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Equilibrium and kinetics studies on the removal of Cd (II) from aqueous solution using hydrochloric acid and sodium hydroxide treated cow hooves

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ABSTRACT

The influence of operation parameters on the removal cadmium ions from aqueous solutions using hydrochloric acid treated (HCH) and sodium hydroxide treated (SCH) cow hooves was investigated. The results obtained showed that pH of 3 and 6, and agitation time of 30 and 60 minutes were sufficient for maximum removal of cadmium by SCH and HCH respectively. The kinetic modeling of the adsorption data was best described by pseudo-second order kinetic equation. Three non-linear isotherm models were used to analysed the data obtained at four different temperatures of 25, 35, 45 and 55 C. The data obtained for both HCH and SCH were best described, based on the R^2 and error function values by Langmuir model at all temperatures considered except the data obtained for HCH at 35 C which was best described by Freundlich model. The maximum adsorption capacities recorded for SCH (7.19-7.92 mgg^{-1}) were higher than those recorded for HCH (2.84-5.51 mgg^{-1}). The information on the FTIR spectra of the biosorbents coupled with those on adsorption energy showed that both chemical adsorption and physical adsorption were involved in the removal of Cd (II) from aqueous solutions.

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KEYWORDS

Adsorption;
Cadmium;
Kinetics;
Equilibrium modeling;
Biosorbents.

INTRODUCTION

The necessity for clean and safe water for public consumption cannot be over emphasized because of the innumerable and invaluable roles water plays for life maintenance and sustenance on the planet earth. It is appreciated that water is involved in all catabolic and anabolic activities like: digestion, assimilation, adsorption, elimination, respiration,

maintaining temperature (homeostasis), etc. taking place in plants and animals. As invaluable as water is, its fitness for life sustenance is being undermined globally on daily basis through the introduction of different contaminants into water bodies. In broad terms, these contaminants can be categorized into two divisions-organic which include industrial solvents, volatile organic compounds, insecticides, pesticides and food processing wastes and inorganic

which include metals, fertilizers and acidity caused by industrial discharges^[1].

Pollution through heavy metals is of great concern because of their non-biodegradability, persistence in the environment and bioaccumulation tendency^[2,3]. Heavy metal pollution has been linked to a lot of diseases and disorders in both plants and animals. Cadmium, which finds its way into water bodies chiefly through industrial activities, is known to be one of the most toxic metals in the world even at low concentration. Its toxic effects include renal dysfunction, hypertension, hepatic injury, lung damage, high blood pressure, destruction of testicular tissue and red blood cells, etc.^[4-6].

In view of the toxicological effects of heavy metals on the environment, and the consequential strict regulations put in place to regulate the amounts of heavy metals introduced into the environment from industrial processes, industries have employed series of chemical and physico-chemical methods to treat their effluents before discharge into the environment. Among these methods are: chemical precipitation, electro-flotation, ion-exchange, reverse osmosis, electro-deposition, solvent extraction, etc.^[7-8]. These methods have been employed industrially with considerable success. However, their industrial applications have been found to be limited by high capital and operational costs, inefficient metal removal particularly at low metal concentration, sensitive operating conditions, and generation of secondary waste which present treatment problems^{[2], [8,9]}.

Adsorption has been proven to be highly effective in the treatment of heavy metal laden wastewaters due to its numerous advantages which include simple design and low operational cost^[8]. Adsorption is also known to be environment friendly. Adsorption using activated carbon is an effective technology in waste water treatment and as such has gained global recognition. However, the use of activated carbon in wastewater treatment is hampered by its high cost and loss during theregeneration process. Hence, the search for cheaper, renewable and more environment friendly organic materials is imperative^[10-12]. Many researchers have worked on the use of biomaterials as adsorbents for sequestering

cadmium from aqueous solution with significant removal efficiency. Some of the explored biomaterials include: cork biomass^[4], rice bran^[13], wheat bran^[14], peels of peas, fig leaves, broad beans, medlar peels^[15], Bagasse fly ash^[16], *Chlamydomonas reinhardtii*^[17], rice straw, soybean hulls, sugarcane bagasse, peanut shells, pecan and walnut shells^[18], chemically modified walnut sawdust^[19], etc.

Majority of the biosorbents that have been explored for cadmium removal are of plant origin. This study was conceived to use cow hooves pretreated with hydrochloric acid and sodium hydroxide solution to remove cadmium from aqueous solution. The influence of operation parameters like pH, contact time and temperature were determined. The equilibrium data obtained at four different temperatures were analysed using Langmuir, Freundlich, Dubinin-Raduskevich non-linear models.

MATERIALS AND METHODS

Collection of cow hooves

Cow hooves were obtained from Ekiti State government abattoir located along Ekiti State University road, 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 and dried in an oven maintained at a temperature of 105^o C. The oven dried hooves were later ground and sieved using sieve of mesh size 212 μ m. The sieved samples were stored in a refrigerator prior to analysis.

Chemical pre-treatment of cow hoof powder

The powdered cow hoof was treated differently with 0.1M HCl, to obtain HCl treated cow hoof (HCH) and 0.1M NaOH to obtain NaOH treated cow hoof. The pre-treatment of the sample was carried out as described in^[20].

General experimental procedure for batch studies

Batch studies were conducted in 150 mL conical flasks containing 25 mL of each metal solution

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using a thermostatic water bath shaker operated at a speed of 120 revolutions per second. Unless otherwise stated, all experiments were carried out by agitating 0.25g of each sample with 50 mgL⁻¹ of Cd (II) solution at room temperature for 60 minutes. The mixture of the biosorbent and the solution was filtered after agitation and the concentration of Cd (II) ion present in the filtrate was determined using atomic absorption spectrophotometer (AAS). The amount of metal ion adsorbed per unit mass of biosorbent was determined according to Equation 1:

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

The percentage Cd removal (%R), was calculated using the following expression:

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

Effect of different parameters on biosorption of Cd (II)

The effect of pH was investigated by equilibrating each sample (HCH and SCH) differently in a series of conical flasks, containing 50 mgL⁻¹ of Cd(II) solution with pH ranging from 2.0 to 8.0. The initial solution pH was adjusted with 0.1M HCl or 0.1M NaOH and the pH measurement was taken using Hanna Instruments (HI 22210) pH meter. Higher pH than 7 was not considered to avoid metal precipitation. The effect of contact time was conducted at different contact times ranging from 0–150 minutes by keeping all other parameters constant as stated

earlier and setting the initial pH of Cd (II) solution at the pH for maximum biosorption by each sample. The effects of both temperature and concentration on the removal of Cd (II) were conducted by agitating 0.25 g each of HCH and SCH with 25 mL of the metal solution maintained at pH of maximum removal agitated at 120 rpm for a period of time required to attain equilibrium as earlier predetermined above. These experiments were conducted at different temperatures of 25, 35 45 and 55° C using initial metal concentrations ranging from 15 to 100 mgL⁻¹.

RESULTS AND DISCUSSION

Effect of pH

The results of the effect of pH on the removal of Cd by both biosorbents are presented in Figure 1. It is evident from the figure that the percentage of cadmium removed by both biosorbents increased with increase in pH. This can be explained based on the fact that the surfaces of the two biosorbents were saturated with hydrogen ions at low pH values. This would definitely bring about low Cd (II) removal based on mutual repulsions between Cd²⁺ and H⁺ ions. Conversely, at high pH values the surfaces of the biosorbents were saturated with low H⁺, this would enhance the amount of Cd (II) removed. For SCH, increase in pH did not have much effect on Cd (II) removal efficiency from pH 3 to 7. Therefore, the pH of 3 was used for further experiments conducted on SCH. For hydrochloric acid treated cow hoof, percentage removal of Cd (II) increased gradu-

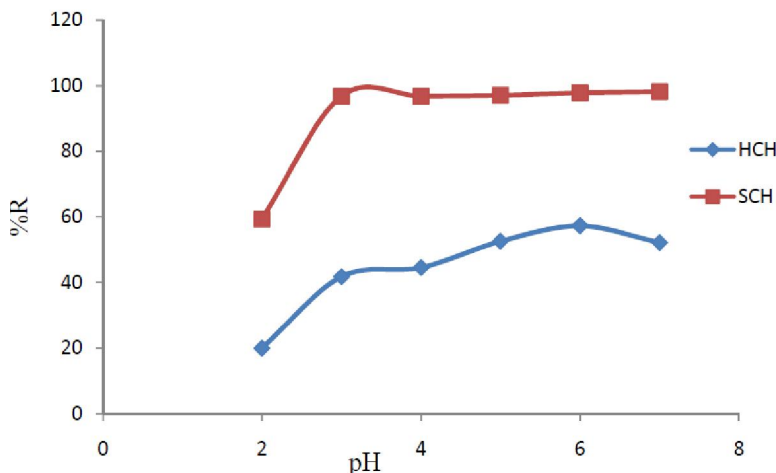


Figure 1 : Effect of pH on the removal of Cd using SCH and HCH

ally with increase in pH until the pH of 6. The maximum removal of cadmium by HCH was observed at a pH of 6. Generally, the amount of Cd (II) removed by SCH was higher that removed by HCH at all pH values.

Effect of contact time and biosorptionkinetic modeling

Figure 2 presents the results of the effect of contact time onthe removal of Cd (II) using HCH and SCH. The results show that the rate of Cd removal by SCH occurred rapidly within the first 10 minutes. The sorption rate continued slowly until equilibrium was reached at 30 minutes. For HCH, the rate of biosorption of Cd was steady from the beginning of the process until equilibrium was reached after 60 minutes of agitation. Biosorption kinetics is paramount in wastewater treatment not only because it describes the soluteuptake, which in turn controls the residence time of a sorbate at the solid–solution interface but also provides valuable insights into the reaction pathways and the mechanism of a sorption reaction^[21-22].

Many kinetic models are available in the literature. But in this study,kinetic data were modeled using the non-linear forms of the pseudo-first and

pseudo-second order kinetics, which are represented as follows:

Pseudo-first order model $q_t = q_e[1 - \exp(-k_1t)]$ (3)

Pseudo-second order model $q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$ (4)

Where q_e is the amount of cadmium biosorbed at equilibrium (mgg^{-1}), q_t is the amount of dye biosorbed at time t (mgg^{-1}), k_1 is the pseudo-first order rate constant (min^{-1}) and k_2 is the pseudo-second order rate constant ($gmg^{-1}min^{-1}$).

In the present study in addition to the widely used, R^2 , an error functionnamely, the sum of the squares of the error (ERRSQ) (Equation 5) was used to minimize the error distribution between the experimental equilibrium data and those predicted by the isotherm models. A spreadsheet was developed using Microsoft Excel to minimize the error distribution between the experimental data and the predicted isotherms by non-linear regressions method. The error minimization was achieved using the solver add-in function, Microsoft Excel, Microsoft Corporation.

$$\sum_{i=1}^n (q_i \text{ model} - q_i \text{ experiment})^2 \tag{5}$$

where $q_i \text{ model}$ is each value of q predicted by the fitted model and $q_i \text{ experiment}$ is each value of q

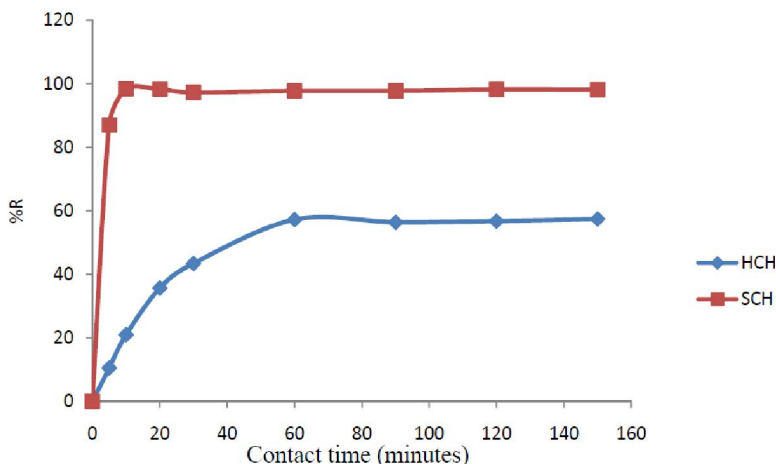


Figure 2 : Effect of contact time on the removal of Cd (II) by HCH and SCH

TABLE 1 : Kinetics parameters for the biosorption of metals using CH at 298K

	Pseudo-first order				Pseudo-second order			
	$q_e(\text{model})$ (mgg^{-1})	k_1 (min^{-1})	R^2	ERRSQ	$q_e(\text{model})$ (mgg^{-1})	k_2 ($gmg^{-1}min^{-1}$)	R^2	ERRSQ
HCH	2.94	0.22	0.9769	0.12	3.09	0.13	0.9913	0.067
SCH	4.83	9.00	0.9873	0.27	4.97	0.37	0.9966	0.07

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measured experimentally, and n is the number of experiments performed. The rate constants, predicted equilibrium uptakes, corresponding correlation coefficients and percentage error values are presented in TABLE 1. It is obvious from the table that pseudo-second kinetic order fitted the kinetic data because it presents lower error values and also higher R^2 values better than the pseudo-first order equation for both biosorbents. The lower is the error function, the lower will be the difference of the q predicted by the model from the q measured experimentally^[23]. Similarly a critical look at Figures 3A and B reveals that the plots for both experimentally determined q and the pseudo-second order kinetic model are very close showing that pseudo-second

order model explains the biosorption of Cd (II) by the two biosorbents better than the pseudo-first order model.

Adsorption isotherms

There are many equations for analyzing experimental adsorption equilibrium data. The isotherm parameters of these models often provide some insight into the adsorption mechanism, the surface properties and affinity of the adsorbent^[24]. In this study, the Langmuir^[25], Freundlich^[26] and DubininRaduskevich^[27] were employed. The non-linear forms of these models are presented below:

$$\text{Langmuir model: } q = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

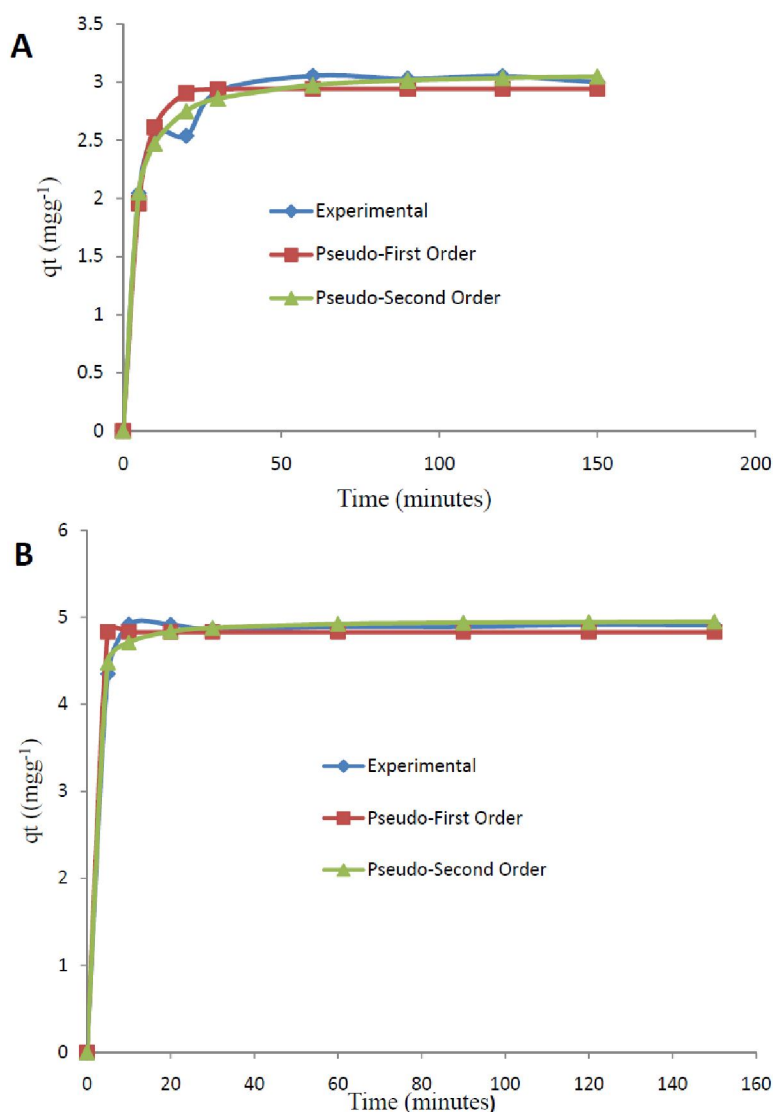


Figure 3 : Kinetic models for the biosorption of Cd (II) using (A) hydrochloric acid treated hooves and (B) sodium hydroxide treated hooves

TABLE 2 : Isotherm parameters for Cd (II) adsorption, using HCH and SCH at four different temperatures

	HCH				SCH			
	25° C	35° C	45° C	55° C	25° C	35° C	45° C	55° C
Langmuir								
$q_m(\text{mgg}^{-1})$	5.51	4.76	3.26	2.84	7.19	7.48	7.55	7.92
$K_L(\text{Lmg}^{-1})$	0.15	0.11	0.11	0.05	1.19	1.47	1.59	2.43
R^2	0.9826	0.8406	0.9890	0.9537	0.8555	0.9079	0.9158	0.9506
ERRSQ	0.17	1.23	0.03	0.08	3.83	2.59	2.57	1.68
Freundlich								
$K_f(\text{mgg}^{-1}(\text{mg L}^{-1}))$	1.3	0.92	0.78	0.55	3.58	3.93	4.03	4.49
N	2.8	2.5	3.10	3.00	4.49	4.87	4.93	4.93
R^2	0.9657	0.8797	0.9821	0.9233	0.8247	0.7953	0.8144	0.8389
ERRSQ	0.34	0.90	0.04	0.22	4.36	5.45	5.05	5.00
D-R								
$q_d(\text{mgg}^{-1})$	4.46	3.59	2.65	2.07	6.87	7.17	7.24	7.56
$E(\text{KJmol}^{-1})$	0.57	0.50	0.38	0.21	1.61	1.93	2.09	2.95
R^2	0.9081	0.6407	0.8441	0.8372	0.8373	0.9230	0.9352	0.9515
ERRSQ	0.91	2.79	0.39	0.29	5.65	3.42	3.17	2.54

$$\text{Freundlich model: } q = K_f C_e^{1/n} \quad (7)$$

DubininRaduskevich:

$$q = q_D \text{Exp} \left[-K \left(RT \ln \left(1 + \frac{1}{C_e} \right) \right)^2 \right] \quad (8)$$

Where q is the uptake (mgg^{-1}), C_e is equilibrium solute concentration, q_m is Langmuir maximum uptake capacity, K_L is Langmuir constant which defines the affinity between the sorbate and the biosorbent, K_f and n are Freundlich constants, q_D is the Dubinin–Radushkevich model uptake capacity and K is the Dubinin–Radushkevich model constant.

The non-linear fitting facilities of solveradd-in function; Microsoft Excel, Microsoft Corporation was also used as described under kinetic modeling to evaluate the differences in the q_e predicted by the models and the q_e determined experimentally (Equation 5). The data predicted by the models are presented in TABLE 2. It can be observed from the table that biosorption of Cd (II) by HCH was best fitted by the Langmuir model at the temperatures of 25, 45 and 55° C judging from the high R^2 and low error values obtained from Langmuir model. However at a temperature of 35° C the biosorption of cadmium was best described by Freundlich model (low error value of 0.90). Similarly, the low error values re-

corded for the removal of cadmium by SCH is a clear pointer to the fact that the removal of cadmium by SCH was best described by Langmuir model at all temperatures considered even though the R^2 values obtained from D-R model are relatively higher than those obtained from Langmuir model. The closeness of the lines obtained for Langmuir model and the experimental q_e values in Figures 4 and 5 further reveals that the biosorption of Cd (II) by both biosorbents was best fitted by Langmuir model.

The maximum adsorption capacities predicted by these models showed that there was increase in the amount of Cd biosorbed by SCH. For example, the maximum adsorption capacity predicted by Langmuir model increased from 7.19 to 7.92 mgg^{-1} when the temperature was raised from 25 to 55° C. However, for HCH, the maximum adsorption capacity decreased with increase in temperature.

The Freundlich constant n is related to intensity of adsorption and an adsorption process is favourable if $1 < n < 10$. Since all n values obtained from the isotherms are higher than 1.0, Cd (II) ions are said to be favourably adsorbed by the two biosorbents at all temperatures studied.

The mechanism of the biosorption of Cd (II) by both HCH and SCH can be explained using the mean energy values obtained from the DubininRaduskevich

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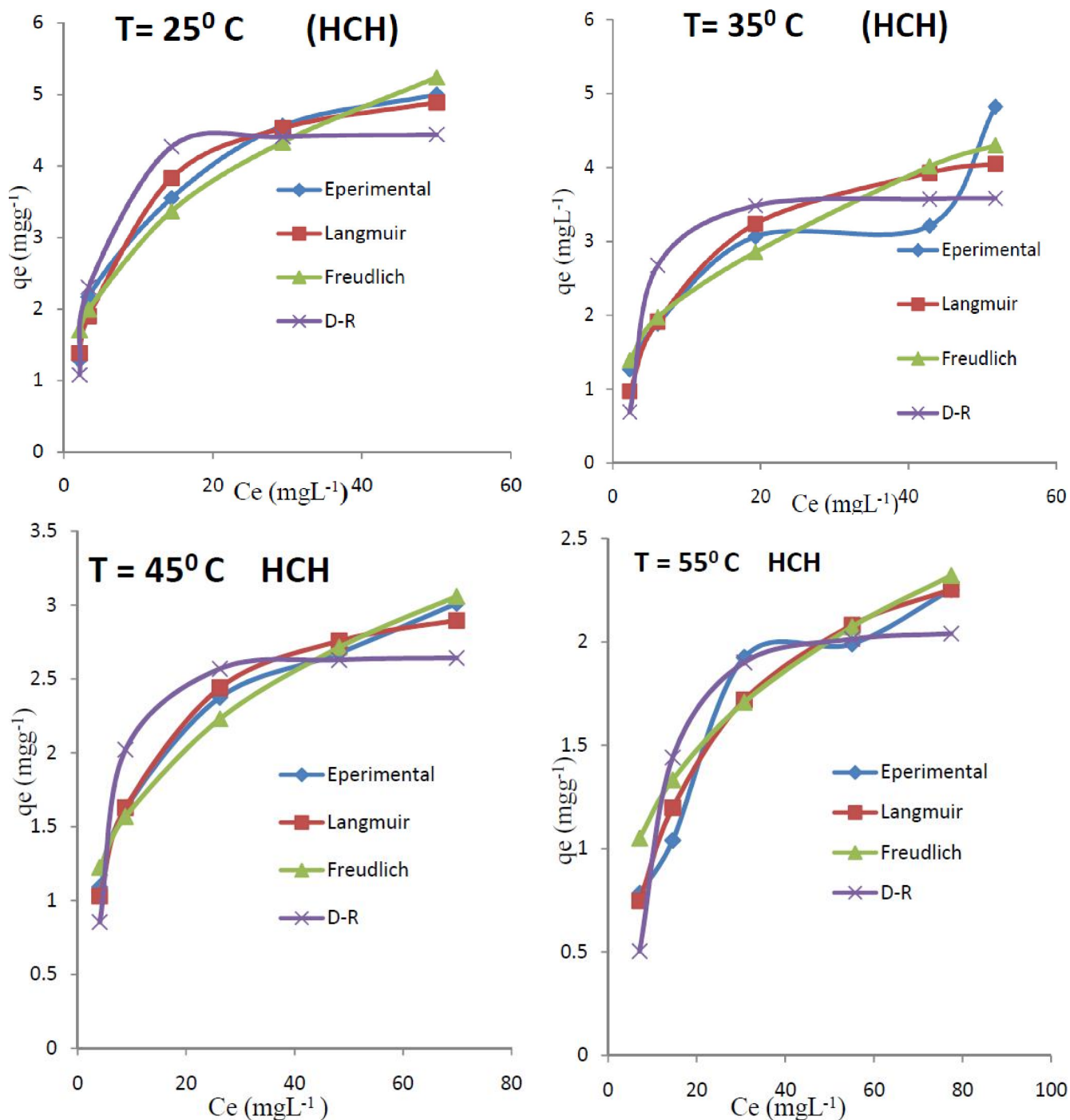


Figure 4 : Adsorption isotherm models for Cd (II) adsorption from aqueous solutions using HCH (biosorbent dosage: 0.25g, pH: 6, and contact time: 60 minutes)

model using equation:

$$E = \frac{1}{\sqrt{2K}} \quad (9)$$

If $E < 8 \text{ kJmol}^{-1}$, the adsorption process is dominated by physical adsorption mechanism and if E is between 8 and 16 kJmol^{-1} , the adsorption process is dominated by chemisorption mechanism^[28]. A criti-

cal look at TABLE 2 reveals that the sorption of cadmium by both HCH and SCH was dominated by physical adsorption.

FTIR spectra of the biosorbents

The FTIR spectra of both biosorbents before and after adsorption of cadmium were obtained to determine the possible involvement of the functional

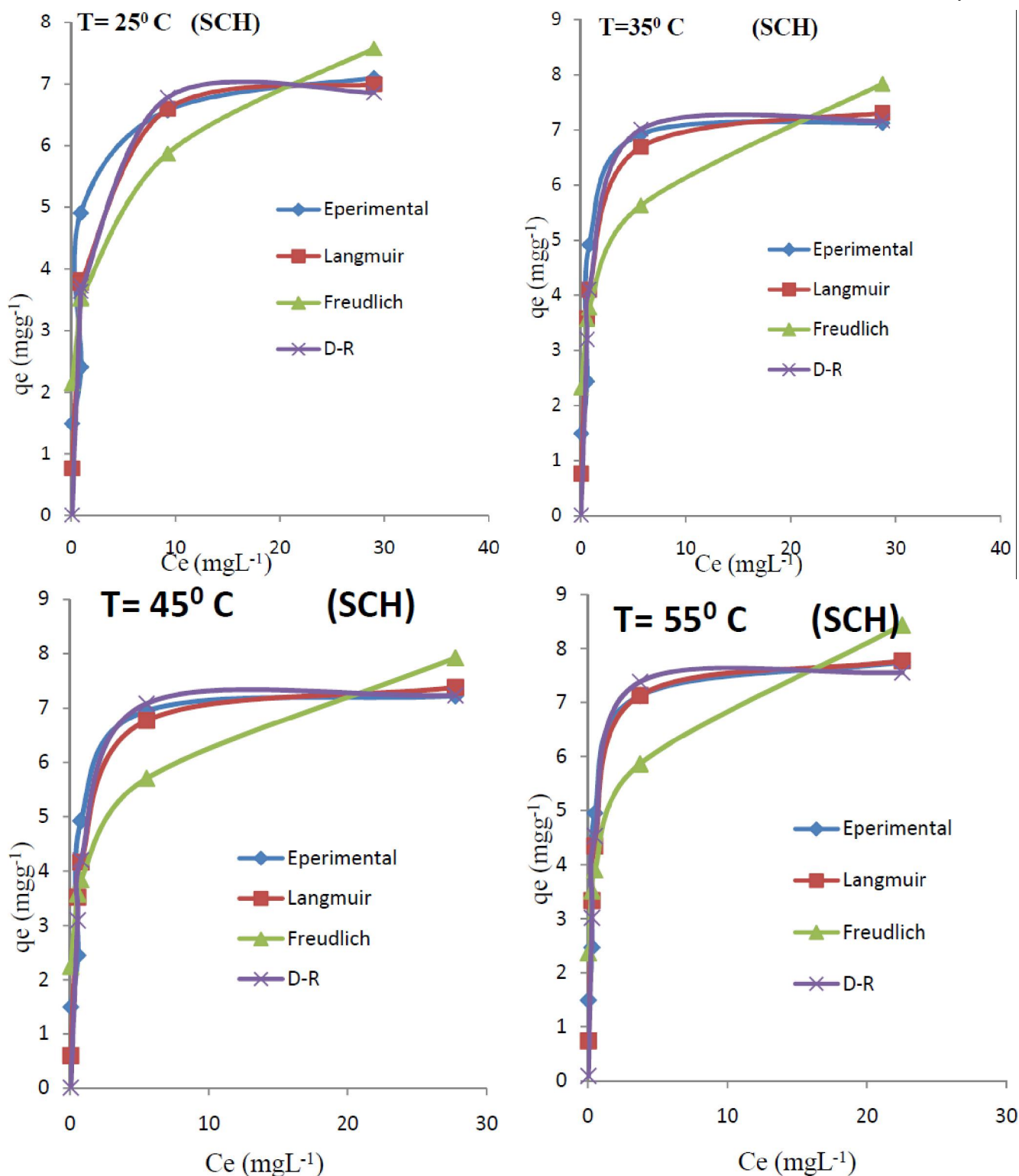


Figure 5 : Adsorption isotherm models for Cd (II) adsorption from aqueous solutions using SCH (biosorbent dosage: 0.25 g, pH: 3, and contact time: 60 minutes)

groups present on the surfaces of the biosorbents on the adsorption process. The spectroscopic characteristics of these spectra are shown in TABLES 3 and 4 while the spectra are presented in Figures 6A

and 6B. The spectra reveal the presence of certain functional groups on the surfaces of the biosorbent before and after adsorption. The spectra for hydrochloric acid treated hooves show that all the peaks

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TABLE 3 : FTIR spectral characteristics of hydrochloric acid modified cow hoof before and after Cd²⁺ adsorption

Frequency (cm ⁻¹) before adsorption	Frequency (cm ⁻¹) after adsorption	Difference	Assignment
3451.42	3429.00	22.42	Bonded -OH
2931.42 2948.57	2931.72	16.85	Aliphatic C-H groups
2377.14	-	-	S-H stretching
1649.48	1651.00	-1.52	C=O stretching of an amide
1541.19	1531.22	9.97	Nitro compound
1241.96	1236.26	5.7	C-N stretching

TABLE 4 : FTIR spectral characteristics of sodium hydroxide modified cow hoof before and after Cd²⁺ adsorption

Frequency (cm ⁻¹) before adsorption	Frequency (cm ⁻¹) after adsorption	Difference	Assignment
3428.00	3435.00	-7	Bonded -OH group
2931.42 2937.14	2931.42	5.72	Aliphatic C-H groups
2382.85	2377.14	5.71	S-H stretching
1653.33	1641.61	11.72	C=O stretching of an amide
1544.04	-	-	Nitrocompound
1239.11	1239.11	0	C-N stretching
1090.93	1068.13	22.8	C-O stretching

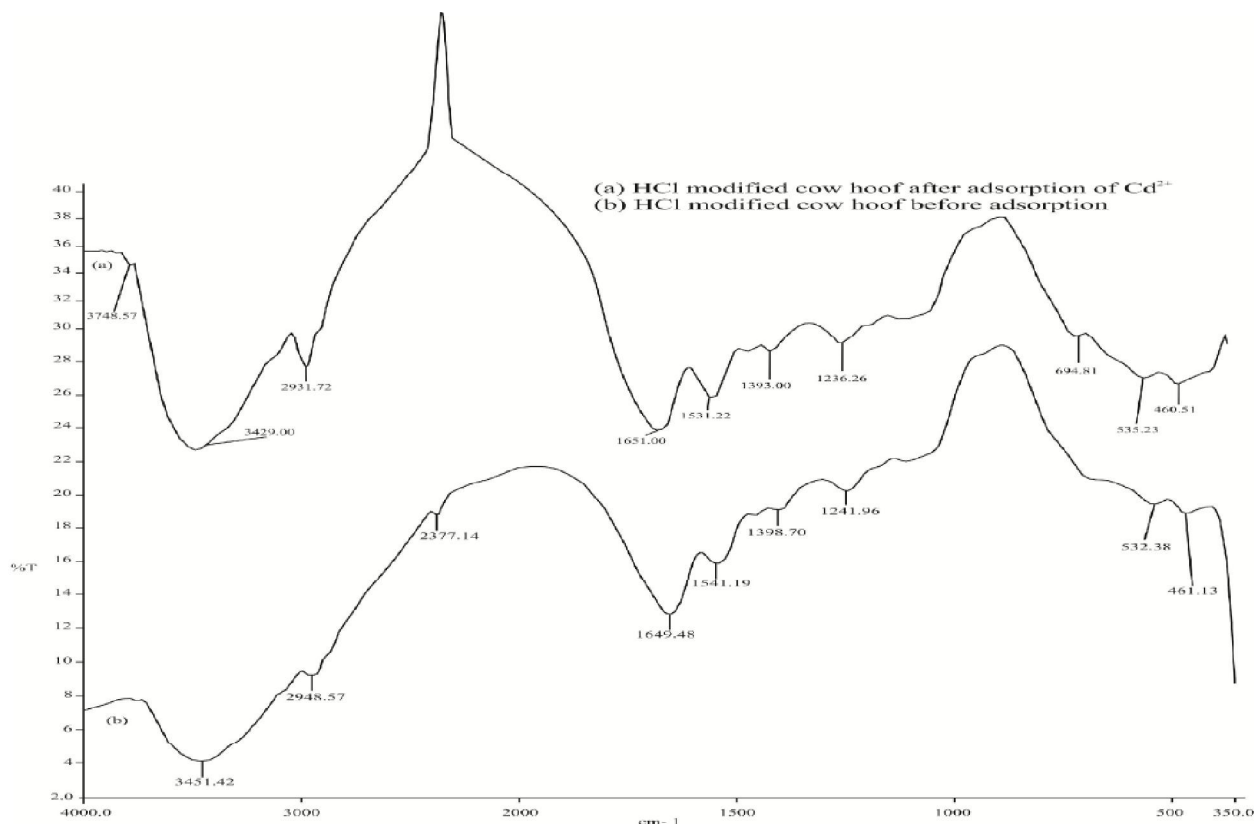


Figure 6A

were shifted and only one peak corresponding to S-H stretching disappeared after cadmium adsorption. This shows that the S-H bond and the functional

groups corresponding to the shifted peaks were likely involved in the adsorption of Cd by HCH.

Similarly, for sodium hydroxide treated hooves,

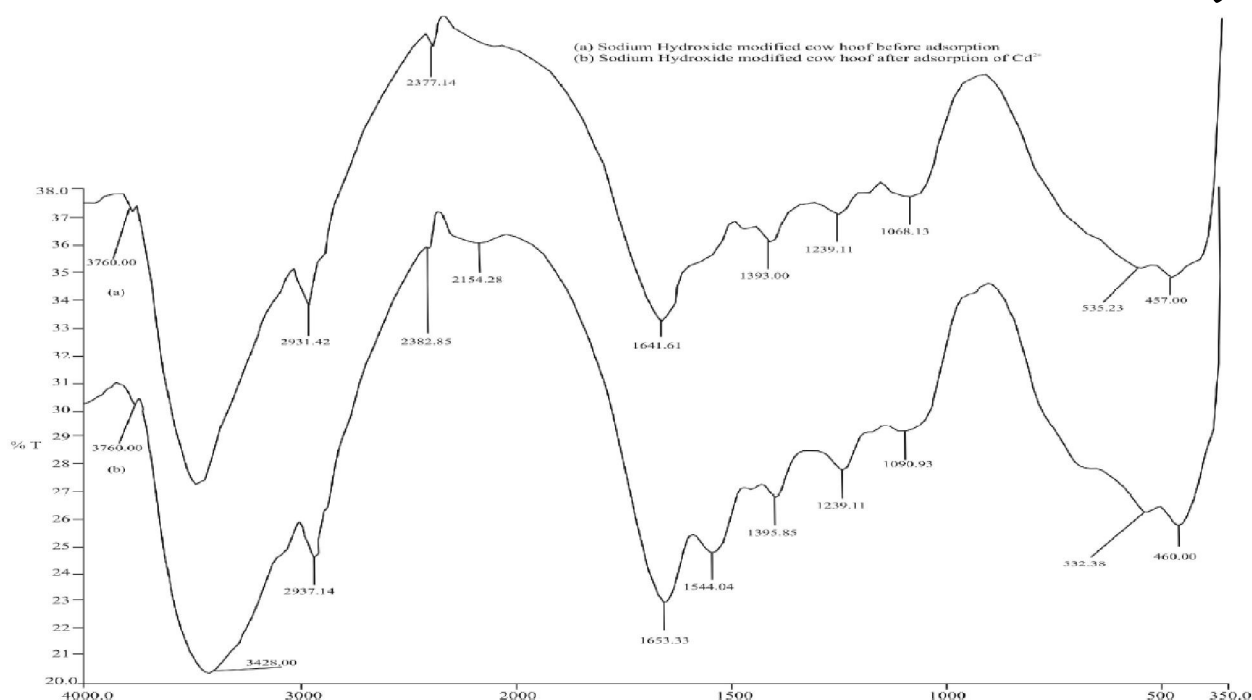


Figure 6B

nearly all the peaks observed before cadmium biosorption were shifted after the biosorption process (Figure 6B and TABLE 4) except the peaks corresponding to amino group and CN stretching. The peak at 1544.04 cm^{-1} (nitro compound) disappeared while the peak at 1239.11 cm^{-1} was retained after cadmium biosorption.

CONCLUSION

Hydrochloric acid treated (HCH) and sodium hydroxide treated (SCH) cow hooves were utilized as alternative adsorbents for removing cadmium ions from aqueous solution. It was established that at pH values of 3 and 6 maximum removals of cadmium ions took place using SCH and HCH respectively. It was also discovered that the removal of cadmium by HCH and SCH was brought to equilibrium after agitation time of 60 and 30 minutes respectively. Two kinetic models were used to analyse the adsorption data and the better fit was the pseudo-second order kinetic model. The equilibrium data obtained were tested with three non-linear isotherm models and it was found out that Langmuir model fitted the data best. This further showed that the removal of cadmium by SCH was favoured by increase

in temperature while its removal by HCH was favoured by decrease in temperature. The mono layer maximum adsorption capacities recorded for SCH was higher than those recorded for HCH at all temperatures considered. The shifts observed in the FTIR spectra peaks for both biosorbents after cadmium adsorption revealed that a bit of chemical interaction occurred between cadmium ions and the functional groups present on the biosorbents. However, the mean adsorption energies evaluated using DubininRaduskevich model obviously revealed that the removal of cadmium by both biosorbents was dominated by physical adsorption

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