

Thermodynamics of Batch Adsorption of Fe^{2+} from Aqueous Solution Using Bamboo-Derived Activated Carbon

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Abstract— In this study the thermodynamics of batch adsorption of iron II ion from aqueous solution using bamboo-derived activated carbon has been investigated. Bamboo was converted into carbon using a pyrolytic reactor. The carbon was then activated using nitric acid. The prepared activated carbon was characterized at two different temperatures with the higher temperature showing a high iodine number. Experimental data obtained from the use of spectrophotometer were analyzed using four model equations; Langmuir, Freundlich, Temkin and Redlich-Peterson. It was found that Langmuir model fits the adsorption most with the highest correlation coefficient $R^2 = 0.992$. Thermodynamics parameters such as Gibbs free energy, enthalpy change, entropy, sticking probability and activated energy were calculated. The value for entropy obtained was positive which signifies a higher decrease of randomness. Sticking probabilities values obtained which are < 1 indicates the probability of the metal to stick on the activated bamboo carbon and activation energy values are all less than 20KJ/mol. The adsorption of Fe^{2+} upon activated carbon from bamboo was found to be spontaneous and endothermic in nature with increase randomness. This study also shows that the adsorption follows physisorption mechanism. It is recommended that other three parameters isotherm be used to evaluate the sorption process.

Keywords— Activated carbon; Bamboo; Batch Adsorption ; Iron (II) ion, Thermodynamics.

I. INTRODUCTION

Water pollution is the introduction of foreign or unwanted matters to the water bodies that makes the water unfit for human consumption, aquatic lives and plant [1]. Heavy metals in water are pollutants which makes water harmful to health. Some heavy metals that occur naturally are mercury, lead, tin, zinc. They are intrinsic part of the earth's crust with relatively high densities, atomic weight or atomic numbers. Heavy

metals can degrade air, water and soil quality and subsequently cause health issues in animals, plants and humans when they accumulate as a result of industrial activities [2]. The roots of heavy metals in the environment are as follows: waste from Industrial, metal manufacturing, fertilizers, emission from vehicles, mining and paint production. Heavy metals enter plants, animals and humans' tissue via ingestion of contaminated food and drinking water, absorption through the skin, manual handling and inhalation [3]. The main entrance route of heavy metals into the food chain is by adsorption by plant roots. Heavy metals affect soil activities by changing the microbial community which synthesizes enzymes. Reduction in the number and activities of soil micro-organisms has been linked to the presence of heavy metals. The concentration of heavy metals in plant has resulted to poor plant growth, decrease in yield and reduction in nutrient uptake by the plant [4]. The effect of heavy metals on human includes lung diseases, kidney damage, disturbance of blood circulation, damage to the nervous system, bone diseases. Iron as a heavy metal is beneficial to man in the right quantity but when in excess can result in the damage of the liver, conjunctivitis and in extreme cases death. Chemical precipitation, coagulation and flocculation, ion exchange, membrane filtration, electro dialysis is some of the methods used for the removal of heavy metals from waste water. Adsorption which involves the adhesion of an ion or molecules onto the surface of another substance e.g. a solid is also used to remove heavy metals from waste water. In recent times, Bio adsorption which is a biological method for the removal of heavy metal from waste water has been adopted. Bio adsorbents which include forest products, agricultural waste, algae, and agricultural products are used for the maximum removal of heavy metals from waste water. Bio adsorption is environmentally friendly and cheap making it preferable to other treatment methods [5]. In recent times, activated carbon has been analyzed as an adsorbent for the removal of heavy metals in water. Due to its high porosity and large surface area, it is considered as an excellent adsorbent for the treatment of water. Apart for its uses as an adsorbent,

activated carbon also has applications as a disinfectant, in the treatment of poison, in the purification of alcoholic drinks and many more application. The knowledge and comprehension of the mechanism of adsorption is therefore relevant and can be obtained from adsorption isotherm [6]. The thermodynamics study which considered parameters such as Gibbs free energy, enthalpy, entropy, sticking probability and activation energy has been used to establish the nature of the adsorption process. Abechi [1] studied the mechanism of adsorption of methylene blue onto activated carbon using thermodynamics tools. He concluded that the adsorption process was characterized by high activation energy and that due to the high value of the enthalpy, the adsorption process is chemisorption. Ademiluyi and Ujile [7] carried out a research work on the kinetics of batch adsorption of iron ii ion from aqueous solution using activated carbon from Nigeria bamboo. They concluded that Langmuir isotherm model produces a better fit.

The objective of this paper was to investigate the thermodynamics of batch adsorption of Iron II ion from aqueous solution using activated bamboo carbon.

II. MATERIALS AND METHODS

MATERIALS

The materials and apparatus used for this research work include waste Nigerian bamboo, a pyrolytic reactor for the carbonization of the bamboo, a condenser attached to the reactor to condense the by-product of the pyrolysis process, nitric acid, Iron (II) salt (both of analytical grade), electronic weighing balance, crucibles, funnels, desiccators, pH tester, filter paper, temperature sensor, crucible, spatula, crusher, sieve, cylinder, petri dish, thermostat water bath, atomic absorption spectrophotometer.

METHODS

Preparation of Bamboo Sample

The sample was obtained from Ozuoba in Emuoha Local Government Area of Rivers State. They were cut into small sizes of about 108mm with a cutting machine, washed thoroughly with distilled water to remove suspended matters and dust. The cleaned sample was then sun dried for 4 hours.

Carbonization

500g of the sun dried bamboo were weighted and introduced into a pyrolysis reactor at about 350^oC for about 5 hours. To the pyrolysis unit, a condenser was attached to monitor the distillate formation rate. At the termination of the carbonization process, the char produced was allowed to cool to room temperature and then kept in a dry clean container (3).

Chemical Activation

The carbonized product of known weighted was crushed with a mechanical grinder. Trioxonitrate (V) acid of known concentration was used as activator. Double activation was used for this process. The crushed bamboo was activated with Trioxonitrate (v) acid in a ratio of 1:2. The mixture was stirred until a paste is formed and then heated in an oven at 105^oC for 2 hours. The activated carbon was further activated with same amount of nitric acid, heated in an oven at 105^oC for 1 hour and then heated in a furnace at 500^oC for two and half hours. The activated bamboo carbon was allowed to cool at room temperature, and then washed several times until a pH value of approximately 7 was obtained. The sample was dried in an oven at temperature of 105^oC for four hours. The activation process was also repeated at a temperature of 550^oC for three and half hours to compare the effectiveness of temperature and time on activation. The final products was sieved to get 75µm particle size and kept in a clean dry air tight container.

Characterization of Activated Carbon

The parameters considered in the characterization of activated carbon include; moisture content, dry matter, bulk density, ash content and iodine number.

Adsorption Experiment

Different concentrations of Iron(II) ion in solution were prepared. The concentration ranges from 50mg/l to 350mg/l. A calibration curve of concentration verses absorbance was prepared before for the Iron(II) ions in solution before the adsorption process. 0.3g of the ABC was weighed and poured into a beaker containing 30ml of 50mg/l concentration of the stock Iron(II) ion solution. The adsorption process was carried out for 10, 15, 30, 60, 90 and 180 minutes agitation time till equilibrium was reached. The process was repeated for concentrations of 100mg/l, 150mg/l, 200mg/l, 250mg/l and 300mg/l. After the agitation time the mixture was filtered with a unicon filter paper. The amount of Iron(II) ion in solution was determined from the filtrate using a spectrophotometer (4).

The amount of Iron (II) adsorbed q (mg/g) was obtained using the equation

$$q = \frac{v(co - ce)}{m} \quad (1)$$

Where, q= amount of Iron(II) ion adsorbed (mg/g)
co= initial concentration of iron (ii)ion in solution (mg/l)
ce= equilibrium concentration of Iron(II) ion (mg/l)
v= volume of the solution (l)
m= mass of activated carbon (g)

Adsorption Isotherm Modeling

Evaluating the equilibrium of the process is important in optimizing the design of the adsorption process. In this research work, the rate of adsorption of Iron(II) ion by ABC was determined using Langmuir [8], Temkin [9], Redlich- Peterson [2], [10], [11] and Freundlich Isotherm Modeling [12], [13], [14]. Four (4) different temperatures which ranges from 10⁰C to 70⁰C was used for this experiment. 0.3g of carbon was weighed and added into a beaker containing 30ml of Iron(II) solution of known concentration for 24 hours at a temperature of 10⁰C while agitating until equilibrium is reached. The mixture was filtered with a filter paper and the filtrate concentration was tested using spectrophotometer. The process was repeated for all the other temperature.

Langmuir isotherm model is used to determine the behavior of the adsorption process (4). Langmuir isotherm is given by the equation (7)

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (2)$$

A plot of C_e/q_e as a function of C_e can be used to determine the values of q_{max} and K_L . The intercept of the plot is $1/q_{max}$ from which q_{max} is determined. K_L is obtained from the slope $1/q_{max}K_L$.

Where q_e = the mass of iron (ii)ion adsorbed per unit mass of carbon at equilibrium (mg/g).

C_e = the equilibrium concentration of Iron(II) ion in solution (mg/l)

q_{max} = maximum adsorption capacity (mg/g)

K_L = Langmuir constant.

The suitability of Langmuir is determined by a dimensionless factor called the Separation factor.

The Separation Factor R_L is expressed as

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

Where C_0 is the initial concentration

K_L is the Langmuir constant

The separation factor shows if the isotherm is favorable, unfavorable, linear or reversible. When separation factor, $R_L > 1$, the isotherm is unfavorable. When $R_L = 1$, it is linear. When $0 < R_L < 1$ it is favorable and when $R_L = 0$ irreversible.

Freundlich isotherm model is applied to heterogeneous surface. It is expressed as

$$\log q_e = \log K_F + 1/n \log C_e \quad (4)$$

For Freundlich $\log q_e$ is plotted as a function of $\log C_e$. The plot gives a straight line with $\log K_F$ as the intercept and $1/n$ as the slope.

Where q_e = the amount of Iron(II) ion adsorbed per unit mass of carbon at equilibrium (mg/g).

K_F = Freundlich constant

n = adsorption intensity

C_e = the equilibrium concentration of the adsorbate (mg/l)

Temkin Isotherm Model is used to represent adsorption behavior between two phases [9]. It is represented linearly as

$$q_e = a + b \ln C_e \quad (5)$$

Where a and b are Temkin constant related to energy and capacity.

A plot of q_e as a function of $\ln C_e$ gives a as the intercept and b as the slope.

➤ Redlich-Peterson is the three parameter isotherm which is expressed as

$$\ln \frac{C_e}{q_e} = \beta \ln C_e - \ln A \quad (6)$$

Where A is Redlich-Peterson constant

B is exponential between 0 and 1

A plot of $\ln C_e/q_e$ as a function of $\ln C_e$ gives $\ln A$ as the intercept and β as the slope

Thermodynamics of adsorption

Thermodynamics deals with heat and temperature change and their relation with energy, work and properties of body of matter. Thermodynamic study of adsorption enables us to determine if the particular adsorption process is physical or chemical, spontaneous or non-spontaneous, exothermic or endothermic.

The thermodynamics parameters considered in this research work include Gibb's free energy change, Enthalpy, Entropy, Sticking probability and Activated Energy. To get these thermodynamic parameters, the adsorption experiment was carried out at different temperatures which include 283K, 298K, 313K and 343K for 6 different concentrations.

Gibb's Free Energy: The equations used for this are

$$\Delta G^0 = -RT \ln K_a \quad (7)$$

$$\ln K_a = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

$$\Delta G^0 = \Delta H - T\Delta S \quad (9)$$

Where ΔG^0 = change in Gibb's free energy

ΔH = Enthalpy change

ΔS = Entropy change

T = Temperature in kelvin

R = Universal gas constant (8.314J/mol/K)

K_a = Langmuir adsorption equilibrium constant.

The values of ΔH and ΔS are gotten from the plot of $\ln K_a$ against $\frac{1}{T}$. The slope obtained is $\frac{\Delta H}{R}$ and the intercept $\frac{\Delta S}{R}$ [16], [17].

Sticking probability can be calculated using the equation (11)

$$\theta = 1 - \frac{C_e}{C_o} \quad (10)$$

$$S^* = (1 - \theta) \exp - \frac{E_a}{RT} \quad (11)$$

The linearized form of this equation is

III. RESULTS AND DISCUSSION

Characterization of the Adsorbent

Table 1 shows the characterization of Activated Bamboo carbon used for the thermodynamics of batch adsorption of Iron(II) ions. The activated of the bamboo carbon was done using nitric acid (HNO_3). The parameters considered for the characterization for the characterization of activated bamboo carbon include iodine number, bulk density, ash content, moisture content and dry matter. The table compares the bamboo carbon activated at $500^\circ C$ for 2.30hr with that activated for $550^\circ C$ for 3.30hr.

TABLE 1. CHARACTERIZATION OF ACTIVATED CARBON FROM BAMBOO

Parameters	Unit	ACB at $500^\circ C$	ACB at $550^\circ C$	Referen ce
Ash content	%	3.2	2.81	<10
Bulk density	g/cm^3	0.42	0.454	0.2-0.6
Moisture	%	3	3	<10
Dry matter	%	97	97	
Iodine number	g of iodine/kg of carbon	825.92	1062.5	600-1100

Adsorption Isotherm

The experimental data obtained from the adsorption process were fitted using adsorption isotherm. The models used to optimize the equilibrium

$$\ln S^* = \ln(1 - \theta) - \frac{E_a}{RT} \quad (12)$$

$$\ln(1 - \theta) = \ln S^* + \frac{E_a}{RT} \quad (13)$$

Where S^* = sticking probability

θ = surface coverage

E_a = activated energy

The plot of $\ln(1-\theta)$ against $1/T$ gives E/R as the slope and $\ln S^*$ as the intercept.

of the sorption process are Langmuir, Freundlich, Temkin and Redlich-Peterson isotherm models.

Langmuir Isotherm Model

A plot of Langmuir isotherm model is presented in Fig. 1 below. The ratio of concentration at equilibrium to the quantity of Iron (II) adsorbed (C_e/Q_e) was plotted against the concentration at equilibrium C_e . The linear relationship exhibited by the plot and the high values at R^2 shows that the plot is consistent with Langmuir model. An increase in the rate of adsorption of Fe^{2+} at lower concentration by the activated bamboo carbon is observed from the plot. The Langmuir isotherm model statistical parameters at temperatures ranging from $10 - 70^\circ C$ are presented in Table 4 with the correlation coefficient values R^2 ranging from 0.9988 to 0.9992. The separation factor R_L was also determined with the values ranging from 0.01941-0.227015 for adsorption temperatures of between $10^\circ C$ to $70^\circ C$ and concentration of between 50mg/l to 300mg/l. The separation factor being less than 1 for all the temperatures and concentrations shows then favorability of the process. Similar results were obtained by Ademiluyi and Ujile [7] with R_L of between 0.02-0.1 for adsorption concentration of between 50mg/l to 200mg/l.

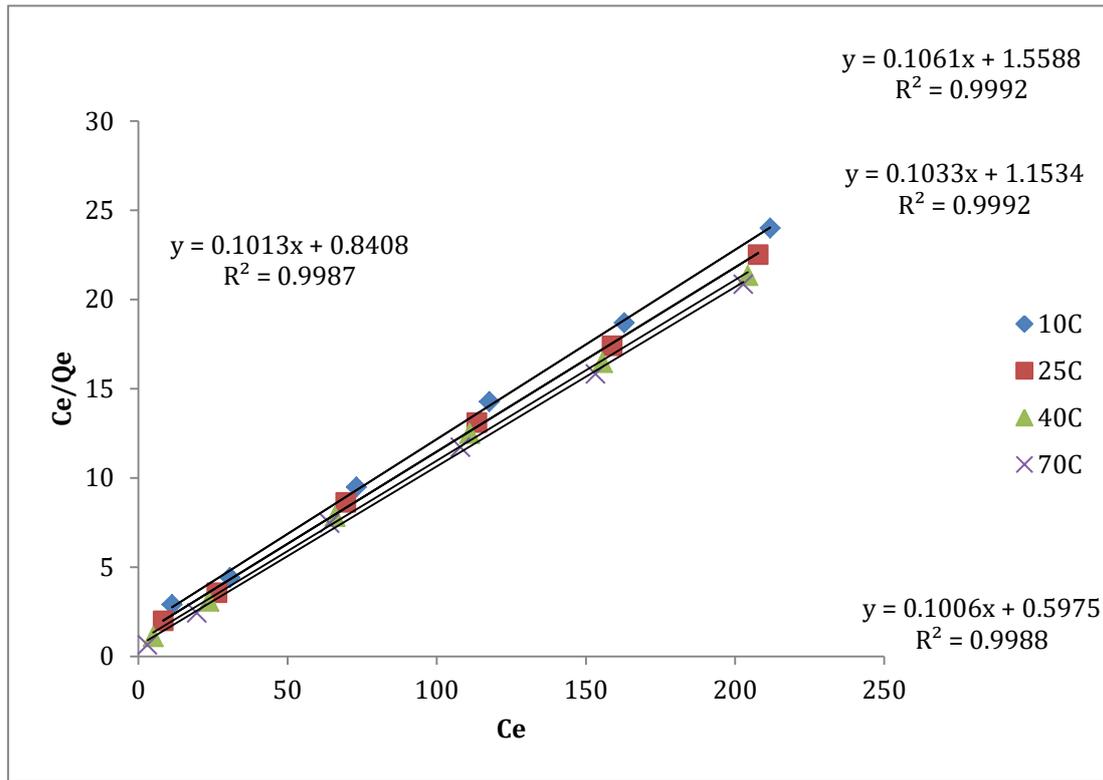


Fig 1. Langmuir adsorption isotherm for batch adsorption of Fe^{2+} at various temperatures.

TABLE 2: EQUILIBRIUM PARAMETERS FOR ADSORPTION OF Fe^{2+}

Co (mg/L)	Ce(mg/L)				Qe (mg/g)			
	Temperature °C							
	10°C	25°C	40°C	70°C	10°C	25°C	40°C	70°C
50	11.256	8.319	4.946	3.0351	3.874	4.168	4.505	4.696
100	30.661	26.319	23.588	19.569	6.933	7.368	7.641	8.044
150	73.064	69.519	65.893	64.108	7.693	8.048	8.411	8.589
200	117.62	113.439	111.065	107.93	8.237	8.656	8.893	9.206
250	162.902	158.799	155.520	153.204	8.709	9.120	9.447	9.679
300	211.774	207.759	204.277	202.781	8.822	9.224	9.572	9.721

TABLE 3: PERCENTAGE OF METAL ADSORBED AT VARIOUS TEMPERATURES

Co (mg/L)	% Iron adsorbed			
	Temperature °C			
	10°C	25°C	40°C	70°C
50	77.487	83.362	90.107	93.930
100	69.338	73.681	76.411	80.439
150	51.290	53.654	56.071	57.261
200	41.188	43.281	44.467	46.031
250	34.839	36.480	37.791	38.718

TABLE 4: LANGMUIR ISOTHERM STATISTICAL PARAMETERS

Statistical Parameters/ Constants			
Temp (°C)	Q_{max} (mg/g)	K_L	R^2
10	9.425	0.0681	0.9992
25	9.6805	0.0896	0.9992
40	9.8717	0.1205	0.9987
70	9.9404	0.1684	0.9988

TABLE 5: SEPARATION FACTOR AT VARIOUS CONCENTRATIONS AND TEMPERATURES

Temp (°C)	Separation factor					
	Concentration, mg/l					
	50	100	150	200	250	300
10	0.2270	0.1280	0.0892	0.0684	0.0555	0.0467
25	0.1825	0.1004	0.0693	0.0529	0.0427	0.0359
40	0.1423	0.0766	0.0524	0.0398	0.0321	0.0269
70	0.1062	0.0561	0.0381	0.0288	0.0232	0.0194

Freundlich Adsorption Isotherm

Freundlich adsorption isotherm for the adsorption of Fe²⁺ on activated bamboo carbon is presented in Fig. 2. The logarithm of the quantity of iron adsorbed at equilibrium (Q_e) was plotted against the logarithm of the concentration at equilibrium C_e of the Fe²⁺. K_f which is Freundlich constant was obtained from the slope and 1/n which is the adsorption intensity was obtained from intercept of the plot. The plot depicts a linear graph with high values of R². The correlation coefficient values ranges from 0.9035 to 0.9789 as shown in table 4.6. The high value of R² shows that it conforms to Freundlich adsorption model. The adsorption intensity n, for Freundlich > 1, (2). From the table it is observed that the values of n ranges from 1.749 - 4.073 and increases with increase in temperature indicating the favorability of Freundlich isotherm.

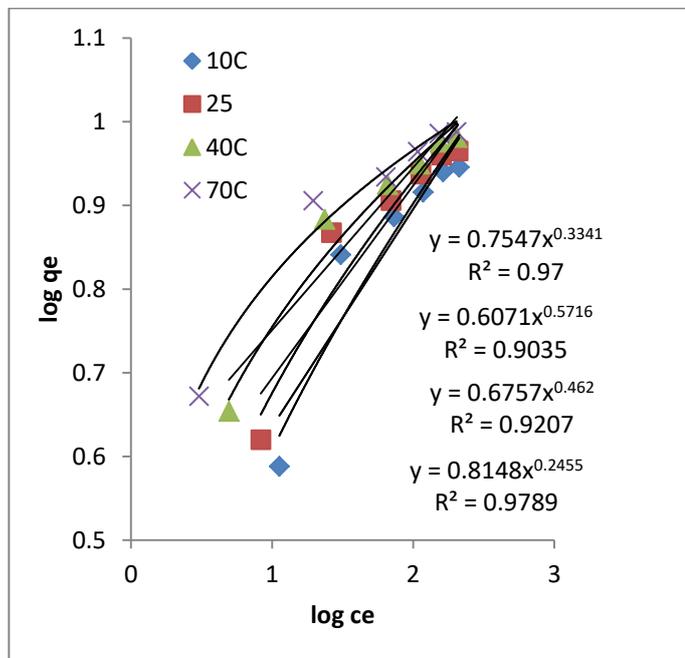


Fig 2. Freundlich adsorption isotherm for batch adsorption of Fe²⁺ at various temperatures.

TABLE 6: FREUNDLICH ISOTHERM STATISTICAL PARAMETERS

statistical parameters			
Temp.(°C)	n	K _f	R ²
10	1.749	4.047	0.9035
25	2.1645	4.7391	0.9207
40	2.993	5.6846	0.97
70	4.073	6.5283	0.9789

Temkin Adsorption Isotherm

The Temkin isotherm model was obtained from the plot of the quantity of Fe²⁺ adsorbed at equilibrium Q_e against the natural logarithm of the concentration at equilibrium. Fig. 3 below depicts a linear relation of the plot. The correlation coefficient obtained at different concentrations were between 0.9263 – 0.961 as shown in Table 7. a and b which are Temkin constants related to energy and capacity were obtained respectively from the intercept and slope of the plot.

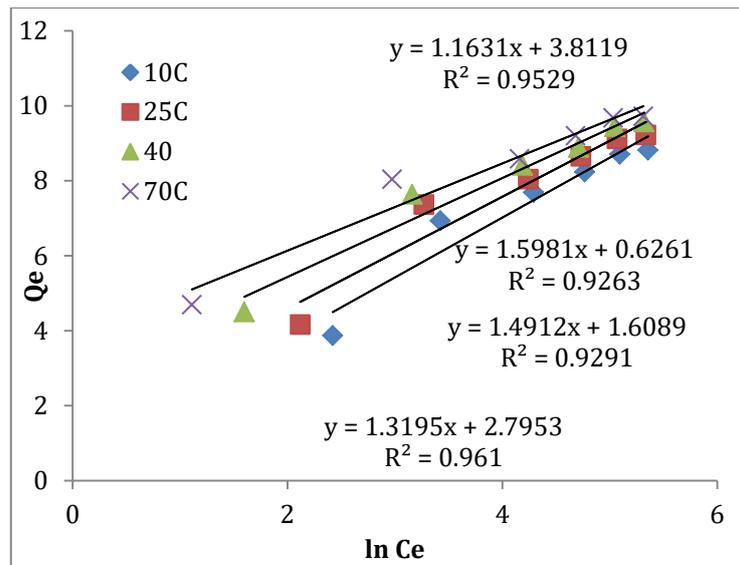


Fig 3. Temkin adsorption isotherm for batch adsorption of Fe²⁺ at various temperatures.

TABLE 7: TEMKIN ISOTHERM STATISTICAL PARAMETERS

Temp. (°C)	statistical parameters/constants		
	a	b	R ²
10	0.6261	1.5981	0.9263
25	1.6089	1.4912	0.9291
40	2.7953	1.3195	0.961
70	3.8119	0.9529	0.9529

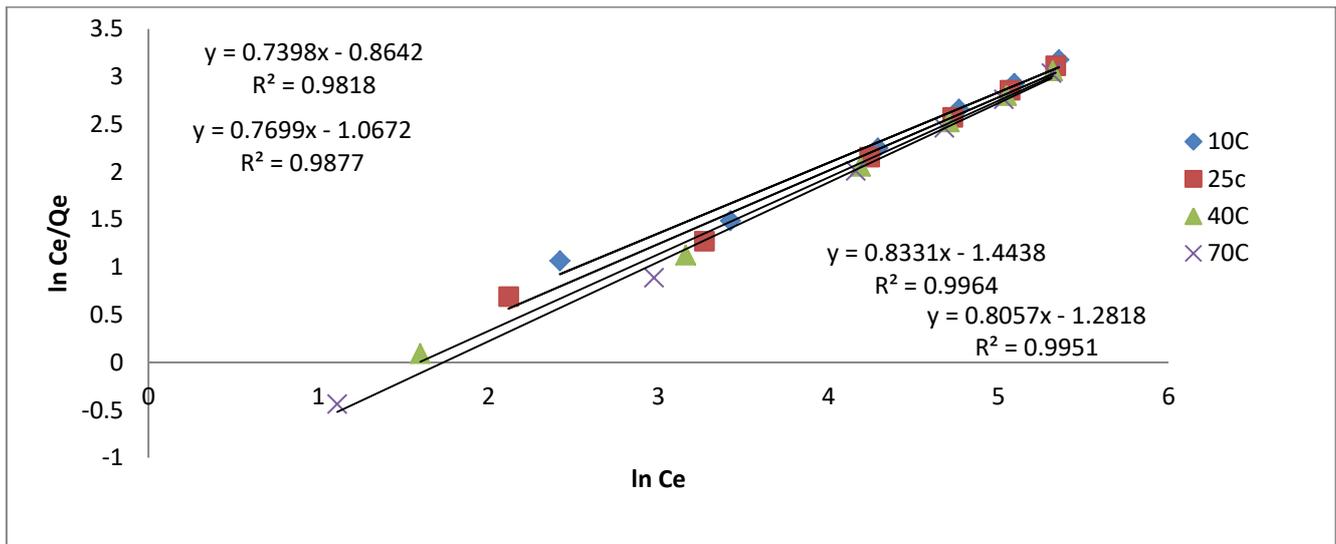


Fig 4. Redlich- Peterson adsorption isotherm for batch adsorption of Fe²⁺ at various temperatures

Redlich-Peterson Adsorption Isotherm Model

The Redlich-Peterson adsorption isotherm model for the adsorption of Fe²⁺ on activated bamboo carbon is presented in Fig. 4. The ratio of the natural logarithm of the concentration at equilibrium to the quantity of iron adsorbed $\ln Ce/Q_e$ was plotted against the natural logarithm of the concentration at equilibrium $\ln Ce$. The linear relationship exhibited by the plots shows that Redlich-Peterson model can be used to predict the sorption of Fe²⁺ on activated bamboo carbon. The Redlich-Peterson statistical parameters are presented in Table 8. The high correlation coefficient R² of between 0.9818 – 0.9964 shows that the isotherm is constant with Redlich-Peterson model.

TABLE 8. REDLICH-PETERSON ISOTHERM STATISTICAL PARAMETERS

Temp. (°C)	statistical parameters		
	A (L/g)	B	R ²
10	2.3726	0.7398	0.9818
25	2.9072	0.7699	0.9877
40	3.603	0.8057	0.9951
70	4.2368	0.833	0.9964

Thermodynamics of adsorption

Thermodynamic parameters considered in the sorption process include Gibbs free energy, enthalpy, entropy, sticking probability and activation energy. Langmuir equilibrium constant K_L was used to calculate some of the parameter by plotting a graph of the natural logarithm of K_L against the reciprocal of temperature in kelvin $1/T$ as shown in Figure 5. From the slope of the plot, enthalpy change ΔH was determined and entropy change ΔS were determined from the intercept. The enthalpy and entropy gotten were in turn used to calculate the change in Gibbs free energy ΔG .

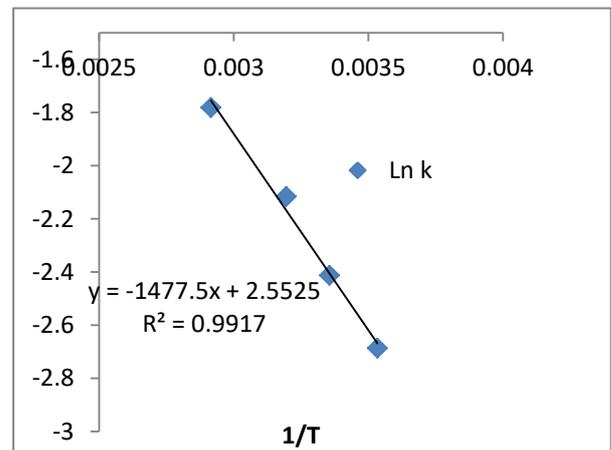
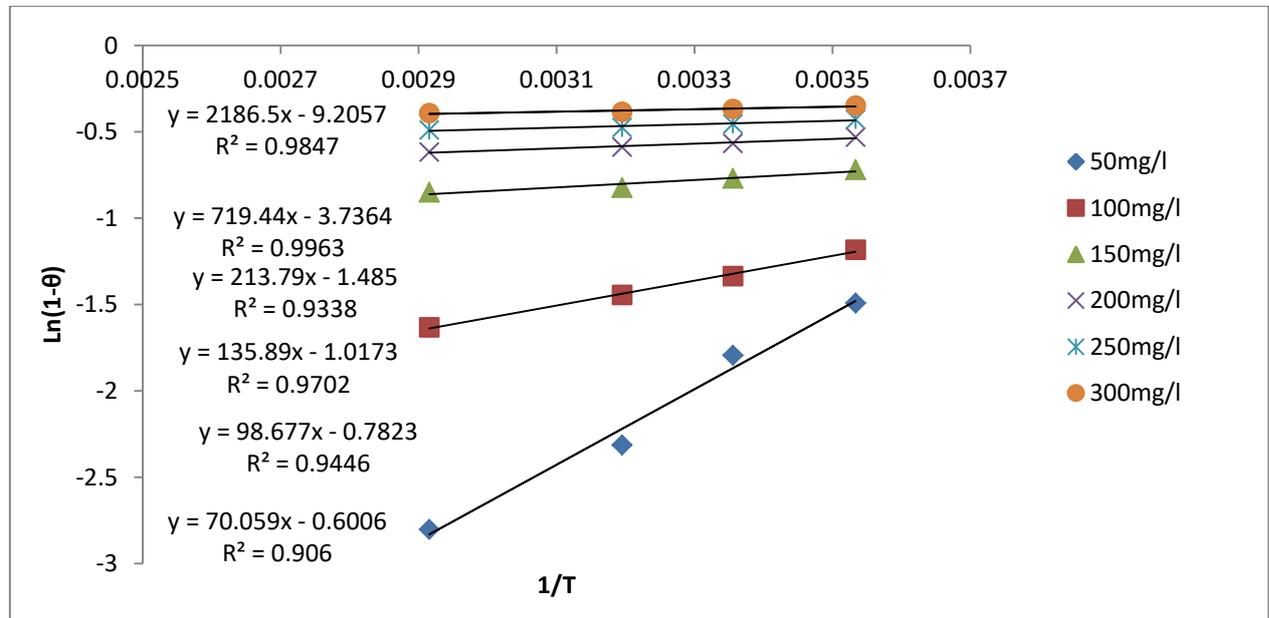


Fig 5. Plot of $\ln K$ (Langmuir constant) against $1/T$

From Table 9 it can be seen that the value of Gibbs free energy change was negative for all temperatures and it decreases with increase in temperature which indicates that the adsorption process occurs spontaneously with rise in temperature. Similar inference was reached by Ahmad [13] who also deduced an increase in spontaneity with temperature. A positive entropy ΔS was obtained which propound that some changes has occurred on the adsorbent and there is increase randomness in the solid/liquid phases during the adsorption process. This results from the fact that at increase temperature, the molecules gain kinetic energy and there is an increase in the random motion of the Fe²⁺ in the solution. The positive enthalpy value obtained signifies that the process is endothermic in nature. The enthalpy value of 12.28 kJ/mol indicates that the process favors physisorption. Another support to this is the increase of metal ion adsorbed with temperature as shown in Tables 2 and 4 since in physisorption, the amount of metal ion adsorbed increases with increase in temperature.

TABLE 9: ADSORPTION THERMODYNAMICS PARAMETERS

Temp. (°C)	ΔG (KJ/mol)	ΔS (J/K/mol)	ΔH (KJ/mol)	R^2
283	-5.993			
298	-6.312	21.2215	12.28	0.992
313	-6.63			
343	-7.267			

Fig 6. Plot of $\ln(1-\theta)$ against $1/T$

Sticking probability and activation energy were estimated from the modified Arrhenius type equation related to surface coverage. The values were calculated from the plot of $\ln(1-\theta)$ against the reciprocal of temperature $1/T$. Activation energy E_a , was gotten from the slope of the plot while sticking probability was calculated from the intercept. The positive values of activated energy E_a as presented in Table 10 indicates an endothermic process and agrees with the conclusion drawn from the enthalpy value. The values for activation energy range from 0.58 – 18.18 kJ/mol with a mean value of 4.73 kJ/mol. This also supports the earlier statement from enthalpy change that the adsorption process favors physisorption since activation energy E_a is less than 20 kJ/mol. The sticking probability $S\Delta$ values as seen from the table above are all less than unity which indicates that the probability of Fe^{2+} to stick on the activated bamboo carbon is high.

IV. CONCLUSIONS

An investigative research of the thermodynamics of batch adsorption of Iron II ion in aqueous solution has been carried out using activated bamboo carbon. The activation of the bamboo carbon was done using two different temperatures, with the highest temperature and time (550°C and 3.30hrs) given a better activation,

which was evident from the higher iodine number of 1062.5g and a lower ash content of 2.81%. From this, it can be deduced that activated bamboo carbon is better achieved at a higher temperature. The data obtained were linearized using Langmuir, Freundlich, Temkin and Redlich-Peterson adsorption isotherm. The isotherms were capable of linearizing the data in all four cases but with Langmuir isotherm model a better fit was obtained with a R^2 value of 0.9992. From the thermodynamics study, the Gibbs free energy was all negative for all the temperatures and decrease with increase in temperature which shows increase in spontaneity. Enthalpy value was found to be 12.28 kJ/mol. The value for entropy obtained was positive which signifies a higher decrease of randomness. Sticking probabilities values obtained which are < 1 indicates the probability of the metal to stick on the activated bamboo carbon and activation energy values are all less than 20 kJ/mol. From all this it can be deduce that the sorption process is endothermic, spontaneous and also favors physisorption mechanism.

TABLE 10. VALUES OF ACTIVATION ENERGY AND STICKING PROBABILITY AT VARIOUS INITIAL CONCENTRATIONS.

C_0	E_a (KJ/mol)	S^Δ	R^2
50	18.18	0.0001	0.9847
100	5.97	0.0238	0.9963
150	1.78	0.226	0.9338
200	1.13	0.362	0.9702
250	0.82	0.457	0.9446
300	0.58	0.548	0.906

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