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Research article

Simultaneous adsorption of toxic metals in binary systems using peanut and sheanut shells biochars

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ABSTRACT

Converting peanut and sheanut shells into biochar is a smart strategy for recycling agricultural waste. Biochar was produced from peanut and sheanut shells at temperatures of 350 ± 5 °C and 700 ± 5 °C. The adsorption capacities for lead (Pb^{2+}), cadmium (Cd^{2+}) and mercury (Hg^{2+}) in the binary systems were evaluated. In the binary systems with concentrations of 5 : 5 mg/L, 10 : 10 mg/L, 25 : 25 mg/L and 50 : 50 mg/L the removal efficiencies of GB350, SB350, GS350, GB700, SB700 and GS700 were 100% for Pb^{2+} and 88.70%–99.46% for Cd^{2+}, 98.20%–100% for Pb^{2+} and 100% for Hg^{2+}, 79.30%–100% for Cd^{2+} and 99.96%–100% for Hg^{2+}. The higher adsorption percentages of Pb^{2+}, Cd^{2+} and Hg^{2+} by the biochar in the binary systems indicated that the pH values of the solutions were good and suitable for adsorption. The biochar from peanut and sheanut shells showed excellent capacity to remove Pb, Cd and Hg in the binary systems. The Langmuir model ($0.3351 \leq R^2 \leq 0.9901$) was more suitable than the Freundlich model ($0.0014 \leq R^2 \leq 0.9994$) for the adsorption of toxic metal ions onto the biochar in the binary systems. The interactive effects of the binary mixtures in the aqueous solution of Pb^{2+}, Cd^{2+}, and Hg^{2+} were found to be either antagonistic or synergistic. Peanut and sheanut shell biochar were rich in calcium, potassium, magnesium, and sodium, and phosphates affected the mechanisms of Pb and Cd adsorption. The high sulphur content might have influenced the mechanism of Hg adsorption in the aqueous solutions on peanut and sheanut shell biochar. These results suggest that peanut and sheanut shell biochar have enormous potential and are suitable for adsorption of Pb^{2+}, Cd^{2+} and Hg^{2+} in wastewater and polluted soil. Therefore, their effectiveness should be further tested in an actual water polluted environment.

1. Introduction

Pollution by potentially toxic elements is a worldwide environmental problem. Major sources of pollution include mining, smelting, and electronic waste disposal, hazardous experimental research (catalysts and spent catalysts), and agricultural activities (pesticides and fertilisers) (Wang and Wang, 2019). Pollution of water bodies with toxic metals such as lead (Pb) and cadmium (Cd) is a major environmental problem, especially in developing countries (Harmesa and Cordova, 2021). The presence of toxic metals in water bodies, even at moderately low concentrations, can lead to long-term risks to human health and ecology (Christou et al., 2017). The search for adsorbents with better metal removal efficiency has attracted serious scientific interest in the last two decades.

In the mixed system of cadmium and mercury (Hg), the Cd removal efficiency was over 99.60% and Hg was 100%; for Cd and Pb, Hg and Pb were both close to 100% in a binary system at the different maximum contamination limits (Duwiejuah et al., 2018). The sorption behaviour of lead and cadmium is similar since they are divalent cations. The sorption of lead and cadmium is based on the same mechanisms and depends on the temperature of pyrolysis and the biochar feedstock (Li et al., 2017). Studies have shown that biochar can effectively remove cadmium and lead from both polluted soils and aqueous solutions by precipitation, adsorption, or functional complexation (Qiu et al., 2021). The main mechanism for Cd and Pb removal is ion exchange (Ca^{2+}) by Ca-rich biochar (Sun et al., 2021). The process of adsorption is influenced by many factors, including adsorption capacity, mechanical stability, and surface area (Khan et al., 2020). The ratios of metal ions exchanged by other competing ions during multicomponent adsorption remain reliable over a wide range of metal concentrations (Chen et al., 2011). Therefore, multimetal studies are essential to accurately estimate the metal binding capacity to biochar in normal environments.

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Biochar produced from agricultural waste can be a successful technique to control toxic metal contamination because it is highly efficient, cost-effective, environmentally sustainable, relatively easy to handle, and reliable in terms of public safety (Wang et al., 2020). Biochar produced from agricultural biomass is widely used for soil remediation due to its high availability and cost-effectiveness (Zhang et al., 2021a). In the production of biochar, the presence of toxic elements must be kept within acceptable limits when using waste materials to allow more environmental benefits, which is usually preferred in the circular economy (Marzeddu et al., 2021). Therefore, the production of biochar and the understanding of the competition between different toxic metals on the adsorbents and their interactions under certain conditions during the adsorption process is crucial for the development of adsorbents and the treatment of the polluted environment. In this study, the efficiency of simultaneous removal of lead, cadmium and mercury ions in binary systems was investigated using peanut shell and sheanut shell biochar.

2. Materials and methods

2.1. Production of biochar

Groundnut and sheanut shells were used to prepare biochar in the Agricultural Sub-sector Improvement Programme laboratory at the University for Development Studies, Nyankpala Campus, Ghana. The groundnut and sheanut shells were collected from Nyohini in Tamale metropolis. The groundnut and sheanut shells were stored in earthen pots and then placed in a Gallenkamp muffle furnace to convert the feedstocks into biochar under limited oxygen conditions. Slow pyrolysis of peanut and sheanut shell biochar was carried out at 350 ± 5 °C for 60 min and 180 min, respectively, in a muffle furnace. Fast pyrolysis of peanut and sheanut shell biochar was performed at 700 ± 5 °C for 45 min and 90 min, respectively, in a muffle furnace. After preparation, the biochars were cooled, crushed, and sieved through 2 mm and used for the experiment.

2.2. Preparation of stock solution and binary aqueous solutions

The experiment was carried out at the University for Development Studies, Spanish Laboratory at Nyankpala Campus, Ghana. 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; ACS reagent, assay; ≥ 99.50%) were obtained from the Spanish laboratory. To prepare the stock solutions, accurately weighed 1.60 g of lead nitrate, 1.93 g of cadmium nitrate and 1.35 g of mercury chloride were dissolved in deionised water to obtain solutions with a concentration of 1000 mg/L. The molecular weight of $Pb(NO_3)_2$ (331.21 g/mol), $Cd(NO_3)_2$ (236.42 g/mol) and $HgCl_2$ (271.50 g/mol) was calculated and divided by the atomic weight of Pb (207.20 g/mol), Cd (122.41 g/mol) and Hg (200.60 g/mol), respectively to obtain the amount of compounds containing 1 mg (1000 ppm) of Pb, Cd, and Hg. The mixtures of toxic metal solutions were prepared in a 1000 mL volumetric flask.

The stock solution was serially diluted to obtain a maximum concentration of 5:5, 10:10, 25:25, and 50:50 mg/L (i.e., the ratio of the cation concentration of lead, cadmium and mercury). These concentrations were established based on previous studies by Duwiejuah et al. (2018) and Quainoo et al. (2019), who reported effective removal of Pb, Cd, and Hg ions at micro concentrations in binary systems using peanut and sheanut shell biochars.

2.3. Experiment for binary systems

The adsorption effect of Pb (II), Cd (II) and Hg (II) by peanut shell biochar prepared at 350 °C (GB350), peanut shell biochar prepared at 700 °C (GB700), sheanut shell biochar prepared at 350 °C (SB350), sheanut shell biochar prepared at 700 °C (SB700), combined peanut and sheanut shells biochar prepared at 350 °C (GS350) and combined peanut and sheanut shells biochar prepared at 7000 °C (GS700) were studied in binary systems. In the binary system of Pb (II) versus Cd (II), Cd (II) versus Hg (II), and Hg (II) versus Pb (II), the concentrations of the co cations were maintained at ratios of 5:5, 10:10, 25:25, and 50:50 mg/L for each metal, respectively. The pH of the solutions was maintained, so no adjustment was made. Sufficient time of 60 min was provided for the system to reach equilibrium at 25 °C constant room temperature. After settling, 50 mL elute was filtered through a Whatman's qualitative filter paper with a particle retention size of 125 mm Ø. A total of 72 elutes (samples) were stored in an ice chest (at 4 °C) and sent to the University of Ghana Ecology Laboratory for analysis using PerkinElmer PIN Accle 900T graphite atomic absorption spectrophotometer (Waltham, United States of America).

2.4. Calculation of binary metals removal efficiency

The adsorption capacity of toxic metal and percentage removal were carried out using Eqs. (1) and (2), respectively.

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

$$R = \frac{C_o - C_e}{C_o} \times 100\% \quad (2)$$

Where $\mathbf{Q_e}$ is the final adsorption capacity of toxic metal (mg/g), $\boldsymbol{R}$ is the percentage removal (%), $\mathbf{C_o}$ represents initial concentrations (mg/L), and $\mathbf{C_e}$ represents final concentrations (mg/L), $\mathbf{V}$ is the volume of aqueous solution (L) and $\mathbf{M}$ is the biochar mass (g).

This study employed Langmuir model (Langmuir, 1918) (Eqn 3) and Freundlich model (Freundlich, 1906) (Eqn 4) for fitting the data.

$$Q_e = \frac{bQ^O C_e}{1 + bC_e} \quad (3)$$

$$Q_e = K_F C_e^{1/n} \quad (4)$$

where $\mathbf{b}$ denotes the Langmuir constant (L/mg), $\mathbf{Q^0}$ denotes the maximum adsorption capacity (mg/g), $\mathbf{n}$ and $\mathbf{K_F}$ are the Freundlich constants (mg/g) (Shen et al., 2019).

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 and Chakravarti, 1974). Adsorption isotherm of Freundlich is often used to describe the heterogeneous surface characteristics of adsorption (Hutson and Yang, 2000). The constant $\mathbf{K_F}$ is an estimated capacity of adsorption indicator, whilst $^1/_{\boldsymbol{n}}$ is a function of the adsorption strength in the process of adsorption (Voudrias et al., 2002). If value of $^1/_{\boldsymbol{n}}$ is below 1 indicates occurrence of a normal adsorption. If $^1/_{\boldsymbol{n}}$ is above 1 shows co-operative adsorption and if $\mathbf{n} = 1$ then the partition amongst the two phases are independent of the concentration (Mohan and Karthikeyan, 1997).

3. Results and discussion

In the binary systems with concentrations of 5:5, 10:10, 25:25 and 50:50 mg/L the removal efficiency of GB350, SB350 and GS350 was 100% for lead ions and 88.70%–98.88% for cadmium ions (Table 1). The minimum removal efficiency of 88.70% for cadmium was recorded by SB350 at a concentration of 5:5 mg/L whilst the maximum of 98.88% was obtained at 50:50 mg/L by GB350 (Table 1). Also, GB700, SB700 and GS700 recorded 100% removal efficiency for lead ions at concentrations of 5:5, 10:10, 25:25 and 50:50 mg/L and ranged from 93.70% to 99.46% for cadmium ions (Table 1). The minimum removal efficiency of 93.70% for cadmium was observed by SB700 at a concentration of 5:5 mg/L, whilst the maximum removal efficiency of 99.46% at 25:25 mg/L was achieved by GB350 (Table 1). In the binary systems of lead and cadmium

Table 1. Removal efficiency of binary toxic metals using biochars (n = 72).

Metal	Conc (mg/L)	Slow pyrolysis			Fast pyrolysis		
		GB350 (%)	SB350 (%)	GS350 (%)	GB700 (%)	SB700 (%)	GS700 (%)
Pb: Cd	5:5	100	100	100	100	100	100
Cd: Pb	5:5	98.70	88.70	97.70	95.02	93.70	94.58
Pb: Cd	10:10	100	100	100	100	100	100
Cd: Pb	10:10	96.81	89.50	97.70	95.02	97.55	96.58
Pb: Cd	25:25	100	100	100	100	100	100
Cd: Pb	25:25	97.44	94.84	98.36	97.79	99.46	99.24
Pb: Cd	50:50	100	100	100	100	100	100
Cd: Pb	50:50	98.88	95.59	98.36	99.23	99.44	99.41
Pb: Hg	5:5	100	100	100	100	100	100
Hg: Pb	5:5	100	100	100	100	100	100
Pb: Hg	10:10	100	100	100	100	100	100
Hg: Pb	10:10	100	100	100	100	100	100
Pb: Hg	25:25	98.30	100	100	100	100	100
Hg: Pb	25:25	99.99	100	100	100	100	100
Pb: Hg	50:50	100	99.86	98.20	100	98.49	100
Hg: Pb	50:50	100	100	100	100	100	100
Cd: Hg	5:5	96.24	79.30	94.42	100	92.8	100
Hg: Cd	5:5	100	99.98	99.96	100	100	100
Cd: Hg	10:10	96.24	79.30	94.42	100	92.79	100
Hg: Cd	10:10	100	99.98	99.96	100	100	100
Cd: Hg	25:25	98.07	94.68	95.02	99.72	99.35	98.53
Hg: Cd	25:25	100	100	99.99	100	99.99	100
Cd: Hg	50:50	97.43	92.31	96.40	99.61	99.30	99.35
Hg: Cd	50:50	100	100	100	100	100	100

ions with concentrations of 5:5, 10:10, 25:25 and 50:50 mg/L, the removal efficiency of GB350, SB350, GS350, GB700, SB700 and GS700 was very effective for lead and cadmium ions. The affinity of biochar for lead ions was greater than for Cd ions in the binary systems. The mixtures of toxic metals exert greater influence on the adsorption capacity typically for the biochar utilisation in the aqueous solution. This is due to the complex contaminants co-existing, which has interaction effects on the removal efficiency in environment. In similar studies, the removal efficiency of cadmium and lead in binary systems by biochar was found to be effective at different lower contamination limits (Duwiejuah et al., 2018). The maximum adsorption capacity of rapeseed was 83.50 mg g^{-1} for Pb and 31.60 mg g^{-1} for Cd (Štefu š ov á et al., 2012). The biochar wheat straw, rice husk, and corncob showed adsorption capacity of 95.38%, 96.41% and 96.92% for Pb^{2+} whilst Cd^{2+} was found to be 93.68%, 94.73% and 95.78% (Amen et al., 2020).

In the binary experiments shown the toxic metals adsorption could be competitive hence increase ionic mobility. In the binary solutions where the Cd^{2+} and Pb^{2+} coexist, Pb^{2+} maximum adsorption capacity was higher than that of Cd^{2+} based on adsorption isotherms and the process of adsorption for Pb^{2+} is more favourable. Ions with high electricity prices and small hydrated ion radii in the reaction are more likely to experience ion exchange. The sorption behaviour of lead and cadmium was similar, as they are divalent cations and their sorption is subject to the same mechanisms, which depend on the temperature of pyrolysis and the biochar feedstock (Li et al., 2017). Zhengtao et al. (2019) found that biochar produced at 500 °C and 700 °C (higher temperatures) shows significantly higher surface areas and pH values than biochar produced during a temperature of 300 °C.

The binary system of lead and mercury ions at concentrations of 5:5, 10:10, 25:25 and 50:50 mg/L recorded removal efficiencies ranging from 98.20% to 100% for lead and 100% for mercury ions in GB350, SB350 and GS350 (Table 1). Except for GB350 that recorded 98.49% removal efficiency for lead ion with concentration of 25:25 mg/L (Table 1). With the exception of GB350, which had a removal efficiency of 98.49% for lead ions at a concentration of 25:25 mg/L (Table 1). The biochar prepared at a pyrolysis temperature of 700 ± 5 °C showed 100% removal efficiency for both lead and mercury ions at concentrations of 5:5, 10:10, 25:25 and 50:50 mg/L (Table 1). The SB700 recorded a 98.49% removal efficiency for lead ions at a concentration of 50:50 mg/L (Table 1). The binary system of lead and mercury ions at concentrations of 5:5, 10:10, 25:25 and 50:50 mg/L recorded high removal efficiencies in GB350, SB350, GS350, SB700 and complete removal in GB700 and GS700 for lead ions and complete removal rates for mercury ions by GB350, SB350, GS350, GB700, SB700 and GS700. The order of adsorption of Pb and Hg ions on biochar was $Hg^{2+} > Pb^{2+}$. In a similar study, each metal in the binary system of Hg and Pb was almost 100% adsorbed at different lower contamination limits (Duwiejuah et al., 2018). Manyuchi et al. (2021) studied of chromium, copper, cyanide, iron, lead, and zinc removal using sawdust-based biochar from gold tailings wastewater shows effectively removal of the heavy metal ions from wastewater by 70%, signifying a strong correlation between the initial concentration of heavy metal ions and the retention time. A wide range of multiple operational factors influence adsorption of toxic metals. These include initial concentration of toxic metal, agitation speed, adsorbent dosage, temperature, adsorbent particle size, effect of pH solution on the adsorption capacity amongst other factors (Chojnacka, 2010).

The removal efficiencies of biochar prepared at a temperature of 350 ± 5 °C with concentrations of 5:5, 10:10, 25:25 and 50:50 mg/L ranged from 79.30% to 98.07% for cadmium and 99.96%–100% for mercury (Table 1). The minimum removal of 79.30% was obtained in SB350 at Cd concentration of 5:5 mg/L and 10:10 mg/L whilst GB350 recorded the maximum removal of 98.07% at concentration of 25:25 mg/L (Table 1). The removal efficiency recorded by GB700, SB700 and GS700 ranged from 92.79% to 100% for cadmium and 99.99%–100% for mercury with concentrations of 5:5, 10:10, 25:25 and 50:50 mg/L (Table 1). The minimum removal of 92.79% was observed by SB700 at Cd concentration of 10 : 10 mg/L whilst GB700 and GS700 recorded the maximum removal efficiency of 100% at concentration of 5:5 mg/L and 10:10 mg/L

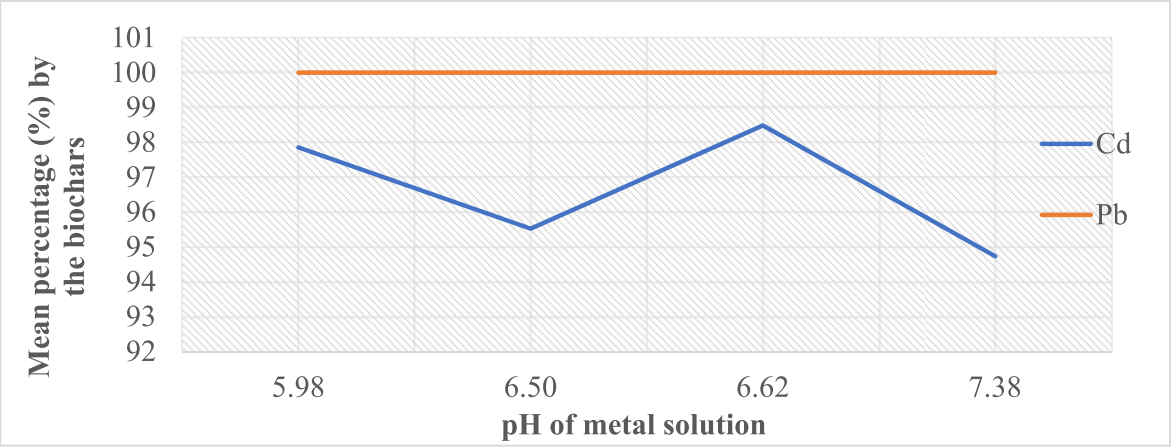

Figure 1. pH solution and mean removal efficiencies of the biochars in lead vrs cadmium.

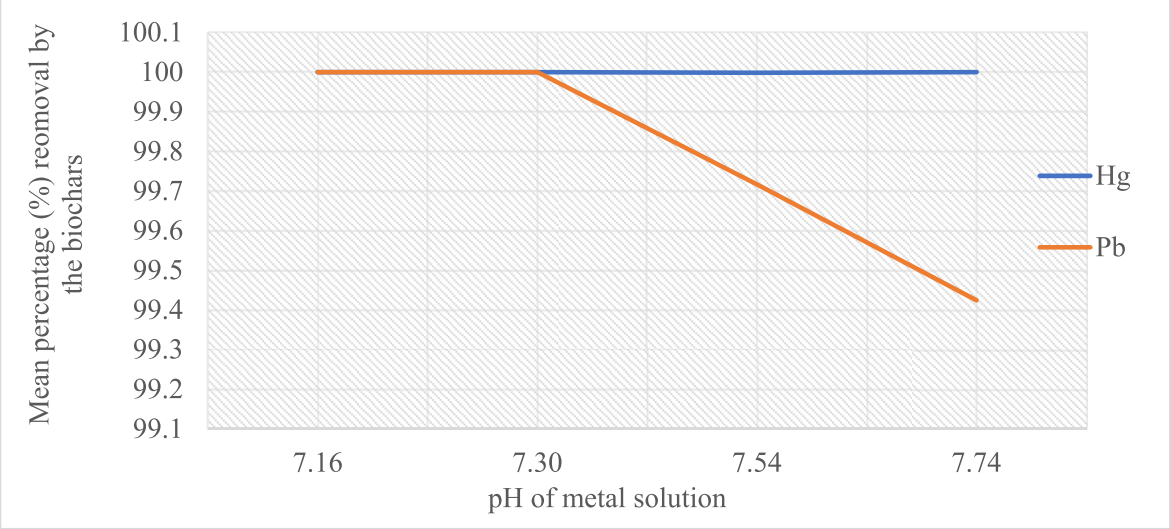

Figure 2. pH solution and mean removal efficiencies of the biochars in lead vrs mercury.

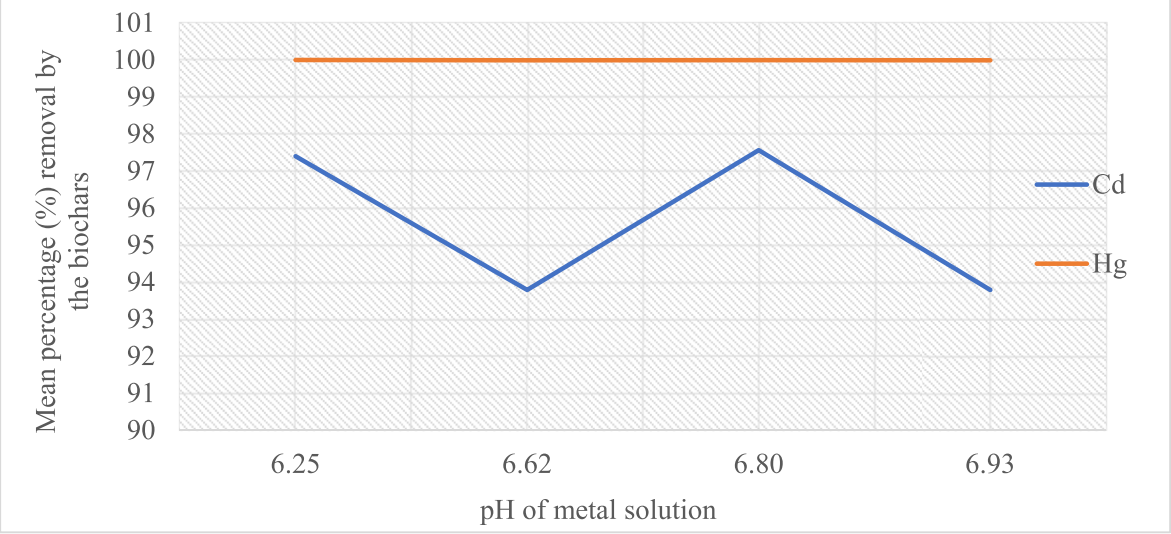

Figure 3. pH solution and mean removal efficiencies of the biochars in cadmium vrs mercury.

for GB700 (Table 1). Only SB700 showed 99.99% removal efficiency for mercury ions at a concentration of 50:50 mg/L (Table 1). The removal efficiencies of GB350, SB350, GS350, GB700, SB700 and GS700 for Cd and Hg with concentrations of 5:5, 10:10, 25:25 and 50:50 mg/L were high on average for cadmium and almost complete for all biochar for mercury. The order of adsorption of Cd and Hg ions on biochar was $Hg^{2+} > Cd^{2+}$. The affinity of biochar for mercury ions in the binary systems was greater than that for Cd ions. The removal rates of SB350 were different from GS350 and GS700. In a similar study, removal efficiencies of over 99.60% for Cd and 100% for Hg were found at different lower contamination limits in the mixed system of Cd and Hg (Duwiejuah et al., 2018). Recently, Yiyi et al. (2019) reported that 32.74 mg g^{-1} and 65.40 mg g^{-1} at 400 °C, and 27.31 mg g^{-1} and 54.60 mg g^{-1} at 700 °C as maximum adsorption capacity at 20 mg L^{-1} initial ion concentration in 24 h for cadmium and nickel ions, respectively. Akeem et al. (2019) reported 83.4 mg/g, 75.9 mg/g, and 72.8 mg/g as the maximum adsorption capacity at a pH of 6 for mercury, copper, and zinc, respectively. The peanut and sheanut shells biochars were effective and highly competitive during toxic metal ion adsorption, and its activity depends on process conditions, including temperature, initial concentration of the toxic metal ion, pH and retention time. Biochar has a distinctive properties and high thermal stability that make it a feasible candidate for a good number of industrial applications such as effective removal and adsorption of toxic metals (Zhang et al., 2021b).

The adsorption of Cd, Pb and Hg by peanut and sheanut biochars is not only related to surface cation exchange capacity, the pore structure, and type and number of biochar functional groups, but is also influenced by the solution pH, biochar dosage, temperature, presence of some cations in aqueous solution, type and initial concentration of toxic metals, and the ageing process of biochar. The effective removal can be attributable to the contact time of 60 min. This positive effect of the contact time of adsorbent enhance the efficient toxic metals removal from aqueous solution can be conclude that the more contact time allows binding in more adsorption sites (Song et al., 2013). The initial toxic metals ions when adsorb occur on the exterior adsorption sites of the biochar surface which can exhibit significant removal of the toxic metals at the initial stage but when adsorption contact time was more increased, the ions will then start to adsorb on the interior sites

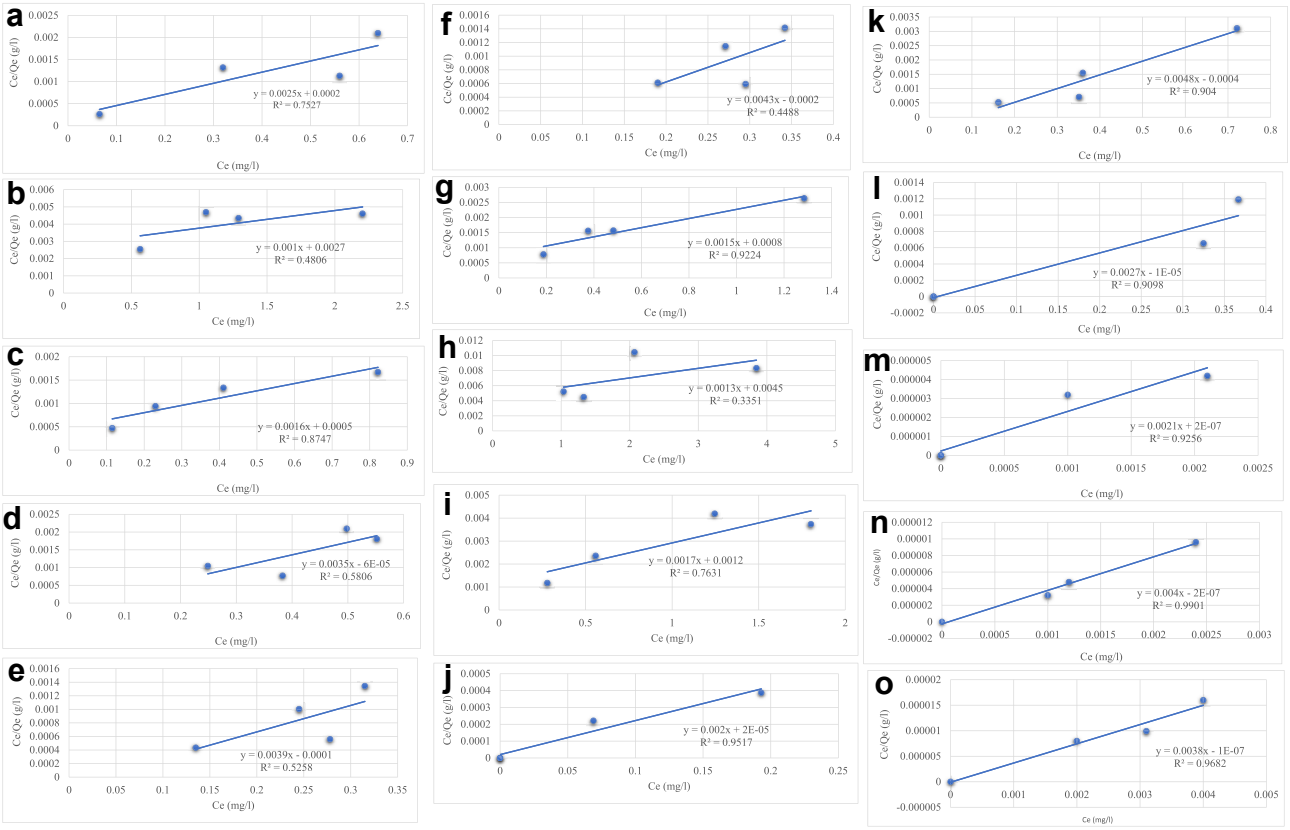

Figure 4. a: Langmuir isotherm for adsorption of **Cd** vrs Pb in binary aqueous solution onto GB350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). b: Langmuir isotherm for adsorption of **Cd** vrs Pb in binary aqueous solution onto SB350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). c: Langmuir isotherm for adsorption of **Cd** vrs Pb in binary aqueous solution onto GS350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). d: Langmuir isotherm for adsorption of **Cd** vrs Pb in binary aqueous solution onto GB700 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). e: Langmuir isotherm for adsorption of **Cd** vrs Pb in binary aqueous solution onto SB700 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). f: Langmuir isotherm for adsorption of **Cd** vrs Pb in binary aqueous solution onto GS700 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). g: Langmuir isotherm for adsorption of **Cd** vrs Hg in binary aqueous solution onto GB350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). h: Langmuir isotherm for adsorption of **Cd** vrs Hg in binary aqueous solution onto SB350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). i: Langmuir isotherm for adsorption of **Cd** vrs Hg in binary aqueous solution onto GS350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). j: Langmuir isotherm for adsorption of **Cd** vrs Hg in binary aqueous solution onto GB700 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). k: Langmuir isotherm for adsorption of **Cd** vrs Hg in binary aqueous solution onto SB700 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). l: Langmuir isotherm for adsorption of **Cd** vrs Hg in binary aqueous solution onto GS700 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). m: Langmuir isotherm for adsorption of **Hg** vrs Cd in binary aqueous solution onto GB350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). n: Langmuir isotherm for adsorption of **Hg** vrs Cd in binary aqueous solution onto SB350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). o: Langmuir isotherm for adsorption of **Hg** vrs Cd in binary aqueous solution onto GS350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min).

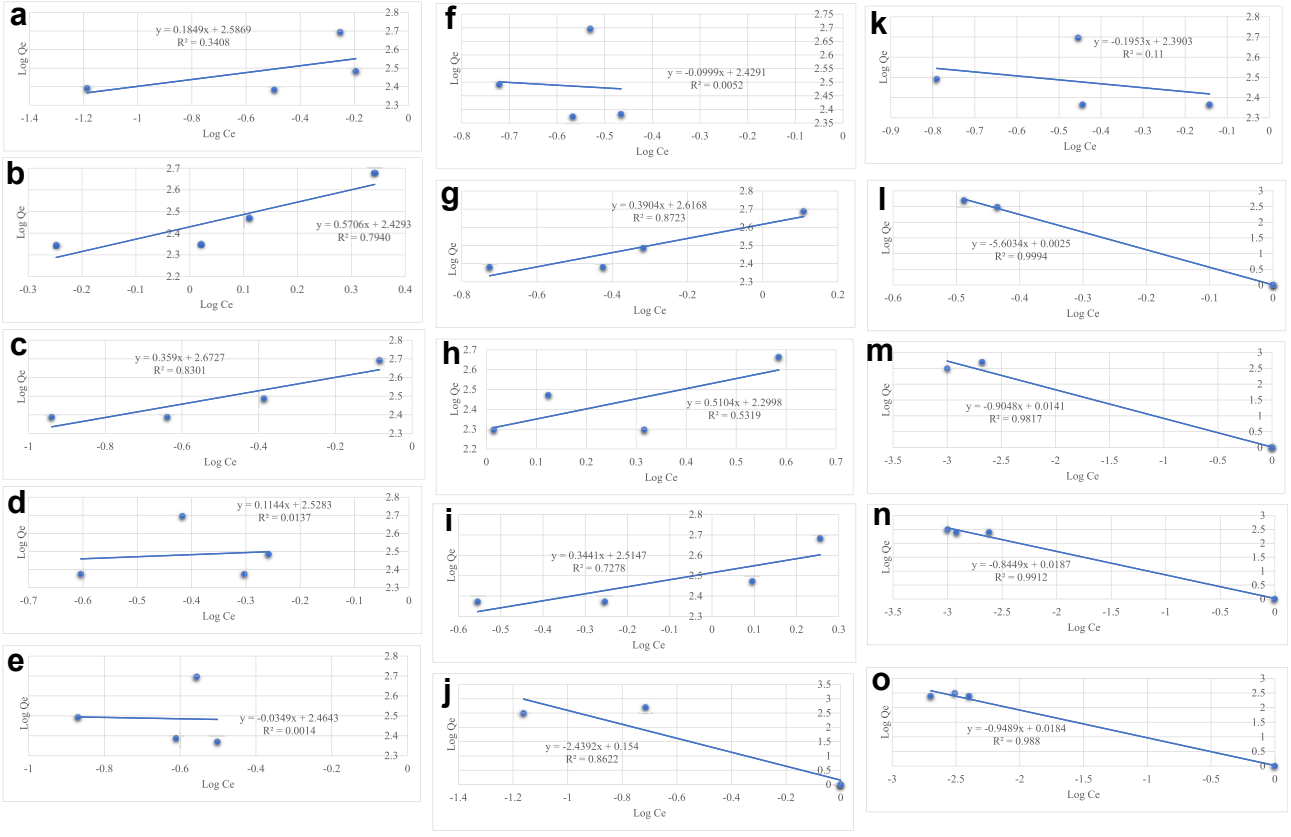

Figure 5. a: Freundlich isotherm for adsorption of **Cd** vrs Pb in binary aqueous solution onto GB350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). b: Freundlich isotherm for adsorption of **Cd** vrs Pb in binary aqueous solution onto SB350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). c: Freundlich isotherm for adsorption of **Cd** vrs Pb in binary aqueous solution onto GS350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). d: Freundlich isotherm for adsorption of **Cd** vrs Pb in binary aqueous solution onto GB700 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). e: Freundlich isotherm for adsorption of **Cd** vrs Pb in binary aqueous solution onto SB700 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). f: Freundlich isotherm for adsorption of **Cd** vrs Pb in binary aqueous solution onto GS700 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). g: Freundlich isotherm for adsorption of **Cd** vrs Hg in mono aqueous solution onto GB350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). h: Freundlich isotherm for adsorption of **Cd** vrs Hg in mono aqueous solution onto SB350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). i: Freundlich isotherm for adsorption of **Cd** vrs Hg in mono aqueous solution onto GS350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). j: Freundlich isotherm for adsorption of **Cd** vrs Hg in mono aqueous solution onto GB700 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). k: Freundlich isotherm for adsorption of **Cd** vrs Hg in mono aqueous solution onto SB700 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). l: Freundlich isotherm for adsorption of **Cd** vrs Hg in mono aqueous solution onto GS700 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). m: Freundlich isotherm for adsorption of **Hg** vrs Cd in mono aqueous solution onto GB350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). n: Freundlich isotherm for adsorption of **Hg** vrs Cd in mono aqueous solution onto SB350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min). o: Freundlich isotherm for adsorption of **Cd** vrs Hg in mono aqueous solution onto GS350 (solution volume: 100 mL; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min).

available on the biochar surface by a distinct mechanism recognised as the ion diffusion (Awwad and Salem, 2012). The peanut and Sheanut shells biochars can be used as cleaners, as there are economical, eco-friendly and potentially sustainable alternative to conventional materials used as adsorbent.

3.1. Relation between pH solution and adsorption performance in binary systems

The pH of Pb vrs Cd solution at 5:5, 10:10, 25:25 and 50:50 mg/L ranged from 5.98 to 7.38 with 100% removal efficiency for Pb and 88.70%–99.46% for Cd for the peanut and sheanut shells biochars (Figure 1). The pH of Pb vrs Hg solution at 5:5, 10:10, 25:25 and 50:50 mg/L ranged from 7.16 to 7.74 with removal efficiencies of 98.20%–100% for Pb and 100% for Hg for the biochar except SB350, which reached 99.99% (Figure 2). The pH of Cd vrs Hg solution at 5:5, 10:10, 25:25 and 50:50 mg/L ranged from 6.25 to 6.93 with removal efficiencies of 79.30%–100% for Cd and 99.96%–100% for Hg for the biochar (Figure 3).

The higher removal rates of Pb, Cd, and Hg by the biochar in the binary systems indicated that the pH solutions were good for adsorption. The high adsorption efficiencies may be a result of the relationship between the functional groups in the peanut and sheanut shells biochars structures and the OH^- (hydroxyl) and H^+ (hydrogen) ions in the solution. The most important factor determining the adsorption performance of the adsorbent is the pH of the solution (Ma et al., 2016). As pH can affect the pollutant and the adsorbent (Nigam et al., 2019).

When the pH changes, the adsorption efficiency changes as the OH^- (hydroxyl) and H^+ (hydrogen) ions in the environment intensely. High concentrations of H^+ protonated functional groups existed on the biochar surface at low pH (Elaigwu et al., 2014). Previous studies reported adsorption of more than 95.10% for Cd (II) and 95.20% for Pb(II) on ragweed biochar and horseweed biochar at pH 5.5 in binary system (Lian et al., 2020), and the highest adsorption capacities were found at an initial pH in the range of 5–6 for biochar derived from rich shells and manure (Kołodyn'ska et al., 2017; Shi et al., 2019). At lower pH, Lin et al. (2016) confirmed that the insoluble crystalline minerals dissolution in biochar will increase leading to the release of large number amount of

Table 2. Langmuir and Freundlich parameters for Pb, Cd and Hg in binary systems using biochars.

Ion	Biochar	Langmuir parameters				Freundlich parameters			
		Q_{max} (mg/g)	K_L (l/mg)	R_L	R^2	$^1/_n$	n	K_F (mg/g)	R^2
Cd vrs Pb	GB350	400.00	0.08	5.00	0.7527	0.18	5.41	386.28	0.3408
Cd vrs Pb	SB350	1000.00	2.70	136.00	0.4806	0.57	1.75	268.72	0.7940
Cd vrs Pb	GS350	625.00	0.31	16.63	0.8747	0.36	2.79	470.65	0.8301
Cd vrs Pb	GB700	285.71	-0.02	0.14	0.5806	0.11	8.74	337.52	0.0137
Cd vrs Pb	SB700	256.41	-0.03	-0.28	0.5258	-0.03	-28.65	291.27	0.0014
Cd vrs Pb	GS700	232.56	-0.05	-1.33	0.4488	-0.10	-10.01	268.60	0.0052
Cd vrs Hg	GB350	666.67	0.53	27.67	0.9224	0.39	2.56	413.81	0.8723
Cd vrs Hg	SB350	769.23	3.46	174.08	0.3351	0.51	1.96	199.43	0.5319
Cd vrs Hg	GS350	588.24	0.71	36.29	0.7631	0.34	2.91	327.11	0.7278
Cd vrs Hg	GB700	500.00	0.01	1.50	0.9517	-2.44	-0.41	1.43	0.8622
Cd vrs Hg	SB700	208.33	-0.08	-3.17	0.9040	-0.20	-5.12	245.64	0.1100
Cd vrs Hg	GS700	370.37	0.00	0.81	0.9098	-5.60	-0.18	1.01	0.9994
Hg vrs Cd	GB350	476.19	0.00	1.00	0.9256	-0.90	-1.11	1.03	0.9817
Hg vrs Cd	SB350	250.00	0.00	1.00	0.9901	-0.84	-1.18	1.04	0.9912
Hg vrs Cd	GS350	263.16	0.00	1.00	0.9682	-0.95	-1.05	1.04	0.9880

Table 3. Mineral composition of the peanut shell and sheanut shell biochars.

Sample	GB350	GB700	SB350	SB700
Al (mg/kg)	1858 ± 32	4326 ± 70	1172 ± 16	1408 ± 17
Ca (mg/kg)	5587 ± 96	13452 ± 34	3977 ± 41	3568 ± 70
Mg (mg/kg)	2498 ± 44	3414 ± 68	1150 ± 25	1694 ± 32
Mn (mg/kg)	170 ± 20	219 ± 30	119 ± 38	92 ± 40
Na (mg/kg)	328 ± 11	411 ± 20	192 ± 11	225 ± 30
K (mg/kg)	16309 ± 15	20873 ± 31	12945 ± 17	19885 ± 22
S (mg/kg)	962 ± 20	781 ± 21	426 ± 80	248 ± 40
P (mg/kg)	1273 ± 90	1948 ± 25	904 ± 26	1298 ± 12

cations (Ca^{2+}, K^+ and Mg^{2+}). Therefore, Pb and Cd, Pb and Hg, Cd and Hg compete at the peanut and sheanut shells biochars surfaces for the adsorption sites.

3.2. Langmuir and Freundlich isotherms for binary systems

The specific plots of adsorption for toxic metals in binary systems are shown Figure 4a to 4p and Figure 5a to 5p. For binary systems, maximum Langmuir capacity ranged from 250.00 to 1000.00 mg/g and 208.33–500.00 mg/g by for biochar prepared at slow and fast pyrolysis temperatures, respectively. The K_L for the binary system ranged from 0.08 to 3.46 l/mg for Cd and 0.00 l/mg for Hg in GB350, SB350 and GS350 and -0.08 to 0.01 l/mg for Cd by GB700, SB700 and GS700 (Table 2). R_L ranged from -3.17 to 174.08 for Cd and 2.00 for Hg in the binary systems. Langmuir R^2 for binary systems ranged from 0.3351 to 0.9901 for GB350, SB350 and GS350 and 0.4488 to 0.9517 for GB700, SB700 and GS700 (Table 2). In general, the n values obtained for binary systems ranged from -28.65 to 8.74 and 1.01 to 470.65 for K_F (Table 2). The Freundlich R^2 values for the binary systems ranged from 0.0014 to 0.9994 for the biochar (Table 2).

In the binary systems, the maximum Langmuir capacity of the Cd ions was greater than that of the Hg ions for the biochar at pyrolysis temperatures of 350 ± 5 °C and 700 ± 5 °C. The K_L (l/mg) and R_L for binary systems were of the order of Cd ion > Hg ion for biochar in binary systems. The separation factor $R_L > 1$ for Cd in binary systems which indicating an unfavourable adsorption process. The K_F, $^1/_n$ and n values for the metals by biochar followed the order of Cd > Hg in the binary systems. The Cd $^1/_n$ and n values are both positive and negative for Cd ion and negative for Hg ion in binary systems. The $^1/_n < 1$ for Cd and Hg means that normal adsorption occurs. The Langmuir model ($0.3351 \leq R^2 \leq 0.9901$) was better than the Freundlich model ($0.0014 \leq R^2 \leq 0.9994$) for the adsorption of toxic metal ions onto the biochar in the binary systems.

3.3. Adsorption mechanism of biochar in the binary systems

Understanding the adsorption mechanism of biochar is very important. There was a strong tendency of divalent cations to hydrate in aqueous solution, which was largely dependent on pH. Metal adsorption on biochar is influenced by inorganic minerals in addition to the cations of biochar. The highly effective removal of Pb in this study may indicate that the adsorption mechanisms of biochar include complexation, precipitation, and cation exchange (Lu et al., 2012). Mg and Ca (Table 3) might have supported the cation exchange that contributed to the adsorption on peanut and sheanut shell biochar, whilst the exchange with Na and K (Table 3) might be responsible for the complexation of Pb with carboxyl and hydroxyl groups. In conclusion, precipitation, cation exchange, and complexation were the main mechanisms responsible for the higher Pb removal rates, as the peanut and sheanut shell biochar were rich in minerals and phosphates.

Electrostatic interactions, precipitation, cation exchange, and surface complexation mechanisms are responsible for higher removal rates of Cd in this study. The peanut and sheanut shells biochars were rich in Ca, K, Mg and Na. A recent study reported that higher Ca and Mg concentrations in biochar played an important role in the adsorption of Pb (II) and Cd (II) in aqueous solutions through cation exchange, physical sorption, precipitation and surface complexation (Zhang et al., 2020). The cations released from water hyacinth biochar (sum of Ca, K, Mg and Na) were almost equal to the amount of adsorbed Cd, indicating that cation exchange plays a dominant role in the sorption of Cd onto biochar (Zhang et al., 2015). The high S and Cl content may have influenced the mechanism of Hg adsorption in the aqueous solutions on peanut and sheanut shell biochar. Different feedstocks used to prepare 36 biochar showed that high S biochar bound the Hg with S, while Hg in low S biochar was largely bound to Cl and O (Liu et al., 2016).

4. Conclusion

The peanut and sheanut shells biochars showed good removal efficiencies of Pb, Cd and Hg in the binary systems. The pH of the solutions was good for the adsorption. Langmuir isotherm model generally best fit the adsorption of toxic metal ions onto the biochars. Peanut and sheanut shells biochars were rich in Ca, K, Mg and Na influenced the mechanisms of Pb and Cd adsorption. The high S and Cl might have influenced the

mechanism of Hg adsorption in the aqueous solutions onto peanut and sheanut shells biochars. Peanut and sheanut shells biochars are of huge potential for toxic metal adsorption hence their effectiveness should be further tested in actual water polluted environment.

Declarations

Author contribution statement

Abudu Ballu Duwiejuah: Conceived and designed the experiments; Performed the experiments; Analysed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Albert Kojo Quainoo & Abdul-Halim Abubakari: Contributed reagents, materials, analysis tools or data; Wrote the paper.

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