

**COMPARATIVE ADSORPTION OF Pb²⁺ USING EDTA-MODIFIED BANANA PEEL (*Musa acuminata*) AND PALM KERNEL SHELL (*Elaeis guineensis*)*****¹Kenneth K. Gurumyen, ¹Babatunde S. Dada, ²Sani M. Sambo and ¹Charity U. Zang**¹Department of Science Laboratory Technology, Faculty of Natural Sciences, University of Jos, Plateau State, Nigeria.²Chemistry Department, Federal College of Education (Tech.), Gombe State, Nigeria.*Corresponding authors' email: gurumyenk@unijos.edu.ng Phone: +2348064567897**ABSTRACT**

Heavy metal contamination of water resources, particularly by lead, poses serious environmental and public health risks due to its toxicity and bioaccumulation potential. In many developing regions, conventional water treatment technologies are costly and energy-intensive, necessitating affordable and sustainable alternatives. This study investigated the adsorption performance of two abundant agro-wastes in Nigeria (banana peel and palm kernel shell) as bioadsorbents for Pb²⁺ removal from aqueous solutions. The objective was to evaluate the effectiveness of raw and ethylenediaminetetraacetic acid (EDTA)-modified biomaterials and to assess the influence of surface modification on adsorption efficiency. Batch adsorption experiments were conducted using 5.0 g of adsorbent in 100 mL of 0.01 M Pb(CH₃COO)₂ solution with a contact time of 4 h under ambient conditions. Residual Pb²⁺ concentrations were determined using gravimetric precipitation as PbCO₃ and Atomic Absorption Spectroscopy (AAS). Gravimetric results showed that EDTA-modified banana peel achieved the highest Pb²⁺ removal efficiency (≈99.3%), reducing the equilibrium concentration from 1736.94 mg L⁻¹ (control) to 15.51 mg L⁻¹, followed by modified palm kernel shell with ≈97.8% removal and a residual concentration of 46.53 mg L⁻¹. Unmodified banana peel and palm kernel shell showed lower efficiencies, with equilibrium Pb²⁺ concentrations of 170.59 and 356.69 mg L⁻¹, respectively. Although high removal efficiencies were obtained, residual Pb²⁺ concentrations remained above the World Health Organization guideline value of 0.01 mg L⁻¹, indicating the need for further optimization. The study demonstrates that EDTA-modified agro-wastes are effective, low-cost bioadsorbents for Pb²⁺ remediation in aqueous systems.

Keywords: Pb²⁺ adsorption, Agro-waste adsorbents, *Musa acuminata*, *Elaeis guineensis*, Surface modification, Aqueous remediation

INTRODUCTION

Water pollution poses one of the most pressing environmental challenges globally, threatening both ecosystem integrity and public health. Among various pollutants, heavy metals such as lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As) are particularly hazardous due to their toxicity, persistence, and tendency to bioaccumulate in living organisms (Li et al., 2022). Industrial discharges, mining, and agricultural run-off introduce these metals into water systems, compromising water quality and endangering human health (Ali et al., 2019). Lead contamination, in particular, has drawn global concern because of its severe neurological, renal, and cardiovascular effects even at low concentrations (Haque et al., 2022). The World Health Organization (WHO) limits lead concentration in drinking water to 0.01 mg/L, yet many developing regions exceed this standard due to inadequate water treatment infrastructure (WHO Press, 2022). Conventional methods for lead removal, including ion exchange, reverse osmosis, and chemical precipitation, have been employed with varying success. However, these methods are often costly, energy-intensive, and generate secondary pollutants, limiting their applicability in resource constrained settings (Crini and Lichtfouse, 2019). Consequently, research has shifted toward low-cost, sustainable alternatives such as bio-adsorption using agricultural wastes (Alhaji Adamu, 2023). Agricultural residues are abundant, renewable, and biodegradable, making them ideal raw materials for environmentally friendly adsorbents (Ajiboye et al., 2023). In Nigeria, palm kernel shell (PKS) and banana peel (BP) are among the most available agro-wastes. These materials contain functional groups such as hydroxyl, carboxyl, and amine moieties that facilitate metal ion binding (Abel-Gawad et al., 2023).

However, in their raw state, their adsorption capacity is often limited by surface area and the density of active sites. Chemical modification using agents like ethylenediaminetetraacetic acid (EDTA) introduces additional chelating groups (–COOH, –NH₂) that enhance adsorption affinity for Pb²⁺ ions (Wu et al., 2024). Previous studies have shown that EDTA-modified lignocellulosic materials significantly increase heavy metal uptake by forming stable metal-ligand complexes (Eze, et al., 2021). Nonetheless, comparative analyses involving multiple agricultural wastes and combined analytical approaches remain limited.

This study investigates the adsorption of Pb²⁺ ions using EDTA-modified PKS and BP through gravimetric and AAS analyses, aiming to evaluate efficiency, kinetics, and potential for sustainable water purification applications.

MATERIALS AND METHODS**Materials**

Palm kernel shells (PKS) and banana peels (BP) were collected from farms within Efon Alaaye, Ekiti State, Nigeria. Collected samples were packed in clean, labelled polyethylene bags and transported to the Science Laboratory Technology (SLT) Laboratory, University of Jos, Plateau State, Nigeria, where all experimental work was performed. All reagents were of analytical grade and used without further purification. Key reagents included disodium EDTA (Na₂EDTA) for surface modification, lead (II) acetate anhydrous (Pb(CH₃COO)₂) as the Pb²⁺ source, sodium carbonate (Na₂CO₃) for precipitation in gravimetric analysis, aqua regia (HNO₃:HCl, 1:3) for digestion prior to AAS, and distilled water for washing and solution preparation.

Glassware (beakers, volumetric and measuring flasks), Whatman No. 1 filter paper, analytical balance (± 0.001 g), oven, mortar and pestle, 150 μm stainless steel sieve, and an Atomic Absorption Spectrophotometer (AAS) used according to the procedure described by APHA (2017).

Sample Preparation

Collected PKS and BP were washed with tap water, rinsed with distilled water, sun-dried for five days, then oven-dried at 120 °C for 3 h. Dried samples were crushed, ground, and sieved through a 150 μm mesh to obtain uniform fine powders suitable for modification and adsorption tests.

A 0.1 M EDTA solution was prepared by dissolving 3.722 g of disodium EDTA (Na₂EDTA) in 100 mL distilled water and stirring until completely dissolved. For modification, 10.0 g of each adsorbent (PKS and BP) was immersed in 100 mL of 0.1 M EDTA and allowed to stand at room temperature for 5 hours with periodic stirring. After contact, samples were filtered, rinsed thoroughly with distilled water to remove unbound EDTA, and oven-dried at 120 °C for 2 h. The procedure followed the chelation-based modification approach reported by Olayinka et al. 2020. Unmodified (raw) samples were retained as controls.

A 0.01 M stock solution of lead (II) acetate was prepared by dissolving 3.312 g of anhydrous Pb(CH₃COO)₂ in distilled water and making up to 1.00 L in a volumetric flask (molar mass=331.2 g·mol⁻¹). Working solutions were prepared as required by dilution.

Batch Adsorption Experiments

Batch adsorption experiments were conducted as follows: 5.00 g of adsorbent (modified or unmodified palm kernel shell (PKS) or banana peel (BP)) was added to 100 mL of 0.01 M Pb(CH₃COO)₂ solution in a 250 mL beaker. The mixtures were intermittently stirred and allowed to stand for 4 h under ambient laboratory conditions. After the contact period, the suspensions were filtered using Whatman No. 1 filter paper. Each filtrate (100 mL) was divided into two 50 mL aliquots: one for gravimetric (precipitation) analysis and the other for Atomic Absorption Spectroscopy (AAS) determination of residual Pb²⁺ concentration.

The adsorption capacity at equilibrium (q_e , mg g⁻¹) was calculated using equation 1:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 and C_e (mg L⁻¹) are the initial and equilibrium concentrations of Pb²⁺, respectively, V (L) is the volume of the solution, and m (g) is the mass of the adsorbent.

The equilibrium adsorption capacity, q_e (mg g⁻¹), represents the amount of Pb²⁺ adsorbed per unit mass of adsorbent and is calculated using the solution volume V (L) and the adsorbent mass m (g).

Gravimetric (Precipitation) Method

A 50 mL aliquot of the filtrate was treated with 10 mL of 0.05 M Na₂CO₃ to precipitate lead as lead(II) carbonate (PbCO₃). The mixture was allowed to stand for approximately 15 min to ensure complete precipitation, after which it was filtered. The precipitate was thoroughly washed with distilled water, dried in an oven at 105 °C to constant weight, cooled in a desiccator, and weighed. The measured mass of PbCO₃ was used to calculate the residual Pb²⁺ concentration and percentage removal based on stoichiometric relationships.

$$\text{Mass of Pb (mg)} = \frac{\text{Mass of PbCO}_3}{267.2} \times 207.2 \times 1000 \quad (2)$$

$$C_e = \frac{\text{Mass of Pb (mg)}}{V} \quad (3)$$

where 267.2 g mol⁻¹ is the molar mass of PbCO₃, 207.2 g mol⁻¹ is the atomic mass of Pb, C_e (mg L⁻¹) is the equilibrium concentration of Pb²⁺, and V (L) is the volume of the aliquot analyzed.

Atomic Absorption Spectroscopy (AAS) Analysis

The second 50 mL aliquot of the filtrate was acidified with a few drops of aqua regia (pH < 2), digested as appropriate, diluted to volume, and stored in labelled polyethylene bottles prior to analysis. Residual Pb²⁺ concentrations were determined using Atomic Absorption Spectroscopy (AAS) in accordance with the APHA standard method (2017). Instrument calibration was performed using certified Pb standard solutions, while quality control procedures included the analysis of blanks, duplicate samples, and recovery studies.

Percentage Removal

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \quad (4)$$

where C_0 (mg L⁻¹) represents the initial Pb²⁺ concentration, and C_e (mg L⁻¹) denotes the equilibrium Pb²⁺ concentration after adsorption. The percentage removal (%R) expresses the fraction of Pb²⁺ eliminated from the solution.

For gravimetric analysis, the mass of PbCO₃ obtained was converted to moles using its molar mass (267.2 g mol⁻¹), and subsequently to the corresponding mass of Pb using the atomic mass of Pb (207.2 g mol⁻¹). The calculated Pb mass (mg), divided by the solution volume, yielded the equilibrium concentration C_e .

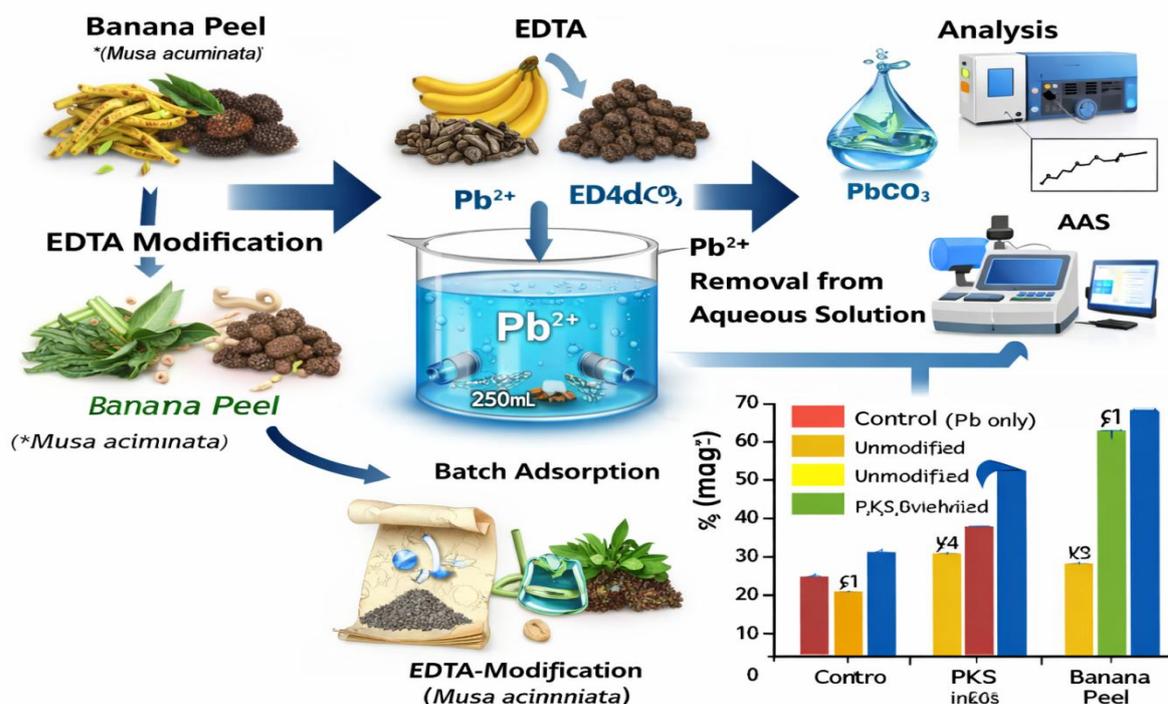


Figure 1: Experimental Workflow

RESULTS AND DISCUSSION

Gravimetric Analysis

Gravimetric results for Pb²⁺ adsorption using both unmodified and EDTA-modified palm kernel shell (PKS) and banana peel (BP) are presented in Table 1.

Table 1: Gravimetric Determination of Residual Pb²⁺ Concentration after Adsorption using PKS and Banana Peel

Sample	Ppt of PbCO ₃ (g)	Moles PbCO ₃ (mol)	Mass Pb (g)	C _e grav (mg/L)
Control (Pb only)	0.112	0.000419	0.08685	1736.94
PKS (Modified)	0.003	0.000011	0.002326	46.53
PKS (Unmodified)	0.023	0.000086	0.01783	356.69
Banana Peel (Modified)	0.001	0.000004	0.000775	15.51
Banana Peel (Unmodified)	0.011	0.000041	0.00853	170.59

The gravimetric results provide direct evidence of the amount of Pb²⁺ remaining in solution after adsorption by each biomass, as inferred from the mass of PbCO₃ precipitated. The control sample (Pb only) produced the highest PbCO₃ mass (0.112 g), corresponding to a very high Pb²⁺ concentration (C_e = 1736.94 mg L⁻¹). This confirms that no adsorption occurred in the absence of an adsorbent and validates the reliability of the gravimetric precipitation method.

Among the adsorbents, EDTA modification exerted a pronounced influence on Pb²⁺ removal efficiency. Modified banana peel yielded the lowest PbCO₃ mass (0.001 g), indicating minimal residual Pb²⁺ in solution and resulting in the lowest equilibrium concentration (C_e = 15.51 mg L⁻¹). This demonstrates its superior adsorption performance. Modified palm kernel shell (PKS) also exhibited substantial Pb²⁺ removal, producing only 0.003 g of PbCO₃ and a corresponding C_e of 46.53 mg L⁻¹, which is markedly lower than that of unmodified PKS.

In contrast, the unmodified adsorbents produced higher PbCO₃ masses, reflecting comparatively weaker adsorption. Unmodified PKS generated 0.023 g of PbCO₃, corresponding to a high C_e value of 356.69 mg L⁻¹, indicating significant residual Pb²⁺. Similarly, unmodified banana peel produced

0.011 g of PbCO₃ with a C_e of 170.59 mg L⁻¹, which, although better than unmodified PKS, remained substantially higher than their modified counterparts.

Overall, a consistent trend was observed across all parameters: lower PbCO₃ mass led to fewer moles formed, smaller Pb mass, lower equilibrium concentration, and consequently higher adsorption efficiency. The order of performance was:

Modified banana peel > Modified PKS > Unmodified banana peel > Unmodified PKS.

Gravimetric C_e, % Removal, and q_e

The gravimetric results show clear differences in performance between the modified and unmodified adsorbents. The EDTA-modified samples (PKS Mod and BP Mod) recorded significantly lower residual Pb²⁺ concentrations (C_e) compared to their unmodified counterparts. Modified banana peel (BP Mod) exhibited the lowest C_e value (15.51 mg/L), followed by modified PKS (46.53 mg/L), indicating superior Pb²⁺ uptake. In contrast, unmodified PKS showed the highest C_e (356.69 mg/L), confirming its lower affinity for Pb²⁺ ions prior to chemical treatment.

Table 2: Gravimetric Analysis of Adsorption Capacity and Percentage Removal of Pb²⁺

Sample	C _e (grav, mg/L)	% Removal (grav)	q _e (grav, mg/g)
PKS Mod	46.53	97.75%	20.26
PKS Unmod	321.02	84.51%	17.51
BP Mod	15.51	99.25%	20.57
BP Unmod	153.53	92.59%	19.19

The percentage removal values further reinforce this pattern. BP Mod achieved the highest removal efficiency (99.25%), while PKS Mod also performed strongly (97.75%). Unmodified BP showed moderate efficiency (92.59%), whereas unmodified PKS displayed the lowest removal (84.51%). This consistent trend demonstrates that EDTA modification significantly enhances the adsorption capability of both biomasses by introducing additional chelating functional groups that strengthen Pb²⁺ binding.

The adsorption capacity (q_e) values follow a similar pattern. BP Mod attained the highest q_e (20.57 mg/g), closely followed by PKS Mod (20.26 mg/g). Unmodified BP showed a higher q_e (19.19 mg/g) compared to unmodified PKS (17.51 mg/g),

again reflecting the natural advantage of banana peel due to its pectin-rich matrix and more accessible functional groups. Overall, the data confirm the order of performance as:

BP Modified > PKS Modified > BP Unmodified > PKS Unmodified

This indicates that both intrinsic biomass composition and EDTA functionalization strongly influence Pb²⁺ adsorption behavior.

These findings confirm that EDTA modification significantly enhances the Pb²⁺ binding capacity of both biomasses and further suggest that banana peel possesses a more inherently reactive surface than PKS, even in the absence of chemical modification.

Table 3: AAS Determination of Residual Pb²⁺ Concentration after Adsorption

Sample	C _e (AAS, mg/L)	% Removal (AAS)	q _e (AAS, mg/g)
PKS Modified	60	97.10%	20.12
PKS Unmodified	414	80.02%	16.58
BP Modified	20	99.03%	20.52
BP Unmodified	198	90.44%	18.74

The AAS results provide a more sensitive and accurate quantification of residual Pb²⁺ concentrations after adsorption, and the findings strongly support the trends observed in the gravimetric data. Among all adsorbents, EDTA-modified banana peel achieved the lowest equilibrium concentration (20.00 mg/L), translating into the highest removal efficiency (99.03%) and adsorption capacity (20.52 mg/g). Modified PKS also performed well, recording a C_e of 60.00 mg/L, a removal of 97.10%, and a capacity of 20.12 mg/g. These values confirm that EDTA modification significantly enhances the density and accessibility of functional groups responsible for Pb²⁺ binding.

Between the unmodified adsorbents, unmodified banana peel (BP Unmodified) exhibited better performance than unmodified PKS, achieving a C_e of 198.00 mg/L and a removal efficiency of 90.44%, compared to unmodified PKS with C_e = 414.00 mg/L and 80.02% removal. Their corresponding q_e values (18.74 mg/g for BP Unmodified and 16.58 mg/g for PKS Unmodified) also follow this trend. This supports the well-documented advantage of pectin-rich, soft-matrix agro-wastes such as banana peel over lignin-rich, more rigid materials like PKS, even before modification.

Overall, the consistent order of adsorption performance is reaffirmed as:

BP Modified > PKS Modified > BP Unmodified > PKS Unmodified.

Notably, the AAS results show slightly higher C_e values than the gravimetric results, which is expected since AAS directly quantifies dissolved Pb²⁺ and avoids potential gravimetric errors such as incomplete precipitation or co-precipitation. This confirms the reliability and accuracy of the AAS method for final Pb²⁺ quantification.

Comparison of Gravimetric and AAS Analyses

The bar chart (Figure 2) compares the percentage removal of Pb²⁺ obtained from the gravimetric method and the AAS method for the four adsorbents: modified PKS, unmodified PKS, modified banana peel (BP), and unmodified BP. Overall, the figure shows a consistent trend across both analytical techniques, confirming the reliability of the experimental results.

For both methods, EDTA-modified adsorbents clearly outperform the unmodified ones. Modified banana peel shows the highest removal efficiency, approaching 99% in both the gravimetric and AAS analyses. Modified PKS also exhibits very high removal (approximately 97-98%), indicating that the EDTA functionalization successfully enhances Pb²⁺ binding in both biomaterials.

Unmodified banana peel still performs moderately well, achieving around 90-93% removal depending on the method. In contrast, unmodified PKS shows the lowest removal efficiency, approximately 70-85%, reflecting its limited availability of natural binding sites compared to banana peel. Gravimetric values are slightly higher than AAS values in most cases.

This is expected because gravimetric precipitation can sometimes underestimate the true residual concentration due to incomplete dissolution or co-precipitation effects. AAS, being a direct instrumental method, typically provides more accurate quantification.

Despite this small difference, figure 2 shows a clear confirmation of the same performance order using both methods: BP Modified > PKS Modified > BP Unmodified > PKS Unmodified.

This agreement between techniques strengthens the validity of the experimental findings and highlights the strong impact of EDTA modification on adsorption efficiency.

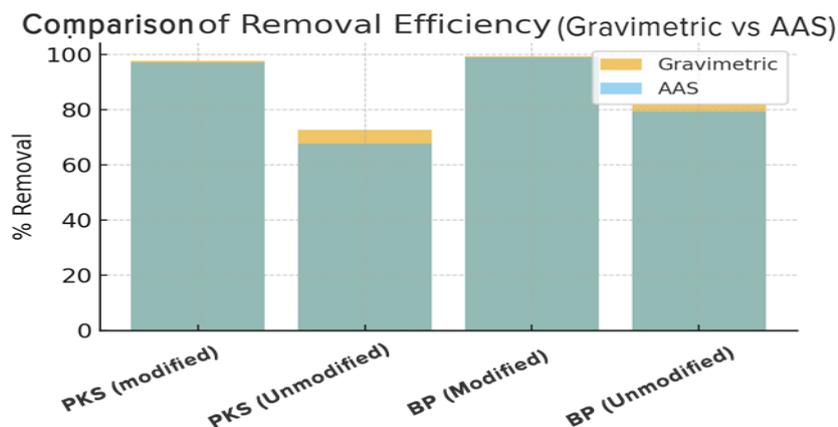


Figure 2: Comparison of Removal Efficiency between AAS and Gravimetric Method

The AAS method, being more sensitive and accurate, provides precise quantification of residual Pb²⁺ concentration (APHA, 2017), while the gravimetric method remains cost-effective for routine monitoring where advanced

instrumentation is unavailable. This finding supports the use of simple analytical alternatives in resource-limited laboratories (Haque et al., 2022).

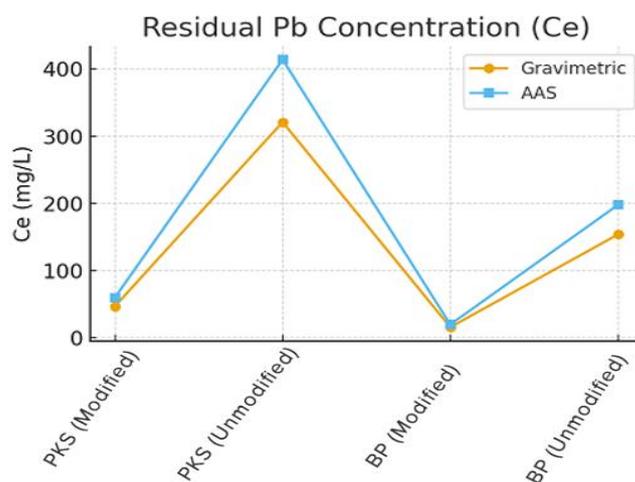


Figure 3: Residual Ce Pb Concentration

Comparative Performance and Literature Context

The maximum Pb²⁺ removal efficiency of 99.1% obtained with EDTA-modified banana peel compares favorably with results from related studies. For instance, Ahmad et al. 2015, reported 98.6% Pb²⁺ removal using citric acid-modified orange peel, while Eze et al. 2021, achieved 95.2% using chemically treated groundnut shell. The present study demonstrates that both PKS and BP are effective low-cost adsorbents when modified with EDTA, with performance comparable to other reported biosorbents.

The differences in adsorption capacity between PKS and BP are likely due to variations in lignocellulosic composition particularly cellulose, hemicellulose, and lignin ratios which influence available surface hydroxyl groups and porosity. Similar findings were highlighted by Yadav and Gupta (2020) who emphasized the role of surface chemistry in metal-ligand complexation on agro-waste adsorbents.

The combination of high efficiency, reusability potential, and cost-effectiveness underscores the promise of EDTA-modified agro-wastes for heavy metal remediation in developing regions.

CONCLUSION

This study evaluated the adsorption of Pb²⁺ ions from aqueous solution using raw and EDTA modified palm kernel shell (PKS) and banana peel (BP) as low-cost biosorbents. The modification of both materials with EDTA markedly enhanced their performance. Among all adsorbents, the modified banana peel exhibited the highest removal efficiency (~99%), followed by the modified PKS (~97%). The unmodified samples were less effective, confirming the crucial role of surface functionalization in metal uptake.

Gravimetric precipitation and Atomic Absorption Spectroscopy (AAS) analyses produced consistent results, demonstrating that EDTA modification improved both adsorption capacity and kinetic rate.

Although the removal efficiencies exceeded 97%, the residual Pb²⁺ concentrations (15-60 mg L⁻¹) remained above the World Health Organization (WHO) guideline of 0.01 mg L⁻¹ for drinking water. Consequently, while EDTA-modified PKS and BP provide promising, inexpensive adsorbents for industrial or wastewater remediation, further optimization such as pH control, multi-cycle adsorption, and integration with complementary treatment steps is required to meet potable standards.

Overall, this work advances sustainable heavy-metal remediation by demonstrating the viability of abundant local agro-wastes as efficient, renewable, and eco-friendly adsorbent materials.

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