

## **Characterization and Utilization of Citric Acid Modified Cow Hoof for Adsorption of Cadmium and Copper from Wastewater**

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### **Authors' contributions**

*This work was carried out in collaboration between all authors. Author IO designed the study, performed the statistical analysis, wrote the protocol, wrote the first draft of the manuscript and managed the literature searches. Authors AOA and AEO managed the analyses of the study. All authors read and approved the final manuscript.*

### **Article Information**

DOI: 10.9734/CSJI/2017/32537

Editor(s):

(1) Georgiy B. Shul'pin, Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia.

Reviewers:

(1) José Ismael Acosta Rodriguez, Universidad Autónoma de San Luis Potosí, México.

(2) Daniel Schwantes, Pontifical Catholic University of Parana, Brazil.

(3) P. N. Palanisamy, Kongu Engineering College, India.

Complete Peer review History: <http://www.sciencedomain.org/review-history/21879>

**Original Research Article**

**Received 1<sup>st</sup> March 2017**  
**Accepted 20<sup>th</sup> March 2017**  
**Published 13<sup>th</sup> November 2017**

### **ABSTRACT**

**Aims:** To investigate the ability of citric acid modified cow hoof (CCH) to remove Cd (II) and Cu (II) from simulated wastewater.

**Place and Duration of Study:** Chemistry Laboratory of Afe Babalola University, Ado – Ekiti, Nigeria.

**Methodology:** The characterization of the citric acid modified cow hoof was carried out through FTIR, SEM and EDX analyses. Batch studies were also conducted to investigate the effect of operation parameters on the adsorption of the metals. Kinetic parameters were analysed using the non-linear forms of pseudo-first order, pseudo-second order and Elovich kinetic models. Non-linear regression analysis of the equilibrium data were carried out using Langmuir, Freundlich, Redlich-Peterson, Dubinin Raduskevich and sips models.

**Results:** The results obtained showed that, the adsorption of the two metals was pH, solute concentration, time and temperature dependent. The kinetic modelling followed pseudo-second-

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order kinetic model for both metals while the equilibrium adsorption data were best described by Redlich-Peterson and Sips isotherm models for Cd (II) and Cu (II) respectively. Thermodynamic parameters obtained showed that the adsorption of both metals was spontaneous and endothermic in nature.

**Conclusion:** Removal of cadmium and copper ions from simulated wastewater using citric acid modified cow hooves (a low-cost adsorbent) is feasible.

*Keywords: Adsorption; cadmium; copper; kinetics; thermodynamics.*

## 1. INTRODUCTION

The threat caused by the presence of heavy metals in the aquatic environment has become a world-wide phenomenon. These metals find their way into the environment principally through anthropogenic activities like: mining, electroplating, smelting, welding, manufacture and indiscriminate disposal of electronic materials, manufacture of fertilizer, oil spillage, application of fertilizer, pesticides and herbicides, manufacture of batteries, etc. Some of these metals are known to be toxic. For example, cadmium and its compounds are listed among the known carcinogens [1] while copper is an essential constituent of about thirty enzymes and glycoproteins. It is required for the synthesis of haemoglobin and for some biological processes [2]. The toxic copper species are  $\text{Cu}(\text{OH})^+$ ,  $\text{Cu}_2(\text{OH})_2^{2+}$  and  $\text{CuCO}_3$  [2]. The harmful potential of these metals has made regulatory agencies set permissible limits for the discharge of heavy metal laden wastewaters into the environment. This necessitates the pretreatment of wastewaters in different industries before discharge into the environment. A lot of methods are conventionally applied for this purpose but most of these methods are limited by one demerit or the other. Adsorption has been found to be one of the most efficient methods for industrial wastewater treatment. In commercial systems, activated carbon is used as adsorbent for purification of dye and heavy metal laden wastewaters. This is because activated carbon presents high adsorption efficiency. This capacity is mainly due to their structural characteristics and their porous texture which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to increase their properties [3]. However, its widespread use is limited due to high costs of manufacturing and regeneration [3].

Consequently, many low-cost adsorbents, including natural materials, biosorbents, and waste materials from industry and agriculture, have been proposed by several authors [4]. In

all, adsorption using dead/inactive plants and animals or their by-products (biosorption) has been found to be economically viable and ecofriendly. Among those biomaterials that have been employed to sequester heavy metals from wastewaters are: cotton waste [5], Bengal gram husk [6], orange mesocarp extract [7], chicken feathers [8], waste tea leaves [9], coconut tree sawdust, eggshell and sugarcane bagasse [10], sulphuric acid modified wheat bran [11,12], tea factory waste [13], papaya wood [14], bagasse fly ash [15], etc.

Piles of cow hooves are freely available in different abattoirs all over Nigeria. This study was conceived to convert these inedible spare parts of cows into a beneficial use as an adsorbent (a way of converting waste to wealth). It is also believed that chemical treatment of hooves can open up or introduce more binding sites for metal uptake. It has been reported that acid treatment of biomaterials can clean up the surface of an adsorbent by removing acid soluble materials which can hinder adsorption process [16]. This study was undertaken to investigate the influence of pH, contact time, adsorbent dosage, initial metal concentration and temperature on the ability of citric acid modified cow hooves to remove copper (II) and cadmium (II) from aqueous solution. Five isotherm models, namely: Langmuir, Freundlich, Redlich-Peterson, Sips and Dubnin-Raduskevich were applied, in their non-linear forms to describe the adsorption data obtained at different concentrations but for a specific temperature.

## 2. MATERIALS AND METHODS

### 2.1 Materials

The chemicals used in this study-copper (II) sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), cadmium nitrate ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), sodium hydroxide (NaOH) and hydrochloric acid (HCl)- were of analytical grade. A stock solution ( $1000 \text{ mgL}^{-1}$ ) of cadmium was prepared by dissolving 2.75 g of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  with distilled water in a 1 L standard flask. This

was made to mark with distilled water. The same procedure was followed to prepare the stock solution for Cu (II) but 3.93 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was weighed into the standard flask. Standard solutions of different concentrations were later prepared from these stocks as required.

### 2.1.1 Preparation of adsorbent

Cow hooves were obtained from a local abattoir in Ado-Ekiti, Nigeria. The hooves were thoroughly washed with detergent and sponge. These were later rinsed thoroughly with distilled water and sun dried for one month. After sun drying, the hooves were again washed with distilled water to remove dust and any adhering debris contracted during sun drying. They were finally dried in an oven maintained at a temperature of  $105^\circ\text{C}$ . The oven dried hooves were later ground and sieved using sieve of mesh size  $212\ \mu\text{m}$ . The sieved sample was stored in a refrigerator prior to analysis. Citric acid modification of the powdered sample was carried out as described by Marshall et al. [17].

### 2.2 Characterization of Adsorbent

FT-IR analysis of the sample in solid state before and after metal removal was carried out using Fourier Transform infrared spectrometer (Perkin-Elmer Spectrum GX, Beaconsfield, UK). This was carried out by mixing 5 mg of CCH homogeneously with dry potassium bromide and made pellets in disc by applying pressure. The spectra of the adsorbent were measured within the range of  $4000 - 400\ \text{cm}^{-1}$ . This was done to obtain qualitative information on the functional groups that could be involved in the process of Cd (II) and Cu (II) adsorption by the CCH. The quantitative and qualitative elemental composition of the adsorbent was determined using an Energy Dispersive X-ray Spectrometer (Oxford X-max 80). The scanning electron micrograph of CCH was taken using Scanning Electron Microscope (Zeissupra 55).

### 2.3 Adsorption Studies

These studies were performed through batch process. Half gramme (0.5 g) of the citric acid modified sample was placed in 150 mL Erlenmeyer flasks containing 50 mL of  $50\ \text{mgL}^{-1}$  solution of each metal. All experiments were performed at ambient temperature except the experiment on variation of temperature. The flasks were agitated for a known period of time. For the determination of the effect of pH, the pH

of each metal solution was adjusted from 2 to 6 using either 0.1 M HCl or 0.1 M NaOH solution. The effect of contact time was verified by varying the contact time from 5 to 150 minutes while the effect of change in adsorbent dosage was verified by varying the mass of CCH from 0.1 to 1.0 g. Adsorption equilibrium data were obtained by equilibrating a fixed amount (0.5 g) of CCH with different concentrations of each metal solution ranging from  $15 - 100\ \text{mgg}^{-1}$ . This was carried out at pH of maximum adsorption and for the period of time required to attain equilibrium for each metal. The experiments on variation of temperature were performed at four different temperatures of 298, 308, 318 and  $328\ \text{K}$ .

At the end of each experiment, the mixture of the solution and CCH was filtered and the concentration of metal present in the filtrate was determined using atomic absorption spectrophotometer. The amount of metal adsorbed in mg per gramme of CCH ( $q$ ) and the percentage metal removal (%R) were calculated using equations (1) and (2) respectively.

$$q = \frac{(C_i - C_f)V}{m} \quad (1)$$

$$\%R = \frac{(C_i - C_f) \times 100}{C_i} \quad (2)$$

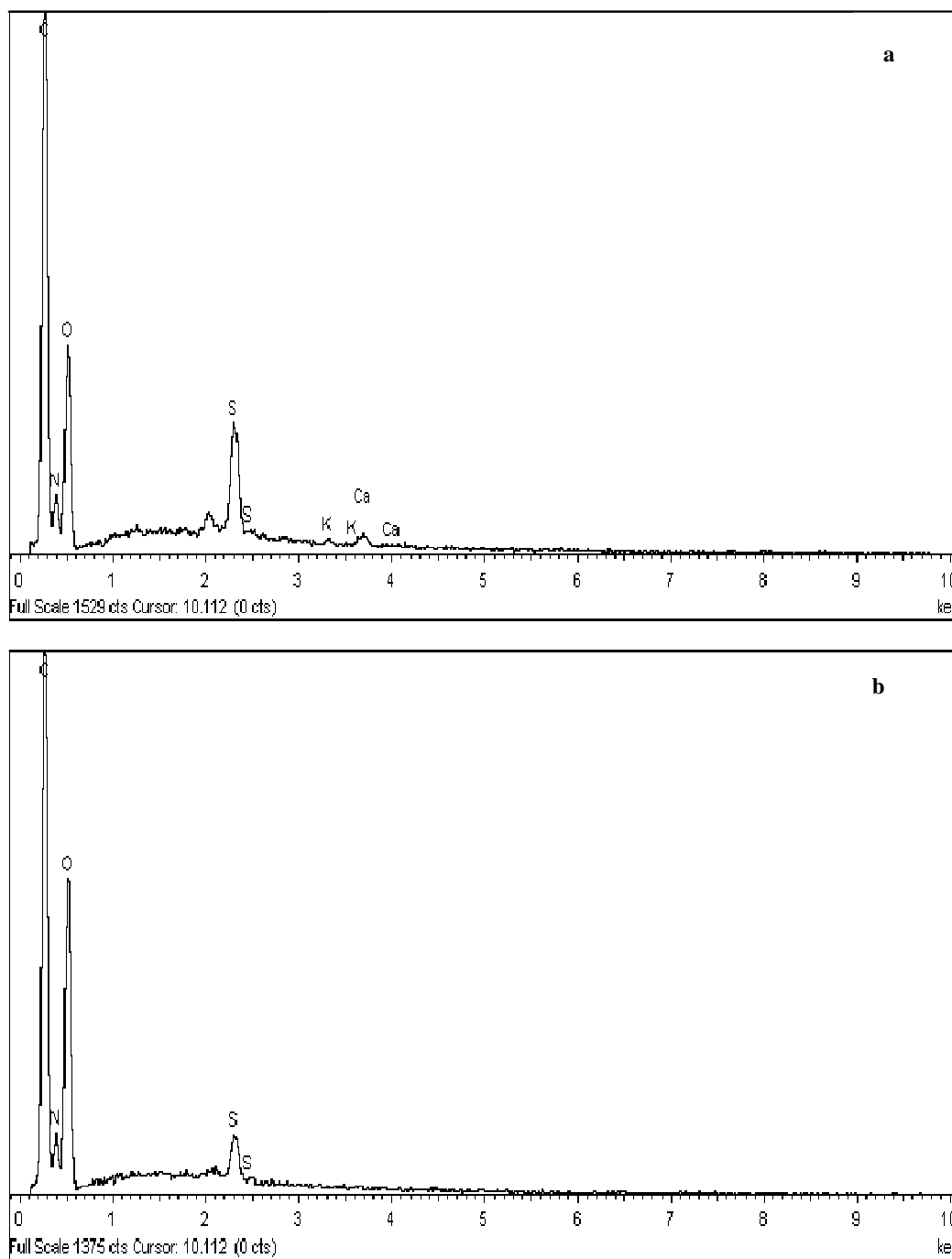
Where,  $m$  is the mass of CCH (g),  $V$  is the volume of the solution (L),  $C_i$  is the initial concentration of metal ( $\text{mgL}^{-1}$ ) and  $C_f$  is the concentration of the metal left in the liquid phase ( $\text{mgL}^{-1}$ ).

## 3. RESULTS AND DISCUSSION

### 3.1 Characterization of the Adsorbent

The scanning electron micrographs of the unmodified and citric acid modified cow hoof are presented in Fig. 1. These micrographs revealed that their surface morphologies were obviously different. This shows that chemical modification with citric acid brought some changes to the surface of the cow hoof after modification. The SEM image of unmodified cow hoof, (Fig. 1a) shows about four large pores which are arranged towards the edges while the SEM image of citric acid modified cow hoof (Fig. 1b) shows an eroded and shrink surface in which the large pores observed for unmodified hoof have been reduced to one small crack towards the lower left





**Fig. 2. Energy dispersion X-ray (EDX) spectrum of (a) unmodified and (b) citric acid modified cow hoof**

**Table 1. Results of elemental analysis of unmodified and citric acid modified cow hoof**

Sample	% Element					
	C	N	O	S	K	Ca
Cow hoof	48.69	18.70	28.50	3.37	0.18	0.56
CCH	39.15	15.18	43.84	1.83	-	-

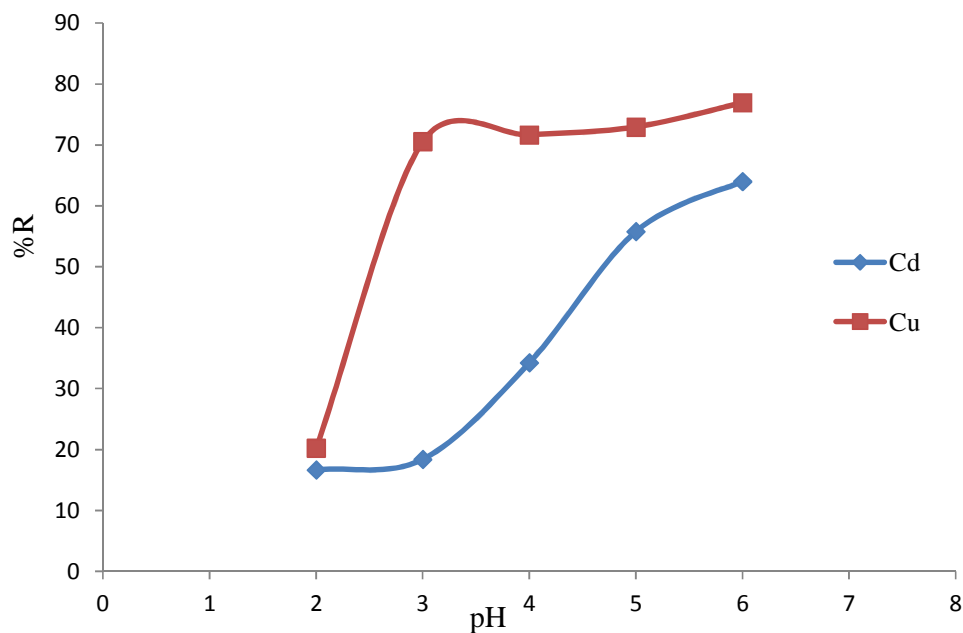
Table 1 compares the percentage composition of the elements contained in the citric acid modified and unmodified cow hoof. The table reveals that carbon had the highest percentage composition in the two samples with its composition in the unmodified sample higher.

### 3.2 Effect of Initial pH

The importance of the effect of pH of a system on the adsorptive removal of a solute molecule from the system cannot be over emphasized. This can be attributed to the influence of pH change on the surface properties of the adsorbent and the chemistry of the solution vis-à-vis: speciation and ionization/dissociation of the adsorbate molecule [19,20]. The adsorption behaviour of both Cd (II) and Cu (II) onto CCH was conducted by adjusting the initial solution pH of each metal solution from 2–6. This was so chosen because many wastewaters including industrial effluents fall within this pH range. These pH values were also chosen to avoid metal precipitation at higher pH values [21]. The results obtained are shown in Fig. 3. The figure indicates that the percentage removal of Cd (II) and Cu (II) by CCH increased with increase in pH of the metal solution. At low pH values, the surface of the adsorbent is saturated with protons thereby making the surface to be positively charged, this discourages the

adsorption of the positively charged Cd (II) and Cu (II) ions onto the surface of the adsorbent.

However, as the pH increases, the concentration of hydrogen ions on the surface of the adsorbent decreases. This encourages the adsorption of the ions thereby giving rise to increase in the amount of metal adsorbed. It can also be observed from the figure that there was a gradual increase in the percentage of Cd (II) adsorbed throughout the pH range considered. However, for Cu (II), there was a sharp increase in the percentage removal when the solution pH was increased from 2 to 3 (a percentage increase of 50%). This cannot be explained based on the speciation of Cu because it is expected that Cu will exist as free  $\text{Cu}^{2+}$  ions within this pH range. Therefore, the ionic states of the functional groups present on the surface of CCH can be used to explain the pH dependency of the removal of  $\text{Cu}^{2+}$  within this pH range. The state of dissociation of the weak acidic groups, particularly, carboxyl groups (COOH) present in biological materials have been used by several authors to explain this observation [5,22,23,24]. Further increase in initial solution pH beyond pH 3 does not seem to have much influence on the percentage removal of Cu (II) as increase in pH from 3 to 6 brought about increase in percentage removal from 70.55 – 76.95%.



**Fig. 3.** Effect of pH on the removal of Cd (II) and Cu (II) using CCH (sorbent mass = 0.5 g, contact time = 60 mins, temperature =  $25\pm 2^\circ\text{C}$ , initial metal concentration =  $50\text{ mgL}^{-1}$ )

### 3.3 Effect of Adsorbent Dosage

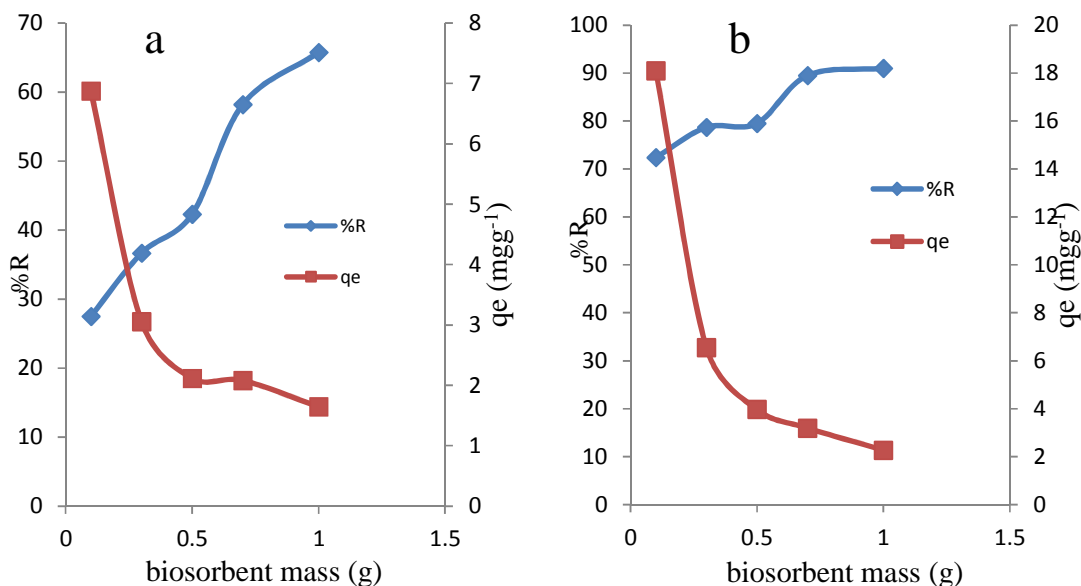
The influence of adsorbent dosage on the adsorption of Cu (II) and Cd (II) by CCH was studied in the range of 0.1–1.0 g and the results obtained are displayed in Fig. 4. The figure shows that adsorption efficiency increased from 27.5 – 65.75% for Cd (II) (Fig. 4a) and from 72.4 – 91% for Cu (II) (Fig. 4b) as the adsorbent dosage was increased from 0.1 to 1 g. The increase in the percentage of metal removed with adsorbent dosage could be attributed to increase in the number of adsorption sites associated with increase in the mass of the adsorbent and this directly increases the surface area, as already reported in the literature [25,26]. It can also be observed that the amount of metal adsorbed per unit mass of CCH ( $q_e$ ) decreased with increase in the mass of CCH dosed. For example, Cd (II) uptake decreased from 6.87 to 1.64  $\text{mgg}^{-1}$  while Cu (II) uptake decreased from 18.10 to 2.28  $\text{mgg}^{-1}$  when the mass of CCH dosed was increased from 0.1 – 1.0 g. This observation may be linked to saturation of adsorption sites due to particulate interaction such as aggregation of adsorbed solute particles [27,28,29].

### 3.4 Adsorption Kinetics

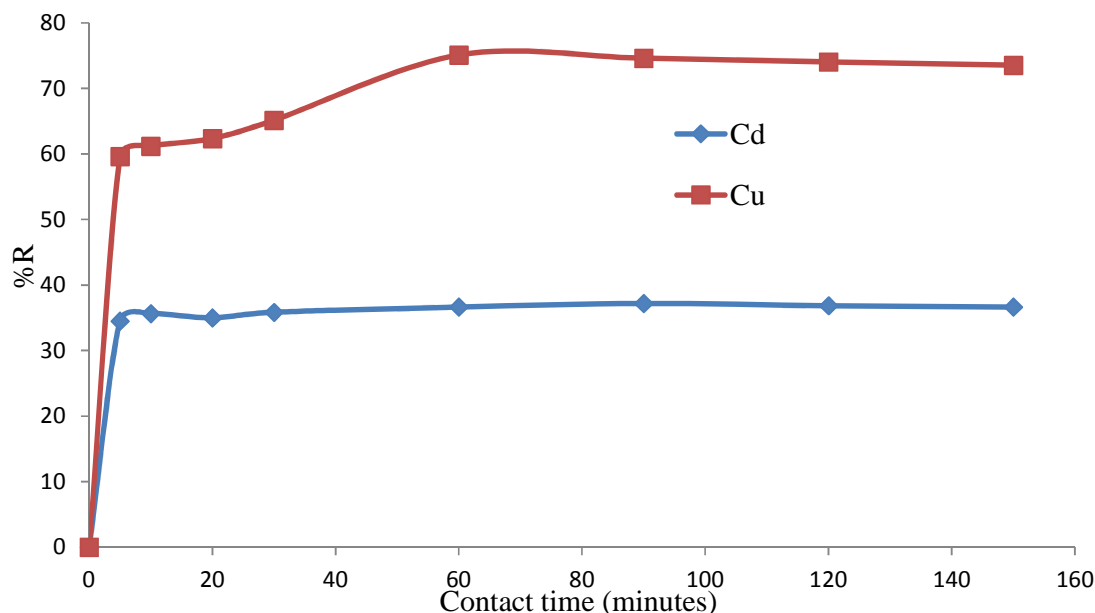
The results in Fig. 5 show that the rate of cadmium (II) removal occurred rapidly within the

first 10 minutes and continued slowly until equilibrium was reached after 60 minutes of agitation. For Cu (II), adsorption was very rapid within the first 5 minutes in such a way that almost 60% of Cu (II) ions were adsorbed within the first 5 minutes of agitation. Sorption rate later continued slowly until equilibrium was established after 60 minutes. The fast adsorption rate observed for the two metals at the initial stages indicates that most of the adsorption occurs on the surface rather than the pores of the samples [8]. The rate of metal sorption could be rapid at the initial stages because the number of unoccupied binding sites which were available for metal sorption at these stages was high. At other stages the number of vacant binding sites becomes less and this decreases adsorption rate progressively until equilibrium is established when all the binding sites have been saturated with metal solutes. This decline in sorption rate can be linked to decrease in total adsorbent surface area [30].

The kinetic parameters of the adsorption process were obtained by analysing the data generated from the effect of contact time using the non-linear forms of pseudo-first order (Equation 5), pseudo-second order (Equation 6) and Elovich (Equation 7) kinetic models. The non-linear forms of these equations were employed because the pseudo-first order equation (in its linear form) has



**Fig. 4.** Effect of adsorbent dosage on the removal of (a) Cd (II) and (b) Cu (II) using CCH (contact time = 60 mins, temperature =  $25\pm 2^\circ\text{C}$ , initial solution pH = 3 for Cu (II) and 6 for Cd (II), initial metal concentration =  $50 \text{ mgL}^{-1}$ )



**Fig. 5. Effect of contact time on the biosorption of Cd and Cu using citric acid modified cow hoof (sorbent mass = 0.5 g, temperature = 25±2°C, initial solution pH = 3 for Cu (II) and 6 for Cd (II), initial metal concentration = 50 mgL<sup>-1</sup>)**

been found not to fit well over the entire contact time range and is generally applicable over the initial periods of the sorption process. This happens because the use of its linearized form requires previous knowledge of the equilibrium sorption capacity ( $q_e$ ) [31]. Conversely, there is no prior need to know  $q_e$  for solving the linear form of a pseudo-second order equation. It is also based on the sorption capacity of the solid phase, which predicts the behaviour over the entire study range [31].

The non-linear form of the pseudo-first order equation [32] is expressed as:

$$q_t = q_e \left[ 1 - \text{Exp}(-k_1 t) \right] \quad (5)$$

While the pseudo-second order kinetic equation [33] can be expressed in its non-linear form as:

$$q_t = q_e \left[ \frac{1}{1 + q_e k_2 t} \right] \quad (6)$$

Where  $q_e$  is the amount of solute adsorbed at equilibrium ( $\text{mgg}^{-1}$ ),  $q_t$  is the amount of solute adsorbed at time  $t$  ( $\text{mgg}^{-1}$ );  $k_1$  is the first order equilibrium rate constant ( $\text{min}^{-1}$ ) and  $k_2$  is the

second order equilibrium rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ ).

The Elovich's equation has been widely used to describe the adsorption of gases onto solid materials; it has also been applied to describe the process of adsorption of metals from aqueous solutions. The model describes the kinetics of the chemisorption process [34].

$$q_t = \frac{1}{\beta} \ln(\alpha \beta t + 1) \quad (7)$$

Where  $\alpha$  and  $\beta$  are constants. The parameter  $\alpha$  represents the rate of chemisorption at zero coverage, the parameter  $\beta$  is related to the extent of surface coverage and to the activation energy for the adsorption.

The model that fitted the adsorption of each of the metals best was adjudged based on the values of the correlation coefficient ( $R^2$ ) and the error function (Err). The model that presented highest  $R^2$  value and lowest E value was adjudged to fit the data best.

The sum of the squares of the error (ERRSQ) (Equation 8) was used to minimize the error distribution between the experimental kinetic



data and those predicted by the kinetic models. Microsoft Excel software was used to minimize the error distribution between the experimental data and the predicted data by non-linear regressions method. The error minimization was achieved using the *solver* add-in function, Microsoft Excel, Microsoft Corporation.

$$\text{Err} = \sum_{i=1}^n (q_{e \text{ cal}} - q_{e \text{ exp}})^2 \quad (8)$$

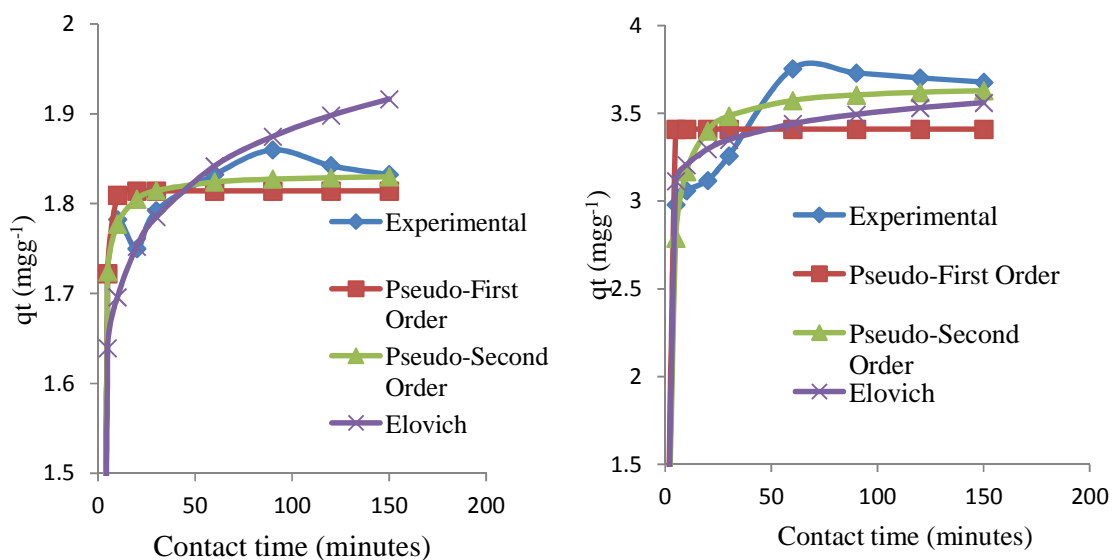
Where  $q_{e \text{ cal}}$  is each value of  $q$  predicted by the fitted model and  $q_{e \text{ exp}}$  is each value of  $q$  measured experimentally, and  $n$  is the number of experiments performed.

The results obtained through non-linear regression analysis of the kinetic models are presented in Table 2. Judging from the  $R^2$  and Err values, it can be seen that pseudo-second order kinetic equation described the adsorption of both metals better than the other two models. It can be noticed from the table that both Elovich and pseudo-second kinetic models described the kinetic data perfectly but the pseudo-second order model was adjudged to describe the adsorption of the metals best based on its low error (Err) values. This shows that chemisorption played an important role in the rate-determining step of the adsorption of Cd and Cu (II) by CCH.

**Table 2. Kinetic parameters for the biosorption of Cd and Cu using CCH at 25°C**

Ion /Model	Cd <sup>2+</sup>	Cu <sup>2+</sup>
$q_{e(\text{exp})}$ (mgg <sup>-1</sup> )	1.86	3.76
<b>Pseudo-first order</b>		
$q_{e(\text{cal})}$ (mgg <sup>-1</sup> )	1.81	3.51
$k_1$ (min <sup>-1</sup> )	0.59	0.33
$R^2$	0.6655	0.6031
Err	0.008	0.51
<b>Pseudo-second order</b>		
$q_{e(\text{cal})}$ (mgg <sup>-1</sup> )	1.83	3.67
$K_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	1.56	0.17
$R^2$	0.8375	0.8382
Err	0.005	0.24
<b>Elovich</b>		
$\alpha$ (mg g <sup>-1</sup> min <sup>-1</sup> )	$8.90 \times 10^6$	$5.46 \times 10^8$
$\beta$ (gmg <sup>-1</sup> )	12.27	7.63
$R^2$	0.9042	0.9346
Err	0.025	0.28

Additionally, Fig. 6 further reveals that the kinetic data predicted by the pseudo-second order model are closer to the experimentally determined kinetic data than those predicted by the other two (considering the closeness of the lines representing the experimental and the pseudo-second order model in Figs. 6a and 6b).



**Fig. 6. Kinetic models for the adsorption of (a) Cd (II) and (b) Cu (II) by CCH (sorbent mass = 0.5 g, temperature = 25±2°C, initial solution pH = 3 for Cu (II) and 6 for Cd (II), initial metal concentration = 50 mgL<sup>-1</sup>)**

### 3.5 Adsorption Isotherm

The Langmuir model [35], which assumes a monolayer adsorption of solutes onto a homogenous adsorbent surface, can be expressed as follows:

$$q = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (9)$$

Where  $q$  is the metal uptake ( $\text{mgg}^{-1}$ ),  $C_e$  is equilibrium solute concentration,  $q_m$ , is the Langmuir constant which denotes the maximum achievable uptake and  $K_L$  is the Langmuir constant which defines the affinity between the adsorbate and the adsorbent. The major assumption of this model is that adsorption takes place at specific homogeneous sites within the adsorbent and once a metal molecule occupies a site, no further adsorption can take place at that site [36].

The Freundlich model [37], expressed mathematically in Equation 10, is an empirical expression that takes into account the heterogeneity of the surface and multilayer adsorption to the binding sites located on the surface of the adsorbent [36].

$$q = K_f C_e^{1/n} \quad (10)$$

Where  $K_f$  and  $n$  are constants which denote the binding capacity and the affinity between the adsorbent and the adsorbate respectively.

Dubnin-Raduskevich equation is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. This model is expressed as:

$$q = q_D \text{Exp} \left[ -K \left( RT \ln \left( 1 + \frac{1}{C_e} \right) \right)^2 \right] \quad (11)$$

Where  $q_D$  is the Dubinin–Radushkevich model uptake capacity and  $K$  is the Dubinin–Radushkevich model constant which determines the mean adsorption energy of the process.

Redlich–Peterson isotherm model, which can be applied either in homogeneous or heterogeneous system, incorporates three parameters into an empirical equation [38]. The model has a linear

dependence on concentration in the numerator and an exponential function in the denominator to represent adsorption equilibria over a wide concentration range. Redlich–Peterson model can be expressed mathematically as:

$$q = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{B_{RP}}} \quad (12)$$

Where  $K_{RP}$  is the Redlich–Peterson model isotherm constant,  $a_{RP}$  is the Redlich–Peterson model constant and  $B_{RP}$  the Redlich–Peterson model exponent. The value of the exponent ( $B_{RP}$ ) lies between 0 and 1. There are two limiting behaviours: the Langmuir form for  $B_{RP} = 1$  and Henry's law form for  $B_{RP} = 0$  [29].

Sips isotherm [39] is a combined form of Langmuir and Freundlich expressions deduced for predicting the heterogeneous adsorption systems [40] and circumventing the limitation of the rising adsorbate concentration associated with Freundlich isotherm model. At low adsorbate concentrations, it reduces to Freundlich isotherm; while at high concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm [41]. The model can be expressed as:

$$q = \frac{K_S C_e^{B_S}}{1 + a_S C_e^{B_S}} \quad (13)$$

Where  $K_S$  is the Sips model isotherm constant;  $a_S$  the Sips model constant and  $B_S$  is the Sips model exponent.

Generally, a minimization procedure was adopted in solving the five isotherm equations by maximizing the correlation coefficient between the experimental data points and the theoretical model predictions with solver add-in function of the Microsoft excel and the results obtained are presented in Table 3. In addition to the commonly employed correlation coefficient ( $R^2$ ), an error function computed using Equation 8 was also employed to judge the model that fitted the equilibrium data best.

It can be observed from the table that adsorption of Cd (II) ion was best fitted by Redlich–Peterson isotherm model while the adsorption of Cu (II) was best fitted by Sips model at all temperatures considered because both models presented lower error values and higher  $R^2$  values than the

other models. This implies that, for Cd (II) ions adsorbed on CCH, the  $q$  fitted by the Redlich-Peterson isotherm model was close to the  $q$  measured experimentally. The same explanation can also be given for Cu (II) ions that the  $q$  fitted by Sips model was close to the experimentally determined  $q$ .

The values of the Langmuir and Dubinin-Raduskevich maximum adsorption capacity  $q_m$  and  $q_D$  calculated by nonlinear regression for Cd (II) when the temperature was increased from 298 – 318 K ranged from 3.01 – 6.19  $\text{mgg}^{-1}$  and 2.34 – 3.19  $\text{mgg}^{-1}$  respectively. The respective values of the maximum adsorption capacity for the two models calculated for Cu (II), within the same temperature range, varied from 9.94 – 12.09  $\text{mgg}^{-1}$  and 5.19 – 5.84  $\text{mgg}^{-1}$ . It is obvious that the adsorption capacity obtained for the two metals increased with increase in temperature.

The values of Freundlich constant  $n$  obtained for the two metals at different temperatures were

found to be between 0 and 10. This is an indication of a strong affinity between CCH and the metal ions. The mean free energy of adsorption  $E$ , estimated from D-R model for the adsorption of both metals by CCH for each temperature considered was found to be  $<8$   $\text{kJ mol}^{-1}$  (Table 3). This shows that the adsorption of Cd (II) and Cu (II) on CCH was dominated by physical adsorption.

### 3.6 FTIR Spectral Characteristics of the Biosorbent

The FTIR spectra of CCH, before and after adsorption of each metal were obtained to determine the possible involvement of the functional groups present on the surface of the adsorbent on the adsorption process. The results of these analyses are presented in Figs. 7a and 7b. The spectra reveal the presence of certain functional groups on the surface of CCH. The major peaks recorded are 3431  $\text{cm}^{-1}$  (-OH group), 2931.42  $\text{cm}^{-1}$  (aliphatic CH groups),

**Table 3. Isotherm parameters for the adsorption of Cd<sup>2+</sup> and Cu<sup>2+</sup> on citric acid modified cow hoof at different temperature**

Isotherm	Cd			Cu		
	298 K	308 K	318 K	298 K	308 K	318 K
<b>Langmuir</b>						
$q_m$	3.01	6.26	6.19	9.94	11.89	12.09
$K_L$	0.07	0.03	0.04	0.03	0.03	0.03
$R^2$	0.9719	0.9838	0.9777	0.9927	0.9957	0.9992
Err	0.11	0.23	0.35	0.22	0.15	0.03
<b>Freundlich</b>						
$K_f$	0.54	0.41	0.50	0.54	0.53	0.64
$n$	2.71	1.76	1.89	1.57	1.47	1.51
$R^2$	0.9614	0.9671	0.9544	0.9921	0.9956	0.9978
Err	0.15	0.47	0.71	0.24	0.16	0.09
<b>Dubinin-Raduskevich</b>						
$q_D$	2.34	3.67	3.94	5.19	5.54	5.84
$E$	0.25	0.18	0.18	0.23	0.24	0.28
$R^2$	0.9215	0.9394	0.9483	0.9418	0.9436	0.9432
Err	0.31	0.96	1.09	2.18	2.36	2.66
<b>Redlich-Peterson</b>						
$K_{RP}$	0.27	0.14	0.15	1.06	1.08	1.20
$a_{RP}$	0.14	0.0007	0.0003	1.24	1.25	1.13
$B_{RP}$	0.90	1.78	2.05	0.45	0.43	0.43
$R^2$	0.9725	0.9902	0.9924	0.9928	0.9942	0.9985
Err	0.11	0.15	0.13	0.22	0.18	0.06
<b>Sips</b>						
$K_s$	0.28	0.10	0.10	0.41	0.42	0.47
$a_s$	0.86	1.27	1.38	0.85	0.84	0.90
$B_s$	0.09	0.02	0.019	0.03	0.023	0.03
$R^2$	0.9727	0.9855	0.9827	0.9932	0.9963	0.9995
Err	0.11	0.20	0.27	0.21	0.13	0.02

2371.42  $\text{cm}^{-1}$  (-SH group) 1638.00  $\text{cm}^{-1}$  (C=O group), 1239.11 (C-N stretching) and 1045.33  $\text{cm}^{-1}$  (C-O stretching). It can be observed that majority of these peaks were shifted after metal adsorption. This reveals that the metal ions actually interacted with the functional groups on the surface of CCH. In fact, in the adsorption of Cd, all the absorption peaks were shifted except the peak corresponding to -OH functional group (3431.00  $\text{cm}^{-1}$ ) that was retained after adsorption. This suggests that all the functional groups were involved in the adsorption of Cd

except -OH group. It is noteworthy that the absorption band corresponding to -SH group (2371.42  $\text{cm}^{-1}$ ) was retained while the absorption band at 3771.14  $\text{cm}^{-1}$  disappeared after the adsorption of copper by CCH. It can be concluded that the metal ions interacted with the functional groups on CCH, and as such, a form of chemical interaction was involved in the process of sequestering cadmium and copper from aqueous solution particularly at the rate-determining step.

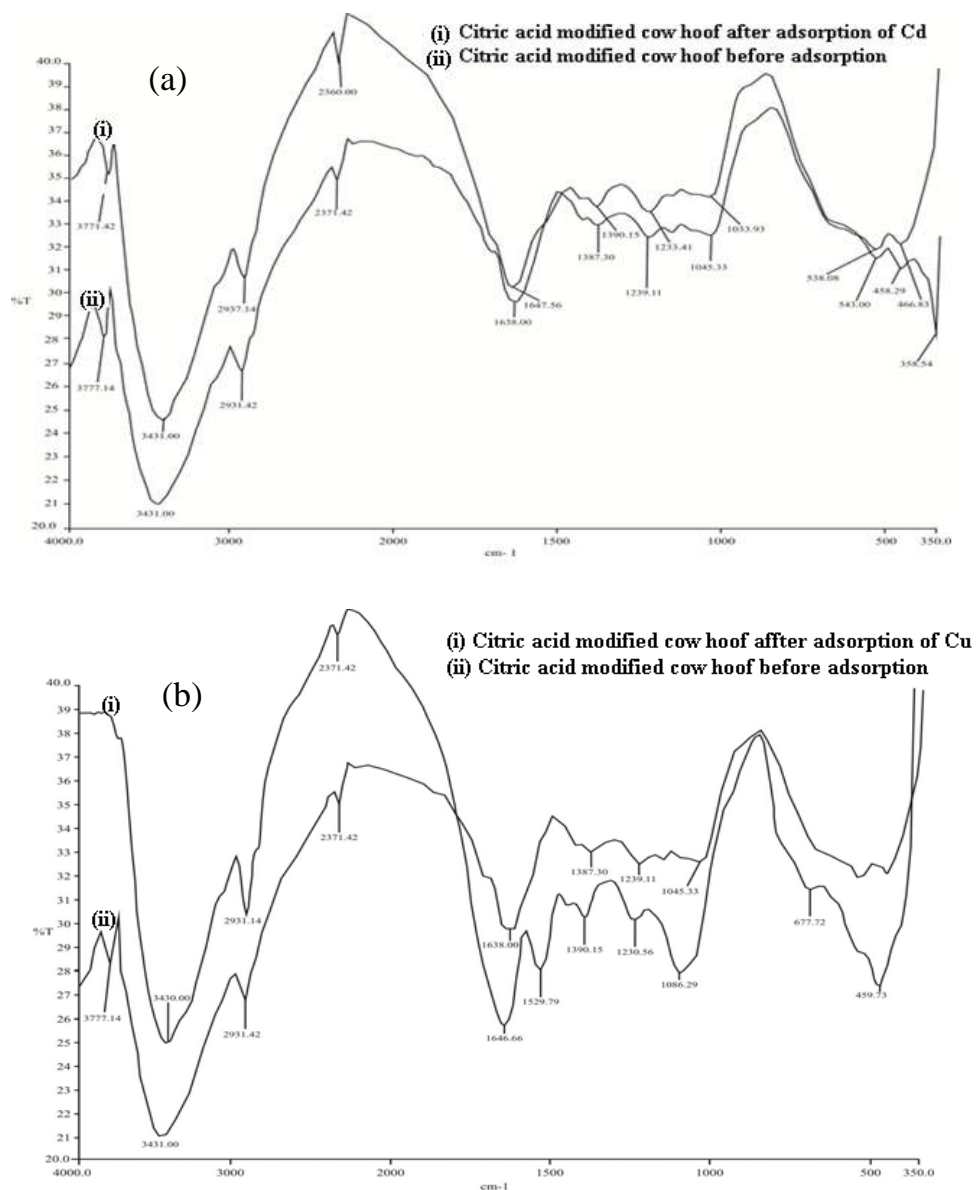


Fig. 7. FTIR spectra of CCH (a) before and after adsorption  $\text{Cd}^{2+}$  and (b) before and after adsorption  $\text{Cu}^{2+}$

**Table 4. Thermodynamic parameters for the adsorption of Cd (II) and Cu (II) by CCH at different temperatures**

Sample	T (K)	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (kJK <sup>-1</sup> mol <sup>-1</sup> )
Cd (II)	298	1.06	23.41	0.075
	308	0.31		
	318	-0.41		
	328	-1.19		
Cu (II)	298	-2.01	2.22	0.14
	308	-2.15		
	318	-2.29		
	328	-2.44		

### 3.7 Adsorption Thermodynamics

The spontaneity of adsorption of Cd and Cu was studied through the determination of the thermodynamic parameters- enthalpy change ( $\Delta H$ ), entropy change ( $\Delta S$ ) and free energy change ( $\Delta G$ ) from studies conducted at different temperatures to obtain the concentration of metal adsorbed at equilibrium ( $C_{Ae}$ ) in mgL<sup>-1</sup> and the equilibrium concentration of the metals remaining in the liquid phase ( $C_e$ ).

The equilibrium constant  $K_e$  was calculated from  $C_{Ae}$  and  $C_e$  values using:

$$K_e = C_{Ae}/C_e \quad (14)$$

Equilibrium constant is related to the entropy and enthalpy of reactions through Equation 15.

$$\ln K_e = \frac{\Delta H}{-RT} + \frac{\Delta S}{R} \quad (15)$$

Where, T is Temperature in Kelvin and R is the gas constant (kJmol<sup>-1</sup>K<sup>-1</sup>).

The values of  $\Delta H$  and  $\Delta S$  were obtained from the slope and intercept of the plot of  $\ln K_e$  against  $1/T$  while values of  $\Delta G$  at different temperatures were obtained using Equation 16.

$$\Delta G = \Delta H - T\Delta S \quad (16)$$

The values obtained for these parameters are presented in Table 4. The positive values of  $\Delta H$  for Cd (II) and Cu (II) adsorbed on CCH further confirms the endothermic nature of the adsorption of both metals. The negative values obtained for the Gibb's free energy change for copper revealed that the removal of Cu (II) was spontaneous at all temperatures considered while the corresponding values obtained for Cd (II) showed that its adsorption was only spontaneous at temperatures greater than or

equal to 318 K. It is interesting to note that the higher the temperature of the process the more negative  $\Delta G$  values become.

### 4. CONCLUSION

This study reveals that the removal of Cd (II) and Cu (II) from aqueous solutions using citric acid modified cow hoof was a function of the operating conditions such as pH, adsorbent dosage, contact time, and temperature. Adsorption of Cd (II) was noticed to be optimum at a pH of 3 while the maximum removal of Cu (II) was attained at a pH of 6. It was also discovered that citric acid modified cow hoof comparatively adsorbed higher amount of copper than cadmium under all operating conditions. The removal of both metals by CCH was favoured by high temperature. The adsorption kinetics of both metals followed pseudo-second-order model indicating that chemisorption was involved in the rate-determining step of the adsorption process even though physical adsorption played a dominating role in the removal of both metals as revealed by the Dubinin-Raduskevich isotherm model. The equilibrium modelling of the adsorption of Cd was perfectly described by Redlich-Peterson model while the removal of copper followed Sips model. The maximum adsorption capacities obtained from both Langmuir and D-R models were found to increase with temperature. The thermodynamic parameters evaluated for the adsorption of both metals showed that the removal of both metals was spontaneous and endothermic in nature. Therefore, citric acid modified cow hoof can be utilized as low-cost adsorbent to sequester Cd and Cu from wastewater.

### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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