

Full Length Research Paper

Adsorption of lead, cadmium, and mercury ions in aqueous solution using groundnut and sheanut shells biochars

Abudu Ballu Duwiejuah^{1*}, Abdul-Halim Abubakari², Albert Kojo Quainoo¹, Yakubu Amadu³ and Abdul-Aziz Bawa⁴

¹Department of Biotechnology, Faculty of Biosciences, University for Development Studies, Tamale, Ghana.

²Department of Horticulture, Faculty of Agriculture, Food and Consumer Sciences, University for Development Studies, Tamale, Ghana.

³Department of Statistics, Faculty of Physical Sciences, University for Development Studies, Tamale, Ghana.

⁴Spanish Laboratory Complex, University for Development Studies, Nyankpala Campus, Tamale, Ghana.

Received 16 March 2022; Accepted 1 June 2022

The adsorption performance of toxic ions and effect of initial pH using groundnut shells and sheanut shells biochars were studied to ascertain the practical and theoretical basis of the use of biochars to remediate water pollution. Biochars were prepared using groundnut and sheanut shells as the feed stocks. The removal efficiencies of lead (Pb) were 100%, > 65.90% for cadmium (Cd) and 96.70% for mercury (Hg) in mono systems of 5, 10, 25 and 50 mg/l. The maximum Langmuir capacity ranged from 400 to 2000 mg/g for Cd and 232.56 to 312.50 mg/g for Hg by biochars. The adsorption of toxic metal ions by groundnut and sheanut shells biochars showed similar removal efficiencies. Adsorption of Pb, Cd and Hg were effective in the varied pH which was largely dependent on the characteristics of groundnut and sheanut shells biochars determined by the pyrolysis conditions and nature of feed stock. Langmuir isotherm was the model that best fit the adsorption of toxic metal ions onto the biochars. Groundnut and sheanut shells biochars have proven to be good candidates for the remediation of water polluted with toxic metals in mono systems.

Key words: Groundnut and sheanut shells biochars, lead, mono systems, removal efficiencies.

INTRODUCTION

Lead, cadmium, mercury are usually considered as priority contaminants due to their toxicity, persistent nature and are released in a large concentration into the environment (Wang and Chen, 2014). The use of biochar to remove toxic metals from water is essential and beneficial for environmental protection and human life.

Biochar has received increasing attention due to its cost and associated physico-chemical properties such as structured carbon matrix, wide surface area, and high porosity in recent years (Lebrun et al., 2019). The exceptional surface chemistry of biochar such as high surface area, high aromaticity, different functional groups

*Corresponding author. E-mail: aduwiejuah@uds.edu.gh. Tel: +233206616055.

and high alkalinity aid its high immobilisation/removal abilities for toxic metals in soil/water (O'Connor et al., 2018).

With the increasing environmental pollution, it is essential to pursue eco-friendly, economically feasible, sustainable and efficient solutions to solve the persistent global problems of food security, environmental pollution, and energy and resource shortages (Chen et al., 2020). Biochar in recent years, has been broadly applied for water treatment (Xing et al., 2020), waste management (Yang et al., 2020), and other purposes owing to its high structural stability, rich porous structure, and large surface area (O'Connor et al., 2018). Cadmium removal efficiency by biochars from *Eichornia crassipes* were more than 90 to 99.24% (Li et al., 2016). Percentage of Pb (II) removal was up to 99% in 40 min from aqueous solution using bamboo biochar and calcium sulphate (Hassan and Kaewsichan, 2016). Cd, Hg and Pb removal efficiency in mono system in lower concentrations was almost 100% onto biochars derived from groundnut, sheanut shells, and a combination of both of them (Duwiejuah et al., 2018).

Harmful components such as polycyclic aromatic hydrocarbons, toxic metals, perfluorochemicals, dioxins, and environmentally persistent free radicals may be produced due to the improper biomass feedstocks selection, conditions and methods preparation although biochar has been widely regarded as an eco-friendly material (Xiang et al., 2021). Recently, most studies are on the negative effects of biochar in the environment because of its potentially toxic components and several interactions with environment (Cui et al., 2021). Cadmium, mercury and lead occurrence in the environment is a major problem due to their toxicity and ability to cause disease. Cd, Hg and Pb are among the notorious toxic metals that has become a considerable global problem in the environment particularly in developing countries with insufficient resources and technological challenges. The utilisation of groundnut and sheanut shells biomasses will be cheaper in terms of cost, efficient and ecologically sustainable adsorbent for Pb, Cd and Hg removal which will guarantee food safety and drinking water by restoring the water contaminated in environment. Hence, the study investigated the adsorption performance of Pb, Cd and Hg ions and effect of initial pH and adsorbent dosage using groundnut shells and sheanut shells biochars.

MATERIALS AND METHODS

Preparation of biochars

Groundnut and sheanut shells were used to produce biochars (Plates 1 and 2) in the Agricultural Sub-sector Improvement Programme Laboratory. The feed stocks were collected from a processing centre, Nyohini, in the Tamale Metropolis. Groundnut and sheanut shells were kept in separate earthen pots and then transferred into a Gallenkamp muffle furnace with internal dimensions of 18" x 8.5" x 7.5" High. The feed stocks were converted into biochar under a limited oxygen condition. The slow

pyrolysis of groundnut shell was done at $350 \pm 5^\circ\text{C}$ for 60 min (GB350: groundnut shells biochar produced at $350 \pm 5^\circ\text{C}$) and fast pyrolysis at $700 \pm 5^\circ\text{C}$ for 45 min (GB700: groundnut shells biochar produced at $700 \pm 5^\circ\text{C}$) in a muffle furnace. The slow pyrolysis of sheanut shell was done at $350 \pm 5^\circ\text{C}$ for 180 min (SB350: sheanut shells biochar produced at $350 \pm 5^\circ\text{C}$) and fast pyrolysis at $700 \pm 5^\circ\text{C}$ for 90 min (SB700: sheanut shells biochar produced at $700 \pm 5^\circ\text{C}$) in a muffle furnace. The difference in residence time of pyrolysis of groundnut and sheanut shells are due to their difference in lignocellulosic biomass (Duwiejuah, 2017). After the pyrolysis step, the biochars were left to cool, crushed and sieved through 2 mm and used for the experiment.

Stock solution preparation and mono aqueous solutions

In the experiments, all chemicals used are at analytical purity and were obtained from Lab Aid, Accra and used without any further treatment. Distilled water was used in all the experiments. Lead nitrate ($\text{Pb}(\text{NO}_3)_2$: grade; GR, assay; 99.50%), cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$ grade; reagent CAS, assay; 99.99%), and mercury chloride (HgCl_2 grade; ACS reagent, assay; $\geq 99.50\%$) were obtained from Lab Aid in Accra, Ghana. The preparation of stock solutions were done by dissolving accurately weighted 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 $\text{Pb}(\text{NO}_3)_2$ (331.21 g/mol), $\text{Cd}(\text{NO}_3)_2$ (236.42 g/mol) and HgCl_2 (271.50 g/mol) were calculated and divided by atomic weight of Pb (207.20 g/mol), Cd (122.41 g/mol) and Hg (200.60 g/mol), respectively to obtain amount of compounds containing 1 mg (1000 ppm) of Pb, Cd, and Hg. Toxic metal solutions were prepared in a 1000 mL volumetric flask. Serial dilutions of the stock solution were done to obtain targeted concentrations of 5, 10, 25 and 50 mg/L.

Experiment for mono metal systems

The experiment was conducted from November to December, 2019. Adsorption studies in the mono metal system of Pb (II), Cd (II), and Hg (II) by GB350, GB700, SB350, SB700, GS350 (combination of groundnut and sheanut shells biochars produced at $350 \pm 5^\circ\text{C}$) and GS700 (combination of groundnut and sheanut shells biochars produced at $700 \pm 5^\circ\text{C}$) were carried out. 100 ml of toxic metal solution of concentration levels of 5, 10, 25 and 50 mg/L with varied adsorbent masses of 2, 4, 8 and 10 g, respectively were agitated at room temperature of 25°C in an orbital shaker (Rotabit orbital shaker with 20 - 230 rpm rotational) with speed rate of 14.6 ± 1 U/min for 60 min. The mono systems experiments were carried out at varied pH solutions that ranged from 5.48 to 7.70. Sufficient time of 60 min was provided for the system to ascertain equilibrium at 25°C constant room temperature. After settling, elute was filtered through a Whatman's qualitative filter paper with 125 mm \emptyset particle retention size. Elutes were preserved in an ice chest and transported to the University of Ghana, Ecological Laboratory, for analysis. The toxic metals' analysis was done using the Perkin Elmer PIN Accle 900T Graphite Atomic Absorption Spectrophotometer (Waltham, United States of America).

Calculation of mono metals removal efficiency

The adsorption capacity of toxic metal Q_e (mg of toxic metal per g of biochar) for each adsorption system was carried out using Equation 1:

$$Q_e = \frac{C_0 - C_e}{M} \times V \quad (1)$$



Plate 1. Groundnut shells biochar.
Source: Authors



Plate 2. Sheanut shells biochar.
Source: Authors

and the adsorption efficiency of cadmium, mercury and lead, Q_e (mg/g) in percentage was determined using Equation 2:

$$Q_e = \frac{(C_0 - C_e)V}{M} \times 100\% \quad (2)$$

where C_0 is initial concentrations (mg/L), and C_e represents final concentrations (mg/L), V is volume of metal solutions (L) and M is the mass of biochar (g).

Adsorption isotherm using Langmuir and Freundlich models

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

model explains the quantitative monolayer formation of toxic metal on the biochar, outer surface and subsequently no further adsorption occurs. 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, Langmuir then exemplified the following Equation 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 Equation 3 to a linear form:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e} \quad (4)$$

Table 1. Removal efficiency of toxic metals using biochars produced during slow and fast pyrolysis (n = 72).

Metal	Conc (mg/L)	Slow pyrolysis			Fast pyrolysis		
		GB350	SB350	GS350	GB700	SB700	GS700
Pb	5	100	100	100	100	100	100
Pb	10	100	100	100	100	100	100
Pb	25	100	100	100	100	100	100
Pb	50	100	100	100	100	100	100
Cd	5	98.24	92.06	100	98.96	97.98	96.24
Cd	10	98.78	98.00	100	98.70	97.00	98.60
Cd	25	98.47	91.95	97.76	99.49	98.82	99.11
Cd	50	96.61	76.90	87.25	99.30	99.36	99.26
Hg	5	99.76	99.94	99.98	99.90	99.36	100
Hg	10	99.78	99.70	99.88	99.49	96.79	100
Hg	25	99.98	99.99	99.94	100	100	99.87
Hg	50	99.99	99.98	100	100	100	100

Source: Authors

where Q_{max} is the adsorption maximum capacity determined by Langmuir model; Q_e = the quantity of toxic metal adsorbed per gram at equilibrium by the biochar (mg/g); Q_0 = maximum capacity of monolayer coverage (mg/g); K_L = constant of Langmuir isotherm (l/mg); and C_e = the toxic metal (adsorbate) equilibrium concentration (mg/L⁻¹). The values of K_L and Q_{max} were determined using the slope and intercept of the plot of C_e vrs C_e/Q_e (Langmuir,

1918). The important feature of Langmuir isotherm may be the expression of equilibrium parameter (R_L), which is a dimensionless constant denoted as separation factor (Webber and Chakravarti, 1974).

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

where K_L = the constant that is associated to the energy of adsorption (Langmuir constant) and C_0 = initial concentration of adsorbate. The R_L is mostly used to ascertain whether the process of an adsorption was thermodynamically favourable or not: when $R_L = 0$, an irreversible adsorption; when $0 < R_L < 1$, favourable adsorption; when $R_L = 1$, a linear adsorption; when $R_L > 1$, an unfavourable adsorption (Gorgievski et al., 2013).

Adsorption isotherm of Freundlich is often used to describe the heterogeneous surface characteristics of adsorption (Hutson and Yang, 2000). Freundlich constants signify the nonlinearity degree between solution concentration and adsorption, and extent of the adsorption, respectively. The data usually fit the proposed empirical Equation 6 by Freundlich:

$$Q_e = K_F C_e^{1/n} \quad (6)$$

where Q_e = the quantity of toxic metal adsorbed per gram at equilibrium by the biochar (mg/g); K_F = Freundlich isotherm constant (mg/g); C_e = the adsorbate equilibrium concentration (mg/L); and n = adsorption intensity. Linearising equation is given as:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

The constant K_F is an estimated capacity of adsorption indicator, whilst $\frac{1}{n}$ is a function of the adsorption strength in the process of adsorption (Voudrias et al., 2002). If value of $\frac{1}{n}$ is below (>)1 indicates occurrence of a normal adsorption. If $\frac{1}{n}$ is above (<) 1, it shows co-operative adsorption and if $n = 1$ then the partition amongst the two phases are independent of the concentration (Mohan and Karthikeyan, 1997).

RESULTS AND DISCUSSION

The lead removal efficiency at concentrations of 5, 10, 25 and 50 mg/L were 100% for groundnut shell biochar (GB350), sheanut shell biochar (SB350) and combination of groundnut and sheanut shells biochars (GS350), groundnut shell biochar (GB700), and sheanut shell biochar (SB700) and combination of groundnut and sheanut shells biochars (GS700) (Table 1). The removal rate of Pb was highly effective by the groundnut and sheanut shells biochars. This may be due to O-containing functional groups that play a vital role in modifying Pb mobility. This is because biochar derived under low temperature pyrolysis gives high amount of O-containing functional groups which generally showed good efficiency for toxic metal stabilisation (Ahmad et al., 2014). Also, biochars produced under high temperature had higher removal rates due to the presence of high pores and surface area. Biochars vary greatly in properties and capacity to adsorb the toxic metals. Other studies

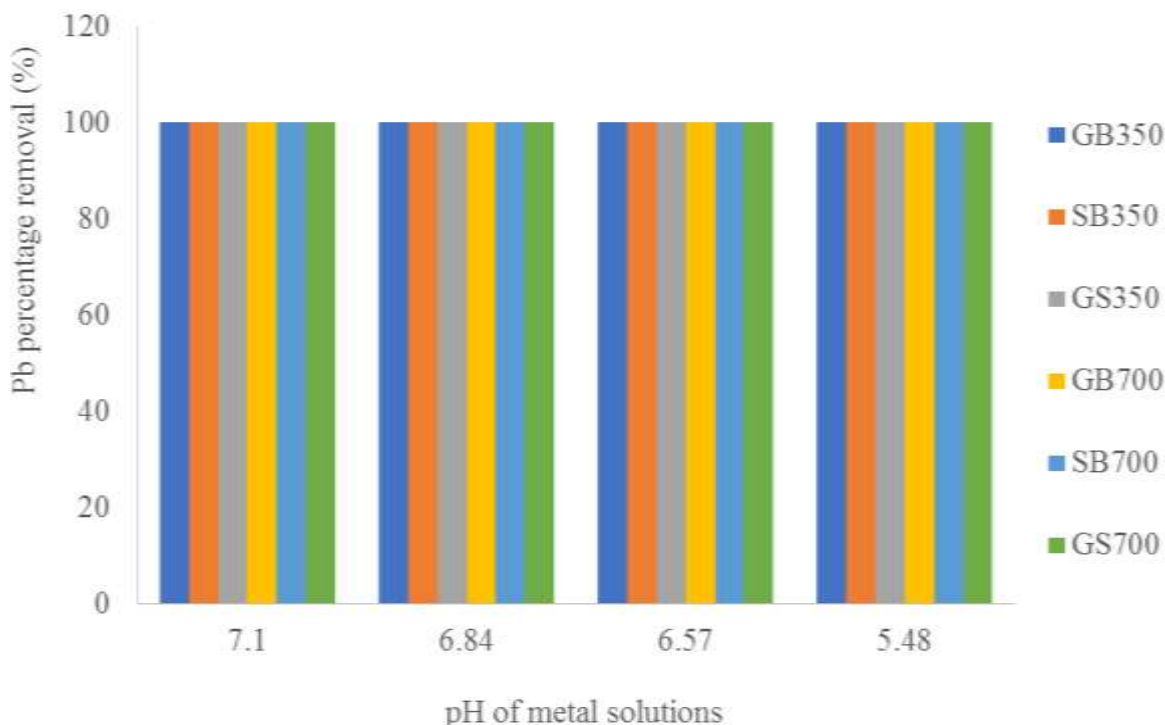


Figure 1. Effect of pH on Pb adsorption in mono system using biochars produced during slow and fast pyrolysis
Source: Authors

conducted with different experimental conditions also show high percentage removal of Pb ion using various natural adsorbents such as chaff (85%), sun flower husk (86%), rice husk (90%), tea waste (98%), sesame husk (100%) (Surchi, 2011), bamboo biochar and calcium sulphate (99%) (Hassan and Kaewsichan, 2016), rice husk biochar (almost 90%) (Sanka et al., 2020) and rice and corn husk-based sorbents (>90%) (Rwiza et al., 2018). Mechanisms of non-electrostatic are deliberated as dominating for Pb (Clemente et al., 2017).

Cadmium removal efficiency at concentrations of 5, 10, 25 and 50 mg/L by groundnut shell, sheanut shell, and the combination of groundnut and sheanut shells biochars produced at temperatures of 350 ± 5 and $700 \pm 5^\circ\text{C}$ ranged from 76.90 to 100% and 96.24 to 99.49%, respectively (Table 1). The groundnut and sheanut shells biochars produced during fast pyrolysis recorded the highest Cd removal rates. Similar studies showed Cd^{2+} removal of almost 100% for municipal sewage sludge biochar (Chen et al., 2014), 90 to 99.24% for *Eichornia crassipes* biochars (Li et al., 2016), 80.60 to 96.90% for orange peel biochars (Tran et al., 2015), and 86.60% for soybean straw and 99.20% for peanut husk biochar (Cheng et al., 2016). Also, wheat straw biochar removal efficiency of Cd was up to ~90% (Cui et al., 2019) and almost 100% by palm waste biochar (700°C) from Cd polluted solutions which was attributed to functional groups (such as $-\text{CO}_3^{2-}$ and $-\text{OH}$ through surface

precipitation and surface complexation, respectively) of the biochar (Usman et al., 2016).

The removal efficiency of mercury ions in the aqueous solution with concentrations of 5, 10, 25 and 50 mg/L by biochars produced from groundnut shell, sheanut shell and the combination of groundnut and sheanut shells at a temperature of $350 \pm 5^\circ\text{C}$ ranged from 99.70 to 100% (Table 1). The biochars produced from groundnut shell, sheanut shell and the combination of groundnut and sheanut shell at temperature of $700 \pm 5^\circ\text{C}$ had removal efficiency ranging from 96.79 to 100% at the concentrations of 5, 10, 25 and 50 mg/L in the prepared aqueous solution (Table 1). The adsorption of toxic metals ions by groundnut and sheanut shells biochars produced during the slow and fast pyrolysis showed similar removal efficiencies. Comparable, high removal of 67.77 to 95.96% for Pb^{2+} and 92.12 to 99.05% for Cd^{2+} from drinking water by biochar obtained from peanut shell, "chonta" pulp and corn cob calcined at 500, 600 and 700°C , respectively (Puglla et al., 2020).

Effect of pH on the adsorption of biochars towards mono metal ions

The pH of solutions of 5.48 to 7.10, 7.30 to 7.70 and 6.20 to 6.91 in the mono systems (Figures 1 to 3) were more effective for Pb, Cd and Hg removal. This was largely

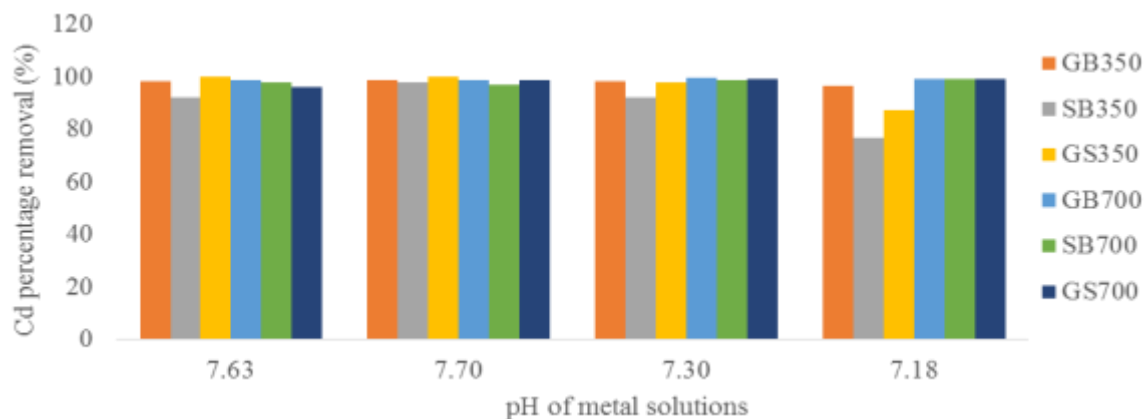


Figure 2. Effect of pH on Cd adsorption in mono system using biochars produced during slow and fast pyrolysis. Source: Authors

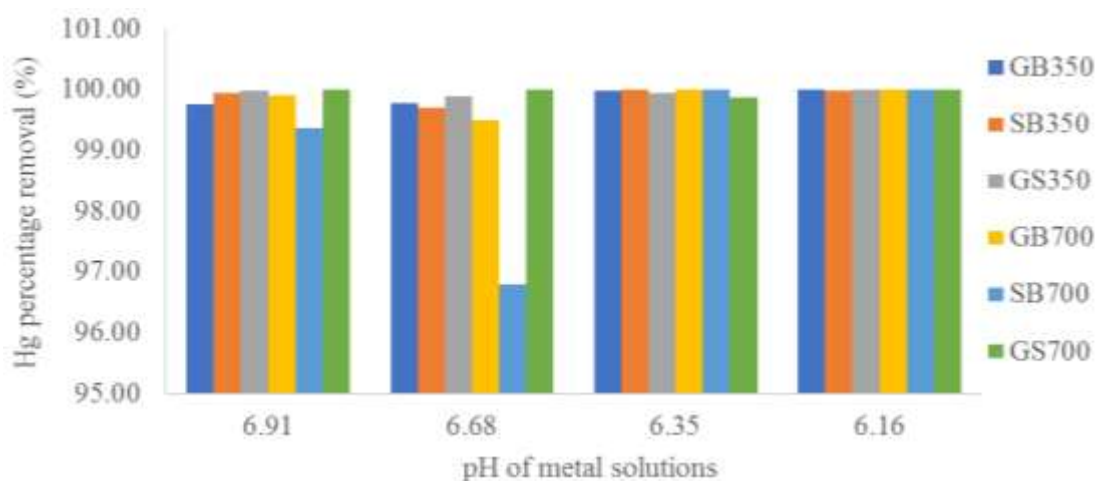


Figure 3. Effect of pH on Hg adsorption in mono system using biochars produced during slow and fast pyrolysis. Source: Authors

dependent on the characteristics of groundnut and sheanut shells biochars determined by the pyrolysis conditions and nature of feed stock. The nutrient content, structure of porosity, phenolic content and pH of biochar depend on the raw material type, temperature and duration of the pyrolysis process (Xu et al., 2021). The surface properties, the adsorbed toxic metal ions distribution, and functional groups protonation on adsorbent are affected by pH of solution (Sun et al., 2014).

Effect of biochar dosage on adsorption performance

The study revealed at biochar dosage of 2 g/5 mg/L, 4 g/10 mg/L, 8 g/25 mg/L and 10 g/50 mg/L Pb removal

efficiency was 100% (Figure 4), 76.90 to 100% for Cd (Figure 5) and 96.79 to 100% for Hg for the biochars (Figure 6). Dosage of biochar affects toxic metal removal in an aqueous solution. The experiment showed the various dosages were effective for metals removal. High amount of biochar 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 sites available for adsorption is followed by increase of an adsorbent specific surface area (Thavamani and Rajkumar, 2013). This causes the higher removal efficiencies by the groundnut and shea nut shells biochars under the various dosages and elevated contaminations limits. The toxic metal ions were nearly completely adsorbed at perspective dosages, and

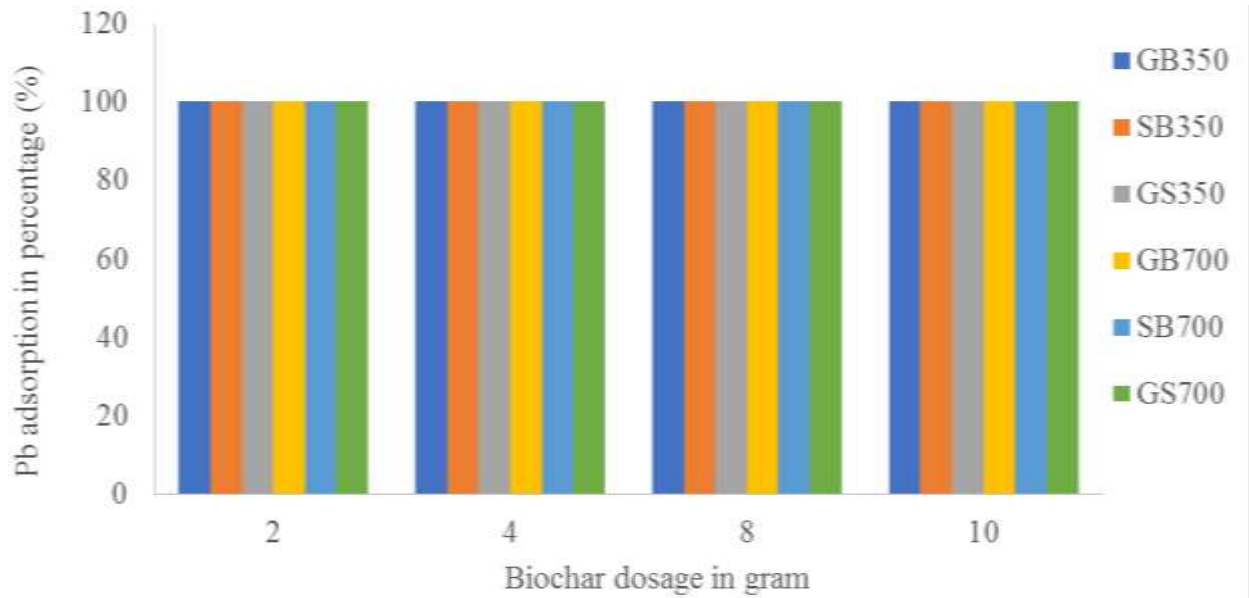


Figure 4. Effect of biochar dosage on Pb in mono system.
Source: Authors

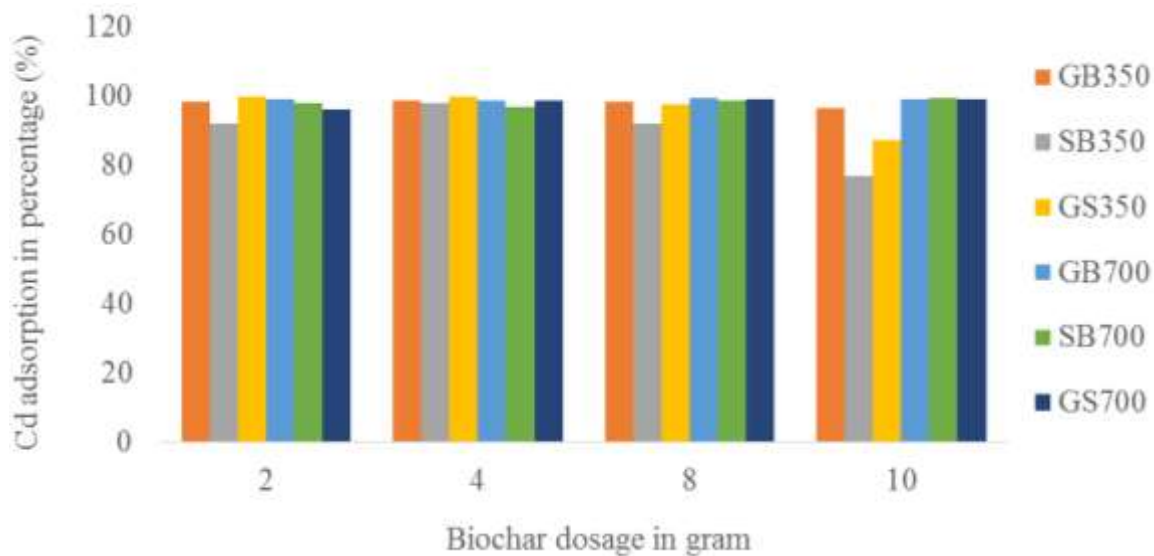


Figure 5. Effect of biochar dosage on Cd in mono system.
Source: Authors

variation of removal efficiencies was negligible with the various biochars.

Adsorption isotherms for mono metals

Langmuir model explains the quantitative monolayer formation of Cd and Hg on the biochar, outer surface and subsequently no further adsorption occurs. The specific

plots of adsorption (C_e/Q_e) against C_e (the equilibrium concentration) for toxic metals that did not ascertain complete adsorption in mono systems (Figure 7a to l as supplementary material). Pb adsorption was complete hence Langmuir graphs could not be plotted. The slope and intercept of the Langmuir graphs were used to compute for the linear isotherm values of Q_{max} and K_L and the R^2 (coefficient of determinations) (Table 2). The

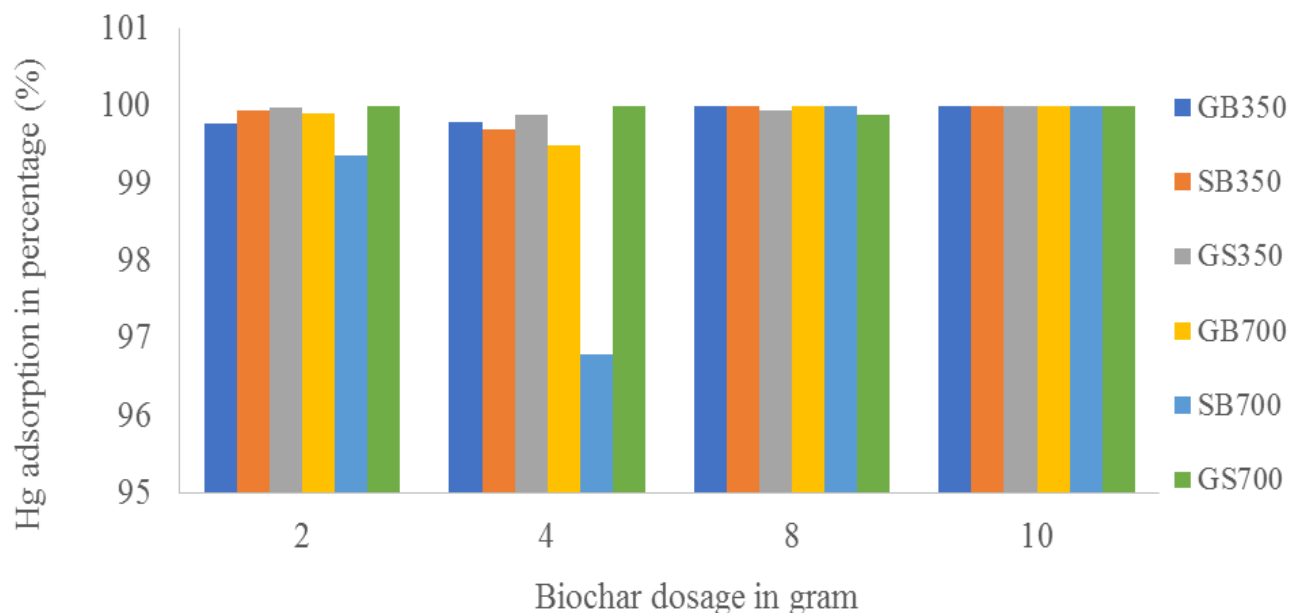


Figure 6. Effect of biochar dosage on Hg in mono system.
Source: Authors

Table 2. Modelling the results of adsorption isotherms of Cd and Hg.

Ion	Biochar	Langmuir parameter				Freundlich parameter			
		Q_{max} (mg/g)	K_L (l/mg)	R_L	R^2	$1/n$	n	K_F (mg/g)	R^2
Cd	GB350	526.32	0.16	8.89	0.9907	0.23	4.27	412.19	0.9711
Cd	SB350	400.00	0.36	19.00	0.9975	0.08	12.82	275.80	0.9123
Cd	GS350	434.78	0.09	5.35	0.9986	1.25	0.80	12.84	0.1500
Cd	GB700	666.67	0.13	7.67	0.8354	0.37	2.71	657.81	0.7673
Cd	SB700	416.67	0.08	5.17	0.4672	0.31	3.26	484.28	0.2543
Cd	GS700	2000.00	1.20	61.00	0.2855	0.78	1.29	1017.42	0.8942
Hg	GB350	232.56	0.00	0.94	0.9982	-0.30	-3.35	73.05	0.7202
Hg	SB350	243.90	0.00	0.93	0.9803	-0.02	-58.82	288.00	0.0039
Hg	GS350	294.12	0.00	1.01	0.9748	-0.87	-1.15	2.29	0.7929
Hg	GB700	250.00	0.00	1.00	1.00	-1.15	-0.87	1.46	0.8642
Hg	SB700	243.90	0.00	0.99	1.00	-1.60	-0.63	2.51	0.6666
Hg	GS700	312.50	0.00	0.99	0.9999	-0.97	-1.03	1.62	0.8578

Source: Authors

maximum Langmuir capacity ranged from 400 to 526.32 mg/g for Cd and 232.56 to 294.12 mg/g for Hg by GB350, SB350 and GS350 and 416.67 to 2000 mg/g for Cd and 243.90 to 312.50 mg/g for Hg by GB700, SB700 and GS700 (Table 2). The maximum Langmuir capacity was in the order of Cd ion > Hg ion and was larger for biochars produced during fast pyrolysis than in slow pyrolysis. The Langmuir constant (K_L) reflects how many the toxic metals interact with the biochar. The bigger constant value implies strong association between the

toxic metal and the biochar and, small constant value indicates weak interaction (Tran et al., 2019). The K_L ranged from 0.09 to 0.36 l/mg for Cd and 0.00 l/mg for Hg by GB350, SB350 and GS350 and 0.08 to 1.20 l/mg for Cd and 0.00 l/mg for Hg by GB700, SB700 and GS700 (Table 2). The K_L (l/mg) was in the order of Cd ion > Hg ion for biochars produced at both 350 ± 5 and $700 \pm 5^\circ\text{C}$. From the results, the value of K_L for Cd and Hg indicates weak interaction. The separation factor R_L was found to be in order of Cd ion > Hg ion. The R_L was found to have

ranged from 5.17 to 61.00 for Cd and 0.93 to 1.01. The $R_L > 1$ for Cd ions indicates unfavourable adsorption process. However, GB350, SB350, SB700 and GS700 for Hg were less than 1 indicating favourable adsorption.

Freundlich isotherm was used to explore the data fitness in terms of the biochars surface heterogeneous nature in toxic metal uptake. The specific plots of $\log Q_e$ against $\log C_e$, give a slope with the value of $1/n$ and an intercept magnitude of $\log K_F$ (Figure 8a to l as supplementary material). Pb adsorption was complete hence Freundlich graphs could not be plotted. The adsorption intensity (n) values were found to have ranged from -58.82 to 12.82 and 1.46 to 1017.42 for K_F (adsorption capacity) (Table 2). The K_F for the metals by biochars followed the order of Cd > Hg. The $1/n$ and n values for the metal ions by biochars followed the order of Cd > Hg. The Cd $1/n$ and n values are positive, and negative for Hg ions. The $1/n < 1$ for Cd and Hg implies a normal adsorption occurred. In the case of Cd, almost all n values were between one and ten, implying the process of adsorption was favourable whilst all n values for Hg were less than 1 implying the degree of nonlinearity between adsorption and solution concentration as physical process. The Langmuir model ($0.2855 \leq R^2 \leq 1.00$) was better fitted for the adsorption toxic metal ions onto biochar than the Freundlich model ($0.0039 \leq R^2 \leq 0.9711$).

Conclusion

The adsorption of Pb, Cd and Hg ions by groundnut and sheanut shells biochars produced during slow and fast pyrolysis temperatures showed similar removal efficiencies. The adsorption performance of groundnut and sheanut shells biochars was highly effective at pH range of 5.48 to 7.70. Langmuir isotherm was the model that best fit the adsorption of toxic metal ions onto the biochars except for SB700 and GS700 that recorded low R^2 . Groundnut and sheanut shells biochars have proven to be good candidates for the remediation of water polluted with toxic metals.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

ACKNOWLEDGEMENTS

The authors are grateful to the staff of Ecological Laboratory of University of Ghana, especially Mr. Prince Owusu (Laboratory Technician) for his swift and timely analysis of the samples. They are grateful to Ghana Government for the provision of the Book and Research Allowance, which was used in funding this study.

REFERENCES

- Ahmad M, Lee SS, Lim JE, Lee SE, Cho JS, Moon DH, Hashimoto Y, Ok YS (2014). Speciation and phytoavailability of lead and antimony in a small arms range soil amended with mussel shell, cow bone and biochar: EXAFS spectroscopy and chemical extractions. *Chemosphere* 95:433-441.
- Chen G, Wang C, Tian J, Liu J, Ma Q, Liu B, Lia X (2020). Investigation on cadmium ions removal from water by different raw materials-derived biochars. *Journal of Water Process Engineering* 35:101223.
- Chen T, Zhang Y, Wang H, Lu W, Zeyua Z, Zhang Y, Ren L (2014). Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge. *Bioresource Technology* 164:47-54.
- Cheng Q, Huang O, Khan S, Liu Y, Liao Z, Li G, Ok GS (2016). Adsorption of Cd by peanut husks and peanut husk biochar from aqueous solutions. *Ecological Engineering* 87:240-245.
- Clemente JS, Beauchemin S, MacKinnon T, Martin J, Johnston CT, Joern B (2017). Initial biochar properties related to the removal of As, Se, Pb, Cd, Cu, Ni, and Zn from an acidic suspension. *Chemosphere* 170:216-224.
- Cui H, Li D, Liu X, Fan Y, Zhang X, Zhang S, Zhou J, Fang G, Zhou J (2021). Dry-wet and freeze-thaw aging activate endogenous copper and cadmium in biochar. *Journal of Cleaner Production* 288:125605.
- Cui L, Noerpel MR, Scheckel KG, Ippolito JA (2019). Wheat straw biochar reduces environmental cadmium bioavailability. *Environment International* 126:69-75.
- Duwiejah AB (2017). Eco-friendly biochars for the adsorption of heavy metals from aqueous phase. Master's thesis submitted in partial fulfillment of the requirements for degree of Master of Philosophy in Biotechnology in University for Development Studies.
- Duwiejah AB, Cobbina SJ, Quainoo AK, Abubakari AH, Bakobie N (2018). Comparative assessment of the adsorption of potentially toxic metals from mono and multi-metal systems groundnut and shea nut shell biochars. *Journal of Health and Pollution* 8(18):6-19.
- Freundlich HMF (1906). Über die adsorption in losungen. *Zeitschrift für Physikalische Chemie (Leipzig)*, 57: 385 - 470.
- Gorgievski M, Božić D, Stanković V, Štrbac N, Šerbula S (2013). Kinetics, equilibrium and mechanism of Cu^{2+} , Ni^{2+} and Zn^{2+} ions biosorption using wheats traw. *Ecological Engineering* 58:113-122.
- Hassan A, Kaewsichan L (2016). Removal of Pb (II) from aqueous solutions using mixtures of bamboo biochar and calcium sulphate, and hydroxyapatite and calcium sulphate. *Environment Asia* 9(1):37-44.
- Hutson ND, Yang RT (2000). Theoretical basis for the Dubinin-Radushkevitch (D-R) adsorption isotherm equation. *Adsorption* 3(3):189-195
- Langmuir I (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of American Chemical Society* 40:1361-1403.
- Lebrun M, Miard F, Nandillon R, Scippa GS, Bourgerie S, Morabito D (2019). Biochar effect associated with compost and iron to promote Pb and As soil stabilization and *Salix viminalis* L. growth. *Chemosphere* 222:810-822.
- Li F, Shen K, Long X, Wen J, Xie X, Zeng X, Liang Y, Wei Y, Lin Z, Huang W, Zhong R (2016). Preparation and characterization of biochars from *Eichornia crassipes* for cadmium removal in aqueous solutions. *PLoS One* 11(2):1-13.
- Mohan S, Karthikeyan J (1997). Removal of lignin and tannin color from aqueous solution by adsorption on to activated carbon solution by adsorption on to activated charcoal. *Environmental Pollution* 97:183-187.
- O'Connor D, Peng T, Zhang J, Tsang DCW, Alessi DS, Shen Z, Bolan NS, Hou D (2018). Biochar application for the remediation of heavy metal polluted land: a review of in situ field trials. *Science of the Total Environment* 619-620:815- 826.
- Puglla EP, Guaya D, Tituana C, Osorio F, García-Ruiz MJ (2020). Biochar from agricultural by-products for the removal of lead and cadmium from drinking water. *Water* 12(10):2933.
- Rwiza MJ, Oh SY, Kim KW, Kim SD (2018). Comparative sorption isotherms and removal studies for Pb (II) by physical and thermochemical modification of low-cost agrowastes from Tanzania.

- Chemosphere 195:135-145.
- Sanka PM, Rwiza MJ, Mtei KM (2020). Removal of selected heavy metal ions from industrial wastewater using rice and corn husk biochar. *Water, Air and Soil Pollution* 231(5):1-13.
- Sun J, Lian F, Liu Z, Zhu L, Song Z (2014). Biochars derived from various crop straws: characterization and Cd (II) removal potential. *Ecotoxicology and Environmental Safety* 106:226-231.
- Surchi KMS (2011). Agricultural wastes as low cost adsorbents for Pb removal: kinetics, equilibrium and thermodynamics. *International Journal of Chemistry* 3(3):103-112.
- Thavamani SS, Rajkumar R (2013). Removal of Cr (II), Pb (II) and Ni (II) from aqueous solution by adsorption on alumina. *Research Journal of Chemical Sciences* 3(8):44-48.
- Tran HN, You SJ, Chao HP (2015). Effect of pyrolysis temperatures and times on the adsorption of cadmium onto orange peel derived biochar. *Waste Management and Research* 34(2):129-138.
- Tran TH, Okabe H, Hidaka Y, Hara K (2019). Equilibrium and kinetic studies for silver removal from aqueous solution by hybrid hydrogels. *Journal of Hazardous Materials* 365:237-244.
- Usman A, Sallam A, Zhang M, Vithanage M, Ahmad M, Al-Farraj A, Ok YS, Abduljabbar A, Al-Wabel M (2016). Sorption process of date palm biochar for aqueous Cd (II) removal: efficiency and mechanisms. *Water, Air and Soil Pollution* 227(12):1-16.
- Voudrias E, Fytianos E, Bozani E (2002). Sorption description isotherms of dyes from aqueous solutions and waste waters with different sorbent materials, global nest. *The International Journal* 4(1):75-83.
- Wang J, Chen C (2014). Chitosan-based biosorbents: Modification and application for biosorption of toxic metals and radionuclides. *Bioresource Technology* 160:129-141.
- Webber TW, Chakravarti RK (1974). Pore and solid diffusion models for fixed-bed adsorbents. *AIChE Journal* 20(2):228-238.
- Xiang L, Liu S, Ye S, Yang H, Song B, Qin F, Shen M, Tan C, Zeng G, Tan X (2021). Potential hazards of biochar: The negative environmental impacts of biochar applications. *Journal of Hazardous Materials* 420:126611. <https://doi.org/10.1016/j.jhazmat.2021.126611>
- Xing W, Zhang M, Liang J, Tang W, Li P, Luo Y, Tang N, Guo J (2020). Facile synthesis of pinecone biomass-derived phosphorus-doping porous carbon electrodes for efficient electrochemical salt removal. *Separation and Purification Technology* 251:117357.
- Xu S, Chen J, Peng H, Leng S, Li H, Qu W, Hu Y, Li H, Jiang S, Zho W (2021). Effect of biomass type and pyrolysis temperature on nitrogen in biochar, and the comparison with hydrochar. *Fuel* 291:120128.
- Yang H, Ye S, Zeng Z, Zeng G, Tan X, Xiao R, Wang J, Song B, Du L, Qin M, Yang Y, Xu F (2020). Utilization of biochar for resource recovery from water: a review. *Chemical Engineering Journal* 397:125502.

Appendix

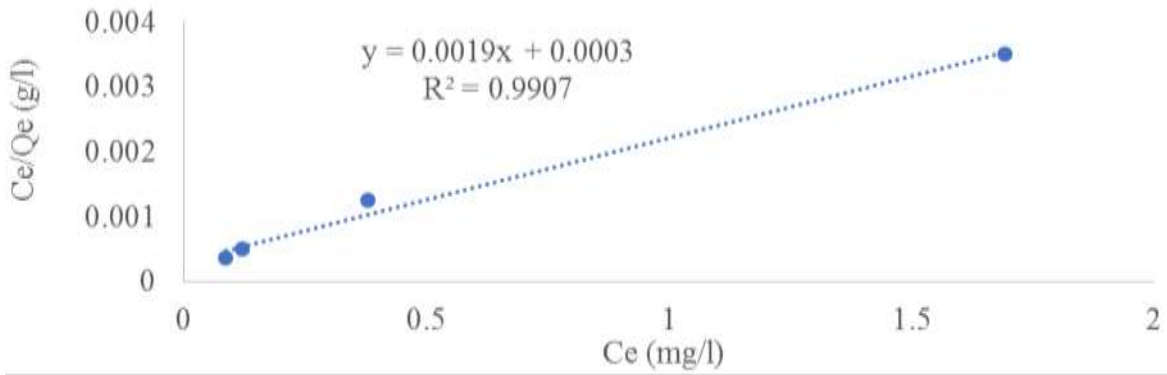


Figure 7a: Langmuir isotherm for adsorption of Cd in aqueous solution onto GB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

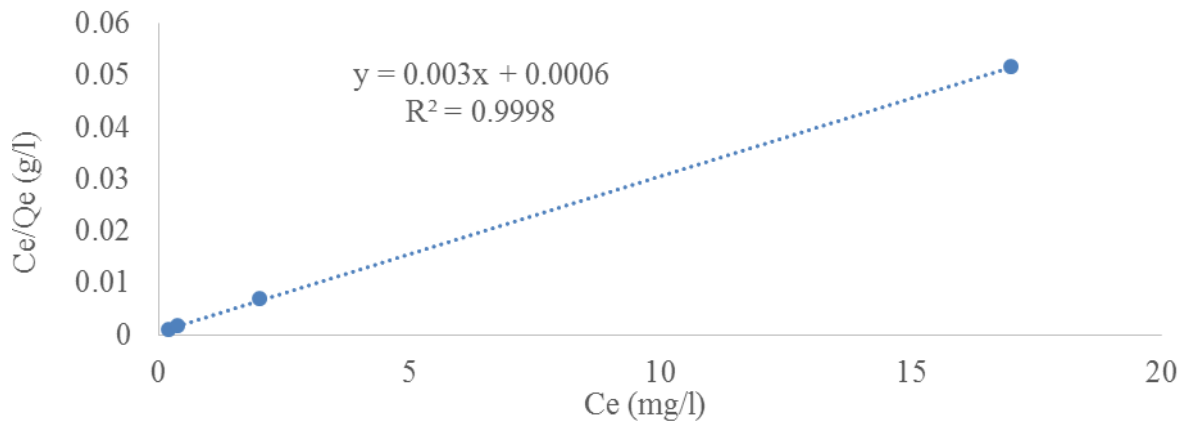


Figure 7b: Langmuir isotherm for adsorption of Cd in aqueous solution onto SB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

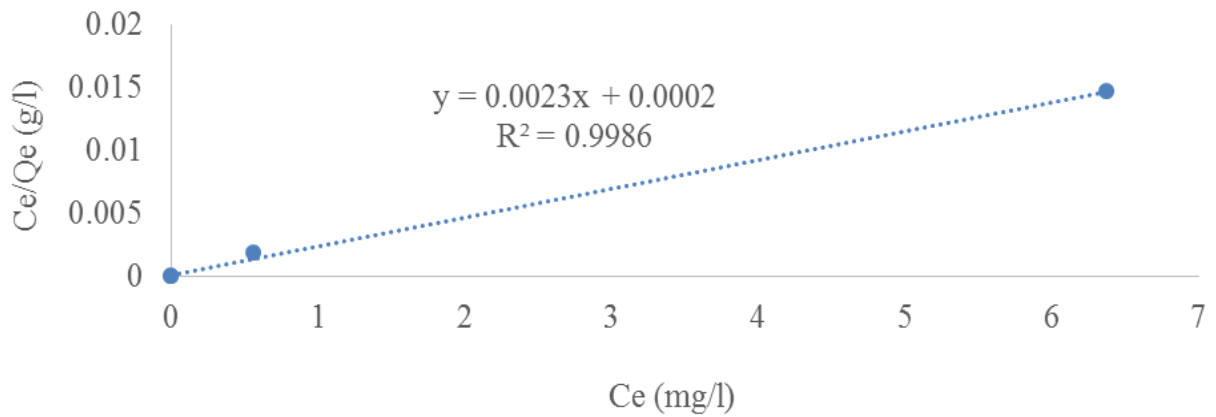


Figure 7c: Langmuir isotherm for adsorption of Cd in aqueous solution onto GS350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

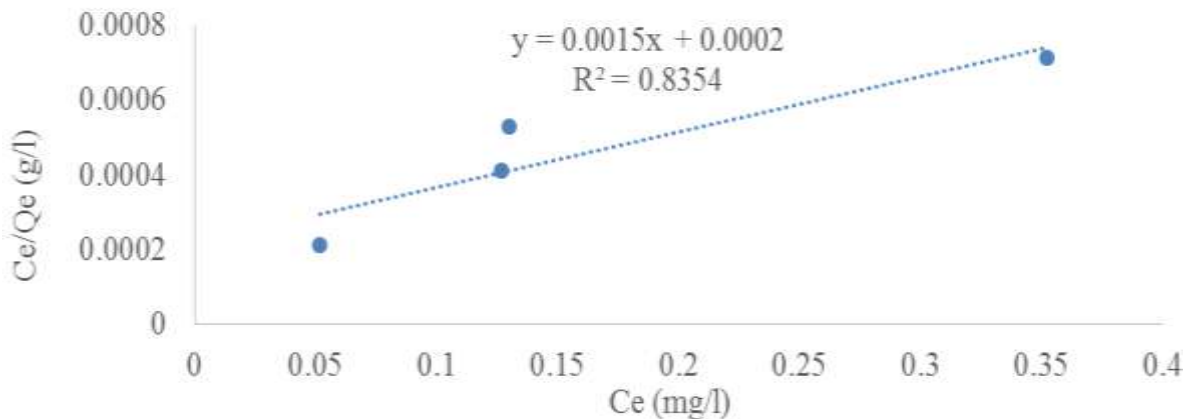


Figure 7d: Langmuir isotherm for adsorption of Cd in aqueous solution onto GB700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

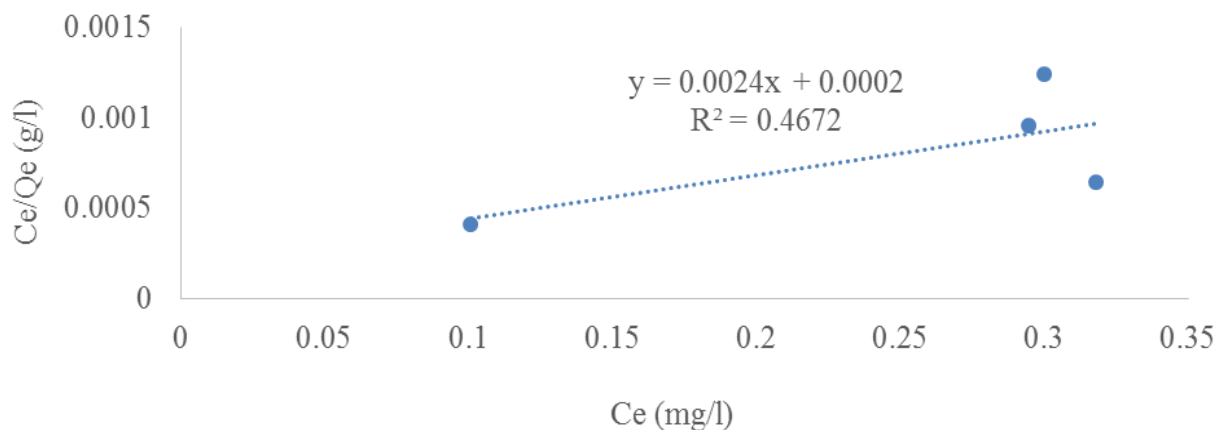


Figure 7e: Langmuir isotherm for adsorption of Cd in aqueous solution onto SB700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

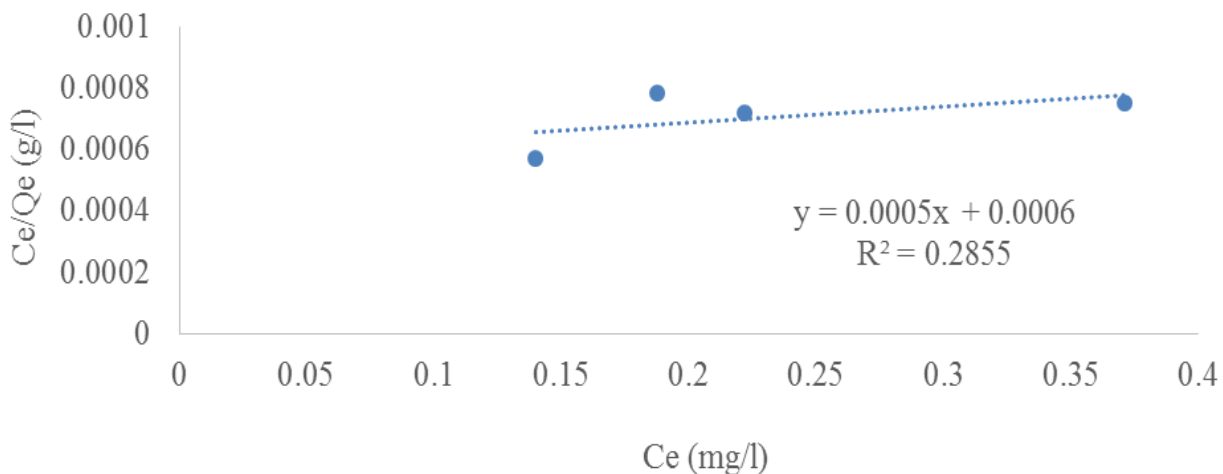


Figure 7f: Langmuir isotherm for adsorption of Cd in aqueous solution onto GS700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

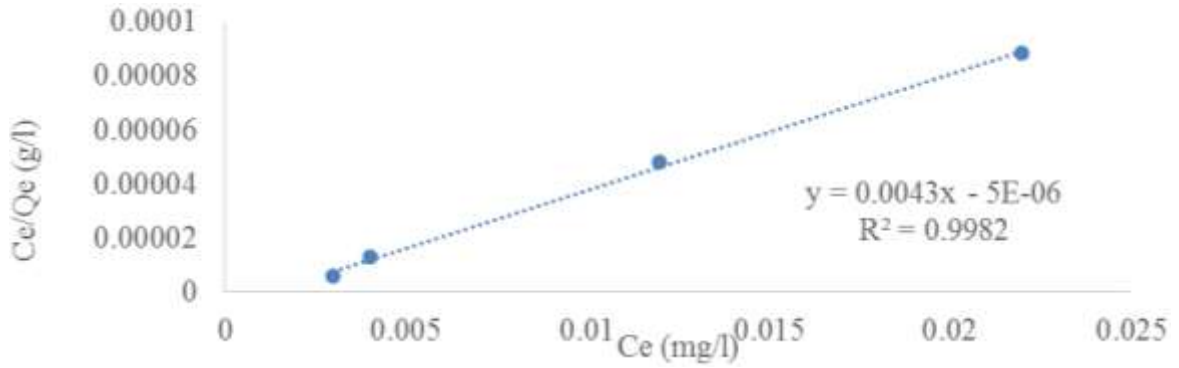


Figure 7g: Langmuir isotherm for adsorption of Hg in aqueous solution onto GB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

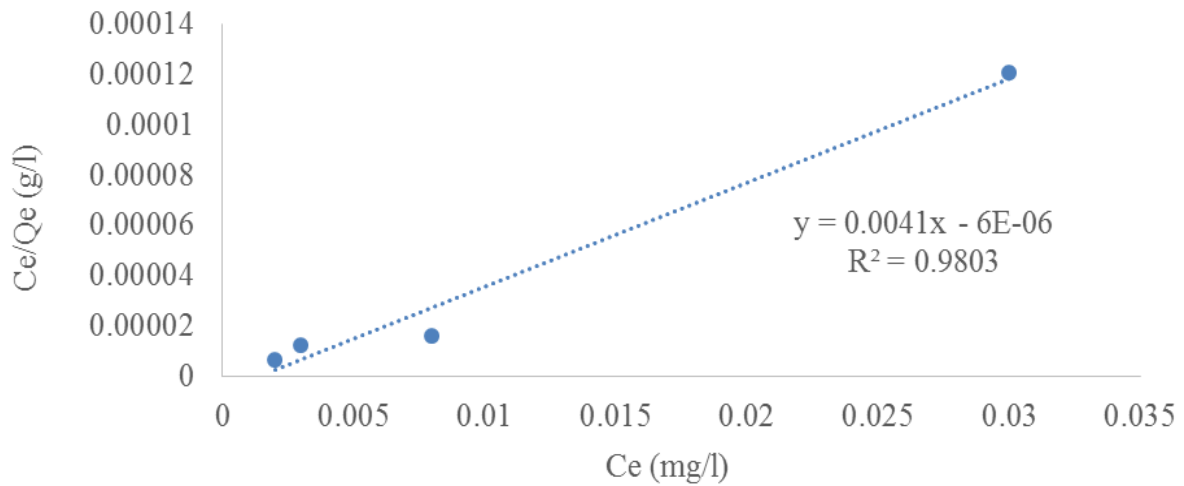


Figure 7h: Langmuir isotherm for adsorption of Hg in aqueous solution onto SB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

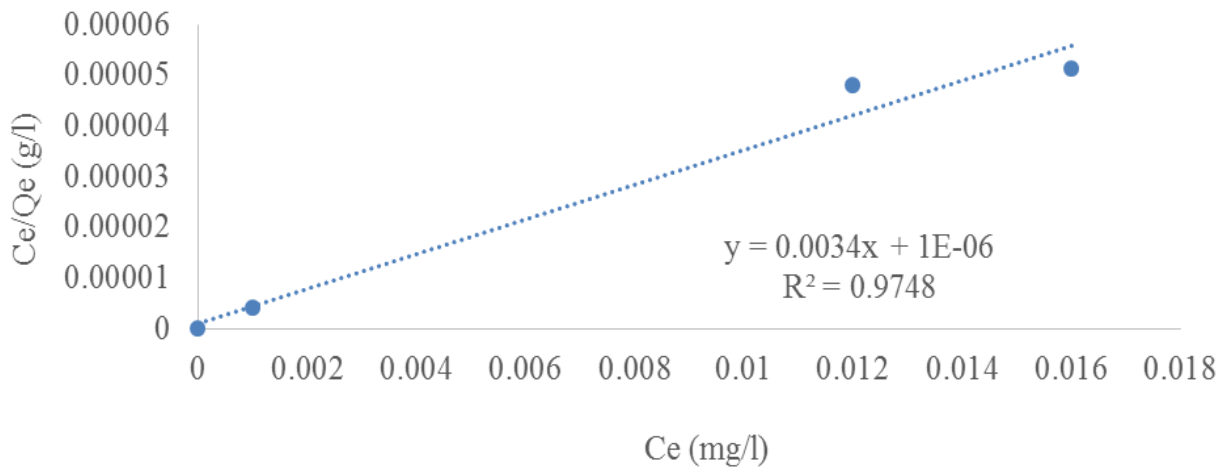


Figure 7i: Langmuir isotherm for adsorption of Hg in aqueous solution onto GS350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

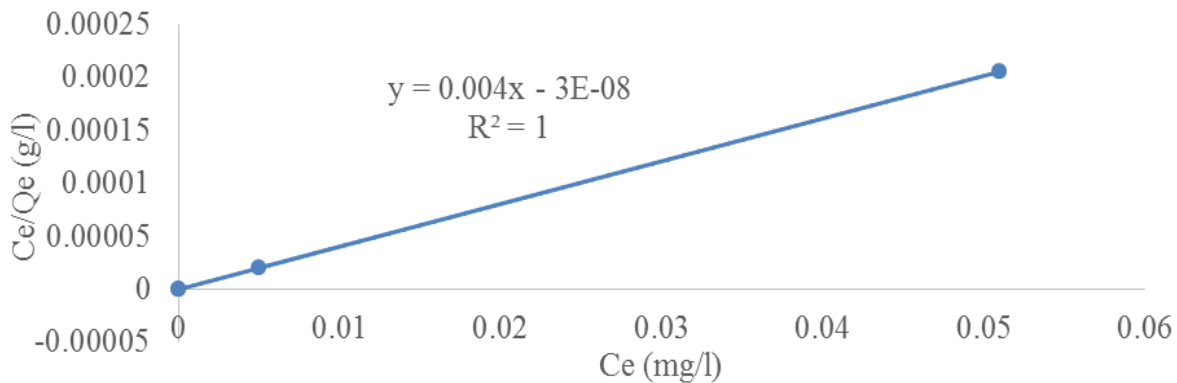


Figure 7j: Langmuir isotherm for adsorption of Hg in aqueous solution onto GB700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

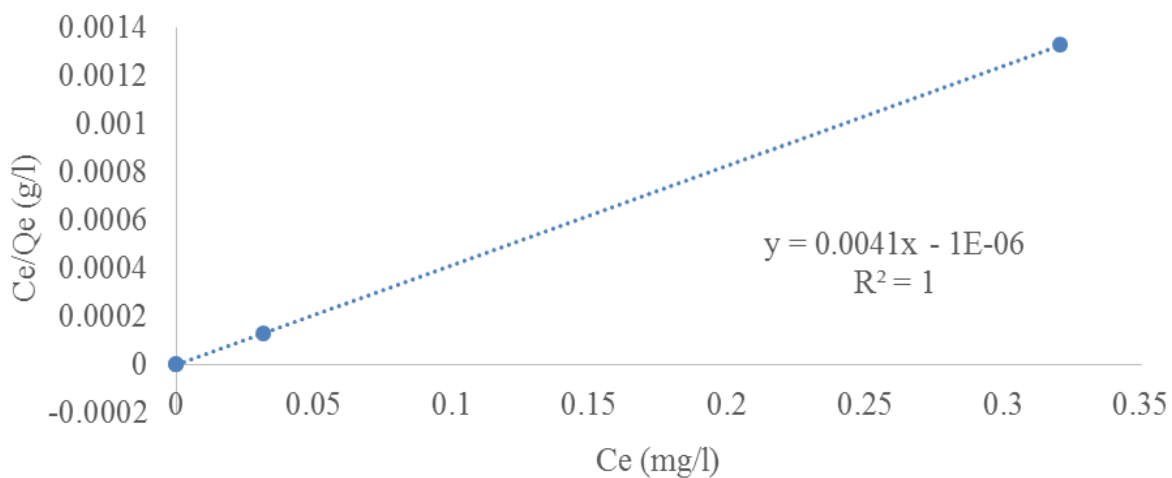


Figure 7k: Langmuir isotherm for adsorption of Hg in aqueous solution onto SB700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

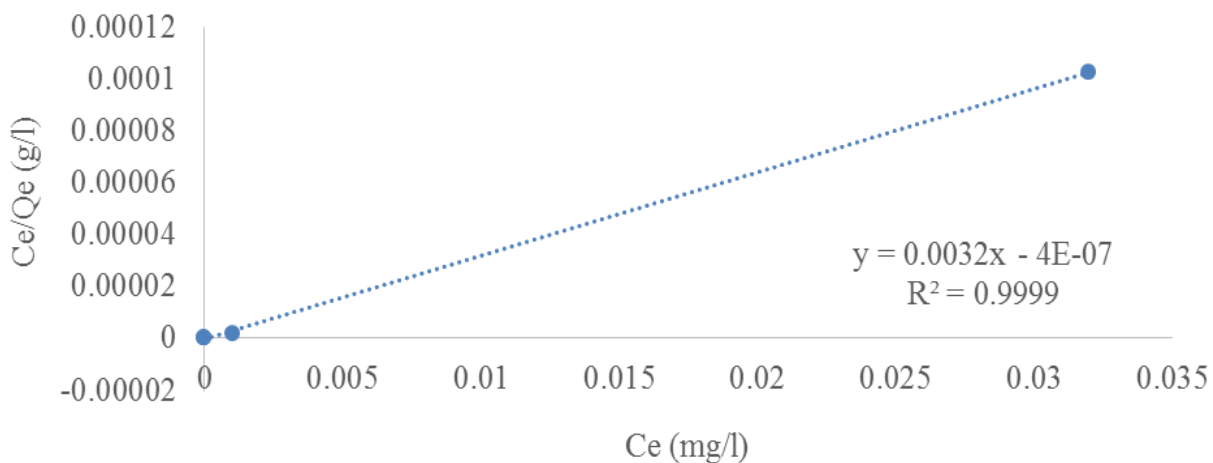


Figure 7l: Langmuir isotherm for adsorption of Hg in aqueous solution onto GS700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

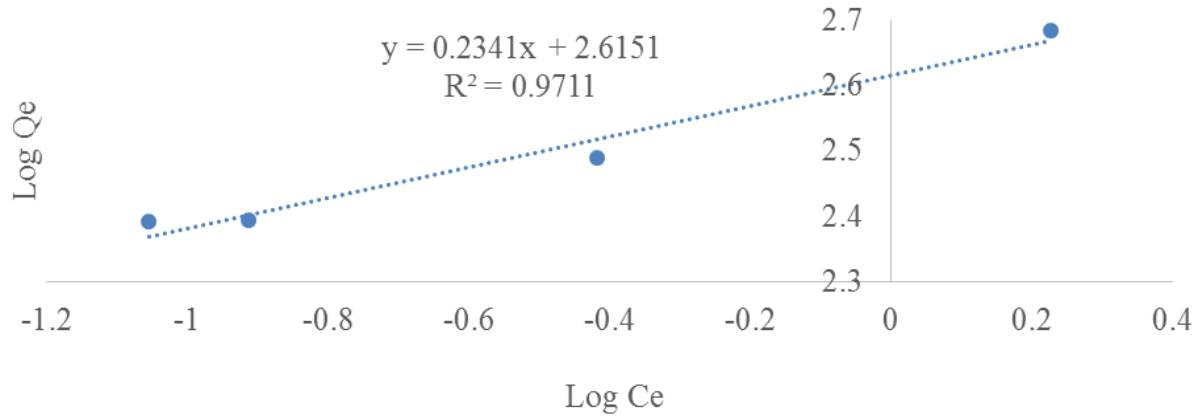


Figure 8a: Freundlich isotherm for adsorption of Cd in aqueous solution onto GB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

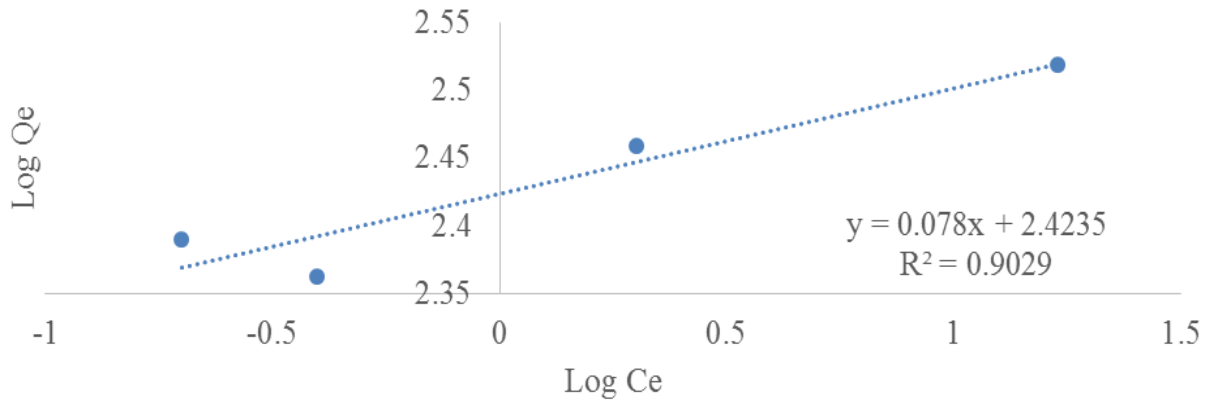


Figure 8b: Freundlich isotherm for adsorption of Cd in aqueous solution onto SB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors'

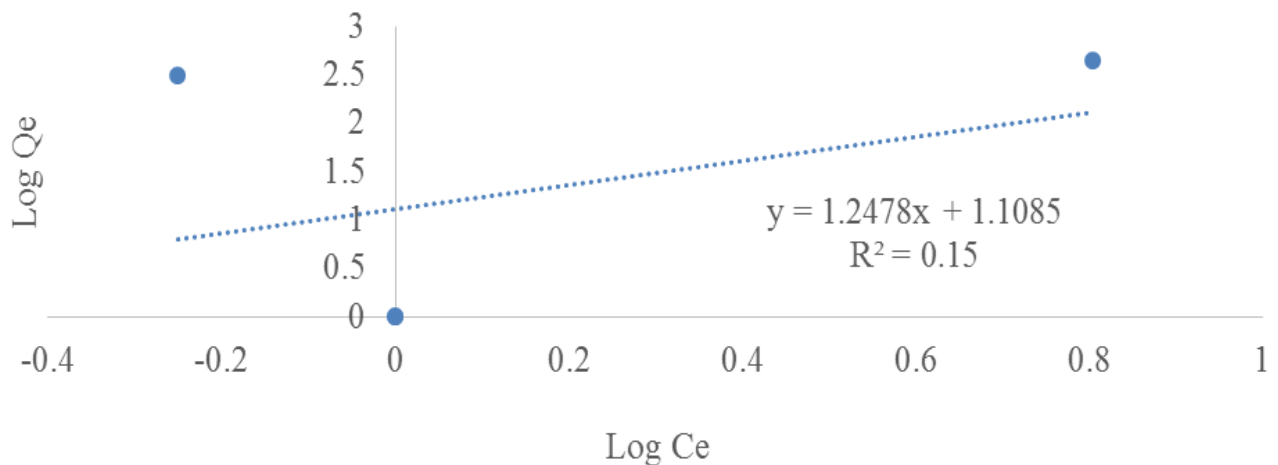


Figure 8c: Freundlich isotherm for adsorption of Cd in aqueous solution onto SB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

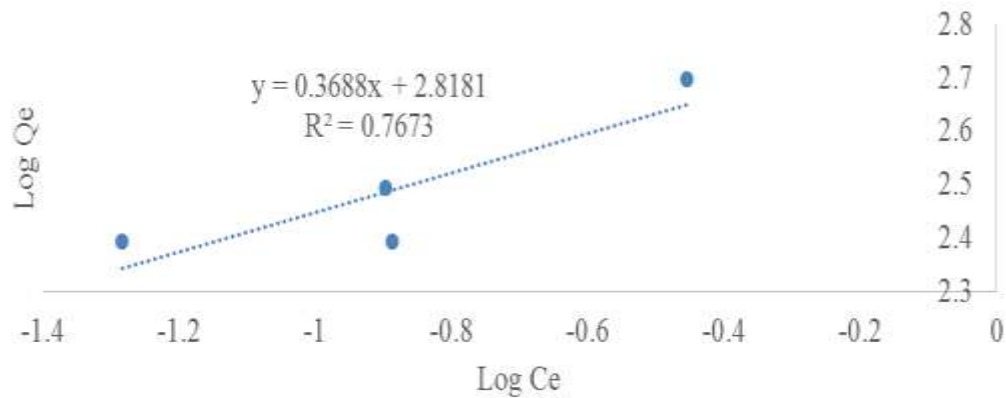


Figure 8d: Freundlich isotherm for adsorption of Cd in aqueous solution onto GB700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

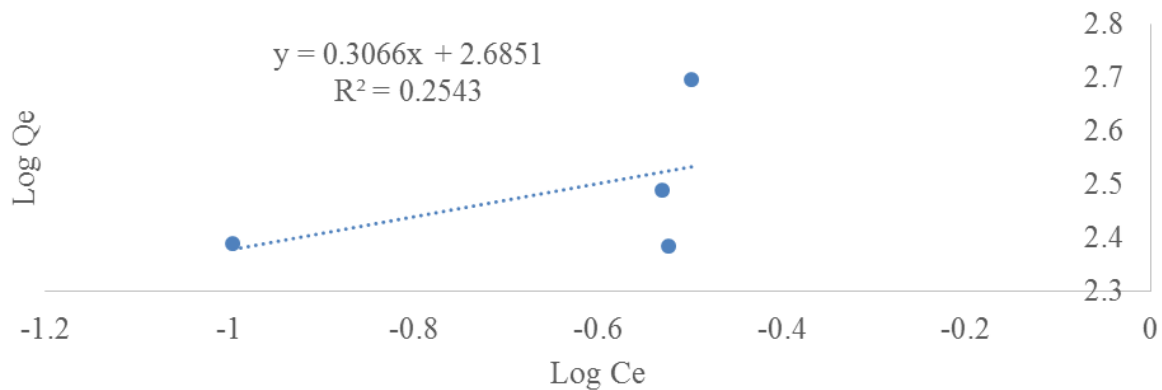


Figure 8e: Freundlich isotherm for adsorption of Cd in aqueous solution onto SB700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

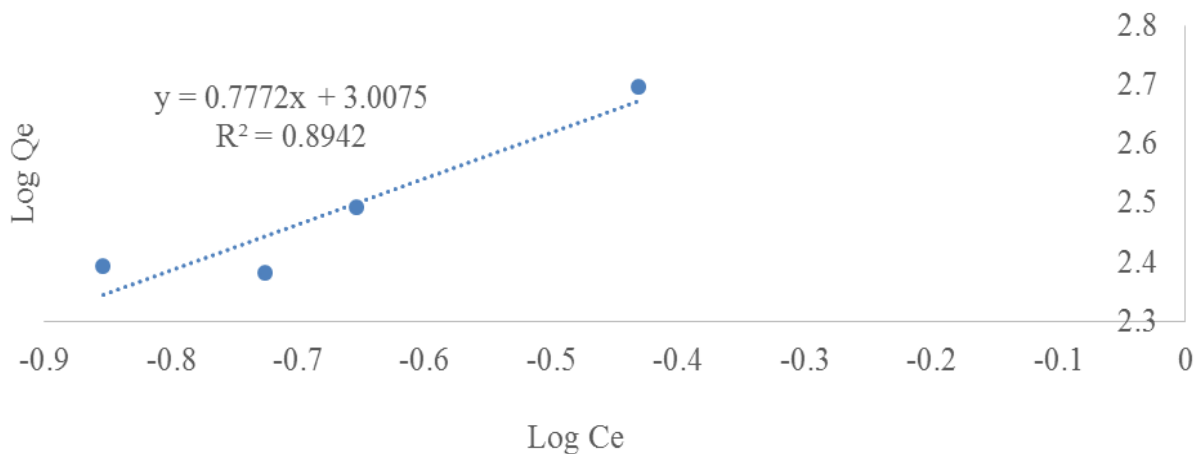


Figure 8f: Freundlich isotherm for adsorption of Cd in aqueous solution onto GS700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

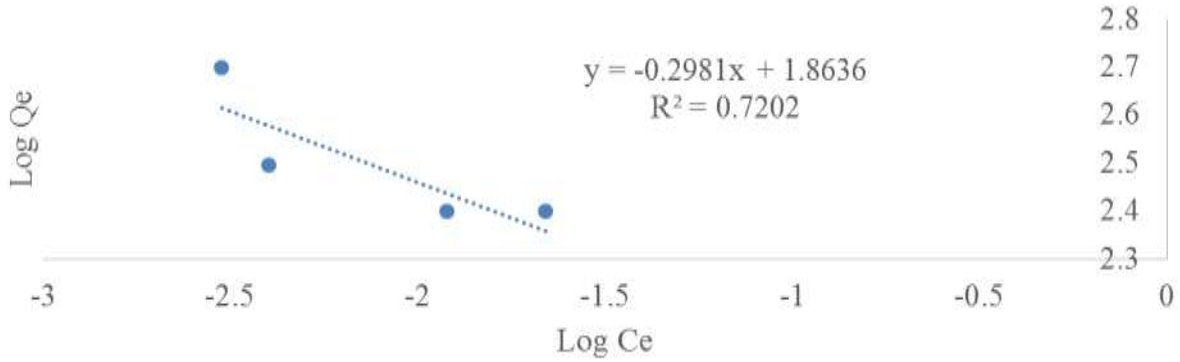


Figure 8g: Freundlich isotherm for adsorption of Hg in aqueous solution onto GB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

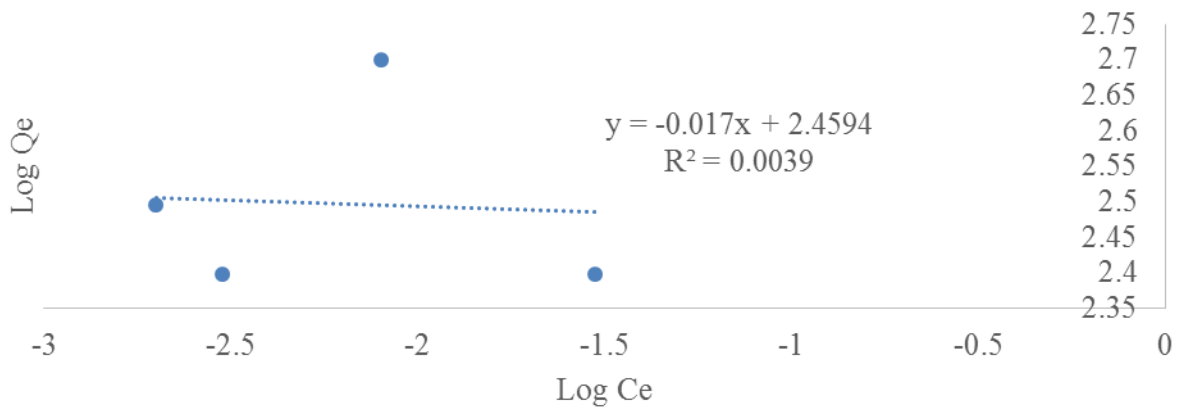


Figure 8h: Freundlich isotherm for adsorption of Hg in aqueous solution onto SB350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

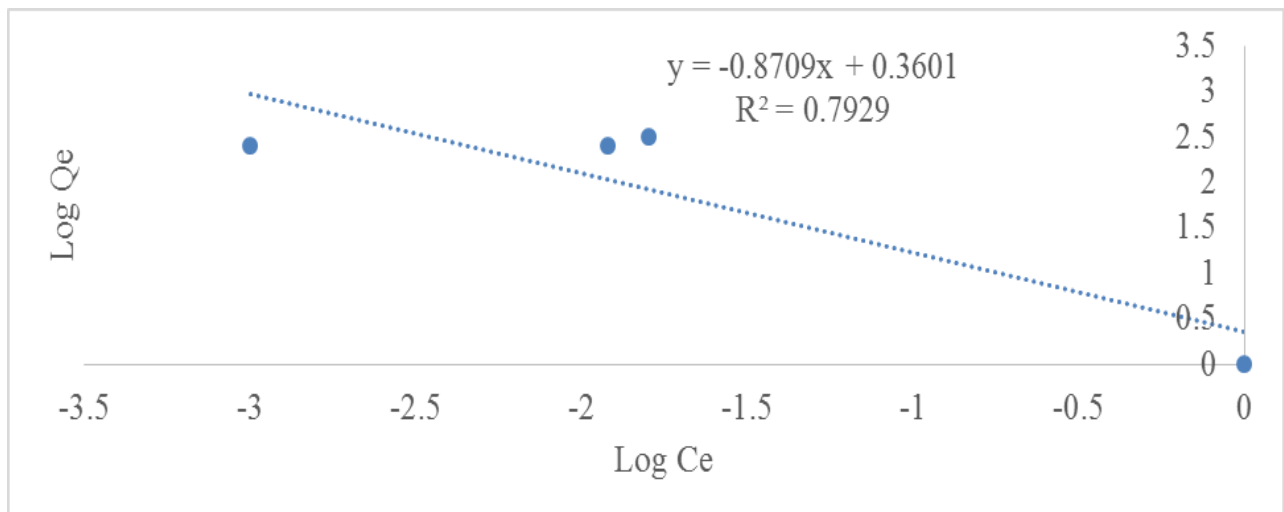


Figure 8i: Freundlich isotherm for adsorption of Hg in aqueous solution onto GS350 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

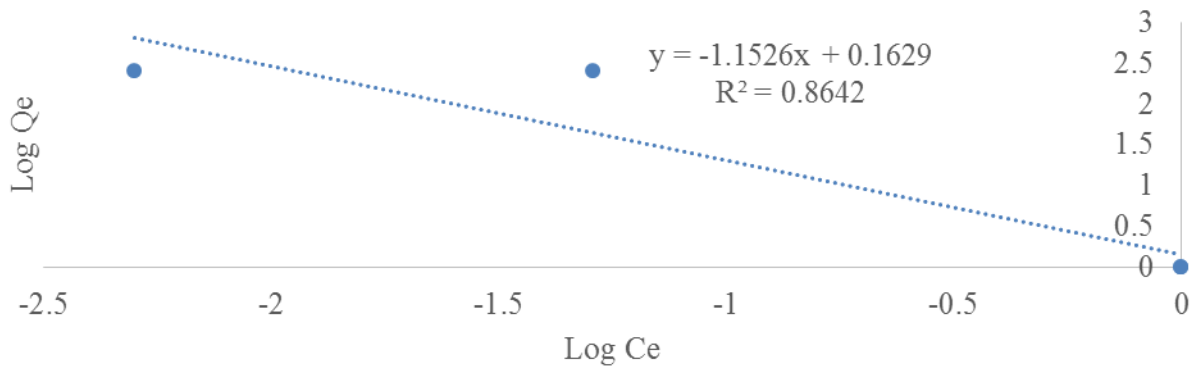


Figure 8j: Freundlich isotherm for adsorption of Hg in aqueous solution onto GB700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

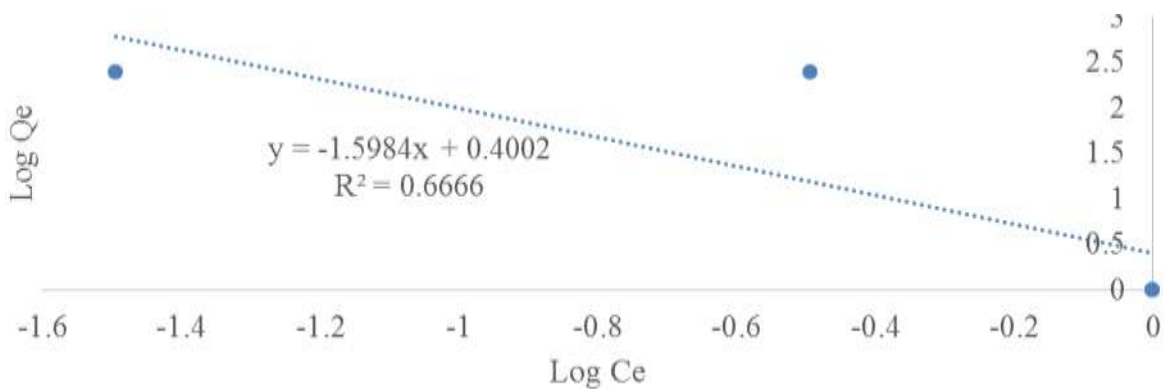


Figure 8k: Freundlich isotherm for adsorption of Hg in aqueous solution onto SB700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses

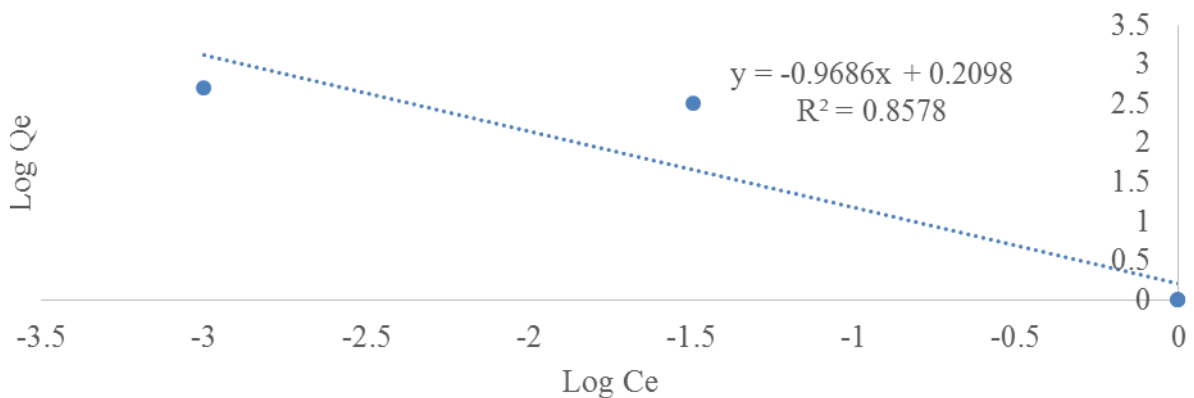


Figure 8l: Freundlich isotherm for adsorption of Hg in aqueous solution onto GS700 (solution volume: 100 ml; adsorbent dose: 2, 4, 8 and 10 g; contact time: 60 min) Source: Authors' analyses