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Kinetics of the bioremoval of selected heavy metal ions from wastewater by the application of modified Nigerian Bambara groundnut shells

Abstract

Nigerian Bambara Groundnut Shells (BGS) were modified to obtain Raw Bambara Groundnut Shell (RBGS), Carbonized Bambara Groundnut Shell (CBGS) and Bambara Groundnut Shell Lignin (BGSL) and used as bio-adsorbents to remove Lead (Pb), Nickel (Ni) and Cadmium (Cd) ions from industrial wastewater. The adsorption study investigated the effects of bio-adsorbent dosage, wastewater pH and contact time. Preliminary analyses which include: an Atomic Adsorption Spectrophotometer (AAS) on the wastewater and Scanning Electron Microscopy (SEM) were carried out on the different modified BGS, while the mechanism of adsorption was described using adsorption kinetic models. AAS analysis revealed that the concentrations of the heavy metals of interest were above WHO permissible limits in wastewater. SEM analysis revealed that the microspores of the bio-adsorbents were covered after the adsorption process. After the adsorption process, 85 – 91% Pb and 80 – 85% Ni and 92 - 98% Cd were removed by the different bio-adsorbents at optimum conditions of adsorption capacity which occurred at 0.8g dosage, pH of 7 and 120 min contact time. Generally, equilibrium occurred within 90 minutes. The mechanism of Pb, Ni and Cd ions adsorption onto RBGS, CBGS and BGSL bio-adsorbents can be described with diffusion and chemisorption processes. Pseudo-second-order kinetics fitted the adsorption process, implying that it is the rate-controlling step. This study found that the modified Bambara groundnut shell bio-adsorbents can be used as an alternative to conventional adsorbents used to treat industrial wastewater effluent

Keywords: bio–adsorbents, wastewater, dosage, adsorption, heavy metals

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Abbreviations: RGBS, raw Bambara groundnut shells; CBGS, carbonized Bambara groundnut shells; BGSL, Bambara groundnut shells; Pb, lead; Ni, nickel; Cd, cadmium; AAS, atomic adsorption spectrophotometer; SEM, scanning electron microscopy; WHO, World Health Organization; H_2SO_4, sulphuric acid; NaOH, sodium hydroxide.

Introduction

In Nigeria, the issue of water availability and the pursuit of sustainable clean water solutions have been complicated by the detrimental impact of pollution stemming from municipal, industrial, and anthropogenic activities.[1,2] The rise in urbanization and industrialization has contributed to the contamination of both ground and surface water sources with heavy metals such as Lead (Pb), Nickel (Ni) and Cadmium (Cd) resulting in a decline in water quality due to the excessive generation of waste.[3,4] Consequently, water bodies have become tainted with untreated or insufficiently treated effluents from various sources, including industrial, commercial, pharmaceutical, agricultural, and domestic sources.[5]

In an effort to mitigate the adverse impacts of water contaminants with these heavy metals in the environment and human health, regulatory authorities establish regulations and limits for the discharge of wastewater into the environment. However, these measures often prove insufficient, necessitating the treatment of wastewater.[6] Various treatment methods are available for the removal of water pollutants, but some of these approaches are associated with high costs and limited effectiveness.[7] Conventional techniques employed to eliminate heavy metals from water include chemical precipitation, flotation, flocculation, sedimentation, solvent extraction, oxidation/reduction, dialysis/electro-dialysis, reverse osmosis, ultra-filtration, electrochemical deposition, ion exchange, and adsorption.[8]

The choice of a suitable technique is predicated on its efficacy and cost-effectiveness.[7] Among the various methods, adsorption has emerged as an effective means of removing heavy metals owing to its numerous advantages. These advantages encompass cost-effectiveness and the ready availability of adsorbents, minimized sludge production, ease of operation, and the potential for adsorbent reuse after undergoing subsequent treatment steps. Adsorption technology operates on a surface-based mechanism, wherein contaminants present in the solution interact with a solid material termed as adsorbents. The porous surface structure of the adsorbent facilitates the adherence of solute molecules, or adsorbate, from the solution onto the adsorbent surface.[7,8]

Apparently, the issue of water pollution, arising from the introduction of heavy metals due to industrial activities and the convectional techniques used for the treatment of industrial wastewater is experiencing a significant concern on a global scale. This is because some convectional adsorbents require synthetic chemicals to reactivate after its use and these chemicals have negative impacts on the environment.[1] Consequently, the quest for environmentally-friendly, cost-effective treatment methodologies to eliminate pollutants has become a prominent area of academic investigations. Biomass, encompassing a wide range of organisms resulting from photosynthesis, comprising animals, plants, and microorganisms, emerges as a valuable biological resource and they are abundant in nature, low pollution and sustainable.[2]

Hence, numerous researchers have used the adsorption technique to remove contaminants from water by using affordable adsorbents prepared locally from plant and animal waste, such as palm fibre,[11] bamboo,[12] soursop,[13] rice husk,[14] garlic and ginger.[2] Locally formulated adsorbent can be modified by means of physical or chemical activation. The activation of these wastes increases the carbon content to over 70% when pyrolised into charcoal with high porosity and large surface area. [9-10] Bambara groundnut shells, an agricultural waste readily available in the local setting, represent an under-utilized resource. The Bambara groundnut, a legume indigenous to Africa, is a significant crop on the continent, with its total annual production surpassing 300,000 tons.[15] Additionally, it serves as a low-cost source of high-quality protein. Leveraging Bambara shell as a natural, cost-effective, safe, and environmentally friendly alternative, it offers promising potential for conventional remediation systems[16] Lignin, extracted from agricultural residues, exhibits notable adsorption capacity and a strong affinity for removing heavy metal.[17,18]

Consequently,[16] investigated carbonized Bambara groundnut shell as an adsorbent for removal of paraquat dichloride from aqueous solution. The authors described the adsorption process as chemisorption, and the kinetics followed the pseudo-second-order kinetics with an R^2 value of 0.999. Also,[20] conducted research on the use of biosorbents derived from the leaves of Ziziphus spina-christi for removing cadmium (Cd^{2+}) ions from aqueous solutions through adsorption. It was discovered that the adsorption process followed the Langmuir isotherm model more closely.

The study conducted by[21] explored the efficacy of biosorbents derived from the leaves and stems of *Calotropis procera* for eliminating chromium ion from aqueous solutions. The adsorption behaviour of chromium ion by the biosorbents was best described by the Freundlich isotherm model and pseudo-second-order kinetic model, as revealed by an evaluation of the isotherm and kinetics of the adsorption process. Also, the authors in[18] used chemically activated carbon from Bambara groundnut shell to remove pendimethalin (PE) (herbicides) and paraquat dichloride (PQ) from aqueous solution. It was found that pseudo-second-order kinetics provided better explanation of PE and PQ removal suggesting that the adsorption was chemisorption.

Similarly, [22] examined how chitosan-modified bamboo charcoal adsorbent could be used to simultaneously adsorb Pb (II) and Cd (II) ions from an aqueous solution. The results revealed that the adsorption kinetics followed the pseudo-second-order model while the adsorption isotherm was best described by the Langmuir isotherm model. Also, [23] investigated the adsorption capacity and optimum condition for adsorption of Arsenic ion (As (V)) onto grapefruit peel biosorbent. They varied the solution pH, temperature, adsorbent dosage, and initial concentration of As (V) to obtain the optimal condition for best removal. The kinetic data indicated that the pseudo-second order model was more appropriate than other kinetic models evaluated in the study.

Therefore, the purpose of this study is to modify Bambara groundnut shells into various forms: Raw Bambara Groundnut Shells (RBGS), Carbonized Bambara Groundnut Shells (CBGS) and Bambara Groundnut Shell Lignin (BGSL). The adsorption capacities of the different Bambara groundnut shell formulations were tested for their ability to remove heavy metals in industrial wastewater collected from a petrochemical plant. Adsorption variables such as the initial concentration of metals, pH level and contact time were studied and the efficiency of the adsorbents and the level of contaminants that can be removed were observed. Furthermore, the understanding of adsorption mechanisms frequently involves the interpretation of kinetic characteristics governing the interplay between the adsorbent and the liquid phase. In this study, the interaction mechanism between the metals (Pb, Ni and Cd) and the modified Bambara adsorbents was assessed using models such as pseudo-first order kinetics, pseudo-second order kinetics, and the intra-particle diffusion model.

Methodology

Collection and preparation of samples

The preparation of Bambara groundnut shells for experimental analysis followed the method described in the work of [16–18] for processing bio-adsorbents intended for use in the adsorption process. The collected shells were thoroughly washed and cleaned with fresh tap water to remove any impurities. Subsequently, they were spread out on a clean surface and allowed to naturally dry for 3 days under ambient conditions. Further drying of the shells was achieved by placing them in an oven at a controlled temperature range of 70 - 100°C for 45 minutes. The dried Bambara groundnut shells were then divided into three portions and subjected to additional processing to obtain the raw sample, carbonized material, and lignin.

Raw Bambara groundnut shell adsorbent

The dried Bambara groundnut shells were cooled and subsequently milled into fine particles to obtain the RBGS adsorbent. These particles were immersed in a 0.1M NaOH solution for a duration of 9 hours. Following this step, they were washed with distilled water and subjected to drying once again. Next, the dried particles underwent a 9-hour immersion in a 0.1M H_2SO_4 solution to eliminate any remaining traces of alkalinity. Subsequently, the particles were thoroughly washed with distilled water and then dried within a desiccator. The resulting dried samples were sieved to achieve a maximum particle size of 1.18mm and were then stored in an airtight container, ready for use in the adsorption process.

Carbonized Bambara groundnut shell adsorbent

A measured quantity of 1.5 kg of dried Bambara groundnut shells was precisely weighed using an analytical weighing balance and introduced into a Pyrolysizer. The pyrolysis process was carried out within a temperature range of 500ºC to 800ºC. Specifically, pyrolysis was conducted at 800ºC, and at approximately 32 minutes into the process. Subsequent to the completion of pyrolysis, the resulting carbonaceous materials were subjected to crushing using a ball mill crusher to achieve fine particles, which were then sieved to obtain a maximum particle size of 1.18mm. These particles were subsequently stored in containers until ready for use in the adsorption process.

Bambara groundnut shell lignin adsorbent

Lignin was isolated from the dried Bambara groundnut shell through a series of steps. Initially, 30g of the dried shells were placed in a beaker, and a 1.0M solution of NaOH was added. The resulting mixture was then subjected to boiling at a temperature of 120 ºC for a duration of 4 hours. After cooling, the mixture underwent filtration, and the pH of the filtrate was adjusted to 2 by the addition of 98% H_2SO_4. The resulting lignin cake was then recovered through oven drying. The obtained lignin was allowed to cool and stored in an airtight container. Following this extraction process, the isolated lignin was utilized as an adsorbent without any further modification.

Initial wastewater analysis

Atomic adsorption spectrophotometer and scanning electron microscopy

The Atomic Adsorption Spectrophotometer (AAS) was used to determine the concentrations of heavy metal (Pb, Ni and Cd ions) contaminants in the wastewater. Scanning Electron Microscopy (SEM, FEI ESEM Quanta 200) was employed to analyze the structural arrangement and pore coverage of the particles before and after the adsorption process, providing insight into the morphology of the raw and carbonized Bambara groundnut shell as well as the lignin.

Batch adsorption experiments

Adsorption experiments followed the procedures recorded in[16–18] as follows:

Effect of dosage

150ml of wastewater was carefully measured and placed into a conical flask. Subsequently, 0.2g of powdered particles of the RBGS was introduced into the flask. The pH of the solution adjusted to 7.0 by the addition of sulphuric acid (H_2SO_4). The flask was then positioned on a rotary disc and stirred magnetically at a rotational speed of 100 rpm for 2 hours to ensure thorough contact between the particles and contaminants in the solution. Following the 2-hour stirring period, the mixture was filtered using filter paper, and the resulting filtrate was subjected to analysis with AAS to determine the concentrations of Pb, Ni, and Cd ions remaining in the solution. This procedure was repeated using dosages of 0.4g, 0.6g, and 0.8g while maintaining the solution pH at 7 and contact time at 2 hours. Likewise, the same procedures were conducted using CBGS and BGSL.

Effect of pH

The impact of wastewater pH on the adsorption process was explored with the modified BGS across four pH levels: 3, 7, 9, and 12. To achieve the desired pH for the wastewater, H_2SO_4 and NaOH were employed for pH adjustment. The investigation followed the same procedures as in the dosage effect study, with a fixed adsorbent dosage of 0.8g while varying the water pH. Additionally, the contact time for each experimental run remained constant at 120 minutes. Upon the completion of the 120-minute contact period, the solution underwent filtration to facilitate the analysis of Pb, Ni, and Cd ion concentrations, which was performed using an AAS.

Effect of contact time

The adsorption processes were examined at varying contact intervals of 30, 60, 90, and 120 minutes with the modified BGS bio-adsorbents. The procedures described earlier for the examination of dosage and pH effects were replicated for all experimental runs at a constant pH of 7.0 and dosage 0.8g. Following a 30-minute contact time, the solution underwent filtration, and the filtrate was subjected to analysis for the concentrations of lead, nickel, and cadmium ions using AAS. A detailed breakdown of the various batch experiments conducted for each formulated adsorbent is outlined in Table 1.

Table 1 Batch adsorption design for each formulated adsorbent

	RBGS			CBGS			BGSL		
	m(g)	pH	t(min)	m(g)	pH	t(min)	m(g)	pH	t(min)
Effect of dosage	0.2	7	120	0.2	7	120	0.2	7	120
	0.4	7	120	0.4	7	120	0.4	7	120
	0.6	7	120	0.6	7	120	0.6	7	120
	0.8	7	120	0.8	7	120	0.8	7	120
Effect of pH	0.8	3	120	0.8	3	120	0.8	3	120
	0.8	7	120	0.8	7	120	0.8	7	120
	0.8	9	120	0.8	9	120	0.8	9	120
	0.8	12	120	0.8	12	120	0.8	12	120
Effect of contact time	0.8	7	30	0.8	7	30	0.8	7	30
	0.8	7	60	0.8	7	60	0.8	7	60
	0.8	7	90	0.8	7	90	0.8	7	90
	0.8	7	120	0.8	7	120	0.8	7	120

Estimation of Adsorption Capacity

The formula used to calculate the percentage of heavy metal adsorbed by the modified Bambara adsorbents is given as:

$$\text{Adsorbed metal}\left(\%\right) = \frac{C_i - C_f}{C_i} \times 100\% \quad (1)$$

The formula used to calculate the adsorption capacity of the modified Bambara adsorbents at any time is expressed as:

$$Q_t = \left(C_i - C_t\right)\frac{V}{m} \quad (2)$$

The formula used to calculate the adsorption capacity of the modified Bambara adsorbents at equilibrium is expressed as:

$$Q_e = \left(C_i - C_e\right)\frac{V}{m} \quad (3)$$

Where:

C_i = Concentration of heavy metal analysed in wastewater before treatment (mg/l)

C_f = Concentration of heavy metal analysed in wastewater after treatment (mg/l)

C_t = Concentration of heavy metal analysed in wastewater after time, t (mg/l)

C_e = Concentration of heavy metal analysed in wastewater at equilibrium (mg/l)

Q_t = Concentration of heavy metal on the surface of adsorbent at time, t (mg/g)

Q_e = Concentration of heavy metal on the surface of adsorbent at equilibrium (mg/g)

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V = Volume of the wastewater (l)

m = Weight of the modified Bambara formulations (g) [23,24,25].

Adsorption kinetics of the modified Bambara groundnut shell bio-adsorbents

Pseudo first-order kinetic model

The rate of adsorption of lead, nickel, and cadmium ions by the modified Bambara bio-adsorbents was studied using the pseudo first-order kinetic model developed by,[26] which is expressed by[27] as:

$$\frac{dQ_t}{dt} = k_1\left(Q_e - Q_t\right) \tag{4}$$

Where:

k_1 = Pseudo first order rate constant (min^{-1})

Q_e = Concentration of heavy metal adsorbed by the adsorbent at equilibrium (mg/g)

Q_t = Concentration of heavy metal adsorbed by the adsorbent with time (mg/g)

t = Contact time (min)

The adsorption capacity at equilibrium and the first-order kinetic rate constant were estimated after integrating equation (4) and linearizing the resulting solution. By integration, we have as follows:

$$\int_{Q_{to}}^{Q_t} \frac{dQ_t}{\left(Q_e - Q_t\right)} = k_1 \int_0^t dt \tag{5}$$

$$\ln Q_e - \ln\left(Q_e - Q_t\right) = k_1 t \tag{6}$$

Rearranging equation (6) gives:

$$\ln\left(Q_e - Q_t\right) = \ln Q_e - k_1 t \tag{7}$$

A plot of $\ln\left(Q_e - Q_t\right)$ against time, t gives the slope of the graph, which corresponds to k_1 and intercept which corresponds to $\ln Q_e$.

Expressing equation (7) in terms of Q_t, we obtained an exponential function given as:

$$Q_e - Q_t = Q_e e^{-k_1 t} \tag{8}$$

By factorization, we obtain

$$Q_t = Q_e\left(1 - e^{-kt}\right) \tag{9}$$

The exponential model, expressed in Equation (9), is used to predict the concentration of heavy metal adsorbed by the modified Bambara bio-adsorbents at any given time.

Pseudo second-order kinetic model

The rate of adsorption of lead, nickel, and cadmium ions by the modified Bambara adsorbents was also studied using the pseudo second-order kinetic model.[27] expressed the pseudo second-order kinetics as:

$$\frac{dQ_t}{dt} = k_2\left(Q_e - Q_t\right)^2 \tag{10}$$

Where:

k_2 = Pseudo second order adsorption rate constant (g/mg.min)

Definition of other parameter remained the same. The adsorption capacity at equilibrium and the second-order kinetic rate constant were estimated after integrating equation (10) and linearizing the resulting solution. By integration, we have as follows:

$$\int_{Q_{to}}^{Q_t} \frac{dQ_t}{\left(Q_e - Q_t\right)^2} = k_2 \int_0^t dt \tag{11}$$

$$\frac{1}{\left(Q_e - Q_t\right)} = k_2 t + C \tag{12}$$

Letting $t = 0$ in equation (12), we have $Q_t = 0$. Hence, $C = \frac{1}{Q_e}$

Replacing C = 1/Qe, equation (12) results to:

$$\frac{1}{Q_e - Q_t} = k_2 t + \frac{1}{Q_e} \tag{13}$$

By rearranging equation (13) and simplifying further, we obtained:

$$\frac{1}{Q_e - Q_t} - \frac{1}{Q_e} = k_2 t$$

$$\frac{Q_t}{Q_e\left(Q_e - Q_t\right)} = k_2 t \tag{14}$$

The pseudo second-order constant and the adsorption capacity at any given time was obtained after rearrangement of equation (14) as follows.

$$Q_t = k_2 t Q_e^2 - Q_t Q_e k_2 t \tag{15}$$

By dividing both sides of equation (15) by $Q_t Q_e^2 k_2$, we have:

$$\frac{1}{Q_e^2 k_2} = \frac{t}{Q_t} - \frac{t}{Q_e} \tag{16}$$

This is further rearranged as:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{Q_e^2 k_2} \tag{17}$$

A plot of $\frac{t}{Q_t}$ against time, t gives the slope of the graph, which corresponds to $\frac{1}{Q_e}$ and intercept which corresponds to $\frac{1}{Q_e^2 k_2}$.

Further simplification equation (17) gives

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \tag{18}$$

Equation (18) is the solution to pseudo second-order kinetic model and it was used to predict the concentration of heavy metal adsorbed by the modified Bambara groundnut shell bio-adsorbents at any given time.

Intra-particle diffusion model

The intra-particle diffusion model is another useful equation for evaluation of adsorption rate, and this is expressed in the work of[28] as:

$$Q_t = K_d \sqrt{t} \tag{19}$$

Where:

Q_t = The amount adsorbed at time t (mg/g)

K_d = Weber and Morris intra-particle diffusion rate constant (mg/g.min$^{0.5}$)

t = Time of adsorption (min)

A plot of Q_t against $t^{1/2}$ gives the slope of the graph, which corresponds to K_d. According to several studies, such as[12] and [25], if the plot is linear, this suggests that the adsorption process is governed by intra-particle diffusion. Nonetheless, if the linear graph does not intersect the origin, then it indicates that intra-particle diffusion is not the rate-limiting step.

Results and discussion

AAS and SEM analysis of Bambara groundnut shell

The results of preliminary analysis carried out on the industrial wastewater effluent sample are given in Table 2.

AAS analysis revealed that all the metals of interest (Pb, Ni and Cd) had levels exceeding the permissible limits specified by the World Health Organization (WHO) for water and wastewater as shown in Table 2. SEM images in Figures 1a–3a exhibited the rough surfaces of RBGS, CBGS and BGSL samples before the adsorption process. These surfaces displayed an irregular pattern of microspores with varying sizes, which contributed to the enhanced adsorption of metals.[29] However, as depicted in Figures 1b–3b, the pores on the surfaces, which were visible prior to the adsorption process, became filled up. This observation suggested that the Pb, Ni and Cd) ions had bonded to the vacant sites on the surfaces of the bio-adsorbents after the adsorption process. Upon careful examination of the images before and after adsorption, it was evident that the surfaces appeared smoother following the adsorption.[30]

Table 2 Concentrations of ions in the wastewater

Parameter	Concentration (mg/l)	WHO limit (mg/l)
Lead	1.27	0.01
Nickel	1.14	0.02
Cadmium	1.06	0.003

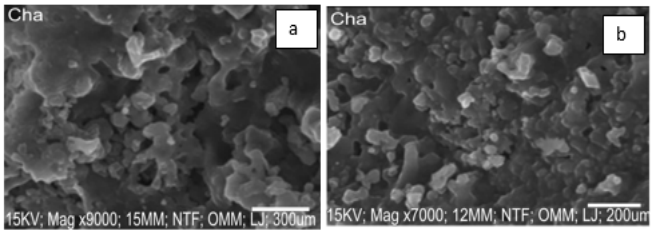

Figure 1 Morphology of Raw Bambara Groundnut Shells before adsorption (a) and after adsorption (b).

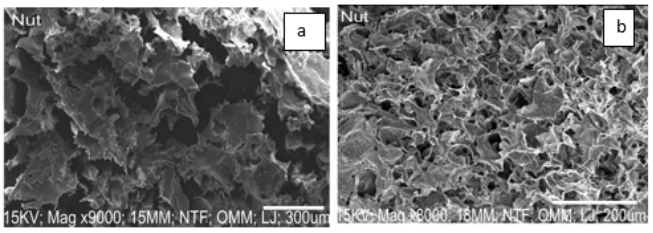

Figure 2 Morphology of Carbonized Bambara Groundnut Shell before (a) and after adsorption (b).

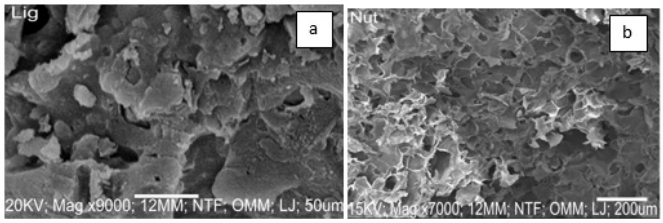

Figure 3 Morphology of Bambara Groundnut Shell Lignin before (a) and after adsorption (b).

Batch adsorption studies

Effect of adsorbent dosage

Figures 4a–4c revealed that as the dosage increased from 0.2g to 0.8g, the percentage of Pb, Ni and Cd ions removed from the wastewater showed an upward trend. The increment in Pb, Ni and Cd ions removal with the increased dosage of the adsorbent can be predominantly attributed to the greater availability of exchangeable binding sites, facilitating the sorption of metal ions. The higher performance observed in the BGSL bio -adsorbent can be attributed to its finer microstructures relative to CBGS and RBGS. This observation is consistent with findings from [15,18] regarding the Bambara groundnut husk adsorbent.

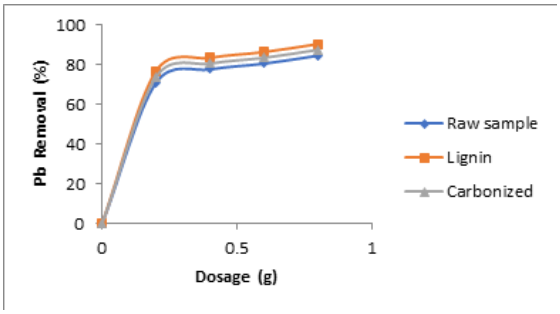

Figure 4a Lead ion removal at various dosages.

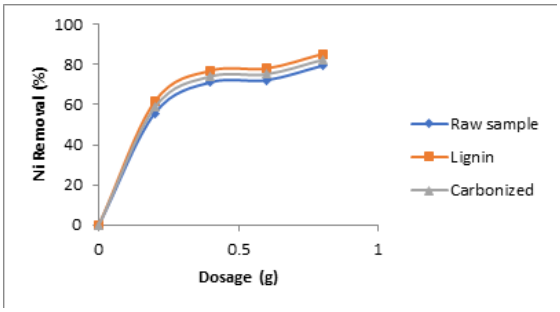

Figure 4b Nickel ion removal at various dosages.

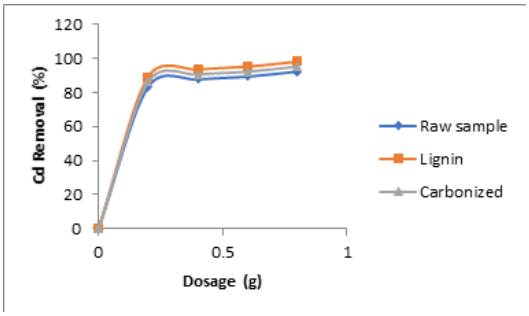

Figure 4c Cadmium ion removal at various dosages.

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The outcomes of the investigation demonstrate that increasing the dosage of RBGS, CBGS, and BGSL substantially bolstered their efficacy in removing Pb, Ni and Cd ions from the wastewater.

Effect of solution pH

Figures 5a–5c illustrates that the percentage of Pb, Ni and Cd ions removed increased as the solution pH ranged from 3.0 to 7.0 for RBGS, CBGS, and BGSL bio-adsorbents. However, the removal efficiency decreased with increasing pH from 9.0 to 12.0. The observed increase in metal adsorption with increasing pH from 3.0 to 7.0 indicates that the surfaces of the adsorbents become more negatively charged, leading to a favorable electrostatic force of attraction with the positively charged metal ions.[34] As explained by [34,35] the pH of a solution influences the chemical state of the binding sites. At low pH values, there is an increased concentration and mobility of hydrogen ions (H+), favoring the adsorption of H+ over metal ions. This creates a competitive scenario between protons and metal ions for the binding sites on the adsorbent.

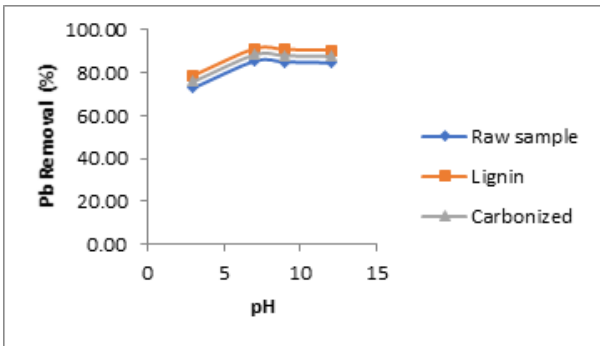

Figure 5a Lead ion removal at various pH of solution.

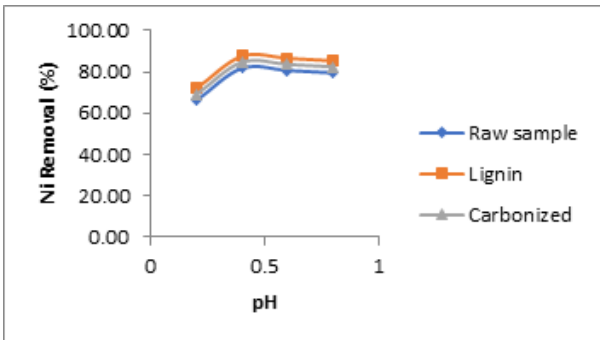

Figure 5b Nickel ion removal at various pH of solution.

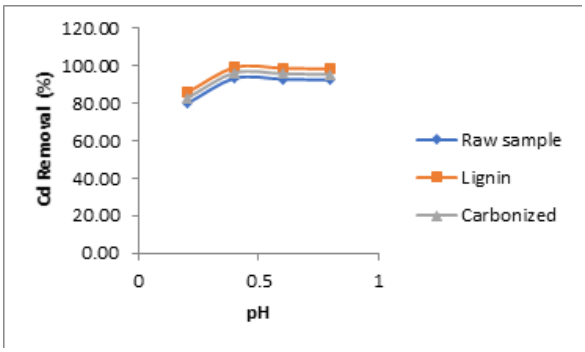

Figure 5c Cadmium ion removal at various pH of solution.

Effect of Contact Time

As depicted in Figures 6a–6c, an increase in contact time, ranging from 30 to 120 minutes, increased Pb, Ni and Cd ion removal. During the initial 30 to 60 minutes of contact time, there was a rapid increase in the percentage removal of Pb, Ni and Cd ions, after which the rate of increase slowed down as the contact time extended further to 120 minutes. Equilibrium adsorption was achieved at approximately 90 minutes for RBGS and CBGS adsorbents and at around 80 minutes for BGSL. After attaining equilibrium, a subsequent increase in contact time did not lead to substantial adsorption. These results indicate that the optimal adsorption onto the modified adsorbents occurred at 120 minutes. A similar study by [16–18,34] reported a maximum adsorption of Pb ions onto Bambara groundnut husk at a contact time of 120 minutes.

The adsorption method demonstrated the effective removal of Pb, Ni and Cd ions from wastewater under optimal conditions as shown in Table 3. However, the values obtained after the adsorption were above the recommended limits set by WHO for drinking water quality. Despite this, the considerable removal levels of Pb, Ni and Cd ions observed after 120 minutes of adsorption suggest that the formulated bio-adsorbents are effective in removing these heavy metals from industrial water. To achieve concentrations of heavy metals below acceptable limits, additional measures can be taken, such as prolonging the contact time or increasing the dosage of the adsorbent. Previous studies have indicated that both contact time and dosage play crucial roles in promoting the removal of water contaminants. [37-39]

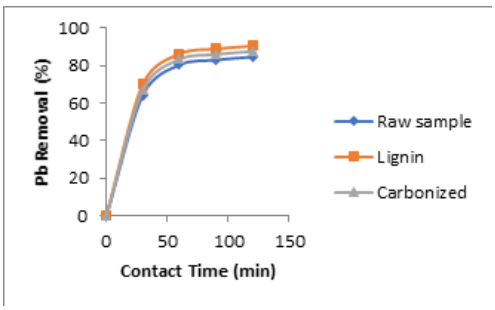

Figure 6a Lead ion removal at various contact time.

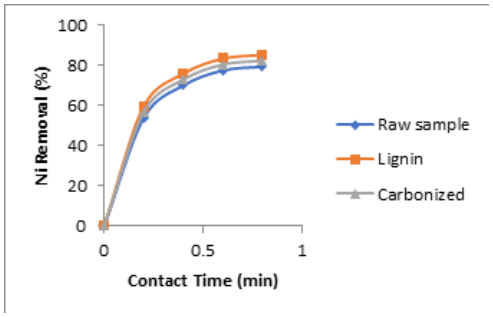

Figure 6b Nickel ion removal at various contact time.

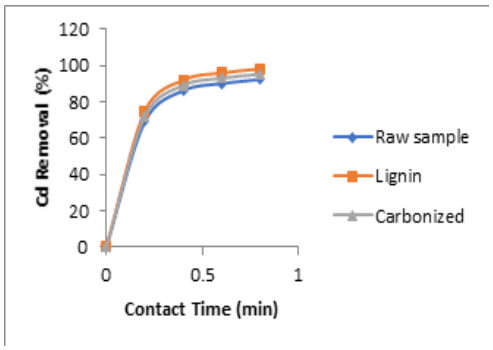

Figure 6c Cadmium ion removal at various contact time.

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Table 3 Industrial wastewater contamination and removal level

Parameter	Initial value	After adsorption			WHO limit	Removal (%)		
		RBGS	CBGS	BGSL		RBGS	CBGS	BGSL
Pb (mg/l)	1.27	0.1948	0.1205	0.1575	0.01	84.66	87.6	90.51
Ni (mg/l)	1.14	0.2177	0.1557	0.1865	0.02	79.46	82.41	85.31
Cd (mg/l)	1.06	0.0868	0.0201	0.0533	0.003	92.39	95.32	98.24

Adsorption kinetics

The kinetic evaluation was performed on results obtained from the investigation of contact time influence between 30 and 120 minutes at wastewater pH of 7.0 and 0.80g dosage of the three formulated Bambara groundnut shell bio-adsorbents.

Plots for determination of kinetic constants

The kinetic constants were determined by fitting results obtained from the experiment into pseudo first-order kinetics, pseudo second-order rate kinetic and intra-particle diffusion model as shown in Figures 7a–7c for RBGS, Figures 8a–8c for CBGS and Figures 9a–9c for BGSL.

Figures 7a–9c shows the linear plots used to evaluate pseudo-first-order kinetic rate constant, pseudo second order kinetic constant, intra-particle diffusion kinetic constant and equilibrium adsorption capacities for the simultaneous adsorption of Pb, Ni and Cd ions onto RBGS, CBGS and BGSL bio - adsorbents. The coefficient of determination, R^2 values for Pb, Ni and Cd ions were obtained from the plots (Table 4). Similarly, a comparison of the linear regression equations with equation (8), showed pseudo first-order rate constant (k_2), pseudo-second order kinetic constant (k_2), intra-particle diffusion kinetic constant (k_d) for Pb, Ni and Cd ions and the adsorption capacity at equilibrium (Q_e) for Pb, Ni and Cd ions for all the bio – adsorbents were predicted and represented in Table 5. Adsorption kinetic analysis helps to establish the mechanism and rate that control step of an adsorption process. The linear lines for the intra-particle diffusion kinetic model do not cross the origin of the graphs. This implied that intra-particle diffusion alone does not control the adsorption of the metals onto the adsorbents, but diffusion and chemisorption both controlled the process[12]; [39-41].

Table 4 Summary of kinetic constant

Parameters	RBGS			CBGS			BGSL		
	Pb	Ni	Cd	Pb	Ni	Cd	Pb	Ni	Cd
Pseudo first order kinetic									
K1 (min-1)	0.0091	0.0094	0.0153	0.0105	0.0105	0.0196	0.0125	0.0119	0.0295
R2	0.8388	0.9264	0.926	0.8495	0.9218	0.9522	0.8657	0.9381	0.9894
Pseudo second order									
K2 (mg/g min)	0.3638	0.2441	0.3283	0.3708	0.2523	0.3344	0.3771	0.2601	0.3402
R2	0.9983	0.9985	0.9989	0.9985	0.9988	0.999	0.9986	0.9989	0.9991
Intra-particle diffusion									
Kd	0.0087	0.0095	0.009	0.0087	0.0095	0.009	0.0087	0.0095	0.009
R2	0.8486	0.9311	0.8836	0.8482	0.931	0.8833	0..8486	0.931	0.8836

Table 5 Predicted concentration of heavy metals

Time (min)	Predicted Q_t (mg/g)			Predicted C_t (mg/l)		
	Pb	Ni	Cd	Pb	Ni	Cd
0	0	0	0	1.27	1.06	1.14
30	0.17274	0.12071	0.16424	0.34872	0.41621	0.26405
60	0.19988	0.15016	0.19275	0.20397	0.25915	0.112
90	0.21093	0.16345	0.20459	0.14504	0.18827	0.04885
120	0.21692	0.17102	0.21108	0.11309	0.14789	0.01424
150	0.22069	0.17591	0.21217	0.09299	0.12181	0.00843
180	0.22327	0.17932	0.2129	0.07923	0.10363	0.00453
210	0.22515	0.18184	0.21308	0.0692	0.09019	0.00357
240	0.22658	0.18378	0.21311	0.06157	0.07984	0.00341
270	0.22771	0.18532	0.2133	0.05555	0.07163	0.0024
300	0.22862	0.18657	0.2135	0.05069	0.06496	0.00133
1000	0.23452	0.19484	0.2136	0.01923	0.02085	0.0008

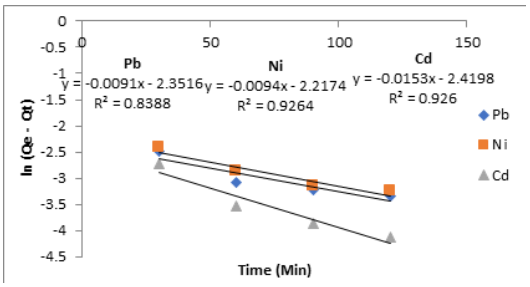

Figure 7a Pseudo-first-order kinetics for adsorption on RBGS.

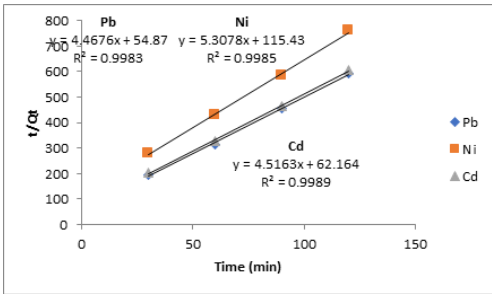

Figure 7b Pseudo second-order kinetics for adsorption on RBGS.

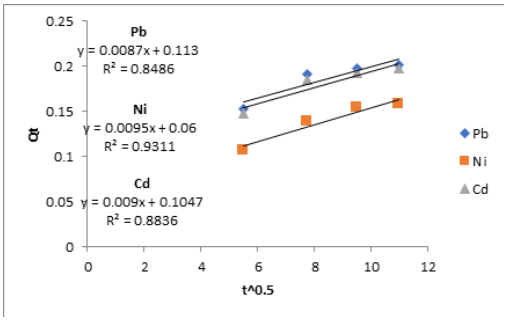

Figure 7c Intra-particle diffusion kinetics for adsorption on RBGS.

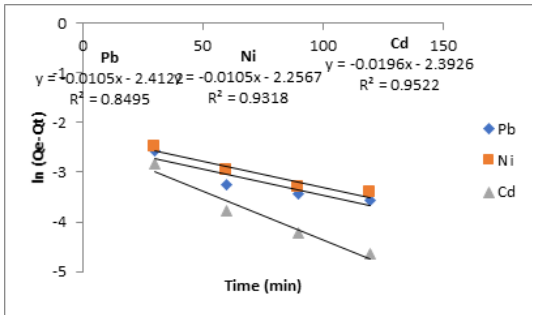

Figure 8a Pseudo first order kinetics for adsorption on CBGS.

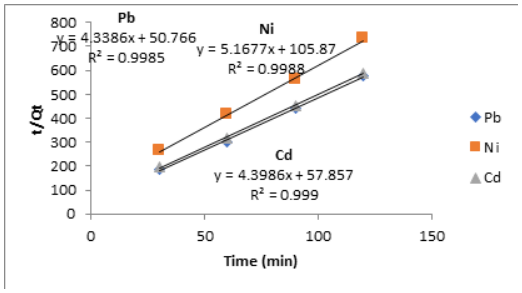

Figure 8b Pseudo second order kinetics for adsorption on CBGS.

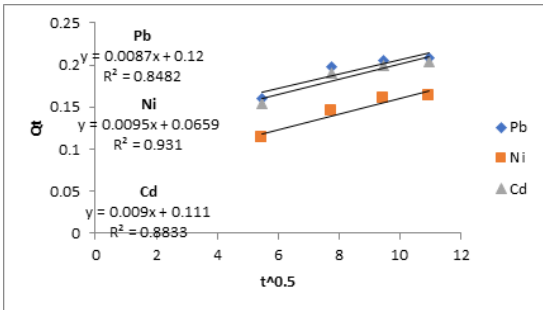

Figure 8c Intra-particle diffusion kinetics for adsorption on CBGS.

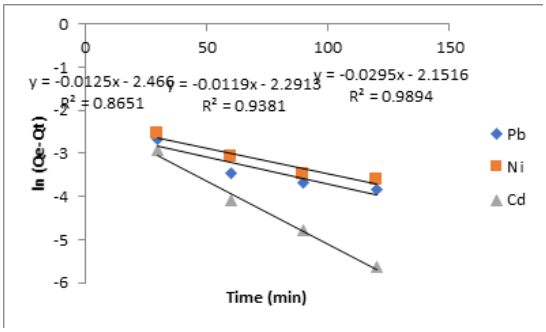

Figure 9a Pseudo first order kinetics for adsorption on BGSL.

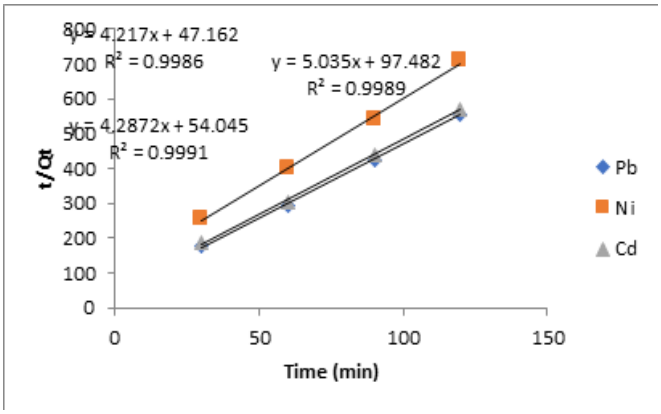

Figure 9b Pseudo second order kinetics for adsorption on BGSL.

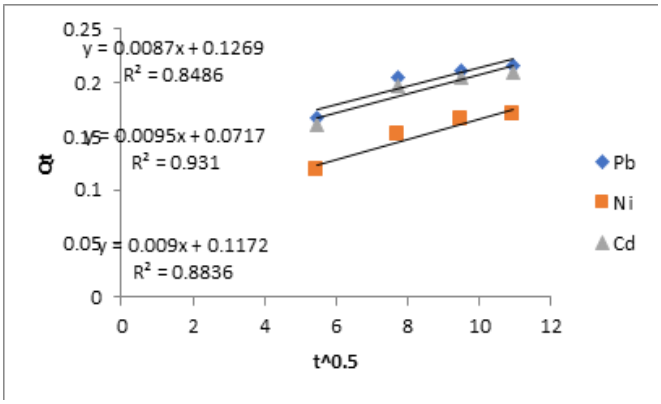

Figure 9c Intra-particle diffusion kinetics for adsorption on BGSL.

In comparison, the second-order pseudo kinetics provided a better fit to the experimental data obtained from the adsorption of lead, nickel, and cadmium onto RBGS, CBGS, and BGL adsorbents than the pseudo-first-order kinetics and intra-particle diffusion model as shown in Table 4. Additionally, the pseudo-second-order was better at predicting the adsorption capacity at equilibrium. The R^2 values obtained from the analysis of the pseudo-second-order kinetic constant were consistently higher than those obtained from the pseudo-first-order kinetic rate constant. As a result, the adsorption of Pb, Ni, and Cd ions by RBGS, CBGS, and BGL was more explained using the pseudo second-order kinetic model. These results are in line with previous studies on adsorption heavy metal using bio-adsorbents.[2,24,42–44] Although,[45] had reported a better experimental fit with pseudo first-order kinetics compared to pseudo second-order for adsorption of Cd onto coconut shell.

The amounts of lead, nickel and cadmium ions in the treated wastewater after 120 minutes (2 hours) of contact time with RBGS, CBGS and BGSL bio – adsorbents were above limits given by WHO for good water quality. Therefore, the kinetic models were used to estimate the time for which the concentration of metals had reduced below WHO minimum limits.[46] In achieving this, the predicted second-order rate constants and equilibrium adsorption capacity were substituted into pseudo second order kinetic model. This kinetic rate model was chosen because it performed better than the other models. Figure 10 demonstrated the capability of the model in predicting the concentration of lead, nickel and cadmium ions in the treated wastewater for BGSL bio – adsorbent at contact time up to 1000 minutes (16.67 hours).

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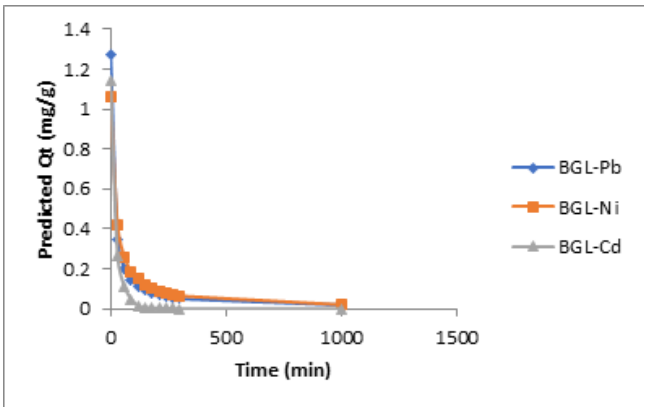

Figure 10 Prediction of heavy metal reduction with time.

The predicted concentration of heavy metals adsorbed onto the bio-adsorbent and concentration in wastewater at any given time, up to 1000 minutes (16.67 hours), are presented in Table 5.

The amounts of Pb, Ni, and Cd ions predicted for BGSL by the pseudo-second-order model were comparable to values obtained from the experiment. However, the results predicted (Table 5) after a contact time up to 1000 minutes (16.67 hours) did not show reduction in the levels of the heavy metals below the standard limit (WHO limits) except Cd, which occurred after 270 – 1000 minutes (4.5 – 16.67 hours). This inability of the adsorbents to remove more of the metal from the wastewater, even up to 1000 minutes of contact time, could be attributed to over saturation of the adsorbents.[47–53] Thus, the dosage of 0.8g used may not be enough to completely or reduce the concentration of lead, nickel and cadmium ions to level below the permissible limits. Therefore, increasing the adsorbent dosage further may remove concentration of heavy metals in the wastewater to levels below WHO recommended standards.

Conclusion and future work

The performance of the different formulations of Bambara groundnut shells as bio-adsorbents for the treatment of wastewater from a petrochemical plant was studied, based on the results, the following conclusions have been drawn:

a) The smoother surfaces of RBGS, CBGS and BGSL after the adsorption process, as revealed by SEM analysis, is an indication that the pore spaces or vacant site were occupied by the lead, nickel and cadmium ions, thereby reducing their concentration in the wastewater.

b) The amount of lead, nickel and cadmium remaining in the wastewater after adsorption process by the RBGS, CBGS and BGSL adsorbents for 120 minutes contact time were above the maximum specified standard limits for good water quality. Also, the predicted values of Pb and Ni ions after 1000 minutes (16.67 hours) contact time were above the maximum specified limits.

c) Therefore, increasing the adsorbent dosage might completely remove or reduce the concentration of Lead, Nickel and Cadmium to the level below the permissible limits. In addition, a minimum of 120 minutes contact time should be maintained with the water pH adjusted to about 7.

d) Based on the findings, it is therefore recommended that further modification of the formulated RBGS, CBGS and BGSL as bio-adsorbents should be carried out to enhance more removal of these heavy metal ions from contaminated industrial effluent below the acceptable limits recommended by World Health Organization.

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None.

Conflicts of interest

The authors declare that they have no competing interests.

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References

1. Ushurhe O, Thadeaus O, Abugor O. Urbanization and surface water quality in Warri, Southern Nigeria. *The International Journal of Humanities & Social Sciences*. 2020;8(8):179–187.
2. Dagde KK, Ndaka JI. Kinetic study of garlic and ginger particles in adsorption of heavy metals in aqueous solution. *Chemical and Process Engineering Research.* 2019;60:25–38.
3. Rahmani K, Mahvi AH, Vaezi F, et al. Bioremoval of lead by use of waste activated sludge. *International Journal of Environmental Research*. 2009;3:471–476.
4. Ibrahim WM, Hassan AF, Azab Y A. Biosorption of toxic heavy metals from aqueous solution by Ulva lactuca activated carbon. *Egyptian Journal of Basic and Applied Sciences*. 2016;3:241–249.
5. Shah BA, Shah AV, Singh RR. Sorption isotherms and kinetics of chromium uptake from wastewater using natural sorbent material. *International Journal of Environmental Science and Technology*. 2009;6:77–90.
6. Abdullah AM, Choudhary A. Removal of oil from seawater using charcoal and rice hull. *Materials Science and Engineering*. 2017;263;32–41.
7. Calderón OAR, Abdeldayem OM, Pugazhendhi A, et al. Current updates and perspectives of biosorption technology: an alternative for the removal of heavy metals from wastewater, Current Pollution Reports. 2020;6(1):8–27.
8. Escudero LB, Quintas PY, Wuilloud RG, et al. Recent advances on elemental biosorption. *Environmental Chemistry Letters*. 2019;17:409–427.
9. Duru CE, Duru IA. Adsorption capacity of maize biomass parts in the remediation of Cu^{2+} Ion Polluted Water. *World News of Natural Science*. 2017;12;51–62.
10. Argun ME, Dursum S. A new approach to modification of natural adsorbent for heavy metal adsorption. *Bioresour Technol*. 2008;99:2516–2527.
11. Ideriah TJ K, David O D, Ogbonna D N. Removal of heavy metal ions in aqueous solutions using palm fruit fibre as adsorbent. *Journal of Environment and Chemical Ecotoxicology*. 2012;4(4),82–90.
12. Ademiluyi FT, Ujile AA. Kinetics of batch adsorption of iron II ions from aqueous solution using activated carbon from Nigerian bamboo. *International Journal of Engineering and Technology*. 2013;3(6):623–631.
13. Ndamitso MM, Mustapha S, Etsuyankpa MB, et al. Removal of Lead, Cadmium and Cobalt from Oil Spill Water onto Soursop (Annonamuricata) Peel. *Science Journal of Analytical Chemistry*. 2016;4(1):7–11.
14. Swarnalakshmi KS, Prakash C, Nivetha S, et al. Use of rice husk ash as an adsorbent to remove contaminants in water and comparison with advanced oxidation process – a study. *Materials Today: Proceedings*. 2018;5:24248–24257.

15. Sebata E, Moyo M, Guyo U, et al. Adsorptive removal of atrazine from aqueous solution using Bambara groundnut hulks (Vigna Subterranean). *International Journal of Engineering Research & Technology*. 2013;2(5):312–321.

16. Ayuba AMM, Nyijime TA. Paraquat dichloride adsorption from aqueous solution using carbonized Bambara groundnut (Vigna Subterranean) shells. *Bayero Journal of Pure and Applied Sciences*. 2019;12(1):167–177.

17. Nyijime T.A, Ayuba AM, Chahul HF. Experimental and computational studies on activated Bambara groundnut (Vigna subterranean) hulls for the adsorptive removal of herbicides from aqueous solution. *Bulletin of the National Research Centre*. 2021;45;189–201.

18. Ayuba AM, Nyijime TA. Removal of pendimethalin herbicide from aqueous solution using untreated Bambara groundnut hulks as a low cost adsorbent. *Journal of Materials and Environmental Science*. 2021;12(1);1–12.

19. Tatah VS, Otitoju O, Onwurah INE. Adsorption isotherm and kinetic studies of Cd (II) and Pb (II) ions bioremediation from aqueous solution using unmodified Bambara groundnut husk (Vigna Subterranean). *American Association for Science and Technology Journal of Environment*.2017;2(3);34–42.

20. Assirey EA, Sirry SM, Burkani HA, et al. Biosorption of cadmium from aqueous solutions by Ziziphus spina-christi leaf powder. *Journal of Environmental Chemical Engineering*. 2020;8(2):103782.

21. Ali N, Jabeen N, Iqbal M, Hussain ST, et al. Biosorption of chromium from aqueous solutions by Calotropis procera leaves and stem powder: equilibrium. *kinetics and thermodynamics studies. Journal of Environmental Chemical Engineering*. 2020;8(6):104339.

22. Anantha RK, Kota S. Removal of lead by adsorption with the renewable biopolymer composite of feather (*Dromaius novaehollandiae*) and chitosan (Agaricus bisporus). Environmental Technology & Innovation. 2016;6(11):11–26.

23. Ngaosuwan K, Ruengyos N, Promchai W. Adsorption of arsenic from aqueous solution using grapefruit peel biosorbent: Equilibrium, kinetic, and thermodynamic studies. *Journal of Environmental Chemical Engineering*. 2022;10(1):108312.

24. Azizi S, Shahri MM, Mohamad R. Green synthesis of zinc oxide nanoparticles for enhanced adsorption of lead ions from aqueous solutions: equilibrium, kinetic and thermodynamic studies. *Journal of Molecules*. 2017;22:831–844.

25. Bhaumik R, Mondal NK, Das B, et al. Eggshell powder as an adsorbent for removal of fluoride from aqueous solution: equilibrium, kinetic and thermodynamic studies. *E-Journal of Chemistry*. 2012;9(3):1457–1480.

26. Lagergren S. About the theory of so-called adsorption of soluble substances. Kungliga Svenska Vetenskapsakademiens, Handlingar, 1898;24:1–39.

27. Ho YS. Citation review of Langer Gren kinetic rate on adsorption reactions. *Journal of Scientomertics*. 2004;59:171–177.

28. Pasavant P, Apiratikul R, Sungkhum V, et al. Biosorption of $Cu^{2+,}$ Cd^{2+}, Pb^{2+}, and Zn^{2+} using dried marine green macroalga *Caulerpa Lentillifera*. *Bioresources Technology*. 2006;97:2321–2329.

29. Sharma PK, Ayub S, Tripathi CN. Isotherms describing physical adsorption of Cr(VI) from aqueous solution using various agricultural wastes as adsorbents. *Civil & Environmental Engineering Research*. 2016;3:1–20.

30. Buvaneswari K, Singanan M. Review on scanning electron microscope analysis and adsorption properties of different activated carbon materials. *Materials Today: Proceedings*. 2020.

31. Hossain MA, Kumita M, Mori S. SEM characterization of the mass transfer of Cr(VI) during the adsorption on used black tea leaves. *African Journal of Pure and Applied Chemistry*. 2010;4(7):135–141.

32. Nirban L, Upendra K. SEM, FTIR and EDAX studies for the removal of safranin dye from water bodies using modified biomaterial – *Bambusa Tulda. IOP Conf Series Materials Science and Engineering*. 2017;225:012105.

33. Setiati R, Siregar SHP, Marhaendrajana T, et al. InfraRed evaluation of sodium lignosulfonate surfactant (SLS). *The International Journal of Science &Technoledge*. 2017;5(3):137–142.

34. Ajala EO, Eletta OAA, Ajala MA, et al. Characterization and evaluation of chicken eggshell for use as a bio-resource. *Arid Zone Journal of Engineering Technology and Environment.* 2018;14(1):26–40.

35. Nyijime TA, Ayuba AM, Chahul HF. Experimental and computational studies on activated Bambara groundnut (*Vigna subterranean*) hulls for the adsorptive removal of herbicides from aqueous solution. *Bulletin of the National Research Centre.* 2021;45:189–201.

36. Millán M, Rodrigo MA, Fernández-Marchante CM, et al. Towards the sustainable powering of the electrocoagulation of wastewater through the use of solarvanadium redox flow battery: a first approach. *Electrochimica Acta*. 2018;270:14-21.

37. Hernandez-Montoya V, Pérez-Cruz MA, Mendoza-Castillo DI, et al. Competitive adsorption of dyes and heavy metals on zeolitic structures. *Journal of Environmental Management*. 2013;116:213–221.

38. Bingol, D, Tekin N, Alkan M. Brilliant yellow dye adsorption onto sepiolite using a full factorial design. *Applied Clay Science*. 2010;50(3):315–321.

39. Li B, Zhou F, Huang K, et al. Highly efficient removal of lead and cadmium during wastewater irrigation using a polyethylenimine-grafted gelatin sponge. *Scientific Reports*. 2016;6:573–581.

40. Kulkarni MR, Revanth T, Acharya A, et al. Removal of crystal violet dye from aqueous solution using water hyacinth: equilibrium, kinetics and thermodynamics study. *Resource-Efficient Technologies.* 2017;3(1):71–77.

41. Okafor PC, Okon PU, Daniel EF, et al. Adsorption capacity of coconut *(Cocos nucifera L.*) shell for lead, copper, cadmium and arsenic from aqueous solutions. *International Journal of Electrochemical Science*, 2012;7:12354–12369.

42. Sharma PK, Ayub S, Tripathi CN. Isotherms describing physical adsorption of Cr(VI) from aqueous solution using various agricultural wastes as adsorbents. *Civil & Environmental Engineering Research.* 2016;3(1):1–20.

43. Chie-Amadi GO, Amagbo LG, Walter C. Performance of plantain pseudo stem for Pb^{+2} adsorption in aqueous solution. *European Journal of Advances in Engineering and Technology.* 2020;7(4):36–44.

44. Thangarajah V, Wijesundara WMYH, Kumari AHML, et al. Aqueous lead removal under optimized conditions using phosphoric acid activated coconut coir activated carbon. *American Journal of Analytical Chemistry.* 2020;11(12):389–405.

45. Eruola AO, Ogunyemi IO. Evaluation of the adsorption capacity of the coconut shell and palm-kernel shell adsorbents powder for the sorption of cadmium (ii) ions from aqueous solution. *IOSR Journal of Environmental Science, Toxicology and Food Technology.* 2014;8(6):55–63.

46. WHO. Guidelines for drinking-water quality: fourth edition incorporating the first addendum. Geneva: World Health Organization. 2017.

47. Odisu T, Edomwonyi-Otu LC, Anih EC. Comparative studies of adsorption of heavy metals from cement waste water using activated carbon from palm kernel husk, coconut and groundnut shells. *Journal of Applied Science and Environmental Management*. 2019;23(5):30–39.

48. Budi E, Umiatin U, Nasbey H, et al. Adsorption and pore of physical-chemical activated coconut shell charcoal carbon. *IOP Conference Series: Materials Science and Engineering*. 2018;335:012007.

49. Muthusamy P, Murugan S. Removal of lead ion using maize cob as a bioadsorbent. *International Journal of Engineering Research and Application.* 2016;6(6):5–10.

50. Gaur N, Kukreja A, Yadav, et al. Adsorptive removal of lead and arsenic from aqueous solution using soya bean as a novel biosorbent: equilibrium isotherm and thermal stability studies. *Applied Water Science*. 2018;8(6):98–109.

51. Okafor PC, Okon PU, Daniel EF, et al. Adsorption capacity of coconut (Cocos nucifera L.) shell for lead, copper, cadmium and arsenic from aqueous solutions. *International Journal of Electrochemical Science*. 2012;7(12):12354–12369.

52. Liang S, Guo X, Tian, Q. Adsorption of Pb^{2+}, Cu^{2+} and Ni^{2+} from aqueous solutions by novel garlic peel adsorbent. *Desalination and Water Treatment*. 2013;51(37–39):7166–7171.

53. Geetha KS, Belagali SL. Removal of dyes and heavy metals using garlic husk. *Nature Environment and Pollution Technology*. 2010;9(2):323–327.

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