

## Research Article

# Equilibrium, Kinetics, and Thermodynamics of the Removal of Nickel(II) from Aqueous Solution Using Cow Hooves

I. Osasona,<sup>1</sup> O. O. Ajayi,<sup>2</sup> and A. O. Adebayo<sup>2</sup>

<sup>1</sup> Department of Chemical Sciences, Afe Babalola University, PMB 5454, Ado-Ekiti, Nigeria

<sup>2</sup> Department of Chemistry, Federal University of Technology, PMB 704, Akure, Nigeria

Correspondence should be addressed to I. Osasona; oosasona@yahoo.com

Received 16 January 2014; Accepted 30 April 2014; Published 19 May 2014

Academic Editor: Jeffrey M. Zaleski

Copyright © 2014 I. Osasona et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The feasibility of using powdered cow hooves (CH) for removing  $\text{Ni}^{2+}$  from aqueous solution was investigated through batch studies. The study was conducted to determine the effect of pH, adsorbent dosage, contact time, adsorbent particle size, and temperature on the adsorption capacity of CH. Equilibrium studies were conducted using initial concentration of  $\text{Ni}^{2+}$  ranging from 15 to 100  $\text{mgL}^{-1}$  at 208, 308, and 318 K, respectively. The results of our investigation at room temperature indicated that maximum adsorption of  $\text{Ni}^{2+}$  occurred at pH 7 and contact time of 20 minutes. The thermodynamics of the adsorption of  $\text{Ni}^{2+}$  onto CH showed that the process was spontaneous and endothermic. Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models were used to quantitatively analysed the equilibrium data. The equilibrium data were best fitted by Freundlich isotherm model, while the adsorption kinetics was well described by pseudo-second-order kinetic equation. The mean adsorption energy obtained from the D-R isotherm revealed that the adsorption process was dominated by physical adsorption. Powdered cow hooves could be utilized as a low-cost adsorbent at room temperature under the conditions of pH 7 and a contact time of 20 minutes for the removal of Ni(II) from aqueous solution.

## 1. Introduction

Heavy metal pollution is a global menace that has threatened the existence of lives for decades. Heavy metals are particularly injurious to plants and animals because of their non-biodegradability, persistency, and bioaccumulation tendency [1, 2]. Nickel can be introduced to the aquatic environment through raw wastewater streams from industrial activities such as mineral processing, paint formulation, electroplating, porcelain enameling, copper sulphate manufacture, manufacture of alloys, silver refining, zinc base casting and storage battery industries, and mining [3–5]. Nickel is an essential micronutrient in animals and cofactor for enzyme urease in plants [4]. It has also been pointed out that an enzyme (a nickel containing enzyme) called carbon monoxide dehydrogenase (CODH) performs an important role in the global carbon cycle. This is because CODH is involved in the interconversion of the environmental pollutant CO and the greenhouse gas  $\text{CO}_2$  [6]. Even though nickel plays

some important roles as an essential micronutrient/enzyme cofactor and carbon dioxide sequestering agent in the environment, excessive concentrations of Ni in animals might cause serious health challenges like gastrointestinal distress, pulmonary fibrosis, skin dermatitis, cyanosis, nausea, tightness of the chest, dry cough and shortness of breath, rapid respiration, and so forth [4, 7, 8].

The maximum allowable discharge concentration of  $\text{Ni}^{2+}$  is 2  $\text{mg/L}$  [9], while its permissible limit in drinking water is 0.5  $\text{mg/L}$  [10]. To attain these standards, aqueous discharge from industrial activities must be treated before being emptied into the environment. To this end, a number of conventional techniques have been used to remove nickel(II) ion from industrial effluents. This includes the use of activated carbon, chemical precipitation and crystallization in the form of nickel carbonate [3], reverse osmosis, coagulation, and floatation [11]. However, these treatment methods are associated with a lot of inherent limitations which include high capital and operational cost, generation of secondary

wastes, and low metal uptake particularly when initial metal concentrations in wastewaters are low [12–14]. This has led to the search for cheap, environmentally friendly, and efficient method of removing heavy metals from wastewaters. Adsorption using activated carbon has proven to be an excellent alternative. However, the use of activated carbon for heavy metal remediation is limited due to its high cost and loss during regeneration [15]. Consequently, attention has been diverted towards the use of low-cost adsorbents and biomaterials which are by-products or the wastes from large scale industrial operations and agricultural waste materials for heavy metal removal from wastewater.

A lot of researchers have worked on different low-cost adsorbents for the removal of Ni(II) from aqueous solution. Examples are *Trichoderma viride* [4], waste tea [16], protonated rice bran [17], chemically modified saw dust (*Dalbergia sissoo*) [18], marine algal biomass [19], corncob [20], and so forth. Most of these low-cost adsorbents have shown high adsorption capacity for Ni(II).

This study was aimed at studying the adsorptive property of cow hoof (an inedible spare part of cows) for the removal of Ni from aqueous solution. The influence of pH, contact time, adsorbent particle size, and sorbent mass on the adsorption capacity of cow hoof were also investigated. The equilibrium data obtained were analysed and modelled using Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models. The feasibility of the adsorption process was determined using the data generated at different temperatures to determine the thermodynamic parameters.

## 2. Materials and Methods

**2.1. Materials.** Cow hooves were obtained from a local abattoir along Ekiti State University Road, Ado-Ekiti, Nigeria. The hooves were thoroughly washed with distilled water and sun dried for a month. After drying, the hooves were again washed with distilled water and dried in an oven maintained at a temperature of 105°C. The oven dried hooves were later ground and sieved using sieves of mesh sizes 212  $\mu\text{m}$ , 425  $\mu\text{m}$ , and 850  $\mu\text{m}$ . A stock solution containing 1000  $\text{mgL}^{-1}$  of Ni(II) was prepared using analytical grade  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  in a 1L standard flask. Standard solutions of different concentrations as might be required were later prepared from this stock.

**2.2. Batch Adsorption Studies.** Unless otherwise stated, all experiments were conducted at room temperature (298 K) for 1 h using 50  $\text{mg L}^{-1}$  Ni(II) solution and 0.5 g CH of particle size 212  $\mu\text{m}$ . Batch adsorption studies were carried out in 150 mL glass stoppered conical flasks each containing 50 mL of Ni(II) solution. A mixture of the adsorbent and Ni solution was agitated at a constant speed using thermostatic water bath shaker (SearchTech 82). The effect of initial solution pH (2, 3, 4, 5, 6, and 7), adsorbent particle size (212  $\mu\text{m}$ , 425  $\mu\text{m}$ , and 850  $\mu\text{m}$ ), adsorbent dose (0.1, 0.3, 0.5, 0.7, and 1 g), and contact time (10, 20, 30, 60, 90, 120, and 150 mins) was evaluated during the present study. HI 2210 pH metre, Hanna Instruments, was used for pH measurement, while 0.1 M HCl or 0.1 M NaOH was used for pH adjustment. The mixture

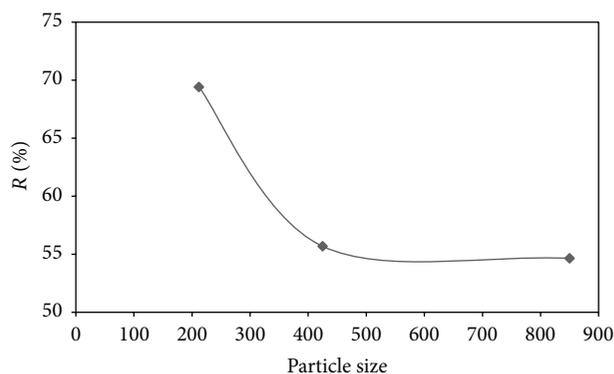


FIGURE 1: Effect of particle size on the percentage removal of  $\text{Ni}^{2+}$ ;  $T = 298 \text{ K}$ .

of the adsorbent and the solution was filtered after agitation and the concentration of  $\text{Ni}^{2+}$  ion present in the filtrate was determined using atomic absorption spectrometer (AAS). The amount of metal ions adsorbed at equilibrium per unit mass of adsorbent was determined according to the following equation:

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

where  $m$  is the mass of adsorbent (g),  $V$  is the volume of the solution (L),  $C_o$  is the initial concentration of Ni ( $\text{mgL}^{-1}$ ),  $C_e$  is the equilibrium concentration of Ni ( $\text{mgL}^{-1}$ ) in the filtrate, and  $q_e$  is the amount of metal adsorbed at equilibrium ( $\text{mgg}^{-1}$ ). The percentage adsorption (%R) was calculated using the following expression:

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

**2.3. Equilibrium Studies.** The isotherm studies for the removal of Ni(II) from aqueous solution using CH were conducted at different temperatures (298, 308, and 318 K) by equilibrating 0.5 g of CH with Ni solution having initial concentration ranging from 15 to 100  $\text{mgL}^{-1}$ . The optimum pH of 7 was maintained for these studies. The samples were then filtered and the filtrates were analysed for Ni(II) using atomic absorption spectrometer (AAS).

## 3. Results and Discussion

**3.1. Effect of Particle Size.** The particle size of an adsorbent plays a vital role in adsorption. Smaller sized particles have a higher surface area, which in turn favours adsorption and results in a shorter equilibration time [21]. This phenomenon was supported by our result for the effect of CH particle size on the removal of Ni as presented in Figure 1. The figure shows that percentage removal of Ni decreased from 69.4% to 54.64% when the particle size was increased from 212  $\mu\text{m}$  to 850  $\mu\text{m}$ . This is due to the fact that adsorbent with smaller particle size will contain higher number of particles (binding

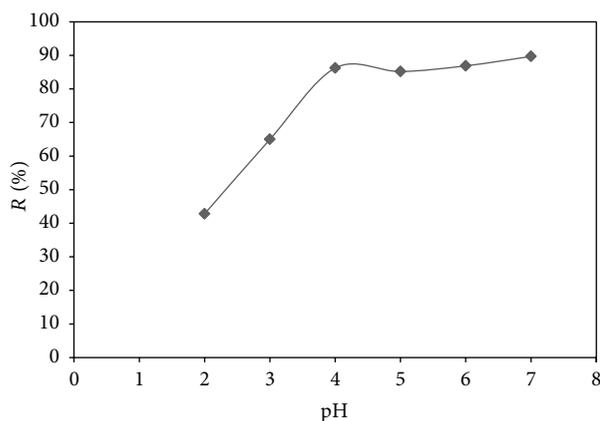
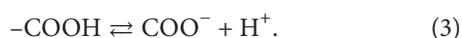


FIGURE 2: Effect of pH on the removal of Ni by cow hoof powder;  $T = 298$  K.

sites) than equal amount of the same adsorbent with higher particle size.

**3.2. Effect of pH.** Solution pH, out of all factors influencing adsorption of metals from solution, has been pointed out to play a major role in adsorption because it affects the solution chemistry of metals and the activity of the functional groups of the adsorbent (particularly biological adsorbents) [22]. The effect of pH on the removal of  $\text{Ni}^{2+}$  from aqueous solution is presented in Figure 2. It can be observed that the removal of nickel(II) ion increased with increase in pH and reached a maximum at pH 7. The percentage removal of Ni was observed to be sharp between pH 2 and pH 4 (from percentage removal of 42.8% to 86.22%), while the extent of removal was observed to be somehow slow between pH 4 and pH 7 (86.22%–89.69%). The sharp increase in nickel uptake between pH 2 and pH 4 cannot be explained by the change in metal speciation, since nickel will exist as free  $\text{Ni}^{2+}$  at pH between 2 and 4 and as such one would expect a very low uptake of  $\text{Ni}^{2+}$  at this region because of the competition that would exist between  $\text{H}^+$  and  $\text{Ni}^{2+}$  ions. Thus the ionic states of the functional groups present on the surface of CH can be used to explain the pH dependency of the removal of  $\text{Ni}^{2+}$  by CH. Meanwhile, it has been reported that biological materials primarily contain weak acidic and basic functional groups [23, 24]. Therefore, in the acidic pH range 2–4, the binding of heavy metal cations is determined primarily by the state of dissociation of the weak acidic groups, particularly, carboxyl groups ( $\text{COOH}$ ) which are the most important acidic groups for metal uptake by biological materials [23, 25]. The dissociation of this weak acidic functional group can be represented as follows [26]:



At low pH, the surface of the adsorbent is saturated with hydrogen ions; this causes the equilibrium to be shifted to the left, thereby decreasing the amount of  $\text{Ni}^{2+}$  adsorbed [26]. As the pH increases the number of hydrogen ions present decreases and this causes more  $\text{COO}^-$  ions to be exposed,

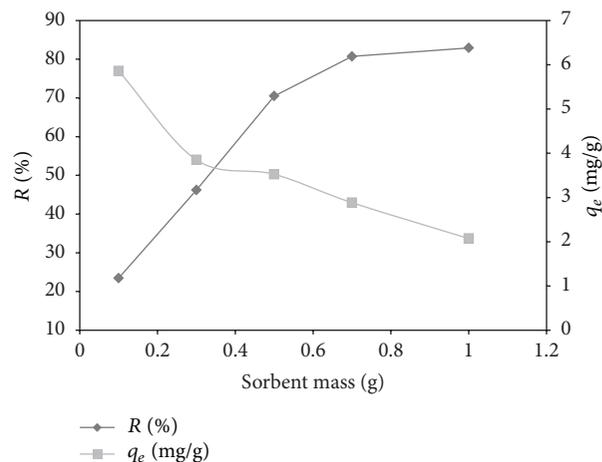


FIGURE 3: Effect of sorbent dosage on the removal of  $\text{Ni}^{2+}$  by cow hoof; pH = 2 and  $T = 298$  K.

thereby increasing the amount of  $\text{Ni}^{2+}$  adsorbed. Summarily, at low pH, the overall surface charge on the adsorbent (CH) became positive and this created a repulsive force between the positively charged Ni(II) ions and the CH surface. Maximum percentage removal of Ni(II) was observed at pH 7; therefore pH 7 was used for other experiments.

**3.3. Effect of Sorbent Dosage.** The influence of sorbent dosage on the percentage removal of Ni is illustrated in Figure 3. It reveals that increase in the amount of CH dosed brought about the increase in the percentage of Ni removed. The percentage of Ni removed from aqueous phase to the CH surface increased from 23.45 to 82.92% when the amount of CH dosed was increased from 0.1 to 1 g. The increase in the percentage Ni(II) adsorption with an increase in adsorbent concentration can be attributed to increase in the surface area of the adsorbent which in turn increased the number of binding sites. Conversely, uptake of Ni(II) per unit weight ( $q$ ) of CH decreased with increase in the concentration of CH dosed. The uptake capacity of Ni(II) decreased from 5.86 to 2.07  $\text{mg g}^{-1}$ , when the concentration of CH was increased from 0.1 to 1 g (Figure 3). This can be linked to the fact that the unchanging amount of solute is insufficient to completely cover the increasing available exchangeable sites on the adsorbent surface. Moreover, interferences could exist among the binding sites at high concentrations of the adsorbent [27, 28].

**3.4. Adsorption Kinetics.** Figure 4 presents the effect of contact time on the adsorption of Ni(II) by cow hoof powder. The optimum percentage (78.5%) adsorption was reached after 20 minutes of agitation. The figure reveals that adsorption of Ni on CH was rapid within the first 10 minutes and the process was brought to equilibrium after 20 minutes of agitation.

A lot of models have been used in the literature to quantitatively describe the kinetic behaviour of adsorption processes of biomaterials. Of these, pseudo-first-order (4)

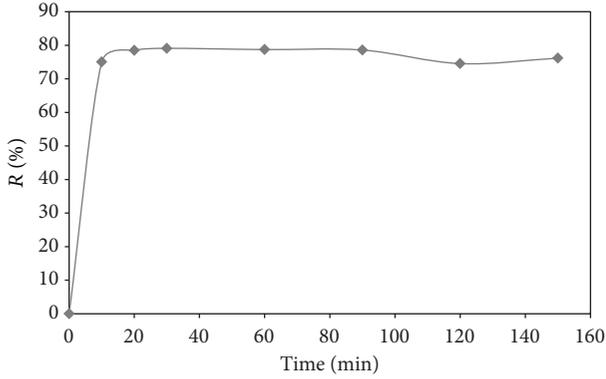


FIGURE 4: Effect of contact time on the percentage removal of  $\text{Ni}^{2+}$  by cow hoof.

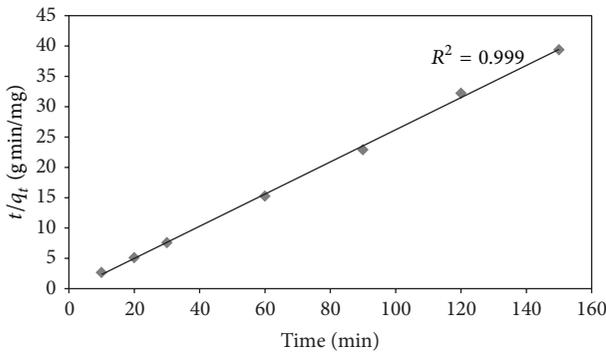


FIGURE 5: Pseudo-second-order kinetic plot for the removal of Ni(II) by CH.

and pseudo-second-order (5) models were used to describe the adsorption kinetic of the removal of Ni(II) by CH.

Consider

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}, \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (5)$$

where  $k_1$  is the rate constant for first-order equation ( $\text{min}^{-1}$ ),  $q_e$  is the amount of metal adsorbed at equilibrium ( $\text{mgg}^{-1}$ ),  $q_t$  is the amount of Ni(II) adsorbed at time  $t$  ( $\text{mgg}^{-1}$ ), and  $k_2$  is the second-order adsorption rate constant ( $\text{gmg}^{-1} \text{min}^{-1}$ ). The adsorption in this study data was well fitted by the pseudo-second-order model with correlation coefficient of 0.999 (Figure 5). The pseudo-first-order model could not describe these data because the process was brought to equilibrium within a short period of time.

**3.5. Adsorption Equilibrium.** The adsorption capacity of CH (at 298, 308, and 318 K) for Ni(II) removal was evaluated using the following two parameters adsorption isotherm models: Langmuir, Freundlich, and Dubinin-Radushkevich (D-R). The Langmuir isotherm is based on the assumption that metal

ions are adsorbed independently at a fixed number of well-defined energetically equivalent sites and that each site can only hold one ion [23]. It is then assumed that once a metal ion occupies a site, no further sorption can take place. This suggests that there is no migration or interaction between the adsorbed ions on the surface of the adsorbent [29]. This model can be expressed as

$$q = \frac{q_m K_L C_e}{1 + K_L C_e}. \quad (6)$$

This can be linearized to obtain

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}, \quad (7)$$

where  $q_m$  ( $\text{mgg}^{-1}$ ) is the maximum adsorption capacity and  $K_L$  ( $\text{Lmg}^{-1}$ ) is a constant related to the affinity of binding sites or bonding energy.

The Freundlich model which is based on the assumption that adsorption occurs on a heterogeneous surface can be expressed as

$$q_e = K_F C_e^{1/n}. \quad (8)$$

This can be linearized by taking the logarithm of both sides of the equation to give

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \quad (9)$$

where  $q_e$  ( $\text{mgg}^{-1}$ ) is the metal uptake at equilibrium,  $C_e$  ( $\text{mgL}^{-1}$ ) is the equilibrium concentration of the metal, and  $K_F$  and  $1/n$  are the Freundlich constants related to adsorption capacity and affinity between the adsorbent and the metal, respectively.

The Dubinin-Radushkevich (D-R) isotherm, which also assumes a heterogeneous surface, is expressed as follows:

$$q_e = q_D e^{-K_D \varepsilon^2}. \quad (10)$$

This can be linearized as

$$\ln q_e = \ln q_D - K_D \varepsilon^2, \quad (11)$$

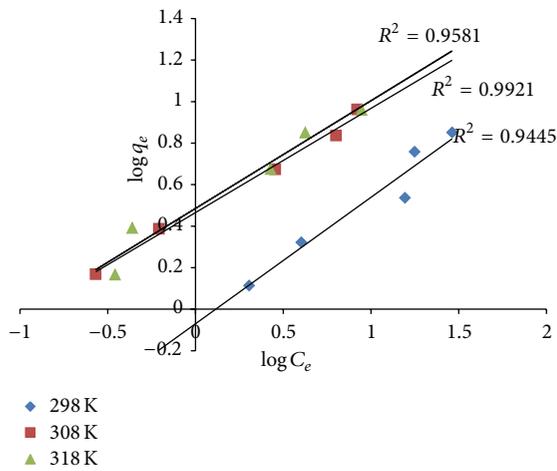
where  $\varepsilon$  is the Polanyi potential =  $RT \ln(1 + 1/C_e)$ ,  $q_D$  is the adsorption capacity of the adsorbent ( $\text{mgg}^{-1}$ ),  $K_D$  is a constant related to the adsorption energy ( $\text{mol}^2 \text{kJ}^{-2}$ ),  $R$  is the gas constant ( $\text{kJK}^{-1} \text{mol}^{-1}$ ), and  $T$  is the temperature (K). The mean adsorption energy can be determined from D-R model using the relationship

$$E = (-2K_D)^{-1/2}. \quad (12)$$

The maximum adsorption capacities, adsorption constants, and the correlation coefficients obtained for the three isotherm models at different temperatures are presented in Table 1. It follows from the table that the Freundlich isotherm model fitted the equilibrium data better than the Langmuir and D-R models at all temperatures (Table 1 and Figure 6).

TABLE 1: Isotherm parameters for the removal of Ni(II) by CH at different temperatures.

Isotherm	Parameter	Temperature (K)		
		298	308	318
Langmuir	$q_m$ (mgg <sup>-1</sup> )	10.23	10.57	11.24
	$K_L$ (Lmg <sup>-1</sup> )	0.0574	0.4188	0.4134
	$R^2$	0.6781	0.9230	0.9516
Freundlich	$K_F$ (L <sup>1/n</sup> g <sup>-1</sup> mg <sup>1/n</sup> )	0.8513	2.9187	3.059
	$n$	1.6425	1.992	1.9286
	$R^2$	0.9445	0.9921	0.9581
D-R	$q_D$ (mgg <sup>-1</sup> )	4.85	6.41	7.122
	$K_D$ (mol <sup>2</sup> KJ <sup>-2</sup> )	-1.4508	-0.1024	-0.1181
	$E$ (KJmol <sup>-1</sup> )	0.587	2.209	2.058
	$R^2$	0.7670	0.8488	0.9171

FIGURE 6: Freundlich isotherm plots for the removal of Ni using cow hoof; pH = 7,  $t = 30$  minutes, and sorbent mass = 0.5 g.

The maximum adsorption capacities ( $q_m$ ,  $K_f$ , and  $q_D$ ) for the three models increased with increase in temperature from 298 K to 318 K. This is an indication of endothermic process.

The Langmuir constant  $K_L$  explains the affinity between the adsorbent and the adsorbate in terms of a dimensionless parameter called separation factor  $R_L$ .  $R_L$  values can be obtained using

$$R_L = \frac{1}{1 + K_L C_o}, \quad (13)$$

where  $C_o$  is the initial concentration of metal (mgL<sup>-1</sup>) and  $K_L$  is Langmuir constant.

If  $R_L = 0$ , the adsorption process is irreversible, if  $0 < R_L < 1$ , the process is said to be favourable, and if  $R_L > 1$ , the process is unfavourable. The  $R_L$  values in this study are shown in Figure 7. The figure indicates that adsorption was favourable at all concentrations considered but more favourable at high Ni(II) concentrations (all  $R_L$  values are less than 1).

This implies that the removal of Ni(II) from aqueous solution increased when the concentration of Ni was increased

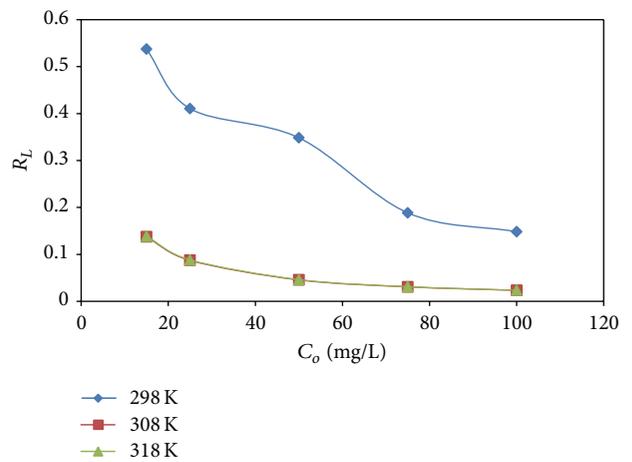


FIGURE 7: Separation factor plots for the removal Ni(II) by CH at different temperatures.

from 15 to 100 mgL<sup>-1</sup>. It can also be observed from the figure that the process was more favourable at high temperatures. This further supports the endothermic nature of the removal of Ni by CH. However, the extent of favourability seems to be insignificant when the temperature was increased from 308 to 318 K (Figure 7).

The Freundlich constant  $n$  can also be used to predict the favourability of the adsorption process [21, 30]. The values of  $n$  in this study are between 1 and 10 (Table 1). This is an indication of favourability of the process.

The Langmuir and Freundlich isotherm constants are useful in predicting the favourability of the removal of Ni(II) by CH but cannot explain the chemical or physical properties of the process. However, the mean adsorption energy ( $E$ ) calculated from the D-R isotherm can provide useful information about these properties [30]. An adsorption process is said to be dominated by physical adsorption if  $E < 8$  kJmol<sup>-1</sup> and by chemical adsorption if  $E > 8$  kJmol<sup>-1</sup> [30]. Therefore, the removal of Ni(II) by CH can be described to be dominated by physical adsorption at all temperatures (Table 1).

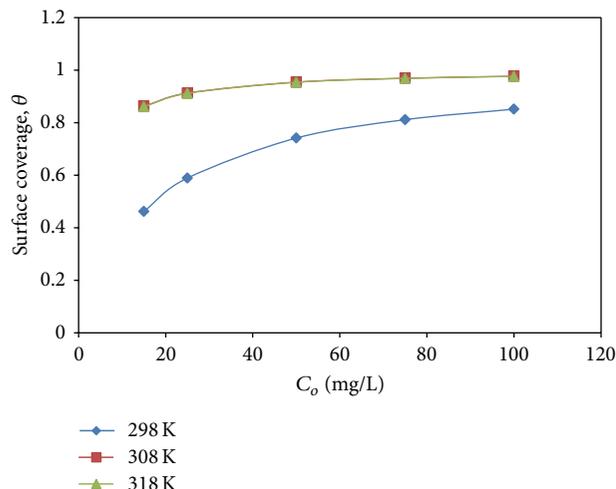


FIGURE 8: A plot of surface coverage against initial Ni(II) concentration.

3.6. *Surface Coverage ( $\theta$ )*. To account for the adsorption behaviour of Ni(II) ions on CH, the Langmuir type equation related to surface coverage was used. The equation is expressed as follows:

$$\frac{\theta}{(1 - \theta)} = K_L C_o, \quad (14)$$

where  $K_L$  is the Langmuir adsorption coefficient and  $C_o$  is the initial Ni(II) concentration ( $\text{mgL}^{-1}$ ). The values of the surface coverage ( $\theta$ ) at all temperatures considered were plotted against initial Ni(II) ions concentration (Figure 8). The figure shows that increase in initial metal ion concentration of nickel brought about increase in the surface coverage on the adsorbent (CH) until the surface was nearly fully covered with a monolayer (Figure 8).

Figure 8 also reveals that increase in temperature from 298 to 308 K increased the surface coverage, while surface coverage seemed to be independent of temperature when the temperature was increased from 308 to 318 K as the plots for both temperatures seem to overlap on each other.

3.7. *Adsorption Thermodynamics*. The changes in Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) for the adsorption process were obtained using the following equations:

$$K_e = \frac{C_{Ae}}{C_e}, \quad (15)$$

$$\ln K_e = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}, \quad (16)$$

$$\Delta G = \Delta H - T\Delta S, \quad (17)$$

where  $C_{Ae}$  is the concentration of Ni(II) ( $\text{mgL}^{-1}$ ) adsorbed at equilibrium,  $C_e$  is the equilibrium concentration of the metal in  $\text{mgL}^{-1}$ ,  $K_e$  is the equilibrium constant,  $T$  is temperature in Kelvin, and  $R$  is the gas constant ( $\text{kJmol}^{-1} \text{K}^{-1}$ ). The value of  $K_e$  can be obtained from the lowest experimental Ni concentration [31].

TABLE 2: Thermodynamic parameters for the removal of Ni by CH at different temperatures.

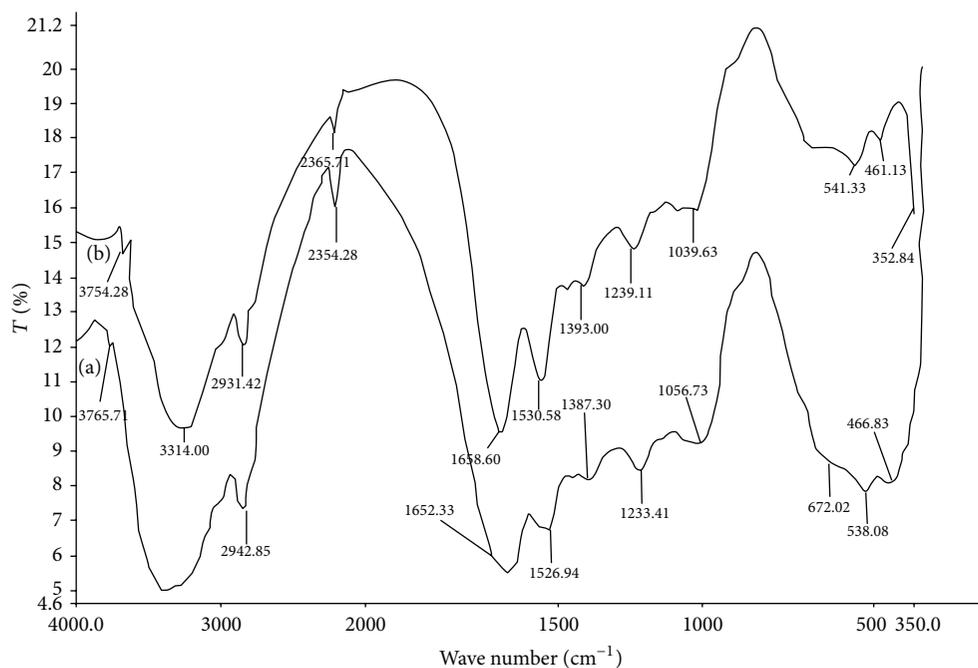
$T$ (K)	$\Delta G^\circ$ ( $\text{kJ mol}^{-1}$ )	$\Delta H^\circ$ ( $\text{kJ mol}^{-1}$ )	$\Delta S^\circ$ ( $\text{kJ mol}^{-1}$ )
298	-5.65	64.76	0.236
308	-8.01		
318	-10.37		

The values of the enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) were calculated from the slope and intercept of the plot of  $\ln K_e$  against  $1/T$  (15), while the values of  $\Delta G$  at different temperatures were obtained using (17). The results of these thermodynamic parameters are presented in Table 2. The negative values recorded for the Gibbs free energy at all temperatures are an indication that the adsorption process was spontaneous and that the degree of spontaneity of the reaction increased with increase in temperature. This coupled with the positive value of the enthalpy change further supports the earlier suggestions that the process was endothermic. The positive value of the entropy change also indicates that entropy increases as a result of adsorption. This occurs as a result of redistribution of energy between Ni(II) ions and the adsorbent. Before adsorption occurs, the heavy metal ions near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state [30].

3.8. *FTIR Analysis*. The FTIR analysis of CH was conducted before and after the adsorption of Ni(II) ions to determine the possible involvement of the functional groups present on CH surface in the adsorption process. The spectra obtained are presented in Figure 9. The spectroscopic characteristics of these spectra are shown in Table 3. A critical observation of Table 3 and Figure 9 shows that virtually all the absorption bands for these functional groups were shifted after adsorption of  $\text{Ni}^{2+}$ . Of all these shifts, five prominent peaks had a decrease in their absorption bands after adsorption of Ni(II) (Figure 9 and Table 3). These include absorption at 2365.71 ( $-\text{S}-\text{H}$ ), 1658.60 ( $-\text{C}=\text{O}$ ), 1530.58 (amino), 1393.00 (nitro compound), and 1239.11. It can be suggested that the functional groups corresponding to these bands played an important role in the adsorption of Ni(II). The involvement of these functional groups (particularly  $\text{C}=\text{O}$  and  $\text{S}-\text{H}$ ) in the removal of Zn and the high positive enthalpy of the process can make one assume that chemisorption took a prominent role in the removal of Ni(II) [26].

## 4. Conclusion

The removal of Ni(II) from simulated wastewater using cow hoof was conducted. Our results revealed that maximum removal of Ni at room temperature could be achieved within a period of 20 minutes and at pH 7. Thermodynamic parameters evaluated from this study showed that the adsorption process was endothermic and spontaneous at all temperatures considered. The kinetic modelling of the adsorption data suggested that chemisorption was the rate determining step since the data fitted well with pseudo-second-order



(a) Cow hoof after adsorption of  $\text{Ni}^{2+}$   
 (b) Cow hoof before adsorption

FIGURE 9: FTIR spectra of CH (a) after adsorption of  $\text{Ni}^{2+}$  and (b) before adsorption.

TABLE 3: FTIR spectral characteristics of CH before and after Ni (II) removal.

IR peak	Frequency ( $\text{cm}^{-1}$ ) before adsorption	Frequency ( $\text{cm}^{-1}$ ) after adsorption	Difference	Functional group
1	3314.00	—	—	Bonded -OH group
2	2931.42	2942.85	11.43	Aliphatic C-H groups
3	2365.71	2354.28	-11.43	S-H stretching
4	1658.60	1652.33	-6.27	C=O stretching
5	1530.58	1526.94	-3.64	Amino/nitro compound
6	1393.00	1387.30	-5.70	Nitro compound
7	1239.11	1233.41	-5.70	C-N stretching
8	1039.63	1056.73	17.10	C-O stretching

model. However the D-R isotherm model suggested that the removal of Ni from aqueous solution using cow hooves was dominated by physisorption. Therefore, it can be concluded that both physical and chemical adsorption played a prominent role in the adsorption process additionally when the enthalpy change for the process was high.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

### References

- [1] L. C. Ajjabi and L. Chouba, "Biosorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  from aqueous solutions by dried marine green macroalga *Chaetomorpha linum*," *Journal of Environmental Management*, vol. 90, no. 11, pp. 3485–3489, 2009.
- [2] I. Osasona, A. O. Adebayo, and O. O. Ajayi, "Biosorption of Pb (II) from aqueous solution using cow hooves: kinetics and thermodynamics," *ISRN Physical Chemistry*, vol. 2013, Article ID 171865, 8 pages, 2013.
- [3] V. Padmavathy, P. Vasudevan, and S. C. Dhingra, "Biosorption of nickel(II) ions on Baker's yeast," *Process Biochemistry*, vol. 38, no. 10, pp. 1389–1395, 2003.
- [4] P. Sujatha, V. Kalarani, and B. N. Kumar, "Effective biosorption of nickel (II) from Aqueous solution using *Trichoderma viride*," *Journal of Chemistry*, vol. 2013, Article ID 716098, 7 pages, 2013.
- [5] M. Sittling, *Toxic Metals—Pollution Control and Worker Protection*, Noyes Data Corporation, Park Ridge, NJ, USA, 1976.
- [6] Y. Kung and C. L. Drennan, "A role for nickel-iron cofactors in biological carbon monoxide and carbon dioxide utilization," *Current Opinion in Chemical Biology*, vol. 15, no. 2, pp. 276–283, 2011.
- [7] C. E. Borba, R. Guirardello, E. A. Silva, M. T. Veit, and C. R. G. Tavares, "Removal of nickel(II) ions from aqueous solution by biosorption in a fixed bed column: experimental and theoretical

- breakthrough curves," *Biochemical Engineering Journal*, vol. 30, no. 2, pp. 184–191, 2006.
- [8] A. K. Meena, G. K. Mishra, P. K. Rai, C. Rajagopal, and P. N. Nagar, "Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent," *Journal of Hazardous Materials*, vol. 122, no. 1-2, pp. 161–170, 2005.
- [9] H. D. Doan, J. Wu, and R. Mitzakov, "Combined electrochemical and biological treatment of industrial wastewater using porous electrodes," *Journal of Chemical Technology and Biotechnology*, vol. 81, no. 8, pp. 1398–1408, 2006.
- [10] World Health Organization, *Guidelines for Drinking-Water Quality, Incorporating First Addendum to Third Edition*, vol. 1, World Health Organization, Geneva, Switzerland, 3rd edition, 2006.
- [11] I. Mobasherpour, E. Salahi, and M. Pazouki, "Removal of nickel (II) from aqueous solutions by using nano-crystalline calcium hydroxyapatite," *Journal of Saudi Chemical Society*, vol. 15, no. 2, pp. 105–112, 2011.
- [12] M. A. Tofighy and T. Mohammadi, "Adsorption of divalent heavy metal ions from water using carbon nanotube sheets," *Journal of Hazardous Materials*, vol. 185, no. 1, pp. 140–147, 2011.
- [13] M. A. Khan, R. A. K. Rao, and M. Ajmal, "Heavy metal pollution and its control through nonconventional adsorbents (1998–2007): a review," *Journal of International Environmental Application and Science*, vol. 3, no. 2, pp. 101–141, 2008.
- [14] N. Kuyucak and B. Volesky, "Biosorbents for recovery of metals from industrial solutions," *Biotechnology Letters*, vol. 10, no. 2, pp. 137–142, 1988.
- [15] D. Sud, G. Mahajan, and M. P. Kaur, "Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions—a review," *Bioresource Technology*, vol. 99, no. 14, pp. 6017–6027, 2008.
- [16] P. E. Aikpokpodion, R. R. Ipinmoroti, and S. M. Omotoso, "Biosorption of nickel (II) from aqueous solution using waste tea (*Camellia cinensis*) materials," *The American-Eurasian Journal of Toxicological Sciences*, vol. 2, no. 2, pp. 72–82, 2010.
- [17] M. N. Zafar, R. Nadeem, and M. A. Hanif, "Biosorption of nickel from protonated rice bran," *Journal of Hazardous Materials*, vol. 143, no. 1-2, pp. 478–485, 2007.
- [18] H. Rehman, M. Shakirullah, I. Ahmad, S. Shah, and H. Hameedullah, "Sorption studies of nickel ions onto sawdust of *Dalbergia sissoo*," *Journal of the Chinese Chemical Society*, vol. 53, no. 5, pp. 1045–1052, 2006.
- [19] P. X. Sheng, Y.-P. Ting, J. P. Chen, and L. Hong, "Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms," *Journal of Colloid and Interface Science*, vol. 275, no. 1, pp. 131–141, 2004.
- [20] Z. Reddad, C. Gerente, Y. Andres, and P. Le Cloirec, "Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies," *Environmental Science and Technology*, vol. 36, no. 9, pp. 2067–2073, 2002.
- [21] K. Vijayaraghavan and Y.-S. Yun, "Bacterial biosorbents and biosorption," *Biotechnology Advances*, vol. 26, no. 3, pp. 266–291, 2008.
- [22] A. Esposito, F. Pagnanelli, and F. Vegliò, "pH-related equilibria models for biosorption in single metal systems," *Chemical Engineering Science*, vol. 57, no. 3, pp. 307–313, 2002.
- [23] L. Norton, K. Baskaran, and T. McKenzie, "Biosorption of zinc from aqueous solutions using biosolids," *Advances in Environmental Research*, vol. 8, no. 3-4, pp. 629–635, 2004.
- [24] M. Riaz, R. Nadeem, M. A. Hanif, T. M. Ansari, and K.-U. Rehman, "Pb(II) biosorption from hazardous aqueous streams using *Gossypium hirsutum* (Cotton) waste biomass," *Journal of Hazardous Materials*, vol. 161, no. 1, pp. 88–94, 2009.
- [25] K. H. Kok, M. I. A. Karim, A. Ariff, and S. A. Aziz, "Removal of cadmium, copper and lead from tertiary metals system using biomass of *Aspergillus flavus*," *Pakistan Journal of Biological Sciences*, vol. 5, no. 4, pp. 474–478, 2002.
- [26] I. Osasona, O. O. Ajayi, and A. O. Adebayo, "Equilibrium, kinetics and thermodynamics of the biosorption of Zn (II) from aqueous solution using powdered cow hooves," *ISRN Physical Chemistry*, vol. 2013, Article ID 865219, 7 pages, 2013.
- [27] J. Tangaromsuk, P. Pokethitiyook, M. Kruatrachue, and E. S. Upatham, "Cadmium biosorption by *Sphingomonas paucimobilis* biomass," *Bioresource Technology*, vol. 85, no. 1, pp. 103–105, 2002.
- [28] G. M. Gadd, P. R. Norris, and D. P. Kelly, "Heavy metal and radionuclide by fungi and yeasts," in *Biohydrometallurgy*, A. Rowe, Ed., Chippenham, Wilts, UK, 1988.
- [29] G. M. Gadd, "Heavy metal accumulation by bacteria and other microorganisms," *Experientia*, vol. 46, no. 8, pp. 834–840, 1990.
- [30] M. E. Argun, S. Dursun, C. Ozdemir, and M. Karatas, "Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics," *Journal of Hazardous Materials*, vol. 141, no. 1, pp. 77–85, 2007.
- [31] R. Han, W. Zou, W. Yu, S. Cheng, Y. Wang, and J. Shi, "Biosorption of methylene blue from aqueous solution by fallen phoenix tree's leaves," *Journal of Hazardous Materials*, vol. 141, no. 1, pp. 156–162, 2007.



**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

