



Biosorption Of Pb(II) Ions from Aqueous Solution Using Tomato (*Lycopersicum*) Roots; Equilibrium, Kinetic, and Thermodynamic Study

J. J. Gongden* • J. Nnebedum • R. A. Lawal • S. Y. Goji

Department of Pure and Industrial Chemistry, University of Jos, Jos Plateau State, Nigeria
gongdenji@gmail.com

Abstract. *Lycopersicum* root, an agricultural waste was used as a biosorbent for the removal of Pb(II) ions from aqueous solution. The biosorptive capacity was determined using Atomic Adsorption Spectrophotometry, (AAS). Optimum metal ion concentration (5.0 mg/l), contact time (30 minutes), contact temperature (15 °C) and pH (5.5), dependence was established with a biosorbent dose of 3.0 g. The experimental data were analyzed using Langmuir, Freundlich, Temkin Dubinin – Radushkevich (D – R) isotherm models. The Freundlich Isotherm best described the biosorption process ($R^2 = 0.9477$), followed by Temkin ($R^2 = 0.9130$), Langmuir ($R^2 = 0.8860$) and D – R ($R^2 = 0.0075$). The kinetics of the adsorption process was evaluated using pseudo-first-order, pseudo-second-order and intra-particle diffusion models. The pseudo-second-order best described the process with $R^2 = 0.9950$ and the q_e , cal (0.0600 mg/g) matched more closely to the q_e , exp (0.0822 mg/g). The thermodynamic analysis showed that the adsorption was spontaneous, feasible and exothermic in nature. Therefore, *Lycopersicum* root can be used as a biosorbent for aqueous removal of Pb(II) ions.

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1. Introduction:

Heavy metal pollution of wastewater is the most strongly connected to human life due to their toxic nature (Davis et al., 2000). This contamination may occur directly by effluents from industries, refineries, and waste treatment plants and indirectly from the atmosphere through rain water or contaminants that enter the water supply from soil/ground water system (Vijayaraghavan & Yun, 2008; Abdel-Raouf & Abdul-Raheim, 2017). Lead is one of such dangerous contaminants released in the natural waters and land from various industrial activities. When the human body is exposed to lead, it accumulates in living tissue such as bone, brain, kidney, muscles and may cause many significant diseases such as anemia, nephropathy, blood and brain disorders and finally death (Halnor, 2015). Due to the toxic effects of lead, the World Health Organization (WHO) established 3 – 10 µg/L as the maximum permissible limits for lead in drinking water. However, the actual concentration of lead in wastewater can be as high as several hundred micrograms per liters. Therefore, the removal of lead from wastewater before its release to natural water bodies is very important to protect public health and the environment at large (Olayebi et al., 2017). Though there are various techniques for the removal of metal ions from wastewaters, the adsorption method has been reported for its eco-friendly, effectiveness and economic

considerations using non-conventional materials such as *Nymphaea ampla* (Gongden et al., 2014), rice husk (Chauhan, 2015), mango peel (Iqbal et al., 2009), sawdust (Bulut, 2007), mushrooms (Amalinei et al., 2012) and groundnut shell (Babarinde & Onyiaocha, 2016).

Lycopersicum is an extensively cultivated plant which serves as a source of nutrient in everyday food preparation in homes. Its production was about 177 tonnes, with China producing 32 % of the total, followed by the European Union, India, the United States and Turkey. Globally, *Lycopersicum* exports were valued at 85 billion US dollars in 2016 (FAO, 2017). Like other plant materials, *Lycopersicum* root contains plenty of floristic fiber made of cellulose, hemicelluloses, and lignin, which suggests that it may be a suitable candidate as an economical and potential biosorbent.

In this study, the potential of *Lycopersicum* root as a low-cost adsorbent for the removal of Pb(II) ions from aqueous solution was investigated. The effects of various experimental parameters on the adsorption process were also examined.

2. Materials & Methods:

Reagents: All the chemicals used were of reagent grade and these include, lead (II) nitrate ($Pb(NO_3)_2$, purity:



98.5%), sodium hydroxide (NaOH, purity: 98%), nitric acid (HNO₃, purity: 71%) BDH Chemicals Limited England, and distilled water.

Equipment's: Instruments used include, digital pH meter (Labtech-14), atomic absorption spectrophotometer (AAS) (Thermo scientific 3000 series), weighing balance (HC-D), air drying oven (memmert BE-200), water bath (DK420) mechanical shaker (ZD-2 Multipurpose). Other materials used were routine laboratory resources.

Sample Preparation and Experiment: The samples (*Lycopersicum* roots) were collected from a farm at Gindiri, Mangu (9.31°N 9.06°E), Nigeria. The roots were washed with distilled water, dried to constant weight, ground, sieved with < 250 μm apertures sieve and kept in an air-tight plastic container as biosorbent. Batch experiments were performed by contacting 3.0 g dose of the biosorbent with separate 50 mL portions of the metal ion solution to determine the effects of initial metal ion concentration (0.5 – 5.0 mg/L), solution pH (5.0 – 7.0), contact time (10 – 120 minutes) and temperature (15 – 50 °C) on the adsorption process. The amount of metal ion adsorbed (q_e) and the adsorption efficiency ($E\%$) were determined using the equations:

$$q_e \left(\frac{mg}{g} \right) = \frac{(C_i - C_e)V}{M} \quad (1)$$

$$E(\%) = \left[\frac{C_i - C_e}{C_i} \right] \times 100 \quad (2)$$

where C_i and C_e are initial and equilibrium metal ion concentrations in mg/L, V (L) is the volume of the metal ions solution and M (g) is the weight of biosorbent.

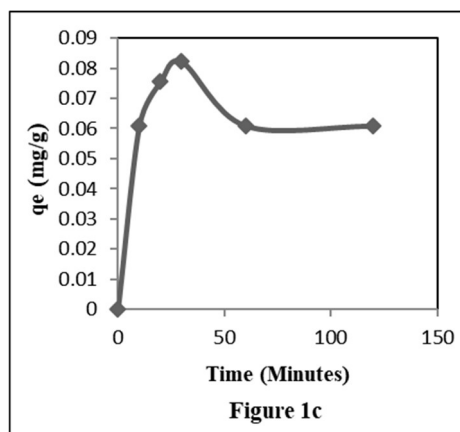
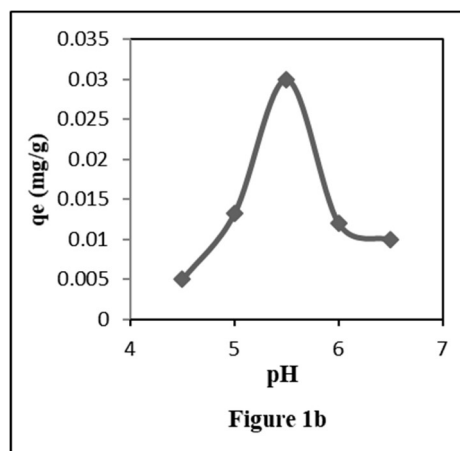
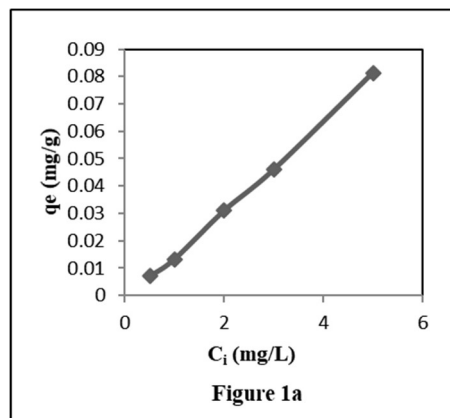
3. Results & Discussion:

3.1. Adsorption Studies

Effect of initial metal ion concentration: The effect of initial metal ion concentration on the adsorption of Pb(II) ions by *Lycopersicum* root biomass is shown in Figure 1a. It could be seen that adsorption capacity increased with increasing initial metal ion concentration. This is due to the greater availability of the adsorbates at higher concentrations and the non-saturation of the active sites on the biosorbent. A higher initial concentration provides the driving forces pertinent to overcome all mass transfer resistance between the metal solution and the *Lycopersicum* root cell wall (Boulaiche *et al.*, 2019).

Effect of solution pH: - The pH of a solution strongly determines the solubility of the adsorbates, its ionization degree and the concentration of the competing ions on the functional groups of the adsorbent (Awoyale *et al.*, 2013). Figure 1b shows that Pb(II) ions uptake was pH-

dependent, with optimum adsorption at pH 5.5 which decreased as the pH of the solution was increased. Pb(II) ions uptake increased from 0.005 mg/g to 0.031 mg/g over pH range from 4.5 to 5.5. This could be attributed to the fact that at low pH (< 5.5) protonation of the active sites at biosorbent surface hindered the formation of bonds between Pb(II) ions and protonated active sites resulting in increased metal uptake (Abudaia *et al.*, 2013). However, with further increase in pH (above 5.5), metal uptake decreased due to precipitation of insoluble lead hydroxides (Tumin *et al.*, 2008).



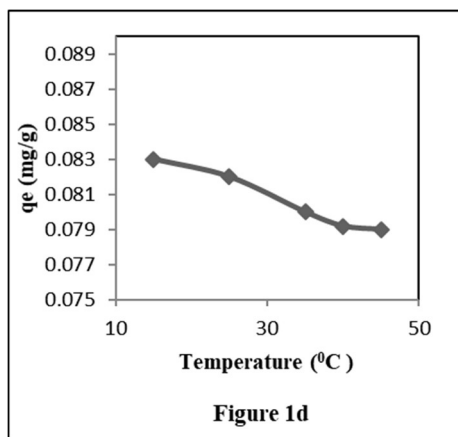


Figure 1. Adsorption profiles showing the effect of: (a) Initial metal ion concentration; (b) pH; (c) Contact time; and (d) Temperature.

Effect of contact time: - Figure 1c presents the influence of contact time on Pb(II) ions adsorption. As can be seen from the figure, adsorption capacity greatly increased in the first 30 minutes, after which there was a mild decrease which remained relatively constant even after a long contact time of 120 minutes. The adsorption rate was initially faster due to the availability of viable sites but as adsorption time increased, the availability of these viable sites gradually diminished until adsorption equilibrium was attained. This result is consistent with that reported by Olayinka *et al.*, (2009) for the removal of chromium and nickel from aqueous solution using rice husk.

Effect of temperature: - The temperature effect on Pb(II) ions adsorption onto *Lycopersicum* root biomass is represented in figure 1d. The figure shows that adsorption capacity decreased with an increase in temperature, though, the amount adsorbed did not change remarkably for the temperature range used. The decrease in uptake could be due to desorption as a result of the weakness of the adsorbing sites as temperature increased and indicates the adsorption process to be exothermic (Jagung, 2011). A similar result was obtained by Nwosu *et al.* (2012) for the removal of Pb(II) and Cd(II) ions on dried *Thevetia nerifolia* nutshell carbon.

Adsorption Isotherm Modeling: Four adsorption models were used to fit the experimental data obtained; these are Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) models. The Langmuir isotherm was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface and its linear form is expressed by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (3)$$

where C_e is the equilibrium concentration of metal ions (mg/L), q_e is the amount of metal adsorbed per specific amount of adsorbent (mg/g), q_{max} is the maximum adsorption capacity (mg/g) and K_L is the Langmuir equilibrium constant (L/mg) related to energy of adsorption which quantitatively reflects the affinity between the adsorbent and adsorbate. The essential features of the isotherm are expressed in terms of a dimensionless constant; separation factor (R_L) defined by the relationship (Langmuir 1918):

$$R_L = \frac{1}{1 + K_L C_i} \quad (4)$$

where C_i (mg/L) is the initial concentration and K_L (L/mg) is the Langmuir equilibrium constant. The value of the separation factor (R_L) provides important information about the nature of adsorption and indicates the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) (Ackacha, 2013).

The Freundlich isotherm, applicable to non-ideal heterogeneous surfaces is used to estimate the adsorption intensity of the bio sorbent and the linear form of the isotherm is represented as:

$$\log q_e = \log K_F + 1/n \log C_e \quad (5)$$

where K_F is the Freundlich constant related to sorption capacity (mg/g) and n is related to the adsorption intensity of the adsorbent (Freundlich, 1906). Temkin isotherm assumes that a decrease in the heat of adsorption is linear and that adsorption is characterized by a uniform distribution of binding energies. Temkin isotherm (Temkin, 1940) is expressed by the following equation:

$$q_e = B \ln A + B \ln C_e \quad (6)$$

where $\frac{RT}{b_T} = B$, T ($^{\circ}\text{K}$) is the temperature, R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), A (L/g) is the equilibrium binding constant corresponding to the maximum binding energy, B (J/mol) is a constant related to heat of sorption and b_T is the Temkin isotherm constant. A plot of q_e versus $\ln C_e$ enables the determination of A and B . The Dubinin-Radushkevich model (D-R) is used to estimate the heterogeneity of the surface energies expressed linearly as (Dubinin and Radushkevich, 1947):

$$\ln q_e = \ln q_m - \beta \epsilon^2; \text{ where } \epsilon = RT \ln \left(\frac{C_e + 1}{C_e} \right) \quad (7)$$



where q_e is the theoretical saturation capacity (mol/g), β is the mean free energy of adsorption per mole of the adsorbate (mol²/J²) and ϵ is the Polanyi potential, C_e (mg/L) is the equilibrium concentration of adsorbate in solution, R (Jmol⁻¹K⁻¹) is the gas constant and T (°K) is the absolute temperature. The D-R constants q_m and β are calculated from the linear plot of $\ln q_e$ versus ϵ^2 . The constant β gives an idea about the mean free energy E (J/mol) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the relationship:

$$E = \frac{1}{\sqrt{2\beta}} \quad (8)$$

The isotherms and their parameters are presented in Figure 2 and Table 1 respectively. From the values of the correlation coefficient (R^2) obtained, the Freundlich model showed the best relationship in the adsorption process followed by the Temkin model with R^2 values of 0.947 and 0.913 respectively. The maximum adsorption capacities (q_{max}) from the Langmuir and D-R isotherms are 0.020 mg/g and 0.004 mg/g respectively. The values of the Langmuir separation factor (R_L) for the adsorption of Pb(II) ions at 30 °C were all less than one (Figure 3) indicating a favorable process (Ackacha, 2013). Also, n value of 1.040 was obtained from the Freundlich equation. According to Batool *et al.* (2018), a value of n greater than 1 is an indication of favorable adsorption. The value of B (0.098 J/mol), which represents the heat of adsorption for the process, was much lower than 20 kJ/mol indicating the predominance of ideal physisorption (Itodo & Itodo, 2011). Also, the E value of 2.3 kJ/mol which was less than the threshold of 8 kJ/mol once more confirmed the predominance of physical binding (Zheng *et al.*, 2009).

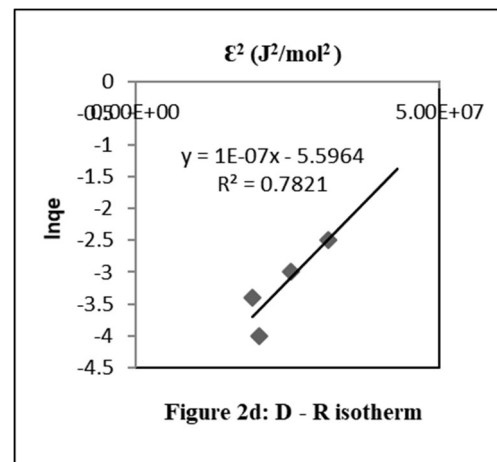
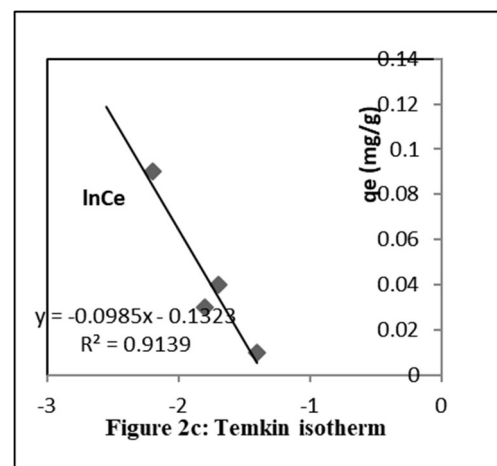
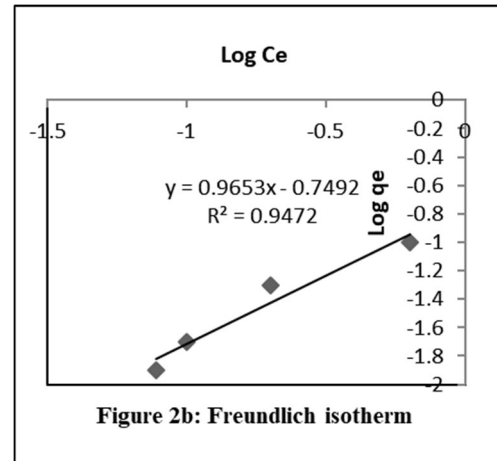
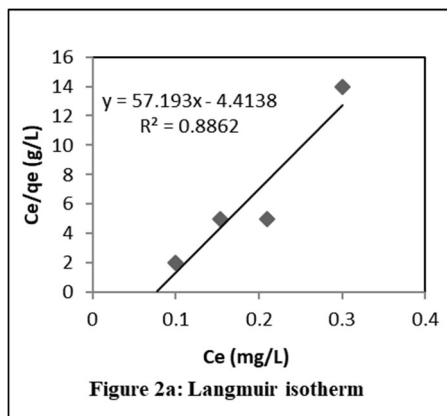


Figure 2. Linearized isotherms for adsorption of Pb(II) ions onto Lycopersicum roots at 30 °C.



Table 1: Isotherm Parameters for Adsorption of Pb(II) Ions onto *Lycopersicum* Roots.

Langmuir Isotherm	Freundlich Isotherm	Temkin Isotherm	D-R Isotherm
$q_{max} = 0.020$ mg/g	$K_F = 0.178$ (mg/g) (L/g) ⁿ	$A_T = 1.144$ L/g	$q_m = 0.004$ mg/g
$K_L = 11.33$ L/mg	$1/n = 0.965$	$B = 0.098$ J/mol	$\beta = 1 \times 10^{-7}$ mol ² /kJ ²
$R^2 = 0.886$	$n = 1.040$ $R^2 = 0.947$	$b_T = 2.5$ $R^2 = 0.913$	$E = 2.3$ KJ/mol $R^2 = 0.782$

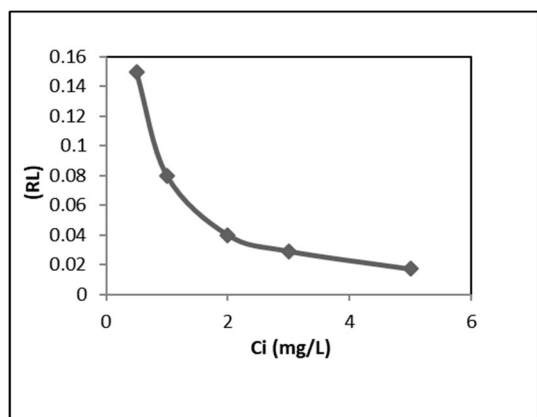


Figure 3. Langmuir Dimensionless Factor

Adsorption Kinetics Modeling: The adsorption kinetics was determined by the method described by Bernard and Jimoh (2013), by measuring adsorptive uptake of Pb(II) ions from aqueous solution at different time intervals from 10 to 120 minutes. Kinetic data were fitted using the Lagergren pseudo-first-order model (Lagergren, 1898), a pseudo-second-order model (Blanchard *et al.*, 1984) and an intraparticle diffusion model (Weber & Morris, 1963) to investigate the mechanism of adsorption and potential rate-controlling steps. The pseudo-first-order Lagergren equation is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (9)$$

The pseudo-second-order equation is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

where q_e (mg/g) is the mass of metal adsorbed at equilibrium, q_t (mg/g) the mass of metal adsorbed at time t , k_1 is the pseudo-first-order rate constant of adsorption (min^{-1}) and k_2 is the pseudo-second-order rate constant of adsorption (mg/g.min). The intra-particle diffusion equation can be written as follows:

$$q_t = K_d t^{1/2} + C \quad (11)$$

where C is the intercept which describes the boundary layer thickness and K_d (mg/g.min^{1/2}) is the rate constant of intra-particle diffusion.

The results obtained from kinetic studies are shown in Figure 4 and Table 2. The pseudo-first-order plot with a very low correlation coefficient ($R^2 < 0.500$) is not suitable for the adsorption process. The results, however, indicated very good compliance with the pseudo-second-order kinetic model with a high correlation coefficient ($R^2 = 0.995$). The large intercept obtained from the intraparticle plot implies that surface adsorption plays a great role in the rate-limiting step (Krishna *et al.*, 2018).

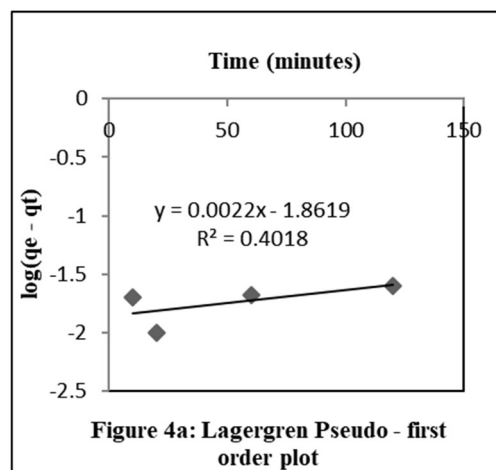


Figure 4a: Lagergren Pseudo - first order plot

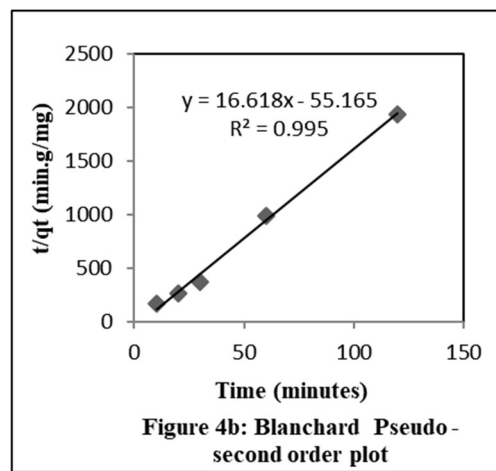


Figure 4b: Blanchard Pseudo - second order plot

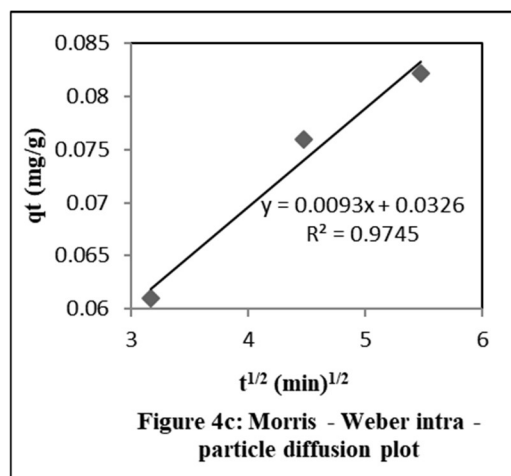


Figure 4c: Morris - Weber intra-particle diffusion plot

Figure 4. Kinetic plots for adsorption of Pb(II) ions onto *Lycopersicum* roots at 30 °C.

Table 2: Evaluated kinetic parameters for Pb (II) ions adsorption.

Pseudo first order	Pseudo second order	Intra-particle diffusion
$q_{e,exp} = 0.0822 \text{ mg/g}$	$q_{e,exp} = 0.0822 \text{ mg/g}$	$K_d = 0.0090 \text{ mg/g.min}^{1/2}$
$q_{e,cal} = 0.0140 \text{ mg/g}$	$q_{e,cal} = 0.0600 \text{ mg/g}$	$C = 0.032$
$K_1 = 0.0046 \text{ min}^{-1}$ $R^2 = 0.4010$	$K_2 = -5.0017 \text{ g/mg/min}$ $R^2 = 0.9950$	$R^2 = 0.9740$

Thermodynamic Study: The thermodynamic parameters estimate the effect of temperature on the adsorption process. The values of Gibb's free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes, activation energy (E_a) and the sticking probability factor were evaluated from the following equations (Jagung, 2011; Saleem & Bhatti, 2011).

$$K_c = \frac{q_e}{C_e} \quad (12)$$

$$\Delta G = -RT \ln K_c \quad (13)$$

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (14)$$

$$\theta = \left(1 - \frac{C_e}{C_i}\right) \text{ and } S^* = (1 - \theta) \exp \frac{-E_a}{RT} \quad (15)$$

where C_e (mg/L) is the equilibrium concentration in solution and q_e (mg/g) is the equilibrium concentration on the sorbent and K_c is the thermodynamic equilibrium constant. T (°K) is the absolute temperature and R is the universal gas constant ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$). θ is the surface coverage.

The values obtained for various thermodynamic parameters are given in Tables 3 and 4. Negative values were obtained for ΔG° at all temperatures and the values increased with an increase in temperature. According to Singha and Das (2011), negative ΔG° values indicate spontaneous and feasible adsorption. The negative ΔH° and ΔS° values represent exothermic and reversible adsorption respectively (Nwosu et al., 2012). The value of $S^* (<1)$ indicated a high sticking probability (Abasi et al., 2011).

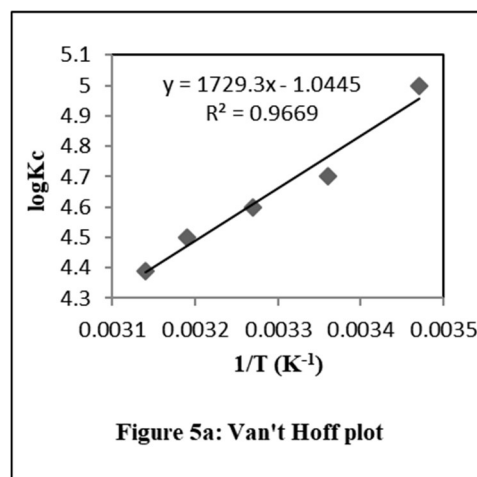


Figure 5a: Van't Hoff plot

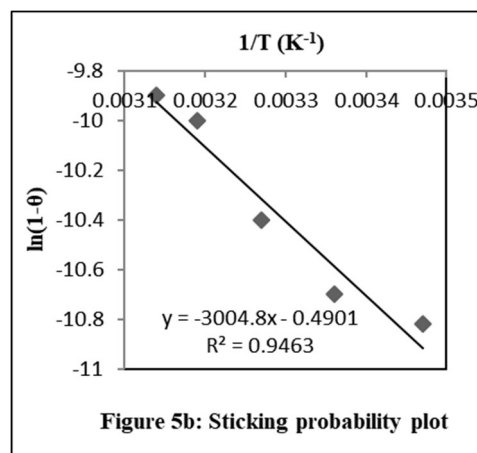


Figure 5b: Sticking probability plot

Figure 5. Thermodynamic plots for adsorption of Pb(II) ions onto *Lycopersicum* roots.

Table 3. Values of Gibb's free energy at various temperatures.

T(°K)	288	298	308	313	318
ΔG° (kJ/mol)	-3.85	-3.98	-4.121	-4.18	-4.25

Table 4. Evaluated thermodynamic parameters for Pb(II) ions adsorption.

ΔS° (kJ/mol)	ΔH° (kJ/mol)	E_a (kJ/mol)	S^*
-0.0200	-33.120	-25.000	0.6126

4. Conclusion

The removal of Pb(II) ions from aqueous solution using *Lycopersicum* root biomass was explored. Various factors such as initial lead (II) ions concentration, solution pH, contact time and temperature were optimized and proved to be an important parameter in adsorption process characterization. Four adsorption isotherms; the Langmuir, Freundlich, Temkin and Dubinin – Radushkevich (D–R) isotherms were applied to adsorption equilibrium data. Arranged in decreasing order according to values of the correlation coefficient (R^2), Freundlich > Temkin > Langmuir > D–R isotherm. The kinetic data obtained fitted best to the pseudo-second-order model ($R^2 = 0.9950$) than pseudo-first-order ($R^2 = 0.4010$) and intraparticle diffusion proved not to be the only adsorption rate-determining step. Also, from thermodynamic analysis, the adsorption process was found to be spontaneous, feasible and exothermic in nature and follows the physical process.

Corresponding Author:

Joel Japhet Gongden, Ph.D.

Department of Pure and Industrial Chemistry, University of Jos, Jos Plateau State, Nigeria.

E-mail: gongdenji@gmail.com

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