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Comparison of the adsorption performance of coconut husk and palm kernel shells biochars for the removal of toxic metals from mining wastewater

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ABSTRACT

Toxic metal in mining wastewater is a significant concern for the environment and human health, prompting improved efforts to develop sustainable and efficient removal methods. This study characterised and compared the performance of coconut husk and palm kernel shells biochars in adsorbing toxic metals from mining wastewater. The biochars were produced through pyrolysis and characterised using Fourier transform infrared spectroscopy. Batch sorption experiments of toxic metals with biochars were conducted to investigate the effects of adsorbent dose, residence times and varied temperatures. The adsorption efficiency for the coconut husk biochar for arsenic ranged from 92.50 % to 97.50 %, 10.79 % to 24.88 % for cadmium, 46.79 % to 57.71 % for chromium and 52.78 % to 59.55 % for nickel at 30 °C for 30 min. The adsorption efficiency for palm kernel shell biochar ranged from 90.00 % to 97.50 % for As, 15.49 % to 48.35 % for Cd, 56.34 % to 91.81 % for Cr, and 34.18 % to 60.15 % for Ni at a temperature of 30 °C for 30 min. The coconut husk and palm kernel shells biochars showed high adsorption effectiveness, which can be attributed to their lignocellulose content, surface area, organic functional groups, and mineral content. Adsorption followed the Langmuir isotherm and pseudo-second order adsorption kinetics for the toxic metals, indicating monolayer chemisorption as the main mechanism. The coconut husk and palm kernel shell biochars are effective adsorbents for treating mining wastewater, with coconut husk biochar showing superior performance due to its higher surface reactivity. There is a need to create guidelines for selecting suitable materials for particular contaminants.

Introduction

Wastewater pollution remains a major global concern, primarily driven by anthropogenic activities such as mining, battery manufacturing, textile production, plastics manufacturing, tannery operations, paper and pulp industries, paint and pigment production, agriculture, domestic waste, and untreated sewage from chemical industries (Wang et al., 2022). Among these, mining operations, particularly artisanal and small-scale mining, are significant contributors to the contamination of water bodies with toxic metals (Karim et al., 2023; Abubakar et al., 2024). Mining wastewater is often laden with cadmium (Cd), chromium (Cr), mercury (Hg), nickel (Ni), arsenic (As), and lead (Pb), with concentrations frequently exceeding regulatory limits set by the Ghana Standards Authority and the World Health Organisation (Karim et al., 2023; Abubakar et al., 2024). In many cases, these excesses result from inadequate treatment infrastructure, operational negligence, or illicit discharge practices.

The presence of toxic metals in wastewater poses severe environmental and public health risks (Mishra et al., 2019). These metals are non-biodegradable, persist in ecosystems, and bioaccumulate in human tissues, leading to cancers, kidney damage, bone disorders, neurotoxicity, and developmental impairments in children (Mishra et al., 2019). Addressing such impacts is crucial not only for safeguarding ecosystems and water resources but also for ensuring the sustainability of mining practices and achieving the United Nations Sustainable Development Goal 6 (SDG 6), which calls for universal access to safe water, sanitation, and hygiene by 2030 (Guterres, 2023).

Various physicochemical methods such as chemical precipitation, coagulation, flotation, flocculation, ion exchange, reverse osmosis, nanofiltration, and ultrafiltration have been applied for heavy metal

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removal from wastewater (Qasem et al., 2021). However, their high operational costs, complex infrastructure, and energy demands limit their application in low- and middle-income countries (Rahman et al., 2020). In contrast, adsorption has emerged as one of the most practical, cost-effective, and efficient approaches for toxic metal removal (Anderson et al., 2022). Biochar, a porous carbonaceous material produced through pyrolysis of biomass under oxygen-limited conditions, has gained prominence as a low-cost and sustainable adsorbent (Mohan et al., 2018). Its high surface area, porous structure, functional groups, and mineral components enable effective binding of toxic metals from aqueous solutions (Fei & Hu, 2022). Compared to commercial adsorbents such as activated carbon, biochar requires minimal processing, can be produced locally, and offers affordability, making it especially relevant for resource-limited settings.

Numerous agricultural residues have been successfully converted into biochar for heavy metal removal. Reported adsorption capacities include banana peel (Cd, 30.7 mg/g; Pb, 45.6 mg/g; Cu, 49.5 mg/g; Cr, 25.2 mg/g), sesame straw (Cd, 86 mg/g; Pb, 102 mg/g; Cu, 55 mg/g; Cr, 65 mg/g), and wheat straw (Cd, 14.56 mg/g; Cu, 7.05 mg/g; Cr, 21.0 mg/g) (Chakraborty et al., 2022; Fei & Hu, 2022). Similar findings have been reported for bagasse, coffee residues, corn straw, peanut husk, and pineapple bran (Inyang et al., 2016; Anderson et al., 2022). Specifically, coconut husk and palm kernel shells have shown excellent adsorption potential, with coconut husk biochar achieving removal efficiencies of 94–97 % for Cd, 52–74 % for Cr, and 98–99 % for Pb (Duwiejuah et al., 2024).

Beyond their adsorption performance, these biomass sources offer broader environmental and economic benefits. Both coconut husk and palm kernel shells are lignocellulosic wastes abundant in Ghana and other tropical regions. Converting them into biochar not only produces effective and low-cost adsorbents but also promotes responsible waste management, supports circular economy principles, and reduces reliance on nonrenewable commercial adsorbents (Duwiejuah et al., 2024). Furthermore, spent biochar can be disposed of more safely than raw waste, as its carbon-rich structure immobilises pollutants and reduces leaching risks (Duwiejuah et al., 2024). Thus, the valorisation of coconut husk and palm kernel shell wastes into biochar presents a sustainable, affordable, and environmentally friendly pathway for removing toxic metals from mining wastewater, offering a promising solution tailored to the socioeconomic and ecological realities of developing countries (Duwiejuah et al., 2024).

Coconut husks and palm kernel shells are predominant agricultural byproducts in Ghana and many other countries. The feedstock choice is usually a very critical determinant of adsorption performance and physicochemical properties of biochar. In this study, the selection of the raw materials, such as coconut husks and palm kernel shells, is owing to their characteristics and local abundance in Ghana and other tropical regions. Coconut husk and palm kernel biochar frequently exhibit superior mechanical strength and chemical stability compared to other agricultural wastes (such as rice husk or sawdust), making them more durable and efficient in water treatment applications. In this study, the most commonly available biomass wastes, like coconut husks and palm kernel shells, were used for the production of biochar, which serves as a low-cost adsorbent. The performance of biochar as an adsorbent largely

Fig. 1. Map of the Tumentu mining site in Ahanta West District, Western Region of Ghana.
Source: Department of Geography and Regional Planning, University of Cape Coast, 2011

depends on different types of biomass material, dosage, residence time, surface functional groups and pH of the aqueous system. Therefore, this study characterised and compared the adsorption performance of coconut husk and palm kernel shells biochars for the removal of toxic metals from mining wastewater.

Materials and methods

Sample collection

The mining wastewater was collected into a gallon from the Tumentu mining site in Takoradi in the Western Region of Ghana (Fig. 1). The water was labelled with a sample code after the collection of samples. The coconut husk and palm kernel shells were gathered and placed in separate sacks and labelled respectively. All the samples were gathered and transported to the Spanish Laboratory Complex. The samples were handled and stored properly.

Biochar production

Vendors of coconuts and palm oil tappers provided the coconut husk and palm kernel shell. Regional agricultural practices greatly impact the availability of agricultural waste materials like palm kernel shells and coconut husk, which are commonly used in biochar production. In tropical developing nations like Ghana, where these materials are plentiful and categorised as waste, they are environmentally and economically feasible for large-scale biochar production. Due to variations in waste management systems and agricultural production, however, such feedstocks might be utilised differently, be in short supply, or not be regarded as waste in industrialised nations. The coconut husk and palm kernel shells were cleaned, broken into small pieces and allowed to air dry for 120 h. Pyrolysis was done using a Kuntan apparatus. The pyrolysis was performed for 30 min to convert coconut husk and palm kernel shell into biochar. After that, the biochar was left to cool.

Biochar characterisation

The biochars were also used to run the Fourier Transform Infrared Spectrometer (FTIR). The functional groups were determined using FTIR (Perkin-Elmer UATR-FTIR Two, Perkin-Elmer, United Kingdom). The IR used the ATR (Attenuated Total Reflectance) with a diamond crystal. The diamond crystal is cleaned with isopropanol, and a background scan is taken. The samples are then placed directly on the crystal, and the pressure gauge is applied to the maximum contact. The samples are then scanned, and the spectrum is generated by scanning through the sample (Sun et al., 2022).

Batch adsorption experiment

Batch sorption experiments of As, Cd, Cr and Ni with biochars were conducted in conical flasks in the water bath to investigate the effects of various factors (adsorbent dose), resident time (30 min and 40 min) and varied temperature (30 °C and 45 °C). The concentrations of the toxic metals in mining wastewater were determined (Table 1). Each 100 mL of mining wastewater was treated with 0.50 g, 1.00 g and 1.50 g of biochar. The mixture was swirled and placed in the water bath at 30 °C and 45 °C for both biochars, respectively. Environmental relevance and scientific objective are reflected in the choice of test temperatures of 30 °C and 45 °C. Typical ambient circumstances in tropical mining regions are mimicked by 30 °C, whilst higher temperatures caused by sunlight or industrial heat are represented by 45 °C. By balancing laboratory control with actual field application, testing within this range enables assessment of the impact of temperature on biochar's adsorption effectiveness under realistic circumstances. This experiment was repeated for different time intervals of 30 min and 40 min. The choice of 30 and 60 minutes as contact times was made by weighing preliminary optimisation results, operational practicality, and adsorption kinetics. Due to the abundance of active sites, the first adsorption in biochar adsorption experiments usually happens quickly. Selecting these time intervals allows us to better understand the kinetics by capturing both the initial rapid uptake phase (30 min) and a near-equilibrium phase (60 min). Due to flow-through system designs and treatment capacity requirements, extended contact times (e.g., many hours) are frequently not feasible in actual mining wastewater treatment situations. Testing at 30 and 60 minutes mimics actual residency durations in batch or continuous treatment systems employing biochar, assuring practical applicability. The two phases were then filtered via a 125 mm Whatman filter paper. An Atomic Absorption Spectrophotometer (AAS) (Waltham, United States of America) was used to determine the toxic metal concentrations in the supernatant phase. The collected filtrate in each bottle was sent back to the Ecological Laboratory for analysis again to determine the concentration of toxic metals, after the adsorption experiment was completed. The percentage elimination of toxic metals from the solution was calculated using the concentration data obtained from the AAS analysis.

Table 1
The initial concentration of the toxic metals.

Heavy metals	Reading 1	Reading 2	Reading 3	Mean
Arsenic	0.004	0.004	0.004	0.004
Cadmium	0.200	0.230	0.210	0.213
Chromium	0.710	0.750	0.740	0.733
Nickel	15.120	14.980	15.070	15.057

Calculation for the adsorption capacity and efficiency of contaminants by biochar

The adsorption efficiency of the toxic metals by the biochars was estimated using Equation 2. The adsorption capacity (Q_e) for each toxic metal at each adsorbent dosage. The adsorption capacity (Q_e) and percentage adsorption were calculated as in equations 1 and 2.

Adsorption isotherm models

Important details regarding the nature of the adsorbate-adsorbent surface interaction can be gleaned from the shape of an adsorption isotherm (Langmuir, 1918). The study used the Freundlich and Langmuir isotherm models. Irving Langmuir proposed the Langmuir isotherm in 1918. It is based on the idea that molecules adsorb in a monolayer without interacting when they are on a surface with a finite number of identical sites (Adeoye et al., 2023). The Langmuir equation is represented by the following equation 3:

Freundlich model

The mathematical representation of the Freundlich adsorption isotherm is equation 5.

Adsorption kinetics

The study of adsorption kinetics examines how adsorption occurs over time. Adsorption is the process by which molecules or particles adhere to a solid or liquid surface. A common model for explaining the kinetics of solute adsorption onto adsorbents is the pseudo-first-order kinetic model. The pseudo-first-order model is based on the idea that the rate of solute uptake changes with time is proportional to the difference between the saturation concentration and the quantity of solid uptake with time (Lagergren, 1898). This model is characteristically applicable in the initial stages of the process of adsorption.

The linearised pseudo first order and pseudo second order models are represented in equations 6 and 7.

A summary of the isotherm and kinetics models used in this study is given in Table 2.

Where Q_e is the adsorption capacity, C_i is the initial concentration of the contaminants, C_f is the final concentration of contaminants after adsorption, M is the amount of dosage of adsorbent, and V is the volume of the solution, C_e is the concentration of the adsorbate at equilibrium (mg/g), K_L is the Langmuir constant (L/mg) and Q_{max}(mg/g) is the amount of adsorbed molecules on the adsorbent surface at any time (Umoren et al., 2023). R_L can also be used as a separation factor. This will help us to better establish the important features of the Langmuir adsorption isotherm model. K_L is the Langmuir constant (mg/g), and C_O is the adsorbate initial concentration. When the$R_L > 1$ = the adsorption could be non-conducive. When the$R_L = 1$, it is linear, when$R_L = 0$, it is irreversible and finally, when $0 < R_L < 1$, it is favourable (Sun et al., 2013).

Where K_F is the adsorption capacity (L mg^{-1}), n denotes the adsorption density, and $\frac{1}{n}$ is the adsorption intensity (Madadgar et al., 2023). Q_e is the toxic metal quantity removed at equilibrium per gram of the adsorbent (mg/g), and C_e is the adsorbate concentration at equilibrium (mg/L). This shows how energy is relatively distributed and how heterogeneous the adsorption sites. If < 1, it means the adsorption is normal. If > 1, it shows that there is co-operation, if $n = 1$, it means there are two-phase partition that does not rely on concentration having occurred (Mahatara and Maskey, 2023). Here, k_1 is the pseudo first order rate constant (min^{-1}), K^2 is the pseudo second order rate constant ($g/mg^{-1}\ min^{-1}$), and qe and qt are the mass adsorbed per unit mass at equilibrium and at time "t", respectively. The adsorption rate is proportional to the concentration square at time t (C_t) according to the pseudo second order model (Rudzinski and Plazinski, 2007).

Results

Coconut husk biochar characterisation

The Fourier transform infrared spectroscopy (FTIR) analysis shows a broad O—H stretching at a peak (3361.72 cm^{-1}, 96.35 %T) for coconut husk biochar (Fig. 2). This is related to the hydroxyl (OH) groups, indicating the phenols, alcohols or moisture in the biochar.

Palm kernel shells biochar characterisations

The FTIR spectra analysis of palm kernel shells biochar displays a C—H stretching vibration in aliphatic hydrocarbons at 2922.09 cm^{-1}, 93.68 %T and 2852.68 cm^{-1}, 94.55 %T (Fig. 3). 1743.19 cm^{-1}, 93.90 % T peak, indicative of C═O stretching of carbonyl bonds of carboxylic groups or conjugated ketone (Fig. 3). 1154.78 cm^{-1}, 92.39 %T peak, associated with C—O stretching vibrations, which are characteristics of alcohols, ethers and phenols (Fig. 3).

Table 2
Summary of adsorption isotherms and kinetic models.

Model	Equation	Number	Source
Adsorption capacity (Q_e)	$Q_e = \frac{C_i - C_f}{m} \times V$	1	
Percentage Adsorption (R(%)	$R(\%) = \frac{C_i - C_f}{C_i} \times 100$	2	
Langmuir isotherm	$\frac{Ce}{Qe} = \frac{1}{K_L qmax} + \frac{Ce}{qmax}$	3	Langmuir, 1918
Separation factor	$R_L = \frac{1}{1 + K_L Ci}$	4	Ayawei et al., 2017
Freundlich isotherm	$Q_e = K_F\ C_e^{1/n}$	5	Freundlich, 1906
Pseudo first order	$Log_{(qe-qt)} = Log_{qe} - \frac{K1}{2.303} t$	6	Lagergren, 1898
Pseudo second order	$\frac{t}{q} = \frac{1}{K_2 q^2} + \frac{1}{qe} t$	7	Rudzinski and Plazinski, 2007

Adsorption of toxic metals by coconut husk biochar and palm kernel shell at 30 °C for 30 min

The adsorption efficiency for the different dosages of coconut husk biochar for arsenic was ≥ 92.50 % at 30 °C for 30 min (Table 3). The adsorption efficiency of coconut husk biochar for cadmium was ≥ 10.79 % at 30 °C for 30 min (Table 3). The adsorption efficiency of coconut husk biochar for chromium was ≥ 46.79 % at 30 °C for 30 min (Table 3). The adsorption efficiency of coconut husk biochar for nickel was ≥ 52.78 % at 30 °C for 30 min (Table 3).

The adsorption efficiency for the different dosages of coconut husk biochar for arsenic was ≥ 90.00 % at 30 °C for 30 min (Table 3). The adsorption efficiency of coconut husk biochar for cadmium was ≥ 15.49 % at 45 °C for 60 min (Table 3). The adsorption efficiency of coconut husk biochar for chromium was ≥ 56.34 % at 30 °C for 30 min (Table 3). The adsorption efficiency of coconut husk biochar for nickel was ≥ 34.18 % at 30 °C for 30 min (Table 3).

Adsorption of toxic metals by coconut husk biochar and palm kernel shell biochar at 45 °C for 60 min

The adsorption efficiency of coconut husk biochar for As recorded 94.00 % at a dosage of 0.5 g and increase to 97.50 % at a dosage of 1.5 g, 15.49 % at dosage of 0.5 g and increase to 20.18 % at a dosage of 1.5 g for Cd, 42.70 % at a dosage of 0.5 g to 49.52 % at a dosage of 1.5 g for Cr and 53.11 % at a dosage of 0.5 g to 54.31 % at a dosage of 0.5 g for Ni at 45 °C for 60 min (Table 3). The palm kernel shell biochar adsorption increases with an increase in dosage from 0.5 to 1.5 g for As, as it ranged from 91.50 % to 97.50 %, 20.18 % to 57.74 % for Cd, 7.23 % to 75.44 % for Cr and 33.07 % to 36.51 % for Ni at 45 °C for 60 min (Table 3).

Langmuir and Freundlich adsorption isotherms for coconut husk and palm kernel shells biochars

Most of the maximum adsorption capacity (q_{max}) for coconut husk biochar was very low and negative for As, Cd, Cr and Ni, showing an unstable adsorption process and weak interaction between metals and coconut husk biochar in the mining wastewater (Table 4). The K_L for the different temperatures of coconut husk biochar and palm kernel shells biochar ranged from 5.78 × 10^{-5} to 1.24 L/mg (Table 4). For Cr and Ni, the $1/_n$ values recorded for coconut husk biochar only were > 2.

The K_F for the different temperatures of coconut husk biochar and palm kernel shells biochar ranged from 1.04 to 0.08 at 30 °C for 30 min (Table 4). The R^2 of coconut husk and palm kernel shells biochar ranged from 0.90 to 0.99 at 30 °C for 30 min (Table 4). The K_F for the different temperatures of coconut husk biochar and palm kernel shells biochar ranged from 15.93 to 1.59 × 10^{16}at 45 °C for 60 min (Table 3). The R^2 of coconut husk and palm kernel shells biochar ranged from 0.96 to 0.66 at 45 °C for 60 min (Table 4).

Adsorption kinetics

The rate at which solutes adsorb onto adsorbents was expressed in the study using the pseudo first order and pseudo second order models. The K_1 for the different temperatures of coconut husk biochar for As, Cd, Cr and Ni ranged from 0.05 to 1.23 $mins^{-1}$ at 30 °C and 45 °C (Table 5). The R^2 of coconut husk biochar for As, Cd, Cr, and Ni ranged from 0.3317 to 0.8941 at 30 °C and 45 °C (Table 5). On the other hand, the K_1 for the different temperatures of palm kernel shells biochar for As, Cd, Cr, and Ni ranged from 0.06 to 1.21 $mins^{-1}$ at 30 °C and 45 °C (Table 5). The R^2 of palm kernel shells biochar for As, Cd, Cr and Ni ranged from 0.2706 to 0.8441 at 30 °C and 45 °C (Table 5).

The K_2 for the different temperatures of coconut husk biochar for As,

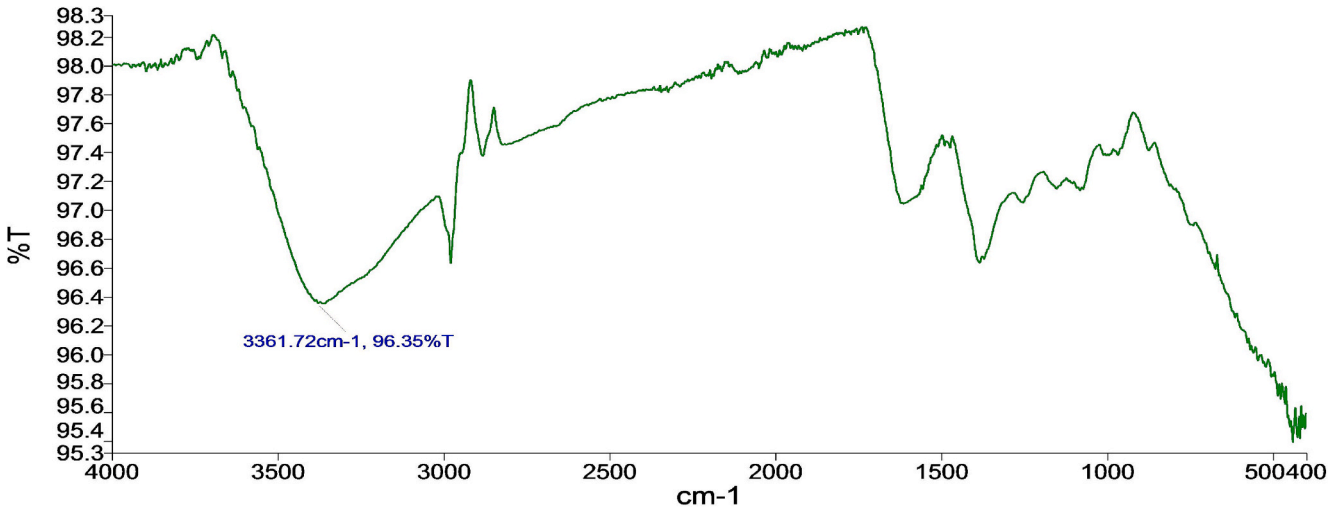

Fig. 2. Fourier transform infrared spectroscopy for coconut husk biochar.

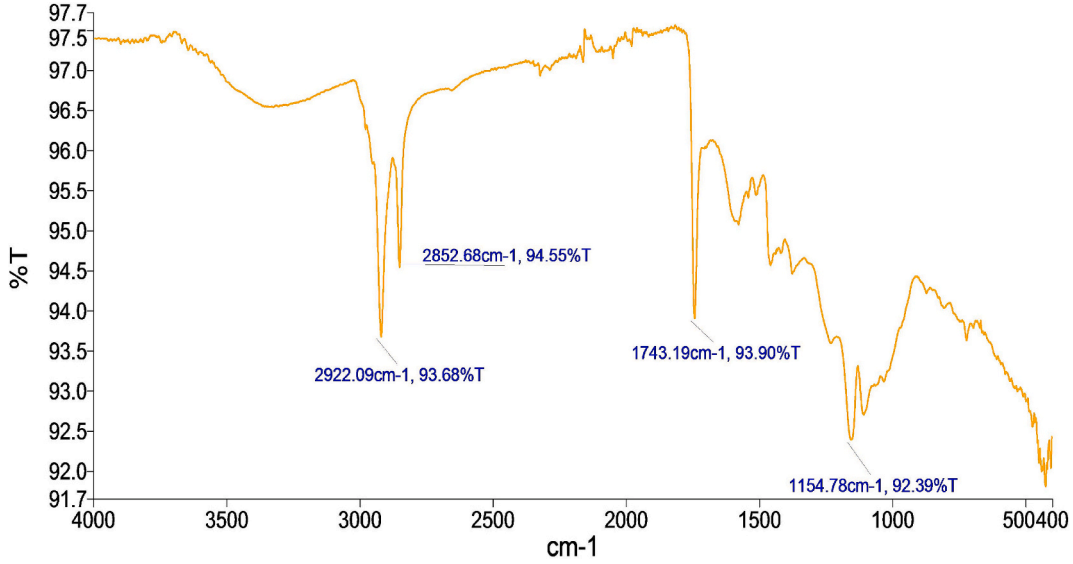

Fig. 3. Fourier transform infrared spectroscopy for palm kernel shells biochar.

Table 3
Removal efficiency of toxic metals by coconut husk biochar and palm kernel shell biochar.

Toxic metal	Dosage	Coconut husk biochar	Palm kernel shell biochar	Coconut husk biochar	Palm kernel shell biochar
		Adsorption efficiency (%)at 30 °C for 30 min	Adsorption efficiency (%) at 30 °C for 30 min	Adsorption efficiency (%) at 45 °C for 60 min	Adsorption efficiency (%) at 45 °C for 60 min
As	0.50	92.50	90.00	94.00	91.50
	1.00	95.00	95.00	96.00	95.50
	1.50	97.50	97.50	97.50	97.50
Cd	0.50	10.79	15.49	15.49	20.18
	1.00	15.49	24.88	15.49	29.57
	1.50	24.88	48.35	20.18	57.74
Cr	0.50	46.79	56.34	42.70	7.23
	1.00	54.97	69.98	44.07	14.05
	1.50	57.71	91.81	49.52	75.44
Ni	0.50	52.78	34.18	53.11	33.05
	1.00	55.76	44.47	53.58	33.20
	1.50	59.55	60.15	54.31	36.51

Cd, Cr and Ni ranged from −3125.00 to 0.24 $g \cdot mg^{-1} \cdot min^{-1}$ at 30 °C and 45 °C (Table 5). The R^2 of coconut husk biochar ranged from 0.8218 to 1 at 30 °C and 45 °C (Table 5). On the other hand, the K_2 for the different temperatures of palm kernel shells biochar for As, Cd, Cr and Ni ranged from −5555.60 to 0.66 $g \cdot mg^{-1} \cdot min^{-1}$ at 30 °C and 45 °C (Table 5). The R^2 of coconut husk biochar ranged from 0.0404 to 1 at 30 °C and 45 °C (Table 5).

Discussion

Coconut husk biochar characterisation

The FTIR analysis discovered a broad O—H stretching of coconut biochar. The hydroxyl groups are linked with this broad peak, which suggests that the biochar contains alcohols, phenols, or moisture. The biochar hydrophilicity is increased by the hydroxyl groups, which enhances the adsorbent's ability to adsorb polar contaminants like heavy metals (Dong et al., 2023). The O—H groups can partake in complexation with toxic metal ions, hydrogen bonding and ion exchange, among other mechanisms of adsorption. This increases the total adsorption ability of the biochar. Furthermore, to indicate unreacted organic matter

Table 4
Langmuir and Freundlich isotherm parameters for toxic metals adsorbed at 30 °C and 45 °C.

Metal	Biochar	Temp.(°C)	Q_{max} (mg/g)	Langmuir parameter			Freundlich parameter			
				R_L	K_L (L/mg)	R^2	$^1/_n$	N	K_F (I/g)	R^2
As	CHB	30	1.00	1.00	4.17×10^{-1}	0.92	9.00×10^{-1}	1.1	1.04	0.90
Cd	CHB	30	−680.34	1.01	−52	0.42	1.25	0.79	0.03	0.38
Cr	CHB	30	−8.00	1.22	−0.25	0.99	3.73	0.26	2.34	0.97
Ni	CHB	30	−0.18	−0.01	−5.55	0.87	6.17	0.16	8.05×10^{-6}	0.93
As	PB	30	1.11×10^{4}	1.00	5.78×10^{-5}	0.99	7.30×10^{-1}	1.36	2.10×10^{-1}	0.97
Cd	PB	30	131.57	1.21	−0.83	0.15	−0.2	−4.81	4.16×10^{-3}	0.15
Cr	PB	30	30.76	0.85	0.24	0.77	0.29	3.35	0.09	0.66
Ni	PB	30	8.59	0.05	1.24	0.84	1.07	0.93	0.08	0.99
As	CHB	45	−10000	1.00	2.80×10^{-4}	0.96	1.20	8.30×10^{-1}	15.93	0.96
Cd	CHB	45	384.61	0.94	0.26	0.01	−0.55	−1.8	2.01×10^{-3}	0.82
Cr	CHB	45	−4.92	1.32	−0.33	0.62	6.11	0.16	10.03	0.71
Ni	CHB	45	−0.02	-9.86×10^{-3}	−6.81	0.95	41.58	0.02	7.83×10^{-36}	0.99
As	PB	45	20,000	1.00	2.50×10^{-5}	0.99	0.84	1.17	0.61	0.98
Cd	PB	45	121.95	1.03	−2.34	0.01	−3.00	−0.33	1.42×10^{-5}	0.89
Cr	PB	45	21.45	2.02	−0.84	0.98	−2.18	−0.45	2.03×10^{-3}	0.88
Ni	PB	45	−0.14	-7.37×10^{-3}	−9.08	0.43	−167.66	−0.06	1.59×10^{16}	0.66

Table 5
Kinetic models for the toxic metals adsorbed onto coconut husks and palm kernel shell biochar.

Metal	Pseudo first order			Pseudo second order		
	q_e (mg·g^{-1})	K_1 (mins^{-1})	R^2	q_e (mg·g^{-1})	K_2 (g·mg^{-1}·min^{-1})	R^2
Coconut husk biochar						
As	0.95	0.05	0.7149	1.40	−2083.38	0.9868
	0.85	0.16	0.7499	1.33	−3125.00	0.9868
	0.80	0.22	0.7500	1.33	0.00	1
Cd	1.20	0.18	0.8941	1.12	−10.56	0.9991
	1.15	0.14	0.8914	1.12	−5.63	0.9959
	1.33	0.29	0.3317	3.01	−2.91	0.9685
Cr	2.05	0.72	0.7332	1.36	−1.74	0.9894
	1.92	0.65	0.7013	1.43	−1.36	0.9643
	1.79	0.58	0.7129	1.40	−2.07	0.8218
Ni	3.41	1.23	0.7506	1.33	−2.01	1
	3.09	1.13	0.7458	1.34	0.24	0.9988
	2.94	1.08	0.7387	1.35	0.11	0.9944
Palm kernel shell biochar						
As	0.94	0.06	0.7102	1.41	−1960.80	0.9926
	0.85	0.16	0.7459	1.34	−5555.60	0.9967
	0.80	0.22	0.7500	1.33	0.00	1
Cd	1.30	0.26	0.8441	1.18	0.07	0.0404
	1.27	0.24	0.8233	1.21	−10.67	0.9987
	1.33	0.29	0.8149	1.23	−6.11	0.9891
Cr	2.97	1.09	0.2706	3.70	0.13	0.7033
	2.54	0.93	0.3302	3.03	0.09	0.4635
	1.95	0.67	0.7085	1.41	0.28	0.4286
Ni	3.19	1.16	0.7467	1.34	0.02	0.9225
	3.35	1.21	0.6866	1.46	0.02	0.8950
	3.16	1.15	0.6846	1.46	0.66	0.9999

or moisture, the broad O—H band on the surface of biochar could impact the material's adsorption abilities (Sun et al., 2022). Though a vital sign about hydroxyl groups and their interactions with hydrogen bonds can be found in the large O—H stretching band. This broadband on biochar surface emphasises the material's hydrophilic properties and ability to participate in a diversity of adsorption processes, which make it useful for removing polar contaminants from water (Murtaza et al., 2024a).

Palm kernel shells biochar characterisations

The FTIR analysis of palm kernel shells displayed a peak of C—H stretching vibrations in aliphatic hydrocarbons. The peaks in this area are linked to the alpha-hydroxylation of carbon in the $–CH_2$ and $–CH_3$ groups (Bangert et al., 2024). These peaks show that aliphatic molecules could be present in the biochar structure, which could be involved in hydrophobic interactions with some organic pollutants. A carbonyl group (C═O) stretching peak is indicative of carbonyl bonds of conjugated systems or carboxylic groups, was observed. The C═O is generally found in aldehydes, carboxylic acids, esters or ketones and is represented by this peak (Marks et al., 2023). For metal ions to be adsorbed through ion exchange or complexation processes, carbonyl groups are vital. Also, the study observed a peak linked with C—O stretching vibrations which usually correlates with ethers, alcohols, and phenols' C—O stretching vibrations. The organic pollutants and toxic metals adsorption is facilitated by the amplified surface reactivity of biochar owing to the C—O functional groups (Xie et al., 2017). Among the key biochar physicochemical characteristics that affect variations in the adsorption of metals are pore size and surface area. Due to their larger surface area and well-developed mesopores (2–50 nm), biochar offers more accessible sites for the adsorption of metal ions. The size of the pores may prevent the movement of bigger hydrated cadmium ions, but arsenic species, which are frequently in smaller oxyanion forms, can move more readily into micro pores. Important functional groups for metal binding include carbonyl (C═O), hydroxyl (–OH), phosphate ($–PO_4$), and carboxyl (–COOH).

Adsorption of toxic metals by coconut husk biochar and palm kernel shell at 30 °C for 30 min

It is remarkable that the adsorption efficiencies of arsenic, Cr and Ni by coconut husk biochar increase with dosage. For arsenic, the hydrophobic property may be the cause of this trend, as it may facilitate interactions with specific functional groups or micro-pores found in the biochar (Murtaza et al., 2023). The Cd adsorption efficiency increased at varied dosages of the coconut husk biochar, but the adsorption efficiency is not high compared to As, Cr and Ni. At all dosages, the Cd and Ni adsorption efficiency increased, but the efficiency is not as high as compared to As and Cr. This suggests that biochar made from palm kernel shells is very good at extracting As and Cr from mining polluted water. The increased availability of adsorption sites is responsible for the small increase in efficiency that occurs with increasing the dosage of biochar (Huang et al., 2023). Arsenic and chromium demonstrated noticeably higher adsorption efficiency than cadmium and nickel. This might be explained by the variations in molecular structures and the biochar made from palm kernel shells' affinity for metal ions. The efficiency of biochar in adsorbing heavy metals may be attributed in part to its high cation exchange capacity. Also, factors such as the physicochemical characteristics of the adsorbates and the binding sites' characteristics should be considered for the interpretation of the differences in the binding affinities of metals (Wang et al., 2017).

Differences in both the chemical properties of the contaminants and the physicochemical characteristics of the biochars explain the considerable variation in adsorption efficiency between arsenic (90–97.5 %) and cadmium (10.79–48.35 %) onto the biochars. Arsenic is commonly found as arsenate As (V) or arsenite As (III), arsenic tends to produce oxyanions in water that engage in strong electrostatic attraction and ligand exchange mechanisms with surface functional groups on biochar, like hydroxyl, carboxyl, and phosphate groups. Cadmium is present as a cation (Cd^{2+}), and its adsorption is highly dependent on ion exchange and surface complexation, processes that may be less advantageous depending on the surface charge and functional groups that are present. Due to their stronger chemical affinities, biochars with higher oxygen-containing functional groups and alkaline pH are generally more effective at adsorbing oxyanions such as arsenic. Cadmium adsorption becomes restricted if the biochar surface has fewer cation exchange sites or is less negatively charged. Depending on their ionic radius and hydration shell size, arsenic species may have better access to micropores and mesopores than cadmium ions, which affects diffusion and adsorption rates. On these biochars, arsenic adsorption may be thermodynamically more advantageous (spontaneous), whereas cadmium adsorption may encounter higher energy barriers, particularly if rival ions (such as Ca^{2+}, Mg^{2+}) are present in the wastewater. The pH at which the tests were carried out may have encouraged the adsorption of arsenic. In general, cadmium absorption is more pH-dependent, with the best uptake typically occurring at higher pH values, where the biochar surface charge is more negative (Wibowo et al., 2025). Cadmium's lower adsorption is related to the weaker affinity of its cationic form under the same circumstances, whereas arsenic's higher adsorption is mostly caused by the stronger interactions between its oxyanion form and the functional groups on the biochar surface. This indicates variations in the adsorption mechanism, with arsenic primarily depending on ligand exchange and electrostatic attraction, whilst cadmium depends more on surface complexation and ion exchange, both of which were less successful in this experiment.

Adsorption of toxic metals by coconut husk biochar and palm kernel shell biochar at 45 °C for 60 min

The key factors influencing adsorption in terms of biochar dosage are the metal ion and the kind of biochar. It proved that increasing the amount of the adsorbent increases the efficacy of adsorption. Increased doses result in an increased number of binding sites, which gives metal ions more chances to interact and stick to the surface of the biochar. This increased availability of binding sites makes the adsorption process easier, which improves the targeted heavy metals' removal effectiveness (Aziz et al., 2023). The type of biochar and the specific heavy metal ions in question are two examples of the many variables that affect how much adsorbent is utilised to attain a certain amount of adsorption. The results of the study demonstrate that raising the dosage of the adsorbent can greatly improve adsorption efficiency, which is important to consider when developing mining wastewater treatment plans and maximising the removal of heavy metals to safeguard the environment and human health. The somewhat higher efficacy with dosage is consistent with research pointing to a method of approaching saturation thresholds with higher dosages of biochar. The observed trend, which shows that greater dosages of biochar result in increased adsorption efficiencies, implies that the porous structure and surface functional groups of palm kernel shell biochar produce an environment that is favourable for cadmium adsorption.

A strong affinity exists between the arsenic, cadmium, chromium, and nickel ions present in mine wastewater and the biochar derived from coconut husk and palm kernel shell. Arsenic had good adsorption efficiency at all dosages. For nickel, the adsorption efficiencies were likewise high. Because of its porous structure or certain chemical capabilities, the adsorbent may offer a favourable environment for nickel adsorption, as evidenced by its consistently high effectiveness (Parmar and Thakur, 2013). The results clearly show that increasing the contact time increases the adsorption efficiency of As, Cd, Cr and Ni. The longer the adsorbent and adsorbate are in contact, the more effectively the As, Cd, Cr and Ni may be removed, as well as the greater the adsorption capacity.

The adsorption efficiency of the coconut husk and palm kernel shell was not significantly different from each other. Differences in the qualities of feedstock are responsible for the varied efficiency of adsorption for toxic metals from the system (Zhao et al., 2019; Singh et al., 2021). Wheat straw, peanut husk, tea-coffee waste and rice bran residues had the highest efficiency of adsorption for Pb (99.8 %), Cd (99.9 %), Pb (96 %) and Pb (74.54 %), respectively (Chakraborty et al., 2022). Biochars with high oxygen-containing functional groups (such as hydroxyl, carboxyl, phosphate) for oxyanionic metals like arsenic. These groups improve ligand exchange mechanisms and electrostatic attraction. Biochars with greater cation exchange capacity and negatively charged surfaces should be prioritised for cationic metals like cadmium because they facilitate ion exchange and complex formation. Biochars with a higher surface area and larger mesopores are better at absorbing larger hydrated ions like cadmium. Biochars made of calcium, magnesium, or silica may provide further adsorption benefits through precipitation and surface complexation, particularly for metals like cadmium. The temperature at which biochar is made influences its functional groups and surface area. Higher temperatures (500 – 700 °C), for example, might increase surface area, which is beneficial for cadmium removal, whilst lower pyrolysis temperatures (300 – 500 °C) tend to retain more functional groups, which may be more favourable for arsenic. Coconut husk and palm kernel shells biochar feedstocks that are locally accessible, affordable, and ecologically friendly to support large-scale wastewater treatment operations. These guidelines can help design treatment systems that are more effective and tailored to the particular chemical behaviour of the targeted metals by coordinating the biochar selection with the chemical behaviour of those metals.

Langmuir adsorption isotherm for coconut husk and palm kernel shells biochars

As, Cd, Cr and Ni had lower values for coconut husk biochar, showing a weaker interaction between metals and the biochars in mining wastewater. The lower constant values showed the weaker interaction between them (Tran et al., 2019). Whilst biochar from palm kernel shell had very high q_{max} values for Cd, As, and Cr, showing a stable process of

adsorption and stronger interaction between Cd, As, and Cr and the palm kernel shell biochar in the mining wastewater. Higher values indicate a stronger interaction between the adsorbents and adsorbate (Tran et al., 2019). The q_{max} for Cd in palm kernel shell biochar was remarkably high, signifying a steady mechanism of adsorption. This study is further supported by the high R_L and R^2 values, which demonstrate a consistent and favourable adsorption process (George et al., 2023). The Langmuir adsorption isotherm was well fitted by the R^2 value, which was greater than 0.70 (Pereira et al., 2023).

The separation factor (R_L) of coconut husk biochar and palm kernel shell biochar for As, Cd and Cr were one, indicating unfavourable adsorption whilst generally Ni ions were smaller than one, favouring the phenomenon of adsorption (Misran et al., 2022). The R_L value, which is less than 1 the adsorption process is favourable, and R_L values greater than 1 the adsorption process is unfavourable. Also, when the $R_L = 1$, the adsorption process is linear (Nethaji et al., 2013). The Langmuir model is the best fit for the adsorption of As, Cd, and Cr onto palm kernel shell biochar based on the q_{max}, R_L and R^2 values. This implies the adsorption of As, Cd, and Cr is effective, physical in nature and the surface of palm kernel shell biochar is a monolayer and possesses a great affinity for As, Cd, and Cr ions in the mining wastewater.

Freundlich adsorption isotherm for coconut husk and palm kernel shells biochars

The linear regression coefficient value of the Freundlich isotherm model verifies that multilayer adsorption means a heterogeneous surface (Chen et al., 2018). For Cr and Ni, the $1/n$ values recorded for coconut husk biochar only were > 2 indicates unfavourable adsorption whilst all the metals (As, Cd, Cr and Ni) adsorption onto palm kernel shell biochar and As and Cd adsorption onto coconut husk biochar is easy to adsorb ($0.5 < {}^{1}/_{n} > 1$) (Desta, 2013).

Generally, the value of n for toxic metals for coconut husk biochar and palm kernel shell biochar was less than one, demonstrating that their removal is a chemical process. The constant n infers the process of adsorption as chemical, linear, or physical (Chen et al., 2018) as it identifies the process of adsorption whether chemical process ($n < 1$), physical process ($n > 1$), desired adsorption ($n = 1$ to 10) or linear process ($n = 1$) (Desta, 2013; Misran et al., 2022). The K_F (l/g) value for coconut husk biochar and palm kernel shell biochar was generally low for As, Cd, Cr and Ni, showing a weaker interaction between metals and biochars. The low constant values showed the weaker interaction between them (Tran et al., 2019).

The Freundlich model is the best fit for the adsorption of As, Cd, Cr and Ni onto coconut husk biochar and palm kernel shell biochar based on the R^2 values only. This implies the adsorption of As, Cd, Cr, and Ni is chemical in nature and the surface of the biowaste biochars are heterogeneous and possesses a great affinity for As, Cd, Cr and Ni ions in the mining wastewater. High R^2 values and interesting adsorption properties were observed for arsenic, chromium, and nickel, highlighting the best match of the Freundlich model. Because of the interactions between metal ions and the adsorbent surface, chromium showed both a high adsorption capacity and adsorption heterogeneity for the biochar made from coconut husks as the temperature rose (Murtaza et al., 2024b).

Adsorption kinetics

In this investigation, PSO had greater qe and R^2 values than PFO, indicating that it suited the data well. The PSO results also suggested that the As, Cd, Cr, and Ni adsorption on coconut husk biochar and palm kernel shell biochar occurs due to chemical processes such as valence force sharing or exchanging electrons between the adsorbents (coconut husk biochar and palm kernel shell biochar) and adsorbate (As, Cd, Cr, and Ni) or by chemical bonding between As, Cd, Cr, and Ni and functional groups. The models showed that the number of empty sites was directly proportional to the metal adsorption rate on the surfaces of the adsorbent (Chidambaram, 2015; Dad et al., 2024). The adsorption rate of PFO kinetics is determined by the adsorbate's process of diffusion (de Caprariis et al., 2017), whereas the kinetics of PSO supports the notion that the rate of adsorption results from a chemical process that includes the valence forces sharing or possibly the electron exchange between the adsorbate and adsorbent (Shakoor et al., 2019).

The PSO kinetics model best fits the data of adsorption since it posits that the rate of adsorption is influenced by the adsorbate concentration and the active availability sites, suggesting that the primary process is chemisorption. This suggests that the mechanism of removal involves not only physical attraction, nonetheless also more powerful chemical interactions such as the exchange or sharing of electrons between contaminant ions and surface functional groups of biochar. In practice, this suggests a steadier and perhaps irreversible process of adsorption, which advances the efficacy and reliability of biochar in treating mining wastewater. The adsorption of As, Cd, Cr and Ni ions in the initial phase onto the coconut husk and palm kernel shells biochar was faster, as the adsorption might have taken place mostly on the biochar surface. This process of adsorption was relatively slow as, Cd, Cr, and Ni gradually diffused into the pores of carbon and reacted with the inner surface of active sites (Kołodýnska et al., 2012). The process of adsorption was a fast reaction, as the reaction rate constants were $k_2 > 1$. The entire adsorption process was separated into two stages: the first stage involved the diffusion of As, Cd, Cr, and Ni to the surface of biochar, and the slope of the fitted line was higher during this stage, indicating that the boundary diffusion process was faster. The slope of the fitted line reduced dramatically in the second stage, showing that the heavy metal adsorption rate was being controlled by biochar at this point.

Conclusion

The biochar made from coconut husk and palm kernel shells has a high adsorption effectiveness, which can be attributed to its lignocellulose content, surface area, organic functional groups, and mineral content. It is imperative to eliminate pollutants from mine effluent to safeguard both human health and the aquatic environment. Coconut husk and palm kernel shells are thought to effectively remove all pollutants when agricultural waste is used.

Real mining effluents have varying pH and mixed pollutants, which might have an impact on adsorption effectiveness when compared to regulated lab settings. In contrast to batch lab tests, continuous flow systems may not allow for enough contact time, resulting in less total pollutant removal. Maintaining biochar's performance through several uses and regenerating it effectively at scale might be difficult. The infrastructure necessary to manufacture, move, and manage significant amounts of biochar may not be readily accessible or affordable. Biochar is heated at moderate temperatures to desorb adsorbed metals and repair active sites. The process of removing toxic metals without harming the structure of biochar uses bases (like NaOH) or mild acids (like HCl). Using saline washes or basic water to treat toxic metals that are only loosely bonded to the biochar surface. These approaches improve the economic viability of biochar-based treatment systems by helping to minimise waste and maintain adsorption capacity. The biochar as an adsorbent utilisation has shown to be very successful and beneficial.

Biochar may have a somewhat lower capacity for adsorbing some pollutants, but its slight processing needs, low manufacturing cost, and option for onsite production make it predominantly well suited for usage in low- and middle-income countries with limited resources for treatment of wastewater. This improves the practicality and scalability of biochar use in actual mining wastewater treatment facilities. Further study should evaluate the efficacy of coconut husk and palm kernel shells waste materials, and create guidelines for the selection of suitable materials for particular contaminants. Also, adopting sustainable practices in wastewater treatment and educating and promoting public

awareness are essential in addressing water pollution.

CRediT authorship contribution statement

Abudu Ballu Duwiejuah: Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Richmond Kow Ntsen Otoo:** Writing – original draft, Investigation, Funding acquisition, Data curation. **Abubakari Zarouk Imoro:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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