



ADSORPTION OF TOXIC METALS ONTO ECO-FRIENDLY AND COST-EFFECTIVE SHEA (*Vitellaria paradoxa*) NUT SHELL BIOCHAR IN AQUEOUS PHASE

****Quainoo, A. K., **Dwiejuah, A. B., **Cobbina, S. J.**

**Department of Biotechnology, Faculty of Agriculture, University for Development Studies*

***Department of Ecotourism and Environmental Management, Faculty of Natural Resources and Environment, University for Development Studies*

Corresponding Author's Email: aquainoo@googlemail.com/aquainoo@uds.edu.gh

Abstract

The present study was to evaluate adsorption of cadmium (Cd), mercury (Hg) and lead (Pb) in mono and multi-metal component systems onto shea nut shell biochar. The adsorption capacity of Cd in mono aqueous phase with contaminant limits of 0.04 mg/l, 0.08 mg/l and 0.20 mg/l onto shea nut shell biochar produced under pyrolysis temperatures of 350 ± 5 °C and 700 ± 5 °C (SB350 and SB700) were 1 mg/g, 2 mg/g and 5 mg/g, respectively. The correlation coefficient values for Langmuir and Freundlich isotherms ranged from 0.28 to 0.99 for mono system and 0.49 to 0.96 for binary and ternary systems by SB350 and SB700. The binary mixtures showed Hg interactions with Cd and Pb ions onto SB350 are antagonistic in nature whilst mercury interaction with ions in ternary systems was synergistic in nature. The study revealed no clear cut difference between adsorption patterns of the mono, binary and ternary metals systems. The study showed complete adsorption of ions in single and competitive systems by shea nut shell biochar that is attributable to the biochar having strong affinity for ions. The mono, binary and ternary adsorption systems are very important in the estimation of toxic metal adsorption efficiencies onto biochar, in accordance with how they are released into receiving waters. For accurate estimation of Cd, Pb and Hg adsorption capacity of shea nut shell biochar, there is the need to conduct further multi-metal adsorption studies in the natural environments.

Keywords: Adsorption, Aqueous Phase, Toxic Metals, Shea Nut Shell Biochar

Introduction

Adsorption capacity of agricultural based biochar is largely dependent on the nature of feed stock and pyrolysis conditions. Biochar is a carbon-rich product produced from biomass that include wood, manure, seeds, husks or leaves that are often heated in a barred vessel with little or no air. Biochar therefore refers to a heterogeneous substance that is rich in minerals and aromatic carbon (Schmidt *et al.*, 2014). 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, Vega, Andrade & Covelo, 2013). Pyrolytic temperature has significant influence on the elemental, morphological and structural properties of biochar (Kołodzyńska *et al.*, 2012). Biochar is a relatively modern development, evolving in coincidence with soil management, carbon

sequestration issues, and control of pollutants (Kajitani, Tay, Zhang & Li, 2013).

Toxic metal contamination originated from rapid industrialisation in which mining activities, smelting activities and fossil fuel combustion intensified the introduction of these metals into ground and surface water bodies (Singha & Guleria, 2014). To mitigate the negative effects of these metals in water bodies, adsorption process is unique and ever promising because of its dependence on adsorbent that can be produced at low cost, besides the process is also easy to adapt, very effective removal and more environmental friendly. Mixtures of metal adsorption studies are also very relevant to evaluate the interference nature of the co-ions and adsorbents efficiency to remove the metal ions from wastewaters (Srivastava, Mall & Mishra, 2006). 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 (Hegazi, 2013).

Agricultural waste can be used as adsorbent for adsorption of contaminants for aqueous environment as it has some advantages that include availability in large quantities, eco-friendly, cost-effective and renewable in nature (Singha & Das, 2013). Many researchers have tried to come out with economically efficient and unconventional adsorbents produced from agricultural/plant wastes (Apaydin-Varol, Pütün & Pütün, 2007). For instance, grinded shea nut shells have proven to be effective in the removal of toxic metals particularly Mn, Fe, Zn and Cu in soils using lettuce as a test crop (Quainoo, Konadu & Kumi, 2015). Shea nut shells are readily available as it is an agricultural residue that is 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). The study of systems with a mixture of contaminants is paramount particularly toxic metals as they usually coexist in the environment. This present study evaluated the adsorption behaviours of toxic metals in mono, binary and ternary components by shea nut shell biochar in order to estimate the toxic metal adsorption capacity of the biochar in natural environments.

Materials and Methods

Materials

Shea nut shells were collected from Shishegu in the Tamale Metropolis, Ghana. Cadmium chloride (CdCl₂ grade; anhydrous, assay; 99.99%), mercury chloride (HgCl₂ grade; ACS reagent, assay; ≥ 99.5%) and lead nitrate (Pb (NO₃)₂: grade; GR, assay;

99.5%) were obtained from the Spanish Laboratory of the University for Development Studies. Stock solutions of 1000 mg/l of each toxic metal were prepared. Separatory funnels, breakers, pipettes, 2 mm standard mesh sieve were among equipment and apparatus used and were also obtained from the Spanish Laboratory of the University for Development Studies at the Nyankpala Campus, Ghana.

Pyrolysis of Shea Nut Shells into Biochar

A muffle furnace was used to convert the samples into biochar under limited oxygen conditions. Shea nut shell biochar was produced at 350 ± 5 °C (slow pyrolysis) for 180 min and 700 ± 5 °C (fast pyrolysis) for 90 min in a muffle furnace. SB350 and SB700 denotes shea nut shell biochar produced at 350 ± 5 °C and 700 ± 5 °C, respectively. Biochar produced by pyrolysis was allowed cool down to room temperature and then gently crushed and sieved to < 2 mm.

Batch Experiment Tests

Batch experiments were carried out using 100 ml separatory funnels, containing 2 g of each type of biochar in 50 ml aqueous solution with different pH conditions (3.25 to 4.63) at laboratory temperature of 24 ± 0.5 °C and constant contact time of 72 min under constant flow rate. The leaching solutions were in composition of one fold, two fold, and five fold value of maximum contaminant level (MCL) for Cd, Hg and Pb ions mono, binary and ternary components in accordance with Saveyn *et al.* (2014) procedure (Table 1). Elutes were then automatically sampled immediately after the whole retention test.

Table 1: Maximum concentration limits (mg/l) of toxic metals in the aqueous phase

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

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

Determination of Toxic metal Concentrations

The 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 the 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 trace metals was done using the Perkin Elmer PIN Accle 900T Graphite Atomic Absorption Spectrophotometer. The detection limit of cadmium was 0.0008 mg/l, mercury was 0.0001 mg/l and lead was 0.003 mg/l.

Adsorption Models

Adsorption efficiency of toxic metals, Q_e (mg/g) was calculated using the following equation 1:

$$Q_e = \frac{(C_o - C_e)V}{M} \quad (1)$$

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).

Adsorption isotherms were determined using the Freundlich and Langmuir models. Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) models were used for fitting the equilibrium data. The Langmuir model usually corresponds to homogeneous monolayer adsorption whilst the Freundlich model explains the adsorption on the adsorbent with heterogeneous surface as follows :

$$Q_e = \frac{Q_{\max} K_l C_e}{1 + K_l C_e}; \text{ Langmuir model} \quad (2)$$

$$Q_e = K_F C_e^{1/n}; \text{ Freundlich model} \quad (3)$$

Where Q_{\max} is the maximum adsorption capacity calculated by Langmuir model, K_l represent the Langmuir constant ($l \text{ mg}^{-1}$), and K_F ($l \text{ g}^{-1}$) and n (dimensionless) are Freundlich constants that signify extent of adsorption and degree of nonlinearity between aqueous solution concentration and adsorption, respectively.

Interactive Behaviour of the Toxic 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 & Chen (1998). The percentage R_i will determine whether the combinations in binary and tertiary system are antagonistic or synergistic in nature.

$$R_i = \frac{\text{Metal } i \text{ adsorption capacity with co-existence of metal } j \text{ and } k}{\text{Metal } i \text{ adsorption capacity without co-existence of metal } j \text{ and } k} \times 100\% \quad (4)$$

Results and Discussion

The study showed adsorption capacity of Cd, Hg and Pb onto shea nut shell biochar produced under slow (SB350) and fast (SB700) pyrolysis in mono-metal system, binary and ternary systems was very effective.

Adsorption in Mono System

The adsorption capacity of Cd in mono aqueous phase with contaminant limits of 0.04 mg/l, 0.08 mg/l and 0.20 mg/l onto SB350 were 1 mg/g, 2 mg/g and 5 mg/g, respectively, whilst at SB700 were 1

mg/g, 2 mg/g and 5 mg/g, respectively (Table 2). The adsorption capacity of Hg in mono aqueous phase with contaminant limits of 0.10 mg/l, 0.20 mg/l and 0.50 mg/l onto SB350 and SB700 were 2.50 mg/g, 5 mg/g and 12.50 mg/g, respectively, and $700 \pm 5 \text{ }^\circ\text{C}$ were 2.50 mg/g, 5 mg/g and 12.50 mg/g, respectively. The adsorption capacity of Pb in mono aqueous phase with contaminant limits of 0.10 mg/l, 0.20 mg/l and 0.50 mg/l onto SB350 were 2.50 mg/g, 5 mg/g and 12.50 mg/g respectively, whilst at SB700 were 2.50 mg/g, 5 mg/g and 12.50 mg/g, respectively.

Table 2: Adsorption of mono metals by shea nut shell biochar

Initial concentration	Cd mg/l	0.04	0.08	0.20
SB350	Cd (mg/g)	1	2	5
SB700	Cd (mg/g)	1	2	5
Initial concentration	Hg (mg/l)	0.10	0.20	0.50
SB350	Hg (mg/g)	2.50	5	12.50
SB700	Hg (mg/g)	2.50	5	12.50
Initial concentration	Pb (mg/l)	0.10	0.20	0.50
SB350	Pb (mg/g)	2.50	5	12.50
SB700	Pb (mg/g)	2.50	5	12.50

Cadmium Adsorption in Binary and Ternary Systems

The adsorption capacity of Cd in binary system of Cd and Hg with contaminant limits of 0.04: 0.10 mg/l, 0.08: 0.20 mg/l and 0.20: 0.50 mg/l onto SB350 was 1 mg/g, 2 mg/g and 5 mg/g. Whilst SB700 adsorption capacity for Cd in the mixture were 1 mg/g, 2.5 mg/g and 5 mg/g, respectively (Table 3). The adsorption capacity of Cd in binary system of Cd and Pb with contaminant limits of 0.04: 0.10 mg/l, 0.08: 0.20 mg/l and 0.20: 0.50 mg/l onto SB350 was 1 mg/g, 1.99 mg/g and 5 mg/g, respectively. Whilst SB700 adsorption capacity of Cd in binary mixture was 1 mg/g, 2 mg/g and 5 mg/g, respectively.

The adsorption capacity of Cd in ternary system of Cd, Hg and Cd with contaminant limits 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 onto SB350 were 0.99 mg/g, 2 mg/g and 5 mg/g, respectively (Table 3). Whilst SB700 adsorption for Cd in the ternary system was 1 mg/g, 2 mg/g and 5 mg/g, respectively.

Table 3: Adsorption of multi-metal component systems by shea nut shell biochar

Biochar	mg/l	0.04 : 0.10	0.08:0.2	0.2:0.5
Slow pyrolysis	Cd (mg/g)	1	2	5
	Hg (mg/g)	2.50	5	12.50
Fast pyrolysis	Cd (mg/g)	1	2.50	5
	Hg (mg/g)	2.50	5	12.50
	mg/l	0.04 : 0.10	0.08 : 0.20	0.20 : 0.50
Slow pyrolysis	Cd (mg/g)	1	1.99	5
	Pb (mg/g)	2.50	5	12.50
Fast pyrolysis	Cd (mg/g)	1	2	5
	Pb (mg/g)	2.48	5	12.50
	mg/l	0.10 : 0.10	0.20 : 0.20	0.50 : 0.50
Slow pyrolysis	Hg (mg/g)	2.48	5	12.50
	Pb (mg/g)	2.50	5	12.50
Fast pyrolysis	Hg (mg/g)	2.50	5	12.50
	Pb (mg/g)	2.47	5	12.50
Biochar	mg/l	0.04 : 0.10 : 0.10	0.08 : 0.20 : 0.20	0.20 : 0.50 : 0.50
Slow pyrolysis	Cd (mg/g)	0.99	2	5
	Hg (mg/g)	2.50	5	12.50
	Pb(mg/g)	2.50	5	12.50
Fast pyrolysis	Cd (mg/g)	1	2	5

Hg (mg/g)	2.50	5	12.50
Pb(mg/g)	2.50	5	12.50

Mercury Adsorption in Binary and Ternary Systems

The adsorption capacity of Hg in binary system of Cd and Hg with contaminant limits of 0.04: 0.10 mg/l, 0.08: 0.20 mg/l and 0.20: 0.50 mg/l onto SB350 was 2.50 mg/g, 5 mg/g and 12.50 mg/g, respectively (Table 3). Whilst SB700 adsorption capacity of Hg in binary system was 2.50 mg/g, 5 mg/g and 12.50 mg/g, respectively. The adsorption capacity of Hg in binary system of Hg and Pb with contaminant limits of 0.10: 0.10 mg/l, 0.20: 0.20 mg/l and 0.50: 0.50 mg/l onto SB350 was 2.48 mg/g, 5 mg/g and 12.50 mg/g, respectively. Whilst SB700 adsorption capacity for Hg in the mixture system was 2.50 mg/g, 5 mg/g and 12.50 mg/g, respectively. The adsorption capacity of Hg in ternary system of Cd, Hg and Cd with contaminant limits 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 onto SB350 were 2.50 mg/g, 5 mg/g and 12.50 mg/g, respectively (Table 3). Whilst SB700 adsorption for Hg in the ternary system was 2.50 mg/g, 5 mg/g and 12.50 mg/g, respectively.

Lead Adsorption in Binary and Ternary Systems

The adsorption capacity of Pb in binary system of Cd and Pb with contaminant limits of 0.04: 0.10 mg/l, 0.08: 0.20 mg/l and 0.20: 0.50 mg/l onto SB350 was 2.50 mg/g, 5 mg/g and 12.50 mg/g, respectively (Table 3). Whilst SB700 adsorption for Pb in binary system was 2.48 mg/g, 5 mg/g and 12.50 mg/g, respectively. The adsorption capacity of Pb in binary system of Hg and Pb with contaminant limits of 0.10: 0.10 mg/l, 0.20: 0.20 mg/l and 0.50: 0.50 mg/l onto SB350 was 2.50 mg/g, 5 mg/g and 12.50 mg/g, respectively. Whilst SB700 adsorption for Pb in the mixture system was 2.47 mg/g, 5 mg/g and 12.50 mg/g, respectively. The adsorption capacity of Hg in ternary system of Cd, Hg and Cd with contaminant limits 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 onto SB350 were 2.50 mg/g, 5 mg/g and 12.50 mg/g, respectively. Whilst SB700 adsorption for Hg in the ternary system was 2.50 mg/g, 5 mg/g and 12.50 mg/g, respectively. The study revealed no clear cut difference between adsorption patterns of mono metal systems and those under competitive adsorption conditions. Though some ions in the binary and ternary systems did not show complete adsorption onto biochar produced

under slow pyrolysis; thus in fold two for Cd and fold one for Hg whilst Pb in fold of the binary system of the aqueous phases did not show complete adsorption onto biochar produced under fast pyrolysis.

The mono, binary and ternary adsorption systems are very important in the estimation of toxic metal adsorption efficiencies onto biochar, in accordance with how they are released into receiving waters. Basically, toxic metals hardly occur alone, they interact and associate with each other. Besides, other components in natural environments are noted to influence their transport and fate between solid surfaces and aqueous solutions (Chen *et al.*, 2011). The adsorption of toxic metals from aqueous phases is largely influenced by multiple factors. The ratios of toxic metal ions relieved by other competitive metal ions in multimetal adsorption remain dependable over a wide range of metal concentrations (Chen *et al.*, 2011). As a result, competitive adsorption studies are necessary in order to accurately estimate the metal retention capacity of biochar in natural environments. It is evident from the results that co-adsorption has no influence in adsorption capacity for other ions using shea nut shells biochar. As the results show complete removal of ions simultaneously in the various binary systems and ternary system under the three contaminants limits for receiving waters.

The complete adsorption of ions in single and competitive systems is attributable to shea nut biochar having strong affinity for ions. Also, some experimental factors such as contact time, dosage of biochar, pH and temperature considered by this study favoured the ions adsorption. Since factors that affect adsorption preference of an adsorbent for toxic metal ions in multi-metal system are basically related to physico-chemical properties of aqueous solutions such as temperature, surface properties of the adsorbent, pH and the metal ionic properties (such as ionic radius, electronegativity and electronic configuration) (Srivastava *et al.*, 2006). Also, relatively less adsorption capacity in multi-component systems is due to competition among various toxic metal ions for available sites for

binding on the adsorbents (Aksu, Acikel & Kutsal, 1999).

Adsorption Isotherms

The Langmuir and Freundlich adsorption isotherms were used for mono, binary and ternary systems. The correlation coefficient (R^2) values for Langmuir isotherm ranged from 0.28 to 0.99 for mono, binary and ternary systems by SB350 and SB700 (Table 4) (Figures 1 a-f). The results showed an order of adsorption capacity of mercury as binary system > mono system > tertiary system. The maximum Langmuir capacity for mono-component system was 0.87 mg/g by SB350 and 0.55 mg/g by SB700, and ranged between 0.04 mg/g and 0.56 mg/g for the binary system and 1.12 mg/g for ternary component system by SB350. The adsorption capacity of -0.17 mg/g for the binary mixture of mercury and lead by SB700 (Tables 4). The negative value of Langmuir constant for mercury suggests that it gives an RL value of more than 1 on SB700 which was very

difficult. It might be due to lead ionic radius increases; the adsorption capacity of biochar decreases for mercury. The order of maximum adsorption capacity of mercury was found to be binary system, mono system and tertiary system.

The correlation coefficient values for Freundlich isotherm ranged from 0.49 to 0.96 for mono, binary and ternary systems by SB350 and SB700 (Table 4) (Figures 2 a-f). The Freundlich isotherm curvature and steepness was determined by n and K_F (Low & Lee, 2000). The affinity of biochar towards toxic metal ion uptake is showed by the value of n (Dada, Ojediran & Olalekan, 2013). When the value of n is ranged between 1 to 10 adsorption processes is favourable (Goldberg, 2005). The n values were between -0.09 to 1.60, so the adsorption can generally be described as a physical process. Only mercury adsorption in mono system with SB350 showed $n > 1$. That showed the degree of nonlinearity between aqueous solution concentration and adsorption as physical processes (Desta, 2013).

Table 4: Langmuir and Freundlich parameters for Cd, Hg and Pb in mono, binary and ternary system

Biochar	Metal system	Langmuir			Freundlich		
		Q_{max} (mg/g)	K_L (l/ mg)	R^2	n	K_F (mg/g)	R^2
SB350	Hg	0.87	115380	0.75	1.60	515.82	0.82
SB350	Hg+Cd	0.56	598700	0.91	-12.27	0.11	0.49
SB350	Hg+Pb	0.04	0	0.28	-12	0.10	0.68
SB350	Hg+Cd+Pb	1.12	148809.5	0.99	-0.09	0.11	0.49
SB700	Hg	0.55	606060.6	0.94	-11.86	0.11	0.55
SB700	Hg+Pb	-0.17	-98039.2	0.99	0.44	1.92×10^{11}	0.96

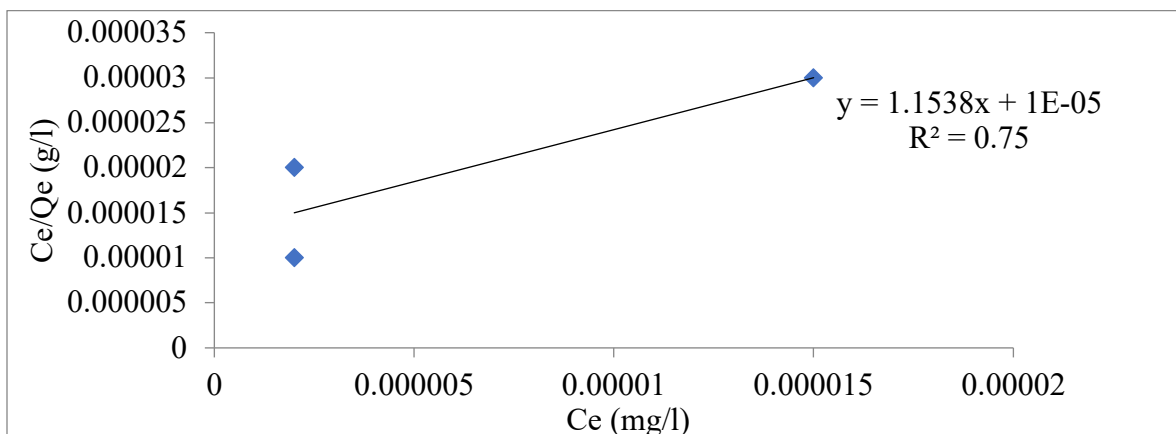


Figure 1a: Langmuir isotherm for adsorption of Hg in mono aqueous phase onto SB350

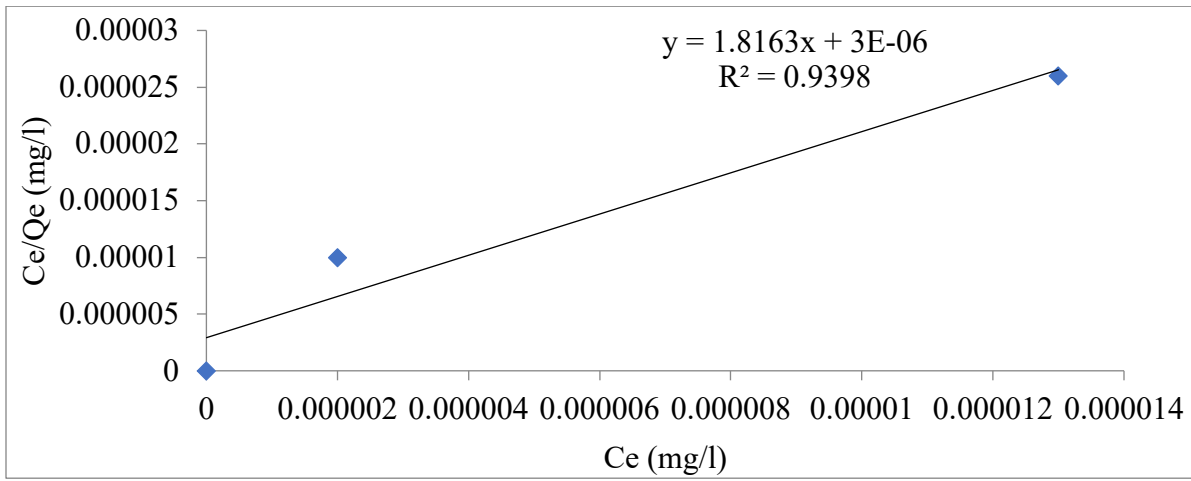


Figure 1b: Langmuir isotherm for adsorption of Hg in mono aqueous phase onto SB700

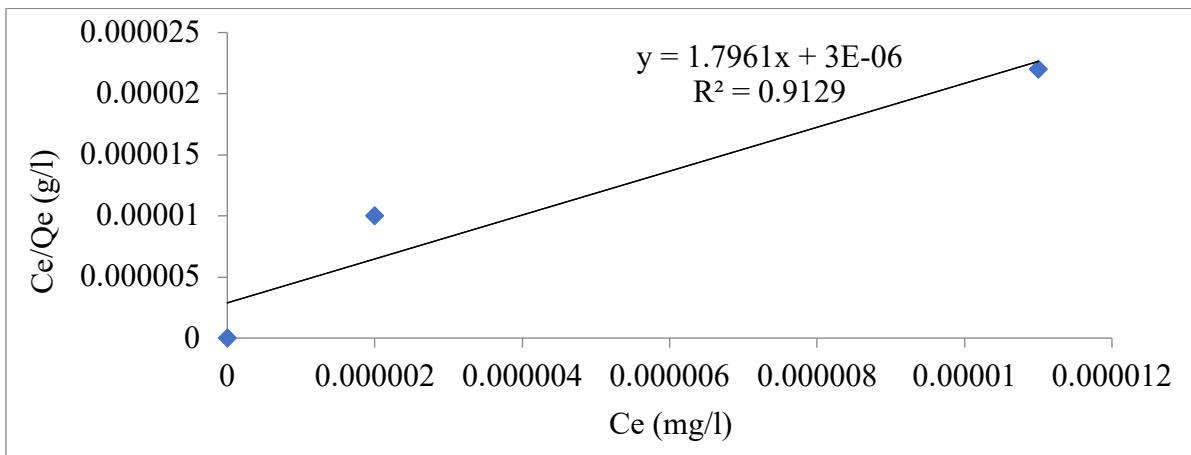


Figure 1c: Langmuir isotherm for adsorption of Hg in Cd vs. Hg aqueous phase onto SB350

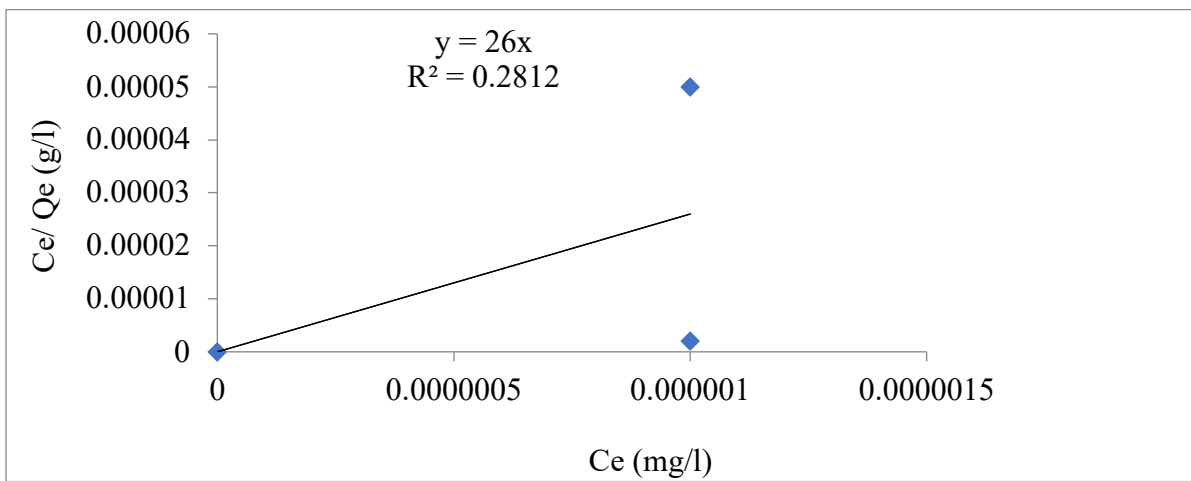


Figure 1d: Langmuir isotherm for adsorption of Hg in Pb vs. Hg aqueous phase onto SB350

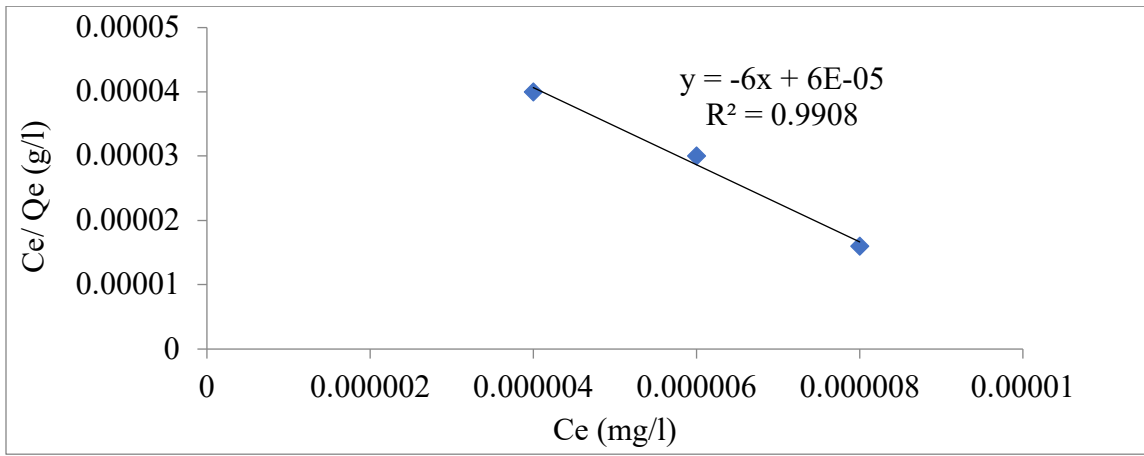


Figure 1e: Langmuir isotherm for adsorption of Hg in Pb vs. Hg aqueous phase on SB700

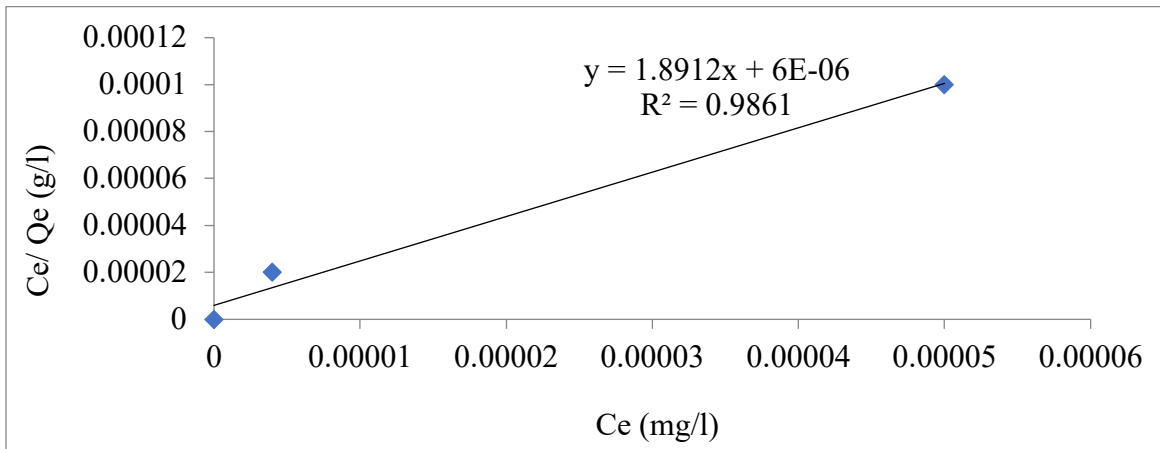


Figure 1f: Langmuir isotherm for adsorption of Hg in Cd vs. Hg vs. Pb aqueous phase onto SB350

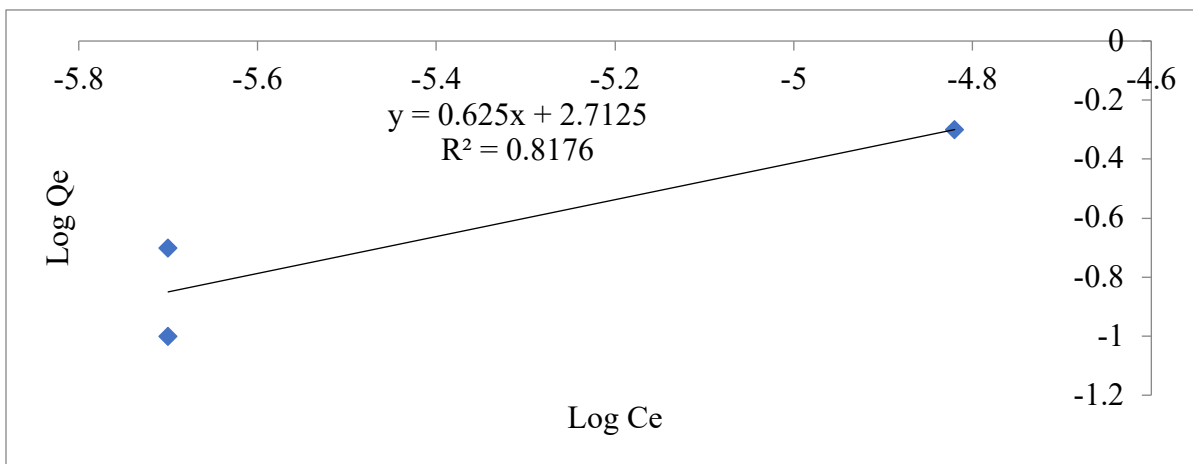


Figure 2a: Freundlich isotherm for adsorption of Hg in mono aqueous phase onto SB350

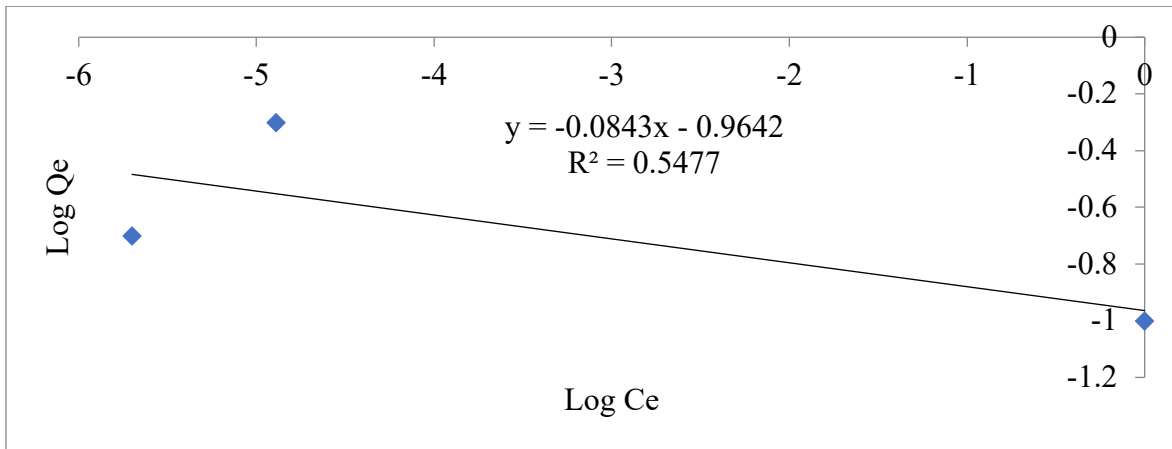


Figure 2b: Freundlich isotherm for adsorption of Hg in mono aqueous phase onto SB700

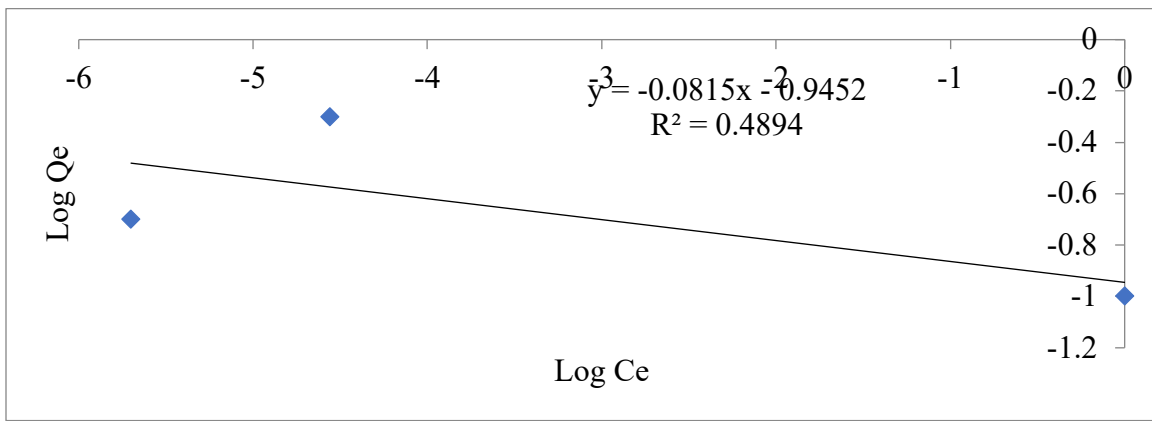


Figure 2c: Freundlich isotherm for adsorption of Hg in Cd vs. Hg aqueous phase onto SB350

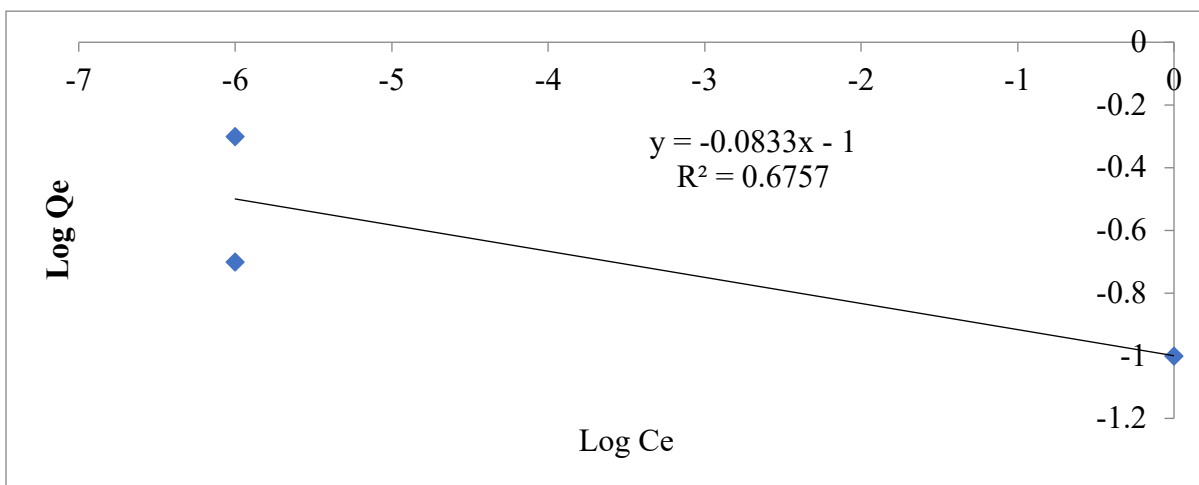


Figure 2d: Freundlich isotherm for adsorption of Hg in Pb vs. Hg aqueous phase on SB350

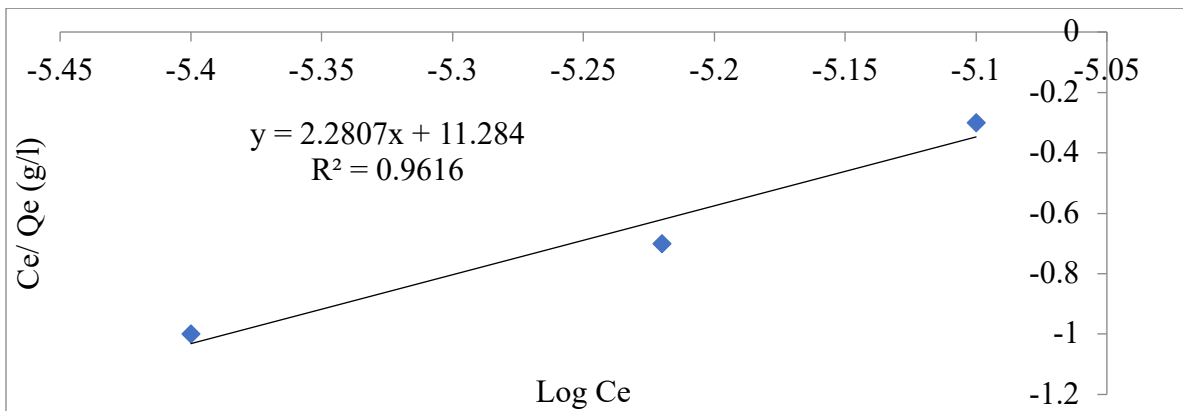


Figure 2e: Freundlich isotherm for adsorption of Hg in Pb vs. Hg aqueous phase onto SB700

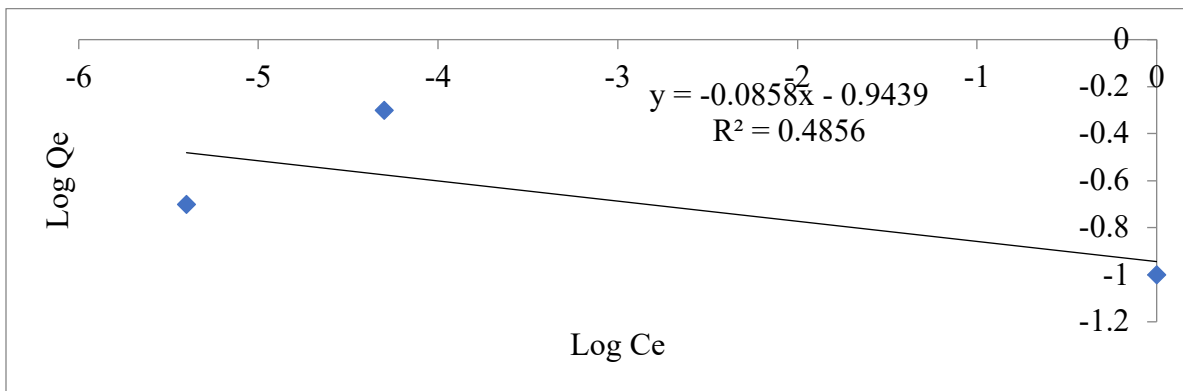


Figure 2f: Freundlich isotherm for adsorption of Hg in Cd vs. Hg vs. Pb aqueous phase onto SB350

Interactive Effect of Metal Ions in Binary and Ternary Systems onto Shea Nut Shell Biochar

The percentage R was used to determine whether the binary and tertiary mixtures are antagonistic, synergistic or non-interactive in nature. The binary mixtures showed mercury interactions with cadmium and lead ions onto SB350 is antagonistic in nature as Ri values were less than 100%. The mixture of mercury and lead aqueous phases with SB700 showed mercury ion behaviour was antagonistic in nature at five but synergistic in nature at fold two (Table 5). The values of Ri were greater than 100% in ternary systems (Table 5) implying the interaction of mercury with cadmium and lead ions is synergistic in nature. Cadmium and lead ions ascertain complete adsorption in the mono systems hence their interaction behaviour cannot be determined in binary and ternary systems.

Mercury ion that is antagonistic in nature implies its 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 binary system. 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 & Kutsal, 1996). However, synergistic nature of mercury ion in this study implies its 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 ternary system.

Table 5: Interactive effect of mixture of metal ions in binary and ternary systems onto shea nut shell biochar produced under slow and fast pyrolysis

SB350		Shea nut shell	
Mixture	Concentration	Ri	Interactive effect
Hg+Cd	0.2	67%	Antagonistic
Hg+Cd	0.5	73%	Antagonistic
Hg+Pb	0.2	33%	Antagonistic
Hg+Pb	0.5	7%	Antagonistic
Hg+Cd+Pb	0.2	1333%	Synergistic
Hg+Cd+Pb	0.5	3333%	Synergistic
SB700			
Mixture	Concentration	Ri	Interactive effect
Hg+Pb	0.2	200%	Synergistic
Hg+Pb	0.5	62%	Antagonistic
Hg+Cd+Pb	0.5	123%	Synergistic

Conclusion

The study evaluated the adsorption behaviours of toxic metals in mono, binary and ternary components onto shea nut shells biochar in order to estimate the toxic metal adsorption capacity of biochar in natural environments. The study revealed no clear cut difference between adsorption patterns of the mono metal systems and those under competitive adsorption conditions. The complete adsorption of ions in single and competitive systems is attributable to shea nut biochar having strong affinity for ions. Also, some experimental factors such as contact time, dosage of biochar, pH and temperature considered by this study favoured the ions adsorption. Based on these results shea nut shell biochar will be eco-friendly, readily available and low-cost adsorbent for effective removal of toxic metals. The mono, binary and ternary adsorption systems are very important in the estimation of toxic metal adsorption efficiencies onto biochar, in accordance with how they are released into receiving waters. As a result, competitive adsorption studies are necessary in order to accurately estimate the metal retention capacity of biochar in natural environments.

Acknowledgements

We are very grateful to Mr. Abdul-Aziz Bawa, Mr. Vincent Ninkun, Mr. Solomon Minyila, Mr. Yoonus Atongi and Mr. Abubakari Adamu for their diverse assistance in conducting the experiment in the laboratory. We also grateful to staff of Ecological

Laboratory of University of Ghana, especially Mr. Prince Owusu (Lab Technician) for his swift and timely analysis of the samples.

Conflict of interest

There is no potential or existing competing interest among authors of this research article.

References

- Aksu, Z., Acikel, U. & Kutsal, T. (1999). Investigation of simultaneous biosorption of copper (II) and chromium (VI) on dried chlorella vulgaris from binary metal mixtures: application of multicomponent adsorption isotherms. *Sep Purif Technol*, 34: 501–524.
- Apaydin-Varol, E., Pütün, E. & Pütün, A. E. (2007). Slow pyrolysis of pistachio shell. *Fuel*, 86(12): 1892-1899.
- Asensio, V., Vega, F. A., Andrade, M. L. and Covelo, E. F. 2013. Tree vegetation and waste amendments to improve the physical condition of copper mine soils. *Chemosphere*, 90(2): 603–610.
- Chang, J.S. & Chen, C.C. (1998). Quantitative analysis and equilibrium models of selective adsorption in multimetal systems using a bacterial biosorbent. *Sep Science Technology*, 33: 611–632.
- Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M.B. & Hay, A.G. (2011). Adsorption of copper and zinc by biochars

- produced from pyrolysis of hardwood and corn straw in aqueous solution. *Bioresources Technology*, 102: 8877–8884.
- Dada, A.O., Ojediran, J.O. & Olalekan, A.P. (2013). Sorption of Pb from aqueous solution unto modified rice husk: isotherm studies. *Adv Chem Phys*, 2013: 9–103.
- Desta, M.B. (2013). Batch sorption experiments: Langmuir and Freundlich isotherm studies for the adsorption of textile metal ions onto Teff Straw (*Eragrostis tef*) agricultural waste. *J Ther- modyn*, 2013: 64–71.
- Freundlich, H.M.F. (1906). Uber die adsorption in losungen. *Zeitschrift f'ur Physikalische Chemie (Leipzig)*, 57: 385–470.
- Goldberg, S. (2005). Equations and models describing adsorption processes in soils. In: Tabatabai MA, Sparks DA (eds) Chemical processes in soils. *Soil Science Society of America, Madison*, pp 489–517.
- Hegazi, H. A. (2013). Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. *HBRC Journal*, 9: 276–282.
- Kajitani, S., Tay, L.H., Zhang, S. & Li, Z.C. (2013). Mechanisms and kinetic modelling of steam gasification of brown coal in the presence of volatile-char interactions. *Fuel*, 103: 7–13.
- Kołodzyńska, D., Wnętrzak, R., Leahy, J. J., Hayes, M. H. B., Kwapiński, W. & Hubicki, H. (2012). Kinetic and adsorptive characterization of biochar in metal ions removal. *Chemical Engineering Journal*, 197: 295–305.
- Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of American Chemical Society*, 40: 1361–1403.
- Low, K.S. & Lee, C.S. (2000). Sorption of cadmium and lead from aqueous solutions by spent grain. *J Process Biochem*, 36: 59–64.
- Quainoo, A.K., Konadu, A. & Kumi, M. (2015). The potential of shea nut shells in phytoremediation of heavy metals in contaminated soil using lettuce (*Lactuca sativa*) as a test crop. *Journal of Bioremediation and Biodegradation*, 6(1): 1-7.
- Sag, Y. & Kutsal T. (1996). Fully competitive biosorption of chromium (VI) and iron (III) ions from binary metal mixtures by *R. arrhizus*: use of the competitive Langmuir model. *Process Biochem*, 31: 573–585.
- Saveyn, H., Eder, P., Garbarino, E., Muchova, E., Hjelmar, O., van der Sloot, H., Comans, R., van Zomeren, A., Hyks, J. & Oberender, A. (2014). Study on methodological aspects regarding limit values for pollutants in aggregates in the context of the possible development of end-of-waste criteria under the EU Waste Framework Directive. Final Report. European Commission Joint Research Centre Institute for Prospective Technological Studies, September, 2014. pp 1-197.
- Schmidt, H.P., Kammann, S.C., Glaser, B., Bucheli, T., Leifeld, J. & Abiven, S. (2014). *Guidelines of the European biochar certificate for a sustainable production of biochar*. Arbaz: European biochar foundation. 21 p.
- Singha, A.S. & Guleria, A. (2014). Chemical modification of cellulosic biopolymer and its use in removal of heavy metal ions from wastewater. *International Journal of Biological Macromolecules*, 67: 409–417.
- Singha, B. & Das, S.K. (2013). Adsorptive removal of Cu (II) from aqueous solution and industrial effluent using natural/agricultural wastes. *Colloids and Surfaces B: Biointerfaces*, 107: 97-106.
- Srivastava, V.C., Mall, I.D. & Mishra, I.M. (2006). Modelling individual and competitive adsorption of cadmium (II) and zinc (II) metal ions from aqueous solution onto bagasse fly ash. *Sep Sci Technol*, 41: 2685–2710.