

Equilibrium, Kinetic and Thermodynamic Studies of the Adsorptive Properties Offonio (*Digitariaiburua*) Husks on Cadmium (II) Ions in Aqueous Solution

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Abstract: This study examined the adsorption characteristics of aqueous Cd(II) ions onto *Digitariaiburua* husks under batch mode. The effects of initial Cd(II) concentration, adsorbent dosage, initial solution pH, contact time and temperature on the adsorption process were studied. Maximum adsorption occurred at initial Cd(II) concentration of 15.0 mg/L, adsorbent dosage of 2.5 g, solution pH of 6.0 and 45 minutes contact time. It was observed that an initial increase in temperature enhanced the adsorption capacity of the adsorbent. The equilibrium data were analyzed using Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models. The results showed that the experimental data were best fitted by the Freundlich model. Kinetic results revealed that the adsorption process followed the pseudo-second order model. The mechanism of adsorption showed that intra-particle diffusion was not the only rate controlling step. From the thermodynamic parameters, it can be said that the adsorption process was feasible, spontaneous, endothermic, random and physical in nature. The results obtained revealed that *Digitariaiburua* husks, an agricultural waste can serve as alternative low-cost adsorbent for the removal of lead metal from aqueous solution like wastewaters.

Keywords: Heavy metals; cadmium; *Digitariaiburua*; adsorption isotherm; kinetics.

I. Introduction

Heavy metals released by a number of industrial processes are major pollutants in marine, ground, industrial and even treated wastewaters. They enter the environment through point sources such as discharges from mining, metal plating, battery, plastic manufacturing, refining ores and fertilizer industries (Kumar *et al.*, 2012; Chigondo *et al.*, 2013). The presence of these heavy metals has become a major threat to plant, animal and human life due to their bioaccumulation tendency and toxicity (Asiagwu, 2012). When they exceed tolerance levels, they have harmful effects on humans and other organisms causing various diseases and disorders such as nervous and renal breakdown, hypertension, brain damage and convulsion (Farooq *et al.*, 2010; Arungandhiet *et al.*, 2015). Conventional water treatment technologies such as chemical precipitation, electro-flotation, ion exchange, reverse osmosis and adsorption onto activated carbon have been found to be effective in reducing heavy metal concentrations (Malamiset *et al.*, 2011; Gongden *et al.*, 2014). These methods, however, have disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal. As a result of these challenges, the use of cheap agricultural wastes such as rice straw, orange residue, apple residue, coconut shell and wheat bran as adsorbents for aqueous phase removal of heavy metals have been reported (El-Sayed *et al.*, 2010; Kumar *et al.*, 2012). In the present study, *Digitariaiburua* husks, an agricultural waste material was studied as a low-cost adsorbent for the removal of Cd(II) ions from aqueous solutions.

II. Materials And Methods

2.1. Sampling and Preparation of Adsorbent

The husks of *Digitariaiburua* were collected from Sot village of Jos-South (9.46°N, 8.48°E), Nigeria. They were washed thoroughly with distilled water and sun dried. The dried husks were ground and sieved through a 250 µm mesh size. The sieved adsorbent was stored in air-tight plastic container for use.

2.2 Reagents / Apparatus

All reagents used were of analytical grade and these included, cadmium (II) nitrate ((Cd(NO₃)₂ · 4H₂O, purity: 98%), sodium hydroxide (NaOH, purity: 98%), nitric acid (HNO₃, purity: 71%) supplied by BDH Chemicals Limited England, and distilled water. Apparatus used included, pH meter (Labtech – 14), weighing balance (Metra/TL 3000), water-bath (B – 465), mechanical shaker (ZD – 2 Multipurpose) and inductively coupled plasma-optical emission spectrometer (ICP – OES; Perkin Elmer Optima 2000 DV). Other materials used were routine laboratory resources.

2.3 Preparation of Cd(II) Solutions

A stock solution of 1000 mg/L was prepared by dissolving 2.8 g of cadmium nitrate in one litre of distilled water. All working solutions were prepared by diluting the stock solution with appropriate amount of distilled water. The pH values of the working solutions were adjusted with 1.0 M nitric acid and 1.0 M sodium hydroxide as the case may be.

2.4 Batch Adsorption Experiments

Batch tests were conducted with 50 mL of Cd(II) solution in 250 mL Erlenmeyer flask to investigate the influence of initial Cd(II) ions concentration (2.5, 5.0, 10, 15 and 20 mg/L), adsorbent dosage (0.5, 1.0, 1.5, 2.0 and 2.5 g), pH (4, 5, 6, 7, 8, 10 and 12), contact time (15, 30, 45 and 60 minutes) and temperature (25, 30, 40 and 60°C) in order to establish optimum values for the adsorption. Adsorbent of particle size <250µm was used in all the experiments. The experimental flasks were agitated at 100rpm speed in a mechanical shaker for a specified time period. At the end of the experiments, the flasks were removed from the shaker, the solutions filtered and the metal ion contents in the filtrates determined using inductively coupled plasma-optical emission spectrometer (ICP-OES). In all cases, measurements were done in triplicate and the mean recorded. The adsorption capacity, q_e (mg/g) and adsorption efficiency, E (%) of *Digitaria iburua* husks were calculated according to the following equations (Jamal *et al.*, 2015):

$$q_e \left(\frac{mg}{g} \right) = \frac{(C_i - C_e)V}{M} \quad (1)$$

$$E (\%) = \left[\frac{C_i - C_e}{C_i} \right] \times 100 \quad (2)$$

Where C_i and C_e are the initial and equilibrium concentration of Cd(II) ions (mg/L), respectively. V (L) is the volume of Cd(II) solution and M (g) is the weight of *Digitaria iburua* husks biomass.

III. Results And Discussion

3.1 Effect of Initial Cd(II) Ion Concentration

Adsorption experiments with the biomass were carried out for solutions containing 2.5 – 20 mg/L Cd(II) ions. As shown in Figure 1, Cd(II) uptake increased from 0.11 mg/g (86.8 %) to 0.89 mg/g (89.5 %) with increase in Cd(II) ion concentration. Maximum adsorption efficiency (96.53 %) occurred at initial Cd(II) ion concentration of 15 mg/L. Such behavior can be attributed to increase in the amount of adsorbate to fixed number of available binding sites on the adsorbent and this is expected to continue until the adsorbent attains saturation (Srinivaset *al.*, 2010).

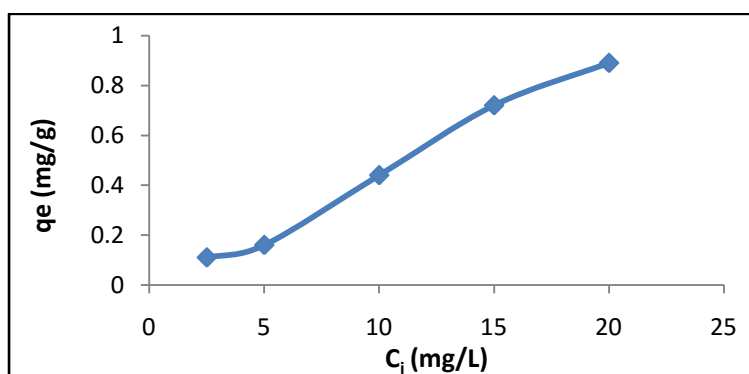


Figure 1: Effect of initial Cd(II) concentration (pH = 5, dose = 1.0 g; time = 45 mins, Temp. = 30 °C)

3.2 Effect of Adsorbent Dosage

The adsorbent dosage is an important factor to be considered for effective adsorption as it determines the sorbent/sorbate equilibrium of the system. The effect of adsorbent dosage on Cd(II) ions adsorption onto *Digitaria iburua* husks was shown in Figure 2. The metal uptake per unit mass of the adsorbent decreased with the increase in adsorbent dosage from 1.36 mg/g to 0.28 mg/g. On the basis of the mass balance relationship in Equation (1), this trend may be attributed to the fact that at high adsorbent dosages, the available metal ions are not able to cover all the exchangeable sites on the adsorbent, resulting in low metal uptake. Cd(II) removal efficiency expressed as a function of only the initial and final Cd(II) ions concentrations in Equation (2), on the other hand, increased with increase in adsorbent dosage from 90.73 % to 92.40 % (Demibrasetal., 2009; Fasotoet *al.*, 2014).

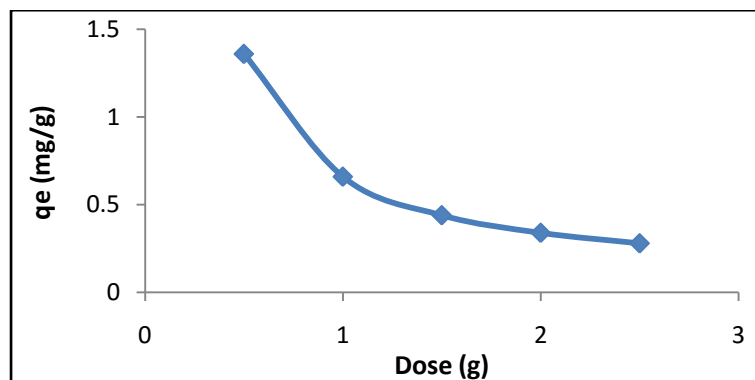


Figure 2: Effect of adsorbent dose ($C_i = 15 \text{ mg/L}$, $\text{pH} = 5$, $\text{time} = 45 \text{ mins}$, $\text{Temp.} = 30 \text{ }^\circ\text{C}$)

3.3 Effect of pH

From Figure 3, it is evident that as pH increased from 4.0 to 8.0, the adsorption capacity increased. Maximum uptake of 0.28 mg/g (93.93 %) was observed at the pH 6.0. Srinivaset al. (2010) stated that low pH depresses adsorption of cadmium due to competition with H^+ ions for binding sites on the adsorbent surface. However, with increasing pH, this competition weakens and Cd(II) ions replaced H^+ ions bound to the adsorbent (or forming part of the surface functional groups such as OH , SO_4^{2-} , etc). After pH 6.0, adsorption capacity decreased due to the presence of hydroxyl ions which resulted in precipitation of the metal ions to form Cd(OH)_2 (Al-Garniet al., 2009). Hence pH 6.0 was chosen as the optimum initial solution pH for the removal of the Cd(II) ions for further investigation of the work. Similar results have been reported by Hassan and El-Kassas (2012) and Gongdenet al. (2016) for Cd(II) adsorption onto *Aspergilluscristatus* and *Luffacylindrica* biomass, respectively.

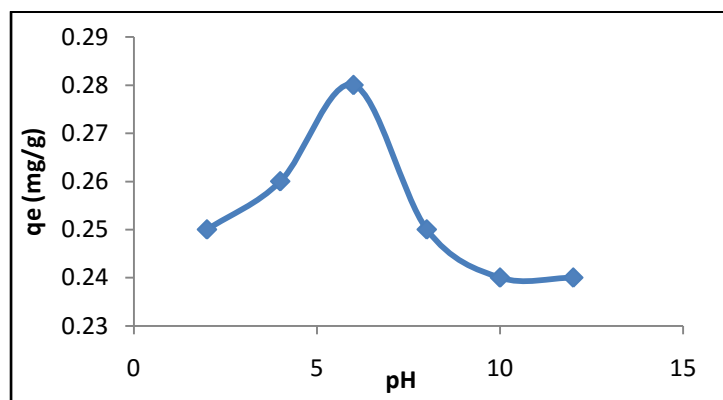


Figure 3: Effect of initial solution pH ($C_i = 15.0 \text{ mg/L}$, $\text{dose} = 2.5 \text{ g}$, $\text{time} = 45 \text{ mins}$, $\text{Temp.} = 30 \text{ }^\circ\text{C}$)

3.4 Adsorption Isotherms

Equilibrium data for the adsorption of Cd(II) ions onto *Digitariaiburuahusk* were fitted into the linearized forms of the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models given by Equations (3), (4) and (5) respectively (Kiranet al., 2010; Dubinin and Radushkevich, 1947). The characteristics of the Langmuir isotherm were determined by a dimensionless constant called the separation factor, R_L given by Equation (6). R_L indicates the nature of adsorption process such that $R_L > 1$, $R_L = 1$, $0 < R_L < 1$, and $R_L = 0$ represent unfavorable, linear, favorable and irreversible adsorption, respectively.

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

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

$$\ln q_e = \ln q_m - \beta \epsilon^2; \text{ where } \epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (5)$$

$$R_L = \frac{1}{1 + K_L C_i} \quad (6)$$

where q_e is the amount of metal adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of metal ions (mg/L), q_{max} is the maximum adsorption capacity (mg/g), K_L is the Langmuir constant (L/mg), K_F is Freundlich constant ($\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$), related to the adsorption capacity, n is a dimensionless empirical parameter related to the adsorption intensity, β is the activity coefficient (mol^2/J^2), ϵ is the Polanyi potential (J/mol), R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$) and T (K) is the absolute temperature. A linear plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ gives the inverse of the intercept as q_{max} and K_L is derived from the slope, the linear plot of $\log q_e$ versus $\log C_e$ gives the inverse of the slope as n and intercept as K_F , while a linear plot of $\ln q_e$ versus ϵ^2 gives the D-R constants β and q_m as slope and intercept respectively. The mean free energy, E (J/mol) of adsorption is calculated from the relationship:

$$E = \frac{1}{\sqrt{2\beta}} \tag{7}$$

For values of E between 8 and 16 kJ mol^{-1} , the sorption process is classified as chemical adsorption, while for values of $E < 8 \text{ kJ mol}^{-1}$, the sorption process is physical in nature (Ackacha, 2013).

The linear plot of the Langmuir, Freundlich and D-R isotherm models were presented in Figures 4, 5 and 6 respectively. The parameters thereof were recorded in Table 1. It can be seen from Table 1 that the correlation coefficient, R^2 obtained from the Freundlich model was closer to unity than those of D-R and Langmuir models, suggesting that the Freundlich isotherm fitted better with the adsorption of Cd(II) ions onto the adsorbent. A basic assumption of the Langmuir isotherm is that adsorption as a chemical phenomenon takes place at specific homogeneous sites within the adsorbent (Saleem and Bhatti, 2011; Jinget *et al.*, 2013). The maximum monolayer coverage capacity (q_{max}) and the Langmuir constant (K_L) which is related to the affinity of the binding sites towards the metal ions were found to be 1.425 mg/g and 0.259 L/mg respectively. R_L values obtained (Table 2) indicated that the equilibrium sorption was favourable. Unlike the Langmuir isotherm, Freundlich isotherm is based on adsorption to heterogeneous surface and it is assumed that the stronger binding sites are occupied first and that the binding strength decreases with increasing degree of site occupation (Wei *et al.*, 2015). The Freundlich adsorption capacity (K_F) and adsorption intensity (n) were found to be 1.633 $\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$ and 1.363, respectively. Ibrahim (2013) stated that n values > 1 indicates favourable physisorption (multilayer) adsorption process. Therefore, the value of $n > 1$ obtained in this study indicated favourable adsorption process. The D-R isotherm expresses adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface (Zhu *et al.*, 2009). As shown in Table 1, q_m was determined to be 1.079 mg/g and the mean free energy, E was 0.071 kJ/mol which indicated a physisorption process.

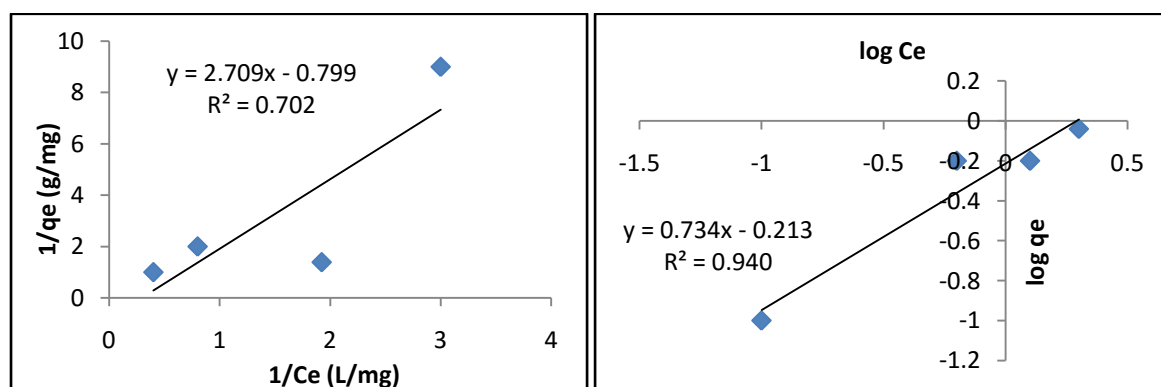


Figure 4: Langmuir isotherm plot Figure 5: Freundlich isotherm plot

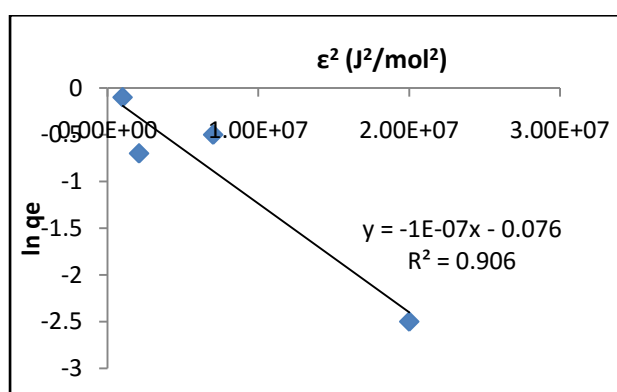


Figure 6:D-R isotherm plot

Table 1: Isotherm constants for Cd(II) ions adsorption onto *Digitariaiburuahusks*

Langmuir Isotherm	Freundlich Isotherm	D-R Isotherm
$q_{max} = 1.425 \text{ mg/g}$	$K_F = 1.633 \text{ mg}^{1-1/n} \text{ L}^{1/n} / \text{g}$	$q_m = 1.079 \text{ mg/g}$
$K_L = 0.259 \text{ L/mg}$	$1/n = 0.734$	$\beta = 1 \times 10^{-4} \text{ mol}^2 / \text{kJ}^2$
$R^2 = 0.702$	$n = 1.363$	$E = 0.071 \text{ kJ/mol}$
	$R^2 = 0.940$	$R^2 = 0.906$

Table 2: Dimensionless Langmuir Separation Factor

Concentration (mg/L)	2.5	5.0	10	15	20
R_L	0.6069	0.4357	0.2786	0.2047	0.1618

3.5 Adsorption Kinetics

Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full scale batch process and for designing batch adsorption systems (King *et al.*, 2007). Figure 7 showed the effect of contact time on the adsorption of Cd(II) ions onto *Digitariaiburua* husks at 30 °C. Cd(II) uptake increased with increase in contact time reaching maximum; 0.281 mg/g (93.53 %) in 45 minutes after which it decreased with further increase in contact time. This may be due to saturation of the binding sites on the adsorbent's surface with Cd(II) ions followed by adsorption and desorption processes which may occur after saturation (Kumar *et al.*, 2012). In order to investigate the controlling mechanism of the adsorption process such as transfer and chemical reaction, pseudo-first order, pseudo-second order, and intra-particle diffusion models were used for analysis of adsorption kinetics. The equation for pseudo-first order kinetics can be written as follows (Lagergren, 1898):

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{8}$$

Pseudo second-order model is represented as (Blanchard *et al.*, 1984):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{9}$$

The intra-particle diffusion equation can be written as follows (Weber and Morris, 1963):

$$q_t = K_d t^{1/2} + C \tag{10}$$

where q_e (mg/g) is the mass of metal adsorbed at equilibrium, q_t (mg/g) the mass of metal adsorbed at time t , k_1 is the pseudo-first order rate constant of adsorption (min^{-1}), k_2 is the pseudo-second order rate constant of adsorption ($\text{mg/g} \cdot \text{min}$), K_d ($\text{mg/g} \cdot \text{min}^{1/2}$) is the rate constant of intra-particle diffusion and C (mg/g) is the intercept which describes the boundary layer thickness. The linear plot of pseudo-first order, pseudo-second order and intra-particle diffusion were displayed in Figures 7, 8 and 9, respectively. The value of q_e , cal obtained from pseudo-second model was in close agreement with that of the experimental value (q_e , exp) than the value obtained from pseudo-first order model (Table 3). Also, the correlation coefficient (R^2) value for pseudo-second order was closer to unity than that of the pseudo-first order model. The study therefore, revealed that the adsorption of Cd(II) ions followed pseudo-second order kinetic model. According to Itodo *et al.* (2010), sorption mechanism assumes an intra-particle diffusivity model if; the line plot of q_t versus $t^{1/2}$ passes through the origin, the R^2 value is high to ascertain applicability and with the intercept, $C < 0$. From the above conditions, the high R^2 value obtained showed the applicability of the model to the adsorption process. The plot not passing through the origin suggested that intra-particle diffusion may not be the only rate controlling step (Ackacha, 2013).

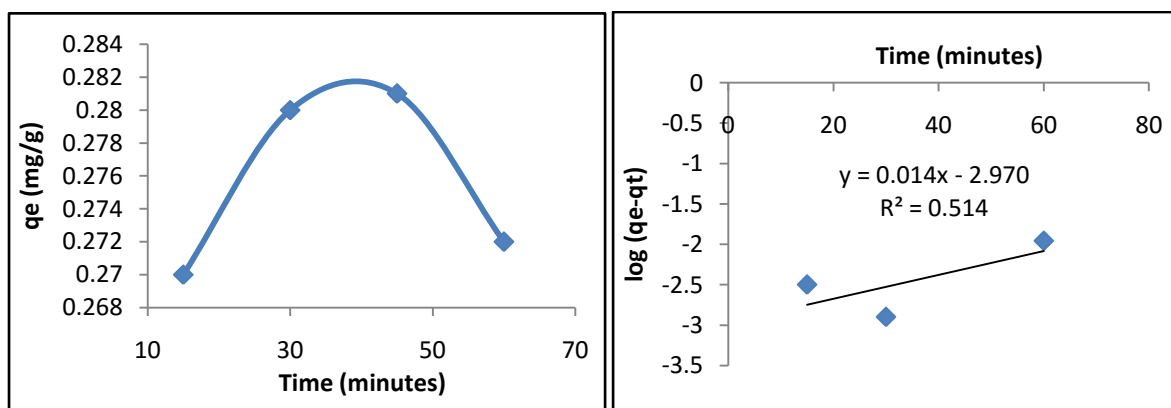


Figure 7: Effect of time ($C_i = 15 \text{ mg/L}$, $\text{pH} = 6$, Figure 8: Pseudo-first order plot dose = 2.5 g, $\text{pH} = 6$, Temp. = 30°C)

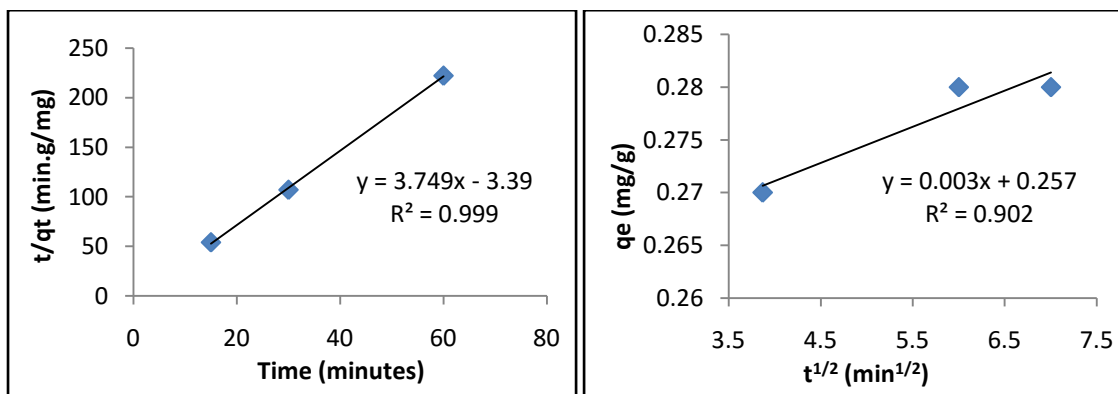


Figure 9:Pseudo-second order plot Figure 10:Intra-particle diffusion plot

Table 3:Kinetic constants for Cd(II) ions adsorption onto *Digitariaiburua* husks

Pseudo-first order	Pseudo-second order	Intra-particle diffusion
$q_e,exp = 0.281 \text{ mg/g}$	$q_e,exp = 0.281 \text{ mg/g}$	$K_d = 0.003 \text{ mg/g.min}^{1/2}$
$q_e,cal = 0.001 \text{ mg/g}$	$q_e,cal = 0.270 \text{ mg/g}$	$C = 0.257 \text{ mg/g}$
$K_1 = 0.032 \text{ min}^{-1}$	$K_2 = 4.146 \text{ g/mg.min}$	$R^2 = 0.902$
$R^2 = 0.514$	$R^2 = 0.999$	

3.5 Thermodynamic Study

The effect of temperature on the adsorption of Cd(II) ions onto *Digitariaiburua* husks was shown in Figure 10. The figure showed clearly that Cd(II) uptake by the adsorbent increased with increase in temperature indicating endothermic process. The sorption percentage increased from 80.60% to 89.69% when the temperature was raised from 25 to 60°C. This could be attributed to acceleration of slow adsorption steps or increase in the number of active sites or surface available for sorption on the adsorbent and enhanced mobility of metal ions from bulk solution (Hashem, 2007; Ofudje *et al.*, 2014).

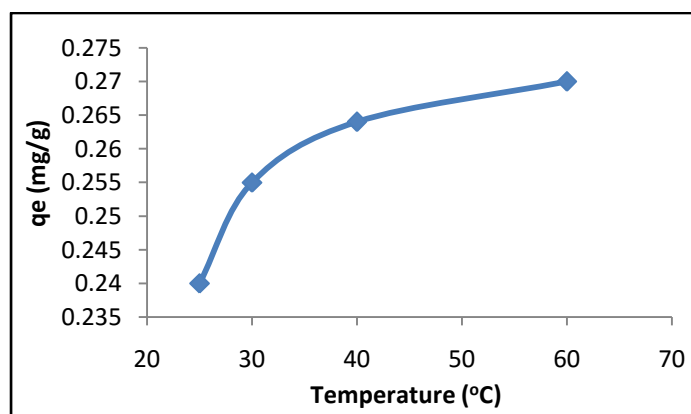


Figure 11: Effect of temperature ($C_i = 15 \text{ mg/L}$, $\text{pH} = 6$, dose = 2.5 g, $\text{pH} = 6$, time = 30 °C)

To further evaluate the feasibility and nature of the adsorption process, thermodynamic parameters including Gibb’s free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) changes were calculated from the following equations (Fu *et al.*, 2012):

$$\Delta G = -RT \ln K_c \tag{11}$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{12}$$

where R is the universal gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), T ($^\circ\text{K}$) is the absolute temperature, K_c is the thermodynamic equilibrium constant which is the ratio of Cd(II) concentration on the adsorbent at equilibrium (q_e) to the remaining Cd(II) concentration in solution at equilibrium (C_e). ΔG° values were estimated from Equation (11), while ΔS° and ΔH° were calculated from the intercept and slope, respectively, of the Van’t Hoff plot ($\ln K_c$ versus $1/T$) (Equation 12). The values of these parameters were given in Table 4.

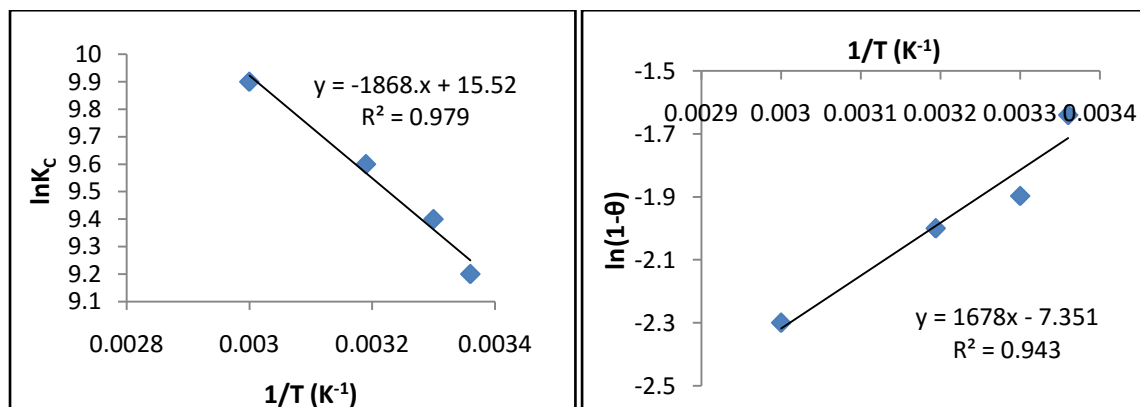


Figure 12: Van't Hoff Plot ($\ln K$ versus $1/T$) **Figure 13:** Plot of $\ln(1-\theta)$ versus $1/T$

Table 4: Thermodynamic parameters for adsorption of Cd(II) ions onto *Digitariaiburuahusks*.

Thermodynamic Parameters					
Temperature T(K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)	E_a (kJ/mol)	S^*
298	-22.63				
303	-23.83	15.53	0.13	13.95	0.00064
313	-25.81				
333	-27.36				

The negative values of ΔG° implied the feasibility and spontaneity of the process (Zeidet *al.*, 2011). The positive value of ΔS° suggested increased randomness at the solid-liquid interface. The positive value of ΔH° (15.53 kJ/mol) showed the endothermic nature of the adsorption process and lies within the range of 1 to 93 kJ/mol indicating physisorption process (Arivoli *et. al.*, 2008). This confirmed the results obtained from D-R isotherm model studies.

In order to ascertain that physical adsorption is the predominant mechanism, the values of activation energy (E_a) and sticking probability (S^*) were estimated from the experimental data using modified Arrhenius type equation related to surface coverage (θ) as follows (Nevine, 2009):

$$\ln(1 - \theta) = \ln S^* + \frac{E_a}{RT} \text{ and } \theta = \left(1 - \frac{C_e}{C_i}\right) \quad (13)$$

The values of E_a and S^* were calculated from slope and intercept of the plot of $\ln(1-\theta)$ versus $1/T$, respectively. $S^* > 1$ indicates no sorption, $S^* = 1$ indicates mixture of physisorption and chemisorption, $S^* = 0$ indicates that chemisorption is the predominant mechanism and $0 < S^* < 1$ indicates that physisorption is the predominant mechanism (Abasiet *al.*, 2011). The sticking probability value (Table 4), indicated that the probability of the Cd(II) ions to stick on surface of the adsorbent was very high as $S^* \ll 1$. The positive value of E_a confirmed the endothermic nature of the adsorption process which is in agreement with the positive value of ΔH° .

IV. Conclusions

Based on the results, it is apparent that Cd(II) adsorption onto *Digitariaiburuahusks* was dependent on initial Cd(II) ions concentration, adsorbent dosage, solution pH, contact time, and temperature. The adsorption of Cd(II) onto the adsorbent fitted best to Freundlich isotherm model indicating multilayer adsorption. The adsorption kinetic experiments revealed that the adsorption process followed the pseudo-second order kinetic model and intra-particle diffusion was not the only rate controlling step. Thermodynamic parameters showed that the adsorption process was feasible, spontaneous and endothermic in nature. The overall results indicated that *Digitariaiburuahusks* could be effectively used as a low-cost and alternative adsorbent for the removal of Cd(II) from aqueous solution.

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