

Nano Sized *Moringa oleifera* an Effective Strategy for Pb(II) ions Removal from Aqueous Solution

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Abstract

Nano-sized *Moringa oleifera* is considered an effective biosorbent with high surface area from agricultural waste, low cost and environment-friendly which can be used for removal of Pb²⁺ from waste water. Thus our study stem to investigate the ability of natural nano-sized biosorbents for removing very toxic Pb²⁺ ions from aqueous solution. The investigated biosorbent (*Moringa oleifera*) was characterized by FTIR, SEM, TEM, XRD and EDX techniques. Moreover, the influence of pH, temperature, adsorbent dosage, contact time and initial metal ion concentration on adsorption process were investigated. The maximum biosorption capacities (q_m) of Pb²⁺ ions by *Moringa oleifera* was 37.9 mg/g. The lowest biosorption was observed (61.4%) for Pb²⁺ ions at pH 2.0 while the highest one (94.36%) at pH 5. The optimum contact time for the adsorption process was found to be at 60 minutes. The amount of Pb²⁺ ions adsorbed increases with increasing in initial metal ion concentration. Moreover, biosorption capacity (q_e) and removal efficiency of Pb²⁺ ions solutions increase as temperature increases. FT-IR data indicated that the adsorption of metal ions occurs on the surface of *Moringa oleifera* powder as the main functional groups that are responsible for metal ions binding are involved in the process. Furthermore, Thermodynamic studies confirmed that the biosorption process was endothermic and the positive value of ΔG° is quite common when an ion-exchange mechanism applies in the biosorption. The Positive value of ΔS° suggested an increase in randomness during the biosorption. The kinetics study of sorption indicates that the pseudo second-order model provides better correlation of the sorption data (R²=0.99) than the pseudo first-order model (R² = 0.91), confirming the chemisorption of metal ions solutions on *Moringa oleifera*. The Freundlich isotherm has a good fit with the experimental data (R² close to 1) compared to Langmuir isotherm (R²=0.99). This study shows that *Moringa oleifera* are available, low cost, effective and environment friendly biosorbent for the removal of Pb²⁺ ions from aqueous environment.

Keywords: Lead, biosorption, Thermodynamics, kinetics, removal efficiency, *Moringa oleifera*, isotherm

1. Introduction

Toxic heavy metals release into the environment such water bodies causes food contamination and so food safety for the human consumption is a serious worldwide public issue [1]. There is evidence that heavy metals present in the environment, even in low concentration, are responsible for producing a variety of illnesses related with the risk of dermal damage, respiratory problems and several kinds of cancer. [2] Owing to longer residence time and ability to form non-biodegradable compounds and its toxic effects, removal of heavy metal from contaminated sites is given priority to restore ecosystem functions and stability [3]. So treatment of waste water as an additional resource to reduce the problem of limited and scarce water resources by the addition of this resource to maximize benefit from the available water resources and reduce the growing gap between available water resources and the required water needs. Heavy metals can be removed from aqueous solutions by several non-effective methods such as ion exchange, chemical precipitation, adsorption and membrane separation [4]. Many studies were conducted to develop an effective, available and environmental-friendly methods for removal of heavy metals by using biosorbents, as microbial biomass, waste materials generated due to agricultural by-products such as: sugar cane bagasse fly ash and peat [5], rice husks and straws [6], soya bean, saw dust, walnut and seeds hull, corn cobs and banana peels [7]. The feasibility of Pb(II) ion removal from aqueous solution onto six natural biosorbents namely rice straw, rice bran, rice husk, hyacinth roots, neem leaves has been investigated [8]. *Moringa oleifera* has been applied in 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 Pb (II) from aqueous systems. It was revealed that the bark is endowed with hydroxyl and/or carboxyl functional groups as the Pb (II) ions were observed to be chelated with these [10]. *Moringa oleifera* has been applied in many water purification studies to remove heavy metals such as Ni, Cu and Zn [11]. *Moringa oleifera* is the most cultivated species of the genus *Moringa*, which is the only genus in the family *Moringaceae* [12]. Many researches on *Moringa oleifera* give a properties as pharmacological properties. which play an important role in medicine [13]. The main amino and carboxylic groups present in the *Moringa oleifera* are found due to protein, some fatty acids, carbohydrates and the lignin units. [14]. Thus, our aim is to convert agricultural waste to useful, economic value biosorbents for the removal of heavy metal from aqueous

solution which would be useful to the environment and to maximize benefit from waste water. As the cheaper biosorbent materials increasing the economic value of this plant, another aim is to indicate the ability of nano sized *Moringa oleifera* for removing Pb^{2+} ions estimating biosorption capacity q_e and removal efficiency under different initial metal ions concentration, pH, contact time, dosage, concentration and temperature.

2. Experiment

$Pb(NO_3)_2$, HCl 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 Brinkann 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 80° at 2θ collected using graphite-monochromatized 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 synthesized nanostructures was also analyzed using (EDAX) unit attached with the FE-SEM. Fourier transform infrared spectroscopy (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. Athermostated 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 Pb^{2+} ions was determined using Flame Atomic Absorption Spectrometer (model, Perkin Elmer, Analyst 200).

2.3. Sample pre-Treatment

Moringa oleifera were washed with de-ionised water to remove dust, and then subjected to drying. *Moringa oleifera* was 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 EDX techniques. The powder was used as biosorbent in the biosorption experiments.

2.4. Preparation of aqueous solution

Aqueous stock solution of Pb^{2+} ions was prepared from its salt by carefully weighing out 1.6 g of $Pb(NO_3)_2$ and dissolved in a 1000 cm^3 volumetric flask and completed with de-ionised water to the mark, the result concentration was 1000 mg/L. Dilution was made to prepare different initial concentrations of Pb^{2+} ions.

2.5. Batch biosorption experiments

2.5.1. Effect of initial metal ions concentration

50 ml of Pb^{2+} 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.

2.5.2. 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). 50 ml of Pb^{2+} 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.

2.5.3. Effect of dosage

In each biosorption experiment, 50 ml of Pb^{2+} 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 ($25^\circ C$) and the mixture was stirred on a shaker at 300 rpm for 1 hr.

2.5.4. Effect of contact time

In the biosorption kinetics experiment, 200 ml of Pb^{2+} 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 at room temperature and the mixture was stirred on a shaker at 300 rpm with a contact times (20, 40, 60, 80, ..., 120) minutes.

2.5.5. Effect of temperature and determination of thermodynamic parameters

50 ml of different concentrations (10, 20 and 50 mg/L) of Pb^{2+} ions solution was added to 300 mg of the biosorbent in 250 ml flat bottom bottle at temperature ($25^\circ C$, $30^\circ C$, $40^\circ C$ and $50^\circ C$). And the mixture was stirred on a

shaker at 300 rpm for 1 hr. After each experiment, the mixture was filtered and centrifuged, 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) [15].

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

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

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

2.5.6. Calculation of metal uptake

The Pb^{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 Pb^{2+} ions absorption capacity, V in liters is the volume of the Pb^{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) Pb^{2+} ion concentrations, respectively. The removal efficiency of the Pb^{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 Pb^{2+} ions removed.

2.4.6. Kinetics study analysis

The mechanism of the adsorption of Pb^{2+} ions was tested using pseudo-first-order [16] and pseudo-second-order kinetic models [17]. 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_t is the Pb^{2+} ions solution uptake in mg/g at time t and q_e is the Pb^{2+} ions solution uptake in mg/g at equilibrium. A plot of $\ln(q_e - q_t)$ against t was made and q_e and k_1 values 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 [17, 18].

3. Results and discussion

3.1. Characteristics of the investigated biosorbent

3.1.1. FT-IR spectral analysis of biosorbent

FT-IR data of biosorbent *Moringa oleifera* (M.O) and Pb^{2+} ions loaded on *Moringa oleifera* (Pb-M.O) were carried out. FT-IR spectrum of the biosorbent, (M.O) exhibits the main functional groups that are responsible for Pb^{2+} ions binding. There are a characteristic IR absorption bands reflecting the complex nature of the *Moringa oleifera*. The main characteristic skeleton cellulose peak in the finger print appears in the region of $1000 - 1200 \text{ cm}^{-1}$ [19]. The appearance of a strong and broad peak at 3295 cm^{-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 3277 cm^{-1} in the spectrum of the metal-loaded *Moringa oleifera* powder indicates the binding of Pb^{2+} ions with amino and hydroxyl groups [20, 21]. 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 1017 cm^{-1} also suggests the involvement of the C-O group in binding of Pb^{2+} ions [20 - 22]. Sharp peaks was also observed at 1738 and 1642 cm^{-1} , which is characteristic of carbonyl group stretching, and is shifted to wave number of 1754 and 1632 cm^{-1} respectively on Pb^{2+} adsorption [23, 24]. Band at 1243 cm^{-1} indicate presence of carboxylic acids which shifted to wave number of 1236 cm^{-1} after Pb^{2+} adsorption [25]. The shifts in the absorption peaks generally observed indicate the existence of Pb^{2+} binding process taking place on the *Moringa oleifera* powder.

3.1.2. Elemental analysis

To determine the composition of the investigated plant, EDS elemental analysis of *Moringa oleifera* is shown in Figure 1.

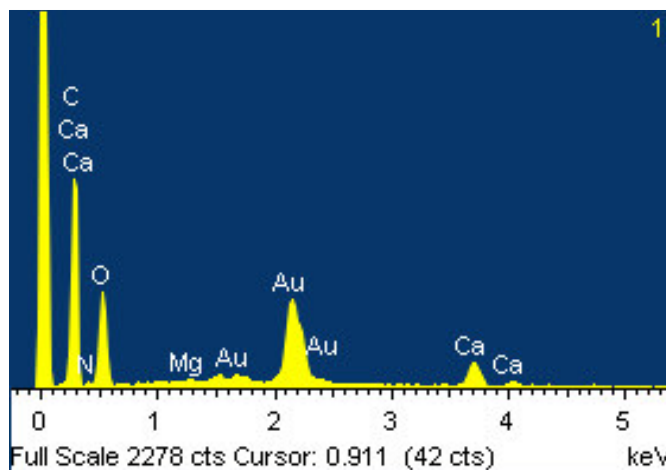


Fig.1: EDS spectrum of the investigated nano sized plant

3.1.3. Scanning electron micrographs SEM

Scanning electron micrographs of biosorbent *Moringa oleifera* (M.O) (Fig. 2) are used to show the morphological features of *Moringa oleifera*. The surface morphology of *Moringa oleifera* exhibits structure porosity for the biomass. The surface morphology of *Moringa oleifera* powder 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 all of them contained a large number of steps surface with edges.

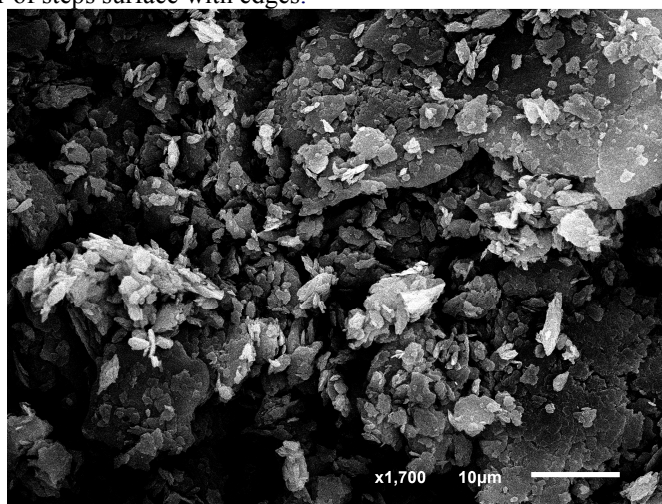


Fig. 2: Scanning electron micrograph of biosorbent *Moringa oleifera* (M.O).

3.1.4. XRD analysis of biosorbent

XRD pattern of the *Moringa oleifera* powder is shown in Fig. 3 indicating the presence of a significant amount of amorphous material due to lignin in the sample. XRD patterns of the adsorbent *Moringa oleifera* powder before and after equilibration with Pb^{2+} ions indicate that the structure of *Moringa oleifera* remained unaltered even after Pb^{2+} adsorption.

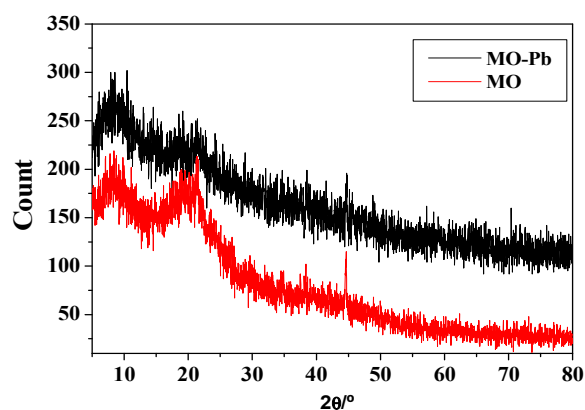


Fig. 3: XRD patterns of the adsorbent *Moringa oleifera* (M.O) powder before and after equilibration with Pb^{2+} ions (M.O)

3.1.5. 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 65 nm (cf. Fig. 4b).

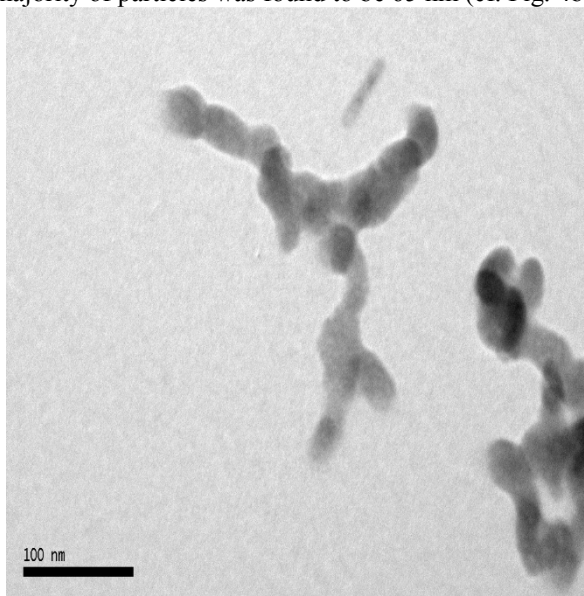


Fig. 4 (a): TEM image of nano sized biosorbent *Moringa oleifera* (M.O).

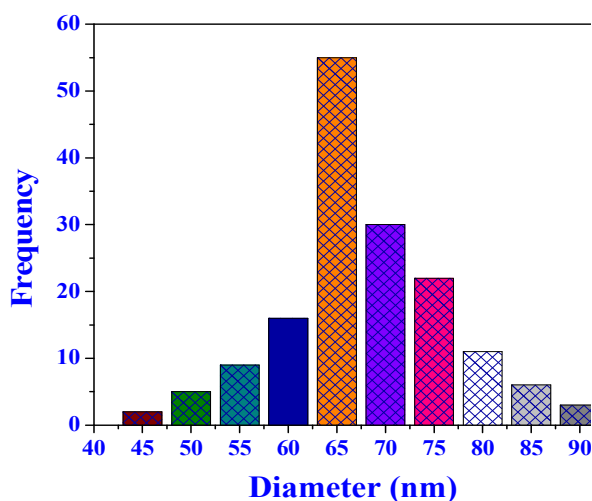


Fig. 4 (b): Calculated Histogram

3.1.6. Effect of initial concentration on the biosorption of Pb^{2+} ions

The effect of initial metal ions concentration on Pb^{2+} ions biosorption is illustrated in Figure 5 and Table 1. The amount of metal ions adsorbed (q_e) increases as the initial concentration rises, as Pb^{2+} ions are available for interaction with the biosorbent increased mass transfer of Pb^{2+} ions to the biosorbent. This biosorption characteristic showed that surface saturation depends on the initial Pb^{2+} ions concentrations. The Pb^{2+} ions removal efficiency for initial concentration 10 and 20 mg/L are 95.83% and 94.36 % respectively and decreases as the initial concentration increases. This suggests the presence of a strong attraction between the biosorbent surface and the Pb^{2+} ions solute. At low concentrations, a greater chance was available for metal removal. Biosorption sites took up the available Pb^{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 Pb^{2+} ions between the aqueous and solid phases. So, initial concentration of Pb^{2+} ions solutions increases the biosorption [26- 29].

Table 1: Pb²⁺ ions Removal Efficiency and q_e at Different Initial Concentration

C _o (mg/L)	C _e (mg/L)	Pb ²⁺ ions R. E %	q _e (mg/g)
10	0.42	95.83	1.6
20	1.13	94.36	3.15
50	4.16	91.68	7.64
100	14.58	85.42	14.24
200	49.32	75.34	25.11
300	93.24	68.92	34.46
400	172.56	56.86	37.91

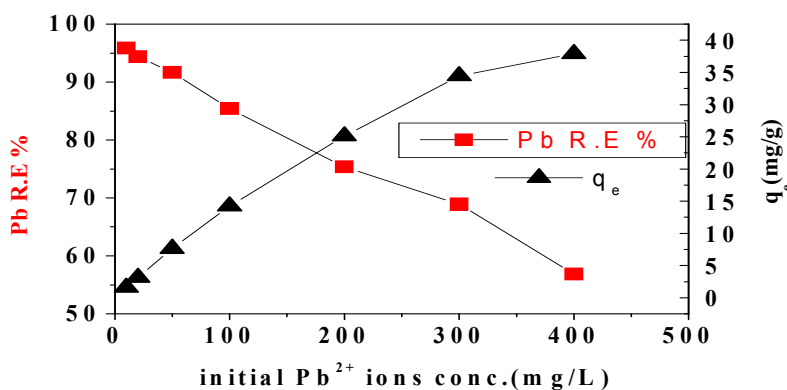


Fig. 5: Effect of initial concentration on Pb²⁺ ions removal efficiency (a) and q_e (b) by *Moringa oleifera*.

3.1.7. Effect of pH on the biosorption of Pb²⁺ ions by *Moringa oleifera*

The effect of pH of a solution is an important factor in the sorption process as shown in Figure 6 and Table 2. The result obtained on the effect of pH on Pb²⁺ ions removal efficiency and q_e showed that both increase as the pH increase. This confirm a strong interaction between the biosorbent and the Pb²⁺ ions in solution that [H⁺] and [OH⁻] could affect both on Pb²⁺ ions removal efficiency and q_e. The amount of Pb²⁺ ions removed by the *Moringa oleifera* at low pH 2 was low (2.04 mg/g) and removal efficiency 61.4 % compared to the highest values removed at pH 6 to 5 were (3.01mg/g and removal efficiency 90.4 % at pH 6, also 3.14 mg/g and removal efficiency 94.36 % at pH 5. This could be explained as follows, at low pH the concentration of hydrogen ions is high [16] and this increase the competition between the hydrogen ions and the metal ions. As H⁺ ions were being removed by the biosorbent, instead of the Pb²⁺ ions, the surface of the biosorbent is surrounded by hydronium ions (H₃O⁺), which prevent the metal ions from approaching the binding sites of the biosorbent [17, 30]. When H⁺ ions at higher concentration, the biosorbent surface becomes more positively charged such that the attraction between biomass and metal cation is reduced[31]. 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 Pb²⁺ ions solution in amount of metal ions sorbed. Maximum adsorption for Pb²⁺ ions occurred at pH 5. The better adsorption observed at pH 5 compared with other higher pHs, As the capacity of the adsorbent reduced, the reduction in adsorption at higher pHs may be due to the increasing of OH⁻ ions, as the precipitation of Pb²⁺ ions as Lead hydroxide occur[32].

Table 2: Pb²⁺ ions removal efficiency q_e at initial concentration of 20 mg/L at different pH values.

pH	C _o (mg/L)	C _e (mg/L)	Pb ²⁺ R. E %	q _e (mg/g)
2	20	7.72	61.4	2.05
4	20	3.65	81.76	2.73
5	20	1.13	94.36	3.15
6	20	1.92	90.4	3.01
7	20	2.1	89.5	2.98
8	20	3.27	83.66	2.79
10	20	3.14	84.28	2.81

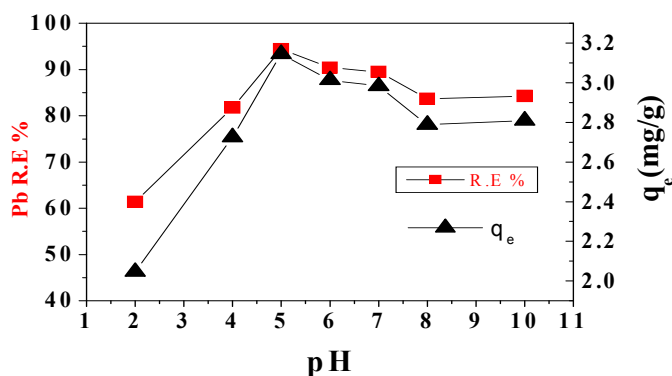


Fig. 6: Effect of pH on Pb²⁺ ions removal efficiency and q_e at initial concentration 20 mg/L at different pH values by *Moringa oleifera*

3.1.8. Effect of biosorbent dosage on the biosorption of Pb²⁺ ions

It is an important parameter to determine the capacity of a biosorbent for a given initial concentration 20 mg/L. As the increase in biosorbent dosage the Pb²⁺ ions, removal efficiency increases with least value of 66.25 % obtained with 25 mg and highest value of 96.36 % 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 Pb²⁺ ions solution and biosorbent with increasing biosorbent dosage bringing about a decrease in the amount of Pb²⁺ ions adsorbed per unit weight of biosorbent. This phenomenon has been reported in previous research[33-35]. These results are shown in Figure 7 and Table 3.

Table 3: Pb²⁺ ions removal efficiency and q_e at initial concentrations 20 mg/L and different biosorbent dosage

Biosorbent dosage	C ₀ (mg/L)	C _e (mg/L)	Pb ²⁺ ions R. E %	q _e (mg/g)
25	20	6.75	66.25	26.5
50	20	5.9	70.5	14.1
100	20	4.14	79.3	7.93
200	20	1.87	90.67	4.54
300	20	1.13	94.36	3.15
400	20	0.96	95.2	2.38
500	20	0.73	96.36	1.93

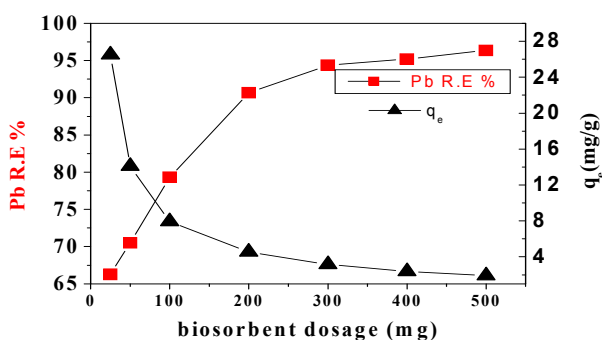


Fig. 7: Effect of biosorbent dosage on Pb²⁺ ions removal efficiency and q_e at initial Concentration 20 mg/L by *Moringa oleifera*.

3.1.9. Effect of contact time on biosorption of Pb²⁺ ions

The result of contact time for the adsorption of Pb²⁺ ions by *Moringa oleifera* is shown in Table 4 and Figure 8. For an initial metal ion concentrations of (10, 30, 50) mg/L, it was observed that the amount of Pb²⁺ ions adsorbed increased with an increase in a contact 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. This may be attributed to long time of contact and availability of active sites, after the equilibrium is reached at 60 minutes. It was followed by a reduction in the metal uptake. There was a slightly increasing or remain constant in the Pb²⁺ 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 [36, 37].

Table 4: Effect of contact time on Pb²⁺ ions removal efficiency and q_e at different Initial concentrations (10, 30, 50) mg/L by *Moringa oleifera*.

Time (min)	Pb R. E % at C ₀ (10 mg/L)	Pb R. E % at C ₀ (30 mg/L)	Pb R. E % at C ₀ (50 mg/L)	q _t (mg/g) at C ₀ (10mg/L)	q _t (mg/g) at C ₀ (30mg/L)	q _t (mg/g) at C ₀ (50mg/L)	C _t at C ₀ (10mg/L)	C _t at C ₀ (30mg/L)	C _t at C ₀ (50mg/L)
20	78.55	73.01	69.3	1.4	4.1	6.69	1.61	5.41	9.84
40	86.3	80.88	80.79	1.52	4.3	7.20	0.9	4.1	6.74
60	95.83	90.76	91.68	1.57	4.53	7.52	0.57	2.81	4.9
80	96.15	91.19	92.2	1.58	4.59	7.54	0.52	2.5	4.75
120	96.21	91.4	92.5	1.58	4.6	7.59	0.503	2.4	4.65

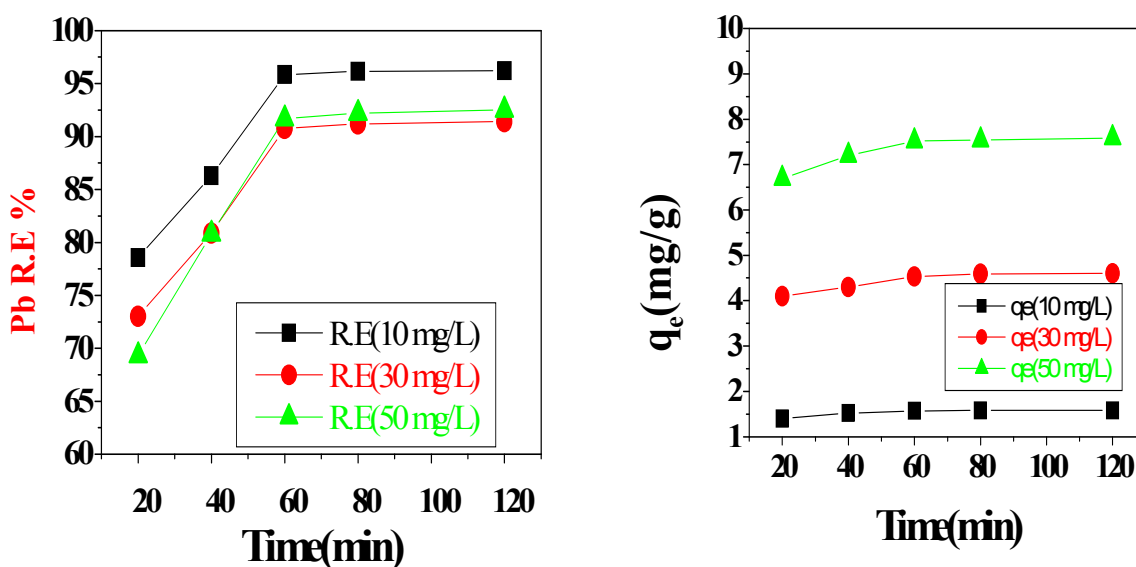


Fig. 8: Effect of contact time on Pb²⁺ ions removal efficiency and q_e at different initial concentrations (10, 30, 50) mg/L by *Moringa oleifera*

3.1.10. Effect of temperature on biosorption of Pb²⁺ ions

Effect of the temperature at different values (25, 30, 40, 50) °C (cf. Fig. 9, Table 5) shows that the Pb²⁺ removal efficiency and q_e at different initial concentrations (10, 20, 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 Pb²⁺ 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 increment 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 on activated carbon [38, 39].

Table 5: Effect of temperature on Pb²⁺ ions removal efficiency and q_e at different initial concentrations (10, 20, 50) mg/L by *Moringa oleifera*

Temp. (°C)	Pb R. E % at C ₀ (10 mg/L)	Pb R. E% at C ₀ (20 mg/L)	Pb R. E % at C ₀ (50 mg/L)	q _e (mg/g) at C ₀ (10mg/L)	q _e (mg/g) at C ₀ (20mg/L)	q _e (mg/g) at C ₀ (50mg/L)	C _e at C ₀ (10mg/L)	C _e at C ₀ 20mg/L)	C _e at C ₀ (50mg/L)
25	95.16	94.36	91.68	1.586	3.15	7.64	0.48	1.13	4.16
30	95.83	94.7	92.2	1.59	3.16	7.68	0.42	1.06	3.9
40	96.7	95.5	93.2	1.61	3.18	7.77	0.33	0.9	3.4
50	96.2	95.3	92.76	1.6	3.178	7.73	0.38	0.93	3.62

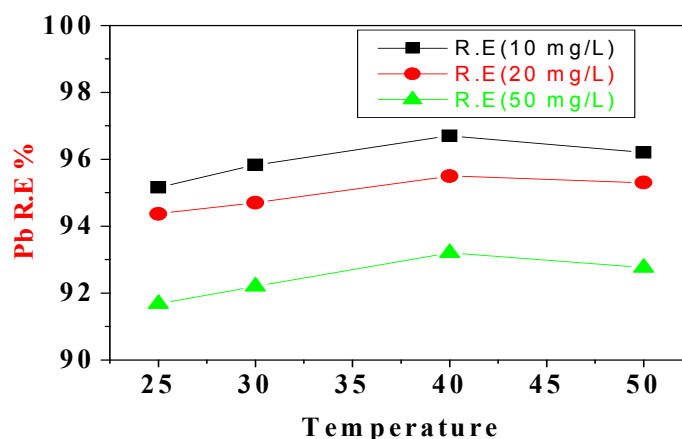


Fig. 9: Effect of temperature on Pb²⁺ ions removal efficiency at different Initial concentrations (10, 20, 50) mg/L by *Moringa oleifera*

3.1.11. Adsorption isotherm

Adsorption isotherms of Pb²⁺ 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 Pb²⁺ adsorbed per unit mass of *Moringa oleifera* increased with the initial concentration of Pb²⁺, as expected [40, 41]. The metal ion distribution between the liquid and solid phases can be described by mathematical model equations such as Langmuir isotherm model and the Freundlich isotherm model [42]. 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 take places on homogeneous surface. These models could be summarized as follows. The linear form of Langmuir isotherm equation is represented by the following equation[43].

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

as, q_e the amount of Pb²⁺ 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.

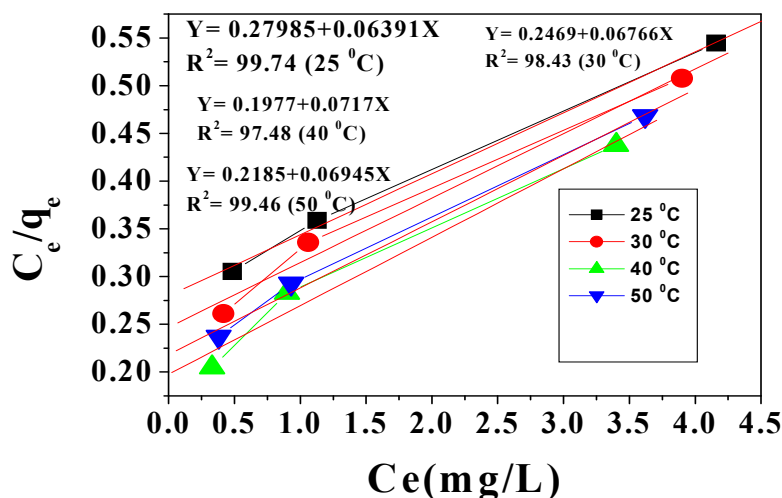


Fig. 10: Linearized biosorption isotherms of Langmuir

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 Lead biosorption isotherms of Langmuir. from the intercept and slope of the plots and are given in Table 6, the Langmuir parameters, b and q_m , are calculated. These values may be used for comparison and correlation of the sorptive properties of *Moringa oliefera*. The Freundlich equation is applicable for isothermal adsorption and has the general form [44].

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

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 Lead 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 [45]. The Freundlich parameters for the adsorption of Lead ions is given in Table 6. 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 [46] stated as:

$$R_L = 1 / (1 + b C^\circ) \quad (9)$$

Mathematical calculation of R_L indicates the shape of isotherm to be either, irreversible ($R_L = 0$), linear ($R_L = 1$), unfavorable ($R_L > 1$) or favorable ($0 < R_L < 1$). From the experiment, R_L varies from 0.053 to 0.303 for different Pb^{2+} ions concentrations (10, 20, 50) mg/L at different temperatures (cf. Table 7). These values ranged between 0 and 1, thus indicating a favorable biosorption. The values of (Freundlich exponent n) were greater than 1. [47] 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 0.674 – 0.727, when the temperature was altered from 293 to 323 K, this indicate that the biosorption of Pb^{2+} onto *Moringa oliefera* is 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 ($R^2 = 0.99$ and 1 respectively) as shown in Table 6 and Figs. 10 and 11. The sorption of metal ion on *Moringa oliefera* follow the Freundlich isotherm model describing the adsorption in aqueous system.

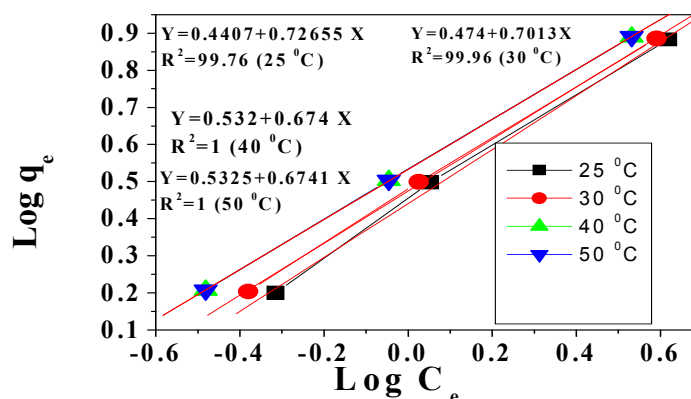


Fig. 11: Linearized biosorption isotherms of Freundlich.

Table6: Isotherm constants of Pb²⁺ ions biosorption on *Moringa oleifera* at various temperatures.

T (K)	Langmuir			Friendlich		
	q _m (mg/g)	b	R ²	n	Kf	R ²
298	15.65	0.23	0.9974	1.38	2.76	0.998
303	14.78	0.27	0.9843	1.43	2.98	0.9996
313	13.94	0.36	0.9748	1.484	3.4	1
323	14.34	0.32	0.9946	1.483	3.41	1

Table 7: A dimensionless constant separator factor (R_L) for Langmuir type biosorption process.

C _o (mg/L)	R _L at			
	25°C	30°C	40°C	50°C
10	0.303	0.27	0.217	0.238
20	0.178	0.156	0.122	0.135
50	0.08	0.069	0.053	0.059

3.1.12 Thermodynamic studies on biosorption of Pb²⁺ 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 Pb²⁺ using Eq. (1). The sorption capacity of the *Moringa oleifera* for Lead 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) [48]. Where ΔG° is the change in free energy (J mol^{-1}), ΔS° is the change in entropy ($\text{J mol}^{-1} \text{K}^{-1}$), ΔH° is the change in enthalpy (kJ mol^{-1}), R is the gas constants ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{K}^{-1}$), 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 8. Positive values of ΔH° suggest the endothermic nature of adsorption of Lead 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[49]. The Positive value of ΔS° suggested an increase in randomness during the biosorption [50]. These kinds of reactions are present in literature [14, 51].

Table 8: Thermodynamic parameters for the biosorption process

Temperature (K)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol)
298	3.47		
303	3.33		
313	3.06	11.51	26.97
323	2.79		

3.1.13. Kinetic studies on the biosorption of Pb²⁺ ions:

The mechanism of the adsorption of Pb²⁺ was tested using pseudo first-order kinetic model and pseudo second order kinetic model[16, 17]. By using the experimental data obtained from sorption time investigation, the adsorption kinetic of the removed Pb²⁺ 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 Pb^{2+} ions uptake at equilibrium in mg/g, k_1 is the rate constant of pseudo-first-order biosorption, and q_t is the Pb^{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 $(1/(k_2q_e^2))$ as intercept from which k_2 can be obtained. Both models are tested for suitability using their correlation coefficient, R^2 [16]. As can be seen from Table 5, the calculated q_e determined from the plot of the pseudo-first-order model for Pb^{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 Pb^{2+} ions ($R^2 = 0.99$) compared to pseudo-second-order model. As their correlation coefficient ($R^2 = 0.99$), the pseudo-second-order model as shown in Table 9 fits the kinetics better, (i.e. $R^2 = 0.99$ for Pb^{2+} ions solutions at various concentrations). The calculated q_e (7.94 mg/g) are very close to the experimental q_e (7.7 mg/g). All these imply that the second order kinetics is good in studying the kinetics of the biosorption of Pb^{2+} ions, suggesting that biosorption is the rate-limiting step; and that biosorption of the Pb^{2+} ions solutions involves two species, in this case, the Pb^{2+} ions and the biosorbent particles [52].

Table 9: Kinetic parameters of Pb^{2+} ions biosorption at different initial concentration

C_0 (mg/L)	Pseudo-first order			Pseudo-second order		Observed q_e (mg/g)
	k_1 (1/min)	q_e (mg/g)	R^2	k_2 (g/mg.min)	q_e (mg/g)	
10	0.089	2.02	0.91	0.221	1.64	1.6
30	0.083	3.53	0.92	0.07	4.67	4.56
50	0.081	10.1	0.92	0.032	7.94	7.7

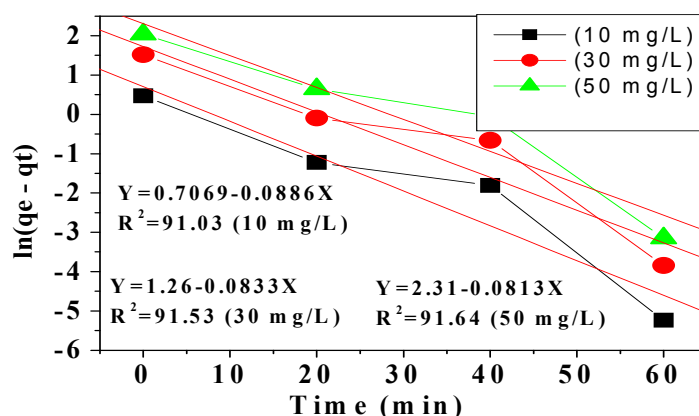


Fig. 12: Pseudo-first order for sorption of Pb^{2+} ions by *Moringa oleifera*.

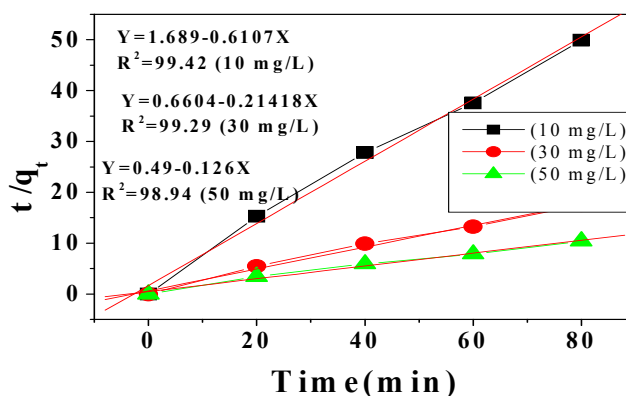


Fig.13. Pseudo-second order for sorption of Pb^{2+} ions by *Moringa oleifera*.

Finally we can say Nano sized *Moringa oleifera* is a good biosorbent for removal of toxic heavy metals compared with larger particle size. Our aims in the future to enhance the removal efficiency more than that we

obtained by chemical treatment or using mixture of biosorbents.

4. Conclusion

Nano sized *Moringa oleifera* was used for adsorption of Pb^{2+} from aqueous solution. The results showed that *Moringa oleifera* biosorbent proved to be a very effective biosorbent in the removal of Pb^{2+} ions from water. The following conclusions can be drawn from this study,

- 1- The biosorption process was pH, Contact time, temperature, dosage and metal ion concentration dependent.
- 2- Biosorption of Pb^{2+} ions solutions obeyed Langmuir and Freundlich isotherms. R_L value from Langmuir and n from Freundlich isotherms show that biosorption of Pb^{2+} ions solutions on *Moringa oleifera* is favorable. Maximum biosorption capacity of Pb^{2+} ions solutions on *Moringa oleifera* is 37.91 mg g^{-1} .
- 3- 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.
- 4- 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 Pb^{2+} ions solutions on *Moringa oleifera*.

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