Adsorptive Removal of Chromium (VI) from Aqueous Solution Using Cow Hooves

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Authors' contributions

This work was carried out in collaboration between all authors. Author IO designed the study, performed the laboratory work under the supervision of the other two authors, wrote the protocol, and wrote the first draft of the manuscript. Authors AOA and OOA managed the literature searches. All authors read and approved the final manuscript.

Research Article

ABSTRACT

Aim: To investigate the use of Nigerian cow hooves for the removal of chromium VI from aqueous solution.
Place and Duration: Chemistry Laboratory, Federal University of Technology, Akure and Chemistry Laboratory of Afe Babalola University, Ado-Ekiti, Nigeria, from September 2011 to June 2012.
Methodology: The adsorption process, which was carried out through batch method, was investigated over a range of pH (2-7), agitation time (0-150 mins) and adsorbent mass (1.0-3.0 g per 50 mL of metal solution). The adsorption isotherms were obtained using initial metal concentrations ranging from 15 to 100 mgL^{-1}. After agitation, the resultant solution was analyzed for Cr (VI) using Atomic Absorption Spectrophotometer.
Results: The optimum operating parameters obtained for the adsorption process are pH 2 (89.5% removal) and time of 30 mins (34.4% removal) while the highest metal uptake (mgg^{-1}) was recorded for 1g of the adsorbent per 50ml of solution. Langmuir, Freundlich and Dubinin-Raduskevich (D-R) isotherm models were applied to describe the experimental data. The Langmuir maximum adsorption capacities of the cow hoof for Cr (VI) at 298, 308 and 318 K were determined to be 3.57, 4.81 and 5.71 mgg^{-1} respectively. Freundlich isotherm model fitted the equilibrium data better than Langmuir and D-R

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models. The mean free energy (E) which was calculated from D-R model indicated that the sorption process was dominated by physisorption mechanism. The adsorption kinetics was found to follow the pseudo-second-order model.

Conclusion: This study revealed that cow hoof powder can be used as a low cost adsorbent for the removal of Cr (VI) from wastewater under the optimum conditions of pH 2 and contact time of 30mins while the thermodynamic parameters- ΔG^0, ΔH^0 and ΔS^0 indicated that the adsorption process was endothermic, feasible and spontaneous.

1. INTRODUCTION

Water is the most important life-sustaining gift of nature after air. The presence of toxic heavy metal ions in water bodies cannot be overemphasized. These heavy metals get into water bodies through two major sources - geogenic and anthropogenic sources, the latter being the chief source. Heavy metal contamination exists in aqueous waste stream of many industries, such as metal plating industry, mining industry, paint and pigment industry, glass industry, and tanneries. Among the toxic heavy metals which present potential danger to human health are Cu, Pb, Cd, Cr and Hg [1]. These heavy metals are not biodegradable and tend to accumulate, like other metals, in living organisms [2] where they react irreversibly with enzymes and proteins thereby causing various diseases and disorders. Chromium is commonly encountered in the environment as chromium (III) and chromium (VI) [3]. Chromium (VI) is said to be more toxic than chromium (III). Chromium (VI) has been reported to cause lung perforation and carcinoma in human beings [4]. Other disorders caused from short or long term exposure to this deadly metal are asthma, pneumonitis and dermatitis, ulcer, irritation of the nasal mucosa and gastrointestinal track, kidney and liver failure, perforation of the nasal septum, lungs cancer, skin [5,6].

If these metals are continuously introduced into our environment without been avoided or treated the lives on earth are in danger. Of course, there are several conventional methods used for removing heavy metals from industrial waste water. These include: chemical precipitation, ion exchange, coagulation, solvent extraction, ultra filtration, reverse osmosis, electro dialysis, etc. [2,7,8]. However, these methods have their attendant disadvantages which include incomplete metal removal, generation of sludge or secondary waste, high running cost, etc. [6]. Adsorption has been pointed out as one of the most efficient methods for the removal of heavy metals from wastewater [9]. Adsorption using activated carbon (AC) is known to be very efficient for heavy metal removal due to its high porosity, large surface area, variable characteristics surface chemistry, high degree of surface activity and high affinity for metals [10,11]. However the use of activated carbon is cost prohibitive thereby limiting its use as adsorbent for heavy metals from industrial wastewater especially in developing countries.

Investigations have been conducted and reported on the use of inexpensive, easily available and environmentally friendly biomaterials for the removal of heavy metals from aqueous solution. High adsorption capacity of these biomaterials has been attributed to the presence of certain functional groups like amino, phosphate, carboxylic, hydroxyl and sulphate groups [7]. Several reports have been made on the adsorption of Cr (VI) on different biomaterials. These include the use of Aeromonas caviae [3], modified oak saw dust [8], eucalyptus bark [6]. Others are Pinus sylvetris, spirogyra, *Rhizopus nigrificans* as listed by Loukidou et al. [3],

sulphuric acid treated sunflower waste, [12], *Rhizopus arrhizus* [13], Cocolumber sawdust, [14]. Most of these biomaterials reported for the removal of chromium (VI) are of plant origin. Hence, the need to investigate the use of fauna wastes for the removal of Cr (VI).

Cow hooves are obtained cheaply in abattoirs in Nigeria where they constitute environmental pollution because they are usually burnt off, thereby contributing to the depletion of the ozone layer. Apart from being inexpensive, cow hooves contain insoluble protein called keratin [15] which contains functional groups (carboxylic and amino groups) which are potential metal binders. Therefore, this work was aimed at investigating the use of cow hooves for the removal of Cr (VI) from aqueous solution since little or no report is available on the use of cow hoof for the removal of this metal. This will also serve as a way of cleaning up the environment and putting cow hooves into significant use.

2. MATERIALS AND METHODS

2.1 Adsorbent and Heavy Metal Solution

The 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 drying, the hooves were ground and sieved using sieve of mesh size 212 μm. A stock solution containing 1000 mgL^{-1} of Cr (VI) was prepared by dissolving 2.82 g of analytical grade $K_2Cr_2O_7$ in distilled water. Standard solutions of different concentrations as might be required were prepared (by dilution) from this stock solution.

2.2 Biosorption Studies

The adsorption experiments were carried out by batch process. 1.0 g of the cow hoof powder (mesh size 212 μm) was placed in Erlenmeyer flasks with 50 mL solution of metal ions of desired concentration. The mixture was equilibrated for a desired period of time at 120 rpm. The mixture of the biosorbent and the solution was centrifuged after expiration of the agitation time 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 at equilibrium per unit mass of biosorbent was determined according to the following equation:

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

Where, m is the mass of adsorbent (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 adsorption (%R), for chromium was calculated using the following expression:

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

2.3 Experimental Conditions

The point of zero charge (pH$_{PZC}$) of the cow hoof was determined by the solid addition method [16]. To a series of 100 mL beakers 55 mL of KNO_3 solution of known strength was

transferred. The pH_i values of the solution were adjusted from 2 to 12 by adding either 0.1 M HNO_3 or 0.1 M NaOH. Then 50 mL of each solution was transferred into a 100 mL conical flask and 0.1 g of cow hoof was added to each flask. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The pH values of the supernatant liquid were noted. The difference between the initial (pH_i) and final pH (pH_f) values ($\Delta pH = pH_i - pH_f$) was plotted against the pH_i. The point of intersection of the resulting curve at which ΔpH is zero gave the pH_{PZC}. The procedure was repeated for different concentrations of KNO_3.

The effect of pH on the sorption of Cr was studied as follows: 100 mL of chromium solution was measured into 250 mL beakers. The pH of the solution in each beaker was adjusted by adding dilute solution of 0.1M HCl or 0.1M NaOH. The pH range used was between pH 2 and pH 7. Then, 50 mL of these solutions was taken into Erlenmeyer flasks and agitated with 1.0 g of adsorbent for 60 minutes at 298 K. After equilibration, the final concentration of metal ions was determined and the percentage of metal adsorbed was calculated. Batch biosorption studies were also conducted to investigate the effect of contact time on the adsorption of chromium onto cow hoof powder. This was done at different contact times ranging from 0-150 minutes with initial metal ion concentration of 50 mgL^{-1}, and biosorbent mass of 1.0 g in 50 mL solution, at 298 K. Experiments to determine the effect of sorbent mass were carried out using 50 mL of 50 mgL^{-1} of chromium ion. The sorbent mass was varied from 1.0-3.0 g and the flasks were agitated for 30mins (optimum time).

2.4 Equilibrium Studies

Equilibrium isotherm studies were conducted by agitating 1.0 g of the adsorbent with 50 mL of chromium solution of pH 2 for 30mins at 298, 308 and 318 K. The initial metal concentration ranged from 15 to100 mgL^{-1}. The samples were then centrifuged and analysed as described earlier.

3. RESULTS AND DISCUSSION

3.1 Effect of pH

pH is an important factor that affects the availability of metal ions in solution (speciation). The value of pH_{ZPC} of cow hoof was determined to be 7.7 (Fig. 1). It has been reported that adsorption of cations is favoured at pH > pH_{PZC}, while the adsorption of anions is favoured at pH < pHPZC. The specific adsorption of cations shifts pHPZC towards lower values, whereas the specific adsorption of anions shifts pHPZC towards higher values [16]. The result obtained for variation of pH in this study agrees well with this general observation (Fig. 1 and 2).
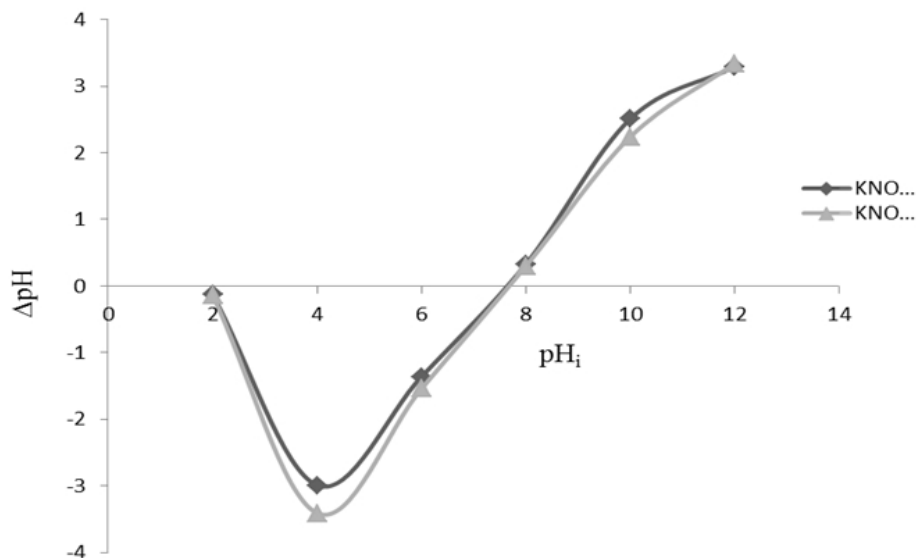
Fig. 1. Point of Zero Charge of cow hoof

Fig. 2 reveals that the maximum uptake of Cr ion took place at pH of 2. This is in agreement with literature reports where the pH for maximum Cr uptakes has been reported to range from 2-4.1 [3,6,7]. There was a decrease in the amount of chromium adsorbed as the pH increased. This can be attributed to the fact that Cr (VI) exists as oxyanions (CrO_4^{2-}, $Cr_2O_7^{2-}$, $HCrO_4^{-}$) in aqueous solution [7,17] of which $HCrO_4^{-}$ and $Cr_2O_7^{2}$ predominate at pH less than 6 [17]. At low pH values the surface of the adsorbent is saturated with protons thereby making the surface of the adsorbent to be positively charged, this enhances the adsorption of the negatively charged Cr oxyanions onto the surface of the adsorbent. However, at high pH values, the surface of the biosorbent is saturated with abundant negative charge. This discourages the adsorption of the chromium oxyanions on to the biosorbent surface since there will be mutual repulsions between the negatively charged biosorbent surface and that of the chromium oxyanions. Furthermore, the presence of the –OH functional group (Fig. 8 and Table 6) on the surface of cow hoof can make one assume that cow hoof is a carbonaceous material which can be represented as C_xOH [18]. Report has it that hydroxylated surface groups are greatly influenced by protonation and deprotonation during pH adjustment as depicted below [18].

At low pH (protonation) we have: $C_xOH + H^+ \leftrightarrow C_xOH_2^+$. This favours adsorption of chromium oxyanion. At high pH deprotonation occurs. i.e. $C_xOH \leftrightarrow C_xO^- + H^+$. This does not favour chromium sorption because of the mutual repulsion that exists between the negatively charged chromium ion and C_xO^-. It has been reported that Cr (VI) is reduced to Cr (III) in acidic medium [17]. At low pH values, the presence of H^+ ions in the solution is high which causes the reduction of Cr (VI) to Cr (III) ions due to high redox potential as shown in the reaction below [17].

$$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O.$$

Literature report has further explained that a redox reaction occurs between the surface groups on the substrate (C_xOH) and Cr (VI) at low pH values [18] (i.e., $3C_xOH + Cr_2O_7^{2-} +$

$4H^+ \leftrightarrow 3C_xO^- + Cr^{3+} + HCrO_4^- + 3H_2O$ or $3C_xOH + HCrO_4^- + 4H^+ \leftrightarrow 3C_xO- + Cr^{3+} + 4H2O$). This observation was confirmed during the adsorption of Cr (VI) on the surfaces of oxidized MWCNTs at low pH [18].
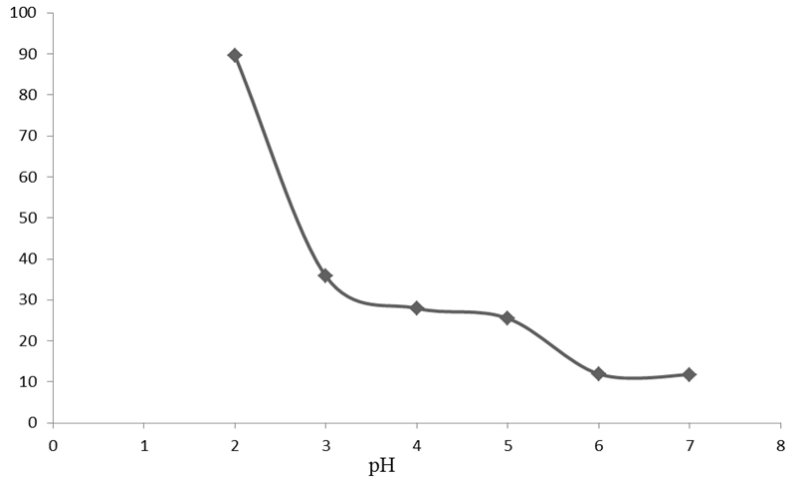

Fig. 2. Effect of pH variation on the removal of chromium using cow hoof powder

3.2 Effect of Contact Time

Contact time is another important factor that affects efficiency of metal uptake in batch adsorption processes. Fig. 3 shows the percentage chromium removal (%R) by cow hoof as a function of contact time. The figure reveals that the maximum adsorption of Cr onto the cow hoof occurred at 30 minutes of agitation with percentage removal of 32.68% (0.817 mgg^{-1}). The extent of adsorption increased rapidly at the initial stage and then became reduced as the agitation time increased beyond 30 minutes. The extent of reduction in the adsorption rate seemed to be insignificant from the agitation time of 60 minutes. There might be possibility of gradual desorption of metal from the biosorbent surface when the agitation time increased from 30 to 60 minutes.
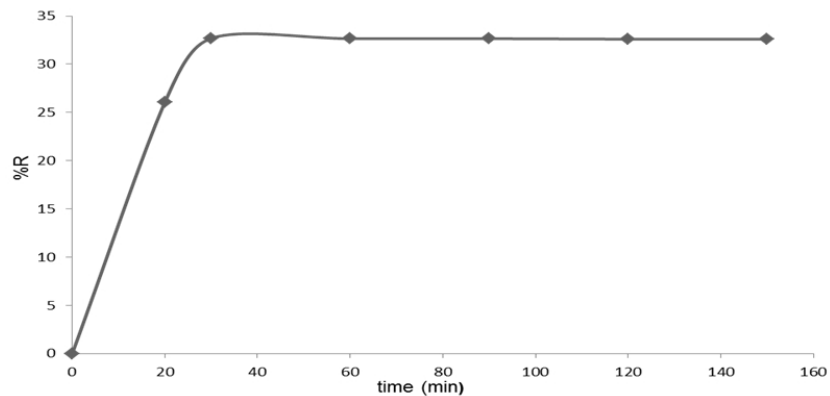

Fig .3. Effect of contact time on the removal of chromium using cow hoof powder

3.3 Effect of Sorbent Mass

The effect of sorbent mass on the adsorption study is shown in Fig. 4. The figure shows that percentage chromium removal (%R) is highly a function of the mass of the biosorbent used. The percentage of metal adsorbed increased with increase in the mass of the sorbent. This is expected because the greater the amount of the adsorbent in solution, the greater the number of binding sites available for metal uptake. Fig. 4 also shows that the amount of metal uptake per gram of adsorbent (q_e) decreased rapidly as the mass of sorbent added increased. This decrease seemed to be steady after the addition of 2.5 g of the sorbent.
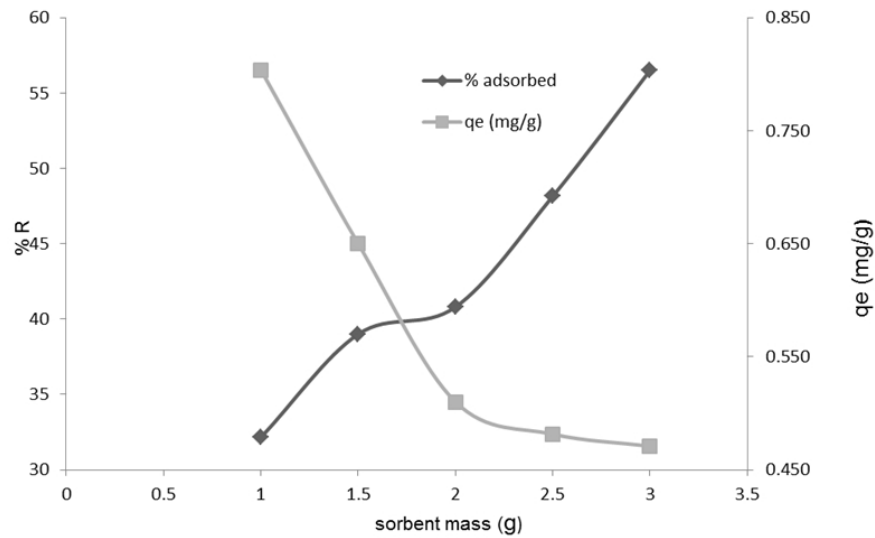

Fig. 4. Effect of sorbent mass on the removal of chromium on cow hoof powder

3.4 Adsorption Isotherms

Adsorption isotherms are of great importance for design purposes since they indicate how metal ions are partitioned between the adsorbent phase and the liquid phase at equilibrium as a function of metal concentration [8]. Several isotherm models are used to describe adsorption data but in this study, Langmuir, Freundlich and Dubinin-Radushkevish (D-R) isotherm models were used to describe the adsorption equilibrium. The Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between the adsorbed ions. The model can take the following linear form:

$$\frac{Ce}{qe} = \frac{1}{Kl\,qmax} + \frac{Ce}{qmax} \tag{3}$$

Where, q_{max} (mgg^{-1} is the maximum adsorption capacity. K_L (Lmg-1) is a constant related to the affinity of binding sites or bonding energy. The plot of C_e/q_e versus C_e gave a straight line (Fig. 5). The Freundlich isothem model is based on adsorption on a heterogeneous surface. It can be expressed linearly as

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{4}$$

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

The plot of $\log q_e$ against $\log C_e$ (Fig. 6a & 6b) shows that the adsorption also follows Freundlich isotherm model. The Dubinin - Radushkevish isotherm which also assumes a heterogeneous surface can be expressed in the following linear form:

$$\ln q_e = \ln X_m - K\varepsilon^2 \qquad (5)$$

Where ε is the Polanyi potential = RT ln(1 + 1/Ce), X_m is the adsorption capacity of the sorbent (mgg-1), K is a constant related to the adsorption energy (mol^2 kJ^{-2}), R is the gas constant (kJK^{-1} mol^{-1}), and T is the temperature (K).

Langmuir parameters can be used to predict the affinity between the sorbate and sorbent using the dimensionless separation factor R_L, defined as

$$R_L = \frac{1}{1 + KLCo} \qquad (6)$$

Where C_0 is the initial concentration of metal (mgL^{-1}) and K_L is Langmuir constant. Separation factor describes the affinity between sorbent and adsorbate as: Irreversible, if R_L = 0; favourable, if 0< R_L <1; linear if R_L= 1and unfavourable if R_L >1. The R_L values in this study are shown in Table 1. The values indicate that the sorption is favourable and this is more favourable at high initial metal concentration for all temperatures considered. The Freundlich constant 1/n can also be used to predict the favourability of the adsorption process [7]. The values obtained for 1/n in this study were between 0 and 1 which is also an indication of the favourability of the process Table 3.

Table 1. Separation factor (R_L) values for chromium ion sorbed on cow hoof

Co (mgL-1)	298K	308K	318K
15	0.706	0.389	0.577
25	0.591	0.277	0.451
50	0.419	0.161	0.291
75	0.325	0.113	0.215
100	0.265	0.087	0.170

The potential of cow hoof for adsorbing chromium can be evaluated by comparing the maximum adsorption capacity of Cr (VI) onto different adsorbents as shown in Table 2. A direct comparison of different biosorbents might be difficult due to varying experimental conditions employed in the studies, yet cow hoof shows fair adsorption efficiency when compared with other biosorbents (Table 2).

The Langmuir, Freundlich and D-R adsorption constants with their respective correlation coefficients are presented in Table 3. The respective maximum adsorption capacities q_m, K_f and X_m for these models ranged from 3.57 to 5.71 mgg-1, 0.155 to 0.622 L1/n g^{-1} mg$^{-1/n}$ and 1.59 to 2.601 mgg-1.

Table 2. Comparison of adsorption capacity (q_m) of cow hoof for Cr (VI) with that of other biosorbents

Biosorbent	pH	q_m (mgg^{-1})	Reference
Modified oak saw dust	3	1.70	[8]
Aeromonas caviae	2.5	124.46	[3]
Chryseomonas luteola	4.0	3.0	[19]
Bacillus megaterium	2.5	30.7	[20]
Bacillus licheniformis	2.5	69.4	[21]
Wallnut shell	NA	1.33	[22]
Zoogloea ramigera	2.0	27.5	[23]
Waste tea	NA	1.55	[22]
Neem sawdust	2	58.82	[24]
Cow hoof	2	5.71	Current study

Table 3 also shows that the adsorption capacity seems to increase with increase in temperature for the three isotherm models. It is obvious from the table that both Langmuir and Freundlich isotherms better fitted the adsorption data than the D-R model. While Langmuir and Freundlich isotherms parameters are important for predicting the affinity between the adsorbent and the adsorbate, the mean adsorption energy (E) calculated from D-R isotherm model can be used to determine the nature of biosorption process. The mean adsorption energy can be calculated using

$$E = (-2K)^{-1/2} \tag{7}$$

If E is < 8 kJmol^{-1}, the adsorption process is dominated by physisorption mechanism and if E is between 8 and 16 kJmol^{-1}, the adsorption process is dominated by chemisorption mechanism and if E is > 16 kJmol^{-1}, the sorption process is dominated by particle diffusion [7, 8]. The mean adsorption energies were 0.224, 0.973 and 0.535 kJmol^{-1} at 298 K, 308 K and 318 K respectively (Table 3). This shows that the adsorption process was dominated by physisorption mechanism.

Table 3. Isotherm parameters for the removal of Cr (VI) by cow hoof at different temperatures

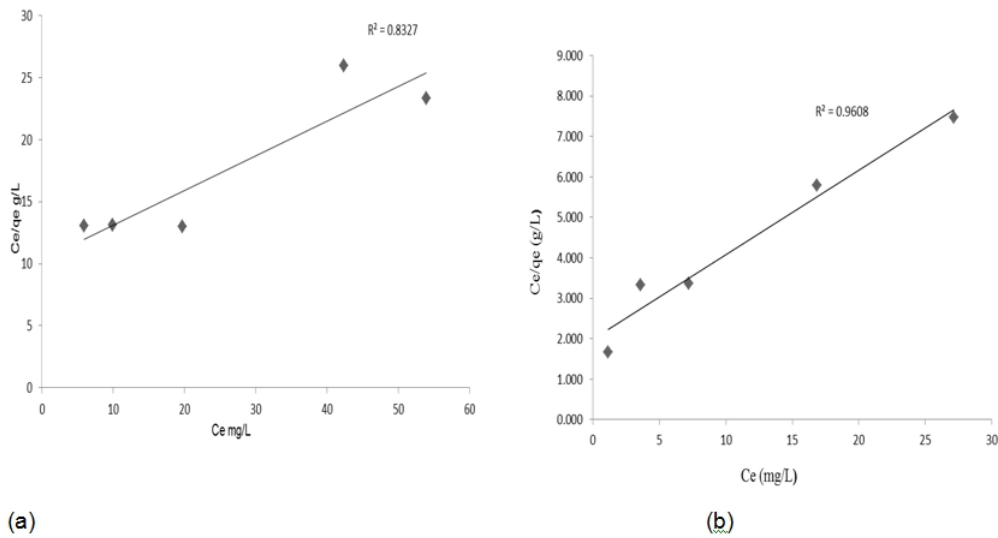| Isotherm	Parameter	Temperature (K)		
		298	308	318
Langmuir	q_{max} (mgg^{-1})	3.57	4.81	5.71
	K_L (Lmg^{-1})	0.028	0.105	0.049
	R^2	0.8327	0.9608	0.9776
Freundlich	K_f (L$^{1/n}$ g^{-1} mg$^{-1/n}$)	0.155	0.622	0.3572
	n	1.4791	1.8305	1.4663
	1/n	0.6761	0.5463	0.682
	R^2	0.9307	0.974	0.976
Dubinin-Radushkevish	X_m (mgg^{-1})	1.59	2.441	2.601
	K (Mol^{2}KJ^{-2})	-9.981	- 0.527	-1.635
	E (KJmol^{-1})	0.224	0.973	0.535
	R^2	0.569	0.6959	0.7315

Fig. 5. Langmuir isotherm plots for adsorption of chromium on cow hoof powder pH=2, (a) at 298 K and (b) at 308 K
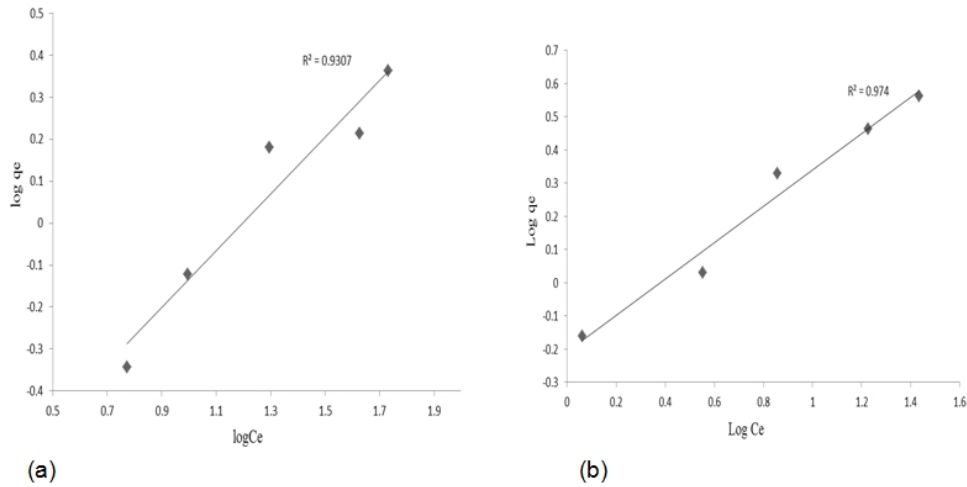

Fig. 6. Freundlich isotherm plots for adsorption of chromium on cow hoof powder pH = 2, (a) at 298 K and (b) at 308 K

3.5 Adsorption Kinetics

The adsorption kinetics of the biosorption process was analysed using the pseudo-first and pseudp-second order kinetic models [10]. The pseudo-first order equation is expressed as follows:

$$\text{Log}(q_e-q_t)=\log q_e-\frac{k1t}{2.303} \tag{8}$$

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Where k_1 = the rate constant for pseudo-first order equation(min^{-1}) and qe = amount of metal sorbed at equilibrium (mgg^{-1}). A plot of log (q_e-q_t) vs. t gave a straight line confirming the applicability of the pseudo-first-order rate equation. Pseudo-second-order sorption rate equation can be expressed as

$$\frac{t}{qt}=\frac{1}{k2\,qe2}+\frac{1}{qe}t \qquad (9)$$

Where k_2 is the pseudo-second-order sorption rate constant (gmg^{-1} min^{-1}). A straight line plot of t/qt vs. t indicates the applicability of pseudo-second-order model.
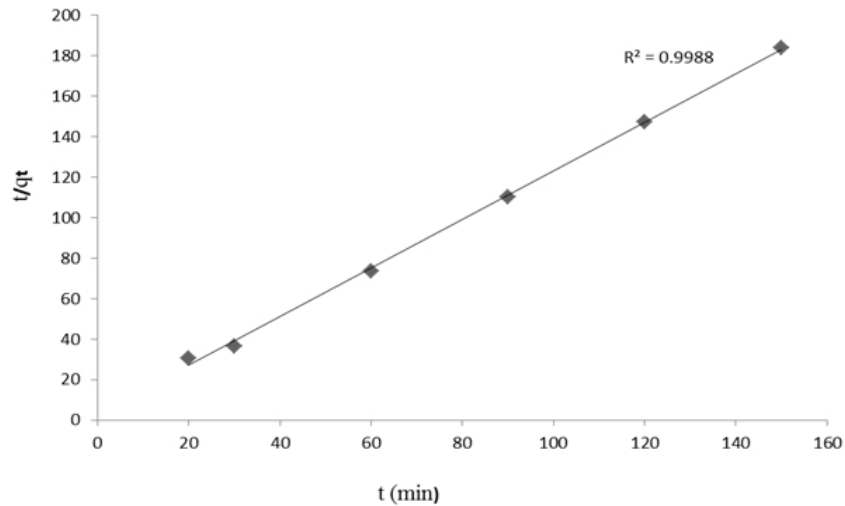

Fig. 7. Pseudo-first order plot for adsorption of chromium on cow hoof powder at T = 298 K

The experimental data fitted both models with pseudo-second order model having a better fit (R^2=0.9988) (Fig. 7). The values of q_e (theo) determined from this models were compared with the q_e (exp) in Table 4. This comparison also indicates that the calculated q_e value for pseudo-second-order kinetic is closer to the experimentally determined value than the one obtained for pseudo-first-order.

Table 4. Pseudo-first-order and pseudo-second-order kinetic constants for the adsorption of chromium ions on cow hoof powder at 298K

Pseudo-first-order				Pseudo-first-order			
k_1 (min^{-1})	q_e(theo) (mgg-1)	q_e(exp) (mgg-1)	R^2	K_2 (gmg^{-1} min^{-1})	q_e(theo) (mgg^{-1})	q_e(exp) (mgg^{-1})	R^2
-0.0433	0.0850	0.817	0.514	2.150	0.8335	0.817	0.9988

3.6 Thermodynamic Studies

The determination of thermodynamic parameters-standard entropy change (ΔS^0), standard enthalpy change (ΔH^0) and standard free energy change (ΔG^0) is important to ascertain the

spontaneity of the adsorption process. Thermodynamic studies were done by carrying out equilibrium studies at various temperatures to obtain corresponding values of C_{Ae} and C_e [25]. The equilibrium constant Ke can be calculated from C_{Ae} and C_e values using

$$K_e = C_{Ae}/C_e \tag{10}$$

where, C_{Ae} represents adsorption in mgL^{-1} at equilibrium; and C_e is the equilibrium concentration of the metal in mgL^{-1}. [26]. Vant Hoff's equation is a useful expression that links ΔH^0 and ΔS^0 with the equilibrium constant as shown below [27]:

$$lnK_e = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{11}$$

where, T is Temperature in Kelvin and R is the gas constant($KJmol^{-1}K^{-1}$). The values of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of the plot of lnK_e against $1/T$ while values of ΔG^0 at different temperatures can be obtained using the equation below.

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

The thermodynamic parameters are shown in Table 5. The positive value of ΔH^0 is an indication of the endothermic nature of the adsorption process. The negative values of the Gibb's free energy (ΔG^0) for all temperatures show that the biosorption process is spontaneous. The table also reveals that the negative values of ΔG^0 increases with temperature. This implies that the degree of spontaneity of the reaction increases with increase in temperature.

Table 5. Thermodynamic constants for the adsorption of Cr (VI) on cow hoof at different temperatures

T (K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (KJ mol^{-1})	ΔS^0(KJ mol^{-1})	R (KJ mol^{-1} K^{-1})
298	-1.707	33.457	0.118	8.314 x 10^{-3}
308	-2.887			8.314 x 10^{-3}
318	-4.067			8.314 x 10^{-3}

This further confirms the endothermic nature of the process. Table 5 also shows that the ΔS^0 value was $0.118KJmol^{-1}$. The positive value of ΔS^0 indicates that entropy increases as a result of adsorption process. Therefore, there is a greater randomness among chromium ions near the adsorbent surface than those ions far from the adsorbent surface. It can also be suggested that the positive value of ΔS^0 is an indication of some structural changes in the adsorbent and adsorbate [28].

3.7 IR Spectroscopy of Cow Hoof

The IR spectra (Fig. 8) of the cow hoof before and after Cr (VI) adsorption were obtained to determine the possible involvement of the functional groups present in the cow hoof on the adsorption process. The spectroscopic characteristics of these spectra are shown in Table 6. The spectra reveal the presence of certain functional groups on the surface of the biosorbent before and after adsorption. It can be observed that many peaks were shifted, two were retained, and two disappeared while one new peak was detected after adsorption.
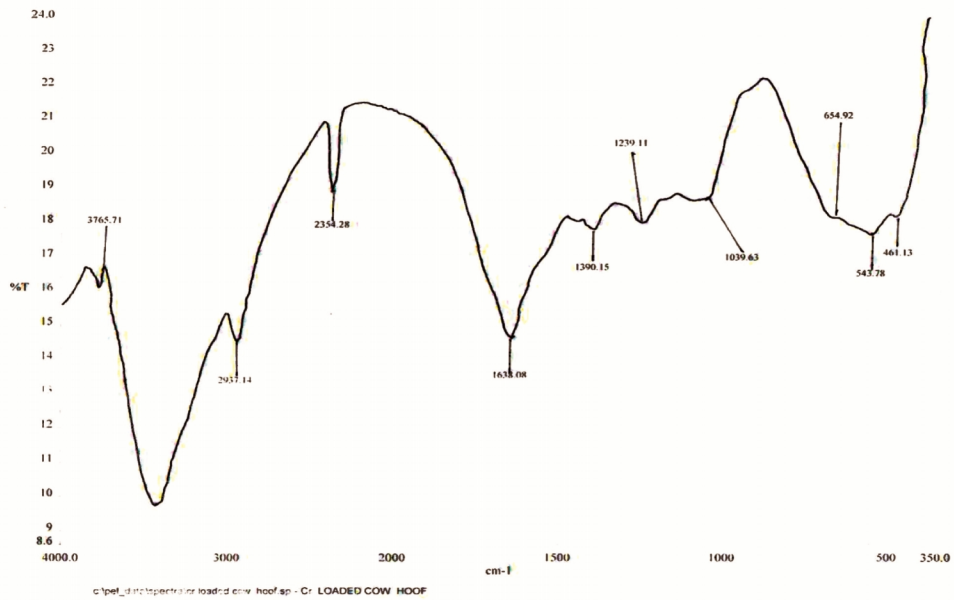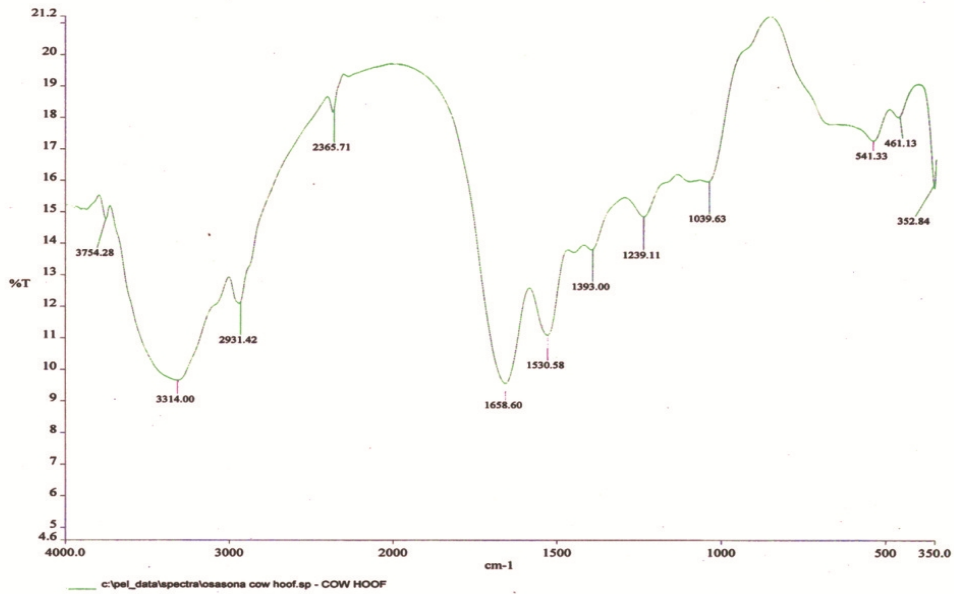
Fig. 8. IR spectra of cow hoof (a) before Cr (VI) and (b) after Cr (VI) sorption

Table 6. IR spectral characteristics of cow hoof before and after Cr (VI) sorption

IR peak	Frequency (cm^{-1}) before adsorption	Frequency (cm^{-1}) after adsorption	Difference	Assignment
1	3754.28	3765.71	-11.43	-NH stretching
2	3314.00	-		Bonded -OH group
3		2937.14	-5.72	Aliphatic C-H groups
4		2354.28	11.43	S-H stretching
5	1658.60	1638.08	20.52	C=O stretching of an amide
6	1530.58	-		N-H bending
7	1393.00	1390.15	2.65	S=O stretching
8		1239.11	0.52	C-N stretching
9	1039.63	1039.63	0	C-O stretching
10	-	654.92		S-O stretching
11	541.33	543.78	-2.45	-C-C- group
12	461.13	461.13	0	

Table 6 clearly shows three significant bands decrease of functional groups at 3754.28, 2931.42 and 541.33 cm^{-1} respectively which correspond to -NH stretching, aliphatic C-H groups and -C-C- group respectively. These significant bands signify the possible involvement of the three functional groups on the adsorption of Cr (VI) onto cow hoof.

4. CONCLUSION

This study revealed that cow hoof powder can be used as a low cost adsorbent for the removal of Cr (VI) from wastewater under optimum conditions of pH 2 and contact time of 30mins. The equilibrium data were better fitted by the Freundlich and Langmuir isotherm than the D-R model. The Freundlich and Langmuir isotherm parameters described the affinity of the cow hoof powder for Cr (VI) ions to be a favourable one while the D-R model revealed the adsorption process to be dominated by physisorption mechanism. The adsorption data were well described by the pseudo second-order kinetic model while the thermodynamic parameters described the sorption of Cr (VI) on cow hoof to be spontaneous and endothermic.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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