHg5FSS	BDL	0.011	PbvrHg5FSS	BDL	0.001
CdvrPb5FSM	0.19	BDL	CdvrHg5FSM	BDL	0.015	PbvrHg5FSM	BDL	0.006

	BINARY		Fast Pyrolysis					
CODE	Cd	Pb	CODE	Cd	Hg	CODE	Pb	Hg
CdvrPb1FFG	BDL	BDL	CdvrHg1FFG	BDL	0.014	PbvrHg1FFG	BDL	BDL
CdvrPb1FFS	BDL	0.96	CdvrHg1FFS	BDL	0.011	PbvrHg1FFS	1.28	0.004
CdvrPb1FFM	BDL	1.81	CdvrHg1FFM	BDL	0.01	PbvrHg1FFM	BDL	0.006
CdvrPb2FFG	BDL	BDL	CdvrHg2FFG	0.007	0.001	PbvrHg2FFG	BDL	BDL
CdvrPb2FFS	BDL	BDL	CdvrHg2FFS	BDL	BDL	PbvrHg2FFS	BDL	0.006
CdvrPb2FFM	BDL	BDL	CdvrHg2FFM	0.043	BDL	PbvrHg2FFM	BDL	0.007
CdvrPb5FFG	BDL	BDL	CdvrHg5FFG	0.036	0.005	PbvrHg5FFG	BDL	BDL
CdvrPb5FFS	BDL	BDL	CdvrHg5FFS	BDL	BDL	PbvrHg5FFS	BDL	0.008
CdvrPb5FFM	BDL	BDL	CdvrHg5FFM	0.213	BDL	PbvrHg5FFM	BDL	0.009

Appendix 3: Result of the ternary system

Ternary	Slow pyrolysis				Fast pyrolysis		
Code	Cd	Pb	Hg	Code	Cd	Pb	Hg
CdvrPbvrHg1FSG	0.38	BDL	0.021	CdvrPbvrHg1FFG	BDL	BDL	0.042
CdvrPbvrHg1FSS	BDL	2.5	BDL	CdvrPbvrHg1FFS	BDL	1.54	1.82
CdvrPbvrHg1FSM	BDL	1.2	0.03	CdvrPbvrHg1FFM	BDL	1.6	0.2
CdvrPbvrHg2FSG	0.43	BDL	BDL	CdvrPbvrHg2FFG	0.009	BDL	0.002
CdvrPbvrHg2FSS	BDL	BDL	0.04	CdvrPbvrHg2FFS	0.01	BDL	BDL
CdvrPbvrHg2FSM	0.04	BDL	0.004	CdvrPbvrHg2FFM	0.05	BDL	BDL
CdvrPbvrHg5FSG	0.62	0.21	BDL	CdvrPbvrHg5FFG	0.05	0.01	BDL
CdvrPbvrHg5FSS	BDL	BDL	0.5	CdvrPbvrHg5FFS	BDL	BDL	0.016
CdvrPbvrHg5FSM	0.2	BDL	0.08	CdvrPbvrHg5FFM	0.3	BDL	0.02

Appendix 4: Parameters for plotting Langmuir, Freundlich and Temkin adsorption isotherm

					Mono						
MBC	Metal	Co (mg/l)	Ce (mg/l)	1/Ce	Log Ce	In Ce	Qe (mg/g)	1/Qe	Log Qe	In Qe	Ce/Qe (g/l)
	Cd	0.04	0	0	0	0	0.04	25	-1.4	-3.22	0
	Slow	0.08	0.000033	30303	-4.48	-10.32	0.08	12.51	-1.1	-2.53	0.000413
		0.2	0.000166	6024.1	-3.78	-8.7	0.20	5	-0.7	-1.61	0.000831
GBC	Cd	0.04	0	0	0	0	0.04	25	-1.4	-3.22	0
	Fast	0.08	0.000026	38462	-4.59	-10.56	0.08	12.5	-1.1	-2.53	0.000413
		0.2	0.000131	7633.6	-3.88	-8.94	0.20	5	-0.7	-1.61	0.000831
MBC	Pb	0.1	0	0	0	0	0.10	10	-1	-2.3	0
	Slow	0.2	0.000636	1572.3	-3.2	-7.36	0.20	5.02	-0.7	-1.61	0.0032
		0.5	0.000817	1224	-3.09	-7.11	0.50	2	-0.3	-0.69	0.00164
GBC	Hg	0.1	0.000011	90909	-4.96	-11.42	0.10	10	-1	-2.3	0.00011
	Slow	0.2	0.000002	500000	-5.7	-13.12	0.20	5	-0.7	-1.61	0.00001
		0.5	0.00001	100000	-5	-11.51	0.50	2	-0.3	-0.69	0.00002
SBC	Hg	0.1	0.000002	500000	-5.7	-13.12	0.10	10	-1	-2.3	0.00002

	slow	0.2	0.000002	500000	-5.7	-13.12	0.20	5	-0.7	-1.61	0.00001
		0.5	0.000015	66667	-4.82	-11.11	0.50	2	-0.3	-0.7	0.00003
SBC	Hg	0.1	0.000002	500000	-5.7	-13.12	0.10	10	-1	-2.3	0.00002
	slow	0.2	0.000002	500000	-5.7	-13.12	0.20	5	-0.7	-1.61	0.00001
	slow	0.5	0.000015	66667	-4.82	-11.11	0.50	2	-0.3	-0.7	0.00003
SBC	Hg	0.1	0	0	0	0	0.10	10	-1	-2.3	0
	Fast	0.2	0.000002	500000	-5.7	-13.12	0.20	5	-0.7	-1.61	0.00001
		0.5	0.000013	76923	-4.89	-11.25	0.50	2	-0.3	-0.7	0.000026

	Binary Cd:Pb	Co (mg/l)	Ce (mg/l)	1/Ce	Log Ce	In Ce	Qe (mg/g)	1/Qe	Log Qe	In Qe	Ce/Qe (g/l)
GBC	Cd	0.04	0.000122	8196.7	-3.91	-9.01	0.04	25.08	-1.4	-3.22	0.0031
	Slow	0.08	0.00061	1639	-3.21	-7.4	0.079	12.6	-1.1	-1.1	0.0077
		0.2	0	0	0	0	0.2	5	-0.7	-1.61	0
MBC	Cd	0.04	0	0	0	0	0.04	25	-1.4	-3.22	0
	slow	0.08	0.000031	0.03	-4.51	-10.38	0.08	12.5	-1.1	-2.53	0.00039
		0.2	0	0	0	0	0.2	5	-0.7	-1.61	0
MBC	Cd:Hg	0.1	0.00001	100000	-5	-11.51	0.1	10	-1	-2.3	0.00001
	HG	0.2	0.000003	333333	-5.52	-12.72	0.2	5	-0.7	-1.61	0.000015
	Slow	0.5	0.000015	66666	-4.82	-11.12	0.5	2	-0.3	-0.7	0.00003
SBC	Hg	0.1	0	0	0	0	0.1	10	-1	-2.3	0
	slow	0.2	0.000002	500000	-5.7	-13.12	0.2	5	-0.7	-1.61	0.00001
		0.5	0.000011	90909	-4.56	-11.42	0.5	2	-0.3	-0.07	0.000022
GBC	Hg	0.1	0.000014	71429	-4.85	-11.18	0.1	10	-1	-2.3	0.00014
	slow	0.2	0.000001	1E+06	-6	-13.82	0.2	5	-0.7	-1.61	0.000005
		0.5	0.000005	200000	-5.3	-12.21	0.5	2	-0.3	-0.7	0.00001
GBC	Fast	0.04	0	0	0	0	0.04	25	-1.4	-3.22	0
	Cd	0.08	0.000007	142857	-5.15	-11.87	0.08	12.5	-1.1	-2.53	0.000088
		0.2	0.000036	27778	-4.44	-10.23	0.2	5	-1.61	-1.61	0.00018
MBC	Cd	0.04	0	0	0	0	0.04	25	-1.4	-3.22	0
	fast	0.08	0.000043	23256	-4.37	-10.05	0.08	12.51	-1.1	-2.53	0.00054
		0.2	0.000213	4695	-3.67	-8.45	0.2	5	-0.7	-1.61	0.0011
GBC	Pb	0.1	0	0	0	0	0.1	10	-1	-2.3	0
	Slow	0.2	0.000156	6410	-3.81	-8.77	0.2	5	-0.7	-1.61	0.00078
		0.5	0.00078	1282	-3.11	-7.16	0.499	2	-0.3	-0.7	0.00156
GBC	Hg	0.1	0.000007	142857	-5.15	-11.87	0.1	10	-1	-2.3	0.000007
	Slow	0.2	0	0	0	0	0.2	5	-0.7	-1.61	0
		0.5	0.00006	16667	-4.22	-9.72	0.5	2	-0.3	-0.7	0.00012
SBC	Hg	0.1	0	0	0	0	0.1	10	-1	-2.3	0
	Slow	0.2	0.000001	1E+06	-6	-13.82	0.2	5	-0.7	-1.61	0.00005
		0.5	0.000001	1E+06	-6	-13.82	0.5	2	-0.3	-0.7	0.000002
MBC	Hg	0.1	0	0	0	0	0.1	10	-1	-2.3	0
	slow	0.2	0.000003	333333	-5.52	-12.72	0.2	5	-0.7	-1.61	0.000015
		0.5	0.000006	166667	-5.22	-12.02	0.5	2	-0.3	-0.7	0.000012
SBC	Hg	0.1	0.000004	250000	-5.4	-12.43	0.1	10	-1	-2.3	0.00004
	Fast	0.2	0.000006	166666	-5.22	-12.02	0.2	5	-0.7	-1.61	0.00003
		0.5	0.000008	125000	-5.1	-11.74	0.5	2	-0.3	-0.7	0.000016
MBC	Hg	0.1	0.000006	166666	-5.22	-12.02	0.1	10	-1	-2.3	0.00006
	Fast	0.2	0.000007	142857	-5.15	-11.87	0.2	5	-0.7	-1.61	0.000035
		0.5	0.000009	111111	-5.05	-11.62	0.5	2	-0.3	-0.7	0.000018

Ternary

MBC	Cd:Hg:Pb	Co (mg/l)	Ce (mg/l)	1/Ce	Log Ce	In Ce	Qe (mg/g)	1/qe	Log Qe	In Qe	Ce/Qe (g/

	HG	0.1	0.00004	25000	-4.4	-10.13	0.1	10	-1	-2.3	0.0004
	Slow	0.2	0.000006	166666	-5.22	-12.02	0.2	5	-0.7	-1.61	0.00003
		0.5	0.000008	125000	-5.1	-11.74	0.5	2	-0.3	-0.7	0.000016
SBC	Hg	0.1	0	0	0	0	0.1	10	-1	-2.3	0
	slow	0.2	0.000004	250000	-5.4	-12.43	0.2	5	-0.7	-1.61	0.00002
		0.5	0.00005	20000	-4.3	-9.9	0.5	2	-0.3	-0.7	0.0001
GBC	Cd	0.04	0.00038	2632	-3.42	-7.88	0.04	25.24	-1.4	-3.23	0.0096
	Slow	0.08	0.00043	2326	-3.37	-7.75	0.08	12.57	-1.1	-2.53	0.0054
		0.2	0.000062	16129	-4.21	-9.69	0.2	5	-1.61	-1.61	0.00031
MBC	slow	0.04	0	0	0	0	0.04	25	-1.4	-3.22	0
	Cd	0.08	0.00004	25000	-4.4	-10.13	0.08	12.51	-2.53	-2.53	0.0005
		0.2	0.0002	5000	-3.7	-8.52	0.2	5	-1.61	-1.61	0.001
GBC	HG	0.1	0.000042	23810	-4.38	-10.08	0.1	10	-1	-2.3	0.00042
	Slow	0.2	0.000002	500000	-5.7	-13.12	0.2	5	-0.7	-1.61	0.00001
		0.5	0	0	0	0	0.5	2	-0.3	-0.7	0
GBC	Cd	0.04	0	0	0	0	0.04	25	-1.4	-3.22	0
	Fast	0.08	0.00009	11111	-4.05	-9.32	0.08	12.51	-1.1	-2.53	0.0011
		0.2	0.00005	20000	-4.3	-9.9	0.2	5	-0.7	-1.61	0.00025
MBC	Fast	0.04	0	0	0	0	0.04	25	-1.4	-3.22	0
	Cd	0.08	0.00005	20000	-4.3	-9.9	0.08	12.51	-1.1	-2.53	0.00063
		0.2	0.0003	3333	-3.52	-8.11	0.2	5	-0.7	-1.61	0.0015

Note: GBC; groundnut biochar, SBC; shea nut biochar and MBC; combined groundnut and shea nut biochar