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Chemical modification of *Moringa oleifera* seed bioadsorbents for enhanced removal of Cd (II) ions from aqueous solutions

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Abstract:

This study assessed the potential of *Moringa oleifera* seeds as novel adsorbents for the removal of cadmium (Cd) (II) ions from synthetic wastewater. The seeds were chemically modified using calcium acetate and sodium hydroxide. Scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) analysis, thermogravimetric analysis (TGA), and Fourier-transform infrared spectroscopy (FTIR) were employed to characterise the bioadsorbents prepared from the Moringa oleifera seeds. The modified bioadsorbent (MOx) exhibited a BET surface area of 171.012 m^2/g, a microporous pore size of 0.103 cm^3/g, and a diameter of 2.138 nm. Results demonstrated that the removal efficiency of the biosorbents for Cd (II) ions was 51.1% for unmodified seeds (MO) and 57.6% for modified seeds (MOx) at a contact time of 90 minutes. At equilibrium, the maximal sorption capacities for MO and MOx were 4.50 and 4.89 mg/g, respectively. The strong coefficient of correlation (R^2) of 0.9938 for the chemically modified seeds and 0.9603 for the unmodified seeds supported the applicability of the Freundlich model, indicating a robust sorption interaction with the Cd^{2+} ions. Pseudo-second-order sorption kinetics were found to be appropriate for Cd (II) sorption onto modified seeds under highly heterogeneous conditions.

Keywords: **adsorption, cadmium ions, *Moringa oleifera* seeds, wastewater treatment.**

Classification numbers: **2.2, 3.5, 5.3**

1. Introduction

Water contamination is a critical global concern, as access to clean water is essential for human survival and socio-economic growth. However, urbanisation, industrialisation, and agricultural activities contribute significantly to environmental pollution, particularly in water bodies, affecting both ecosystems and human populations [1].

Among the various pollutants, heavy metals are of particular concern due to their non-biodegradable nature, ability to bioaccumulate in living organisms, and potential to enter the food chain. They are often ingested through contaminated food and water, posing significant risks to public health [2, 3]. In addition to their concentration and persistence, these metals are hazardous and mobile in the environment, endangering public health and ecosystems [4, 5].

Cadmium (Cd), for instance, is a hazardous metal with no known biological function, and its accumulation in the human body can lead to severe renal damage. Consequently, Cd has been classified as a priority pollutant by the European Economic Community and the UK Department of Environment [6].

According to the US Environmental Protection Agency, cadmium is classified as a category B1 carcinogen. As recommended by the World Health Organisation, the authorised limit for cadmium in drinking water is 0.005 mg/l, similar to that in China. Therefore, effective Cd removal methods for aquatic environments must be developed [7].

Industrial effluents can be treated to remove heavy metals using various techniques, such as ion exchange, chemical precipitation, electrocoagulation, and reverse osmosis. However, most of these methods have drawbacks, including high costs, technological requirements for setup and maintenance, and the production of hazardous byproducts [8]. Due to its simplicity in design, affordability, high efficiency, and ease of use, adsorption is a promising option [9]. While the adsorption method may effectively and economically remove harmful compounds from wastewater, it also offers additional benefits, including reusability and an environmentally-friendly approach [10-12].

Large-scale use of activated carbon (AC), the most widely used heavy metal adsorbent, is limited by its high cost and challenging regeneration. Recent research has shifted focus towards developing low-cost adsorbents derived

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from agricultural waste, including materials such as fruits, bagasse, rice husks, straws, coconut husks, coffee grounds, vegetable peels, sludges, and steel slag. These materials demonstrate the potential of agricultural and industrial waste products for treating heavy metal-contaminated wastewater. Indeed, such low-cost adsorbents have already shown the capacity to remove Cd (II) ions with at least 90% or higher efficiencies than activated carbon.

Thrift stores and agricultural operations generate large amounts of waste that impact air, water, and soil [13]. Industrial waste can include dust, other refuse, and waste residue discharged during industrial processes, while agricultural waste originates from livestock breeding, agricultural production, processing, and rural household activities [14]. If not effectively treated, these wastes can cause serious environmental problems [9]. Generally, the treatment methods are expensive, complex, and prone to cross-contamination. Transforming these wastes into valuable resources could significantly reduce pollution [15, 16].

Agro-industrial products like *Moringa oleifera* seeds contain water, lignin, lipids, proteins, simple sugars, hemicellulose, and pectin. Due to the high content of carboxyl and hydroxyl groups, these materials are helpful to adsorption processes. However, if not appropriately handled, agro-industrial wastes may lead to excess organic carbon, restricted adsorption capacity, and elevated chemical and biological oxygen demand [17]. Therefore, agro-industrial waste must be processed to eliminate soluble organic components to enhance their adsorption capacity before its use to remediate wastewater, especially in adsorption-based treatment methods such as biofiltration [17]. Additionally, the type of material used to support the bed affects both treatment costs and the extent of contaminant removal [18].

Therefore, this study aims to evaluate the adsorption capabilities of chemically modified *Moringa oleifera* seeds for Cd (II) ion removal from synthetic wastewater. By transforming agricultural waste into valuable resources, this research highlights the potential of sustainable solutions for environmental pollution mitigation.

2. Materials and methods

2.1. Materials

Moringa oleifera seeds were sourced from the University of Lagos Lagoon Front. Analytical-grade reagents, including calcium acetate and sodium hydroxide, were procured from Sigma-Aldrich. Cadmium nitrate tetrahydrate was used to prepare a 40 mg/l stock solution, from which experimental concentrations were derived.

2.2. Preparing and characterisation of the bioadsorbents

2.2.1. Preparation of the biosorbents

Moringa oleifera seeds were separated from pods, cleaned with water, and dried at 25°C. The seeds were then blended into a fine powder.

To remove lignin, 25 g of powder was treated with 1 M nitric acid or 1 M sodium hydroxide solutions, heated at 100°C for 30 minutes, and neutralised to pH 5-7. The samples were further treated with 150 ml of 2.5 M sodium hypochlorite at 60°C for 30 minutes to remove low-molecular-weight carbohydrates. Finally, the samples were dried in a convection oven at 60°C for 5-7 hours [18].

2.2.2. Physico-chemical characterisation of the dry biosorbents

The powdered samples were subjected to chemical modification through consecutive treatments with 1 M NaOH and $Ca(CH_3COO)_2$. Initially, 15 g of *Moringa* seed powder was stirred at 1000 rpm for two hours in 100 ml of 1 M NaOH. The samples were then washed with water until the supernatant reached a neutral pH (pH 7) and subsequently dried at 45°C for four hours [15]. The elemental compositions of both the modified and unmodified adsorbents were analysed using a BRUKER EDX two-dimensional VANTEC-500 detector. Fourier transform infrared spectroscopy (FT-IR) was performed using a Spectrum 200 spectrometer within the 4000-500 cm^{-1} range to identify the principal functional groups of the bioadsorbents, both before and after metal absorption. The morphology of the bioadsorbents was examined using a PSEM eXpress scanning electron microscope (SEM) operating at 20 kV. The specific surface area, pore volume, and pore diameter were assessed using the Brunauer-Emmett-Teller (BET) method. An N_2 gas adsorption analysis was conducted on both modified and unmodified *Moringa oleifera* seeds using a Quantachrome Nova station [17].

2.3. Adsorption experiments

The adsorption process was evaluated by varying the initial concentration of metal ions in solution, contact time, and the temperature of the batch sorption process [18]. For the sorption experiment, a specific amount of adsorbent was agitated in each aqueous solution using a rotary shaker within 250 ml conical flasks. At a designated temperature, 0.5 g of the modified *Moringa oleifera* seed powder was added to 100 ml of the aqueous solution and stirred at 200 rpm for a predetermined duration. Following centrifugation at 5000 rpm for 10 minutes, the concentrations of the metal ions were determined using atomic absorption spectroscopy (AAS).

2.3.1. Effect of dosage on sorption

The following criteria were used to assess the effect of adsorbent dosage on sorption: adsorbent dosage ranging from 0.1 to 1.0 g of modified biosorbents (MOx) in 100 ml of solution; metal ion concentration of 2 ppm; pH of 7.85 for all sorption studies; and a shaking duration of 1.5 hours [18].

2.3.2. Effect of pH on sorption

The effect of pH on sorption was examined under the following conditions: adsorbent dosage of 0.5 g of MOx in 100 ml of solution; Cd^{2+} concentration of 2 ppm; pH levels of 2, 4, 6, 8, and 10; and a shaking duration of 1.5 hours at 27.5°C.

2.3.3. Effect of Cd (II) Ion concentration on sorption

The effect of Cd^{2+} ion concentration on sorption was studied using 0.5 g of biosorbent in 100 ml of metal ion solution, with metal ion concentrations ranging from 2 to 10 ppm. The pH was maintained at 7.85, and the shaking duration was 1.5 hours at 27.5°C.

2.3.4. Effect of contact time on sorption

The rate of sorption was determined using the following parameters: a shaking duration of 150 minutes, 0.5 g of biosorbents (MO/MOx) per 100 ml of solution, an initial metal ion concentration of 2 ppm, and a pH of 7.85 at 27.5°C.

2.3.5. Effect of temperature on sorption

Thermodynamic data for sorption were obtained using the following parameters: an adsorbent dose of 0.5 g (MO/MOx) in 100 ml of solution, a metal ion concentration of 2 ppm Cd^{2+}, a pH of 7.85, and a shaking duration of 1.5 hours. Sorption tests were conducted at temperatures of 10, 20, 30, 40, and 50°C [19, 20].

$$Q_t = Q_e\,(1 - e^{-k_1 t}) \qquad (1)$$

where the pseudo-first-order rate constant (min^{-1}) is denoted by k_1, the sorption amount at time t is Q_t (mg/g), and the sorption amount at equilibrium is Q_e (mg/g).

$$Q_t = \frac{k_2 Q_e 2t}{(k_2 Q_e t + 1)} \qquad (2)$$

where Q_e (mg/g) is the sorption amount at equilibrium, k_2 (g/(mg•min)) is the pseudo-second-order rate constant, and Q_t (mg/g) is the sorption amount at time t.

We utilised Eqs. (3) and (4) to ascertain the MO_x's ions sorption capacity and ion adsorption efficiency (η), in that order [19, 20]. Each experiment was performed three times, and the average was used to determine the final sorption capacity.

$$Q_e = \frac{V(C_0 - C_e)}{m} \qquad (3)$$

$$\eta = \frac{C_0 - C_e}{C_0} \qquad (4)$$

The ions concentration at the adsorption equilibrium and initial concentration are denoted by C_e (mg/l) and C_0 (mg/l), respectively; the volume of the ions solution used in the experiment is indicated by V (l); and the dry weight of the biosorbent added to the ions solution is indicated by m (mg). The MO_x ion sorption capacity is denoted by Q_e (mg/g).

The isothermal adsorption of ions onto MO/MOx was characterised using the Langmuir (Eq. 5) and Freundlich (Eq. 6) models [21, 22]

$$\text{Langmuir } Q_e = \frac{Q_m K_L C_e}{(1 + K_L C_e)} \qquad (5)$$

$$\text{Freundlich } Q_e = K_F C_e\, n \qquad (6)$$

where Q_m (mg/g) is the maximal adsorption capacity under ideal conditions; K_F (l/mg) denotes the Freundlich constant; n is a measure of heterogeneity. K_L (l/mg) denotes the Langmuir constant. C_e (mg/l) is a measure of the Cd^{2+} ion concentration at adsorption equilibrium. At adsorption equilibrium, the adsorption capacity is indicated by Q_e (mg/g). Fig. 1 describes the schematic of the bioadsorption process of *M.oleifera*.

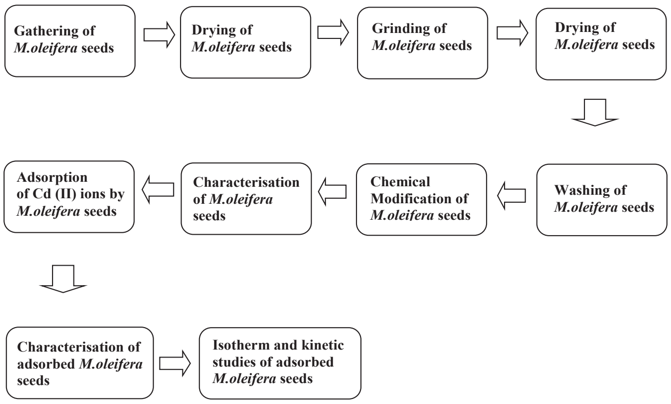

Fig. 1. Schematic of the bioadsorption process of *Moringa Oleifera* seeds [23].

3. Results and discussion

3.1. Characterisation of the bio-adsorbents

The modified bioadsorbent (MOx) exhibited a BET surface area of 171.012 m^2/g. The pores in MOx were characterised by a volume of 0.103 cm^3/g and a diameter of 2.138 nm. According to the International Union of Pure and Applied Chemistry (IUPAC), MOx is classified as having microporous pore sizes [20]. Micropores are defined as having diameters of less than 2 nm, mesopores range from 2 to 50 nm, and macropores exceed 50 nm [24].

An adsorbent's specific surface area, total pore volume, and pore width are critical factors influencing its interaction with the adsorbate and its adsorption efficiency. The surface area of MOx was significantly greater than that of the unmodified adsorbents. This enhanced surface area contributed to improved cadmium ion adsorption, as adsorption is a surface-dependent phenomenon [24]. Consequently, MOx is expected to outperform unmodified bioadsorbents in metal ion adsorption [25-28]. This improvement can be attributed to the removal of hemicellulose, lignin, and other residues through chemical alkali treatment, which increases the quantity of cellulose exposed on the fibre surface.

The application of NaOH and calcium acetate alters the transformation of cellulose types within the fibres, enhancing the capacity of microfibrils to rearrange and improving the fibres' load capacity. This treatment reduces the helix angle of the fibres, further increasing their load capability. Additionally, alkali treatment removes certain amounts of lignin, wax, and oils from the fibre surface, exposing short-length crystals. By removing hemicelluloses, the rigidity and density of the fibrils decrease, allowing for easier formation of fibril structures. The inherent toughness of natural cellulose has drawn significant attention from researchers [5-28].

Alkali treatment increases the cellulose proportion by dissolving lignin and hemicellulose. Calcium acetate treatment further enhances the matrix-fibre interfacial bond by modifying surface polarity and increasing fibre roughness.

Table 1. Surface characteristics of the biosorbents before and after activation [26].

Biosorbents	BET surface *Area (m²/g)*	Pore volume *(cm³/g)*	Average pore *Diameter (nm)*	References
MO	90.25	0.078	0.198	
MO_x	171.012	0.103	2.138	
Bagasse	0.487	1.422	57.2	[26]

Using energy dispersive X-ray (EDX), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM), the modified and unmodified *Moringa oleifera* seed particles were analysed.

Figure 2 illustrates the SEM micrographs of unmodified (MO) and modified (MOx) biosorbents. The SEM micrograph of MO (Fig. 2A) at 8000x magnification and 20 kV revealed spherical particles with a size of 10 µm, resulting in a rough surface and porous structure. As the magnification increased from 8000 to 10000x, the pore size decreased from 10 to 100 µm, with Fig. 2B displaying the optimal porosity.

In contrast, the SEM micrograph of MOx at 8000x magnification (Fig. 2C) and 15 kV revealed irregular particles of 10 µm with a broad dispersion of 10.2 µm. At 9000x magnification, the particles exhibited improved clustering, attributable to the treatment, which generated a greater specific surface area, enhancing Cd (II) adsorption efficiency [26].

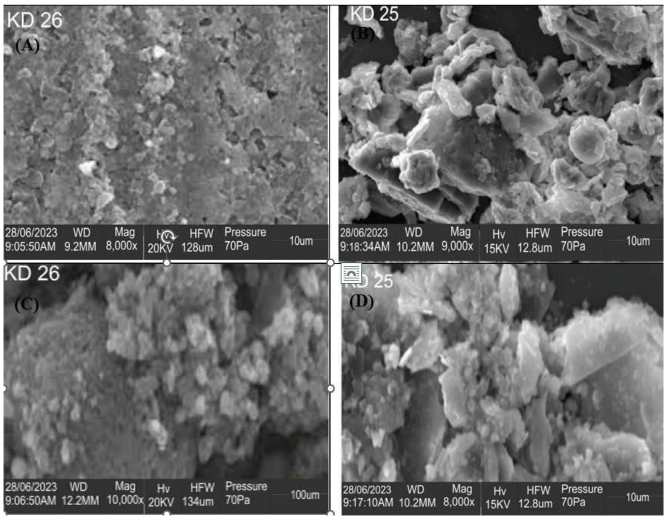

Fig. 2. Scanning electron microscopy micrographs of unmodified adsorbent (MO) (A and B) and the chemically treated adsorbent with 10 ppm modifiers (MOx) (C and D, respectively).

Figure 3 presents the elemental composition of the unmodified and modified *Moringa oleifera* seeds. Silicon (Si) exhibited the highest peak for MO, followed by oxygen (O), with sodium (Na) showing the lowest peak. In the case of MOx, silicon maintained the highest peak, followed by oxygen, while calcium (Ca) displayed the lowest peak.

Investigations of *Moringa oleifera* seeds revealed that they contain significant levels of sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg), which are essential minerals for the seeds [27].

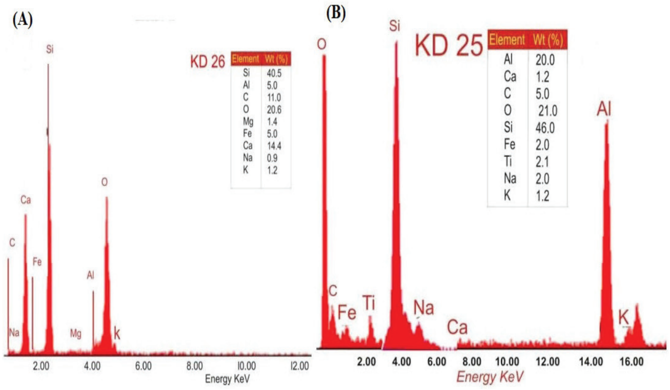

Fig. 3. Dispersive X-ray spectra of (A) MO and (B) MO_x.

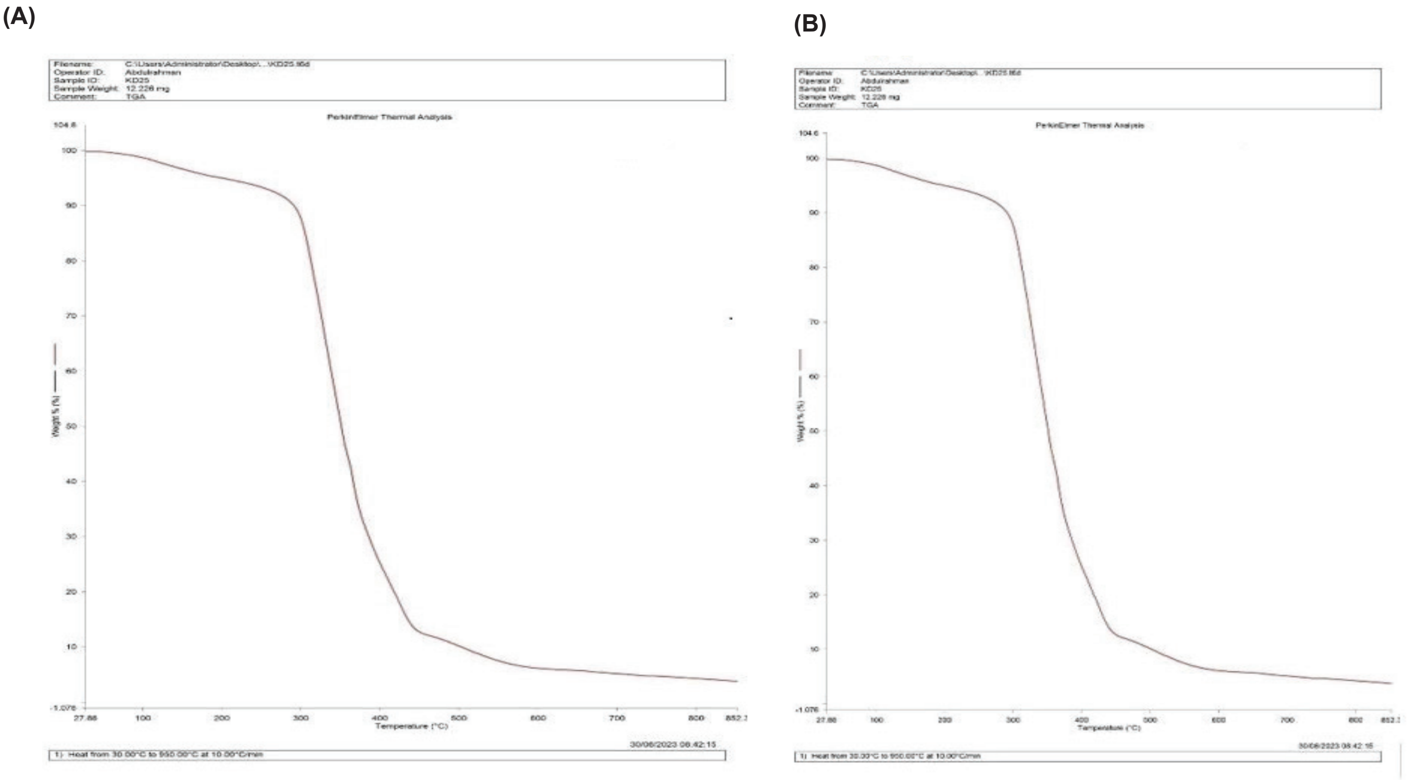

Fig. 4. Thermogravimetric analysis profiles of (A) MO and (B) MO$_x$.

TGA analysis indicates that the decomposition process occurs in multiple stages, as shown in Fig. 3. The thermogravimetric curve confirms the heterogeneity of the sample, given that the intermediates formed are a mixture of various components.

The thermogram of the unmodified adsorbent (MO), shown in Fig. 4A, reveals an initial weight loss of 2.5% between 70 and 100°C, attributed to the loss of water. Between 220 and 430°C, an additional weight loss of 62% occurs, corresponding to the hydrolysis of hemicellulose and the release of organic and/or aqueous components such as pectin and proteins. This indicates a reduction in the volatile matter present in *Moringa* seeds.

A third stage of weight loss, observed between 430 and 590°C, is due to the decomposition of major seed constituents, including fatty acids. For example, oleic acid has a boiling point of 360°C. At temperatures above 590°C, the breakdown of cellulose and lignin into CO_2, H_2O, and ash resulted in a residual weight of 8% [16, 25].

The thermogram for the modified adsorbent (MOx), shown in Fig. 4B, follows a similar progression to that of MO. However, due to the presence of ash and possibly inorganic oxides, a reduced residue of approximately 3% was observed beyond 590°C.

3.2. Adsorption isotherms of Cd (II) ions using Moringa oleifera

Figure 5 illustrates the effect of varying the initial Cd(II) ion concentration from 2 to 10 mg/l at a specific adsorbent dosage of 0.5 g, a temperature of 27.5±1°C, and a pH of 7.85. The removal efficiency of Cd(II) ions by MOx peaked at 10 mg/l, with values of 51.1% for MO and 57.6% for MOx. This result can be attributed to the ample active sites on the sorbent, which facilitate the adsorption of metal ions at low concentrations due to the favourable ratio of initial metal ion concentration to available binding sites. These findings are consistent with previous studies showing

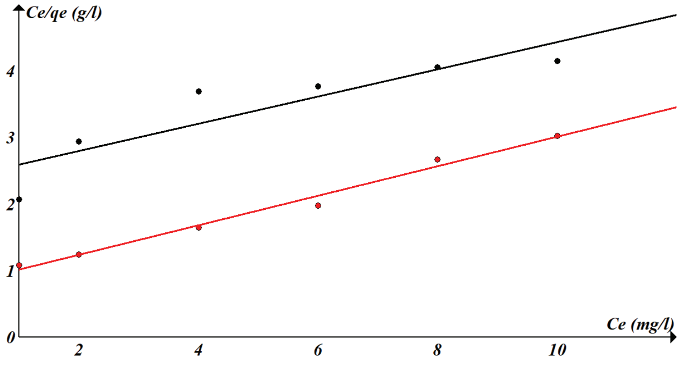

Fig. 5. Langmuir isotherm for the sorption of Cd (II) for MO/MOx.

that metal ion adsorption increases with rising adsorbate concentrations [26-32].

The adsorption of Cd (II) ions was examined using the Langmuir and Freundlich isotherm models, as shown in Figs. 5 and 6. Adsorption isotherms describe the interaction between adsorbate molecules and the adsorbent surface, providing insights into the distribution of adsorbate molecules between the liquid and solid phases [33-36]. The applicability of these isotherm equations was evaluated through correlation coefficients (R^2).

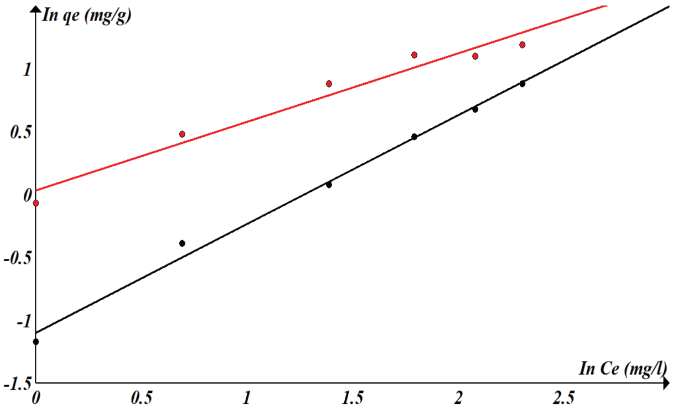

Fig. 6. Freundlich isotherm for the sorption of Cd (II) ions by MO/MOx.

The Langmuir isotherm assumes a uniform adsorbent surface, with no interactions between adsorbate molecules and a monolayer adsorption mechanism. Equilibrium data for Cd (II) ion concentrations ranging from 2 to 10 mg/l at 27.5±1°C were analysed using the linear form of the Langmuir equation (Equation (5)). The plot of *Ce/qe* versus *Ce* for the removal of Cd (II) ions using MO/MOx is shown in Fig. 5.

The Langmuir model provided a good fit for the adsorption data, with R^2 values of 0.7986 for MO and 0.9879 for MOx (Table 2). The monolayer adsorption of Cd (II) ions onto MOx was indicated by these results, with maximal sorption capacities (q_e) of 4.50 mg/g for MO and 4.89 mg/g for MOx. According to Table 2, the maximal sorption capacities (q_e) for MO and MOx were 4.50 and 4.89 mg/g, respectively. Thus, Table 2 illustrates that the adsorption capacity and removal efficiency of MO/MOx strongly correlate with the size of the metal ions.

The Freundlich equation-derived adsorption capacities (K_f) for Cd (II) were 0.3 and 1.03 mg/g, respectively. For favourable adsorption of Cd (II) ions onto MO/MOx, the Freundlich constant "*n*" values were 1.16 and 1.83, respectively, meeting the requirement of $0<n<10$. The Freundlich-type adsorption isotherm indicates the heterogeneity of MOx's surface, demonstrating that MOx's surface comprises tiny, heterogeneous pores conducive to the physical process of adsorption (Fig. 6).

A dimensionless constant separation factor describes the affinity between the sorbate and sorbent. Figs. 5 and 6 demonstrate the favourable adsorption of the Cd (II) ion processes using MOx. Previous research utilising sesame husk as an adsorbent to remove Cu (II) ions from aqueous solution and Jatropha seed husk for lead removal corroborates these findings [37, 38].

In an aqueous solution, the state of metal ions is determined by two factors: the pH of the mixture and the ratio of the material's remaining functional groups to the concentration of metal ions. The concentration was adjusted while maintaining a constant pH of 7.85, the ideal level for metal ion sorption.

Metal ion sorption is significantly influenced by the structural features of the MOx backbone. The metal ion absorption of cadmium was more excellent for MOx than for MO, as demonstrated in Figs. 5 and 6; this is attributed to the increased number of pores created by the improvement and modification of the functional groups, which tend to attract cadmium ions more effectively than MO. Generally, the metal ions' electronegativity and hydration values affect the amount of metal ions absorbed by the ion exchanger [39-43].

The model's applicability, which implies a strong interaction for the Sorption of Cd^{2+} onto the MO/MOx, was supported by the high Freundlich coefficient of correlation (R^2) for MO (0.9603) and MOx (0.9938). Due to a batch factor, the computed values aligned closely with the experimental values, indicating that the Freundlich model provided a satisfactory fit for the equilibrium data. This suggests that the MO/MOx sorption process considered the heterogeneity of the sorption sites on the adsorbents' surfaces. The isotherm fits indicate that there was more to the sorption onto the adsorbents than just a physical process.

Table 2. Isotherm constants of two isotherm models for the sorption of Cd^{2+}.

Isotherm model	Constants	Cd^{2+}
Langmuir	q_{max} (mg/g)	4.50*(4.89)
	η (%)	51.1*(55.0)
	K_L (l/mg)	0.086*(0.280)
	R^2	0.7986*(0.9879)
Freundlich	K_F [mg/g(l/mg)$^{1/n}$]	0.33*(1.03)
	n	1.16*(1.83)
	R^2	0.9938*(0.9603)

*(MO) Values are in parenthesis.

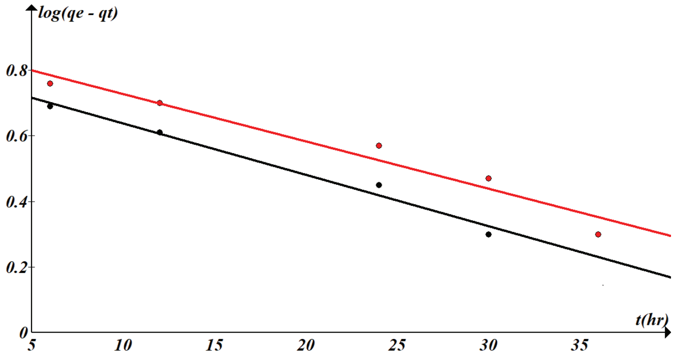

Fig. 7. Langmuir kinetics of sorption for MO/MOx.

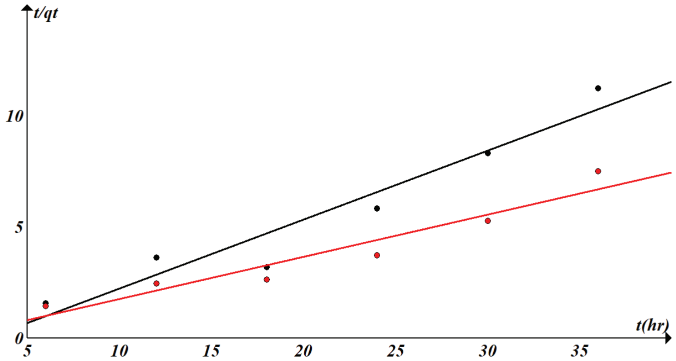

Fig. 8. Second-order kinetics of Cd^{2+} sorption for MO/MOx.

Table 3. Kinetic parameters of the kinetic models for the sorption of Cd^{2+}.

Kinetic model	Parameter	Cd^{2+}
Langmuir pseudo first order	q_e, e$^{(mg/g)}$	2.10*(2.98)
	q_e, calc(mg/g)	6.23*(7.45)
	$K_1 \times 10^{-3}$ (hr^{-1})	6.74*(6.25)
	R^2	0.9396*(0.9252)
Pseudo second order	q_e, calc(mg/g)	3.22*(5.27)
	K_2 (hr^{-1})	0.11*(0.26)
	R^2	0.9288*(0.9239)

*(MO) values in parentheses.

3.3. Sorption kinetics of Cd^{2+} by Moringa oleifera seeds (MO/MOx)

The kinetic performance of an adsorbent is as crucial as its adsorption capacity in determining its feasibility for pilot-scale applications. Kinetic analysis provides insights into the solute absorption rate and the residence time required to complete the adsorption reaction. This information is essential for determining the size and operational efficiency of adsorption systems. The adsorption kinetics play a pivotal role in the performance of flow-through systems, whether fixed-bed or otherwise.

Plots of the pseudo-first-order and pseudo-second-order equations for Cd^{2+} ions are displayed in Figs. 7 and 8. During the sorption period, linear relationships were observed between *log(t)* and *t*, as well as *t* versus *t*, with high correlation coefficients ($R^2>0.9$) for both models, as shown in Table 3. This indicates a strong agreement between the experimental data and the theoretical predictions of the models. The sorption kinetics onto MO and MOx can be explained using a pseudo-second-order Langmuir model.

Table 3 summarises the kinetic parameters for the sorption of Cd^{2+} by MO and MOx, including initial concentrations and other key parameters derived from linear regression. These parameters are critical for predicting the sorption rate and designing batch and flow-through adsorption systems. When selecting optimal operating conditions for large-scale batch operations, it is essential to consider the kinetic characteristics of sorbate uptake [40-45]. The kinetic parameters help forecast the sorption rate and provide essential data for the design and modelling of sorption systems.

3.4. Sorption thermodynamics of Cd^{2+} by the MO/MOx

The effect of temperature on the sorption of metal ions onto the MO/MOx was investigated by evaluating three thermodynamic factors: Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS). The Gibbs free energy change was calculated using the following equation:

$$-RT = \Delta G \ln K$$

where R is the gas constant (8.314 $JK^{-1}mol^{-1}$), T is the absolute temperature (K), and K is an equilibrium constant that may be obtained by calculating the Langmuir constant K_L ($Lmol^{-1}$). ΔG represents the change in Gibbs free energy ($KJ\ mol^{-1}$).

By graphing ΔG against T, one may determine the enthalpy changes (ΔH) and entropy (ΔS) by calculating the slope and intercept of the van't Hoff equation, which is $\Delta G = \Delta H - T\Delta S$ [41-45].

The thermodynamic feasibility of the sorption process was assessed using the calculated parameters. Positive ΔH values indicated the endothermic nature of the sorption process. Although specific ΔH values could not definitively classify the sorption type, sorption enthalpy typically falls within the range of 20 to 420 kJ/mol. This range corresponds to temperatures for chemical reactions and is commonly interpreted as indicative of chemical sorption processes [43-45].

Gibb's free energy shift (ΔG^{o}) adsorption must be negative for significant sorption. The near feasibility and non-spontaneity of the adsorption process at temperatures below 323 K are shown by a positive Gibbs free energy change (ΔG^{o}) as illustrated in Table 4. Since the adsorbate has a stronger affinity for the adsorbent at higher temperatures and its mobility of molecules and ions in the solution rises with temperature, a drop in the positive value of this should generally be possible. On the other hand, positive ΔG^{o} values increase with temperature, indicating that a lower temperature promotes adsorption [44-48].

Table 4. Thermodynamics parameters for the sorption of Cd^{2+} MO/MOx.

Parameters	MO	MOx
(mg/g)	2.10	2.98
R^2	0.9839	0.9745
K_L (l/mg)	0.083	0.112
ΔG (kJ/mol)	6.378	5.593
ΔH (kJ/mol)	12.936	27.636
ΔS (J/mol.K)	20.952	70.424

MO/MOx: ΔH: Enthalpy, ΔS: Entropy, ΔG: Gibbs free energy.

Additionally, the value of ΔH^{o} can provide insight into the type of sorption mechanism. Chemisorption processes typically occur within a temperature range of 80-200 kJ mol^{-1}, while the heat generated during physical adsorption is in the range of 2.1-20.9 kJ mol^{-1}, which is comparable to the heat of condensation. As shown in Table 4, the adsorption of heavy metal ions by MO/MOx appears to involve a physico-chemical sorption mechanism rather than a purely physical or chemical process [45-48].

A positive ΔS^{0} value indicates a significant affinity of the adsorbent for the adsorbate species. Moreover, an elevated ΔS^{0} value suggests potential structural modifications in both the adsorbent and adsorbate, as well as increased instability at the solid-solution interface [46-48].

3.5. Effect of dosage and pH on sorption

The effect of solution pH on the removal of Cd (II) ions is illustrated in Fig. 9. The pH of the aqueous medium had a substantial impact on sorption capacity. The adsorption of Cd (II) ions increased by 92.95% as the pH was raised from 2 to 7.5, reaching an optimal sorption capacity at pH 7.5. However, beyond this pH level, the removal efficiency of cadmium ions decreased.

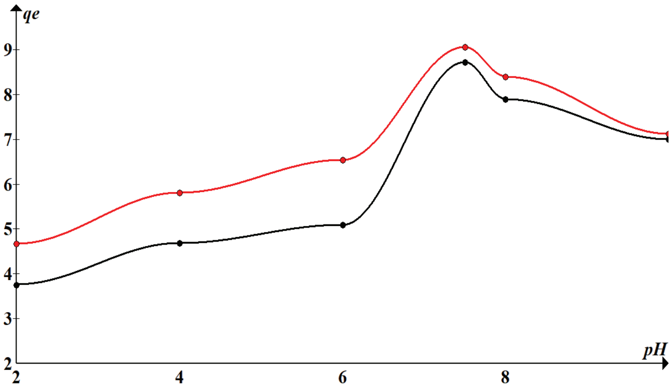

Fig. 9. Effect of pH on the sorption of Cd (II) ions by MO/MOx.

The medium's pH influenced sorption capacity through two primary mechanisms: the solubility of metals and the overall charge of the functional groups on MO/MOx. The optimal pH for maximum adsorption performance was determined to be approximately 7.5, which aligns with the natural pH of most freshwater aquatic systems [47-52].

Figure 10 illustrates the impact of MO/MOx dosage on the adsorption capacity for Cd (II) ions from aqueous solutions. Cadmium biosorption increased proportionally with a rise in adsorbent concentration in the metal solution. This improvement may be attributed to an increase in available free binding sites due to the higher concentration of MO/MOx or the enhanced exchange of functional groups, which facilitated cadmium adsorption from the solution [48-53].

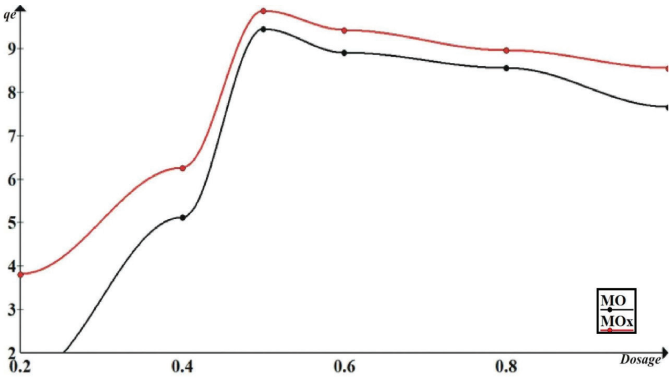

Fig. 10. Effect of dosage on the sorption of Cd (II) ions by MO/MOx.

4. Conclusions

Bio-adsorbents derived from *Moringa oleifera* seeds, an agro-industrial material, were evaluated for their capacity to remove Cd (II) ions from synthetic water samples. The study investigated the role of the starting material and its chemical modification on the performance of the final adsorbent product. The bioadsorbents were chemically treated with NaOH and $Ca(CH_3COO)_2$ to enhance their adsorption capacity. The results demonstrated that an increase in the concentration of these chemical modifiers further improved the adsorbents' efficacy. The highest Cd (II) ion removal efficiency, 57.6%, was achieved within 1.5 hours.

Although the adsorption process with these sorbents is complex, the enhanced removal efficiency can be attributed to the increased availability of binding sites resulting from chemical treatments and the inherent composition and structure of *Moringa oleifera* seeds. This study highlights the potential to develop effective adsorbents for metal ion removal using agro-industrial materials and innovative green technologies.

The modified bioadsorbent derived from *Moringa oleifera* seeds is an inexpensive and efficient material for the removal of heavy metals from polluted effluents. The research suggests that chemically modified agricultural and industrial materials can be employed in processes where adsorption serves as the primary method for pollution remediation.

For effective metal ion extraction from polluted water, strict protocols must be followed, governed by multiple factors and trends. The findings of this study demonstrated the effectiveness of MO/MOx in removing Cd (II) ions from aqueous solutions. Adsorption performance was shown to depend on parameters such as adsorbent dosage, pH, and the concentrations of both the adsorbent and adsorbate. Equilibrium was reached in approximately 1.5 hours, with an optimal pH of 7.5 for Cd (II) removal.

The experimental results were well represented by Freundlich and Langmuir adsorption models, with the data fitting the Freundlich isotherm model particularly well. This analysis confirms that *Moringa oleifera* is an effective agent for the removal of heavy metals from aqueous solutions, achieving the overall objectives of the study.

CRediT author statement

Olu Lawrence Ekebafe: Supervision, Conceptualisation, Methodology; Kelechi Daniel Obodo: Writing, Reviewing, Editing; Jehoshaphat Izunobi: Software, Validation, Reviewing, Editing.

COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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