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Cow hoof as a low-cost adsorbent for comparative removal of cadmium and copper from simulated and industrial wastewater

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Abstract : Cow hoof was exploited as an adsorbent for removing Cd(II) and Cu(II) from aqueous solution through batch experiments. The optimum conditions established were applied to industrial wastewater. The removal efficiencies of this low-cost adsorbent recorded for aqueous solution were higher than those recorded for real industrial wastewater. The data obtained were best described by the pseudo-second-order kinetic equation. Equilibrium studies conducted at different temperatures were best described by Langmuir (Cd) while data obtained for Cu obeyed both Freundlichmodel. Evaluated thermodynamic parameters of the process showed that Cd(II) and Cu(II) removal was spontaneous and endothermic. Therefore, the use of cow hoof as a low-cost adsorbent to remove Cd(II) and Cu(II) from wastewater is feasible.

Keywords : Equilibrium studies; Thermodynamic parameters; Cow hoof powder; Cadmium.

INTRODUCTION

Metals are extensivelyused in several industries, including mining, metallurgical,electronic, electroplating and metal finishing. The presence ofmetal ions in final industrial effluents is extremely undesirable, asthey are toxic to both lower and higher organisms[1]. The presence of these metals in the environment has become a matter of public concern because of their persistence and bioaccumulation tendencies. Cadmium is one of the most toxic heavy metals. It is chiefly generated and introduced into the environment through industrial activities like metal plating,mining, manufacture of Cd–Ni batteries, and production of phosphate fertilizer, pigments, stabilizers and alloys[2]. Cd (II) has been implicated in causing different human disorders like irritation to the respiratory tract, renal dysfunction, bone degeneration, liver damage, anemia, tooth decay, high blood pressure, kidney damage and destruction of testicular tissue and redblood cells etc.[2-5]. The evidence of carcinogenicity of cadmium and cadmium compounds in humans has been reported[5]. Copper is an essential trace metal which is not as toxic as cadmium but its continuous industrial application and accumulation in the environment could be detrimental to animal and human health. It has also been reported that copper is toxicto a variety of aquatic organisms, even at very low concentration[4].

In view of the environmental and health implications of heavy metals, most industrialisedcountries have introduced strict environmental regulationsto regulate the amount of these metals and other contaminants being discharged into the environment from industrial activities. This development has made most industries develop/adopt some methods of treating their wastewaters so as to reduce the concentrations of metals in them to acceptable levels beforedischarge into the environment. However, most of these methods are inefficient, cumbersome, not environmentally friendly or capital intensive. Adsorption using low cost adsorbent has proved to be a better alternative to this important industrial demand. Some recently utilized low-cost adsorbents with high metal removal efficiency include: *Opuntiaficusindica*[6], coconut tree sawdust[7], eggshell[7], sugarcane bagasse[7],*Chaetomorphalinum*[8], cotton waste[9], acid treated cashew nut shell[10], modified oak saw dust[11], modified chitosan[12, 13], alkali treated tea residue[14], carbonaceous adsorbents[15], etc.

Cow hoof, a keratin containing inedible by-product from cows, can be obtained freely from local abattoirs in Nigeria. The presence ofCOOH and NH_2 on the surface of cow hoof can enhance the capability of cow hoof as a low-cost adsorbent.

This study was undertaken to investigate the feasibility of using cow hoof as an adsorbent for removing cadmium and copper from aqueous solution and to determine the effect of different parameters (pH, contact time, temperature) on the adsorption efficiency of cow hoof. The optimum conditions obtained for metal removal were also applied to treat wastewaters obtained from two industries in Nigeria. The kinetic, equilibrium isotherm and thermodynamic parameters of the process were also determined.

MATERIALS AND METHODS

Materials

Cow hooves were obtained from a local abattoir in Ado-Ekiti, dried, ground and sieved using a sieve of mesh size 212µm. The hooves were thoroughly washed with sponge. These were later rinsed thoroughly with distilled water and sun dried for one month. After sun drying, the hooves were again washed with distilledwater and dried in an oven maintained at a temperature of 105^0 C. The oven dried hooves were later ground and sieved using sieve of mesh size 212 µm. The sieved samples were stored in a refrigerator prior to analysis.

Preparation of metal ions solutions

A stocksolution containing 1000 mgL^{-1} of each metal was prepared separately by dissolving appropriate weight of analytical grade salt of each metal ($Cd(NO_3)_2$.4H2O) and ($CuSO_4.5H_2O$) with distilled water in a 1 L standard flask. This was made to mark with distilled water. Standard solutions of different concentrations, as might be required, were later prepared from these stocks.

General procedure for batch studies

Unless otherwise stated, batch adsorption studies were carried out at room temperaturefor 1 h using 0.5g per 50mL of 50 mg/L metal solution. The mixture of each metal solution and cow hoof powder was agitated at a constant speed of 120 rpm. The effect of pH on the removal of Cd and Cu was conducted byvarying the initial solution pH from 2 to 6. The pH of each solution was adjusted using 0.1M HCl or 0.1M NaOH. The pH of maximum metal removal was noted and other subsequent experiments were performed at this pH. The influence of contact time was investigated by agitating a mixture of cow hoof and metalsolution for a period of time ranging from zero to 150 minutes. The range of 0.1-1.0g of cow hoof was used to investigate the effect of sorbent mass. Experiments on the effects of concentration and temperature were performed by varying the initial concentration of the metal concernedfrom 15 to 100 ppm at four different temperatures of 298, 308, 318 and 328 K. Each experiment in this case was conducted for 2 h for attainability of equilibrium.

The resultant mixture was filtered at the end of each agitation and the concentration metal present in the resultant filtrate was determined using Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 presents the results of the effect of pH on the removal efficiency of $Cd^{2+}$and Cu^{2+}. The figure reveals that the percentage of metal removed increased from 95.08- 99.48% for Cd^{2+} and from 66 – 95.92% for Cu^{2+} when the pH was increased from 2 to 6. This trend can be explained based on the fact that the surface of the adsorbent (cow hoof) is saturated with hydrogen ions at low pH and with hydroxyl ions at high pH. The amount of Cd^{2+} and Cu^{2+} adsorbed at low pH was low because of the competition that existedfor the available binding sites between hydrogen ions and the metal ions(Cd^{2+} andCu^{2+}).

Similarly, repulsive forces between the metal ions and hydrogen ions could have decreased the amount of metal adsorbed at low pH. At high pH the concentration of H^+ ions would be low. This enhanced the amount of Cd^{2+} and Cu^{2+}adsorbed. The percentage of cadmium and copper adsorbed increased gradually with increase in pH until the pH of 4 and 5 respectively where increase in pH seemed not to give an appreciable increase in the percentage of metal adsorbed. These results are in close agreement with literature reports[16, 17]. Thus, the removal of Cd and Cu by cow hoof can be maximized at a pH of 4 and 5 respectively. This pH of maximum removal of each metal was used for subsequent experiments.

The results of the effect of contact time on the removal of Cd^{2+} and Cu^{2+} are presented in Figure 2. The figure clearly shows that the amount of $Cd^{2+}$and Cu^{2+} adsorbed increased with increase in contact time until equilibrium was established after agitation time of 60 minutes. It is obvious from the figure that three distinct stages were involved in the removal of these metals from aqueous solution by cow hoof. The first five minutes of metal removal in each case was rapid. This can be basically explained by the fact that the number of binding sites available at the beginning is higher thanthose present at any other stage of the process. This was followed by a region of steady increase in the amount of metal adsorbed. This occurred between the agitation time of 5 and 60 minutes (Figure 2). The third stage, agitation period of 60 minutes and beyond, was characterized with negligible or no increase in the amount of metal adsorbed. This occurred basically because there is a limit to the amount of metal a given mass of an adsorbent can adsorbed at a constant temperature. In other words, at a period of time above 60 minutes, the surface of the adsorbent (cow hoof) has

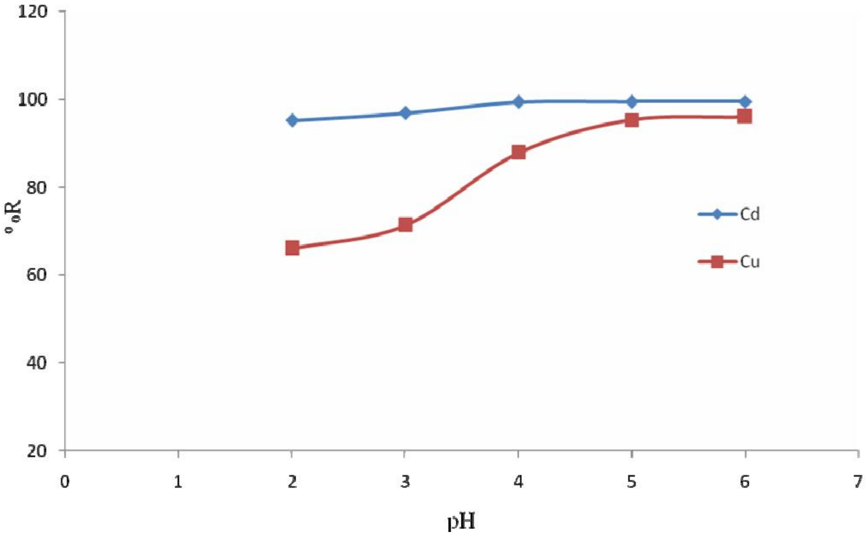

Figure 1 : Effect of pH on the removal of cadmium and copper by cow hoofcladodes: C_0= 50 mg/L, particle size 212 µm, sorbent mass = 0.5 g, contact time = 60 min, andtemperature = 298 K

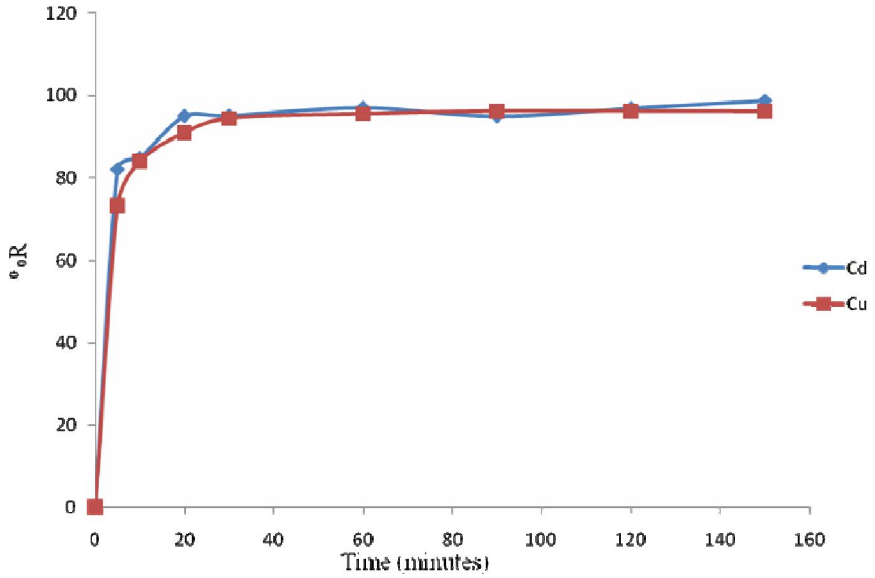

Figure 2 : Effect of agitation time on the adsorption of Cd and Cu by cow hoof:C_0 = 50 mg/L, particle size 212 µm, sorbent mass = 0.5 g, temperature = 298 K and pH = 4(Cd); 5 (Cu)

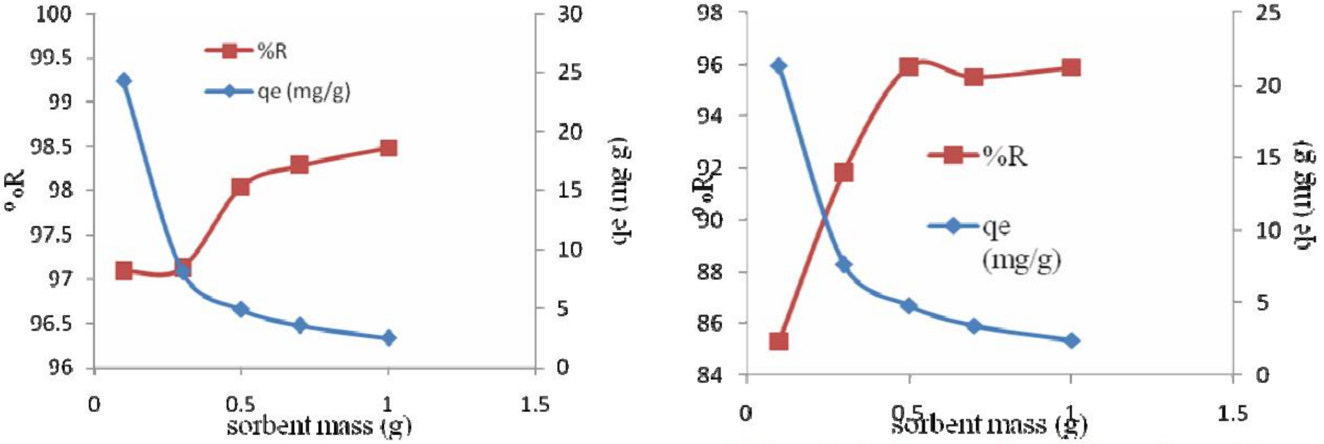

Figure 3 : Effect of sorbent mass on the adsorption of Cd and Cu by cow hoof: C_0 = 50 mg/L, particle size 212 µm, contact time = 60 minutes, temperature = 298 K and pH = 4(Cd); 5 (Cu)

been saturated with maximum amount of solute (Cu and Cd in each case).

Figure 3 displays the results of the effect of sorbent mass on the removal of cadmium and copper from aqueous solution by cow hoof. The percentage removal of both $Cd^{2+}$and Cu^{2+}increases with increase in the amount of cow hoof dosed. This can be attributed to the fact that number of binding sites increases as the amount of cow hoof dosed increases. The percentage removal of Cd^{2+} increased from 97.08 - 98.48% when the amount of cow hoof dosed increase from 0.1 – 1 g (Figure 3a). For copper, the percentage removal increased from 85.28 – 95.88% (Figure 3b) within the same range of cow hoof dosage. Conversely, the values of metal uptake obtained in mgg^{-1}for the two metals decreased with increase in biosorbent dosage. The uptake capacity of Cd(II) and Cu (II) decreased from 24.27-2.46mgg^{Š1} (Figure 3a) and 21.32 –2.39 mgg^{-1}(Figure 3b) when the amount of adsorbent was increased from 0.1 to 1 g. This may be due to interferences among the binding sites at high concentrations of adsorbent which can be caused by over-crowding of the adsorbent particles[15].

Adsorption isotherms

Adsorption isotherms express the mathematical relationship between thequantity of adsorbate and equilibrium concentration of adsorbateremaining in the solution at a constant temperature[3]. The equilibrium data generated using different concentration of metal solution at different temperaturesof 298, 308, 318 and 328 K were modelled using three isotherm models namely: Langmuir, Freundlich and Dubinin Raduskevish (D-R).

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 sorption can take place on that site. The model can take the following linear form**[18]**:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (1)$$

where, q_m (mgg^{-1}) is the maximum adsorption capacity, K_L(L/mg) is a constant related to the affinity of binding sites orbonding energy. Plots of Ce/qe against Ce were made for different temperatures and therespective values of $q_m$and K_L were obtained from the slope and intercept of the plots.

The empirical Freundlich isotherm,which is based on adsorptionon a heterogeneous surface, can be expressed linearly as follows**[19]**:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (2)$$

Where K_F($L^{1/2}g^{-1}mg^{-1/n}$) and n (dimensionless) are the Freundlichconstantsrelated to adsorption capacity and affinity between the adsorbent and the metal, respectively. The respective values of n and $K_F$were obtained from the slope and intercept of the linear plots of log qe versus log Ce.

The Dubinin–Radushkevich (D–R) isotherm**[20]**, whichassumes a heterogeneous surface, is expressed as follows:

$$\mathbf{\ln q_e = \ln q_D - K_D \varepsilon^2} \qquad (3)$$

Where ε is the Polanyi potential = RT ln(1 + 1/Ce), q_D is the DubininRaduskevich adsorption capacity of the adsorbent (mgg^{-1}), K_D is DubininRaduskevich constant relating to the adsorption energy (mol^2 kJ^{Š2}), R is the gas constant (kJK^{Š1} mol^{Š1}), and T is the temperature (K). Linear plots of ln qe versus ε^2 were obtained for different temperatures and the values of K_D and $q_D$were evaluated from the slope and intercept respectively. The values of the isotherm constants and the coefficient of determination(R^2) values associated with each isotherm model are given in TABLE 1. It is obvious from these tables that equilibrium data were best fitted by Langmuir model for Cd (II) while the data obtained for Cu (II) were best described by Freundlichmodel. The high values of coefficient of determination (R^2 = 0.9943- 0.9975) obtained from Langmuir model for Cd (II) confirms the monolayer adsorptionof Cd (II) onto the cow hoof surface. All the models revealed that the maximum adsorption capacity of Cd^{2+} adsorbed increased with increase in temperature.

The values of the maximum adsorption capacity obtained for cow hoof compare favourably with those reported in literature for some low-cost adsorbents (TABLES 2a and 2b).

The separation factor,R_L, which is a measure of adsorption favourability, was obtained from the Langmuir constant $K_L$using Equation 4 below:

$$R_L = \frac{1}{1 + K_L C_o} \qquad (4)$$

Where C_o is the initial concentration of metal (mgL^{-1}). The values of R_L obtained for Cd (II) and Cu (II) are presented in TABLE 3. The values of $R_L$ranged from 0.004 to 0.035 for Cd (II)and from 0.125 to

TABLE 1 : Isotherm parameters for the removal of Cd^{2+} by cow hoof

Metal	T (K)	Langmuir			Freunlich			DR		
		q_m (mgg^{-1})	K_L (Lmg^{-1})	R^2	K_f ($L^{1/2}g^{-1}mg^{-1/n}$)	n	R^2	q_D (mgg^{-1})	E (kJ)	R^2
Cd	298	8.63	1.83	0.9943	3.89	3.13	0.8375	7.34	2.96	0.9695
	308	9.03	1.69	0.9975	4.44	3.05	0.8442	8.01	3.31	0.9857
	318	9.30	2.38	0.9956	4.93	3.07	0.8645	8.20	3.79	0.9802
	328	9.51	2.65	0.9945	5.26	3.04	0.8466	8.33	4.11	0.9316
Cu	298	9.30	0.02	0.8070	0.24	1.34	0.9784	3.5	0.21	0.8653
	308	10.6	0.02	0.7188	0.28	1.24	0.9217	4.48	0.23	0.9089
	318	9.13	0.04	0.8463	0.50	1.42	0.8868	4.76	0.35	0.8295
	328	15.13	0.03	0.9620	0.64	1.32	0.9963	5.46	0.25	0.8657

0.711 for Cu (II). This confirms the favourability of the adsorption of Cd (II) and Cu(II) by cow hoof since ($0 < R_L < 1$). Similarly, the values of Freundlich constant n, which fell within the range 1<n<10 also shows that the affinity between the metal ions and cow hoof was high.

The values of adsorption energy, E evaluated from the D-R model (Equation 5) shows that the adsorption of both Cd (II) and Cu (II) was dominated by physical adsorption since E values are less than 8 kJ (TABLE 1).

$$E = (-2K_D)^{-1/2} \qquad (5)$$

Adsorption kinetics

The adsorption kinetics of Cd(II) and Cu(II) were modelled using pseudo-first order (equation 6), pseudo-second order (equation 7) and Elovich kinetic equations (equation 8). The linear forms of these equations are presented below.

$$Log(q_e - q_t) = L\,og\,q_e - \frac{k_1 t}{2.303} \qquad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{2}} + \frac{1}{q_e} t \qquad (7)$$

TABLE 2a: Comparison of maximum adsorption capacity (q_m) estimated from Langmuir isotherm model for Cd (II) with that of other biosorbents

Biosorbent	Temperature (K)	q_m (mgg^{-1})	Reference
Sea weeds: *Padina sp.*	295	84	[4]
Sargassum sp.	295	85.12	
Ulva sp.	295	64.96	
Gracillaria sp.	295	33.6	
Acid treated cashew nut	303	436.7	[10]
Pseudomonas putida	NA	8.0	[21]
Waste tea	NA	1.63	[22]
Walnut shell	NA	1.5	[22]
Nut shell	NA	1.3	[22]
Exhausted coffee	NA	1.48	[22]
Rice husk ash	NA	20.24	[23]
Tea factory waste	298	20	[24]
Cow hoof	328	9.51	Current study

TABLE 2b : Comparison of maximum adsorption capacity (q_m) estimated from Langmuir isotherm model for Cu (II) with that of other biosorbents

Biosorbent	Temperature (K)	q_m (mgg^{-1})	Reference
Sea weeds:*Padina sp.*	295	72.39	[4]
Sargassum sp.	295	62.87	
Ulva sp.	295	47.63	
Gracillaria sp.	295	37.47	
Coco nut tree saw dust	NA	3.89	[7]
Egg shell	NA	34.48	[7]
Sugarcane bagasse	NA	3.65	[7]
Modified chitosan	298	12.6	[12]
Modified chitosan	NA	19.8	[13]
Pseudomonas putida	NA	6.6	[21]
Tea factory waste	298	6.13	[24]
Enterobactersp. J1	298	32.5	[25]
Bacillus sp. (ATS-1)	298	16.6	[26]
CH	328	15.13	Current study

TABLE 3 : Separation factor (RL) values for cadmium ion sorbed on modified and unmodified cow hoof

Sample	Co (mg/L)	298 K	308 K	318 K	328 K
Cd^{2+}	15	0.035	0.034	0.027	0.025
	25	0.021	0.021	0.017	0.015
	50	0.012	0.010	0.008	0.007
	75	0.007	0.007	0.006	0.005
	100	0.005	0.005	0.004	0.004
Cu^{2+}	15	0.488	0.690	0.649	0.711
	25	0.364	0.571	0.526	0.597
	50	0.222	0.400	0.357	0.425
	75	0.160	0.308	0.270	0.330
	100	0.125	0.250	0.217	0.270

TABLE 4 : Kinetic parameters for the removal of CdandCu^{2+}by cow hoof at 298 K

	Pseudo-first- order				Pseudo-second- order			Elovich		
Metal	q_e(exp) (mg/g)	q_e(cal) (mg/g)	k_1 (min^{-1})	R^2	q_e(cal) (mg/g)	k_2	R^2	α(gmg$^{?1}$)	B (mgg$^{?1}$h$^{?1}$)	R^2
Cd^{2+}	4.85	1.17	0.09	0.8613	4.85 - 3.277 0.9993	0.28	0.9993	18836636	4.72	0.7716
Cu^{2+}	4.78	2.03	0.12	0.9915	4.87	0.16	1	24255	3.27	0.8194

TABLE 5 : Thermodynamic parameters for the adsorption of Cd and Cu by cow hoof

Sample	T (K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0(kJmol^{-1}K^{-1})
Cd	298	- 11.04	19.59	0.104
	308	-12.42		
	318	-13.48		
	328	-14.52		
Cu	298	-0.47	35.89	0.122
	308	-1.68		
	318	-2.91		
	328	-4.13		

Where $q_t$is the metal uptake per unit weight of cow hoof (mg g^{-1}) at time t, q_e is the metal uptake per unit weight of ofcow hoof(mg g^{-1}) at equilibrium, and k_1 (min^{-1}) and k_2 (g mg^{-1}min$^{”1}$)are the rate constants of the pseudo-first-order and pseudo-second-order kinetic equations respectively. The values of k_1 and its corresponding q_e values were respectively determined from the slope and intercept oftheplotof log q_e–$q_t$versus time (Equation 8). While $k_2$and its corresponding qe values were respectively determined from the intercept and slope of the plot of t/q_t versus time(Equation9).

$$q_t = \frac{1}{\beta}\ln \alpha\beta + \frac{1}{\beta}\ln t \qquad \textbf{(8)}$$

where, β (mg g^{-1} min^{-1}) is the initial adsorption rate and α (gmg^{-1})is the desorption constant related to the extent of the surface coverageand activation energy for chemisorption. The respective values of and were obtained from the slope and intercept of the plot between qtand lnt.

The kinetic parameters obtained for the three models and their corresponding coefficient of determination (R^2) values are presented in TABLE 4. A close observation of the R^2values in the table shows that the adsorption of both metals was best described by the pseudo-second order equation. Similarly, the closeness of the estimated qe value from the pseudo-second order equation and the experimental qe values for the two metals also supports this assertion.

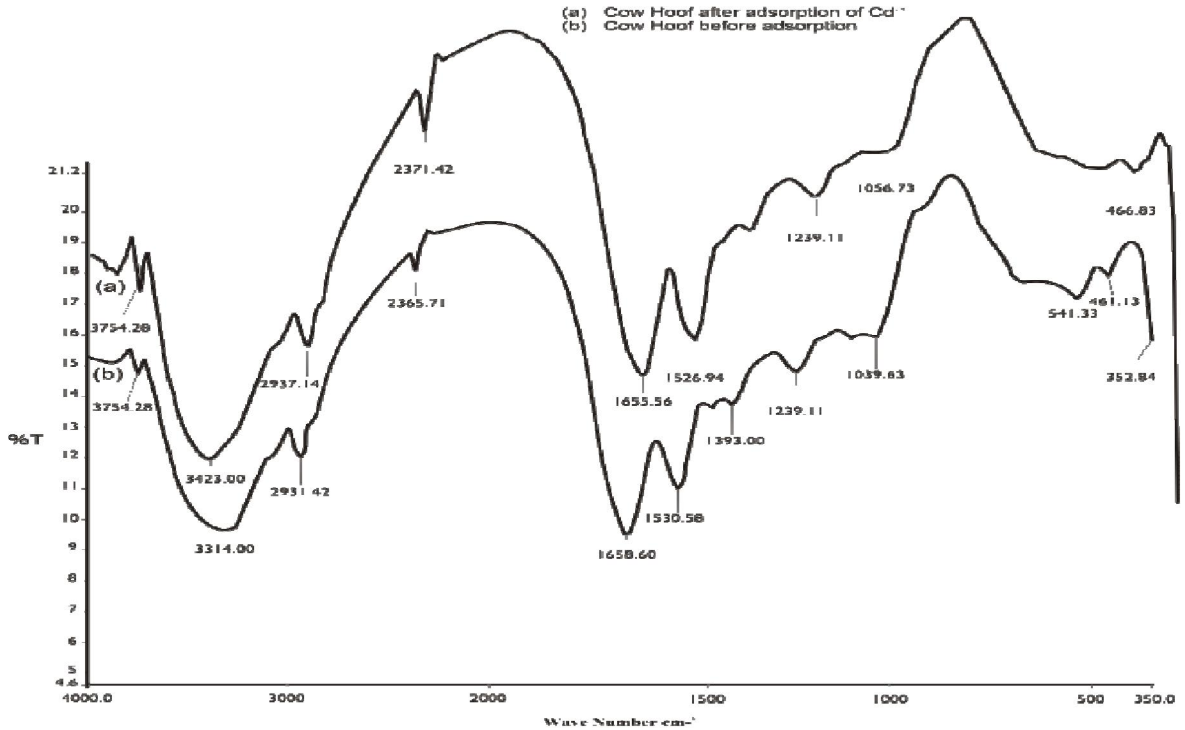

Figure 4A : FTIR spectra of (a) Cd loaded cow hoof and (b) unloaded cow hoof

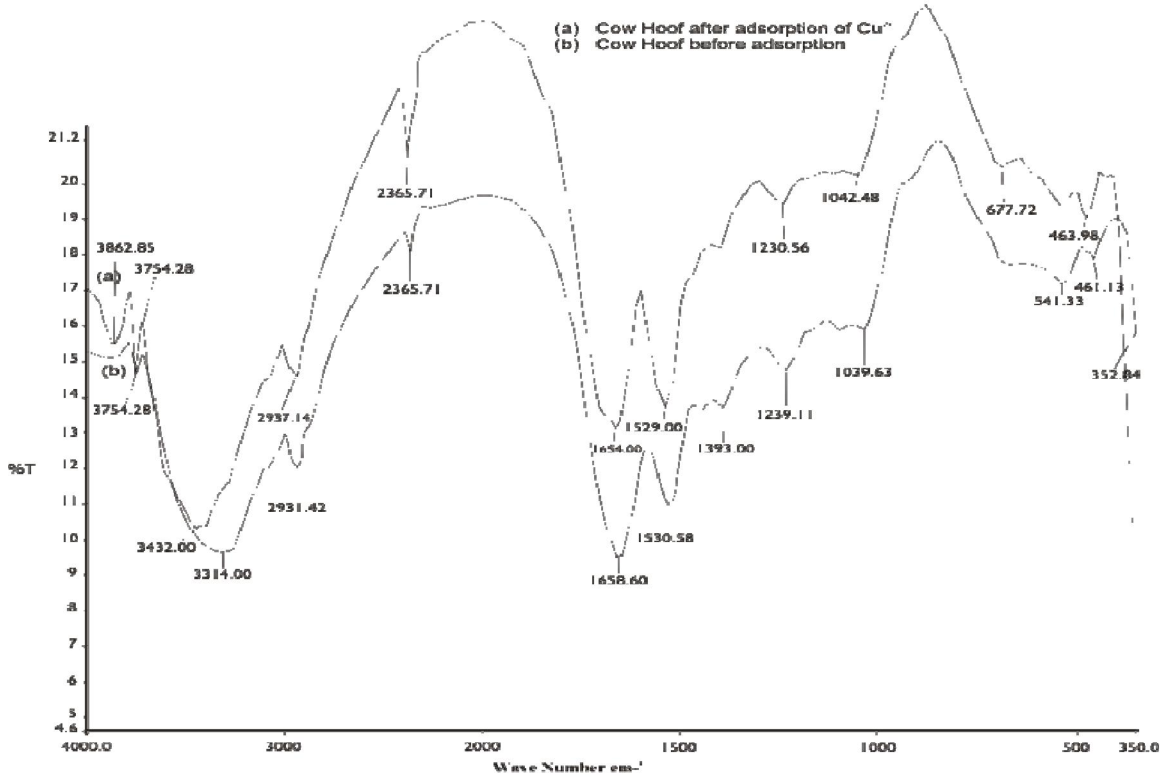

Figure 4B : FTIR spectra of (a) Cu^{2+} loaded CH and (b) unloaded CH

Adsorption thermodynamics

The feasibility of the adsorption of Cd (II) and Cu (II) was assessed through the evaluation of the 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:

$$K_e = \frac{C_{Ae}}{C_e} \tag{9}$$

$$\ln K_e = \frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{10}$$

Where, Ke is the equilibrium constant, Ce is the equilibrium metal ion concentration in solution (mgL^{-1}), C_{Ae} is the amount of metal ions adsorbed on the adsorbent 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 plot oflnK$_e$ against 1/T while the values of ΔG^0 at different temperatures were determined using the equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{11}$$

The results of the different parameters are presented in TABLE 5. The negative values of the Gibbs free energy recorded for the two metals at all temperatures show that the adsorption process was spontaneous. It is glaring from TABLE 5 that the negative valuesof $\Delta G^0$for the two metalsincrease with increase in temperature. This shows that the degree of spontaneityof the adsorption increases with increase in temperature. The enthalpy change recorded for the two metals reveal that the adsorption of both Cd (II) and Cu (II) by cow hoof was endothermic in nature. This observation further supports the earlier observation on isotherm parameters that revealed that the maximum adsorption capacityof cow hoof for the two metals increased with increase in temperature. The value of ΔS obtained for each metal shows that entropy increases as a result of adsorption. This impliesthat Cd (II) and Cu (II) ions adsorbed onto the surface of the adsorbent were more loosely arranged than those that were yet to be adsorbed. This shows that the ions of these metals adsorbed to the surface of cow hoof were weakly bonded to the surface. This is an indication of physical adsorption.

FTIR spectral characteristics of the adsorbent

The FTIR spectra (Figures 4A and 4B) of cow hoof before and after adsorption of metals were obtained todetermine the possible involvement of the functional groups present on its surface ontheadsorption process. The spectroscopic characteristics of these spectra are shown in TABLE 5. The spectra reveal the presence of certain functional groups on the surface of the adsorbent before and after adsorption. It can be observed that many peaks were shifted after adsorption of both metals. The peaks at 1239.11 (corresponding to C-N stretch) and 2365.71 (corresponding to S-H stretching) were retained after the adsorption of Cd and Cu respectively (Figures 4A and 4B). These observations can make one suggest that those functional groups (e.g. OH, C-O and C=O) that had their absorption bands shifted after metal adsorption might be directly involved while functional groups like C-N and S-H were not directly involved in the adsorption of Cd (II) and Cu (II) by cow hoof.

TABLE 6 : FTIR spectral characteristics of cow hoof before and after adsorption of Cd^{2+} and Cu^{2+}

IR peak	Frequency (cm^{-1}) before adsorption	Metal Ion	Frequency (cm^{-1}) after adsorption	Difference	Assignment
1	3314.00	Cd^{2+}	3423.00	-109	Bonded -OH group
		Cu^{2+}	3432.00	-118	
2	2365.71	Cd^{2+}	2371.42	-5.71	S-H stretching
		Cu^{2+}	2365.71	0	
3	1658.60	Cd^{2+}	1655.56	3.04	C=O of an amide
		Cu^{2+}	1654.00	4.60	
4	1530.58	Cd^{2+}	1526.94	3.64	Amino group
		Cu^{2+}	1529.00	1.58	
5	1239.631239.11	Cd^{2+}	1239.11	0	C-N stretching
		Cu^{2+}	1230.56	8.55	
6	1039.63	Cd^{2+}	1056.73	-17.1	C-O stretching
		Cu^{2+}	1042.48	-2.85	

TABLE 7 : Some physicochemical characteristics of industrial wastewater collected

Metal	Real Industrial wastewater
Conductivity	956±0.02
Ph	7.84±0.11
Temperature (^{0} C)	25.7±0.20
TS (mg/L)	2773±5.12
TSS (mg/L)	2200±3.01
TDS (mg/L)	573±2.23
Total hardness as $CaCO_3$(mg/L)	259.70±0.3
Cadmium(mg/L)	0.15±0.02
Chromium(mg/L)	0.10±0.01
Copper (mg/L)	0.15±0.05
Nickel(mg/L)	0.35±0.03
Lead(mg/L)	0.13±0.02
Zinc(mg/L)	0.85±0.01
Iron (mg/L)	0.10±0.03

TABLE 8 : Efficiencies of cow hooffor metal removal from simulated and Industrial wastewater

Metal	Simulated Wastewater qe (mgg^{-1})	%R	Industrial Wastewater qe (mgg^{-1})	%R
Cd	4.68	99.49	3.75	75.00
Cu	4.79	95.92	2.75	55.01

Biosorption studies using industrial wastewater

The effect of competing ions on the removal of Cd(II) and Cu(II) by cow hoof was studied by collecting wastewater sample from a company which specialises in the production of colour coated roofing sheets. The physico-chemical characteristics of these samples, which were determined by standard analytical methods, are presented in TABLE 7. The wastewater sample was filtered and 50 mL portions were measured into 150 mL conical flasks. The pH of each was adjusted to the pH of maximum removal of each metal. Then 0.5 g of cow hoof powder was weighed into each flask and the mixture was agitated at constant speed of 120 rpm for120 minutes and the mixture was filtered. The filtrate was analyzed for metal concentration using Atomic Absorption Spectrometer AAS. The results obtained are presented in TABLE 8.

The results presented in TABLE 8 show that both percent removal and uptake capacity recorded for real industrial wastewaterwere lower than the corresponding values obtained for simulated wastewater sample. The decrease in the amount of metal biosorbed by cow hoof from the industrial wastewater compared to the amount biosorbed from the aqueous solution can be attributed to the presence of other ions and impurities which may compete with Cd or Cu or even block the available binding sites present on the surface of the biosorbent.

CONCLUSION

This study revealed that powdered cow hooves can be utilized to remove $Cd^{2+}$and Cu^{2+}under the optimum condition of pH4 (Cd), pH5 (Cu) and contact time of 60 minutes. The process is also thermodynamically feasible under an endothermic condition. It was observed that the presence of co-ions and other impurities in real industrial wastewater decreased the efficiency of cow hoof for Cd (II) and Cu (II) removal

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