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ORIGINAL RESEARCH

Kinetics, isotherms and thermodynamics studies of Pb^{2+} and Mn^{2+} adsorption from model wastewater solution using raw *Phoenix dactylifera* L. seed

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Abstract

Introduction: Adsorption has been extensively reported as a successful method for removing potentially toxic metals from wastewater. **Aim:** This study investigated the efficiency of raw Phoenix dactylifera L. as an adsorbent for the removal of Pb (II) and Mn (II) ions from model wastewater. **Method:** Batch adsorption process. **Results:** The initial and the equilibrium metal ion concentrations were determined using the atomic absorption spectroscopy, while the raw Phoenix dactylifera L was characterized using the scanning electron microscope and Fourier transform infrared spectroscopy (FTIR). The effects of metal ion concentrations, the kinetics, pH, adsorbent dosage, and temperature on the metal ion bio-sorption were also investigated. The pH-dependent adsorption of the metal ions revealed an optimum pH of 3.0, and a maximum percentage removal of 93.37% for Pb (II) and 97.57% for Mn (II) across the entire concentrations range. The results of the modelling analysis of the adsorption isotherms showed that the correlation coefficient for Temkin was the highest with 0.976 for Pb (II) and 0.955 for Mn (II) ions. The kinetic studies of both ions followed the pseudo-second-order reaction kinetic while the thermodynamic analysis (maximum adsorption) indicated that the process was spontaneous and exothermic with value of ΔG of -183.91 kJ/molK for Pb (II), and -379.31 kJ/molK for Mn (II).and ΔH values of -0.065 kJ/mol for Pb (II) and -0.841 kJ/mol for Mn (II) respectively. **Conclusion:** Overall, the adsorbent demonstrated a significant potential for effective removal of the metal ions of interest.

Keywords: Biosorption, Isotherms, Pseudo-second order, phoenix dactylifera L. seed

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All co-authors agreed to have their names listed as authors.

1. INTRODUCTION

Industrial activities have greatly contributed to the rise in environmental challenges. A common type of pollution the world is currently struggling with is water pollution [1]. Water pollution from industrial wastewater is a dominant environmental problem due to the presence of heavy metals [2]. These pollutants are more pronounced in the effluents of industries such as metallurgical industries, surface coating and metal plating facilities, electrolysis and battery manufacturing, metal-complex dye production, and paints industries. Heavy metals in industrial wastewater are not visible to the naked eye, non-biodegradable, and are mostly found in the environment, hence, their exposure and accumulation increase at an alarming rate as water demand and consumption increases as a result of an increase in the development and human population [3]. Also, it has been reported that heavy metals persist in the environment and cause several adverse health effects; heavy metal exposure continues and these adverse health effects increase in many parts of the world [7]. Heavy metals are significant environmental pollutants and their toxicity increasingly constitutes serious ecological, evolutionary, nutritional, and environmental concerns [8, 9]. The most commonly found heavy metals in wastewater include arsenic, cadmium, chromium, copper, lead, nickel, and zinc, all of which cause risks to human health and the environment [10]. Heavy metals are mostly found in the surroundings by natural means and through human activities [11]. Various sources of heavy metals include soil erosion, natural weathering of the earth's crust, mining, industrial effluents, urban runoff, sewage discharge, insect or disease control agents applied to crops, and many others [12].

Heavy metals are increasingly worrisome due to their potential harmful effects prospective influences on the environment and human health [13]. Owing to their physical and chemical properties, they have been extensively disseminated into the surroundings through several human activities such as industrial, agricultural, medical and domestic activities [14]. Industrial effluents are a major source of environmental pollution and exposure to human beings [15]. Heavy metals are often present in water bodies, and most of them are regarded as highly lethal even in very small amounts [16]. Heavy metals, for instance, lead, cadmium, chromium, cobalt, arsenic, mercury and nickel, are listed as very toxic elements [17]. These metals are assumed to be ubiquitous toxicants, and their deadliness is influenced by many factors, for instance, the amounts of heavy metal doses, types of elements and exposure route. Heavy metals can be transported into the human body via many sources, for instance, water, air, skin and food, and can become more lethal in the human body when they are not completely digested and stored in the muscle [18]. They may damage various vital human organs such as gastrointestinal, kidneys, bones, endocrine glands and central nervous system [19].

Furthermore, prolonged exposure to heavy metal has been associated with a number of deteriorating illnesses of these human vital organs and may increase the threat of cancer diseases [20]. A few heavy metals are also important for life and show a unique role in the metabolic system of human beings, for instance, the functioning of acute enzyme locations; however, they can damage the organism in higher amounts [21].

To standardize the uncontrollable release of these unsafe toxins in water, either originating from natural or wastewater sources, innovative and modern water treatment tools are offered worldwide. Industries used several different conventional methods for the removal of heavy metals from water such as: ion exchange, membrane separation, ultrafiltration, adsorption, activated carbon and other methodologies [19]. However, these conventional methods seem to be inappropriate to apply in the elimination of heavy metals at low levels, and most importantly, the techniques involved require secondary treatment step and are therefore expensive. In addition, they harm both natural life and the environment. In recent years, the adsorption method, particularly bio-sorption, has been found to be appropriate for the removal of contaminants from polluted water samples.

The adsorption method comprises of the separation and aggregation of target analytes from one stage to another. The adsorption system is quite easy to work with and is very effective in the elimination of deadly contaminants at low levels. Moreover, the adsorption method has been the most extensively accepted process because of its simplicity, versatility, ecofriendly, and being highly cost-effective [22]. Agricultural wastes, natural materials or industrial by-products are locally available in large quantities and can thus be utilized as low-cost adsorbent. Specifically, there is a rising demand to discover effortlessly obtainable, highly efficient, very cost-effective, easy-to-use, eco-friendly, and highly effective absorbents for the absorption of Pb(II) and Mn (II) ions. Cashew nut-shell, sawdust, spent grain, wheat straw, pine cone powder, herbaceous peat, peanut hull and sugar beet pulp are examples of the effective adsorbents that have been used to remove the aforementioned heavy metals [22]. Due to the great obtainability and low cost of these adsorbents, a complex regeneration method is not needed, thus this cheaper adsorption system has elicited the need to discover more eco-friendly natural adsorbents.

This study, therefore, explores the equilibrium and kinetics of using raw *phoenix dactylifera* L. seed as an adsorbent for the removal of Pb(II) and Mn(II) ions from model wastewater in a batch process. The kinetics of the adsorption process was tested using pseudo-first-order and pseudo second order kinetic models. The Langmuir, Freundlich, and Temkin isotherm models were used to describe equilibrium isotherms. The adsorption mechanisms of Pb(II) and Mn(II) ions from model wastewater unto raw date seeds (RDS) were also evaluated in terms of thermodynamic properties.

2. MATERIAL AND METHODS

2.1. Collection and Preparation of Adsorbent

The date fruits (*Phoenix dactylifera* L.), 5 kg, were purchased from Alaba rago, Ojo Local Government Area, Lagos State, Nigeria (6.464 ^{o}N, 3.196^{o} E). The date pits were removed and thoroughly rinsed with distilled water to exclude any remnants of edible portion and dust materials. It was sun-dried for many days and later dried in an oven at 80 °C for 2 hr. The date pits were mechanically crushed and processed in a ball mill, homogenized, and sieved at 120 μm. Figures 1a, 1b and 1c showed images of the date fruits, date pits, and date seeds powder.

Figure 1: (a) Raw date fruits (*Phoenix dactylifera* L seed.) (b) Date pits (c) Date seeds powdered

2.2. Characterization

The FT-IR spectra of the sample for the adsorption processes were recorded within 650 – 4000 cm^{-1} using the Fourier Transform spectrophotometer SHIMADZU FT-IR- 8400S model. The scanning electron microscope (SEM) model Carl Zaiss Leo Supra 50VP Field Emission equipped with Oxford INCA-X energy dispersive microanalysis system (EDX) was used to examine the surface morphology and the elemental distribution.

2.3 Batch Adsorption Experiments

Removal of heavy metal ions was carried out through batch adsorption studies. 0.6 g of the date seed powder was put into several previously cleaned and dried 100 mL Erlenmeyer flasks. Thereafter, lead and manganese metal solutions of different concentrations (Co) of 500, 400, 300, 200 and 100 mg/L were introduced into the flasks. The resulting solutions were equilibrated on a shaker (vibrator) for 2 hours at a speed of 100 rpm. The mixtures were then filtered and stored in a cool and dry place. At equilibrium, the concentration of metal ions, Ce, was quantitatively determined by atomic absorption spectroscopy (AAS) using Thermo Scientific Evolution 600 spectrometer. The pH value was adjusted to 7 by adding 0.1 M HNO_3 or 0.1 M NaOH solution.

The percentage adsorption (%) removal (R), and metal ions removal capacity of the adsorbents at equilibration time (Qe) and at arbitrary time t, (Qt) were calculated according to Equations (1)–(3):

$$\% \mathrm{R} = \frac{\mathrm{Co}-\mathrm{Ce}}{\mathrm{Co}} \times 100 \qquad (1)$$

$$\mathrm{Q_e} = \frac{(\mathrm{Co}-\mathrm{Ce})}{\mathrm{m}} \times \mathrm{V} \qquad (2)$$

$$\mathrm{Q_t} = \frac{(\mathrm{Co}-\mathrm{Ct})}{\mathrm{m}} \times \mathrm{V} \qquad (3)$$

Where Co, Ce, and Ct are the initial, equilibrium, and at-time-t concentrations (mg/L) respectively, of the heavy metal ions present in the solution; V is the volume (L) of the heavy metal solution; and m is the mass (g) of the adsorbents. The adsorption capacities, both (Qe) and (Qt), were calculated as mg/g.

The effect of operational parameters on the adsorption process was thereafter studied.

2.4. Adsorption Isotherm Models

Adsorption isotherms, which explain how an adsorbate interacts with an adsorbent, are crucial for maximizing the effectiveness of any adsorbent. The shape of an isotherm offers details on the stability of the interactions between adsorbent and adsorbate as well as the molecular adsorption affinity [23]. Adsorption isotherms are expressed mathematically in a variety of ways. Some of these expressions are based on simplified physical descriptions of adsorption, while others are empirical and requires correlating experimental data. The data obtained from the equilibrium studies was used to check the applicability of Langmuir, Freundlich, and Temkin isotherms under specific conditions: pH of 7, adsorbent dose of 0.8 g, agitation speed of 150 rpm, and contact time of 2.5 hr.

2.5 Adsorption kinetics

Adsorption kinetics describes the rate of retention or release of a sorbate from aqueous solution to a solid-phase interface. In adsorption, linear or non-linear analysis of the kinetics is applied. The kinetics of adsorption onto the surface of the date seed adsorbent is ascertained using the pseudo-first order (also known as Largagren model) and pseudo-second order [23, 24]. The kinetic studies were carried out using 0.8 g of RDS in 50 ml of the metal ion solutions at pH 7 and different contact time at 0, 30, 60, 90, 120, and 150 min.

2.6. Adsorption thermodynamics

The thermodynamic studies were conducted at various temperatures at 27, 37, 47, 57, and 67 °C with an initial metal ion concentration of 500 mg/L at pH 7 to investigate the thermodynamic parameters [25]. 0.8 g of the *Phoenix dactylifera* L. powder was added to conical flasks containing 50 mL of the metal ion solutions. The flasks were agitated for 2.5 hours to ensure equilibrium. Subsequently, the adsorbents were removed via filtration, and the final concentrations of the metal ions in the filtrates were analyzed.

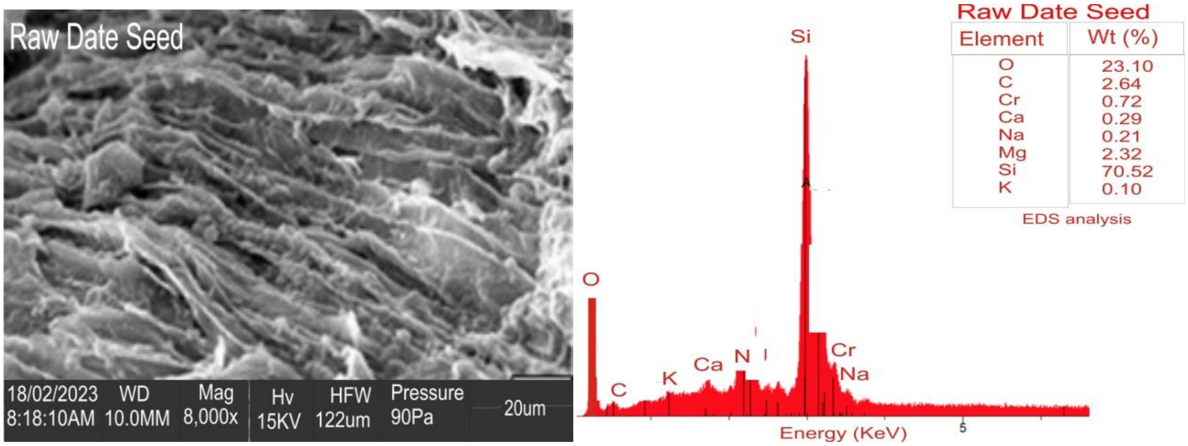
3. RESULTS AND DISCUSSION

3.1. Characterization of Raw Date Seed (RDS)

3.1.1 SEM/EDX Analysis

The morphology and physical properties of the adsorbent surfaces of the date seed were evaluated using SEM/EDX [26]. The images of *Phoenix dactylifera* L. seed before and after adsorption of lead and manganese ions are presented in Figures 2-4. Numerous fragmented particles resembling spots are visible in the SEM image of raw *Phoenix dactylifera* L. seed before adsorption (Figure 2), demonstrating the porous nature of the adsorbents which would be suitable for target metal adsorption. The SEM images (Figure 3) of the adsorbent obtained after the adsorption experiment exhibited smoother surface for lead adsorption compared to the raw powder (Figure 2). This indicated that the pores present on the raw *Phoenix dactylifera* L.seed before adsorption have been successfully occupied by the metal ions after adsorption. The EDX analysis of the adsorbents before and after adsorption was conducted to evaluate the composition of the active components present in the adsorbent. The EDX images were presented in Figures 2 and 4.

The presence of various elements on bio-sorbent materials could facilitate the adsorption of metal ions of interest through electrostatic interaction [26]. The raw *Phoenix dactylifera* L. seed adsorbent comprised silicon as the major element (70.52%) and other elements such as oxygen (23.10%), Cr (0.72 %), Ca (0.29%), Mg (2.32%) and K (0.1%). Figures 4 confirmed the adsorption of lead (4.40%) and manganese (3.30%) on the surface after the adsorption process.



Element	Wt (%)
O	23.10
C	2.64
Cr	0.72
Ca	0.29
Na	0.21
Mg	2.32
Si	70.52
K	0.10

Figure 2: Images of raw *Phoenix dactylifera* L. surface showing (a) the SEM image and, (b) EDX image. The SEM image shows a rough surface indicating high porosity suitable for adsorption while EDX image indicates highest concentration of elemental silicon at the surface of the raw *Phoenix dactylifera* L. powder.

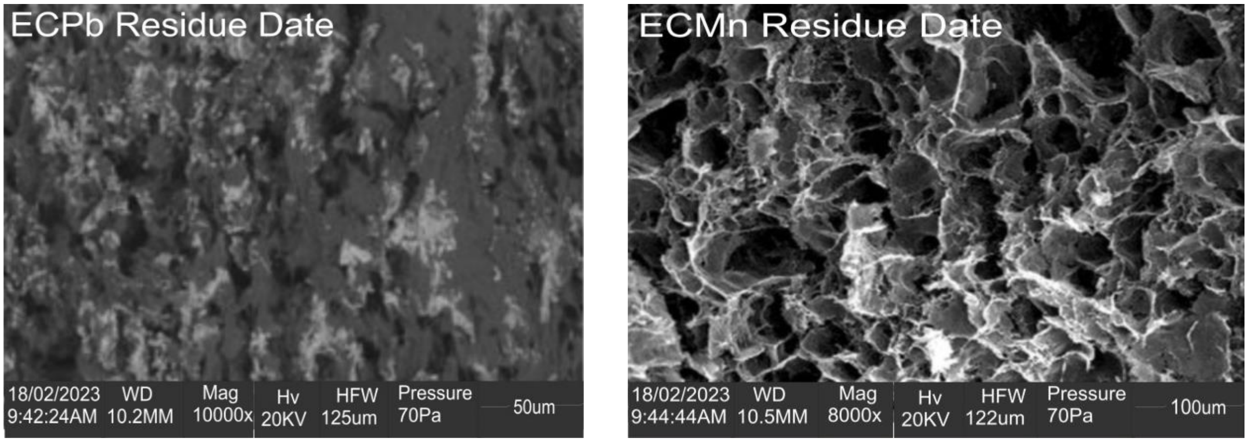
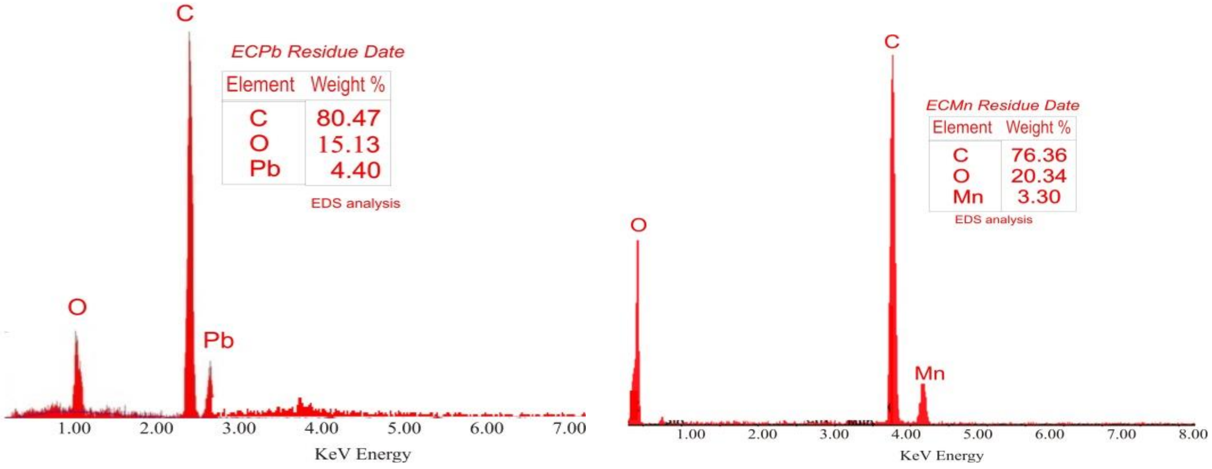


Figure 3: Images of *Phoenix dactylifera* L. surface after adsorption showing (a) the SEM image of adsorption with Pb and (b) the SEM image of adsorption with Mn.



(a) (b)

Figure 4: EDX spectra of *Phoenix dactylifera* L. surface after adsorption (a) with Pb and (b) with Mn ions, showing the adsorption of Pb and Mn ion at the at the surface of the adsorbents.‘

3.1.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Fourier-transform infrared spectroscopy (FTIR) was conducted to identify the surface functionalities and adsorption mechanism for the raw *Phoenix dactylifera* L. seed for the adsorption process. Figure 5 illustrates the FTIR spectral data for Phoenix dactylifera L powder. The seeds of *Phoenix dactilifera* L. are classified as lignocellulosic adsorbents, comprising cellulose, hemicellulose, and lignin. The spectra exhibited a broad band at 3528.7 cm^{-1}, which is attributed to the stretching vibration of amine groups (N-H) on the surface of the *Phoenix dactylifera* L. seed The band at 3023.9 cm^{-1} can be ascribed to the stretching vibration of C-H from aromatic compounds. The band at 2373.9 cm^{-1} can be ascribed to the stretching vibration of the thiol functional group (S - H) [25]. The band at 1740.7 cm^{-1} was associated with the vibration of C═O bond stretching of aldehydes. The peak at 1221.9 cm-1 represents the C-O stretching vibration in the lignin structure [27].

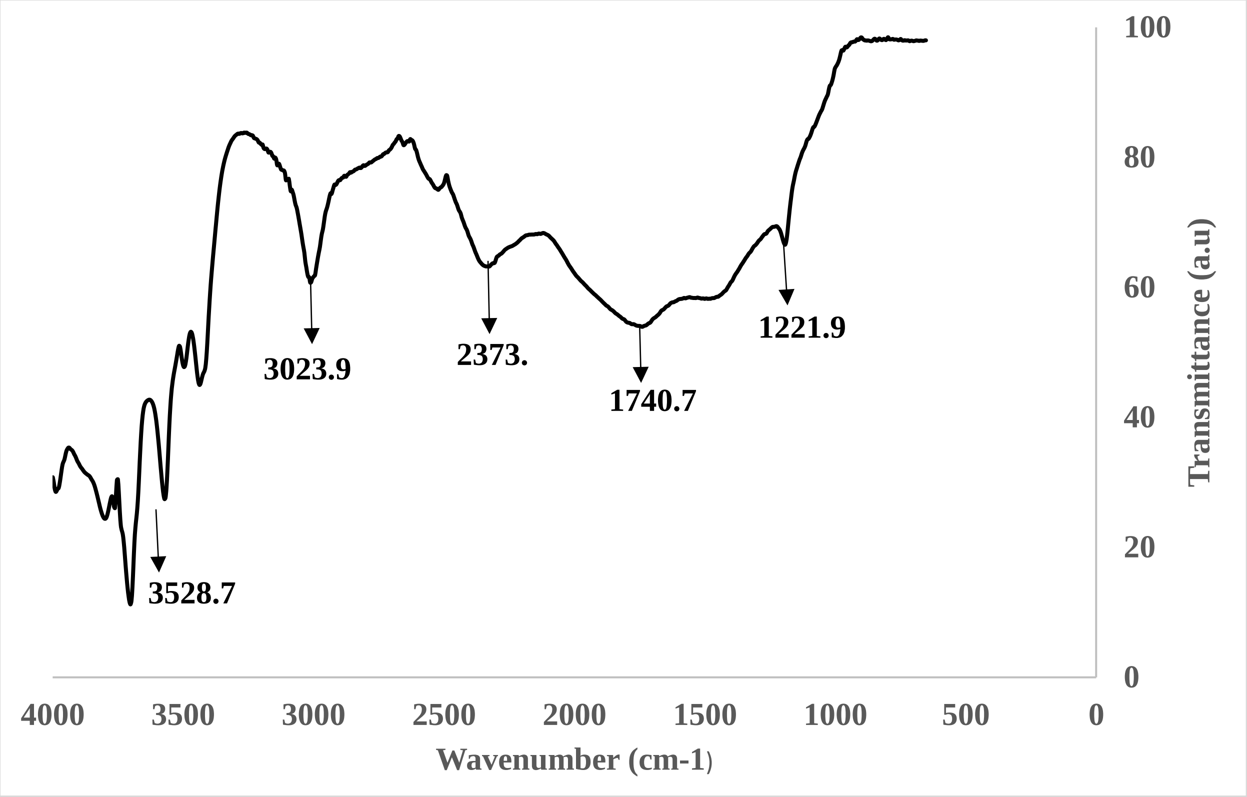


Fig. 5: The FTIR result of *Phoenix dactylifera* L. seed

Adsorption Isotherm

The research examined the adsorption of lead and manganese ions onto *Phoenix dactylifera* L. seed surface using the Langmuir, Freundlich, and Temkin isotherm models. The results of the study, as presented in Table 2, indicate that the Langmuir and Temkin models provide a good fit for the data, with R^2 values ranging from 0.989 for lead and 0.972 for manganese. The correlation coefficient values suggest that the Langmuir model is a better fit for lead (II) and the Temkin model is a better fit for the manganese (II) adsorption process. Langmuir's isotherm model suggests that monolayer adsorption was involved in the adsorption of lead (II) ions unto the *Phoenix dactylifera* L. surface [17]. The positive values of the Temkin constant (BT) of lead (II) (1.6805) and manganese (II) (2.679) indicated that the adsorption process was exothermic [28]. Langmuir isotherm assumes monolayer coverage on a homogeneous surface with identical adsorption sites; for gas adsorption on solid surfaces [29]. However, in solution-solid systems, with the hydration forces and mass transport effects, the system is much more dynamic and complex, and obeying the isotherm does not necessarily reflect the validity of the aforementioned assumptions. In this system, the isotherm adequacy may be significantly affected by the experimental conditions, in particular, the range of concentration of the solute [28]. These results suggest that Langmuir and Temkin's isotherms followed a good fit for Pb (II) and Mn (II) adsorption with Phoenix dactylifera L. surface, respectively. Since the values of RL and BT for Pb (II) and Mn (II) ions are between 0 and 1, and 1 and 5 respectively, this indicateed the adsorption of these metal ions unto Phoenix dactylifera L. surface [30]. The non-linear and linear forms of the Langmuir model, Freundlich, and Temkin models are expressed by Equations (4-9), respectively.

Langmuir nonlinear equation $Q_e = \frac{Q_m K_L C_e}{1+K_L}$ (4)

Langmuir linear equation: $\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m}$ (5)

Freundlich nonlinear equation $Q_e = K_f C_e^{1/n}$ (6)

Freundlich linear equation $\mathrm{Ln}Q_e = \mathrm{Ln}K_f + \frac{1}{n} LnC_e$ (7)

Temkin nonlinear equation $Q_e = \frac{RT}{B_t} \ln A_t + \frac{RT}{B_t} \ln C_e$ (8)

Temkin linear equation $Q_e = B_T \ln A_T + B_T \ln C_e$ (9)

Langmuir Isotherm Model

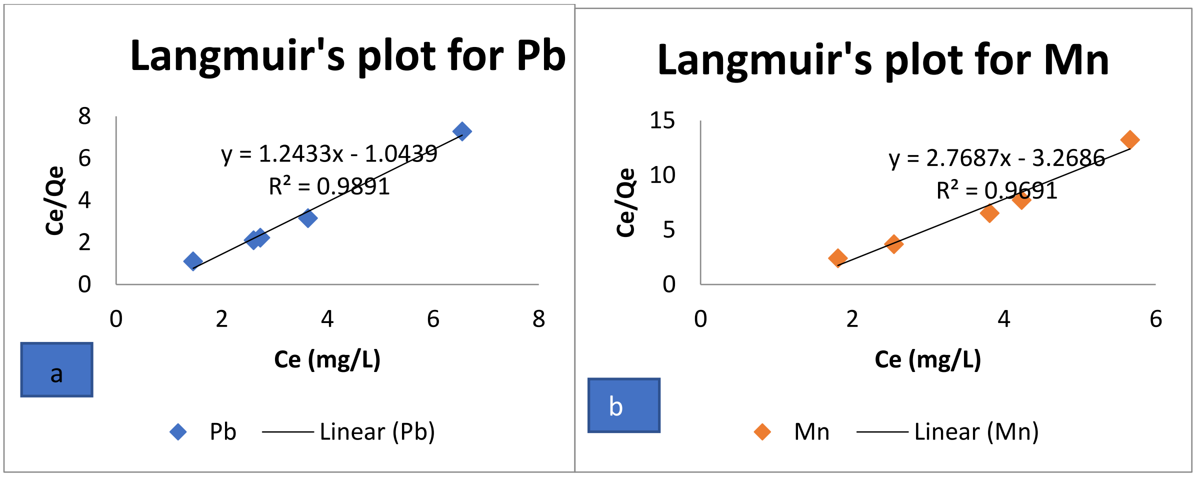


Fig. 6. Langmuir adsorption isotherm of (a) Pb (II), (b) Mn (II) onto *Phoenix dactylifera* L. seed

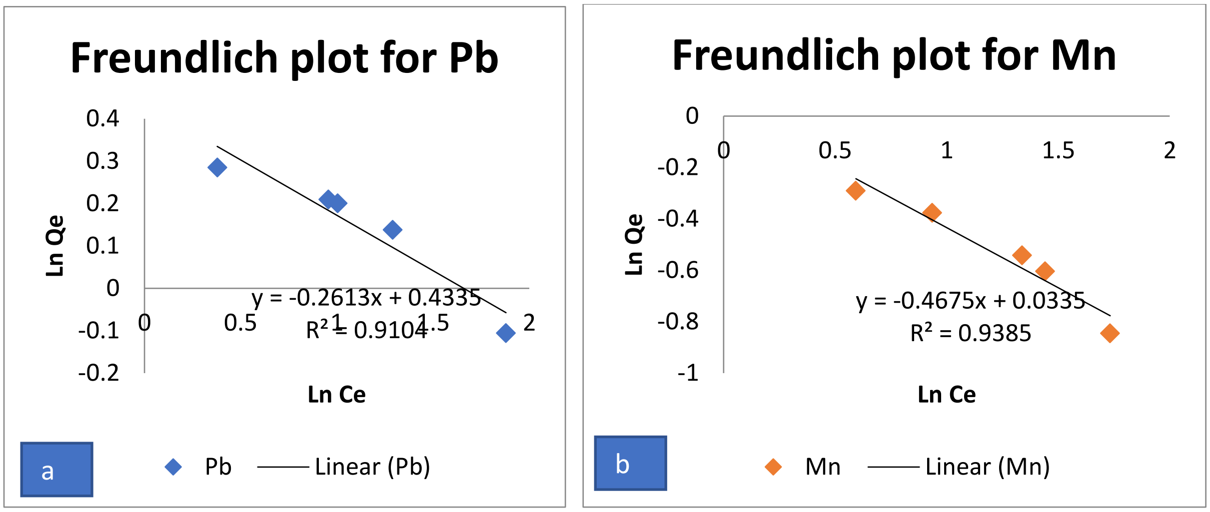


Figure 7: Freundlich adsorption isotherm of (a) Pb (II), (b) Mn (II) unto *Phoenix dactylifera* L. seed

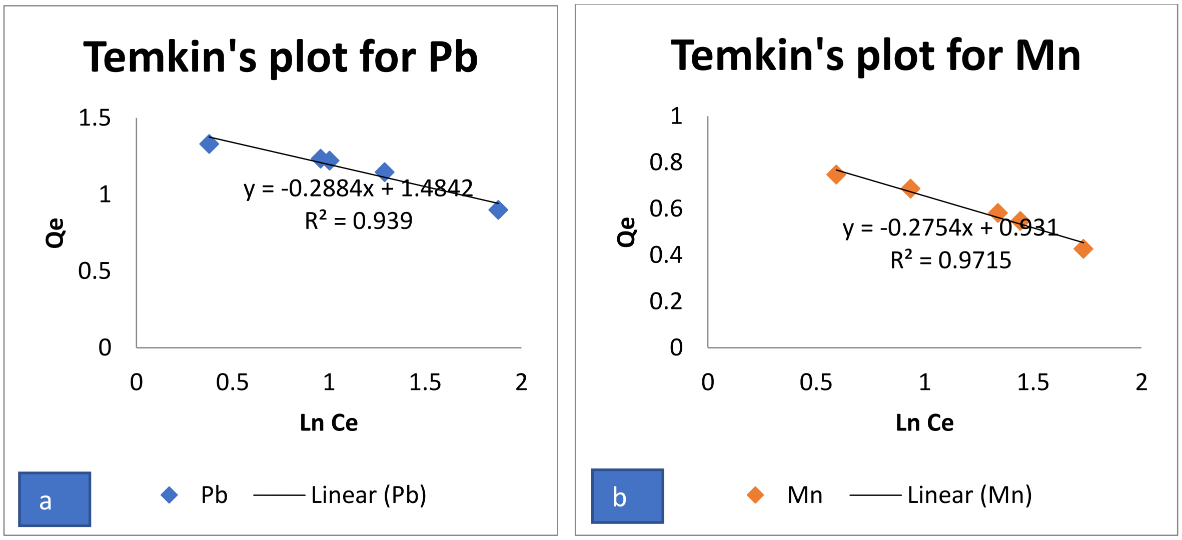


Figure 8: Temkin adsorption isotherm of (a) Pb (II), (b) Mn (II) unto *Phoenix dactylifera* L. seed

Table 1: Adsorption isotherm parameter for the adsorption of Pb (II), and Mn (II) ions onto *Phoenix dactylifera* L. seed

ISOTHERMS	Pb (II)	Mn (II)
Langmuir		
Q_{max}	0.804	0.361
K_L	1.191	0.847
R_L	0.046	0.099
R^2	0.989	0.969

Freundlich		
N	3.8270	2.139
K_F	1.5426	1.034
R^2	0.9104	0.939
Temkin		
B_T	1.6805	2.679
K_T	0.8234	0.744
R^2	0.939	0.972

3.3. Adsorption kinetics

Kinetic models were used to describe the relationship between the adsorption capacity and contact time to explain the adsorption process and the potential rate-limiting step and pseudo second order models were applied to simulate the adsorption data. The equations 3 and 4 are given as:

$$\log\,(q_e\text{-}q_t) = \log\,(q_e) - (\frac{K_t}{2.303})t \qquad (10)$$

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{1}{q_e}t \qquad (11)$$

where qe and qt are the amounts of metal ions adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k1 (1/min) is the rate constant of first-order adsorption. The values of k1 are calculated using the plots of log (qe - qt) versus t. The k2 (g/mg min) is the rate constant of the second-order adsorption. The plots are presented in Figures 9 and 10, and the kinetic parameters together with the regression coefficients (R^2) are calculated and shown in Table 2. It can be observed that the R^2 of the pseudo-second-order model is higher than that of the pseudo-first-order model. The value of the correlation coefficient R^2 for the pseudo-second-order adsorption model is much higher (0.9998) than the value of R^2 for the pseudo-first-order model (0.9805). The results indicate that the adsorption of lead (II), and manganese (II) ions onto *Phoenix dactylifera* L. seed surface has a more precise fitting towards the pseudo-second-order equation. Therefore, it was concluded that the pseudo second order adsorption model is more suitable to describe the adsorption kinetics of metal ions uptake by phoenix dactylifera L adsorbent [31].

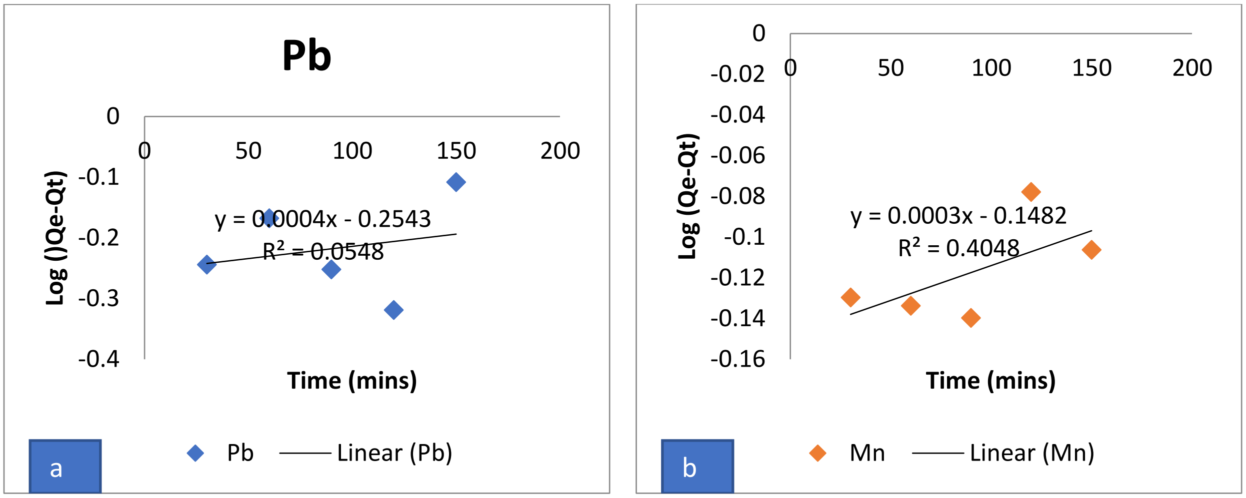


Figure 9: Pseudo-first order kinetics of (a) Pb (II), (b) Mn (II) unto *phoenix dactylifera* L. seed

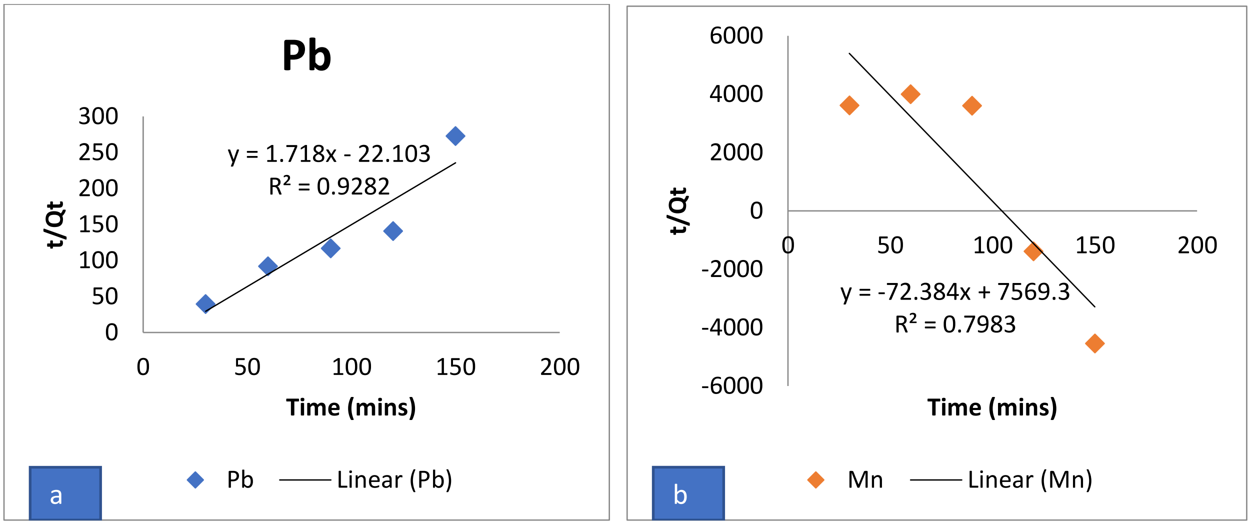


Figure: 10. Pseudo-second order kinetics of (a) Pb (II), (b) Mn (II) unto *Phoenix dactylifera* L. seed

Table 2: Parameters for various kinetic models of Pb (II), and Mn (II) ions unto raw *Phoenix dactylifera* L.

Kinetic Models	**Pb (II)**	**Mn (II)**
Pseudo-first order		
q_e (mg/g)	7.4534	6.762
K_1 (min^{-1})	0.0794	0.065
R^2	0.0548	0.405
Pseudo-second order		
q_e (mg/g)	8.7522	7.675
K_2 (mg/g.min)	0.0452	0.055
R^2	0.9282	0.798

3.4. Adsorption Thermodynamics

The feasibility of the adsorption process was estimated by the determination of thermodynamic parameters of free energy change (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) which are calculated from equations 12 and 13.

$\Delta G° = -RT \ln Kc$ (12)

$\ln Kc = (\Delta S°)/R - (\Delta H°)/RT$ (13)

where Kc is the equilibrium constant, ΔG°, ΔH°, and ΔS° are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol), and entropy (J/mol), respectively; R is the gas constant (8.314 J/molK), and T is the temperature (K).

The values of ΔH° and ΔS° can be obtained from the slope and intercept of a plot of ΔG° versus 1/T (Fig. 11), respectively. The parameters for the adsorption process are listed in Table 3. From the result, it was found that the value of negative ΔG° increases with an increase in temperature from 288 to 318 K. The negative value of Gibbs free energy changes indicates that the adsorption process was favorable and spontaneous. The negative values of ΔH° and the positive values of ΔS° indicated the exothermic nature and randomness during the adsorption of manganese (II) ion.. This was also supported by the increase in adsorption capacity of metal ions with an increase in temperature [20]. The enthalpy values indicated the possible domination of chemical forces in the lead (II) and manganese (II) ions adsorption system. The increase in the randomness may be associated with the fact that the adsorbed water molecules which were replaced by the adsorbates species gained more translational entropy, which allowed the prevalence of randomness in the system [32].

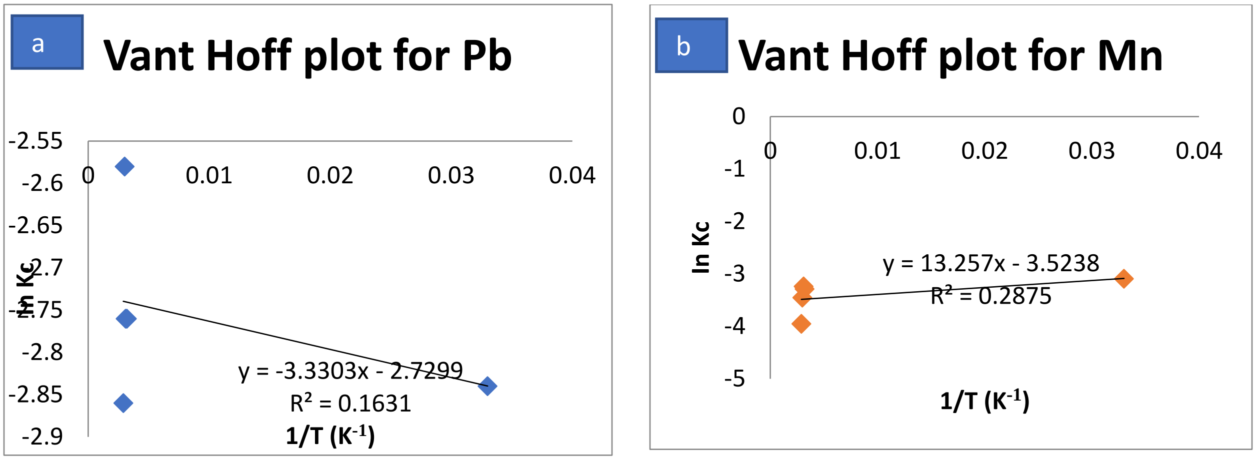


Fig.11. Vant Hoff plot of (a) Pb (II), (b) Mn (II) onto *phoenix dactylifera* L.

Table 3: Thermodynamic parameters for the adsorption of Pb (II), and Mn (II) ions unto *Phoenix dactylifera* L

Metal Ion	Temp (K)	ΔH (KJ/mol)	ΔS (KJ/mol/K)	ΔG (KJ/mol)
Pb (II)	298	-0.065	0.597	-177.95
	303			-180.93
	308			-183.91
	313			-186.89
	318			-189.88
Mn (II)	298	-0.841	1.229	-367.02
	303			-373.17
	308			-379.31
	313			-385.46
	318			-391.60

4. CONCLUSION

Raw *Phoenix dactylifera* L. seed powder was used as an adsorbent for the removal of lead and manganese (II) ions from an aqueous solution. According to the values of correlation coefficients, R^2, the pseudo-second order kinetic model fits very well with the adsorption data. The Temkin model agrees very well with the equilibrium isotherm. The RL values showed that *Phoenix dactylifera* L. seed was favorable for the adsorption of lead and manganese (II) ions. The thermodynamic analysis showed that the adsorption process of lead and manganese ions using phoenix dactylifera L. seed was spontaneous and exothermic in nature with ΔH values of -0.065 kJ/mol and – 0. 847 kJ/mol respectively. Overall, the present investigation showed that raw date seed was a promising low-cost adsorbent to be used in the removal of lead and manganese (II) ion from aqueous solutions thereby serving as a potential bio-remediator for industrial waste water treatment.

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COMPETING INTERESTS

We declared that there is no conflicting interest in the publication of this study.

AUTHORS' CONTRIBUTIONS

Osundiya M. O. was involved in the conceptualization, methodology and writing of the original draft of the manuscript. Sobola A. O. was involved in the conceptualization, methodology and writing of the original draft of the manuscript was involved in the formal writing of the manuscript. Oyewole T. S. was involved in the conceptualization, methodology and writing of the original draft of the manuscript. Tovide O. O was involved in methodology and formal data analysis, Nwinee S.A was involved in methodology and formal data analysis. Kohra S.B. was involved in methodology and formal data analysis, Olowu, R. A. was involved in the conceptualization and methodology of the study.

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