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Biosorption Potential of *Arachis hypogaea* Peel-Derived Biochar for Mercury-Contaminated Wastewater Treatment

[1]Verwiyeh Silas Tatah, [1]David Chinonso Anih, [2]Michael Chibuzor Okere, [3]Ugo Nwitte-Eze, [4]Efagene Clifford, [5]Godswill Igenewari Yellowe, [6]Amola Augustine Inalegwu, [7]Nwanze Tobechukwu Joseph, [8]Asogwa, Chikaodili Dorothy and [9]Emmanuel Ndirmbula Linus

[1]Department of Biochemistry, Faculty of Biosciences, Federal University Wukari, Taraba, Nigeria
[2]Department of Marine Science, Faculty of Sciences, University of Lagos, Lagos, Nigeria
[3]Department of Chemical Engineering, Federal University of Technology, Akure, Ondo, Nigeria
[4]Department of Chemical Engineering, Faculty of Engineering, Enugu State University of Science and Technology, Enugu, Nigeria
[5]Department of Civil and Environmental Engineering, Faculty of Engineering, University of Port Harcourt, Rivers, Nigeria
[6]Department of Biological Sciences, Faculty of Sciences, Taraba State University, Jalingo, Nigeria
[7]Department of Civil and Environmental Engineering, University of Lagos, Akoka, Lagos, Nigeria
[8]Department of Physics and Astronomy, University of Nigeria Nsukka, Enugu, Nigeria
[9]Department of Pharmacology and Therapeutics, Faculty of Basic Clinical Sciences, University of Maiduguri, Borno, Nigeria

ABSTRACT

Background and Objective: Mercury contamination in water remains a pressing global challenge due to its persistence, toxicity, and ability to bioaccumulate through food chains, posing serious ecological and health risks. Conventional treatment technologies, though effective, are often costly and energy-intensive, limiting their application in resource-constrained settings. This study explored the potential of groundnut (*Arachis hypogaea*) peel-derived biochar as an economical biosorbent for mercury removal from aqueous solutions. The work aimed to evaluate the influence of operational parameters, adsorption kinetics, and equilibrium behavior, while also considering the broader implications for waste valorization and sustainable water treatment. **Materials and Methods:** Groundnut peels collected from local sources were washed, oven-dried, and converted into biochar through slow pyrolysis at 450°C. The resulting biochar was ground, sieved, and applied in batch adsorption experiments. Parameters including adsorbent dosage (1.5-5.0 g), initial mercury concentration (5-25 mg/L), pH (2.4-9.1), and contact time (5-120 min) were systematically varied at 30°C. Residual mercury concentrations were determined using atomic absorption spectrophotometry. Adsorption data were modeled using Langmuir and Freundlich isotherms, while kinetic behavior was assessed with pseudo-first-order and pseudo-second-order models. Statistical analyses were performed using ANOVA at $p<0.05$. **Results:** Mercury removal efficiency increased steadily with biochar dosage, reaching 84.96% at 5 g. Adsorption was rapid within the first 40 min, then slowed as equilibrium approached, reflecting external film diffusion followed by intraparticle transport. Optimum removal occurred at pH 6.0 (70.78%), while efficiency declined under strongly acidic or alkaline conditions due to proton competition and hydroxide precipitation. Removal remained above 66% up to 20 mg/L but decreased at higher concentrations due to site saturation. The Langmuir model provided the best fit (q_{max} = 20.01 mg/g, R^2 = 0.932), indicating monolayer adsorption, while kinetic data aligned more closely with the pseudo-first-order model ($k1$ = 0.107 min^{-1}, R^2 = 0.978), suggesting physisorption dominance. **Conclusion:** Groundnut peel biochar demonstrated promising potential as a sustainable, low-cost sorbent for mercury removal, combining moderate adsorption capacity with rapid uptake and pH-sensitive performance. While effective under laboratory conditions, further studies on surface modification, regeneration, and column applications are recommended to enhance efficiency and support real-world deployment. This work highlights the dual benefit of mitigating mercury pollution while valorizing agricultural waste within a circular economy framework.

KEYWORDS

Groundnut peel biochar, mercury removal, heavy metal adsorption, adsorption isotherms, adsorption kinetics, agricultural waste valorization, pH effect, water treatment, sustainable remediation

ISSN: 2151-7908 (Online)
ISSN: 1819-3579 (Print)
https://doi.org/10.3923/tasr.2025.88.98

Received: 17 Sep. 2025
Accepted: 11 Nov. 2025
Published: 12 Nov. 2025

INTRODUCTION

Mercury (Hg) is a globally recognized priority pollutant due to its extreme toxicity, environmental persistence, and pronounced tendency to bioaccumulate and bio magnify within aquatic food webs, posing severe ecological and human health risks. Once released into the environment, mercury undergoes complex transformations, including methylation, which amplifies its toxicity and facilitates its transfer through trophic levels. Consequently, the development of efficient, sustainable, and cost effective remediation strategies remains an urgent scientific and policy priority. Among the various approaches explored, adsorption has emerged as a particularly promising method for Hg^{2+} removal, owing to its operational simplicity, adaptability, and potential for regeneration. Recent studies have elucidated the adsorption mechanisms of Hg^{2+} onto diverse biochar fractions, revealing that feedstock type, pyrolysis temperature, and surface chemistry critically influence sorption performance[1].

Beyond mercury, adsorption technologies have been successfully applied to other contaminants, such as fluoride, using advanced sorbents like metal organic frameworks[2]. Agricultural solid wastes, including fruit and vegetable peels, have attracted significant attention as low-cost, renewable feedstocks for adsorbent production[3]. Such valorization aligns with circular economy principles, as demonstrated by the conversion of potato peel waste into biofuels[4], and complements other biorefinery pathways, such as the extraction of protein-polysaccharide complexes from brown algae[5]. The cation exchange capacity of biochars, a key determinant of their metal binding potential, varies widely with feedstock composition and nutrient ratios[6].

While membrane-based technologies can achieve high removal efficiencies for heavy metals, they are often hindered by high energy demands, fouling, and operational costs[7]. Meanwhile, global mercury emissions are projected to rise under current socioeconomic trajectories, intensifying the need for scalable, low-cost sorption solutions[8]. Plant-derived materials, such as banana peel extracts rich in phenolic compounds, have demonstrated notable metal binding capacities[9], and nano modification of biochar has been shown to enhance active site density and adsorption kinetics[10]. Comprehensive reviews confirm the versatility of biochar-based composites in removing both organic and inorganic pollutants from aqueous systems[11-13], while magnetic biochars derived from waste wood have proven effective in arsenic remediation[14].

The broader literature underscores biochar's multifunctional role in environmental management, from soil amendment to water purification[15-17]. However, certain agro residues remain underexplored despite their abundance and favorable physicochemical properties. Groundnut (*Arachis hypogaea*) peel, a lignocellulosic byproduct of peanut processing, is one such resource. Its high carbon content, porous structure, and surface functional groups make it a promising precursor for biochar production. When subjected to controlled pyrolysis, groundnut peel biochar can offer a high surface area, abundant active sites, and tailored surface chemistry conducive to Hg^{2+} adsorption.

This study investigates the potential of groundnut peel biochar as an efficient biosorbent for mercury-contaminated wastewater. Specifically, it evaluates the effects of initial Hg^{2+} concentration, pH, contact time, and adsorbent dosage on removal efficiency, while applying isotherm and kinetic models to elucidate the underlying sorption mechanisms. By integrating waste valorization with water treatment, this work contributes to sustainable remediation strategies that address both environmental contamination and agricultural waste management.

MATERIALS AND METHODS

Study area and sample collection: This study was conducted over six months, from January to June, 2024, at the Microbiology Laboratory of Federal University, Wukari, located in Taraba State, Nigeria. Wukari is a culturally rich city with deep historical roots, once part of the former Gongola State.

Geographically, Wukari sits between Taraba and Benue States. It shares boundaries with Benue State to the south, Gassol Local Government Area (LGA) to the North, Donga LGA and Takum to the East, and Ibi LGA to the West. The city spans an area of approximately 4,308 km^2 and had a recorded population of about 241,546 during the 2006 census.

Wukari experiences a wide range of relative humidity, varying from 14 to 77%, and is known not only for its environmental diversity but also for its vibrant cultural heritage. The city is home to a traditional state that embraces a rich tapestry of customs, values, and social norms that continue to shape its identity today.

Reagents and apparatus: Experiments employed an atomic absorption spectrophotometer, Whatman No. 1 filter paper, orbital shaker, analytical balance, pH meter, mortar and pestle, and DHG-902A oven.

Preparation of synthetic mercury solution: A stock solution of 1000 ppm Hg^{2+} was prepared by dissolving 1.48 g of Mercury Sulfate ($HgSO_4$) in 1 L of distilled water. Working solutions of 5, 10, 15, 20, and 25 ppm were obtained by serial dilution of the stock solution.

Preparation of groundnut peel biochar: Groundnut (*Arachis hypogaea*) peels were collected from local agricultural waste sources, thoroughly washed with distilled water to remove dirt and impurities, and air-dried for 48 hrs. The peels were then oven-dried at 105°C for 24 hrs to eliminate residual moisture[18,19].

The dried biomass was converted into biochar through slow pyrolysis in a muffle furnace under limited oxygen conditions at 450°C for 2 hrs. After cooling to room temperature in a desiccator, the biochar was ground with a mortar and pestle and sieved to a particle size of less than 250 μm. The prepared biochar was stored in airtight containers until use[18,19].

Batch adsorption experiments: Batch adsorption studies were conducted in acid-washed polyethylene bottles at 30±2°C using an orbital shaker. The following parameters were varied systematically:

- **Adsorbent dosage:** 1.5, 2.0, 3.0, 4.0, and 5.0 g
- **Solution volume:** 100 mL of mercury solution per flask
- **Contact time:** 5, 20, 40, 60, 90, and 120 min
- **Shaking speed:** 100 rpm to ensure uniform mixing
- **pH adjustment:** The pH of the solutions was adjusted to 2.4, 6.0, 7.0, 8.52, and 9.13 using 0.1 M H_2SO_4 or 0.1 M NaOH, measured with a calibrated pH meter[18-20]

At each time interval, 10 mL aliquots were withdrawn, filtered through Whatman No. 1 filter paper, and analyzed for residual mercury concentration using an Atomic Absorption Spectrophotometer (AAS). All experiments were conducted in duplicate, and mean values were reported by researchers[18-21].

Adsorption isotherm and kinetics: Equilibrium data were analyzed using the Langmuir and the Freundlich isotherm models to describe adsorption behavior. Kinetic studies were performed using pseudo-first-order and pseudo-second-order models to determine the rate-controlling mechanism[18-21].

Statistical analysis: All experiments were performed in duplicate, and results are presented as Mean±Standard Deviation (SD). Data fitting for isotherm and kinetic models was carried out using linear regression analysis, and the coefficient of determination (R^2) was used to evaluate the goodness of fit. Differences between treatments (such as pH, dosage, or contact time) were assessed using One-way ANOVA at a significance level of $p<0.05$[22-24].

RESULTS AND DISCUSSION

Effect of biochar dosage: The Hg^{2+} removal increased from 50.14% at 1.5 g to 84.96% at 5.0 g, reflecting enhanced surface area and active site availability[25].

Figure 1 illustrates the influence of groundnut-peel biochar dosage on mercury adsorption. Removal efficiency increased progressively from 1.5 to 5.0 g, confirming the positive correlation between sorbent mass and surface area availability.

These findings validate the dosage optimization described and highlight the role of active sites in enhancing Hg^{2+} uptake.

Table 1 summarizes how increasing biochar dosage influenced Hg^{2+} removal. Removal improved steadily between 1.5 and 5.0 g, reflecting greater availability of adsorption sites. These data corroborate the discussion on dosage optimization for effective mercury uptake.

Effect of contact time: Rapid uptake occurred within the first 40 min; removal reached 52.54% at 120 min, indicating initial external diffusion followed by intraparticle transport[26].

Figure 2 depicts how adsorption efficiency varies with contact time. Removal increased sharply during the first 40 min, then gradually approached equilibrium. This trend supports the kinetic, showing that most Hg^{2+} uptake occurs rapidly before stabilizing.

Effect of pH: Maximum removal (70.78%) was observed at pH 6.0. Below this pH, proton competition reduces Hg^{2+} binding; above pH 7.0, $Hg(OH)_2$ formation and deprotonation lower efficiency[27].

Figure 3 illustrates the variation of mercury removal with pH. Adsorption efficiency increased steadily from acidic to near-neutral conditions, peaking at pH 6. This confirms the role of pH in optimizing surface charge and promoting Hg^{2+} binding.

Effect of initial Hg^{2+} concentration: Removal remained above 66% up to 20 ppm but declined at 25 ppm due to active site saturation. Adsorption capacity increased with concentration, plateauing as sites filled[28].

Figure 4 presents the relationship between starting Hg^{2+} concentration and adsorption capacity. Capacity increased with concentration up to ~20 ppm, reflecting enhanced driving force for mass transfer. Beyond this level, q_e approached a plateau, consistent with surface saturation noted in this study.

Adsorption isotherms: Langmuir modelling produced q = 20.013 mg/g (R^2 = 0.932), indicating monolayer adsorption. Freundlich parameters (1/n = 0.841, R^2 = 0.841) suggested weaker, multilayer sorption[29-34].

Figure 5 shows the Langmuir adsorption plot derived. The linear trend between and indicates a good fit to the Langmuir model. This supports the assumption of monolayer adsorption on a uniform surface.

Figure 6 illustrates the Freundlich adsorption plot. The straight-line fit between log q_e and log C_e demonstrates that adsorption also conforms to the Freundlich model. This supports the presence of heterogeneous surface sites and multilayer sorption behavior.

Table 2 presents the Langmuir and Freundlich constants. The high R^2 values indicate good agreement between experimental data and both models. These results confirm the suitability of the isotherms for describing Hg^{2+} uptake by the biochar.

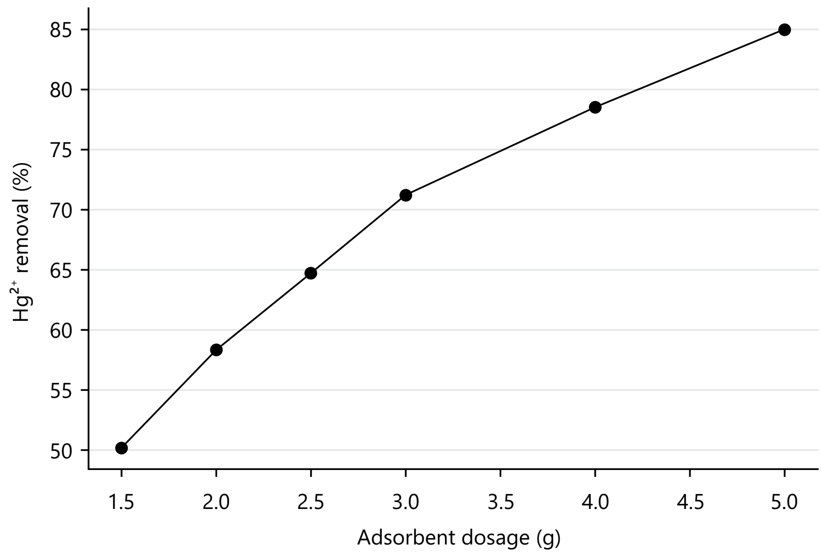

Fig. 1: Effect of adsorbent dosage on mercury (Hg^{2+}) removal efficiency (self-generated)
Removal percentage of Hg^{2+} from solution as a function of biochar dosage (1.5-5.0 g). Data show a steady rise in adsorption efficiency, reaching ~85% at the highest dosage tested. Points represent measured values, and the connecting line indicates the overall trend

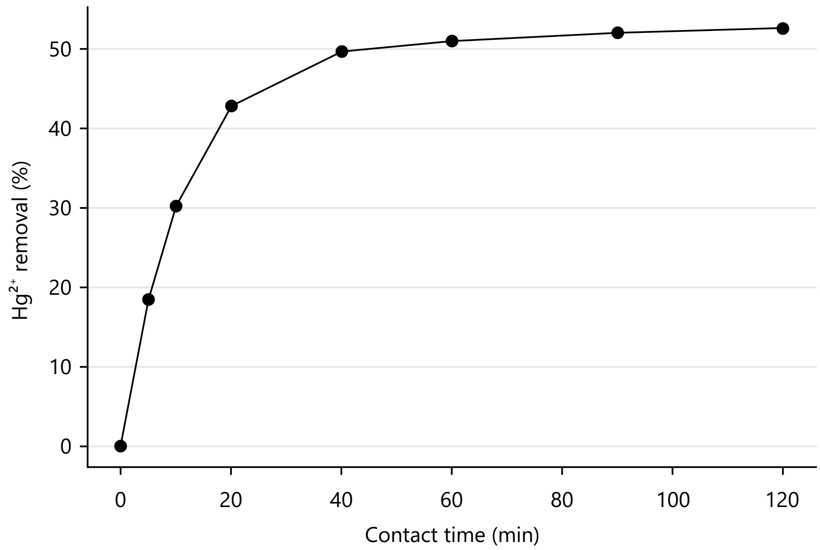

Fig. 2: Effect of contact time on mercury (Hg^{2+}) removal by groundnut-peel biochar (self-generated)
Mercury removal percentage plotted against contact time (0-120 min). Adsorption rose quickly at early intervals and levelled off near 52% at 120 min. Symbols denote experimental values, and the line shows the adsorption trend

Table 1: Effect of adsorbent dosage on mercury (Hg^{2+}) removal efficiency

Adsorbent dosage (g)	Hg^{2+} removal (%)
1.5	50.14
2.0	58.3
2.5	64.7
3.0	71.2
4.0	78.5
5.0	84.96

Adsorbent dosage values (1.5-5.0 g) with corresponding Hg^{2+} removal percentages. Removal efficiency rose consistently with increasing dosage, reaching about 85% at 5 g. Numbers represent measured means from the adsorption study

Table 2: Langmuir and the Freundlich isotherm parameters for mercury (Hg^{2+}) adsorption

Isotherm	Parameter 1	Parameter 2	R^2
Langmuir	q_{max} = 20.013 mg/g	b ≈0.20 L/mg	0.932
Freundlich	K_f ≈ 1.20	1/n = 0.841	0.841

Values of q_{max}, b, K_f, and 1/n for Hg^{2+} adsorption on biochar. Both models display strong fits, with Langmuir suggesting monolayer coverage and Freundlich reflecting surface heterogeneity. Parameters were derived from equilibrium adsorption data

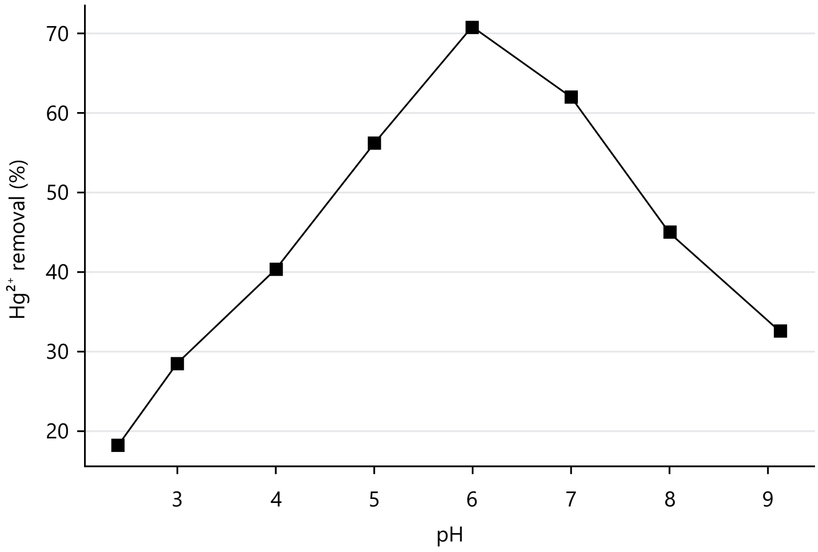

Fig. 3: Influence of solution pH on mercury (Hg^{2+}) adsorption by groundnut-peel biochar (self-generated)

Percentage of Hg^{2+} removed from solution across pH 2.4-9.1. Removal rose from ~18% in strongly acidic media to ~71% at pH 6, then declined at higher pH. Points represent experimental values, while the line traces the observed adsorption trend

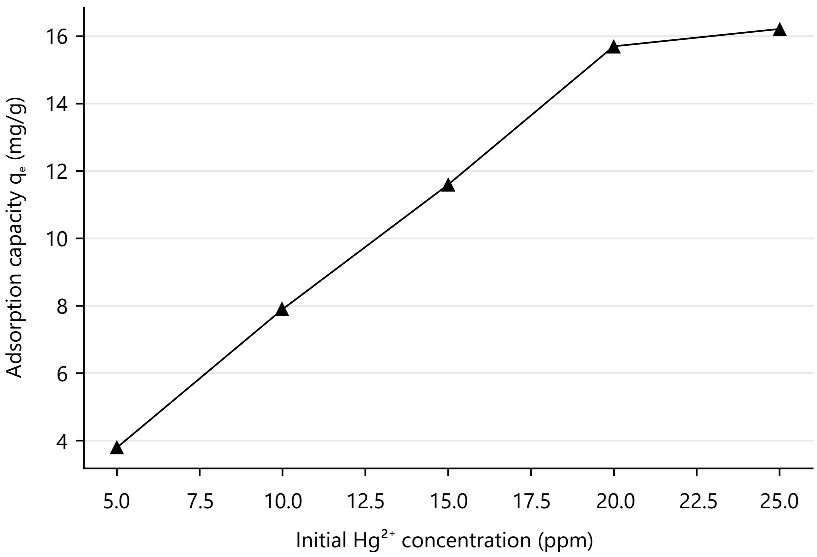

Fig. 4: Effect of initial mercury concentration on adsorption capacity (q_e) of groundnut-peel biochar (self-generated)

Adsorption capacity (q_e, mg/g) plotted against initial Hg^{2+} concentration (5-25 ppm). Capacity rose steadily, reaching ~16 mg/g at higher concentrations. Data points show measured values; the connecting line illustrates the saturation trend

Adsorption kinetics: Pseudo-first-order kinetics (k = 0.107 min^{-1}, R^2 = 0.978) fit marginally better than pseudo-second-order (k = 0.509 g/mg/min, R^2 = 0.971), indicating dominance of physical adsorption mechanisms.

Table 3 summarizes the kinetic constants and R^2 values. Both pseudo-first-order and pseudo-second-order models were evaluated, with high coefficients of determination. These results highlight the good fit of the kinetic models to Hg^{2+} adsorption.

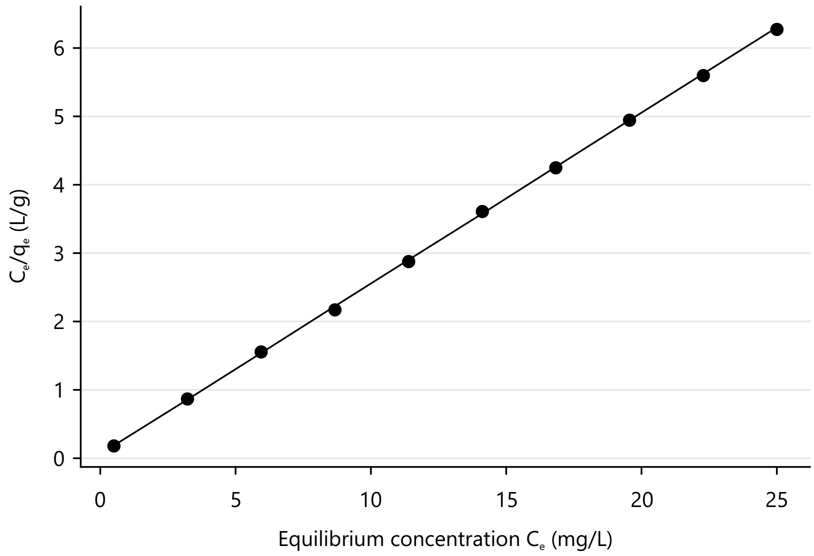

Fig. 5: Langmuir isotherm for mercury (Hg^{2+}) adsorption onto groundnut-peel biochar (self-generated)
Linear plot of versus for Hg^{2+} adsorption. Points represent experimental values, while the line depicts the Langmuir fit. The slope and intercept provide the adsorption capacity and Langmuir constant

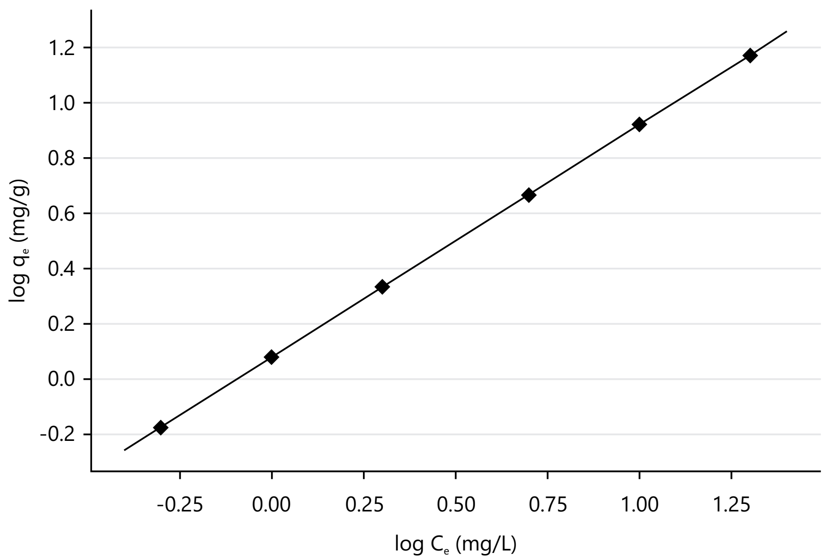

Fig. 6: Freundlich isotherm for mercury (Hg^{2+}) adsorption onto groundnut peel biochar (self-generated)
Logarithmic plot of adsorption capacity (q_e) versus equilibrium concentration (C_e). Data points show experimental values, with the line indicating the Freundlich fit. The slope (1/n) and intercept (K_f) characterize adsorption intensity and capacity

Table 3: Kinetic parameters for Hg^{2+} sorption onto groundnut-peel biochar

Kinetic model	Rate constant	R^2
Pseudo-first-order	k1 = 0.107 min^{-1}	0.978
Pseudo-second-order	k2 = 0.509 g/mg/min	0.971

Rate constants (k1, k2) and R^2 values for pseudo-first-order and pseudo-second-order adsorption. The second-order model shows slightly higher R^2, indicating closer agreement with experimental uptake. All parameters were calculated from contact-time adsorption data

The current study shows that groundnut peel biochar is a promising, low cost sorbent for mercury removal from aqueous solutions. It was observed that removal efficiency increased steadily with higher biochar dosage, a classic effect of greater site availability. This trend is consistent with the observations of Liang *et al.*[11] and Qiu *et al.*[13], who reported that increasing sorbent mass enhances the number of accessible binding sites and improves overall removal. Sen[3] also emphasized that agricultural residues represent abundant and renewable feedstocks for low cost adsorbents, which aligns well with the performance of groundnut peel biochar in this work.

The adsorption kinetics revealed a rapid uptake phase within the first 40 min, followed by a slower sapproach to equilibrium[35,36]. This two stage process, initial external film diffusion and surface adsorption, then intraparticle diffusion, has been widely described in biochar systems. Duan *et al.*[36] highlighted that such kinetic behavior is typical of porous carbons and has important implications for reactor design. Similarly, Ahmad *et al.*[22] noted that lignocellulosic chars often display fast initial uptake followed by diffusion controlled stages. Our results therefore, reinforce the general kinetic patterns of biochars while providing specific evidence for groundnut peel as a viable precursor.

The pH was another decisive factor in adsorption performance. Maximum removal occurred near neutral pH, while efficiency declined under strongly acidic or alkaline conditions. This can be explained by the interplay between surface protonation states and mercury speciation. Guo *et al.*[1] demonstrated that oxygen and nitrogen containing functional groups on biochar surfaces play a key role in metal complexation, and that proton competition at low pH reduces binding. Liang *et al.*[11] further showed that deprotonated sites at near neutral pH favor cation uptake, which supports our findings.

The equilibrium data fitted the Langmuir model better than the Freundlich model, with a moderate maximum adsorption capacity (q_{max} = 20.01 mg/g). This suggests that mercury adsorption onto groundnut peel biochar occurs primarily as monolayer coverage on a relatively uniform surface. However, the reasonable fit to the Freundlich model also indicates the presence of heterogeneous, lower affinity sites. Liang *et al.*[11] and Qiu *et al.*[13] reported similar mixed signatures for unmodified lignocellulosic biochars, while Ahuja *et al.*[10] observed that unmodified chars often exhibit moderate capacities compared with engineered materials. Our results, therefore, position groundnut peel biochar as a useful baseline sorbent, with potential for further enhancement through modification.

Kinetic modeling confirmed that pseudo first order behavior (R^2 = 0.978) described the data slightly better than pseudo second order (R^2 = 0.971). This indicates that physisorption and diffusion are the dominant mechanisms under the tested conditions. Kołodyńska *et al.*[18] emphasized that pseudo first order behavior often reflects diffusion limited uptake in porous carbons. Nevertheless, the reasonable fit of the pseudo second order model suggests that some degree of stronger surface interaction may also be occurring, consistent with the mixed physisorption-chemisorption mechanisms reported by Ahmad *et al.*[22] and Shi *et al.*[31].

When compared with modification strategies reported in the literature, our unmodified groundnut peel biochar provides a useful baseline. Chen *et al.*[14] demonstrated that magnetic impregnation not only improves uptake but also facilitates easier separation. Likewise, Ahuja *et al.*[10] and Wu *et al.*[34] showed that nano modifications and heteroatom doping can significantly increase active site density and selectivity. These approaches represent promising directions for future work, particularly if higher adsorption capacity or reusability is required.

It is also important to acknowledge the limitations of this study. Our experiments were conducted using synthetic Hg^{2+} solutions, which do not fully capture the complexity of real wastewater matrices. Park *et al.*[19] documented how competing cations, dissolved organic matter, and variable ionic strength can reduce effective adsorption capacity in other biochar systems. Therefore, testing with real effluents is essential before field scale application can be recommended.

Finally, the techno economic viability of groundnut peel biochar depends on its regeneration and reuse potential. Ahmad *et al.*[22] stressed that repeated sorption-desorption cycles and capacity retention data are critical for cost modeling. Without such data, it is difficult to determine whether the material is best used as a single use sorbent or as a regenerable medium. Moreover, the rapid initial uptake observed in this study suggests that compact treatment units with short residence times could achieve meaningful removal. However, achieving higher fractional removals would require deeper beds, higher sorbent loading, or improved affinity through modification. Liang *et al.*[11] and Qiu *et al.*[13] emphasized the importance of column studies and breakthrough curves to translate batch results into continuous flow systems.

CONCLUSION

Groundnut peel biochar exhibited effective mercury (Hg^{2+}) adsorption, achieving up to 85% removal under optimal conditions. Adsorption followed the Langmuir model with moderate monolayer capacity, while kinetic analysis indicated pseudo-first-order behavior dominated by physisorption and diffusion control. Maximum uptake occurred near neutral pH, confirming the influence of surface deprotonation and mercury speciation. Overall, the biochar's rapid adsorption, low cost, and sustainable origin highlight its potential for mercury remediation in wastewater. Future studies should focus on detailed surface characterization, testing with real wastewater matrices, and exploring cost-effective modifications to enhance reusability and capacity. Pilot-scale column and techno-economic analyses are also recommended to support large-scale applications. Finally, fixed-bed column experiments and techno-economic analyses will provide data for scale-up and integration into practical mercury removal systems.

SIGNIFICANCE STATEMENT

Groundnut peel biochar demonstrates a viable, low-cost strategy for removing Hg^{2+} from aqueous solutions, combining rapid initial uptake with moderate monolayer capacity. By valorizing an abundant agricultural residue, this approach advances sustainable, circular-economy remediation options for resource-limited settings. The material's pH-sensitive performance and diffusion-limited kinetics clarify operational windows and guide reactor design. With targeted surface characterization, real-effluent testing, and simple modification or regeneration steps, the sorbent could be translated into practical treatment systems. This work therefore provides both a proof of concept and a clear roadmap for developing affordable, scalable mercury-removal technologies.

ACKNOWLEDGMENTS

We sincerely appreciate the invaluable contributions of our colleagues, collaborators, peers, and mentors whose insights and feedback enriched this study. We gratefully acknowledge Federal University Wukari for its unwavering institutional support and the enabling environment provided. Special thanks go to the Microbiology Laboratory, where the batch experiments were meticulously conducted with expert technical assistance. Finally, we thank our families and friends for their constant encouragement throughout the course of this work.

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