

## Kinetics And Thermodynamic Studies Of Biosorption Of Cadmium (Ii) From Aqueous Solution Onto Sweet Potato Skin (Sps)

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**Abstract:** - The biosorption of Cadmium onto Sweet Potato Skin (SPS) from aqueous solution were investigated in this study. The amount of Cd(II) adsorbed was found to be dependent on the pH of the solution, contact time and initial concentration of Cd(II). The equilibrium data were analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) Isotherm equation. The Freundlich Isotherm model fits the experimental data than the others. The values of the separation factors ( $R_L$ ) are in the range of 0.2-0.7 which indicates favourable biosorption. Results also showed that the pseudo-second order equation provided the best model for the biosorption process. Various thermodynamic parameters such as  $\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$  were evaluated. A positive value of  $\Delta H^\circ$ , indicates the endothermic nature of the process. The negative values of the Gibbs free energy at all the temperature showed that the adsorption process was spontaneous and the positive value of  $\Delta S^\circ$  reflects good affinity of Cadmium ions towards the biosorbent.

**Keywords:** - Biosorption, Sweet Potato Skin, Cadmium, Isotherm, Thermodynamic.

### I. INTRODUCTION

The term "heavy metals" refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration [1]. Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), Arsenic (As), Silver (Ag), Chromium (Cr), Copper (Cu), Iron (Fe), and the platinum group elements. Continuous discharge of industrial, domestic and agricultural wastes in rivers and lakes causes deposit of pollutants in sediments. Such pollutants include heavy metals, which endanger public health after being incorporated in food chain.

These Heavy metals cannot be destroyed through biological degradation, as is the case with most organic pollutants [2]. The presence of the heavy metals in the environment is thus of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even in relatively low concentration [3]. Arsenic and cadmium for instance, can cause cancer. Mercury can cause mutations and genetic damage, while copper, lead, and mercury can cause brain and bone damage.

Cadmium is a rare element and is present in the natural environment in form of its various compounds, at a relatively low level. The oxidation state of almost all cadmium compounds is +2, although a few compounds have been reported in which it is +1. Cadmium occurs in the earth's crust at an abundance of 0.1–0.5 ppm and is commonly associated with zinc, lead, and copper ores [4]. Cadmium is widely and increasingly used in industries for corrosion- protection coating as it is highly corrosion resistant, nickel-cadmium batteries, Cadmium pigmented plastic, ceramics, glasses, paints and enamels, Cadmium stabilized Polyvinyl chloride (PVC) products, and Cadmium coated ferrous and Non-ferrous products, Cadmium alloys, Cadmium electronic compounds, Cement and Phosphate fertilizers. It may enter the aquatic and ambient environment as a toxic pollutant from various anthropogenic sources such as zinc, copper and lead mining, various industries, Iron & steel, non-ferrous metals, cement production etc, electroplating, phosphate fertilizers, nickel-cadmium batteries, coal utilization and tobacco smoking. In high concentrations, cadmium may affect human health. Cadmium contamination of the fishes was the main cause for the episodal pollution and endemic bone disease "itai-itai" reported from Japan, during which several hundreds of peoples were affected. Water sources near cadmium-emitting industries, both with historic and current operations; have shown a marked elevation of cadmium in water sediments and aquatic organisms [5]. The World Health Organization (WHO) has set a maximum guideline concentration of 0.003mg/L for Cd in drinking water [6]. With this adverse effect of Cadmium metal and with increase in paint and plastic industry in Nigeria, there is considerable interest in the development of techniques to remove cadmium from contaminated water before they are discharged into receiving bodies.

There are so many methods available for the removal of metal ions from effluents. The technologies are divided into three categories, biological, chemical and physical [7]. The major method of industrial wastewater treatment involves physical and chemical processes. They have their own advantages and drawbacks because of high cost and disposal problems [7]. A combination of different processes is often used to achieve

the desired water quality in the most economical way. Chemical methods involved coagulation combined with flotation and filtration, electro flotation, electro kinetic coagulation, conventional oxidation methods by oxidizing agents, irradiation and electro chemical processes [7]. These technologies are very expensive and have disposal problems. Although these methods are efficient for treatment of water contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and consumption of chemical reagents are common problems [7]. Physical methods are membrane filtration and adsorption. Membrane filtration processes are nanofiltration, reverse osmosis, electro dialysis etc. The major disadvantage of this membrane filtration is limited lifetime before membrane fouling occurs. Adsorption is one of the most popular methods for the removal of pollutants from effluents since proper design of the adsorption process will produce high quality treated effluents. This process provides an attractive alternative for treatment of contaminated water, especially if the adsorbent is inexpensive and does not require an additional pre-treatment step before application [7].

The use of activated carbon exhibits high efficiency, but the high cost of activated carbon sometimes limits its applicability for heavy metal removal [8], together with its regeneration and disposal of used activated carbon is often very difficult. Therefore, the interest of researchers is increasing using alternative materials, which are quite low cost, easily available and extremely effective adsorbents. Alternatively, low cost and unconventional adsorbents such as rice husk, fly ash, peat, lignite, saw dust etc. are used for removal of toxic metals which is effective and economical [7]. These adsorbents have distinct advantages over the conventional methods which include: reusability of biomaterial, low operating cost, and selectivity for specific metal, short operation time and no chemical sludge [9]. Most of the biosorption studies reported in literatures have been carried out with living microorganisms. However due to certain inherent disadvantages, use of living microorganisms for metal removal and recovery is not generally feasible in all situations. For example, industrial effluents contain high concentrations of toxic metals under widely varying pH conditions. These conditions are not always conducive to the growth and maintenance of an active microbial population [2]. The disadvantages of using microorganisms can be overcome by using low cost adsorbents. In general, a sorbent can be assumed to be "low cost" if it requires little processing and is abundant in nature, or is a by-product or waste material from another industry, which has lost its economic or further processing values [2].

Sweet Potato Skin is an agricultural waste from food industries; which are available abundantly at no or low costs, they do not have any immediate use and are discarded as waste in many parts of the country or are used as land-fills or just ordinarily burnt as a form of disposal method. It is therefore important to explore a possibility of utilizing these waste materials to remove Cadmium (II) from aqueous solution as an alternative to high cost commercial adsorbent materials.

## **II. MATERIALS AND METHODS**

### **2.1 Materials**

#### **2.1.1. Adsorbent material**

The Sweet Potato skins (SPS) were collected from a food restaurant in Choba, Obi-Akpor Local Government area of River State, Nigeria. The collected Sweet Potato skins were washed thoroughly with clean water for several times to remove the earthy matter and all the dirt particles and then rinsed with de-ionized water. They were cut into smaller bits and sun-dried for 72 hours. After drying, the dried SPS was grounded and sieved to get the average adsorbent size of 1.7mm. For preservation, it was kept in plastic-stopper bottles (containers) and to minimize contact with humidity all these bottles were preserved in desiccators before the time of use. No other physical and chemical treatments were given to the biosorbent prior to the experiments.

#### **2.1.2. Adsorbate solution**

A stock solution (1000 mg/l) of Cd (II) ion was prepared by dissolving the required amount of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Merck) in distilled water. Cadmium solutions of desired concentrations were prepared by adequate dilution of the stock solution with distilled water. 0.1N of HCL and KOH used to adjust the pH to the required value were also prepared.

### **2.2. Methods**

#### **2.2.1 Characterization of the biosorbent**

The Fourier transform infrared spectroscopy (FTIR) was used to determine the functional groups on the carbon. The infrared spectra of the biomass samples before and after metal uptake were recorded, using a Bulk-Scientific infrared Spectrophotometer Model 530. Characterisation was performed in order to identify chemical functional groups present on the SPS that might be involved in the metal uptake procedure.

#### **2.2.2 BATCH ADSORPTION PROCESS**

Batch adsorption processes were carried out to determine the effect of adsorbent dosage, pH of the solution, contact time, initial concentrations and temperature on the adsorption of Cd(II) ions on the SPS.

Cadmium ion uptake (Adsorption capacity) at a particular time  $q_t$  [10] and the uptake percentage (% removal of metal ion) [11] were determined by mass balance, as follows:

$$q_t = \frac{(C_o - C_t)V}{W} \dots \dots \dots (1)$$

$$\text{uptake percentage} = \frac{(C_o - C_t)V}{C_o} * 100 \dots \dots \dots (2)$$

Where “ $q_t$ ” is the amount of metal ion adsorbed (mg per g of sorbent) at time “ $t$ ”, “ $V$ ” is the volume of the sample solution, “ $W$ ” denotes the weight of sorbent (g), “ $C_o$ ” and “ $C_t$ ” are the metal concentration in the aqueous solution (mg/l) at the initial and at time “ $t$ ”, respectively.

Cadmium ion uptake (Adsorption capacity) at equilibrium  $q_e$  was determined by mass balance using Equation 3 [10]:

$$q_e = \frac{(C_o - C_e)V}{W} \dots \dots \dots (3)$$

Where,  $q_e$ , is the equilibrium adsorption capacity (mg/g);  $C_o$  and  $C_e$ , the initial and equilibrium Cadmium concentrations in the water (mg/l), respectively;  $V$ , volume of used solution (l); and  $m$ , the mass of used bioadsorbent (g).

### **Determination of the Effect of adsorbent dosage on the Biosorption of Cd (II)**

The effect of adsorbent dosage on the amount Cadmium ion removal was analyzed over the range of (0.2 – 1)g of the adsorbent. 15ml of the metal solutions of 50mg/l was taken in plastic tube and are agitated with the various mass of adsorbent at the natural pH of SPS at 200rpm for 2hrs at room temperature. The samples were filtered using whatmann filter paper no 1, and the concentrations of the initial solution and the filtrate/solution were analyzed using Atomic Absorption spectrophotometer (Buck Scientific Atomic Absorption/Emission Spectrophotometer 200 Spectra).

### **Determination of the Effect of pH on the Biosorption of Cd (II)**

The effect of pH on the amount Cadmium ion removal was analyzed over the pH range of 2 to 10. In this study, 15ml of the metal solutions of 50mg/l was taken in plastic tube and are agitated with 0.4g of SPS at 200rpm for 2hrs at room temperature. The samples were filtered using whatmann filter paper no 1, and the concentrations of the initial solution and the filtrate/solution were analyzed using Atomic Absorption spectrophotometer (Buck Scientific Atomic Absorption/Emission Spectrophotometer 200 Spectra).

### **Determination of the Effect of Agitation Time**

By keeping all other variable constant the effect of contact time on the amount of removal of Cadmium ion from the solution were also determined by contacting 15ml of 60mg/L of the Cadmium solution with 0.4g of the adsorbents at the optimum pH and room temperature. The samples were agitated for the time of 20mins, 40mins, 60mins, 80mins, 100mins and 120mins respectively in plastic tube. Then, the samples were filtered with Whatmann filter paper no.1 and the concentrations of the initial solution and the filtrate/solution at each time were analyzed using Atomic Absorption spectrophotometer (Buck Scientific Atomic Absorption/Emission Spectrophotometer 200).

### **Determination of the Effect of Initial Concentration of Cd (II)**

The effect of initial concentration of the metal ions solutions were carried out by contacting 0.4g of GAG with 15ml of Cadmium solution of different initial concentrations (10,20,40,60,80 and 100mg/L) in 20ml plastic tube. The samples were then agitated at 200rpm at the equilibrium time. After which equilibrium concentrations were analyzed as before.

### **Effect of Temperature**

To measure the thermodynamic parameters, the experiments were conducted at different temperatures in the range of 25<sup>0</sup>C to 70<sup>0</sup>C for Cadmium adsorption. By keeping all other variable constant the effect of temperature on the amount of removal of Cadmium ion from the solution were also obtained by contacting 20ml of 40mg/L of the Cadmium solution with 0.4g of the adsorbents at the optimum pH and time agitated at 200rpm.

## **3. Results and Discussion**

### **3.1 FT-IR Analysis**

FTIR spectroscopy was applied to identify the major functional groups responsible for Cd(II) adsorption on the biosorbent and the results are shown in Fig. 1 and 2. By comparing the FTIR spectra of SPS before and after adsorption using IR correlation table [12], there were remarkable shifts in some bands (Table 1). These bands are the functional groups of SPS that participate in Cd(II) biosorption.

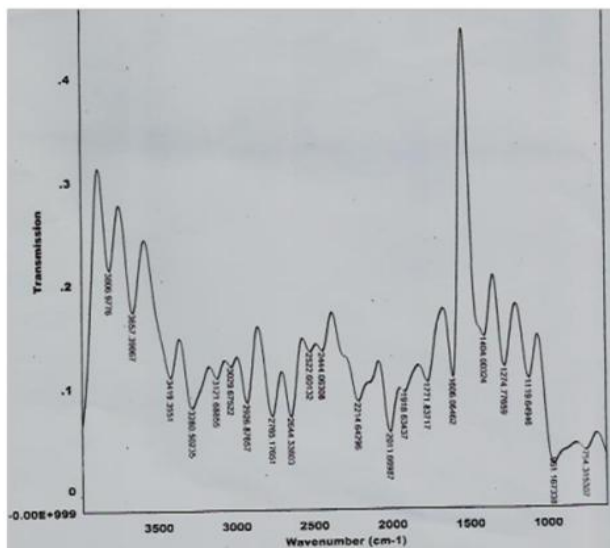


Fig 1: FTIR of SPS unloaded

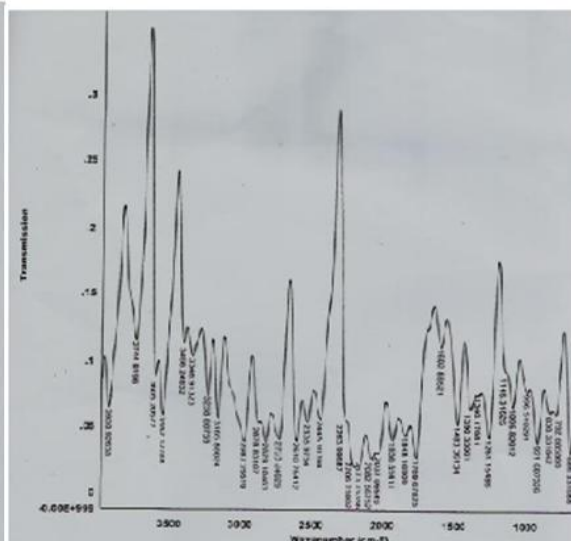


Fig 2: FTIR of SPS loaded with Cadmium.

Table 1: FTIR spectral characteristics of SPS before and after biosorption of Cd(II).

Transmission band (cm <sup>-1</sup> )		Assignment
Peak before adsorption	Peak after adsorption	
961.167	921.607	Methylene group
1404.003	1145.3163	Methylene group
1606.885	1602.885	Methylene group
2214.643	2206.759	Methylene group
2765.177	2733.840	Methylene group
1119.649	1095.82	Amine group
3280.502	3238.808	Amine group
3419.355	3408.248	Amine group
3657.391	3605.206	Amine group
1119.649	1095.82	Carboxylic Acid group
1274.777	1261.54	Carboxylic Acid group
3806.978	3744.82	Hydroxyl group

### 3.2 EFFECT OF ADSORBENT DOSAGE

The biosorbent dosage is an important parameter because this determines the capacity of a biosorbent for a given initial concentration. The Effect of Adsorbent Dosage On the amount of Cadmium(II) adsorbed (mg/g) at fixed agitation time, fixed adsorbate concentration at room temperature and at original pH of the solution is presented in Fig. 3 and 4. As the mass of adsorbent is being increased from 0.2g – 1g, the amount of Cadmium adsorbed decreases from 3.06mg/g to 0.61mg/g. This is as a result of large quantity of the adsorbent competing for the available Cd (II) ion thereby decreasing the amount adsorbed. Also From Fig. 3, there is a slight increase in the percentage of Cadmium removed as the mass of adsorbent is increased, which shows that small mass of the adsorbent can effectively remove Cadmium metal from waste water.

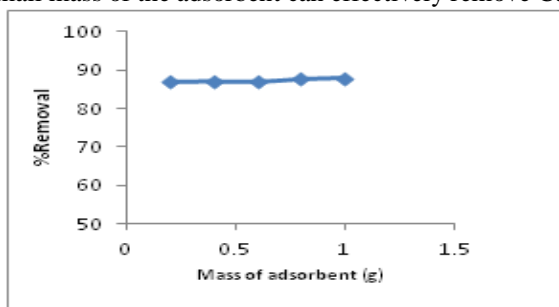


Fig. 3: Effect of Adsorbent dose on the % Removal of Cadmium

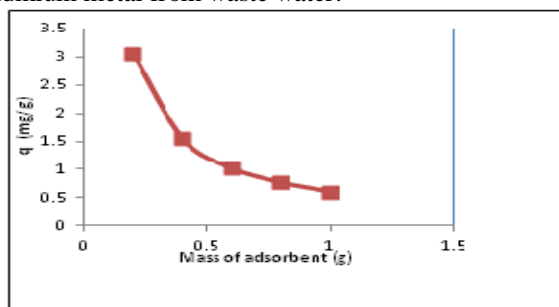
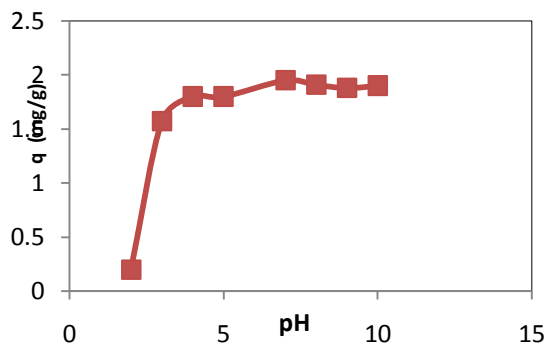


Fig. 4: Effect of Adsorbent dose on the amount of Cadmium adsorbed

### 3.3 EFFECT OF pH

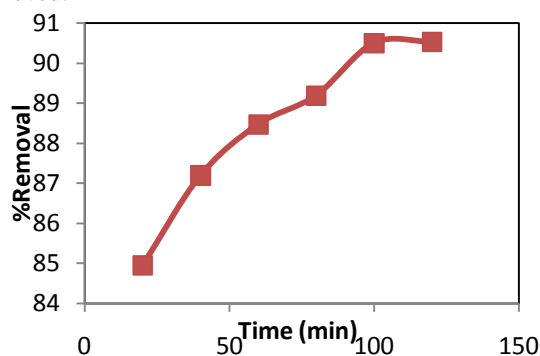
The pH of the solution is one of the important factors governing the adsorption of metal ions [13]. Figure 5 shows the adsorption capacity of Cd(II) as a function of pH of the adsorbate at fixed adsorbent dose, fixed agitation time, fixed adsorbate concentration at room temperature. Cadmium adsorption was found to increase with increasing pH of the solution within the range studied. At pH of 2, only 0.2 mg/g of Cd(II) was adsorbed, but as the pH increases to 7, 1.95mg/g of Cd(II) was adsorbed. According to [14], as pH of the solution increased the cadmium uptake increased probably due to the decreased hydronium ions concentration that provided more adsorption sites for cadmium ions.



**Fig. 5: Effect of pH on the amount of Cadmium adsorbed.**

### EFFECT OF CONTACT TIME

The effect of contact time on Cd(II) Removal (%) at fixed adsorbent dosage, fixed pH and fixed adsorbate concentration at room temperature is presented in Figure 6. From the figure the minimum amount of time required for considerable adsorption to take place is 20 min, further increase resulted in slight increase in percentage of Cadmium removed. The equilibrium time for the adsorption of Cd(II) is achieved at 80 min, with 90.5% of the Cd(II) removed.



**Fig 6: Effect of contact time on the % Removal of Cadmium metal  
Effect of the Initial Concentration of Cd (II)**

The effect of the initial concentration of Cd(II) was investigated at the equilibrium time, optimum pH and at room temperature. From Fig. 7, the metal biosorption capacity increases with an increase in the initial metal ion concentration from 0.29mg/g to 2.23mg/g for SPS, this is due to the fact that an increase in initial ion concentration provides a larger driving force to overcome all mass transfer resistance between solid and aqueous phase, thus resulting in higher metal ion adsorption[15]. While the % removal of Cd(II) decreases from 78.3% to 53.41% (Fig. 8) , this according to [16] is that at high-level concentrations, the available sites of adsorption become fewer and therefore the rate of adsorption decreases.



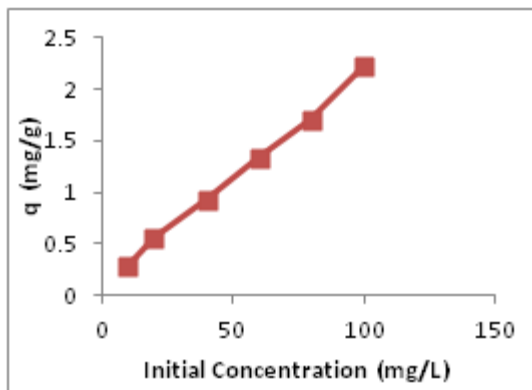


Fig.7: Effect of initial concentration on Amount of Cadmium adsorbed.

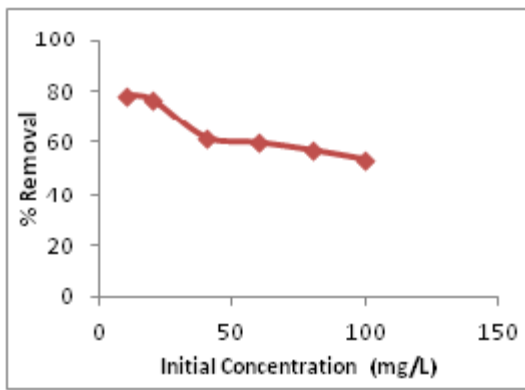


Fig.8: Effect of initial concentration on %Removal of Cadmium

**3.5 BIOSORPTION ISOTHERMS**

The biosorption Isotherms was evaluated using four Isotherm equations namely; Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) Isotherm.

Linear form of Langmuir model [17] is given as:  $\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_m} + \frac{C_e}{q_m}$  ... .. (4)

Where;  $q_e$  is the amount of adsorbate adsorbed on the adsorbent at equilibrium (mg/g),  $q_m$  is the maximum adsorption capacity corresponding to a complete monolayer coverage on the adsorbent surface (mg/g),  $K_L$  is the Langmuir constant (L/g), and  $C_e$  is the concentration of adsorbate at equilibrium (mg/L).

The Values of Langmuir parameters  $q_{max}$  and  $K_L$  were calculated from the slope and intercept of the linear plot of  $C_e/q_e$  versus  $C_e$  Figure9. Values of  $q_{max}$ ,  $K_L$  and regression coefficient  $R^2$  are listed in Table 2. The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter,  $R_L$  expressed as [18]:  $R_L = \frac{1}{(1+k_1C_i)}$  ... .. (5) Where  $C_i$  is the initial concentration and  $K_L$  is the Langmuir constant.

The value of separation parameter  $R_L$  provides important information about the nature of adsorption. The value of  $R_L$  indicates the type of Langmuir isotherm to be irreversible ( $R_L=0$ ), favourable ( $0 < R_L < 1$ ), linear ( $R_L=1$ ) or unfavourable ( $R_L > 1$ ). The  $R_L$  was found to be in the range of 0.2 – 0.7 for concentration of 10–100 mg/L of metal ions indicating favourable biosorption.

Freundlich[18]:  $\log q_e = \log K_F + \frac{1}{n} \log C_e$  ... .. (6)

Where  $K_F$  is Freundlich constant (L/mg) relating to the bonding energy.

Freundlich equilibrium constants were determined from the plot of  $\log q_e$  versus  $\log C_e$ , Figure 10. The  $n$  value indicates the degree of non-linearity between solution concentration and adsorption as follows: if  $n = 1$ , then adsorption is linear; if  $n < 1$ , then adsorption is a chemical process; if  $n > 1$ , then adsorption is a physical process[18]. The  $n$  value was determined to be 1.56. Since the  $n$  value is greater than 1, this indicates the biosorption of Cadmium (II) onto SPS is a physical process.

Temkin[17]:  $q_e = B_1 \ln K_T + B_1 \ln C_e$  ... .. (7)

Where  $K_T$  is equilibrium binding constant (lit/mg) corresponding to maximum binding energy.

Where:  $B_1 = \frac{RT}{b}$  ... .. (8)

$B_1$  is a constant relating to the heat of adsorption.

Temkin Isotherm constants were determined from the plot of  $q_e$  versus  $\ln C_e$  of Figure 11 which enables the determination of isotherm constants  $K_T$  and  $B_1$ .

D–R[19]:  $\ln q_e = \ln q_d - \beta \epsilon^2$  ... .. (9)

Where  $q_d$  is the D–R constant ( $mgg^{-1}$ ),  $\beta$  is the constant related to free energy ( $mol^2/kJ^2$ ) and  $\epsilon$  is the Polanyi potential which is defined as:

$$\epsilon = RT \ln \left[ 1 + \frac{1}{C_e} \right] \dots \dots \dots (10)$$

The constant ( $\beta$ ) is pertained to the mean free energy of adsorption per mole of the adsorbate (kJ/mol) as it is transferred to the surface of the solid from infinite distance in the solution. This energy can be computed using the following relationship:

$$E = \frac{1}{\sqrt{2\beta}} \dots \dots \dots (11)$$

Dubinin–Radushkevich(D–R) isotherm constants were determined from the plot of  $\ln q_e$  against  $\epsilon^2$  of Figure 12. The calculated D-R constants and mean free energy for adsorption are shown in Table 2. The mean adsorption

energy was determined to be in the range of 0-1 kJ/mol, which is in the energy range of physical adsorption reaction.

Fitting of the data to Langmuir, Freundlich, Temkin and D-R Isotherms suggests that the biosorption of Cadmium ontoSPS can be explained by the Isotherms as outlined in Table 2.It is apparent that the Freundlich model describes the biosorption process of Cd(II) onto SPS favourably on the basis of Correlation factor R<sup>2</sup>.

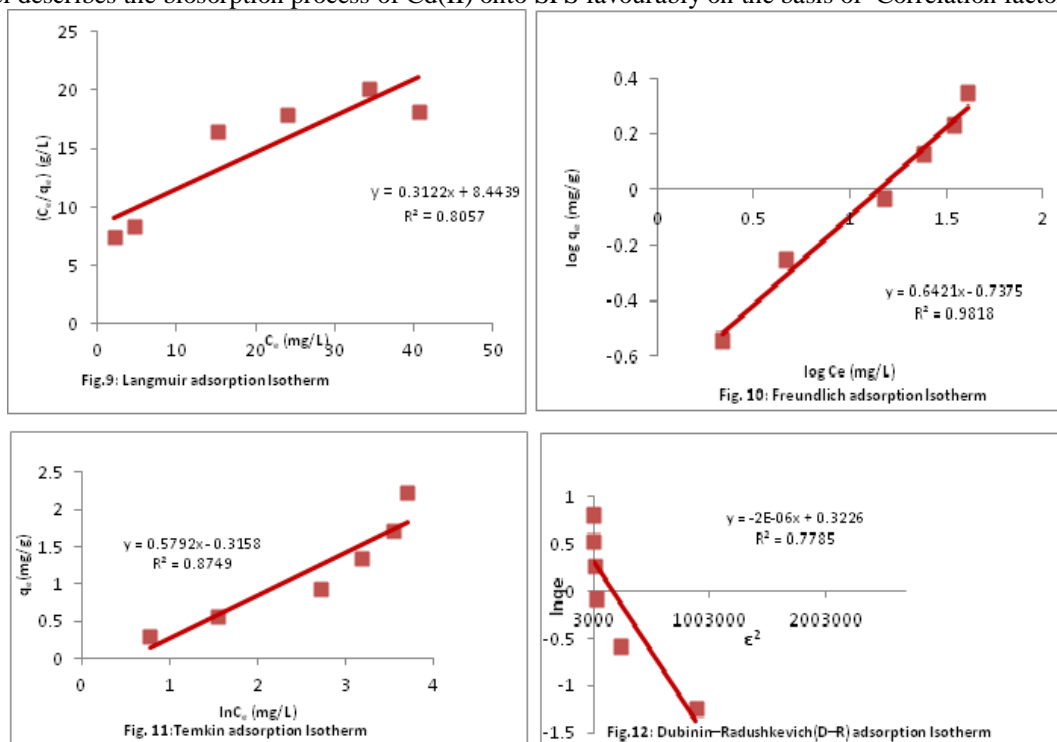


TABLE 2: ISOTHERM CONSTANTS FOR THE ADSORPTION OF Cd(II) ONTO SPS

Isotherm Model	Parameters	Values	Isotherm Model	Parameters	Values
Langmuir	q <sub>m</sub> (mg/g)	3.21	Temkin	B <sub>1</sub> (kJ/mol)	0.579
	K <sub>L</sub> (L/mg)	0.04		K <sub>T</sub> (L/mg)	0.58
	R <sup>2</sup>	0.806		R <sup>2</sup>	0.8749
Freundlich	K <sub>f</sub> (L/g)	5.47	D-R	q <sub>m</sub> (mg/g)	1.38
	n	1.56		β (mol <sup>2</sup> /kJ <sup>2</sup> )	2e <sup>-06</sup>
	R <sup>2</sup>	0.982		R <sup>2</sup>	0.779
				E(KJ/mol)	0.5

3.6 KINETICS OF ADSORPTION

In order to investigate the biosorption process of Cd (II) onto SPS, pseudo-first-order of Lagergren rate equation, Natarjan and Khalaf equation, Bhattacharya and Venkobacharya equation, pseudo-second-order, intraparticle and Bangham’s diffusion model were used to find out the best fit kinetic model for the adsorption of Cd(II)SPS.

$$\text{Lagergren rate equation [18]} \frac{dq_t}{dt} = k_1(q_e - q_t) \dots \dots \dots (12)$$

Integrating this for the initial and end conditions; t = 0 to t = t at q<sub>t</sub> = 0 to q<sub>t</sub> = q<sub>t</sub>, equation (12) may be rearranged for linearized data plotting to give:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \dots \dots \dots (13)$$

Where q<sub>e</sub> and q<sub>t</sub>(mg/g) are amount of metal ion adsorbed per unit mass of adsorbent at equilibrium and at time t (min). K<sub>1</sub> is the rate constant for first-order adsorption.

Figure 13 shows the Lagergren pseudo-first order kinetic plot for the adsorption of Cadmium ions onto SPS. The calculated values and their corresponding linear regression correlation coefficient values are shown in Table 3. The linear regression correlation coefficient value was determined to be 0.811, the value of the calculated adsorption capacity ( $q_{e,calculated}$ ) were far much lower than experimental one ( $q_{e,experimental}$ ), suggesting that the adsorption process did not fit the pseudo-first order model .

Natarajan Khalaf equation [20] is given as:  $\log(C_i / C_t) = (k_{ad} / 2.303) t$ ..... (14)

Where;  $C_i$  and  $C_t$  are the concentration of the adsorbate (in mg/L), at time zero and time t.  $k_{ad}$  is the first order rate constant ( $\text{min}^{-1}$ ) for adsorption.

Figure 14 shows the Natarajan and Khalaf pseudo-first order kinetic plot for the adsorption of Cadmium ions onto SPS. The linear regression correlation coefficient of the plot  $\log(C_0 / C_t)$  against time (t) value shows that this model cannot be applied to predict the adsorption kinetic model.

The rate equation for pseudo first order given by Venkobacharyaand Bhattacharya[20] is: $\text{Log} (1- U(T)) = - (k/2.303) t$  .....(15)

Where,  $U (T) = [(C_i - C_t) / (C_i - C_e)]$ ..... (16)

$C_e$  is the equilibrium time metal ion concentration and  $k$  is the pseudo first order rate constant

plot of  $\text{Log} (1- U(T))$  against t. Figure 15 shows the Bhattacharya and Venkobacharyapseudo-first order kinetic plot for the adsorption of Cadmium ions onto SPS. The linear regression correlation coefficient value shows that this model cannot be applied to predict the adsorption kinetic model.

Pseudo-second order equation[21]:  $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \dots \dots \dots (17)$

Figure 16 shows the pseudo-second order kinetic plot for the adsorption of Cadmium ions onto SPS, from which  $q_e$  and rate constant were determined from the slope and intercept presented in Table 3. From Table 3 the linear regression correlation coefficient  $R^2$  value is higher than the Pseudo first order kinetics. The higher values confirm that the adsorption data are well represented by pseudo-second order kinetics[18]. The calculated maximum adsorption capacity value of  $q_e$  (calculated) which are quite close to the experimental value,  $q_e$  (experimental) for adsorption of cadmium onto SPS, which indicates that the pseudo second order model fits with the kinetic data very well.

Intra-particle diffusion model [22]:  $q_t = k_{id} \sqrt{t} + I$  ..... (18)

The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model[22] equation 18. Plot of  $q_t$  versus  $\sqrt{t}$  is shown in Figure 17, Where  $k_{id}$  is the intra-particle diffusion rate constant ( $\text{mg/g min}^{1/2}$ ), this is gotten from the slope of the plot of  $q_t$  versus  $\sqrt{t}$  and  $I$  ( $\text{mg/g}$ ) is a constant that gives idea about the thickness of the boundary layer. Since the Weber-Morris plot of  $q_t$  versus  $\sqrt{t}$  did not pass through the origin, which is an indication of some degree of boundary layer control and this further shows that the intra-particle diffusion is not the only rate limiting step, but also other kinetic models may control the rate of adsorption all of which may be operating simultaneously [23].

Bangham equation[24] is given as:  $\log \log \left( \frac{C_0}{C_0 - q_t M} \right) = \log \left( \frac{K_0 M}{2.303 V} \right) + \alpha \log(t) \dots \dots \dots (19)$

Where;  $C_0$  is the initial concentration of the adsorbate in solution ( $\text{mg/L}$ );  $V$ , the volume of solution ( $\text{mL}$ );  $q_t$  = the amounts of metal ion adsorbed ( $\text{mg/g}$ ) at time,  $m$ =the weight of the adsorbent used ( $\text{g/L}$ ); and  $\alpha (<1)$  &  $k_0 [\text{ml}/(\text{g/l})]$  = the diffusion constant

The possibility of pore diffusion was explored by using the Bangham equation model. Figure 18 yields a satisfactory linear curve for the removal of Cd (II). The correlation coefficient indicates that the diffusion of adsorbate into the pores of the adsorbent also control the rate of adsorption.

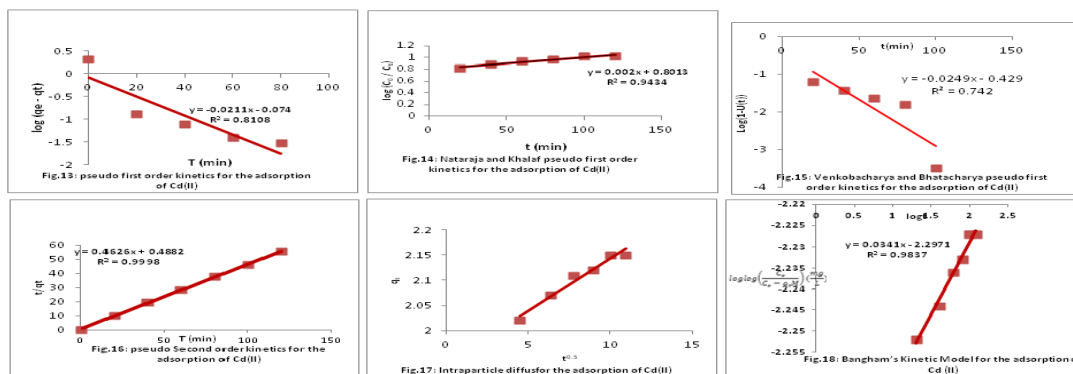


TABLE 3: KINETIC PARAMETERS FOR THE ADSORPTION OF Cd(II) ONTO SPS



KINETIC MODEL	PARAMETER	SPS	KINETIC MODEL	PARAMETER	SPS
Lagergren Pseudo first order equation	$K_1$	0.048	pseudo Second order kinetics	$K_2$	0.44
	$q_{e(\text{exp})}$	0.84		$q_{e(\text{exp})}$	2.15
	$q_{e(\text{cal})}$	2.15		$q_{e(\text{cal})}$	2.16
	$R^2$	0.811		$R^2$	0.99
Nataraja and Khalaf pseudo first order kinetics	$K_1$	0.005	Intra particle diffusion	$K_d$	0.026
	$R^2$	0.943		$C$	1.937
Venkobacharya and Bhatacharya	$K$	0.058	Bangham's Kinetic Model	$R^2$	0.963
	$R^2$	0.74		$K_o$	0.00044

**EFFECT OF TEMPERATURE**

When the temperature were increased from 25°C to 80°C, the biosorption capacity and percentage removal of Cd(II) increased. The higher uptake at higher temperature may be attributed to the availability of more active sites on the surface of SPS, the same result was obtained by Al-Dujaili et al [25] on the Biosorption of cadmium (II) onto loquat leaves(Eriobotrya japonica) and their ash from aqueous solution, equilibrium, kinetics, and thermodynamic studies..

**ADSORPTION THERMODYNAMICS**

Thermodynamic parameters such as standard free energy change ( $\Delta G^\circ$ ), standard enthalpy change ( $\Delta H^\circ$ ), and standard entropy change ( $\Delta S^\circ$ ) were evaluated. The free energy of adsorption process considering the adsorption equilibrium constant  $K_o$  is given by the equation [26]:

$$\Delta G^\circ = -RT \ln K_o \dots \dots \dots (20)$$

Where  $\Delta G^\circ$  is the free energy of adsorption (kJ/mol), T is the temperature in Kelvin and R is the universal gas constant (8.314 Jmol<sup>-1</sup>K<sup>-1</sup>).

The adsorption distribution coefficient may be expressed in terms of enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) as a function of temperature.

$$\ln K_o = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \dots \dots \dots (21)$$

Where  $\Delta H^\circ$  is the standard heat change of sorption (kJ/mol) and  $\Delta S^\circ$  is standard entropy change (kJ/mol). The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  can be obtained from the slope and intercept of plot of  $\ln K_o$  against 1/T [26].

According to [22] and [27]:  $K_o = \frac{C_{solid}}{C_{liquid}}$  where  $K_o$  is the equilibrium constant,  $C_{solid}$  is the solid phase concentration at equilibrium (mg/L),  $C_{liquid}$  is the liquid phase concentration at equilibrium (mg/L).

Also the Gibb's free energy change is also related to the enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) at constant temperature by the van't Hoff equation:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \dots \dots \dots (22)$$

Equations (20) and (22) can be written as:

$$-RT \ln K_o = \Delta H^\circ - T \Delta S^\circ \dots \dots \dots (23)$$

Or

$$\ln K_o = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \dots \dots \dots (24)$$

The values of enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were calculated from the slope and intercept of the plot of  $\ln K_o$  vs. 1/T, Figure 19. The calculated values of the thermodynamic parameters  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  for the biosorption of Cd(II) onto SPS are reported in Table 4. Positive value of  $\Delta S^\circ$  and  $\Delta H^\circ$  showed increased randomness and that the adsorption process is endothermic [18]. A negative value of the free energy ( $\Delta G^\circ$ ) at all the temperature indicates the process to be feasible and spontaneous; the same result was gotten by [18] and also [25].

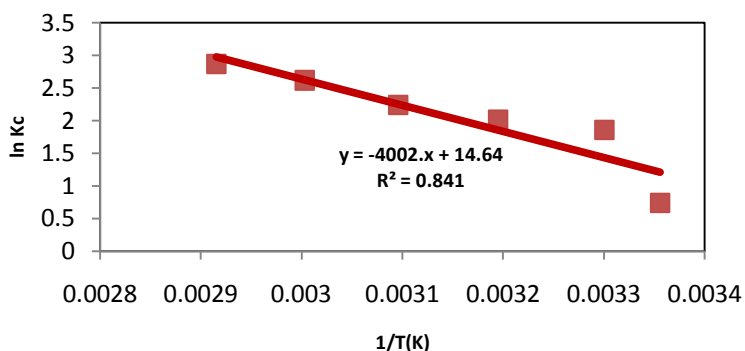


Fig.19: Van't Hoff plot for adsorption of Cd(II) on SPS

TABLE 4: THERMODYNAMIC PARAMETERS OF ADSORPTION OF Cd(II)

SPS			
T(K)	$\Delta G^\circ$ (KJ/MOL)	$\Delta H^\circ$ (KJ/MOL)	$\Delta S^\circ$ (KJ/MOL)
298	-1.83	33.28	0.1
303	-4.69		
313	-5.26		
323	-6.05		
333	-7.25		
343	-8.18		

For physical adsorption free energy change ( $\Delta G^\circ$ ) ranges from (-20 to 0) kJ/ mol and for chemical adsorption it ranges between (-80 and -400) kJ mol<sup>-1</sup>[18]. The  $\Delta G^\circ$  for Cd(II) biosorption onto SPS was in the range of -1.83 to -8.67 kJ mol<sup>-1</sup> indicating the biosorption process to be physical process.

### III. CONCLUSION

This study has showed that Sweet Potato Skin has good adsorption capacity for Cadmium and the minimum amount of time required for adsorption to take place is 20 min. Sweet Potato Skin can therefore be used in the treatment of effluents from cadmium industries.

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