

Full Paper

Utilizing of nano sized *Moringa oleifera* in removing highly toxic Cd(II) ions from aqueous media

Badriah Saad Al-Farhan¹ and Mallak Megalea Zikry²

¹ Department of Chemistry, Faculty of Girls for Science, King Khalid University, 61421 Abha, King Saudi Arabia, KSA

² Medicinal and Aromatic Plants Researches Department, Horticulture Research Institute (HRI), Agri. Res. Center (ARC), 12619 Giza, Egypt.

Email: shahd_bb@hotmail.com

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Abstract

Leaves of *Moringa oleifera* in nano scale was prepared and characterized by FTIR, SEM, TEM, XRD and EDS techniques. In addition to, study of the effect of nano sized *Moringa oleifera* on adsorption of Cd²⁺ ions from aqueous solution was checked. The influence of pH, temperature, adsorbent dosage, contact time, metal ion concentration and chemical treatment of biomass were investigated. The maximum adsorption capacity (q_m) of Cd²⁺ ions biosorption by *Moringa oleifera* was 40.53 mg g⁻¹. The removal efficiency was 93.74%. The amount of Cd²⁺ ions adsorbed increases with increasing in adsorbent dosage and metal ion concentration. Biosorption of Cd²⁺ ions slightly increases as increasing the temperature. IR spectra showed that the main functional groups are responsible for Cd²⁺ ions binding in the biosorption process. Thermodynamic studies confirmed that the biosorption process is endothermic. The obtained positive value of ΔG° indicated that the ion-exchange mechanism applies in the biosorption. The sorption process was fitted to pseudo second order kinetics. The Freundlich isotherm has a good fit with the experimental data compared to Langmuir isotherm. The results obtained from the current research suggested that *Moringa oleifera* is available agricultural, low cost, environment friendly biosorbent for the removal of toxic heavy metals from aqueous environment.

Keywords: Cadmium, Biosorption, Kinetics, Removal efficiency, *Moringa oleifera* powder, isotherm.

1. Introduction

The addition of treated waste water as a resource to maximize benefit of the available water resources and reduce the growing gap between available water resources and the required water needs and to maintain international water security. Water bodies and waste water are contaminated with toxic heavy metals. There is evidence that heavy metals are responsible for illnesses related to the risk of dermal damage, respiratory problems and several kinds of cancer [1]. Heavy metal contamination affects ecosystem functions. Owing to ability to form non-biodegradable compounds, removal of heavy metal from contaminated sites is an important process to restore ecosystem functions [2]. Cadmium is one of the common heavy metals causing pollution of natural water, which affects human and animals health as retardation of growth, the risk of cancer and damage to the liver and the kidneys [3], [4]. Cd^{2+} ions can be removed from aqueous solutions by several methods such as ion exchange, chemical precipitation, adsorption and membrane separation. These methods contain several restrictions of the removal of Cd^{2+} ions from water [5]. Many studies were conducted to develop effective, available and environmental-friendly methods for removal of heavy metals by using different low-cost agricultural materials for the adsorption of heavy metals from aqueous solutions [6], [2], [7]. Many researches are operated on the removal of Cd^{2+} ions from aqueous solution using adsorbents derived from low-cost tree leaves such as Maize [8]. *Moringa oleifera* has been applied for water purification process to remove heavy metals, as contain functional groups such as hydroxyl, carboxyl, amines,

phenolic, hydroxyl groups which are responsible for the adsorptive capability of heavy metals. The plant is generally chemically composed of a large protein molecule [9]. The removal efficiency of the bark of *Moringa oleifera* was also investigated for $\text{Pb}(\text{II})$ from aqueous systems. It was revealed that the bark is endowed with hydroxyl and/or carboxyl functional groups as the $\text{Pb}(\text{II})$ ions were observed to be chelated with these groups [10]. *Moringa oleifera* has been applied to many water purification studies to remove heavy metals such as $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ [11], [12] and recoveries of up to 60.21% for $\text{As}(\text{III})$ and 85.60% for $\text{As}(\text{V})$ [13]. *Moringa oleifera* is the most cultivated species of the genus *Moringa*, which is the only genus in the family *Moringaceae* [14]. Many researches on *Moringa oleifera* give a properties as water purification and pharmacological properties which play an important role in medicine. The main functional groups amino and carboxylic present in the *Moringa oleifera* have are found due to protein, some fatty acids, carbohydrates and the lignin units [15]. Treating biomass with a base like NaOH and a subsequent citric acid modification stabilizes the biomass due to insertion and cross linking to carboxyl groups and thus increases its cation uptake ability [16]. *Moringa oleifera* (MOL) were washed with base and citric acid, and obtained chemically modified MOL biosorbent (CAMOL) for removing Pb^{2+} ions from aqueous solution [17], also was used for the removal of Cd^{2+} , Cu^{2+} and Ni^{2+} ions from aqueous solution [18]. The sorption process mechanisms include chemisorption, adsorption-complexation on surface, ion

exchange, and surface adsorption [19],[20]. There are a large quantities of solid agricultural waste that cause a big problem, this needs to convert this waste to useful, economic value products for the removal of heavy metal from aqueous solution which would be useful to the environment. The cheaper adsorbent materials increasing the economic value of this plant. As far as we know, no previous studies related to the use of nano sized scale of waste agricultural plants in removal of toxic ions had been found. Thus, this work aims to indicate the ability of nano sized *Moringa oleifera* for removing Cd^{2+} ions estimating maximum biosorption capacity q_m and removal efficiency.

2. Experimental

$Cd(NO_3)_2 \cdot 4H_2O$, HCl, citric acid and NaOH were purchased from Sigma-Aldrich and used without further purification

2.1 Sample collection

The *Moringa oleifera* leaves were collected from Medicinal and Aromatic Plants Researches Department, Agriculture Research Center, Giza, Egypt.

2.2 Instruments

The investigated samples of *Moringa oleifera* powder were grinded to nano size using Retsch Muhle Brinkmann Spectro Mill MS Micro-Grinding Mixing. The structure of investigated plant was characterized by X-ray powder diffraction by a Philips X' Pert PRO MPD, being the X-ray patterns from 5° to 90° at 2θ collected using graphite-mono chromatized Cu $K\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$), operating at 45 kV and 40 mA. The morphology of sample was studied using

field-emission scanning electron microscopy, and was performed on a JSM-6100 microscope with an acceleration voltage. The chemical composition of the prepared nano structures was also analyzed using (EDS) unit attached with the FE-SEM. Fourier transform infrared spectroscope (FTIR-2000, Perkin-Elmer) was used for detection of the surface functional groups on the prepared biosorbents. Transmission electron microscopy images were obtained with a 2000 EX II microscope (JEOL, Japan) at an acceleration voltage of 200 kV. AD1000 and AD1020 pH/mV/ISE/temperature bench Meters was used to adjust pH of the prepared solutions. A thermostated shaker bath (Heidolph MR 3001) was used for shaking. EBA 20 Zentrifugen D-78532 tuttlingen was used to centrifuge the sample after the adsorption process. The concentration of Cd^{2+} ions was determined using Flame Atomic Absorption Spectrometer (model, PerkinElmer, Analyst 200).

2.3 Sample pre-Treatment

Moringa oleifera leaves were washed with doubly distilled water to remove dust, and then subjected to drying. *Moringa oleifera* leaves were grinded and sieved to obtain a very fine powder less than 100 nm and was kept in an airtight plastic container for further sorption studies. The powders obtained were characterized using FTIR, SEM, TEM, XRD and EDS techniques. The powder was used as biosorbent in the biosorption experiments.

2.4 Treatment of *Moringa oleifera* (MO) by citric acid

Chemical modification of nano sized powder *Moringa oleifera* (MO) using NaOH followed by citric acid treatment. CAMO was prepared as followed, 200 grams of the powder was placed in 4L of 0.1N NaOH, then was stirred at 300 rpm for 1h at 23°C to remove NaOH. The powder was rinsed with water and added to 4L of distilled water. This biomass was mixed with citric acid (CA) in a ratio of 1.0 g powder to 7.0 mL of CA (0.6 M). The acid/powder Slurry was dried overnight at 50°C. Then citric acid (CA) treated MO powder (CAMO) was filtered and washed in a Buchner funnel under vacuum with 150 - 200 mL of distilled water per gram of the product to remove excess CA. This volume of water was sufficient to remove unreacted CA since no turbidity from cadmium citrate was observed when the washed powder was suspended in 10 mL of water to which 10 mL of 0.1M cadmium nitrate was added. The modified powder was dried at 50°C overnight [21]; [17], [18].

2.5 Preparation of aqueous solution

Aqueous stock solution of Cd²⁺ ions was prepared from its salt by carefully weighing out 2.726 g of Cd(NO₃)₂·4H₂O and dissolved in a 1000 cm³ volumetric flask then completed with de-ionized water to the mark, the result concentration was 1000 mg/L. Dilution was made to prepare different initial concentrations of Cd²⁺ ions.

2.6 Batch biosorption experiments

2.6.1 Effect of initial metal ions concentration

A 50 ml of Cd²⁺ ions solution of different initial concentrations (10, 20, 50, 100,

200, 300 and 400 mg/L) was added to 300 mg of the biosorbent in 250 ml flat bottom bottle and the mixture was stirred on a shaker at 300 rpm for 1 hr.

2.6.2 Effect of pH

Biosorption experiments were carried out at different pH (2 - 10), initial pH was adjusted by using 0.1M sodium hydroxide (NaOH) or 0.1M hydrochloric acid (HCl). A 50 ml of Cd²⁺ ions solution of initial concentration (20 mg/L) was added to 300 mg of the biosorbent in 250 ml flat bottom bottle at room temperature and different pH values, the mixture was stirred on a shaker at 300 rpm for 1 hr.

2.6.3 Effect of biosorbent dosage

In each biosorption experiment, 50 ml of Cd²⁺ ions solution of initial concentration (20 mg/L) was added to different dosage of the biosorbent (25, 50, 100, 200, 300, 400 and 500 mg) of the biosorbent in 250 ml bottle at room temperature (25°C) and the mixture was stirred on a shaker at 300 rpm for 1 hr.

2.6.4 Effect of contact time

In the biosorption kinetics experiment, 200 ml of Cd²⁺ ions solution of different initial concentrations (10, 30 and 50 mg/L) was added to 1.2 g of the biosorbent in 250 ml flat bottom bottle and the mixture was stirred on a shaker at 300 rpm with a contact times (20, 40, 60, 80, ... and 120) minutes.

2.6.5 Effect of temperature on the biosorption processes and determination of thermodynamic parameters

A 50 ml of different concentrations (10, 20 and 50 mg/L) of Cd²⁺ ions solution was added to 300 mg of the biosorbent in 250 ml flat bottom bottle at

temperatures (25, 30, 40 and 50 °C). Then, the mixture was stirred on a shaker at 300 rpm for 1 hr. After each experiment, the mixture was centrifuged, and the concentration of each was determined using Flame Atomic Absorption Spectrometer. The thermodynamic parameters, ΔH° , ΔS° , and ΔG° for the biosorption process were calculated using the relationships (1) and (2) [22].

$$\ln b = \Delta S^\circ/R - \Delta H^\circ/RT \quad (1)$$

Where, b (Langmuir constant related to energy). The plot of $\ln b$ versus $1/T$ yields a slope and intercept whose values correspond to $\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively. These values can then be used to compute ΔG° by applying the Gibbs relationship:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

2.7 Calculation of metal uptake

The Cd^{2+} ions uptake at equilibrium was calculated by:

$$q_e = \frac{V(C_o - C_e)}{W} \quad (3)$$

where q_e in mg/g is Cd^{2+} ions absorption capacity, V in liters is the volume of the Cd^{2+} ions solution and W in gram is the amount of the biosorbent, C_o and C_e in mg/L are initial and final (equilibrium) Cd^{2+} ions concentrations, respectively. The removal efficiency of the Cd^{2+} ions was also determined using;

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

Where, R. E. % is the percentage of Cd^{2+} ions removed.

2.5.7. Kinetics study analysis of adsorption processes

The mechanism of the adsorption of Cd^{2+} ions was tested using pseudo-first-order [23] and pseudo-second-order kinetic models. Pseudo-first-order and pseudo-second order models are giving by Equations 5 and 6, respectively in a linear form

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$(t/q_t) = 1/(k_2 q_e^2) + (t/q_e) \quad (6)$$

Where, k_1 is the rate constant of pseudo first order, q_e is the Cd^{2+} ions solution uptake in mg/g at equilibrium and q_t is the Cd^{2+} ions solution uptake in mg/g at time t . $\ln(q_e - q_t)$ against (t) is plot was made and q_e and k_1 were obtained from the slope and intercept, respectively. k_2 is the rate constant of pseudo-second order. Plot of (t/q_t) against t gives $(1/k_2 q_e^2)$ as intercept from which k_2 can be obtained and $(1/q_e)$ as slope. Both models are tested for suitability using correlation coefficient, R^2 [24]; [25].

2.5.8. Effect of chemical treatment

A 50 ml of Cd^{2+} ions solution of initial concentration (20 mg/L) was added to 300 mg of the chemically treatment biosorbent (CAMO) in 250 ml flat bottom bottle at room temperature, the mixture was stirred on a shaker at 300 rpm for 1 hr. After each experiment, the mixture was centrifuged, and the concentration of each was determined using Flame Atomic Absorption Spectrometer.

3. Results and discussion

Characterization of the investigated biosorbent

FT-IR spectral analysis of biosorbent

FT-IR data of biosorbent *Moringa oleifera*(MO) (Fig.1a) and Cd²⁺ ions loaded on *Moringaoleifera*(Cd-MO) (Fig.1a) were carried out. FT-IR spectrum of the biosorbent, (MO) exhibits the main functional groups that are responsible for Cd²⁺ions binding. There are significant changes in the characteristic FTIR absorption bands (Fig. 1a) reflecting the complex nature of the *Moringa oleifera*. The main characteristic skeleton cellulose peak in the finger print appears in the region of 1000 - 1200 cm⁻¹[26]. The appearance of a strong and broad peak at 3295cm⁻¹, could be attributed to the stretching vibration of the N-H bond of amino groups and indicative of bonded hydroxyl group. The shift in the peak position to 3275 cm⁻¹ in the spectrum of the metal-loaded *Moringa oleifera* powder indicates the binding of cadmium ions with amino and hydroxyl groups[27-29]. The intense band appeared at 1025 cm⁻¹ can be assigned to the C-O of alcohols and carboxylic acids and confirms the lignin structure of *Moringa oleifera*. The shift of the peak to 1028cm⁻¹ also suggests the involvement of the C-O group in binding of Cd²⁺ ions [27-30]. Sharp peak was also observed at 1738 and 1642 cm⁻¹, which is characteristic of carbonyl group stretching, and is shifted to lower wave number of 1732 and 1634 cm⁻¹respectively on Cd²⁺ adsorption [31];[32]. Band at 1243 cm⁻¹ indicate presence of carboxylic acids which shifted to wave number of 1237 cm⁻¹after

Cd²⁺ adsorption [17]. Also FTIR for detection the functional groups on the modified biosorbents[citric acid (CA) treated MO powder (CAMO) before adsorption(CAMO)and after adsorption of Cd²⁺ ions (Cd-CAMO) was shown in Fig. 1b

Comparison of the IR spectra of samples of MO and CA modified MO revealed that acharacteristic stretching vibration absorption band of carboxyl group at 1725 cm⁻¹ is present in the IR spectrum of CAMO samples. This confirms the esterification between alcohol groups of cellulose in MO and citric acid[16],[18]. The broad absorptions around 2500–3500 cm⁻¹centered at 3278 confirm the existence of carboxylic OH groups and free COOH groups after CA modification. A change in peak position to 3281 cm⁻¹ in the spectrum of the Cd²⁺ loaded CAMO indicates the binding of these metal ions with hydroxyl groups. peak at 1725 cm⁻¹ shifted to 1730cm⁻¹ in the spectrum of the Cd²⁺loaded CAMO indicating the binding of metal ions to carboxylic groups also. These showed that Cd²⁺ adsorbed mainly to the active groups such as hydroxyl groups (OH) and carboxylic groups (COO⁻) [10]; [18].The shifts in the absorption peaks generally observed indicate the existence of Cd²⁺ binding process taking place on the *Moringa oleifera* powder[2],[7].

Elemental analyses

To determine the chemical composition of the investigated plant, and used as a primary fast test to identify the ability of biomass to adsorb the metal ions on its surface[7]. EDS elemental analysis of *Moringa olieifera*is shown in Figure 2.

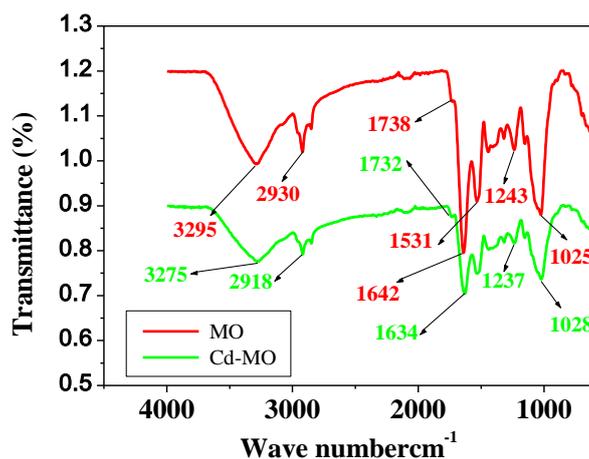


Fig. 1a: FT-IR spectral analysis of biosorbent *Moringa oleifera* (MO) and Cd²⁺ loaded *Moringa oleifera* (Cd-MO).

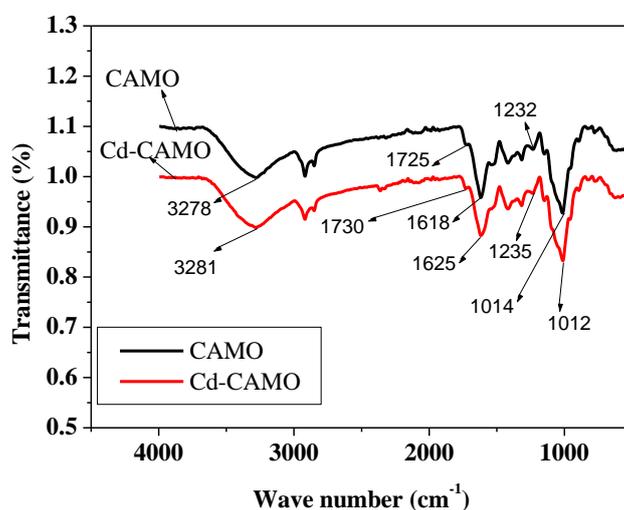


Fig. 1b: FT-IR spectral analysis of the modified biosorbent *Moringa oleifera* (CAMO) and Cd²⁺ loaded the modified *Moringa oleifera* (Cd-CAMO).

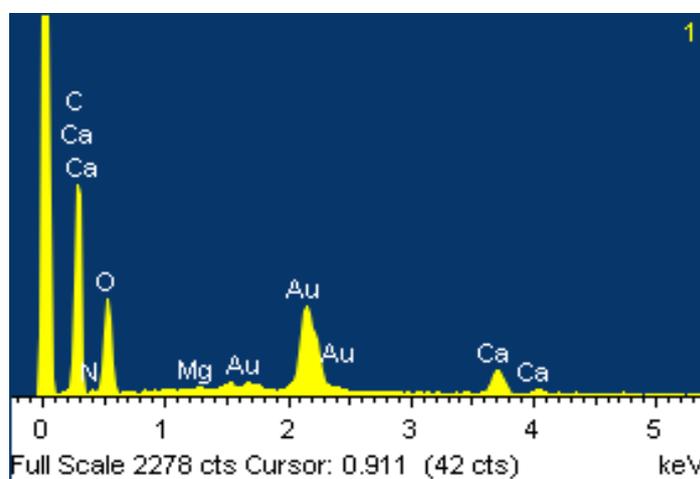


Fig. 2: EDS spectrum of the investigated nano sized plant

Scanning electron micrographs SEM

Scanning electron micrographs of biosorbent *Moringa oleifera*(MO) (Fig. 3) are used to show the morphological features of *Moringa oleifera* powder and exhibits structure porosity for the biomass. The morphology of *Moringa oleifera* powder surface showed that the powder was an assemblage of fine particle which did not have regular, fixed size and shape. The particles were of various dimensions and contained number of steps surface, with edges.

XRD analysis of biosorbent

XRD pattern of the biosorbent *Moringa oleifera* powder indicates the presence of a significant amount of amorphous material due to lignin in the sample. The amorphous nature of the biosorbent suggested that Cd^{2+} could easily penetrate into the surface of MO biosorbent. XRD patterns of the adsorbent *Moringa oleifera* powder(M O)before and after equilibration with Cd^{2+} indicate that the structure of MO remained unaltered even after Cd^{2+} adsorption [17],[7].

Transmission electron microscopy (TEM)

The grinding sample was subjected to TEM analysis (cf. Fig. 4a) to examine the particle size and the size of the majority of particles was found to be 30nm (cf. Fig. 4b).

Effect of initial metal ions concentration on the biosorption of Cd^{2+} ions by *Moringa oleifera*

The effect of initial metal ions concentration on Cd^{2+} ions biosorption is illustrated in Figure 5 (a, b). The amount of metal ions adsorbed (q_e) increases as

the initial concentration rises, as Cd^{2+} ions are available for interaction with the biosorbent increased mass transfer of Cd^{2+} ions to the biosorbent. This biosorption characteristic showed that surface saturation depends on the initial Cd^{2+} ions concentrations. The Cd^{2+} ions removal efficiency for initial concentrations 10 and 20 mg/L are 93.74and 92.1 % respectively and decreases as the initial concentration increases. This suggests the presence of a strong attraction between the biosorbent surface and the Cd^{2+} ions solute. At low concentrations, a greater chance was available for metal removal. Biosorption sites took up the available Cd^{2+} ions rapidly when increasing concentrations to high concentration as saturation occurred quickly, the rate of diffusion became slow. The initial concentration give a significant force in overcoming mass transfer resistances of the Cd^{2+} ions between the aqueous and solid phases. So, initial concentration of Cd^{2+} ions solutions increases the biosorption[33 - 37],[2],[7].

Effect of pH on the biosorption of Cd^{2+} ions by *Moringa oleifera*

The effect of pH of a solution is an important factor in the sorption process as shown in Figure 7. The result obtained on the effect of pH on Cd^{2+} ions removal efficiency and q_e showed that both increase as the pH increase. This confirm a strong interaction between the biosorbent and the Cd^{2+} ions in solution that $[H^+]$ and $[OH^-]$ could affect both on Cd^{2+} ions removal efficiency and q_e . The amount of Cd^{2+} ions removed by the *Moringaoleifera*at low pH 2 was low(0.92 mg/g)and removal efficiency 27.7 % compared to the amounts

removed at pH 4 to 10 were ranged from (2.92 mg/g and removal efficiency 87.8% at pH 8 to 3.07 mg/g and removal efficiency 92.1% at pH 5. This could be explained as follows, at low pH the concentration of hydrogen ions is high [24]. This increase the competition between the hydrogen ions and the metal ions. As H^+ ions were being removed by the biosorbent, instead of the Cd^{2+} ions, the surface of the biosorbent is surrounded by hydronium ions (H_3O^+), which prevent the metal ions from approaching the binding sites of the biosorbent [25]; [38] when H^+ ions at higher concentration, the biosorbent surface becomes more positive charge so, the attraction between biomass and metal cation is reduced [39]. When pH increases, the number of the positively charged sites decreases while the negatively charged sites increases, the surface of the sites gets negatively charged thus increases electrostatic force of attraction for the positively charged Cd^{2+} ions solution in amount of metal ions sorbet. Maximum adsorption for Cd^{2+} ions occurred at pH 5. The better adsorption observed at pH 5 compared to other higher pH may be due

to the large number of H^+ ions present, which neutralizes the negative charges on adsorbent surface, reducing hindrance to the diffusion of organics at higher pH. As the capacity of the adsorbent reduced, the reduction in adsorption may be due to the increasing of OH^- ions, as the precipitation of Cd^{2+} ions as cadmium hydroxide occur [40].

Effect of biosorbent dosage on the biosorption of Cd^{2+} ions

It is an effective factor to study the capacity of a biosorbent for a given initial concentration 20 mg/L. As biosorbent dosage Cd^{2+} ions increases, removal efficiency increases with least value of 79.5 % obtained with 25 mg and highest value of 98.1% with 500 mg of the biosorbent. This is due to the increase in surface area and availability of biosorption sites. But biosorption capacity q_e decreases as a result of the splitting effect of the concentration gradient between the Cd^{2+} ions solution and biosorbent with increasing biosorbent dosage bringing about a decrease in the amount of Cd^{2+} ions adsorbed per unit weight of biosorbent as shown in Figure 7 [41-45], [37], [36].

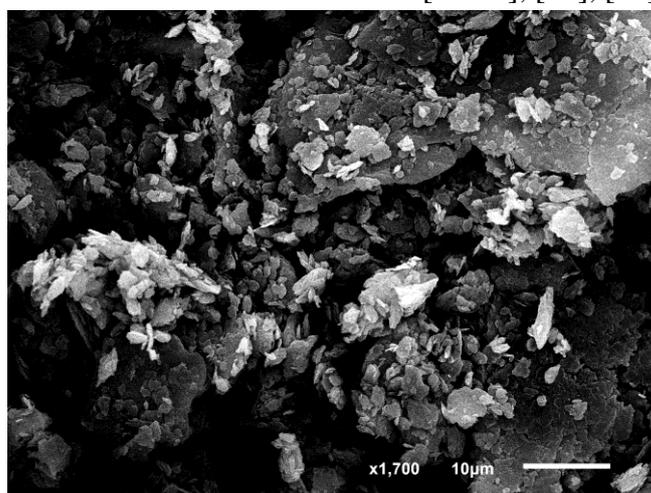


Fig. 3: Scanning electron micrograph of biosorbent *Moringa oleifera* (MO).

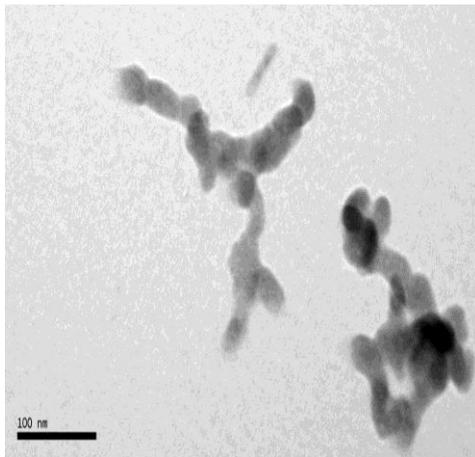


Fig. 4 (a): TEM image of nano sized Biosorbent *Moringa oleifera* (MO).

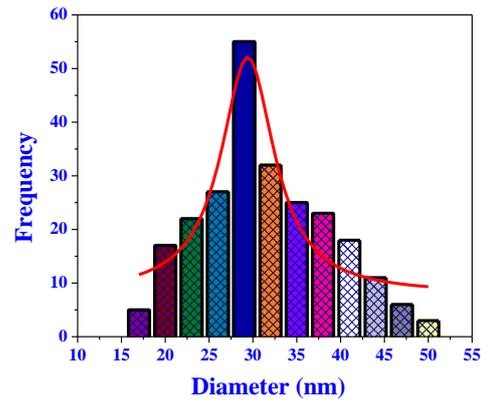


Fig. 4(b): particle size distribution for the investigated biosorbent.

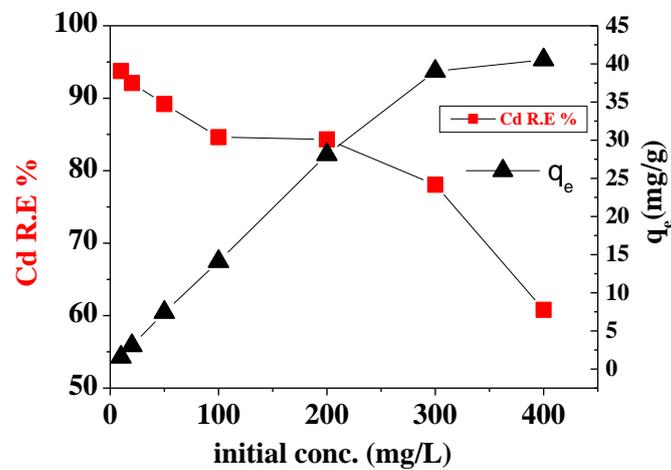


Fig. 5: Effect of initial Cd^{2+} ions concentration on Cd^{2+} ions removal efficiency(a) and q_e (b) by *Moringa oleifera*

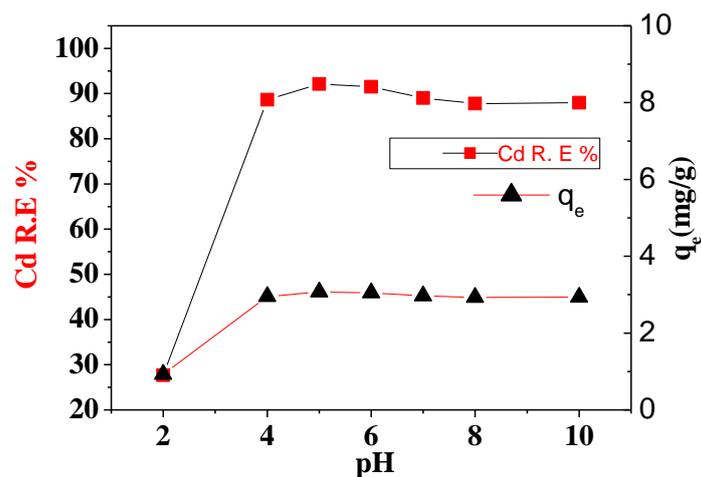


Fig. 6: Effect of pH on Cd^{2+} ions removal efficiency and q_e at initial concentration 20 mg/L at different pH values by *Moringa oleifera*

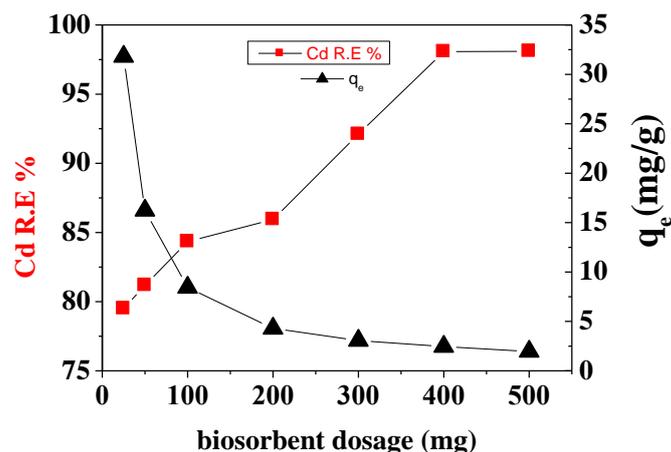


Fig. 7: Effect of biosorbent dosage on Cd^{2+} ions removal efficiency and q_e at initial concentration 20 mg/L by *Moringa oleifera*.

Effect of contact time on biosorption of Cd^{2+} ions

The result of contact time for the adsorption of Cd^{2+} ions by *Moringa oleifera* is shown in Figure 8. For an initial metal ion concentrations of (10, 30, 50) mg/L, it was observed that the amount of Cd^{2+} ions absorbed increased with increase in time and reach equilibrium in 60 minutes. The removal efficiency of metal ions increases with the increase of the adsorption time. And it remains constant after an equilibrium time of 60 minutes. This may be attributed to long time of contact and availability of active sites, after the equilibrium is reached at 60 minutes. There was a slightly increasing or remain constant in the Cd^{2+} ions removal, as the sites are less available as the capacity of the adsorbent gets exhausted, the rate of uptake was controlled by the rate at which the adsorbate was transported from the solution to the sites of the biosorbent particles and leaving the process to be attachment controlled [45-46],[2].

Effect of temperature on biosorption of Cd^{2+} ions

Effect of the temperature at different values (25, 30, 40 and 50) $^{\circ}\text{C}$ (cf. Fig. 9) shows that the Cd^{2+} removal efficiency and q_e at different initial concentrations (10, 20 and 50) mg/L by *Moringa oleifera* increases while the temperature is increasing. The increase in capacity q_e with temperature suggested that the active sites have increased with temperature. The increase of the temperature encourages the process of biosorption. This process due to increase in the movement of the Cd^{2+} ions which occurs at higher temperatures. The increase in adsorption capacity of *Moringa oleifera* with temperature indicates an endothermic process. The increase in adsorption with temperature may be due to pore size change causing intra particle diffusion within the pores or increase in the chemical interaction of the metal cations to the surface of adsorbent leading to chemical interaction to occur during adsorption process which results into increase in adsorption capacity. At higher temperatures, the possibility of diffusion of solute within

the pores of the adsorbent may not be ruled out as reported by researchers for the adsorption of cations [47-49],[37] concentrations (10, 20, 50) mg/L by *Moringa oleifera*.

Adsorption isotherm

Adsorption isotherms of Cd^{2+} ions on *Moringa oleifera* are presented as a function of the equilibrium concentration of metal ions in the aqueous solution in Fig. 10. The amount of Cd^{2+} adsorbed per unit mass of *Moringa oleifera* increased with the initial concentration of Cd^{2+} , as expected [50],[51]. The maximum adsorption capacity is 16.47 mg/g of *Moringa oleifera*. The metal ions distribution between the liquid and solid phases can be described by mathematical model equations such as Langmuir isotherm model and the Freundlich isotherm model [52]. The Langmuir and Freundlich models are used because of its ability to describe experimental data in wide range of concentrations. Freundlich and Langmuir adsorption isotherms are also classical models to describe the equilibrium between metal ions adsorbed onto adsorbent and metal ions in solution. Both isotherm models can be easily transformed into linear forms, just by linear regression. Langmuir's isotherm model suggests that uptake takes place on homogeneous surface. These models could be summarized as follows. The linear form of Langmuir isotherm equation is represented by the following equation [53],[2],[36],[37].

$$C_e / q_e = 1/q_m b + C_e / q_m \quad (7)$$

as, q_e the amount of Cd^{2+} ions adsorbed at equilibrium (mg g^{-1} adsorbent), C_e is the equilibrium concentration of adsorbate (mg L^{-1}), b (L mg^{-1}) and q_m (mg g^{-1}) are

the Langmuir constants related to energy and the adsorption capacity, respectively. Plot of C_e/q_e against C_e give a straight line with slope $1/q_m$ and intercept $1/q_m b$ is obtained (Figs. 10), which shows cadmium biosorption isotherms of Langmuir. From the intercept and slope of the plots, the Langmuir parameters, b and q_m , are calculated. These values may be used for comparison and correlation of the sorptive properties of *Moringa oleifera*. The Freundlich model is applied for isothermal adsorption and has the general form [54].

$$\log q_e = \log K_f + 1/n \log C_e \quad (8)$$

as, C_e is the equilibrium concentration (mg L^{-1}) of adsorbate, q_e is the amount of adsorbate (mg g^{-1} adsorbent), n and K_f are the Freundlich constants. When $\log q_e$ is plotted against $\log C_e$, a line with slope $1/n$ and intercept $\log K_f$ is obtained (cf. Fig. 11). This reflects the satisfaction of Freundlich isotherm model for the adsorption of cadmium ions. The intercept, $\log K_f$, is an indicator of the adsorption capacity and the slope, $1/n$, is an indicator of intensity of adsorption [55]. To ascertain if the biosorption phenomenon is favorable or unfavorable, for Langmuir type biosorption process, isotherms can be classified by R_L , a dimensionless constant separator factor [56] stated as:

$$R_L = 1 / (1 + b C_0) \quad (9)$$

Mathematical calculation of R_L indicates the shape of isotherm to be either, irreversible ($R_L = 0$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or favorable ($0 < R_L < 1$). From the experiment, R_L varies from 0.101 to 0.374 for different Cd^{2+} ions concentrations (10, 20, 50) mg/L at

different temperatures(cf. Table 1). These values ranged between 0 and 1, thus indicating a favorable biosorption. The values of (Freundlich exponent n) were greater than 1[57]. Moreover, the value of n indicates better biosorption mechanism and formation of relatively stronger bond between adsorbate and biosorbent as $1/n$ values are found in the range of 0.72–0.74, when the temperature was altered from 293 to 323 K, this indicate that the biosorption of Cd(II) onto

*Moringa oliefera*s favorable under the conditions studied as $1/n$ values between 0 and 1. The fitting of the linear form of the models was examined by using linearity coefficient (R^2). The Langmuir model has a less fitting model than Freundlich model according to linearity coefficients ($R^2 = 0.9946$ and 0.9999 respectively) as shown in Figs. 10 and 11. The sorption of metal ion on *Moringa oliefera* follows the Freundlich isotherm model describing the adsorption in aqueous system.

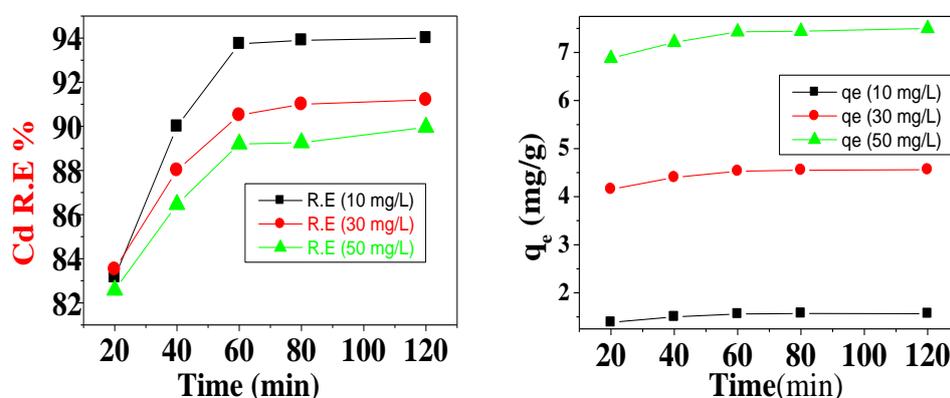


Fig. 8: Effect of contact time on Cd²⁺ ions removal efficiency and q_e at different initial concentrations (10, 30, 50) mg/L by *Moringa oliefera*

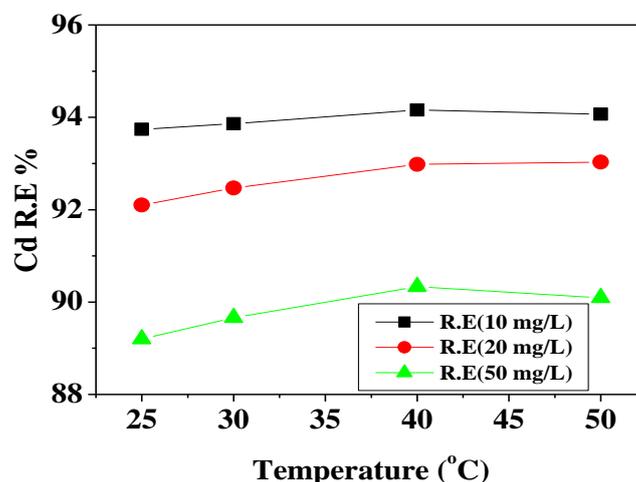


Fig. 9: Effect of temperature on Cd²⁺ ions removal efficiency at different initial concentrations (10, 20, 50) mg/L by *Moringa oliefera*

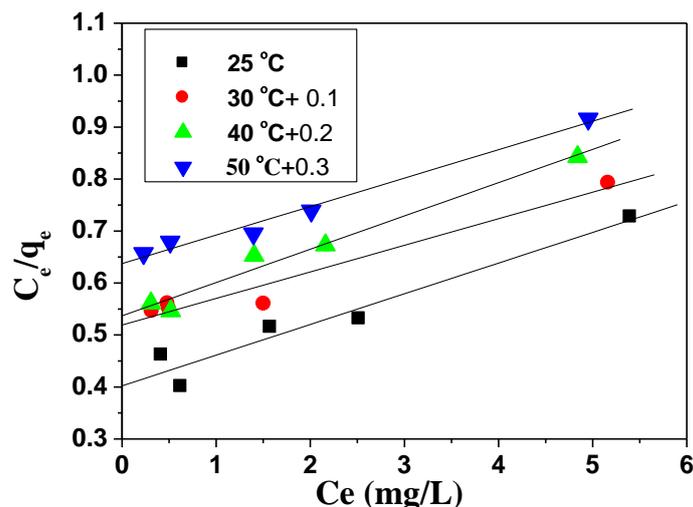


Fig. 10: Linearized biosorption isotherms of Langmuir

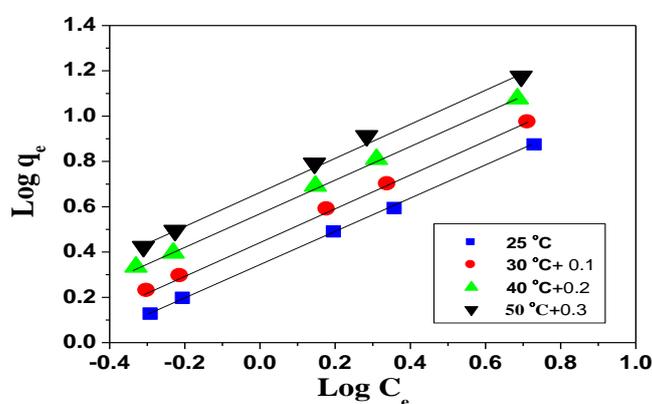


Fig. 11: Linearized biosorption isotherms of Freundlich.

Table 1: A dimensionless constant separator factor (R_L) for Langmuir type biosorption process.

C_0 (mg/L)	R_L at 25°C	R_L at 30°C	R_L at 40°C	R_L at 50°C
10	0.373	0.374	0.367	0.359
20	0.226	0.230	0.225	0.219
50	0.106	0.107	0.104	0.101

Thermodynamic studies on biosorption of Cd²⁺ ions

The obtained thermodynamics equilibrium constant was used to calculate all other thermodynamic parameters from a plot $\ln b$ against $1/T$. The entropy, enthalpy and Gibbs free energy for the adsorption process were obtained at different temperatures for Cd(II) using

Eq. (1).

The sorption capacity of the *Moringa oleifera* for Cadmium increased with increasing temperature, this means the sorption process was endothermic. Thermodynamic parameters such as enthalpy change, free energy change and entropy change were determined using the equations (1),(2) [58];[45];[59].

Where ΔG° is the change in free energy (KJ mol^{-1}), ΔS° is the change in entropy ($\text{J mol}^{-1} \text{K}^{-1}$), ΔH° is the change in enthalpy ($\text{kJ mol}^{-1} \text{K}^{-1}$), R is the gas constant ($8.314 \times 10^{-3} \text{kJ mol}^{-1} \text{K}^{-1}$), T is the absolute temperature (K), and b is the equilibrium constant of adsorption. When $\ln b$ is plotted against $1/T$, the slope $\Delta H^\circ/R$, and intercept $\Delta S^\circ/R$ are obtained. From the slope and intercept of the Van't Hoff plots of $\ln b$ versus $1/T$ the values of ΔH° and ΔS° were obtained. The thermodynamic parameters are given in Table 2. Positive values of ΔH° suggest the endothermic nature of adsorption of Cadmium ions on the *Moringa oleifera*. The positive ΔG° values were obtained in this study. It has been suggested that a positive value for ΔG° is quite common when an ion-exchange mechanism applies in the biosorption of cationic sorbate because of the activated complex formed by the cationic sorbate with the biosorbent [60]. The magnitude of ΔG° also increased with increase in the temperature that the biosorption was more favorable at higher temperatures [22]; [61].

Kinetic of the adsorption Cd^{2+} ions

The Kinetic of the adsorption of Cd(II) was tested using pseudo first-order kinetic model and second order kinetic model [24]; [25]. By using the experimental data obtained from sorption time investigation, the adsorption kinetic of the removed Cd^{2+} ions from aqueous solution was studied (cf. Figs. 12, 13). The linear forms by Equations 5 and 6 of Pseudo-first-order and pseudo-second order models, respectively are used. Where, q_e is the Cd^{2+} ions uptake at equilibrium in mg/g , k_1 is the rate constant of pseudo-first-order biosorption, and q_t is the Cd^{2+} ions uptake at time, t in mg/g . Values of k_1 and q_e were obtained from the slope

and intercept, respectively of plot of $\ln(q_e - q_t)$ against t . k_2 is the rate constant of pseudo-second order model. A plot of (t/q_t) against t gives $(1/q_e)$ as slope and $(1/(k_2 q_e^2))$ as intercept from which k_2 can be obtained. Both models are tested for suitability using their correlation coefficient, R^2 [24]. The calculated q_e determined from the plot of the pseudo-first-order model for Cd^{2+} ions solutions at various concentrations differs from the experimental q_e . This implies that pseudo-first-order model is not good in studying the kinetics of the biosorption of Cd^{2+} ions. As their correlation coefficient is close to 1, the pseudo-second-order model fits the kinetics better, (i.e. 0.999 for Cd^{2+} ions solutions at various concentrations). The calculated q_e (7.5 mg/g) are very close to the experimental q_e (7.44 mg/g). All these imply that the second order kinetics is good in studying the kinetics of the biosorption of Cd^{2+} ions, suggesting that biosorption is the rate-limiting step; and that biosorption of the Cd^{2+} ions solutions involves two species, in this case, the Cd^{2+} ion.

Effect of chemical treatment of the biosorbents on biosorption efficiency

The effect of chemical modification of the biosorbents by esterifying with NaOH followed by citric acid treatment (CAMO) on the removal efficiency compared with (MO) was studied and shown in Table. 3. It was observed that the R. E.% of metal ions by (CAMO) was higher than the R. E.% of metal ions by (MO) and this was due to the treating with a base like NaOH and a subsequent citric acid modification stabilizes the biomass due to insertion and cross linking of carboxyl groups and thus increases its cation uptake ability [16-18].

Table 2: Thermodynamic parameters for the biosorption process

Temperature(K)	ΔG° (KJ/m l)	ΔH° (KJ/mol.k)	ΔS° (J/mol. K)
298	4.44	1.99	8.24
303	4.48		
313	4.57		
323	4.65		

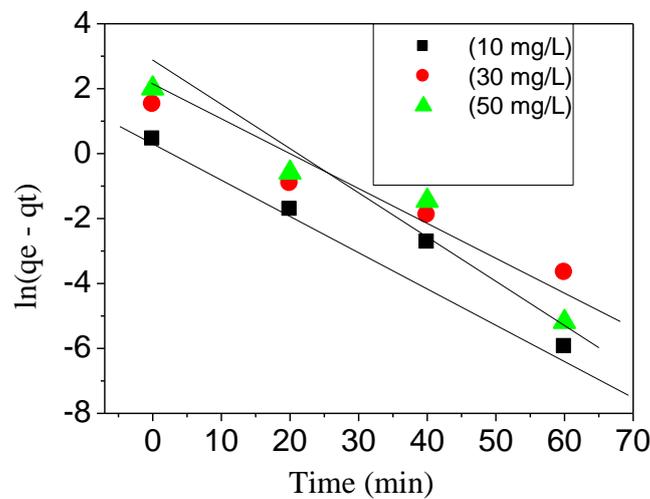


Fig. 12: Pseudo-first order for sorption of Cd²⁺ ions by *Moringa oleifera*

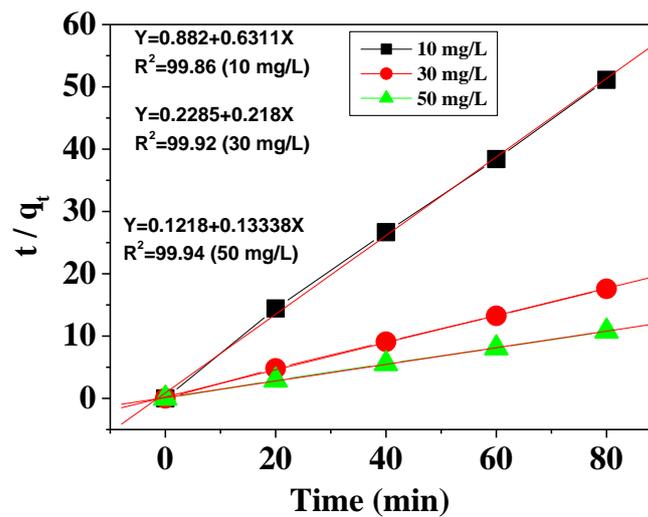


Fig.13: Pseudo-second order for sorption of Cd²⁺ ions by *Moringa oleifera*

Table 3: Effect of chemical treatment of biosorbent on biosorption efficiency

Biosorbent	<i>Moringa oleifera</i>			
	MO		CAMO	
C ₀ (20 mg/L) of metal ions	C _e (mg/L) ± sd ^a	R. E.% ± sd ^a	C _e (mg/L) ± sd ^a	R. E.% ± sd ^a
Cd ²⁺	1.58 ± 0.01	92.10 ± 0.12	0.385 ± 0.01	98.10 ± 0.43

Conclusion

Nano sized of *Moringa oleifera* biosorbent was used for adsorption of Cd²⁺ ion from aqueous solution. The results showed that *Moringa oleifera* biosorbent proved to be a very effective biosorbent in the removal of Cd²⁺ ions from water. The following conclusions can be drawn from this study,

- 1- The biosorption process was affected by pH, contact time, temperature, dosage and metal ion concentration dependent.
- 2- The Freundlich isotherm has a good fit with the experimental data compared to Langmuir isotherm. R_L value from Langmuir and n from Freundlich isotherms show that biosorption of Cd²⁺ ions solutions on *Moringa oleifera* is favorable.
- 3- Maximum biosorption capacity of Cd²⁺ ions solutions on *Moringa oleifera* is 40.53 mg g⁻¹.
- 4- Thermodynamic studies confirmed that the biosorption process was endothermic; a positive value for

ΔG° is quite common when an ion-exchange mechanism applies in the biosorption of cationic sorbate.

5- The kinetics study of sorption indicates that the pseudo second-order model provides better correlation of the sorption data than the pseudo first-order, confirming the chemisorption of Cd²⁺ ions solutions on *Moringa oleifera*.

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