

# Comparing the Different Methods Used in the Determination of Thermodynamic Parameters Using Adsorption of Pb(II) on to Chicken Feather as an Example

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## Authors' contributions

This work was carried out in collaboration between both authors. Author SAO designed the study and performed the statistical analysis. Authors SAO and CCO wrote the protocol and wrote the first draft of the manuscript. Author SAO managed the analyses of the study. Authors SAO and CCO managed the literature searches. Both authors read and approved the final manuscript.

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## ABSTRACT

**Background:** Thermodynamic parameters are important in determining the feasibility and spontaneity of an adsorption process. They are also vital in estimating adsorptive mechanisms (i.e., physisorption, ion exchange or chemisorption). Accurate calculation of these thermodynamic parameters is highly dependent on the equilibrium constant  $K_c$ . Many authors make use of constants obtained from various isotherm models, partition constant and distribution coefficient in calculating the thermodynamic parameters especially the Gibbs free energy. According to the provisions of the International Union of Pure and Applied Chemistry, the standard equilibrium constant ( $K^\circ$ ) for calculating Gibbs free energy change ( $\Delta G^\circ$ ) must be a dimensionless parameter.  
**Results:** In this work various methods have been employed in determining the thermodynamic parameters. Fourier Transform Infra-red Spectroscopy (FTIR) analysis confirmed the presence of

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carboxyl, hydroxyl, amino and sulphur-containing functional groups in chicken feathers. There were no substantial variations in the chicken feather spectra before and after biosorption as confirmed by FTIR Spectroscopy spectroscopy which can be an indication of the possible reuse of chicken feather.

**Conclusion:** Negative values of  $\Delta G$  show a spontaneous process with spontaneity increasing with temperature. Finally, scanning electron microscope images of the chicken feather were found to have rough and uneven surfaces.

**Keywords:** Chicken feather; heavy metals; lead; thermodynamic; enthalpy; entropy; Gibb's free energy.

## ABBREVIATIONS

AAS	: Atomic absorption spectrophotometer
BET	: Brunauer-Emmett-Teller
CF	: Chicken feather
FTIR	: Fourier Transform Infra Red Spectroscopy
$\Delta G^\circ$	: Gibb's energy change
$\Delta H^\circ$	: Change in enthalpy
$K^\circ$	: Standard equilibrium constant
$K_C$	: Equilibrium constant
$K_F$	: Freundlich adsorption constant
$K_L$	: Langmuir adsorption constant
$K_P$	: Partition constant
$1/n$	: Freundlich heterogeneity factor
Pb	: Lead
pH	: Potential of hydrogen
Q	: Metal uptake
$Q_{max}$	: Maximum metal uptake
$R^2$	: Coefficient of determination
Rpm	: Revolution per minute
$\Delta S^\circ$	: Change in entropy
SEM	: Scanning Electron Microscopy
T	: Temperature

## 1. INTRODUCTION

Adsorption is the transfer of molecules, ions or atoms from one phase (solid, liquid or gas) to another phase (liquid or solid). It differs from absorption being a surface phenomenon while absorption is a bulk phenomenon. The type of bonding may be ionic, covalent or metallic and this depends on the properties of the species concerned and the resulting process is generally classified as being physisorption, chemisorption or electrostatic sorption [1]. Adsorption is considered to be a fast physical or chemical process, and its rate is governed by the type of process. In other words, it can be defined as a general term for several passive accumulation processes which in any particular case may include ion exchange, coordination, complexation, chelation, adsorption and micro-precipitation [2]. One of the potential sorbents is

keratin biomaterials like wool, feather, hair etc which are receiving increasing attention for the heavy metal removal due to their availability, low cost and high uptake capabilities.

Keratin is a family of fibrous structural proteins that protects epithelial cells from damage and makes up the outer layer of human skin. It is the major structural component of wool, hair, feathers, horn and nail providing them with the required strength and toughness for masticatory organs, such as the tongue [3]. Keratinous materials are readily available around us as waste and have been used to adsorb metal ions from solution either in their native state or after pretreatment with a suitable chemical to enhance their uptake of metals. Feathers consist of about 91% keratin, 1.3% fat, and 7.9% water, making them a suitable sorbent for heavy metals removal.

Thermodynamic studies are important to interpret adsorption behaviour most importantly for equilibrium of the process [4]. Sorption behaviour/nature can be obtained from thermodynamic parameters like change in Gibb's energy change ( $\Delta G^\circ$ ), change in enthalpy ( $\Delta H^\circ$ ) and change in entropy ( $\Delta S^\circ$ ) associated with the uptake process. These parameters are highly dependent on the dimensionless thermodynamics equilibrium constant  $K_C$ . This thermodynamic equilibrium constant  $K_C$  can be obtained from the constant of various isotherm models like Langmuir (of various linearization type), Freundlich, Brunauer-Emmett-Teller (BET), Henry, Frumkin, Flory-Huggins and Redlich-Peterson etc. Thermodynamics equilibrium constant  $K_C$  can also be obtained from partition constant, distribution coefficient etc. the use of these various approaches might lead to discrepancies in the values of calculated thermodynamic parameters, hence the right approach must be sought.

The objectives of this work are to study the nature of adsorption of Pb(II) unto chicken

feathers and to compare the thermodynamic parameters calculated using different thermodynamic equilibrium constants ( $K_C$ ) that were obtained from the isotherm constants of various types of Langmuir isotherm linearization and Freundlich isotherm.

## 2. MATERIALS AND METHODS

### 2.1 Biosorption Thermodynamics

Chicken feathers (CFs) were obtained from a public slaughter point in Gwagwalada area council of the Federal Capital Territory-Abuja. The CFs have been washed, dried and cut into smaller sizes which have been used in the biosorption experiments.

Thermodynamics studies have been carried out using a single metal solution of Pb(II) aqueous solution at a pH of 4.0 using 0.05 g of CF in 50 cm<sup>3</sup> aqueous solution at a speed of 250 rpm on a magnetic stirrer varying the aqueous solution

temperature between 10 to 50°C. The resulting mixture has been filtered after stirring and the filtrate analyzed for metal concentration using AAS.

The metal uptake ( $Q$ , in mg/g) and the percentage biosorption (%) have been calculated using the equations:

$$\frac{(C_i - C_f) * V}{W} \tag{1}$$

$$\frac{(C_i - C_f)}{C_i} * 100 \tag{2}$$

$C_i$  = Initial metal concentration (mg/l)

$C_f$  = Final metal concentration (mg/l)

$V$  = Volume of solution (L)

$W$  = Weight of CF (g)

## 3. RESULTS

Results obtained from this work are presented in Tables 1 to 8 and Figs. 1 to 3 as follows:

**Table 1. Langmuir parameters for Pb(II) adsorption onto the chicken feather**

Langmuir type	T	$Q_{max}$		$K_L$		$R^2$
	(K)	(mg/L)	(mmol/L)	(L/mg)	(L/mmol)	
I	283	71.43	0.3447	0.3461	71.71	0.9065
	293	68.44	0.3303	0.3001	62.18	0.9591
	303	62.50	0.3016	0.2461	50.99	0.9692
	313	60.50	0.2943	0.2011	43.72	0.9394
	323	57.14	0.2758	0.1463	30.31	0.9618
II	283	47.17	0.2277	0.4896	101.45	0.9736
	293	46.30	0.2235	0.4011	83.11	0.9808
	303	45.25	0.2184	0.3896	80.73	0.9817
	313	43.86	0.2117	0.3022	62.62	0.9361
	323	43.85	0.2116	0.2211	45.82	0.9802
III	283	57.81	0.2790	0.6112	126.64	0.7702
	293	56.81	0.2742	0.5740	118.93	0.8355
	303	50.66	0.2445	0.5190	107.66	0.7169
	313	49.71	0.2399	0.5023	104.08	0.7748
	323	46.42	0.2240	0.4888	101.28	0.8024
IV	283	68.88	0.3324	0.4992	103.43	0.8940
	293	66.59	0.3214	0.4163	86.26	0.8355
	303	54.68	0.2639	0.4166	86.32	0.8069
	313	50.11	0.2418	0.3246	67.26	0.8148
	323	49.58	0.2393	0.2998	62.19	0.8214
V	283	50.11	0.2418	0.4821	99.89	0.9233
	293	49.94	0.2410	0.4101	84.97	0.9808
	303	46.36	0.2237	0.3922	81.26	0.9817
	313	44.70	0.2157	0.3301	68.40	0.9361
	323	34.68	0.1674	0.2667	55.26	0.9802

**Table 2. Freundlich parameters for Pb(II) adsorption onto the chicken feather**

T (K)	$K_F$ (mg/g)(L/mg) <sup>1/n</sup>	$K_F$ (mmol/g)(L/mmol) <sup>1/n</sup>	n	1/n	R <sup>2</sup>
283	5.87	0.49	1.875	0.5332	0.9824
293	7.28	0.51	2.001	0.4997	0.9922
303	28.50	3.13	1.707	0.5859	0.7714
313	19.36	0.70	2.650	0.3773	0.8910
323	14.90	0.43	2.965	0.3373	0.9586

**Table 3. Thermodynamic parameters obtained from Langmuir constant using  $K_c = 55.5 * 1000 * 207 * K_L$  (in L/mg)**

Linear forms of Langmuir	T(K)	van't Hoff equation	Kc	$\Delta G^\circ$ (KJ/mol)	$\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/mol)	R <sup>2</sup>
I	283	y = 1927.8x + 8.4421	3976170	-35.75	-16.03	70.19	0.9667
	293		3447699	-36.67			
	303		2827320	-37.42			
	313		2310337	-38.13			
	323		1680768	-38.49			
II	283	y = 1697.3x + 9.5876	5624770	-36.57	-14.11	79.71	0.9194
	293		4608037	-37.38			
	303		4475920	-38.58			
	313		3471825	-39.19			
	323		2540107	-39.60			
III	283	y = 534.12x + 13.869	7021771	-37.09	-4.44	115.31	0.9598
	293		6594399	-38.25			
	303		5969425	-39.30			
	313		5770674	-40.51			
	323		5615579	-41.73			
IV	283	y = 1157.2x + 11.474	5735059	-36.62	-9.62	95.39	0.9348
	293		4782663	-37.47			
	303		4786109	-38.75			
	313		3729167	-39.38			
	323		3444252	-40.42			
V	283	y = 1272.8x + 11.05	5538606	-36.53	-10.58	91.87	0.9498
	293		4711434	-37.43			
	303		4505790	-38.60			
	313		3792354	-39.42			
	323		3063983	-40.11			

**Table 4. Thermodynamic parameters obtained from Langmuir constant using  $K_c = 55.5 * 1000 * K_L$  (in L/mmol)**

Linear forms of Langmuir	T(K)	van't Hoff equation	Kc	$\Delta G^\circ$ (KJ/mol)	$\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/mol)	R <sup>2</sup>
I	283	y = 1882.7x + 8.6018	3979905	-35.76	-15.65	71.52	0.9508
	293		3450990	-36.67			
	303		2829945	-37.42			
	313		2426460	-38.26			
	323		1682205	-38.50			
II	283	y = 1697.1x + 9.5896	5630475	-36.57	-14.11	79.73	0.9194
	293		4612605	-37.38			
	303		4480515	-38.58			
	313		3475410	-39.19			
	323		2543010	-39.61			

Linear forms of Langmuir	T(K)	van't Hoff equation	Kc	$\Delta G^\circ$ (KJ/mol)	$\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/mol)	R <sup>2</sup>
III	283	y = 534.05x + 13.870	7028520	-37.09	-4.44	115.32	0.9598
	293		6600615	-38.25			
	303		5975130	-39.31			
	313		5776440	-40.52			
	323		5621040	-41.73			
IV	283	y = 1155.1x + 11.482	5740365	-36.62	-9.60	95.46	0.9347
	293		4787430	-37.47			
	303		4790760	-38.75			
	313		3732930	-39.38			
	323		3451545	-40.43			
V	283	y = 1272.7x + 11.051	5543895	-36.54	-10.58	91.88	0.9498
	293		4715835	-37.43			
	303		4509930	-38.60			
	313		3796200	-39.42			
	323		3066943	-40.11			

**Table 5. Thermodynamic parameters obtained from Langmuir constant using  $K_c = 10^6 K_L$  (in L/mg)**

Linear forms of Langmuir	T(K)	van't Hoff equation	Kc	$\Delta G^\circ$ (KJ/mol)	$\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/mol)	R <sup>2</sup>
I	283	y = 1927.8x + 6.0007	346100	-30.01	-16.03	49.89	0.9667
	293		300199	-30.72			
	303		246100	-31.27			
	313		201100	-31.78			
	323		146300	-31.94			
II	283	y = 1697.3x + 7.1463	489600	-30.83	-14.11	59.41	0.9194
	293		401100	-31.43			
	303		389600	-32.43			
	313		302200	-32.84			
	323		221100	-33.05			
III	283	y = 534.12x + 11.428	611200	-31.35	-4.44	95.01	0.9598
	293		574000	-32.30			
	303		519600	-33.15			
	313		502300	-34.16			
	323		488800	-35.18			
IV	283	y = 1157.2x + 9.0326	499200	-30.87	-9.62	75.10	0.9348
	293		416300	-31.52			
	303		416600	-32.60			
	313		324600	-33.02			
	323		299800	-33.87			
V	283	y = 1272.8x + 8.6083	482100	-30.79	-10.58	71.57	0.9498
	293		410100	-31.48			
	303		392200	-32.45			
	313		330100	-33.07			
	323		266700	-33.55			

**Table 6. Thermodynamic parameters obtained from Freundlich constant using  $K_c = 10^3 k_f [\text{in (mg/g)(L/mg)}^{1/n}]$**

T(K)	Van't Hoff equation	Kc	$\Delta G^\circ$ (KJ/mol)	$\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/mol)	R <sup>2</sup>
283	y = -2675x + 18.31	5870	-20.84	22.24	152.23	0.4864
293		7280	-22.36			
303		28500	-23.86			
313		19360	-25.41			
323		14900	-26.93			

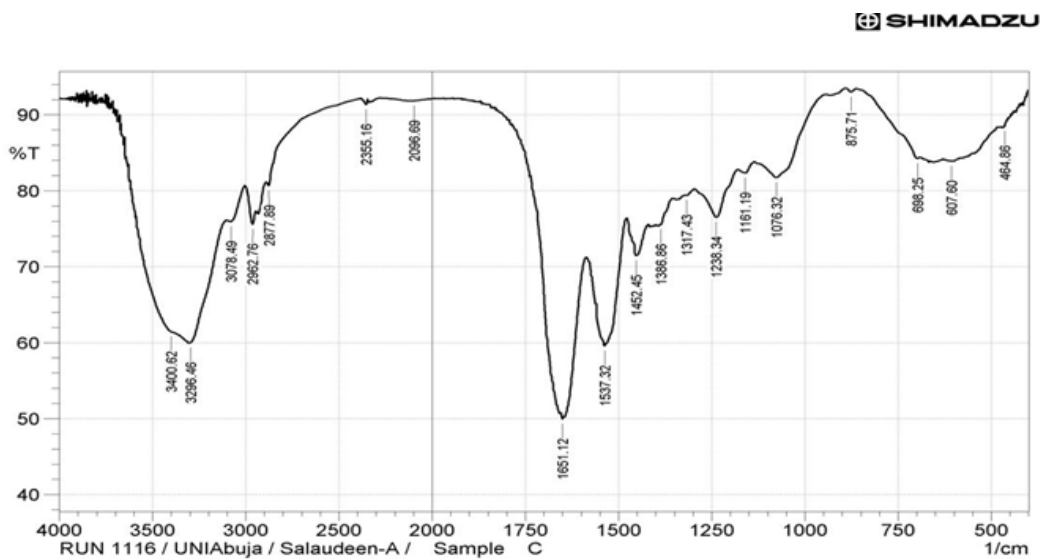
**Table 7. Thermodynamic parameters obtained from Freundlich constant using**

$$K_c = K_F \rho \left(\frac{10^6}{\rho}\right)^{(1-1/n)}$$

T(K)	Van't Hoff equation	Kc	$\Delta G^\circ$ (KJ/mol)	$\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/mol)	R <sup>2</sup>
283	y = -9034x + 39.8	3710.5	-18.53	75.11	330.90	0.8784
293		7310.2	-21.84			
303		8698.5	-25.15			
313		105464.3	-28.46			
323		141054.3	-31.77			

**Table 8. FTIR spectra bands and assignments of chicken feather**

Assignments	Wavenumbers (cm <sup>-1</sup> )
N-H stretch	3296.46
Methyl C-H asym/sym. Stretch	2962.76/2877.89
Amide I, 80% C=O stretch and 20% N-H bend	1651.12
Amide II, 60% N-H bend and 40% C-N stretch	1537.32
Amide III, 40% C-N stretch, 30% N-H bend and O=C=N bend	1238.34
Sulphonate S-O asym. Stretch	1161.19
Sulphonate S-O sym. Stretch	1032.11
Cystine dioxide (R-SO <sub>2</sub> -S-R)	1238.34
Cystine monoxide (R-SO-S-R)	1076.32
Cystine	1176.62 – 1031.95



**Fig. 1. FTIR spectra of virgin chicken feather**

SHIMADZU

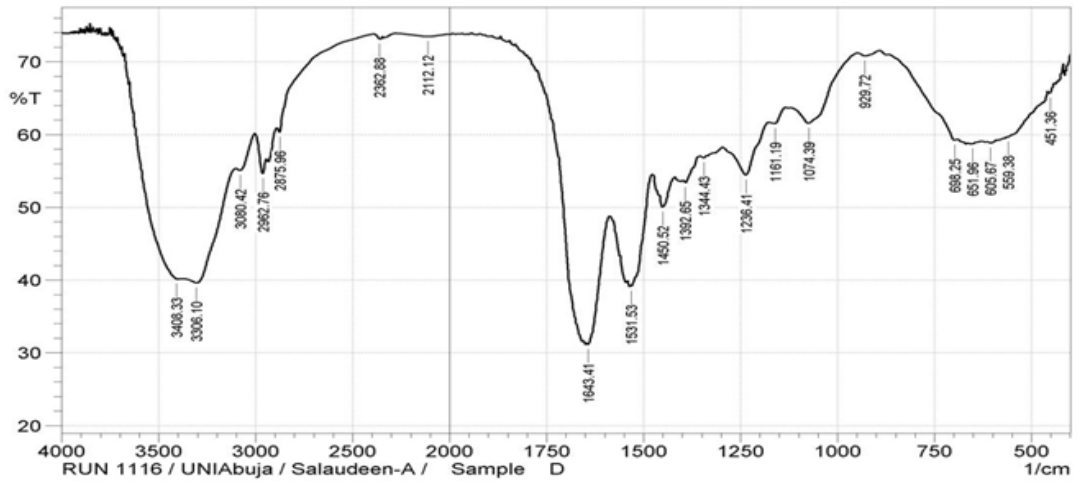
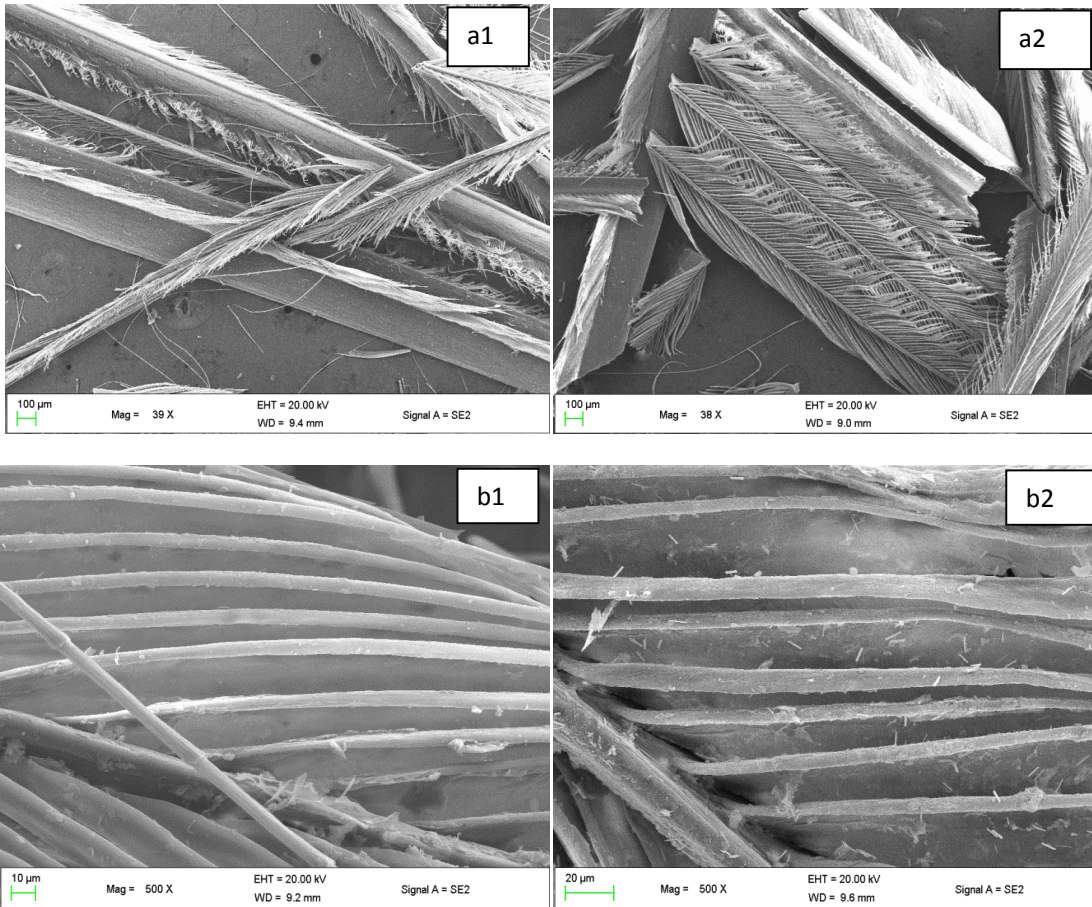
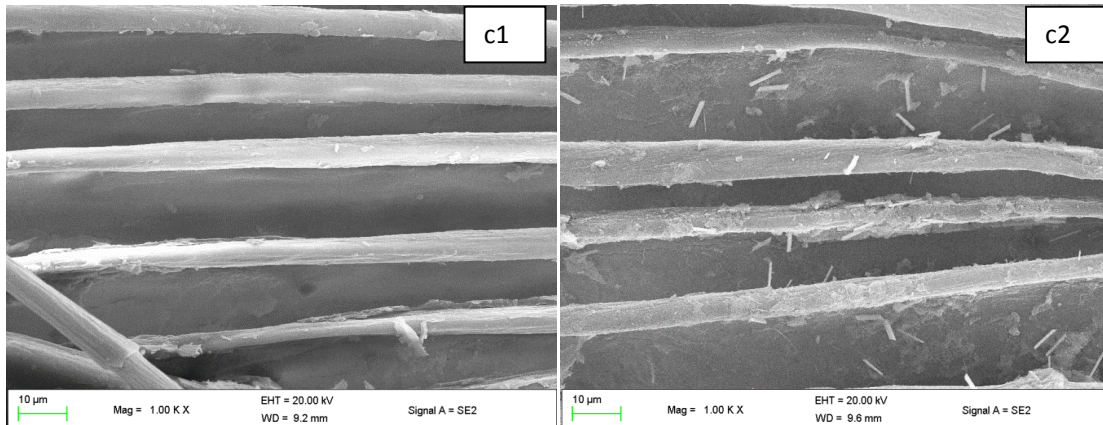


Fig. 2. FTIR spectra of metal loaded chicken feather





**Fig. 3. Scanning electron micrograph of CF: (a1) virgin and (a2) loaded at 40X mag.; (b1) virgin and (b2) loaded at 500X mag.; and (c1) virgin and (c2) loaded at 1000X magnification**

## 4. DISCUSSION

### 4.1 Isotherm Models

The Langmuir equation [5] is based on the following assumptions

- The adsorbent surface has a finite number of identical sites with uniform energies
- Amount of adsorbate adsorbed is independent of adsorption rate i.e adsorbed species do not interact
- Only a monolayer can be formed even after the saturation of adsorption sites.

The non linear form of Langmuir equation is given as [5]

$$q_e = \frac{Q_{max}K_L C_e}{1 + K_L C_e} \quad (3)$$

Its linearized forms are given below

#### Type I

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_{max}}\right) C_e + \frac{1}{Q_{max}K_L} \quad (4)$$

#### Type II (Lineweaver-Burk Linearization)

$$\frac{1}{q_e} = \left(\frac{1}{Q_{max}K_L}\right) \frac{1}{C_e} + \frac{1}{Q_{max}} \quad (5)$$

#### Type III (Eadie-Hoffsie Linearization)

$$q_e = \left(\frac{-1}{K_L}\right) \frac{q_e}{C_e} + Q_{max} \quad (6)$$

#### Type IV (Scratchard Linearization)

$$\frac{q_e}{C_e} = -K_L q_e + Q_{max} K_L \quad (7)$$

#### Type V

$$\frac{1}{C_e} = -K_L Q_{max} \frac{1}{q_e} - K_L \quad (8)$$

Where

$Q_{max}$  = Saturated amount of adsorbed adsorbate, (mg/g)

$C_e$  = Equilibrium concentration of adsorbate in solution, (mg/L)

$K_L$  = Langmuir adsorption constant, (L/mg)

$q_e$  = Uptake at equilibrium (mg/g)

The Freundlich equation is based on adsorption onto heterogeneous surface [6]. It can be expressed as

$$q_e = k_f C_e^{1/n} \quad (9)$$

Where

$k_f$  = Freundlich adsorption constant, (mg/g)

$C_e$  = Equilibrium concentration of adsorbate in solution, (mg/L)

When linearized, the below equation is obtained

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (10)$$

## 4.2 Thermodynamic Parameters

Thermodynamic studies are useful in determining the spontaneity and feasibility of an adsorption



process. They are necessary for interpreting adsorption behaviours [7]. Thermodynamic parameters like  $\Delta H^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  can be obtained from Langmuir equilibrium constant ' $K_L$ ', Freundlich equilibrium constant ' $K_f$ ', partition constant ' $K_p$ ' etc. correct and accurate values for these thermodynamic parameters are largely dependent on equilibrium constant. Looking at previously published works, one would observe series of anomalies in the calculation of these parameters using most especially the Langmuir constant with various units such as L/mg, L/mol, L/g, L/mmol etc. with Gibb's free energy ( $\Delta G$ ), the level of spontaneity of adsorption can be determined. More negative values of  $\Delta G$  indicate energetically favourable adsorption. The van't Hoff equation is important in determining the  $\Delta G$  as it provides a relationship between temperature in Kelvin and equilibrium constant ' $K_c$ '.

$$\Delta G = -RT \ln K_c \quad (11)$$

$$\Delta G = \Delta H - T \Delta S \quad (12)$$

Substituting equation 11 into 12

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (13)$$

From the plot of  $\ln K_c$  vs  $\frac{1}{T}$ , entropy change  $\Delta S$  and enthalpy change  $\Delta H$  of the adsorption process can be obtained from the intercept and slope of the plot respectively.

From equation 11,

R = universal gas constant (8.314 Jmol<sup>-1</sup>K<sup>-1</sup>)

T = temperature (K)

Kc = equilibrium constant

The unit of  $\Delta G$  is J/mol, the term RT also has the unit J/mol (from Jmol<sup>-1</sup>K<sup>-1</sup> x K), therefore the equilibrium constant  $K_L$  must have no unit i.e dimensionless. It is therefore very incorrect to use  $K_L$  values with unit in the calculation of  $\Delta G$ .

### 4.3 Calculating Equilibrium Constant from Langmuir Constant $K_L$

For an adsorption process taking place in an aqueous medium, the Langmuir constant  $K_L$  can easily be converted to dimensionless equilibrium constant Kc using the equations

$$K_c = K_L \times M_w \times 55.5 \times 1000 \quad (14)$$

$$K_c = K_L \times 55.5 \times 1000 \quad (15)$$

Equation 14 is used for  $K_L$  values in L/mg while equation 15 is used for  $K_L$  values in L/mmol, where  $M_w$  is the molecular weight/atomic mass of adsorbate as may apply. This was initially proposed by Milonjic [8] and then developed by Zhou and Zhou [9] and Liu [10].

The factor 55.5 (dm<sup>3</sup>mol<sup>-1</sup>mol<sup>-3</sup>) is dimensionless and it is the number of moles of pure water per litre of solution. It is obtained by dividing ~1000 g/L by 18 g/mol. Multiplying by this factor makes equations 14 and 15 dimensionless.

Substituting equation 14 into equation 11

$$\Delta G = -RT \ln(K_L \times M_w \times 55.5 \times 1000) \quad (16)$$

Substituting equation 14 into equation 13

$$\ln(K_L \times M_w \times 55.5 \times 1000) = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R} \quad (17)$$

Equation 17 is now in the form of  $y = mx + c$

Where  $\ln(K_L \times M_w \times 55.5 \times 1000) = y$ ,  $x = \frac{1}{T}$

The thermodynamic parameters obtained by applying equation 14 to 17 are given in Tables 3 and 4. From the table, it is obvious that the Kc values obtained from the five linearizations of the Langmuir equation are different. The ranges of Kc values obtained are 1680768-3976170, 2540107-5624770, 5615579-7021771, 3444252-5735059 and 3063983-5538606 for type I, II, III, IV and V respectively. The trend for the Kc values obtained are: Type III > Type IV > Type V > Type II > Type I. The Kc values tend to decrease with increasing temperature indicating Kc is temperature-dependent. With the large difference in Kc values, there was only a small difference in  $\Delta G$  values obtained.

Milonjic [8,11] proposed that Kc can be obtained as a dimensionless constant by multiplying  $K_L$  in L/mg by 10<sup>6</sup>

$$K_c = K_L \times 10^6 \quad (18)$$

$$\Delta G = -RT \ln(K_L \times 10^6) \quad (19)$$

$$\ln(K_L \times 10^6) = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R} \quad (20)$$

10<sup>6</sup> factor is assumed to be solution density taking the density of pure water to be 1.0 g/ml

Thermodynamic parameters obtained by using equation 18 to 20 are given in Table 5.

It is obvious from the  $K_c$  values obtained that its magnitude is highly dependent on the type of linearization used on the Langmuir equation and the method used to make  $K_c$  dimensionless constant using equation 21

$$K_c = K_F \rho \left(\frac{10^6}{\rho}\right)^{(1-1/n)} \quad (21)$$

for  $K_F$  in (mg/g)(mg/L)<sup>1/n</sup>

$$K_c = K_F \rho \left(\frac{10^6}{\rho} \cdot M_W\right)^{(1-1/n)} \quad (22)$$

for  $K_F$  in (mmol/g)(mmol/L)<sup>1/n</sup>

$$\ln\left[K_F \rho \left(\frac{10^6}{\rho}\right)^{(1-1/n)}\right] = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R} \quad (23)$$

and as used by Tran and Chao [12]

$$K_c = K_F \times 10^3 \quad (24)$$

$$\ln(K_F \times 10^3) = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R} \quad (25)$$

The units of  $K_F$  can be converted using

$$K_F = K_F^* \cdot (M_W)^{(1-1/n)} \quad (26)$$

$K_F$  is in (mg/g)(mg/L)<sup>1/n</sup>

$K_F^*$  is in (mmol/g)(mmol/L)<sup>1/n</sup>

$\rho$  = density of pure water (~1.0 g/ml)

The Gibb's free energy obtained from the Freundlich equilibrium constant were consistent with those obtained from Langmuir constant in sign but not in magnitude, with a higher correlation coefficient from Langmuir plots.

#### 4.4 FTIR Analysis

FTIR analysis has carried out to identify the functional groups which could be responsible for biosorption. FTIR spectra were recorded using Shimadzu FTIR-8400S. The FTIR spectra of chicken feathers were carried out pre and post sorption and shown in Figs. 1 and 2. The approximate assignments and wavenumbers of the vibrational modes for both spectra are listed in Table 8. The spectra obtained for the virgin and metal loaded chicken feather are very similar, indicating that the main functional groups on the chicken feather did not change significantly during the biosorption process, indicating the possibility of regeneration and re-use. However, the metal-loaded chicken feather and the virgin one showed some differences in their spectra.

The slight differences in the spectra around 930, 1078, 1400, 1535 and 3300 cm<sup>-1</sup> are probably due to the presence of the metal ions on the biosorbent surfaces.

#### 4.5 SEM Analysis

SEM micrographs of CF were scanned before and after metal sorption using Scanning Electron Microscope JEOL JSM 6100 at magnifications of 40, 500 and 1000 to determine their surface morphology and are presented in Fig. 3.

From the micrographs, it is evident that there are no significant or pronounced differences in the surface morphology of the adsorbent before and after biosorption experiments, which is advantageous in terms of the possibility of re-use of the sorbent. SEM micrographs of CF resemble the human ribs with a rough and uneven surface. It is seen that the surface of the CF after metal biosorption became rougher and cavities became closer than they were before biosorption, indicating that the superficial layers on the sorbent are closed after biosorption possibly due to acidic nature of the aqueous solution before the biosorption experiments.

It is also evident from the micrographs that CF has a high surface area possibly leading to a relatively good adsorption capacity.

#### 5. CONCLUSION

From this work, the following conclusions can be drawn:

1. Equilibrium constant  $K_c$  is temperature-dependent i.e inversely proportional to temperature.
2. The thermodynamic parameters  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  calculated from the different linearization of Langmuir constants all have the same sign.
3. Negative values of  $\Delta G$  show a spontaneous process with spontaneity increasing with temperature.
4. From the FTIR spectra obtained, hydroxyl, carboxyl, amino and sulphur-containing groups are present in chicken feather with no significant difference in the spectra before and after sorption.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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