

Research Article

Biosorption of Pb(II) from Aqueous Solution Using Cow Hooves: Kinetics and Thermodynamics

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Biosorption of Pb(II) ions from aqueous solution by cow hooves (CHs) was investigated as a function of initial pH, contact time, and biosorbent dosage through batch studies. Equilibrium experiments were performed at three different temperatures (298, 308, and 318 K) using initial Pb^{2+} concentration ranging from 15 to 100 mgg^{-1} . This study revealed that maximum uptake (96.2% removal) of Pb^{2+} took place within 30 minutes of agitation, and the process was brought to equilibrium within 60 minutes of equilibration. The equilibrium data were modelled using Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models. The Langmuir isotherm model fitted the data best at all temperatures considered. The Lagergren second-order kinetic model fitted the biosorption process better than the first-order model. The negative values obtained for both Gibb's free energy change and enthalpy change are an indication of the spontaneous and exothermic nature of the sorption of Pb^{2+} onto CH. A study of the FTIR spectral obtained before and after Pb^{2+} sorption showed that carbonyl, hydroxyl, amino, and carboxyl groups were involved in the sorption process.

1. Introduction

The presence of heavy metals in the environment, particularly the aquatic environment, cannot be over emphasized. Their presence in the environment has become a great threat all over the years because of their nonbiodegradability, toxicity, persistency, and bioaccumulation tendency [1, 2]. Heavy metals are introduced majorly into the environment through wastewater generated from various industrial activities such as mining, electroplating, metal finishing, dyeing, battery manufacturing processes, and production of paints and pigments [3, 4]. Lead is one of the most toxic heavy metals and important contaminants in aquatic environments. Lead can exist in organic and inorganic forms. Both forms have been identified to be poisonous with the former being more poisonous [5]. The maximum allowable limit of Pb considered safe in drinking water by the World Health Organization (WHO) is 50 ppb, whereas less than 15 pp is adopted by the United States Environmental Protection Agency (US EPA) [6]. The permissible limit of lead for effluent discharge to inland surface water is 0.1 mg/L [7].

Therefore, to conform to these standards and to keep a safe environment, it becomes absolutely necessary to reduce the amount of this deleterious metal from aqueous wastes generated from industries before they are released into the environment. This necessity has seriously enhanced the demand for new technologies for metal removal from wastewater [8]. Various treatment technologies have been developed for the removal of heavy metals from wastewater. The most widely used conventional methods for removing heavy metals from wastewater include ion exchange, chemical precipitation, reverse osmosis, evaporation, and electro dialysis [3, 9]. But most of these treatment technologies are associated with a lot of demerits which include high chemical or energy requirements (which implies high capital and operational cost) and generation of toxic sludge or other secondary products that need to be disposed [8, 10, 11]. Besides, the conventional methods have inadequate efficiencies at low metal concentrations, particularly in the range of 1–100 mg/L [12].

In recent decades, adsorption has proved to be one of the simplest and most effective treatment methods for

the removal of heavy metals from wastewater. Adsorption of heavy metals from wastewater using activated carbon has gained a wide acceptability industrially because of its high porosity, large internal surface area, relatively high mechanical strength, high degree of surface activity, and high affinity for metals [12–14]. However, the use of activated carbon is highly expensive, thereby limiting its use as adsorbent for heavy metal removal from industrial wastewater especially in the third-world countries [15, 16]. This has necessitated the search for low-cost adsorbents, which are cheaply available and environmentally friendly, that can be effective as or even more effective than activated carbon.

Biosorption can be defined as the passive uptake of toxicants by dead/inactive biological materials or by materials derived from biological sources [17]. The major advantages of biosorption over conventional treatment methods include low cost, good efficiency, minimization of chemical and biological sludge, regeneration of biosorbent, and possibility of metal recovery [18]. A number of low-cost biosorbents have been exploited for the removal of lead from wastewaters. These include *Pleurotus florida* and *Trichoderma viride* [18], *Streptovercillium cinnamomeum* waste biomass [19], *Pseudomonas putida* [20], *Pleurotus ferulae* [21], and native and chemically modified corn corb [22], *Corynebacterium glutamicum* [23].

Cow hoof is an inedible byproduct that can be obtained freely from local abattoirs in Nigeria. Cow hoof is known to contain insoluble protein called keratin [24] which contains some functional groups such as amino and carboxyl, which may likely enhance biosorption processes. Thousands of cow hooves are burnt off in different abattoirs in Nigeria every day. It has been reported that keratin extracted from cow hooves has been exploited in making a special fire extinguishing foam specifically designed to quell the hotter, high-intensity fires triggered by aviation fuel across the UK [25]. This study is another attempt aimed at turning this agricultural waste into valuable use.

This study was aimed at investigating the feasibility of using cow hoof powder as an alternative biosorbent for the removal of Pb^{2+} ions from aqueous solution. The Langmuir, Freundlich, and Dubinin-Raduskevich (D-R) isotherm models were used to fit the equilibrium data while Lagergren kinetic models were used for kinetic modelling.

2. Experimental

2.1. Materials. Cow hooves were obtained from an abattoir along Ekiti State University Road, Ado Ekiti, Nigeria. The hooves were thoroughly washed with distilled water and sun-dried for a month. After sun drying, the hooves were washed again with distilled water and oven-dried at $105^{\circ}C$. The dried hooves were ground and sieved using sieve of mesh size $212\ \mu m$. A stock solution containing $1000\ mgL^{-1}$ of $Pb(II)$ was prepared by weighing $1.5984\ g$ of analytical grade $Pb(NO_3)_2$ into a 1 L standard flask. This was dissolved and made to mark with distilled water. Standard solutions of different concentrations as might be required were prepared (by dilution) from this stock solution.

2.2. General Procedure for Biosorption Studies. The influence of different parameters like solution pH, equilibration time, and sorbent dosage on the removal of $Pb(II)$ was investigated through batch experiments at 298 K. Half gramme ($0.5\ g$) of CH was suspended in 50 mL of $50\ mgL^{-1}$ $Pb(II)$ solution in 150 mL conical flasks for each experimental run. This mixture was agitated using thermostatic water bath shaker (SearchTech 82) for 60 minutes unless stated otherwise at a constant speed. The effects of solution pH on the biosorption process were assessed by adjusting the solution pH between 2.0 and 6.0 using dilute HCl or dilute NaOH solution. The solution pH was not adjusted above 6 because precipitation was noticed at pH above 6. HI 2210 pH metre, Hanna Instruments, was used for pH measurement. The effect of contact time was investigated by varying the agitation time from 0 to 150 minutes. For each experimental run, the mixture of the biosorbent and the solution was centrifuged after agitation and the concentration of metal ion present in the liquid phase (supernatant) was determined using atomic absorption spectrometer (AAS). The amount of metal ions adsorbed per unit mass of biosorbent was determined according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m}, \quad (1)$$

where m is the mass of CH (g), V is the volume of the solution (L), C_0 is the initial concentration of metal (mgL^{-1}), C_e is the final concentration of $Pb(II)$ in the liquid phase (mgL^{-1}), and q_e is the amount of metal biosorbed at equilibrium (mgg^{-1}). The percentage biosorption (%R), for $Pb(II)$, was calculated using the following expression:

$$\%R = \frac{(C_0 - C_e) \times 100}{C_0}. \quad (2)$$

2.3. Equilibrium Studies. Equilibrium isotherm studies were conducted by agitating $0.5\ g$ of CH with 50 mL of lead(II) solution (pH of 3.5) for 60 minutes at 298, 308, and 318 K. The initial metal concentration ranged from 15 to $100\ mgL^{-1}$. The samples were then centrifuged and analysed as described earlier.

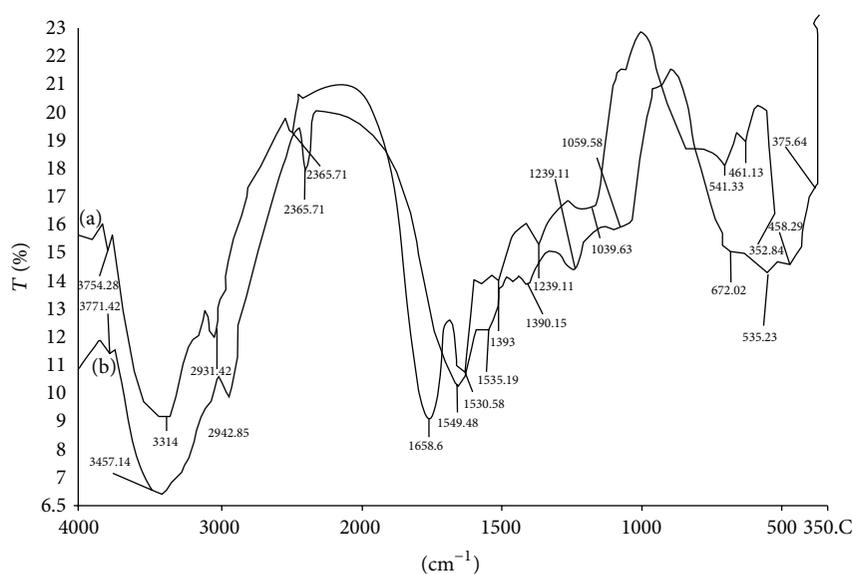
3. Results and Discussion

3.1. FTIR Analysis. The possibility of functional groups involvement in the biosorption of $Pb(II)$ by CH was determined using FTIR spectroscopic analysis. The major functional groups that can be noticed on the biosorbent surface are OH ($3314\ cm^{-1}$ band), C=O ($1658.6\ cm^{-1}$ absorption, band), C-O ($1239.11\ cm^{-1}$ and $1039.63\ cm^{-1}$), C-C ($2931.42\ cm^{-1}$), and amino group ($1530.58\ cm^{-1}$ and $1393\ cm^{-1}$) (Figure 1(a)). Most of these absorption bands were altered after $Pb(II)$ biosorption (Figure 1(b) and Table 1), which is an indication of the involvement of these functional groups in the biosorption process.

3.2. Effect of pH on Pb Removal. The effect of pH on the biosorption of $Pb(II)$ by CH is presented in Figure 2.

TABLE 1: FTIR spectral characteristics of cow hoof before and after Pb(II) biosorption.

FTIR peak	Frequency (cm ⁻¹) before adsorption	Frequency (cm ⁻¹) after adsorption	Difference	Assignment
1	3754.28	3771.42	-17.14	-NH stretching
2	3314.00	3457.14	-143.14	Bonded -OH group
3	2931.42	2942.85	-11.43	Aliphatic C-H groups
4	2365.71	2365.71	—	S-H stretching
5	1658.60	1649.48	9.12	C=O stretching of an amide
6	1530.58	1535.19	-4.61	Amino/nitro compound
7	1393.00	1390.15	2.85	Nitro compound
8	1239.11	1239.11	—	C-N stretching
9	1039.63	1059.58	-19.95	C-O stretching



(a) Cow hoof before biosorption
(b) Cow hoof after Pb biosorption

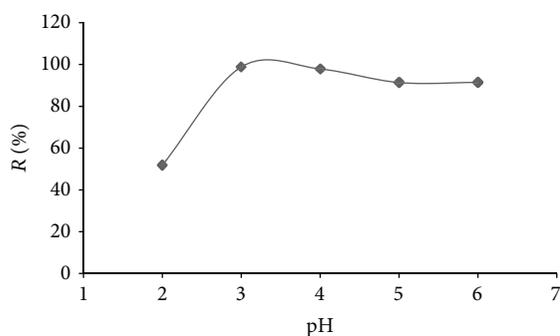
FIGURE 1: FTIR spectra of (a) unloaded CH and (b) Pb²⁺ loaded CH.

FIGURE 2: Effect of pH on the percentage removal of Pb using cow hoof.

The figure reveals that the biosorption of Pb onto CH was pH dependent. There was little removal of Pb under highly

acidic conditions. The biosorption of Pb onto CH increased gradually from pH of 2 (about 50% Pb removal) to 3.5 (about 99% Pb removal) while a decrease in the percentage removal of Pb was noticed at pH above 4. The maximum removal percent of Pb occurred between the pH of 3 and 4. The pH dependence of metal biosorption can be explained by both solution chemistry and the functional groups present on the surface of the biosorbent [26]. At low pH, the surface of the biosorbent is saturated with hydrogen/hydroxonium ions. This creates a competition between the Pb cation and the hydrogen ions for the active sites on the biosorbent surface. This competition brings about decrease in the amount of Pb(II) adsorbed at low pH.

3.3. Effect of Contact Time on Biosorption of Pb(II). Figure 3 presents the effect of contact time on the adsorption capacity and percentage removal of Pb(II) by CH biomass. The result presented in Figure 3 indicates that there was a rapid removal

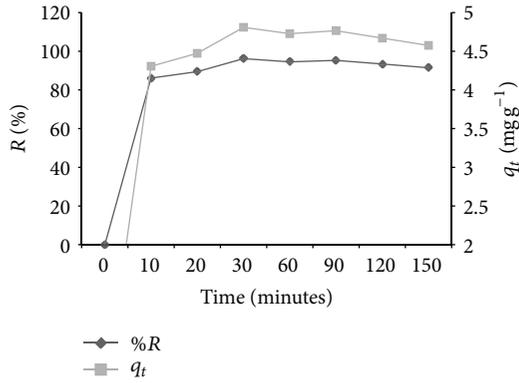


FIGURE 3: Effect of contact time on the removal of Pb(II) by CH, pH = 3.5, $T = 298$ K.

of Pb(II) within the first ten minutes. In fact, more than 80% removal of Pb(II) occurred within this period. The biosorption rate increased gradually until equilibrium was attained after 60 minutes of agitation. Therefore, an equilibration time of 60 minutes was used for further experiments. The initial high biosorption rate might be linked to the abundance of free binding sites on the biosorbent, which become saturated resulting in decreased biosorption rate [22]. The optimum adsorption capacity (q_t) and percentage removal were 4.81 mgg^{-1} and 96.2%, respectively.

3.4. Effect of CH Dosage. The effect of biosorbent dosage on the removal of lead (II) ions by CH was investigated by agitating CH powder of different masses ranging from 0.3 g to 2.5 g with 50 mL of 50 mgg^{-1} Pb(II) solution at 298 K. The result of this investigation is presented in Figure 4. The figure reveals that the removal of lead is a function of the mass of CH used. The percentage of metal biosorbed slightly increased from 94.24% to 95.48% when the amount of cow hoof was increased from 0.3 g to 2.5 g. This could happen because the greater the mass of the adsorbent in solution, the greater the number of binding sites available for metal uptake. Conversely, the amount of metal adsorbed per unit mass of CH decreased from 7.85 to 0.95 mgg^{-1} when the sorbent mass used was increased from 0.3 to 2.5 g.

3.5. Biosorption Isotherms. Analysis of the equilibrium data is important to develop an equation which could be used for design purposes [27]. Several isotherm equations are available for equilibrium modelling in biosorption processes. The biosorption data in this study were described using Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models.

The Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer biosorption without any interaction between the biosorbed ions. The linear form of this model can be expressed as

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}, \quad (3)$$

TABLE 2: Separation factor (R_L) values for Pb (II) ion biosorbed on cow hoof.

Co (mgL^{-1})	298 K	308 K	318 K
15	0.093	0.072	0.114
25	0.058	0.045	0.071
50	0.029	0.023	0.037
75	0.020	0.015	0.025
100	0.013	0.012	0.018

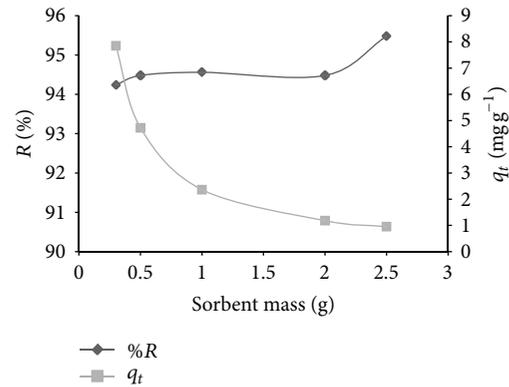


FIGURE 4: Effect of sorbent mass on the removal of Pb, pH = 3.5, $T = 298$ K.

where q_m (mgg^{-1}) is the maximum adsorption capacity and K_L (Lmg^{-1}) is a constant related to the affinity of binding sites or enthalpy of biosorption and should vary with temperature [34]. Straight lines were obtained when a plot of C_e/q_e versus C_e was made for different temperatures (Figure 5). Langmuir parameters are important in predicting the affinity between the biosorbate and biosorbent using the dimensionless separation factor R_L , defined as

$$R_L = \frac{1}{1 + K_L C_0}, \quad (4)$$

where C_0 is the initial concentration of metal (mgL^{-1}) and K_L is Langmuir constant. The affinity between biosorbent and adsorbate is described as irreversible, if $R_L = 0$; favourable, if $0 < R_L < 1$; linear if $R_L = 1$, and unfavourable if $R_L > 1$. The R_L values in this study are shown in Table 2. The values indicate that the biosorption of Pb(II) is favourable and this is more favourable as both the initial metal concentration and temperature increased.

The Freundlich isotherm model gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies [34]. This model can be expressed linearly as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e, \quad (5)$$

where K_f and n are Freundlich constants which are related to sorption capacity and intensity, respectively.

TABLE 3: Isotherm parameters for the removal of Pb (II) by cow hoof at different temperatures.

Isotherm	Parameter	Temperature (K)		
		298	308	318
Langmuir	q_m (mgg ⁻¹)	8.640	8.912	9.52
	K_L (Lmg ⁻¹)	0.65	0.85	0.52
	R^2	0.9854	0.9969	0.9888
Freundlich	K_f (L ^{1/n} g ⁻¹ mg ^{-1/n})	3.097	3.394	2.909
	n	2.503	2.50	2.164
	R^2	0.7478	0.8388	0.824
D-R	q_D (mgg ⁻¹)	5.719	6.948	7.38
	K_D (Mol ² KJ ⁻²)	-0.0878	-0.0935	-0.1742
	E (KJmol ⁻¹)	2.386	2.312	1.694
	R^2	0.6802	0.8472	0.8803

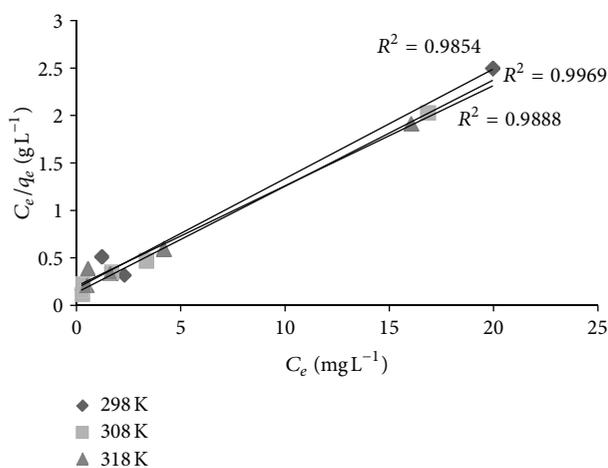


FIGURE 5: Langmuir plots for the removal of Pb(II) by CH at pH 3.5, agitation time of 60 minutes, and different temperatures.

The Dubinin-Radushkevich isotherm which also assumes a heterogeneous surface can be expressed in the following linear form:

$$\ln q_e = \ln q_D - K_D \varepsilon^2, \quad (6)$$

where ε is the Polanyi potential = $RT \ln(1 + 1/C_e)$, q_D is the adsorption capacity of the biosorbent (mgg⁻¹), K_D is a constant related to the adsorption energy (mol² kJ⁻²), R is the gas constant (kJK⁻¹ mol⁻¹), and T is the temperature (K). D-R isotherm model is important for determining the mean adsorption energy. This sorption energy can be estimated by using the following relationship:

$$E = (-2K_D)^{-1/2}. \quad (7)$$

The magnitude of the mean adsorption energy E is useful for estimating the nature of the biosorption process. If the value of E is less than 8 kJmol⁻¹, the biosorption process can be explained by physisorption mechanism, if E is between 8 and 16 kJmol⁻¹, the process is dominated by ion exchange

mechanism, and if E is >16 kJmol⁻¹, the biosorption process is dominated by chemisorption [35].

The Langmuir, Freundlich, and D-R isotherm parameters at different temperatures are presented in Table 3. A critical look at the correlation coefficients (Table 3) for the three isotherm models reveals that the biosorption process was best fitted by Langmuir model at all temperatures. The maximum adsorption capacities, q_m , calculated from Langmuir equation at 298 K, 308 K, and 308 K are 8.64, 8.912, and 9.52 mgg⁻¹, respectively. The maximum adsorption capacities obtained from Freundlich and D-R models at these temperatures are 3.097, 3.394, and 2.909 L^{1/n} g⁻¹ mg^{-1/n}, and 5.719, 6.948, and 7.38 mgg⁻¹, respectively. The mean biosorption energies were 2.386, 2.312, and 1.694 kJmol⁻¹ at 298 K, 308 K, and 308 K, respectively (Table 3). This shows that the biosorption process was dominated by physisorption mechanism.

A comparison of the adsorption capacities for the biosorption of Pb(II) ions on different biosorbents used in the literature with cow hoof is summarized in Table 4. Although direct comparison of adsorption capacities of different biosorbents is difficult due to the differences in experimental conditions, yet the adsorption capacity of Pb by CH compares favourably well with those reported in the literature.

3.6. Adsorption Kinetics. The adsorption kinetics of the biosorption of Pb(II) were analysed using Lagergren first-order and Lagergren second-order kinetic models [36]. The Lagergren first-order equation is expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}, \quad (8)$$

where k_1 is the rate constant for Lagergren first-order equation (min⁻¹) and q_e = amount of metal biosorbed at equilibrium (mgg⁻¹). A plot of $\log(q_e - q_t)$ versus t gave a straight line confirming the applicability of the Lagergren first-order rate equation. Lagergren second-order sorption rate equation can be expressed as

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (9)$$

TABLE 4: Comparison of biosorption capacity (q_m) of cow hoof for Pb (II) with those of other biosorbents.

Biosorbent	Temperature (K)	q_m (mgg ⁻¹)	Reference
Wheat bran	293	68.97	[2]
<i>Pseudomonas putida</i>	NA	56.2	[20]
<i>Pleurotus ferulae</i>	NA	2.79	[21]
<i>Bacillus</i> sp. (ATS-1)	298	92.3	[28]
<i>Pseudomonas aeruginosa</i>	323	0.7	[29]
<i>Pinus pinaster</i> bark	NA	1.59	[30]
Modified peat	NA	230	[31]
<i>Enterobacter</i> sp. J1	298	50.9	[32]
Corn cob	NA	8.29	[33]
Corn starch	NA	28.8	[33]
Cow hoof	298	8.42	Current study

TABLE 5: Kinetics' parameters for the biosorption of Pb (II) onto CH at 298 K.

	$q_{e(\text{exp})}$ (mgg ⁻¹)	$q_{e(\text{cal})}$ (mgg ⁻¹)	k_1 (min ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R^2
First order	4.81	1.9525	0.0145	—	0.6780
Second order	4.81	4.76	—	0.248	0.9983

TABLE 6: Thermodynamic constants for the biosorption of Pb onto CH at different temperatures.

T (K)	ΔG^0 (Jmol ⁻¹)	ΔH^0 (Jmol ⁻¹)	ΔS^0 (Jmol ⁻¹)	R (Jmol ⁻¹ K ⁻¹)
298	-10280.4	-33265.14	-77.13	8.314
308	-9509.1			8.314
318	-8737.8			8.314

where k_2 is the second-order rate constant (gmg⁻¹ min⁻¹). A straight line plot of t/q_t versus t indicates the applicability of second-order model.

The rate constants k_1 , k_2 , the calculated equilibrium adsorption capacity q_e (cal) from first-order and second-order equations, and the experimental equilibrium adsorption capacity q_e , (exp) (mg/g) are presented in Table 5. It can be observed from the table that the equilibrium adsorption capacity calculated from the first-order equation is different from the experimental q_e value. This coupled with its correlation coefficient can make one conclude that the biosorption process was not properly described by the first-order kinetic. On the other hand, the calculated q_e from the second-order kinetic model is similar to the experimentally determined q_e . Furthermore, the correlation coefficients R^2 (Table 5 and Figure 6) for the second-order equation is higher than the corresponding value for the first-order model. This shows that the biosorption of Pb(II) onto CH is better described by Lagergren second-order model suggesting that chemisorption was the rate-determining step.

3.7. Determination of Thermodynamic Parameters. Thermodynamic parameters are important factors that determine the feasibility and spontaneity of an adsorption process. These parameters were determined by carrying out equilibrium

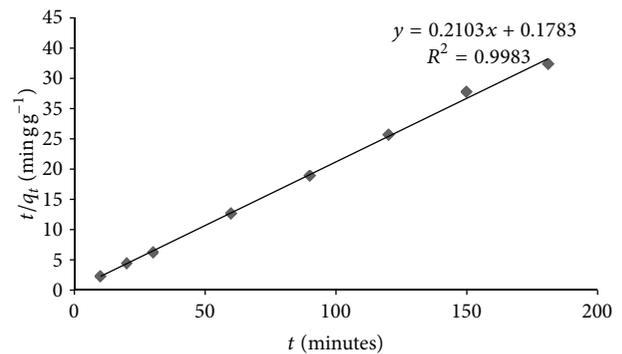


FIGURE 6: Second-order kinetic plots for the biosorption of Pb(II) onto CH at 298 K.

studies at different temperatures to obtain corresponding values of C_{Ae} and C_e . The equilibrium constant K_e can be calculated from C_{Ae} and C_e values using

$$K_e = \frac{C_{Ae}}{C_e}, \quad (10)$$

where C_{Ae} represents adsorption in mgL⁻¹ at equilibrium and C_e is the equilibrium concentration of the metal in mgL⁻¹. The value of K_e can be obtained from the lowest experimental metal concentration [37]. Vant' Hoff's equation is a useful expression that links ΔH^0 and ΔS^0 with the equilibrium constant (K_e) as shown below [38]:

$$\ln K_e = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}, \quad (11)$$

where T is the temperature in Kelvin and R is the gas constant (kJmol⁻¹ K⁻¹). The values of the standard enthalpy change

(ΔH^0) and standard entropy change (ΔS^0) were calculated from the slope and intercept of the linear plot of $\ln K_e$ against $1/T$ while the values of ΔG^0 at different temperatures were determined using the equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0. \quad (12)$$

The thermodynamic parameters are shown in Table 6. The negative values of ΔG^0 at all temperatures considered indicate the spontaneous nature of the biosorption process. The removal of Pb by CH can further be described as exothermic based on the negative value of ΔH^0 . The low value of ΔS^0 indicates that no remarkable change on entropy is associated with the biosorption process, and its negative value is an indication that the biosorption process is spontaneous at low temperatures precisely at temperatures less than 432 K (159°C).

4. Conclusions

It can be concluded from this study that powder obtained from cow hooves can be utilized as a low-cost biosorbent for the removal of Pb^{2+} from aqueous solutions with 96.2% efficiency within 30 minutes of agitation. The biosorption process is a function of the biosorbent dosage, the initial solution pH, and temperature. The efficiency of Pb^{2+} removal increased with increase in the amount of CH dosed while the pH of 3.5 was recorded for maximum Pb^{2+} removal. The isotherm studies revealed that Langmuir model fitted the equilibrium data better than Freundlich and D-R models. The Langmuir maximum adsorption capacities increased from 8.64 to 9.52 mgg^{-1} when the temperature was raised from 298 K to 318 K. The FTIR spectral of the unloaded and Pb^{2+} loaded CH revealed that carbonyl, carboxyl, hydroxyl, and amino groups played a vital role in the biosorption process. The thermodynamic parameters revealed that the biosorption process was exothermic and spontaneous.

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