Research Article

Equilibrium, Kinetics, and Thermodynamics of the Biosorption of Zn(II) from Aqueous Solution Using Powdered Cow Hooves

Ilesanmi Osasona,[1] Olubode O. Ajayi,[2] and Albert O. Adebayo[2]

[1] *Department of Chemical Sciences, Afe Babalola University, PMB 5454, Ado-Ekiti 360101, Nigeria*
[2] *Department of Chemistry, Federal University of Technology, PMB 704, Akure 340252, Nigeria*

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

The capability of cow hoof (CH) to remove Zn(II) from aqueous solution under the influence of sorbent size, solution pH, contact time, and sorbent dosage was investigated through batch studies. Equilibrium studies were conducted at three different temperatures (298, 308, and 318 K) by contacting different concentrations of Zn(II) solution with a known weight of cow hoof. The biosorption of Zn onto cow hoof was found to increase with increase in the mass of sorbent used while the biosorption efficiency was found to decrease with increase in sorbent particle size. The optimum conditions of pH 4 and contact time of 60 minutes were required for maximum removal of Zn(II) by cow hoof (mesh size 212 μm). The equilibrium data were modelled using Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models. The data were best fitted by Langmuir model. The kinetic data were analysed using Lagergren kinetic equations and these were well fitted by the pseudo-second-order kinetic model. The thermodynamic parameters showed that the biosorption process was feasible, spontaneous, and endothermic.

1. Introduction

Water is an essential life-sustaining natural resource and as such, its fitness for life sustenance should be constantly maintained and preserved. Unfortunately, heavy metals and other pollutants generated from different industrial and agricultural activities constantly put the purity and life-sustaining ability of this important natural resource under threat. The threat generated by the presence of heavy metals becomes particularly worrisome because of their nonbiodegradability, toxicity, persistency, and bioaccumulation tendency [1–3]. These metals have been implicated in causing health challenges such as accumulative poisoning, cancer, brain damage, lung damage, and hepatic and renal damage [4, 5]. Zinc is a trace element that is essential for human health. It is important for the physiological functions of living tissues and regulates many biochemical processes. But excessive ingestion of zinc, especially at levels of 100–500 mg/day, can bring about serious health problems, which include stomach cramps, skin irritations, vomiting, nausea, and anaemia [1, 6].

There are strict environmental regulations in most developed and developing countries with regard to contaminants discharged from industrial operations. This means that industries need to develop on-site or in-plant facilities to their own effluents and minimize the contaminant concentrations to acceptable limits prior to their discharge [7]. This necessity has seriously enhanced the demand for new technologies for metal removal from wastewater [8]. A number of technologies have been developed to remove toxic heavy metals from industrial wastewater. These include reduction and precipitation, coagulation, ion exchange, reverse osmosis, and evaporation. But most of these treatment technologies have their attendant limitations which include high chemical demand, high capital and operational cost, and generation of toxic sludge or other secondary wastes. In addition, these methods are ineffective at low metal concentrations, particularly in the range of 1–100 mg/L [9]. Therefore, there is a need for a cost effective treatment method that is capable of removing heavy metals from solution even at low metal concentrations.

Biosorption seems to be the answer to this important industrial demand based on the following advantages: low cost, good efficiency, minimization of chemical and biological sludge, regeneration of biosorbent, and possibility of metal recovery [10, 11]. Some of the biosobents that have been exploited for the removal of Zn from aqueous solution include marine green macroalga *Chaetomorpha linum* [1], biosolids [11], *Fontinalis antipyretica* [12], marine algal biomass [13], metal imprinted chitosan [14], dried animal bones [15], chitosan [16], maize cob and husk [17], Algerian sheep hoof [18], and waste tea leaves [19].

Cow hoof is an inedible spare part of cows which can be obtained free-of-charge from local abattoirs in Nigeria. Thousands of cow hooves are thrown into dumpsites in various abattoirs in Nigeria every day thereby constituting environmental nuisance. Cow hooves are known to contain an insoluble protein called keratin. The presence of keratin in cow hooves can enhance its biosorption capacity since amino and carboxylic functional groups have been identified as parts of the functional groups that are responsible for high metal removal efficiency of biomaterials [20]. Therefore, this study was targeted at investigating the feasibility of using cow hooves as a low-cost adsorbent for the removal of zinc from aqueous solution. The influence of pH, contact time, biosorbent particle size, biosorbent mass, and initial Zn(II) concentration on the biosorption property of cow hoof was also investigated. The equilibrium data obtained were analysed and modelled using Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models.

2. Experimental

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 sieve of mesh sizes 212 μm, 425 μm, and 850 μm. A stock solution containing 1000 mgL^{-1} of Zn(II) was prepared by dissolving 4.39 g of analytical grade $ZnSO_4 \cdot 7H_2O$ in a 1 L standard flask. This was made to mark with distilled water. Standard solutions of different concentrations were later prepared from this stock.

2.2. Biosorption Studies. Biosorption experiments were carried out through batch process in 150 mL conical flasks containing 50 mL Zn(II) solution using a thermostatic water bath shaker operated at a constant speed. The influence of pH and mass of CH on the biosorption process was investigated by equilibrating 0.5 g of CH (particle size of 212 μm) in a series of conical flasks, containing 50 mgL^{-1} of Zn(II) solution with pH ranging from 2.0 to 6.0 and with biosorbent mass ranging from 0.3 to 2.0 gL^{-1}, respectively. The effect of contact time and CH particle size on the removal of Zn(II) was conducted at different contact times ranging from 0 to 120 minutes and different particle sizes of 212 μm, 425 μm, and 850 μm, respectively, using 50 mgL^{-1} Zn(II) solution. All experiments were
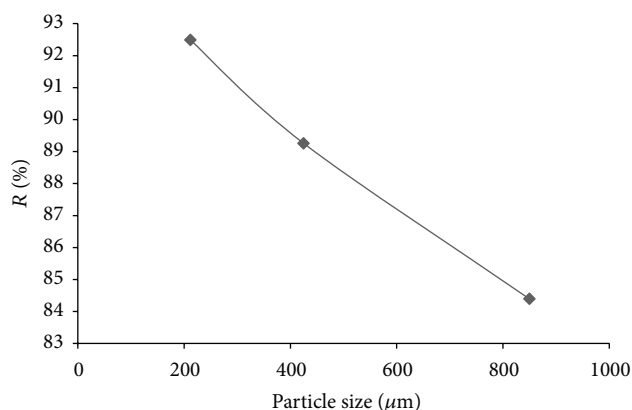

FIGURE 1: Effect of particle size on the sorption of zinc onto cow hoof.

carried out at 298 K. The mixture of the biosorbent and the solution was centrifuged after agitation and the concentration of metal ion present in the 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:

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

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 equilibrium concentration of the adsorbate in the liquid phase (mgL^{-1}), and q_e is the amount of metal adsorbed at equilibrium (mgg^{-1}). The percentage removal (%R) of zinc was calculated using the following expression:

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

2.3. Equilibrium Studies. Equilibrium isotherm studies were conducted by agitating 0.5 g (particle size of 212 μm) of CH with 50 mL of zinc solution of pH 2 for 30 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. Effect of Particle Size. The results of experiments conducted on the effect of particle size are summarized in Figure 1. The figure shows that percentage removal increased with decrease in particle size. This could be linked to the fact that equal quantity of a given biosorbent with different mesh sizes would present different numbers of binding sites. It is obvious that the smallest particle size will provide the highest number of active sites due to its high surface area because the larger the particle size, the smaller the surface area and the fewer the number of active sites present.

3.2. Effect of pH. The effect of pH on the biosorption of Zn(II) by cow hoof is presented in Figure 2. It is obvious from the
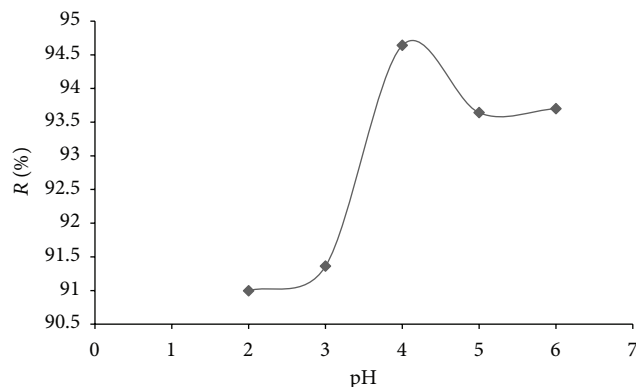
FIGURE 2: Effect of pH on the sorption removal of zinc by cow hoof.

FIGURE 3: Effect of contact time on the removal of zinc by cow hoof.

FIGURE 4: Effect of sorbent mass on the removal of zinc by cow hoof.

figure that the percentage removal of Zn^{2+} increased from 90.99 to 94.64% when the pH was raised from 2 to 4. The pH dependence of metal uptake can be related to the functional groups of the biosorbent and also to solution chemistry. At pH values less than 4 metals are in their free ionic form (Zn^{2+}) and as such the sharp increase in metal uptake between pH 2 and 4 cannot be described by the change in metal speciation [11, 21]. One would expect a very low metal uptake at this region because of the repulsive forces that exit between the H^+ and Zn^{2+} ions. This can make one assumes that the functional groups present on the surface of the biosorbent and their associated ionic state are responsible for this extent of biosorption.

Carboxyl groups (–COOH) are the important groups for metal uptake by biological materials [11, 21]. The dissociation of this acidic functional group can be represented as follows:

$$-COOH \longleftrightarrow COO^- + H^+ \qquad (3)$$
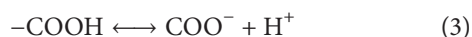
At low pH, there is high concentration of hydrogen ions; this shifts the equilibrium to the left, thereby decreasing the amount of Zn^{2+} biosorbed. Apart from this, there is a competition for the active site between the Zn^{2+} and H^+ at low pH values. But as the pH increases, the amount of hydrogen ions present will be decreased. This favours the production of more negative ions (i.e., COO^-) which enhances the biosorption of Zn^{2+}. At pH higher than 4 a decrease in the amount of zinc removed was noticed; this could be due to the formation of anionic hydroxide complexes and lower polarity of zinc ions at higher pH values [1, 21]. Literature reports have it that maximum uptake of Zn^{2+} for most biosorbents takes place between pH 4 and 5 [1, 11, 22].

3.3. Effect of Contact Time. The result for the effect of contact time on the removal of Zn by CH is presented in Figure 3. The result shows that the rate of metal removal occurred rapidly within the first 10 minutes of the biosorption process, and after this the process proceeded slowly. This indicates that most of the biosorption occurs on the surface rather than the pores of the cow hoof [23]. The figure also reveals that maximum uptake (94.5%) of zinc took place after 60 minutes
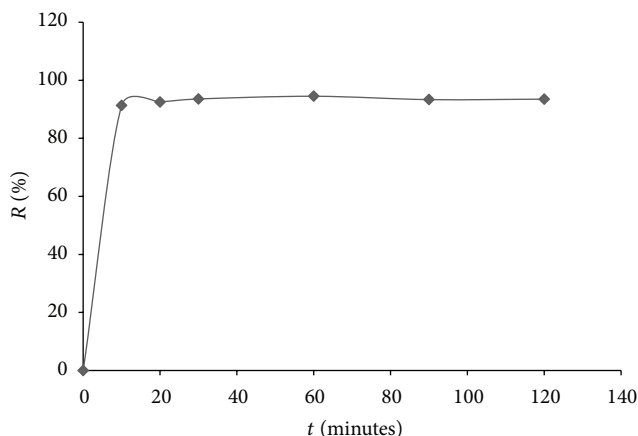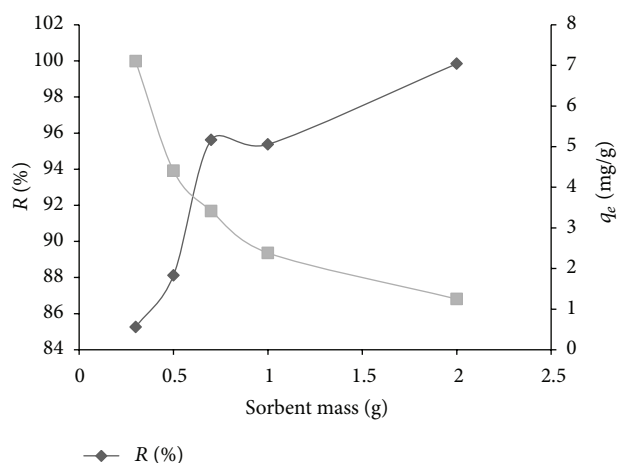
of agitation, beyond which there was no appreciable increase in the percentage removal of zinc; instead there was a small decrease in biosorption rate. This might be due to saturation of the biosorbent surface with zinc followed by adsorption and desorption after saturation [5].

3.4. Effect of Sorbent Mass. Figure 4 presents the results of the influence of mass of CH on the percentage removal and the amount of zinc biosorbed at equilibrium (mgg^{-1}). It is clear from the figure that the percentage of Zn^{2+} adsorbed increased gradually (from 85.26 to 98.84%) while the uptake capacity in mgg^{-1} decreased (from 7.1 to $1.25\,mgg^{-1}$) with increase in the mass of CH used. This may be due to increase in the number of binding sites available at high concentrations of the biosorbent.

3.5. Biosorption Kinetics. The biosorption kinetics of the removal of Zn^{2+} by cow hoof was analysed using Lagergren

TABLE 1: Kinetic parameters for the biosorption of zinc on CH.

Pseudo-first-order				Pseudo-second-order		
k_1 (min^{-1})	q_e (th) (mgg^{-1})	q_e (ex) (mgg^{-1})	R^2	k_2 (gmg^{-1} min^{-1})	q_e (th) (mgg^{-1})	R^2
−0.00713	0.108	4.725	0.4472	2.565	4.68	0.999
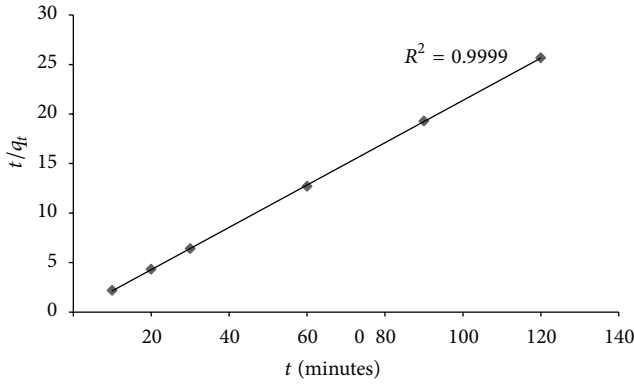
FIGURE 5: Second-order kinetic plot for the removal of zinc by cow hoof, T = 298 K, pH = 4, biosorbent mass = 0.5 g.

first-order and second-order kinetic equations represented by, respectively,

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

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

where k_1 = the rate constant for first-order equation (min^{-1}), q_e = the amount of metal biosorbed at equilibrium (mgg^{-1}), q_t = the amount of sorbate biosorbed at time t (mgg^{-1}), and k_2 is the second-order adsorption rate constant (gmg^{-1} min^{-1}). Straight line graphs were generated for the two equations and the kinetic parameters are listed in Table 1.

The value of the theoretical equilibrium uptake, q_e (th), and the experimental value q_e (ex) obtained for second-order equation are in good agreement (Table 1). This, coupled with the high correlation coefficient (Table 1 and Figure 5), indicates that the biosorption of zinc onto CH is better described by the second-order equation suggesting that chemisorption was the rate determining step.

3.6. Biosorption Isotherms. Several isotherm equations are available for equilibrium modelling of adsorption processes. In this study, Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models were used to analyse the equilibrium data obtained at 298, 308, and 318 K. The Langmuir equation assumes a monolayer adsorption in which all adsorbed ions do not interact with each other and once a metal ion occupies a site, no further adsorption can take place on that site. The model can take the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}, \tag{6}$$

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 bonding energy.

Both Freundlich and D-R isotherm models are based on the assumption that adsorption occurs on a heterogeneous surface. The Freundlich model can be expressed linearly as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e, \tag{7}$$

where q_e (mgg^{-1}) is the uptake at equilibrium concentration, C_e (mgL^{-1}), and K_f and $1/n$ are the Freundlich constants related to biosorption capacity and biosorption intensity, respectively. The Dubinin-Radushkevich isotherm can be expressed in the following linear form:

$$\ln q_e = \ln q_D - K_D \varepsilon^2, \tag{8}$$

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

$$E = \left(-2K_D\right)^{-1/2}. \tag{9}$$

The magnitude of the energy E is useful for estimating the type of adsorption. If this value is less than 8 kJ mol^{-1}, the adsorption process is said to be dominated by physical adsorption, between 8 and 16 kJ mol^{-1} the process is dominated by ion exchange, and if E is greater than 16 kJ mol^{-1} the adsorption process is dominated by a stronger chemical adsorption than ion exchange [5].

The biosorption constants and the correlation coefficients for the three isotherm models are presented in Table 2. The respective maximum adsorption capacities q_m, K_f, and q_D for these models increased from 10.93 to 11.58 mgg^{-1}, 4.095 to 7.58 L$^{1/n}$ g^{-1} mg$^{-1/n}$, and 7.35 to 11.19 mgg^{-1} when the system temperature was increased from 298 K to 318 K. This observation indicates that the biosorption process is endothermic. This may be due to the mobility of molecules which increases generally with increase in temperature [24]. The mean biosorption energies computed from D-R model (Table 2) at all temperatures reveal that physisorption dominated the biosorption of zinc on CH, since all values of E are less than 8. This clearly shows that other biosorption mechanisms may be involved in the removal of Zn by CH since kinetic modeling has earlier revealed chemisorption to be the rate determining step.

The R^2 values for the three models clearly show that Langmuir model described the biosorption process better than the two other models especially at all temperatures.
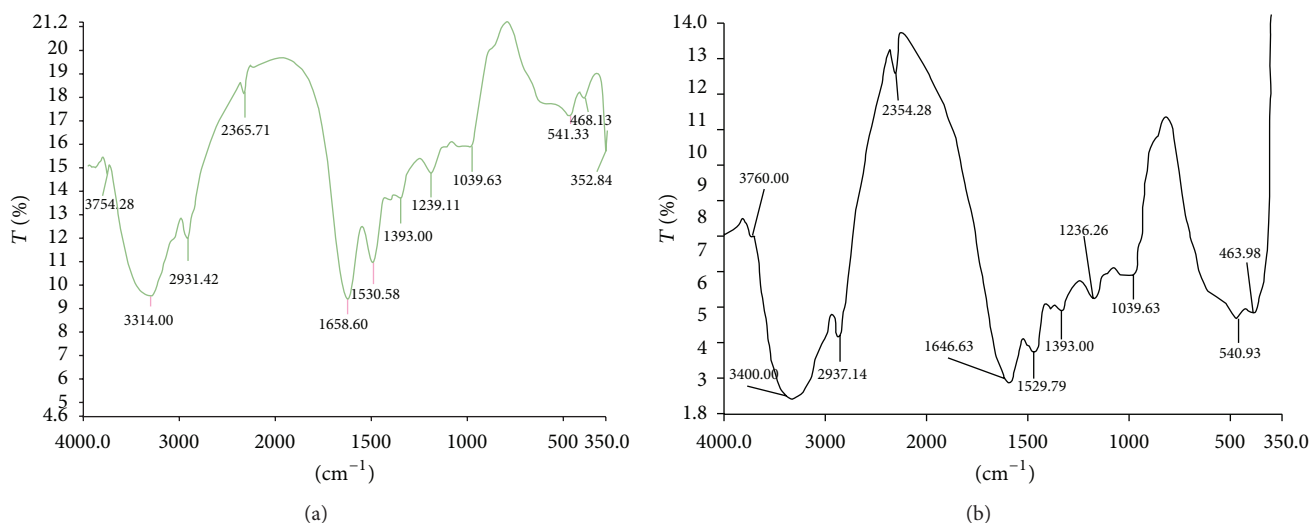
(a)

(b)

FIGURE 6: FTIR spectra of (a) unloaded CH and (b) Zn^{2+} loaded CH.

TABLE 2: Isotherm parameters for the removal of Zn(II) by CH at different temperatures.

Isotherm	Parameter	Temperature (K)		
		298	308	318
Langmuir	q_m (mgg^{-1})	10.93	11.53	11.58
	K_L (Lmg^{-1})	0.776	2.121	2.181
	R^2	0.9495	0.9774	0.9637
Freundlich	K_f (L$^{1/n}$ g^{-1} mg$^{-1/n}$)	4.095	7.413	7.58
	n	2.056	1.868	1.889
	R^2	0.9014	0.7828	0.7617
D-R	q_D (mgg^{-1})	7.35	11.05	11.19
	K_D (moL^2 KJ^{-2})	−0.0755	−0.0574	−0.0491
	E (KJ moL^{-1})	2.57	2.951	3.191
	R^2	0.8112	0.9766	0.9441

TABLE 3: Thermodynamic parameters for the biosorption of Zn onto CH at different temperatures.

T (K)	ΔG^0 (kJ moL^{-1})	ΔH^0 (kJ moL^{-1})	ΔS^0 (J moL^{-1})
298	−10.14	42.792	177.61
308	−11.912		
318	−13.687		

plot of $\ln K_e$ against $1/T$ while the values of ΔG^0 at different temperatures were determined using the equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0. \tag{12}$$

The values of the different thermodynamic parameters are listed in Table 3. The negative value of ΔG^0 is an indication that the process was feasible and spontaneous while the enthalpy of the process confirms the endothermic nature of the biosorption process. The positive value of ΔS^0 indicates that there is an increase in the randomness in the system solid/solution interface during the biosorption process. This further indicates that cow hoof has a great affinity for Zn^{2+} ions and there are some structural changes at Zn and CH interface [25].

3.8. FTIR Analysis.
The interaction between zinc and the active functional groups on the surface of CH was studied using FTIR spectroscopic analysis. The FTIR spectrum of cow hoof is shown in Figure 6(a) and a list of the major functional groups on the adsorbent surface before and after Zn biosorption is shown in Table 4. The following functional groups could be easily identified on the surface of CH: carbonyl, hydroxyl, amine, amide, aliphatic C–H groups, and so forth. Some of the absorption bands for these functional groups were shifted while others were retained after the biosorption of Zn^{2+}. Three prominent bands decrease of functional group can be identified on the cow hoof surface

3.7. Biosorption Thermodynamics.
The equilibrium amount of Zn adsorbed onto the cow hoof at different temperatures was examined to obtain thermodynamic parameters such as Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0). These were calculated using the following expressions:

$$K_e = \frac{C_{Ae}}{C_e}, \tag{10}$$

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

where K_e is the equilibrium constant, C_e is the equilibrium metal ion concentration in solution (mgL^{-1}), C_{Ae} is the amount of metal ions adsorbed on the biosorbent at equilibrium (mgL^{-1}), T is temperature in Kelvin, and R is the gas constant (JmoL^{-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

TABLE 4: FTIR spectral characteristics of CH before and after Zn(II) biosorption.

IR peak	Frequency (cm^{-1}) before adsorption	Frequency (cm^{-1}) after adsorption	Difference	Functional group
1	3314.00	3400	86	Bonded –OH group
2	2931.42	2937.14	5.72	Aliphatic C–H groups
3	2365.71	2354.28	−11.43	S–H stretching
4	1658.60	1646.63	−11.37	C=O stretching
5	1530.58	1529.79	−0.79	Amino/nitro compound
6	1393.00	1393.100	0	Nitro compound
7	1239.11	1236.26	−2.85	C–N stretching
8	1039.63	1039.63	0	C–O stretching

after biosorption (Figure 6 and Table 4) at 2365.71 (−S–H), 1658.6 (−C=O), and 1530.58 (amino). This is an indication of the possible involvement of these three functional groups in the biosorption of Zn onto CH. In comparing the involvement of these functional groups (particularly C=O and S–H) in the biosorption of Zn and the high positive enthalpy of the process, one can assume that chemisorption took a prominent role in the removal of Zn(II). Therefore, the biosorption of Zn(II) by powdered cow hooves can be described by both physical and chemical adsorption since the mean energy evaluated from the D-R isotherm model had earlier suggested that the removal of Zn from aqueous solution using cow hooves was dominated by physisorption.

4. Conclusions

The biosorption of Zn^{2+} on cow hoof was found to be influenced by the different parameters considered. The maximum uptake of Zn^{2+} occurred under the following conditions: pH of 4, particle size 212 μm, contact time of 60 minutes and biosorbent mass of 2 g. It has been observed that C=O and S–H functional groups present on the surface of the biosorbent were involved in the removal of zinc ions from aqueous solution. The biosorption process was feasible, spontaneous, and endothermic in nature while the kinetic parameters obviously revealed that the biosorption process followed the pseudo-second-order kinetic model.

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