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ADSORPTION PERFORMANCE OF GROUNDNUT AND SHEANUT SHELLS BIOCHARS IN TERNARY SYSTEM OF TOXIC METALS

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ABSTRACT

The choice of biomass is influenced by its availability, potential characteristics such as abundance of functional groups and large surface area. This study explored the removal of toxic metal ions from aqueous solution using groundnut and sheanut shells biochars. Groundnut and sheanut shells biochars pyrolysed at 350 ± 5ºC and 700 ± 5°C and used to remove lead (Pb), cadmium (Cd) and mercury (Hg) in ternary systems. Initial toxic metal concentrations and residual concentrations after the biochars application were measured using atomic absorption spectrophotometer. The adsorption efficiency of groundnut and sheanut shells biochars pyrolysed at 350 ± 5ºC and 700 ± 5°C in the ternary system ranged from 81.28% to 100% for lead, cadmium ranged from 43.66% to 100% and mercury ranged from 96.38% to 100%. The higher removal rates of Pb, Cd and Hg by the biochars showed the pH solutions were favourable for the adsorption. Langmuir isotherm was the model that best fit the adsorption of toxic metal ions. Groundnut and sheanut shells biochars qualify as a feasible and economic option for toxic metals removal. Hence, studies should be conducted in real polluted water to ascertain the actual effectiveness of these biochar treatments.

Keywords: Cadmium, groundnut shells biochars, removal efficiency, ternary system, toxic metals

Introduction

In polluted water treatment, it is preferable to constantly employ remediation measures that are sustainable and eco-friendly adsorbents (Kumar *et al.,* 2021). There are numerous biological, physico-chemical, and electrochemical treatment methods, but, the long processing time, high cost, use of toxic agents, and the secondary pollution generation make these treatment techniques industrially unsuitable (Rafique *et al.,* 2021). So, eco-friendly and effective process are required to remove toxic metal from polluted water.

Biochar has been trending for some time now because of its low-cost, eco-friendly, high adsorption capacity, high surface area and high porosity (Jiang *et al.,* 2018). Biochar has been used as an eco-friendly product for agricultural or mining to chelate toxic metals, soil improvement, control of pollution water, reduction of greenhouse gas emission among others. Hence, adsorption with the use of green adsorbent which is easy to operate, regenerate, high efficiency, low energy requirements,

economic feasibility and flexibility in the direction of primary contaminant and secondary contaminant, this method has gained the needed attention than the other processes (Hazrati *et al.,* 2021).

Biochar produced from biomass has been given momentous attention, particularly for the effective removal of toxic metals and contaminants from wastewater and water. One of the possible environmental functions is to reduce the bio-availability or mobility of the toxic metals such as lead and cadmium in water systems, depending on its cation exchange capacities and high surface area (O'Connor *et al.,* 2018; Palansooriya *et al.,* 2020). Biochar has distinctive properties and high thermal stability that make it a good candidate for a lot of industrial applications including effective removal and adsorption of toxic metals (Zhao *et al.,* 2021). Biochar from industrial and agricultural waste has also gained attention owing to its biodegradable features, economic feasibility and low-cost nature. The adsorption of metal ions onto biochar mostly depends on the ion exchange surface, the chemical cross-linking amongst toxic metals and biochar surface functional groups.

The interactions of toxic metals and biochar include mechanisms like precipitation with soluble minerals, ion exchange and binding with functional groups (Wang *et al.,* 2019). The adsorption process is influenced by many factors that play a vital role including the adsorption capacity, mechanical stability and surface area (Khan *et al.,* 2020). The ratios of toxic metal ions exchanged by other competitive ions in multicomponent adsorption remain dependable over an extensive range of toxic metal concentrations (Chen *et al.,* 2011). Metal ions in multicomponent systems interact with each other in an antagonistic, non-interactive or synergistic way and the results cannot be projected on the monometal studies basis (Ting & Teo, 1994). Toxic metals contamination of aqueous environments is a considerable concern for most developing countries. The presence of toxic metals can cause toxicity to plants and living organisms in the environment which can heavily affect human health. Pollution is predominant in developing countries where treatment or recycling of solid waste and wastewater is inadequate due to the lack of suitable management processes and affordable treatment technologies. Hence, this study sought to ascertain and discuss the adsorption performance of ternary systems for the removal of lead, cadmium and mercury ions using groundnut and sheanut shells biochars.

Experimental

Preparation of biochars and stock solution

Groundnut and sheanut shells collected from Nyohini in the Tamale Metropolis were used to produce biochars using a Gallenkamp muffle furnace. The groundnut shell and sheanut shells biochar was produced at 350 ± 5°C (slow pyrolysis) for 60 min and 180 min, and at 700 ± 5°C (fast pyrolysis) for 45 min and 90 min, respectively. They biochars were then left to cool, crushed and passed through a 2 mm sieve and used for the experiment.

Lead nitrate (Pb $(NO_3)_2$ grade; GR, assay; 99.50%), cadmium nitrate ($Cd(NO_3)_2$ grade; reagent CAS, assay; 99.99%), and mercury chloride ($HgCl_2$ grade; reagent ACS, assay; ≥ 99.50%) were obtained from the Spanish Laboratory. The preparation of stock solutions were done by dissolving 1.60 g of lead nitrate, 1.93 g of cadmium nitrate and 1.35 g of mercury chloride in deionised water to obtain solutions of 1000 mg/L concentration. Molecular weight of 331.21 g/mol for $Pb(NO_3)_2$, 236.42 g/mol for $Cd(NO_3)_2$ and 271.50 g/mol for $HgCl_2$ were calculated and divided by 207.20 g/mol atomic weight of Pb, 122.41 g/mol atomic weight of Cd and 200.60

g/mol atomic weight of Hg, respectively to obtain 1 mg (1000 ppm) of Pb, Cd and Hg. Toxic metal in ternary systems were prepared in a volumetric flask.

Experiment for ternary systems

The experiment was conducted in the University for Development Studies, Spanish Laboratory at Nyankpala Campus. The adsorption effect of Pb^{2+}, Cd^{2+} and Hg^{2+} by groundnut shell biochar derived at 350 ± 5°C (GB350), groundnut shell biochar derived at 700 ± 5°C (GB700), sheanut shell biochar derived at 350 ± 5°C (SB350), sheanut shell biochar derived at 700 ± 5°C (SB700), groundnut and sheanut shells biochar derived at 350 ± 5°C (GS350) and groundnut and sheanut shells biochar derived at 700 ± 5°C (GS700) were studied in ternary systems. The experimental design used in the ternary system of Pb (II) viz Cd (II) viz Hg (II) was in a ratio of 5 : 5 : 5 mg/L, 10 : 10 : 10 mg/L, 25 : 25 : 25 mg/L and 50 : 50 : 50 mg/L. The pH of the aqueous solutions were not adjusted. Sufficient time of 60 minutes was provided for the system to attain equilibrium. After settling, 50 mL elute was filtered through a Whatman's qualitative filter paper (125 mm Ø particle retention size). Elutes were analysed using the Perkin Elmer PIN Accle 900T Graphite Atomic Absorption Spectrophotometer (Waltham, United States of America) at the University of Ghana, Ecological Laboratory.

The quantity of toxic metal adsorbed (qe, mg/g) and removal efficiency were calculate using the following equations;

$$q_e = \frac{(C_o - C_e)\,x\,V}{W} \quad [1]$$

$$R_e = \frac{(C_o - C_e)}{C_o}\ x\ 100 \quad [2]$$

Where removal efficiency is denoted as the R_e, initial concentration (mg/L) is denoted as the C_o, concentration at equilibrium (m/L) is denoted as the C_e, volume of the aqueous solution (L) is denoted as the V and mass of biochar (g) is denoted as W.

Data modelling using Langmuir and Freundlich equations in ternary systems

The Langmuir model assumes uniform adsorption energies on the surface and no toxic metal transmigration in the plane of the biochar surface. Based on these assumptions that Langmuir then exemplified the following in [3]:

$$Q_e = \frac{Q_{max} K_l C_e}{1 + K_l C_e} \quad [3]$$

Adsorption parameters of Langmuir model were assessed by changing the Langmuir [3] to a linear form:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_o K_l C_e} \quad [4]$$

Where Q_{max} is the adsorption maximum capacity determined by Langmuir model; $\mathbf{Q}_e$ = the quantity of toxic metal adsorbed per gram at equilibrium by the biochar (mg/g); $\mathbf{Q}_o$ = maximum capacity of monolayer coverage (mg/g); $\mathbf{K}_l$ = constant of Langmuir isotherm (l/mg); and $\mathbf{C}_e$ = the toxic metal (adsorbate) equilibrium concentration (mg/L). The values of $\mathbf{K}_l$ and $\mathbf{Q}_{max}$ were determined using the slope and intercept of the plot of Ce vrs C_e/Q_e (Langmuir, 1918). The important feature of Langmuir isotherm may be the expression of R_L (equilibrium parameter), which is a dimensionless constant denoted as separation factor or equilibrium parameter (Webber & Chakravarti, 1974).

$$R_L = \frac{1}{1 + K_l C_0} \quad [5]$$

Where, $\mathbf{K}_L$ = the constant that is associated to the energy of adsorption (Langmuir constant) and $\mathbf{C}_0$ = initial concentration of absorbate. $\mathbf{R}_L$ value designates the nature of adsorption to be either, irreversible if $\mathbf{R}_L = 0$, unfavourable if $\mathbf{R}_L > 1$, favourable if $0 < \mathbf{R}_L < 1$and linear if $R_L = 1$. Adsorption isotherm of Freundlich is often used to describe the heterogeneous surface characteristics of adsorption (Hutson & Yang, 2000). The data usually fit the proposed empirical equation by Freundlich:

$$Q_e = K_f C_e^{1/n} \quad [6]$$

Where $\mathbf{Q}_e$ = the quantity of toxic metal adsorbed per gram at equilibrium by the biochar (mg/g); $\boldsymbol{K}_f$ = Freundlich isotherm constant (mg/g); $\mathbf{C}_e$ = the adsorbate equilibrium concentration (mg/L); and **n** = adsorption intensity.

Linearising equation:

$$\log Q_e = \log K_f + {}^1/_n \log C_e \quad [7]$$

The $\mathbf{K}_f$ is an estimated capacity of adsorption indicator, whilst ${}^1/_n$ is a function of the adsorption strength in the process of adsorption (Voudrias *et al.*, 2002). If value of ${}^1/_n$ is below 1 indicates occurrence of a normal adsorption. If ${}^1/_n$ is above 1 shows co-operative adsorption and if **n** = 1 then the partition amongst the two phases are independent of the concentration (Mohan & Karthikeyan, 1997).

Results and discussion

Removal efficiency of ternary toxic metals by biochars

The removal efficiency of GB350, SB350 and GS350 in the ternary system for lead ranged from 81.28% to 100%, cadmium ranged from 43.66% to 97.62% and mercury ranged from 96.38% to 100% (TABLE 1). The efficiency of GB700, SB700 and GS700 adsorption of lead, cadmium and mercury ions in the ternary systems was 100% for lead ion, and ranged from 71.42% to 100% for Cd and 100% for mercury ion (TABLE 1). The removal efficiency of GB350, SB350 and GS350 for ternary systems on average was high for Pb, Cd and Hg ions. There was total removal of Pb and Hg ions by GB700, SB700 and GS700 in the ternary systems. There was high efficiency of toxic metal adsorption by the groundnut and sheanut shells biochars produced during slow and fast pyrolysis.

TABLE 1

Removal efficiency of ternary toxic metals using biochars

		Slow pyrolysis			Fast pyrolysis		
Metal	Conc (mg/L)	GB350	SB350	GS350	GB700	SB700	GS700
Pb	5:5:5	100%	92.92%	100%	100%	100%	100%
Pb	10:10:10	81.28%	89.69%	100%	100%	100%	100%
Pb	25:25:25	81.96%	100%	93.10%	100%	100%	100%
Pb	50:50:50	91.73%	93.27%	100%	100%	100%	100%
Cd	5:5:5	91.46%	43.66%	72.26%	87.38%	71.42%	96.50%
Cd	10:10:10	84.99%	86.27%	97.62%	98.83%	100%	99.38%
Cd	25:25:25	97.45%	66.66%	92.01%	100%	97.54%	100%
Cd	50:50:50	92.48%	77.22%	93.63%	98.80%	99.42%	98.97%

Hg	5:5:5	100%	99.98%	100%	100%	100%	100%
Hg	10:10:10	99.25%	99.79%	100%	100%	100%	100%
Hg	25:25:25	96.38%	100%	99.86%	100%	100%	100%
Hg	50:50:50	100%	99.99%	100%	100%	100%	100%

Effect of pH solution on biochar adsorption performance in ternary systems

The pH of Pb vrs Cd vrs Hg solution at 5 : 5 : 5 mg/L, 10 : 10 : 10 mg/L, 25 : 25 : 25 mg/L and 50 : 50 : 50 mg/L in the ternary systems ranged from 6.71 to 7.31 with 81.28% to 100% removal efficiency for Pb (Fig. 1) was 43.66% to 100% for Cd (Fig. 2) and 96.38% to 100% for Hg for the biochars (Fig. 3). The biochars removal at pH of 6.71 to 7.31 of Pb vrs Cd vrs Hg solution can be considered effective and fairly good on average for removal of Pb, Cd and Hg. The surface properties, the adsorbed toxic metal ions distribution, and functional groups protonation on adsorbent are greatly affected by pH of solution (Sun *et al.,* 2014).

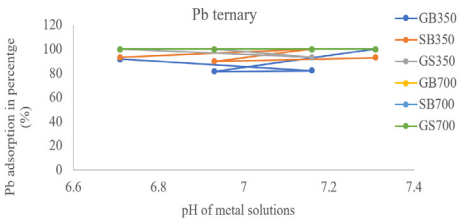


Fig. 1: Effect of pH on Pb adsorption in ternary system using biochars

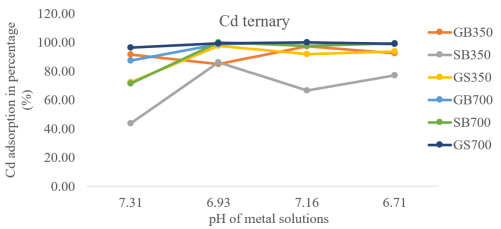


Fig. 2: Effect of pH on Cd adsorption in ternary system using biochars

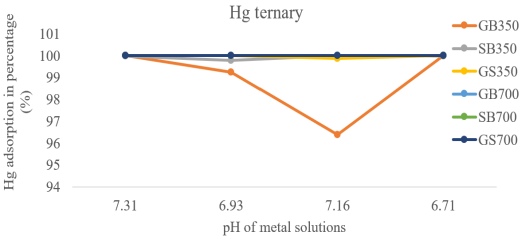


Fig. 3: Effect of pH on Hg adsorption in ternary system using biochars

Effect of biochar dosage in the ternary systems

In the ternary systems of Cd vrs Pb vrs Hg with biochar dosage of 2 g / 5 : 5 : 5 mg/L, 4 g / 10 : 10 : 10 mg/L, 8 g / 25 : 25 : 25 mg/L and 10 g / 50 : 50 : 50 mg/L in the ternary systems of Pb vrs Cd vrs Hg, Pb removal efficiency ranged from 81.28% to 100% (Fig. 4), 43.66% to 99.46% for Cd (Fig. 5) and 96.38% to 100% for Hg for the biochars (Fig. 6). The ternary system experiment showed the various dosages were effective for metals removal. High amount of biochar adsorbents in process of adsorption can guarantee availability of more sites and specific surface areas for adsorption, which usually contribute to great adsorption capacity. The increases in number of adsorption sites available is followed by increase of an adsorbent specific surface area (Thavamani & Rajkumar, 2013). This cause the higher removal efficiencies by the groundnut and sheanut shells biochars under the various dosages and elevated contamination limits.

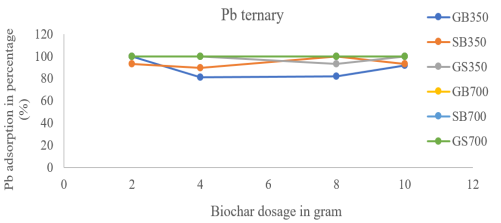


Fig. 4: Effect of biochar dosage on Pb in ternary system of Pb, Cd and Hg

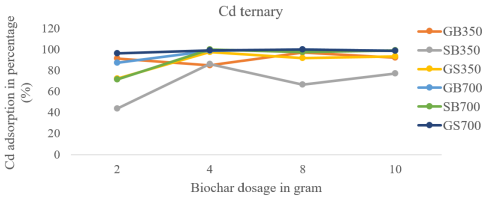


Fig. 5: Effect of biochar dosage on Cd in ternary system of Pb, Cd and Hg

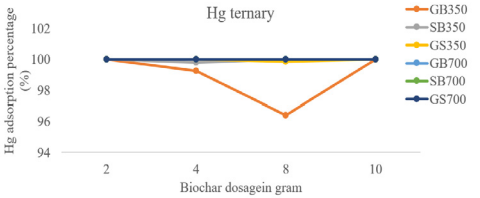


Fig. 6: Effect of biochar dosage on Hg in ternary system of Pb, Cd and Hg

Langmuir and Freundlich isotherms for Pb, Cd and Hg in ternary systems

The specific plots of adsorption (Ce/Qe) against Ce (the equilibrium concentration) for toxic metals in ternary systems are presented in Figs. 7a to 7j and Figs. 8a to 8j. The maximum Langmuir capacity ranged from 454.55 to 555.56 mg/g and 172.41 to 526.32 mg/g for ternary systems by biochars produced at 350 ± 5°C and 700 ± 5°C, respectively (TABLE 2). The K_L for ternary systems ranged from 0.95 to 5.68 l/mg for Cd by GB350, SB350 and GS350 and 0.37 l/mg and 0.50 l/mg for Pb and 0.01 l/mg and 0.00 l/mg for Hg by GB350 and SB350 and -0.12 to 0.05 l/mg for Cd by GB700, SB700 and GS700 (TABLE 2). For ternary systems, the maximum Langmuir capacity and K_L (l/mg) was in the order of Cd ion > Pb ion > Hg ion and were larger for biochars formed during slow pyrolysis than in fast pyrolysis. The R_L was found to be ranged from -38.76 to 285.09 for Cd, 19.33 and 26.00 for Pb, 0.96 and 1.30 for Hg in the ternary systems. The R_L was found to be in order of Cd ion > Pb ion > Hg in the ternary systems. The separation factor $R_L > 1$ for both Cd and Hg ions which indicates favourable adsorption process. Langmuir R^2 for ternary system ranged from 0.5223 to 0.9997 for GB350, SB350 and GS350 whilst only Cd in ternary system did not attain complete removal or adsorption hence showed R^2 of 0.7415 for GB700, 0.9619 for SB700 and 0.8646 for GS700 (TABLE 2).

TABLE 2

Langmuir and Freundlich parameters for Pb, Cd and Hg in ternary systems using biochars

		Langmuir parameters					Freundlich parameters		
Ion	Bio-char	Q_{max} (mg/g)	K_L (l/mg)	R_L	R^2	$^1/_n$	n	K_F (mg/g)	R^2
Cd vrs Pb vrs Hg	GB350	526.32	0.95	48.37	0.7556	0.24	4.15	280.22	0.4367
Cd vrs Pb vrs Hg	SB350	454.55	5.68	285.09	0.5223	0.29	3.44	135.74	0.3037
Cd vrs Pb vrs Hg	GS350	555.56	1.39	70.44	0.5248	0.18	5.71	268.66	0.2482
Cd vrs Pb vrs Hg	GB700	303.03	0.01	1.30	0.7415	-1.56	-0.64	21.30	0.2614
Cd vrs Pb vrs Hg	SB700	172.41	-0.12	-5.03	0.9619	-1.93	-0.52	37.22	0.2148
Cd vrs Pb vrs Hg	GS700	526.32	0.05	3.63	0.8646	-1.49	-0.67	10.68	0.3995
Pb vrs Cd vrs Hg	GB350	333.33	0.37	19.33	0.7651	3.48	0.29	3.18	0.7553
Pb vrs Cd vrs Hg	SB350	500.00	0.50	26.00	0.8824	0.43	2.33	68.68	0.0191
Hg vrs Pb vrs Cd	GB350	303.03	0.01	1.30	0.9997	-0.57	-1.74	21.76	0.3290
Hg vrs Pb vrs Cd	SB350	143.90	0.00	0.96	0.9771	-0.88	-1.31	2.24	0.7989

The n values found for ternary systems ranged from -1.74 to 5.71 and 2.24 to 280.22 for K_F (TABLE 2). Freundlich R^2 values for ternary systems ranged from 0.0191 to 0.7989 onto the biochars (TABLE 2). For ternary systems, K_F for the metals by biochars followed the order of Cd > Pb > Hg and was greater in biochar produced at 350 ± 5°C than in 700 ± 5°C. The $^1/_n$ and n values for the metal ions by biochars followed the order of Pb > Cd > Hg in the ternary systems. The $^1/_n$ and n values were both positive and negative for Cd ion, positive for Pb and negative for Hg ion which were < 1 implying normal adsorption occurs except for Pb with GB350. In some cases of Cd and Pb n is between one and ten implying the process of adsorption was favourable except for GB700, SB700 and GS700 for Cd and GB350 for Pb. Whilst in all cases of Hg n is less than 1 implying the degree of nonlinearity between adsorption and solution concentration as physical process. The adsorbent affinity towards the toxic metal ion uptake is showed by the n value (Dada *et al.,* 2013). The process of adsorption is favourable when n is in range of 1 to 10 (Goldberg, 2005), and when n > 1, degree of nonlinearity between adsorption and solution is physical process (Desta, 2013). Langmuir isotherm was the model that best fit the adsorption of toxic metal ions onto the biochars in the ternary systems.

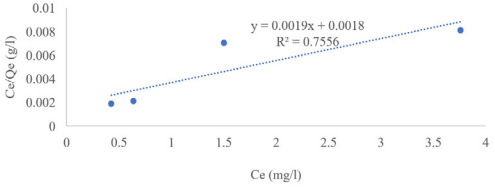


Fig. 7a: Langmuir isotherm for adsorption of **Cd** vrs Pb vrs Hg in ternary aqueous solution onto GB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

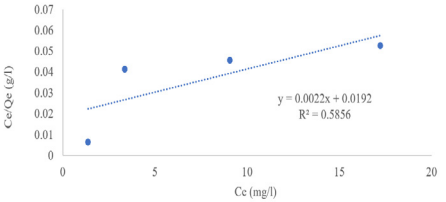


Fig. 7b: Langmuir isotherm for adsorption of **Cd** vrs Pb vrs Hg in ternary aqueous solution onto SB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

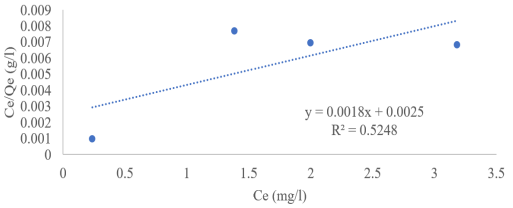


Fig. 7c: Langmuir isotherm for adsorption of **Cd** vrs Pb vrs Hg in ternary aqueous solution onto GS350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

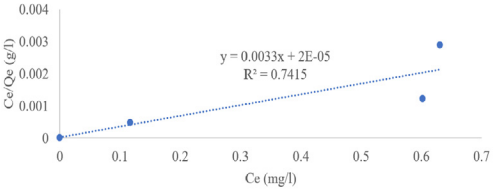


Fig. 7d: Langmuir isotherm for adsorption of **Cd** vrs Pb vrs Hg in ternary aqueous solution onto GB700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

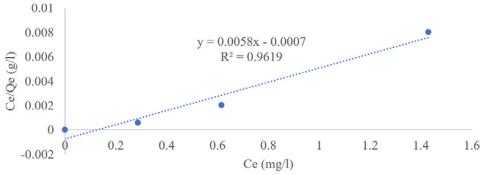


Fig. 7e: Langmuir isotherm for adsorption of **Cd** vrs Pb vrs Hg in ternary aqueous solution onto SB700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

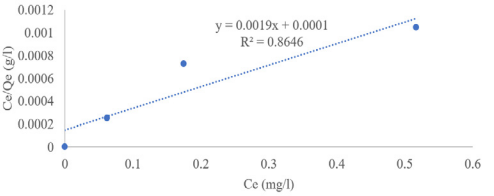


Fig. 7f: Langmuir isotherm for adsorption of **Cd** vrs Pb vrs Hg in ternary aqueous solution onto GS700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

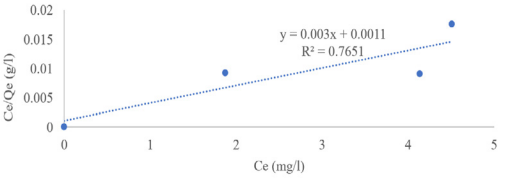


Fig. 7g: Langmuir isotherm for adsorption of Cd vrs **Pb** vrs Hg in ternary aqueous solution onto GB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

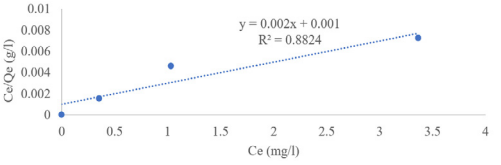


Fig. 7h: Langmuir isotherm for adsorption of Cd vrs **Pb** vrs Hg in ternary aqueous solution onto SB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

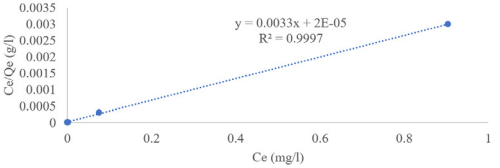


Fig. 7i: Langmuir isotherm for adsorption of Cd vrs Pb vrs **Hg** in ternary aqueous solution onto GB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

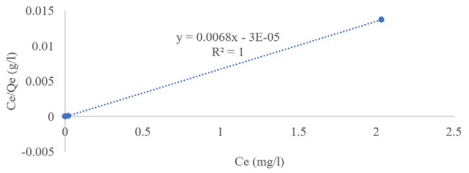


Fig. 7j: Langmuir isotherm for adsorption of Cd vrs Pb vrs **Hg** in ternary aqueous solution onto SB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

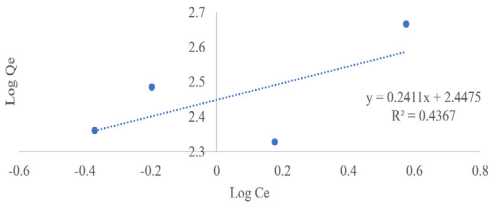


Fig. 8a: Freundlich isotherm for adsorption of **Cd** vrs Pb vrs Hg in ternary aqueous solution onto GB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

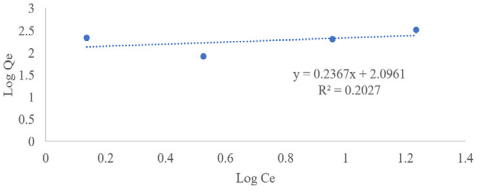


Fig. 8b: Freundlich isotherm for adsorption of **Cd** vrs Pb vrs Hg in ternary aqueous solution onto SB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

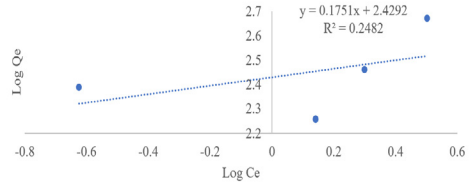


Fig. 8c: Freundlich isotherm for adsorption of **Cd** vrs Pb vrs Hg in ternary aqueous solution onto GS350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

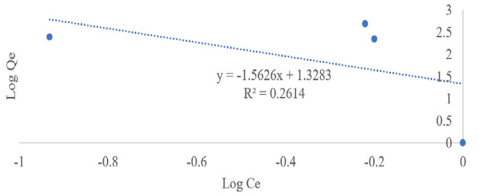


Fig. 8d: Freundlich isotherm for adsorption of **Cd** vrs Pb vrs Hg in ternary aqueous solution onto GB700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

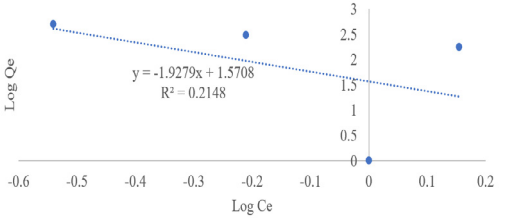
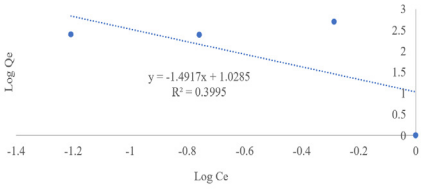


Fig. 8e: Freundlich isotherm for adsorption of **Cd** vrs Pb vrs Hg in ternary aqueous solution onto SB700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)



Pb vrs Hg in ternary aqueous solution onto GS700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

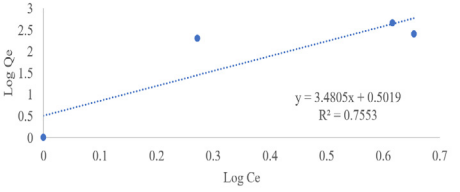


Fig. 8g: Freundlich isotherm for adsorption of Cd vrs **Pb** vrs Hg in ternary aqueous solution onto GB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

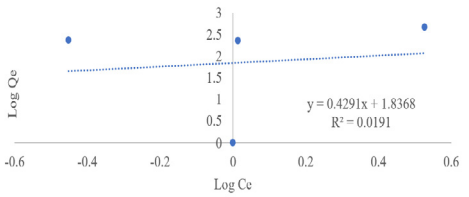


Fig. 8h: Freundlich isotherm for adsorption of Cd vrs **Pb** vrs Hg in ternary aqueous solution onto SB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

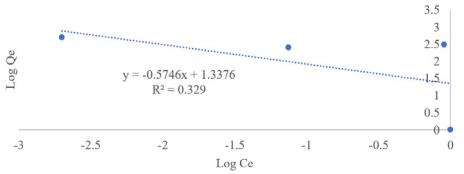


Fig. 8i: Freundlich isotherm for adsorption of Cd vrs Pb vrs **Hg** in ternary aqueous solution onto GB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

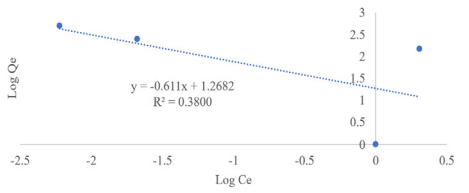


Fig. 8j: Freundlich isotherm for adsorption of Cd vrs Pb vrs **Hg** in ternary aqueous solution onto SB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min)

Adsorption mechanism of biochar in the ternary systems

Different toxic metals demonstrates diverse valence states or species at different conditions of pH which influence and determine the type of adsorption mechanisms. Metal adsorption onto biochar is influenced by the inorganic minerals in addition to the biochar cation ions. The highly effective removal of Pb in this study could imply adsorption mechanisms by the biochars include precipitation, cation exchange and complexation (Lu *et al.*, 2012). The rich Mg and Ca could aid in cation exchange contributing to the adsorption onto groundnut and sheanut shells biochars whilst exchange with Na and K could have accounted for Pb complexation with hydroxyl and carboxyl groups. It has been reported that the predominant mechanism of adsorption for Pb by biochars derived from oak bark and oak wood was cation exchange which was related to the release of cations (Mohan *et al.*, 2007). 62% sorption of Pb onto bagasse biochar produced at 500 °C by means of cation exchange (Ding *et al.*, 2014). Higher temperature of pyrolysis can promote faster removal of Pb(II) by biochar and the dominant mechanism was precipitation (Shen *et al.,* 2019). Phosphate materials used in scavenging Pb(II) had excellent cooperation capability with Pb in environments (Huang *et al.,* 2018). In conclusion, precipitation, complexation, and cation exchange are the main mechanisms responsible for Pb higher removal rates as the groundnut and sheanut shells biochars were rich in minerals and phosphates.

Electrostatic interactions, precipitation, cation exchange, and surface complexation mechanisms may be responsible for Cd higher removal rates in this study because the groundnut and sheanut shells biochars were rich in Ca, K, Mg and Na and phosphates (Duwiejuah *et al.,* 2022). A recent study showed surface complexation and ion exchange were the key mechanisms for scavenging of Cd(II) (Luo *et al.,* 2019). Also, precipitation accounted for 88% Cd adsorption due to relatively high soluble carbonate and phosphate concentrations with 12% being from π bonding of Cd in dairy manure biochar (Xu *et al.*, 2013).

The high S and Cl may have influenced the mechanism of Hg adsorption in the aqueous

solutions onto groundnut and sheanut shells biochars. Biochars have proven very effective owing to high sulfur to precipitate above 90% of Hg^{2+} as $Hg(OH)_2$ or $HgCl_2$ mostly over co-precipitation with biochars anions such as S, O and Cl (Kong *et al.,* 2011; Liu *et al.,* 2016). Chemical reduction is also responsible for Hg sorption. Besides $Hg(OH)_2$ precipitation, complexation, and cation exchange, Hg^{2+} has also be abridged to Hg_2Cl_2 in Cl^- presence, which was on the biochar surface then precipitated (Xu *et al.*, 2016). It is possible that the mechanism for toxic metal adsorption by groundnut and shea shells biochars involve coordination between the toxic metal ions and the functional groups, which is largely dependent on the solution pH (Cheng *et al.,* 2016).

Conclusion

The removal efficiency of GB350, SB350 and GS350 for ternary systems on average were high for Pb, Cd and Hg ions and GB700, SB700 and GS700 was complete removal for Pb and Hg, highly appreciable for Cd. Groundnut and sheanut shells biochars qualified as a feasible and economic option for toxic metals removal. Hence, studies should be conducted in real water polluted environments to ascertain the actual effectiveness of these biochar treatments in water processing.

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