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Thermodynamic Studies on the Biosorption of Cd^{2+} from Aqueous Solution by Cocoa (*Theobroma cacao*) Pod Husk

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ABSTRACT

The biosorption of Cd^{2+} *by Cocoa (Theobroma cacao) pod husk was investigated in single metal solution. Equilibrium biosorption studies were carried out to delineate the effect of temperature variation on biosorption capacity of cocoa pod husk. The result showed that unmodified cocoa pod husk (UCPH) and modified cocoa pod husk (MCPH) exhibited maximum biosorption of 97.8 % and 99.5 % respectively at 303 K. Thermodynamic parameters such as* ΔG°_{ads}, ΔH°_{ads}, ΔS°_{ads}, E_{Aads} *and* S^{*}_{ads} *related to Gibbs free energy, enthalpy, entropy, activation energy and sticking probability were evaluated. The result of thermodynamic investigations indicated that the biosorption reactions were spontaneous* ($\Delta G^{\circ}<0$)*, exothermic* ($\Delta H^{\circ}<0$)*, irreversible* ($\Delta S^{\circ}>0$)*, diffusion controlled* ($-E_A$) *and physisorption mechanism* ($S^{*}<1$)*.*

Key words: Aqueous solution, Biosorption, Cadmium, Cocoa pod husk, Thermodynamic parameters.

INTRODUCTION

The tremendous increase in the amount of heavy metals released into the aquatic environment has become a major concern in the present decade. Among these heavy metals is cadmium, an extremely toxic metal commonly found in industrial workplaces, particularly where any ore is being processed or smelted [1]. Due to its low permissible exposure limit (PEL), over-exposures may occur even in situations where trace quantities of cadmium are found in the parent ore or smelter dust. However, the drinking water standard recommended by the World Health Organization (WHO) is 0.005 mg/L of cadmium while the permissible limit is 0.01 mg/L in irrigation water [2, 3].

Cadmium is introduced into water bodies from smelting, metal plating, cadmium-nickel batteries, phosphate fertilizer, mining, pigments, stabilizers, alloy industries and sewage sludge [2]. Toxicological studies have shown that long-term effects from cadmium (II) poisoning include kidney damage and changes to the constitution of the bone, liver and blood. Short-term effects include nausea, vomiting, diarrhoea and cramps [4]. As a result, minimizing production of hazardous waste and heavy metals became one of the most important environmental challenges that the world faces today.

Many methods for treatment of metal ions from aqueous solutions have been described which include chemical and surface chemistry processes such as precipitation, adsorption, membrane processes, ionic exchange, floatation and others [5]. However, these techniques have their own inherent limitations such as less efficiency, sensitive operating conditions and production of secondary sludge requiring further costly disposal [6]. These disadvantages, together with the need for more economical and effective methods for recovery of metals from wastewater have resulted in the development of alternative separation technologies. One of such alternatives is biosorption, where certain types of biomass are able to bind and concentrate metals from even very dilute aqueous solution [7, 8]. In fact, biosorption offers a number of advantages when compared to the conventional methods currently used [9].

Agricultural by-products have been used by many researchers to remove metal ions such as cadmium from aqueous solutions [10 – 14]. These agricultural by-products are usually composed of lignin and cellulose as their major constituents and may also include other polar functional groups of lignin such as alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups [15]. These groups have the ability to bind heavy metal ions to a large extent by donation of an electron pair from these groups to form complexes with the metal ions in solution [16].

In this study, modified and unmodified cocoa pod husks were used for the removal of Cd^{2+} from aqueous solutions. The major objective of this study is to investigate the biosorption efficiency of Cd^{2+} by cocoa pod husk using thermodynamic parameters for the prediction of the mechanisms involved in Cd^{2+} biosorption.

MATERIALS AND METHODS

Preparation of biosorbent

The cocoa *(Theobroma cacao)* pod husk used was obtained from a waste disposal site at Cocoa Research Institute of Nigeria, Ibeku Sub-station, Umuahia, Abia State, Nigeria. The pod husk was washed thoroughly with deionized water to remove dirt and other particulate matter and then cut into small particles. These particles were air-dried and crushed into powdery forms using a manually operated grinder. The meal obtained was dried further in the oven at 50°C for 12 h. The meal was then sieved through sieve No. 250 µm. 100 g of 250 µm particle size of cocoa pod husk(s) were activated by soaking in 2 % (v/v) dilute nitric acid (HNO_3) solution for 24 h in a round bottom flask. The mixture was filtered after 24 h and washed copiously with deionized water until neutral pH of the filtrate was observed. The biosorbent was then dried in an oven at 110°C for 12 h. Thereafter the biosorbent was removed from the oven and was labeled unmodified cocoa pod husk (UCPH) and stored in a dessicator. The activation of the biosorbent with 2 % (v/v) nitric acid helps to dissolve any soluble biomolecule and to remove any debris from the surface of the biosorbent which might interfere with metal ions during biosorption process. It also aids in opening up the pores of the biosorbent in readiness for biosorption process [17 – 19].

Modification of biosorbent

50 g of the 250 µm particle sized activated unmodified coca pod husk (UCPH) was taken from the bulk for chemical modification process. The biosorbent was modified by thiolation using the method of Okieimen and Okundaye [20]. Specifically, 50 g of UCPH was thiolated with 550 ml of 0.3 M solution of thioglycollic acid for 24 h at 29°C. After 24 h, the mixture was filtered, washed with deionized water and then with methanol. It was finally washed with deionized water and dried at 50°C in the oven for 12 h. After 12 h, the biosorbent was stored in an air-tight, moisture free container and labeled modified cocoa pod husk (MCPH).

Biosorbent characterization

The surface characteristics of the cocoa pod husk were determined according to the method outlined by Santamarina *et al* [21]. Parameters such as specific surface area (S_{AA}), specific charge density, particle density and cation exchange capacity (CEC) were determined.

Preparation of metal solution (biosorbate)

All reagents used were of AR grade chemicals. Stock solution of 1000 mg/L Cd^{2+} was prepared in deionized water using cadmium chloride ($CdCl_2$). Working solutions of 100 mg/L were prepared from the stock solution by appropriate dilution with deionized water.

Biosorption studies

Batch mode biosorption studies were carried out to determine the biosorption of Cd^{2+} by UCPH and MCPH respectively. A 50 ml volume of Cd^{2+} solution with a concentration of 100 mg/L was transferred into various 250 cm^3 conical flask. An accurately weighed biosobent sample 1 g was then added to the solution. A series of such conical flasks in triplicates (nine containing UCPH and Cd^{2+} solution and another nine containing MCPH and Cd^{2+} solution) were then corked and labeled for different temperatures 303 K, 323 K and 343 K respectively. The conical flasks with their content were then shaken at a constant speed of 100 rpm in a shaking water bath with temperatures 303, 323 and 343 K, respectively for 1 h, maintaining the pH at 5.0. After agitation for 1 h, each reaction mixture was filtered into sample bottle using Whatmann filter paper No. 42. The filtrate was analyzed for the remaining cadmium ion concentration using atomic absorption spectrophotometer (AAS: UNICAM Solar 969).

The amount of metal ions adsorbed by the biosorbent was determined using a mass balance equation expressed as:

$$q_e = (C_o - C_e)\, V/m \qquad (1)$$

where q_e is the amount of metal ion adsorbed (mg/g) by the biosorbent at equilibrium, C_o is the initial concentration of metal ion in the solution (mg/L), C_e is the equilibrium concentration or final concentration of metal ion in the solution (mg/L), V is the volume of initial metal ion solution used (mL), m is the mass of the biosorbent (g). To minimize error, the mean value of the triplicate values for each case was used for calculation.

The percent biosorption (%) was also calculated using equation (2):

$$\% \text{ biosorption} = C_o - C_e / C_o \times 100 \qquad (2)$$

RESULTS AND DISCUSSION

Surface characterization of the biosorbent

The surface characteristics of the cocoa *(Theobroma cacao)* pod husk are reported on Table 1. The specific surface area (S_{AA}) and specific charge density (SCD) are very high which depicts that the biosorbent have very high tendency for metal ions biosorption.

Table 1: Surface characteristics of unmodified and modified cocoa pod husk

Parameter		Value (unit)	Parameter	Value (unit)
Bulk density:	UCPH	0.072 (g/cm^3)	Specific surface area (S_{AA}):	2.280 x 10^{26} (m^2/g)
	MCPH	0.080 (g/cm^3)		2.32 x 10^{24} (g/cm^3)
Particle density:	UCPH	0.262 (g/cm^3)	Surface charge density (SCD):	6.20 x 10^{24} (meq/m^2)
	MCPH	0.302 (g/cm^3)		6.42 x 10^{25} (meq/m^2)
Pore volume:	UCPH	3.9 (cm^3)	Particle size:	250 (µm)
	MCPH	4.2 (cm^3)		250 (µm)
Cation exchange capacity (CEC):	UCPH	34.2 (mg/50g)	pH:	5.41
	MCPH	35.3 (mg/50g)		5.02
Porosity:	UCPH	20.10 (%)	Colour:	Dark Brown
	MCPH	22.01 (%)		Dark Brown

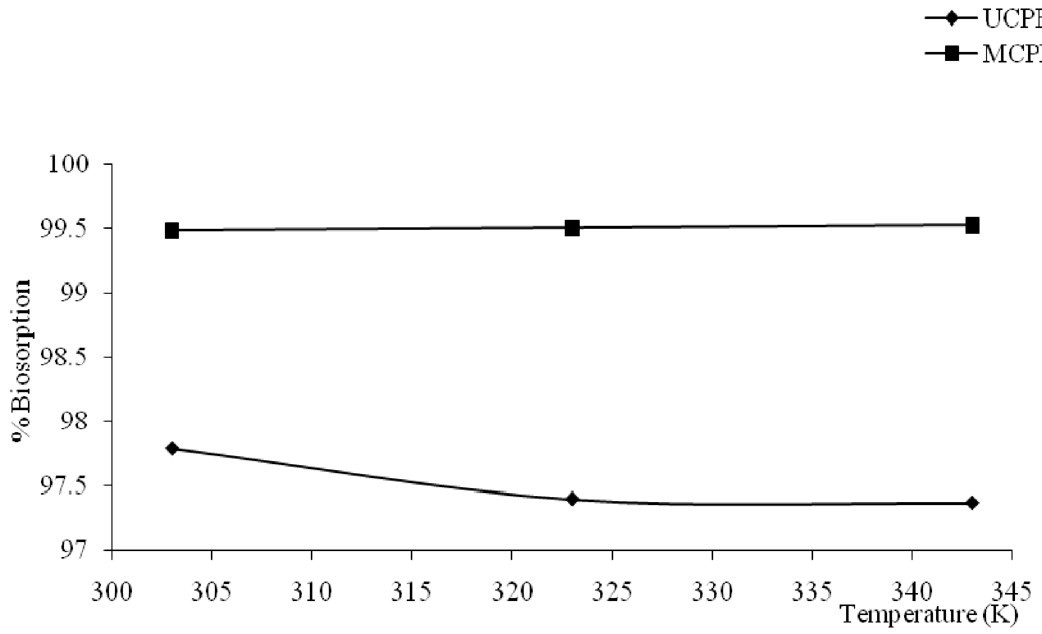

Fig 1: Effect of temperature on percent biosorption of Cd (II) ions by modified and unmodified cocoa pod husk

Effect of temperature on biosorption

Investigation of biosorption capability of modified and unmodified cocoa pod husk is illustrated in Fig.1. From the figure, the equilibrium uptake of Cd^{2+} by unmodified cocoa pod husk (UCPH) was affected by temperature and decreased with increasing temperature up to 343 K which is the optimum temperature in relation to this work. For modified cocoa pod husk (MCPH), the equilibrium uptake of Cd^{2+} also decreased at 323 K and slightly increased at 343 K but was insignificant to the percent adsorbed at 303 K. Succinctly, the trend was the higher the temperature, the lower the biosorption of Cd^{2+}. This trend also suggests that the biosorption process was exothermic in nature. Other researchers have also reported this with other metal ions [22 – 24]. This implies that increase in temperature resulted in corresponding increase in the solubility of the biosorbate (metal ion solution) and consequently a decrease in the chemical potential which resulted in a decrease in biosorption [24, 25]. At high temperature, the thickness of the boundary layer is expected to decrease due to the increased tendency of the metal ions to escape from the surface of the biosorbent to the solution phase as a result of the increase in kinetic energy of the ions, hence there is bound to be weak biosorption interactions between the biosorbent and the biosorbate. A similar finding was also observed by Elaigwu *et al* [26]. However, this decrease in biosorption of Cd^{2+} with increasing temperature which suggests weak biosorption interaction between biomass surface (biosorbent) and the metal ions also suggests and supports physisorption mechanism. Other researchers have reported same [17, 19].

Thermodynamic study

The thermodynamic parameters such as Gibbs free energy (ΔG°_{ads}), enthalpy change (ΔH°_{ads}), entropy (ΔS°_{ads}), activation energy (E_{Aads}) and sticking probability (S^*_{ads}) were determined to evaluate the feasibility and nature of the biosorption of Cd^{2+} onto modified and unmodified cocoa pod husk. The thermodynamic parameters were calculated from the following equation [27 – 29]:

$$K = C_{ad}/C_e \qquad (3)$$

$$\ln K = \Delta S^\circ_{ads}/R - \Delta H^\circ_{ads}/RT \qquad (4)$$

$$\Delta G^\circ_{ads} = - RT \ln K \qquad (5)$$

where K is the equilibrium constant, C_{ad} is the amount adsorbed or metal ion concentration on the biosorbent at equilibrium (mg/g) and C_e is the equilibrium concentration of the metal ion in solution (mg/L), R is universal gas constant (8.314 JK^{-1} mol^{-1}), T is the absolute temperature (K).

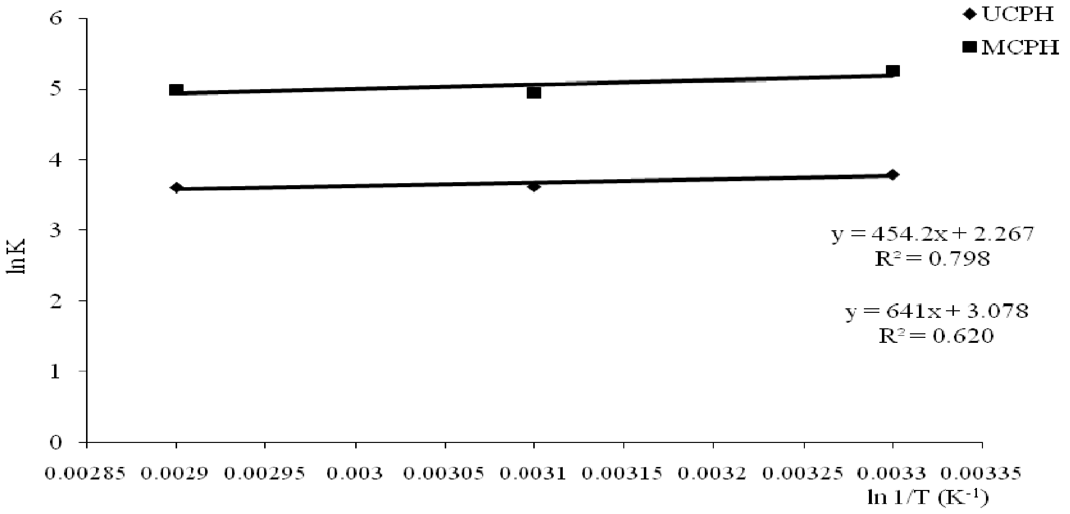

Fig 2: Vant Hoff plot for biosorption of Cd (II) ions by modified and unmodified cocoa pod husk

The plot of ln K versus 1/T (Van't Hoff plot) for the biosorption of Cd^{2+} onto modified (MCPH) and unmodified (UCPH) cocoa pod husk is shown on Fig. 2. The regression equations and R^2 values are also shown on the figure. Using the linear regression equation, values of ΔH°_{ads} and ΔS°_{ads} were calculated from the slopes and intercepts of the plot. Using equation (5), the values of ΔG°_{ads} were calculated at different temperatures. The values obtained for the thermodynamic parameters are shown on Table 2. From Table 2, the negative values of ΔG°_{ads} confirm the feasibility of the process and the spontaneous nature of biosorption with a high preference of Cd^{2+} on cocoa pod husk. The values of enthalpy change, ΔH°_{ads} obtained were negative which further confirm the exothermic nature of the biosorption process. This is similar to findings by other researchers [30 – 32]. The positive values of entropy, ΔS°_{ads} corresponds to an increase in the degree of freedom of the adsorbed species [28, 29]. Positive values of ΔS°_{ads} also reflect that some changes occurred in the internal structure of cocoa pod husk during the biosorption process.

Similar type of observation has been reported by other researchers [28, 33 – 34]. Nonetheless, values of ΔS°_{ads} denoted feasibility and irreversibility of the biosorption process.

Table 2: Thermodynamic parameters of Cd^{2+} biosorption by unmodified and modified cocoa pod husk

Biosorbent	Temp (K)	ΔG°_{ads}(KJ mo^{-1})	ΔH°_{ads}(KJ mo^{-1})	ΔS°_{ads}(JK mo^{-1})	E_{Aads} (KJmol^{-1})	S^{*}_{ads}
UCPH	303	-9554.60	-3776.63	18.85	-3685.18	0.09
	323	-9728.75				
	343	-10297.78				
MCPH	303	-13229.02	-5329.27	25.59	-5296.02	0.05
	323	-13292.03				
	343	-14244.25				

Values of activation energy (E_{Aads}) and sticking probability (S^{*}_{ads}) were used to ascertain the nature and mechanism of the biosorption respectively. Sticking probability was also used to ascertain the probability of the metal ion remaining on the surface of the biosorbent. Thus, sticking probability equation is given by:

$$S^{*}_{ads} = (1 - \Theta) \exp - (E_A/RT) \qquad (6)$$

where Θ is known as the surface coverage and is given by:

$$\Theta = (1 - C_e/C_o) \qquad (7)$$

where C_e and C_o are equilibrium and initial metal ion concentrations respectively. The plot of ln (1 - Θ) versus 1/T (sticking probability plot) is shown on Fig. 3. The regression equation and R^2 values are also shown on the figure. Using the linear regression equation, the values of E_{Aads} and S^{*}_{ads} were calculated from the slopes and intercepts of the plot. The values obtained for E_{Aads} and S^{*}_{ads} are also shown on Table 2. For the activation energy of biosorption, E_{Aads}, the values were negative indicating that lower solution temperature favours Cd^{2+} removal by biosorption onto UCPH and MCPH. Negative E_{Aads} values also signify reduced E_{Aads} and increased reaction rate. It also suggests that the biosorption process is exothermic in nature. More so, relatively low values of E_{Aads} suggest that Cd^{2+} biosorption is a diffusion controlled process. Other researchers have also made similar observation [32, 35]. The sticking probability, S^{*}_{ads}, is a function of the biosorbate/biosorbent system under consideration and must lie in the range 0<S<1 and it is always dependent on temperature and also indicates the measure of the potential of a biosorbate to remain on the biosorbent indefinitely. Hence, S^{*}_{ads} values obtained fall within the range 0 and 1. These values further confirm that the biosorption of Cd^{2+} was of physisorption mechanism.

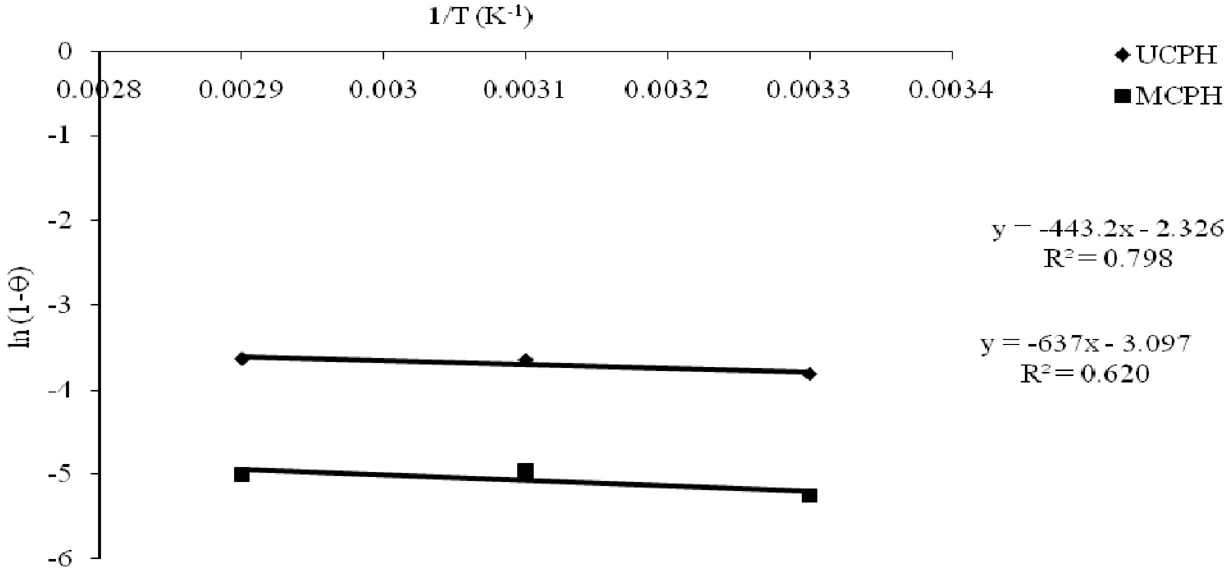

Fig 3: Sticking probability plot for biosorption of Cd (II) ions by modified and unmodified cocoa pod husk

CONCLUSION

Cocoa *(Theobroma cacao)* pod husk has been shown to be a potentially useful biosorbent to remove Cd^{2+} from aqueous solutions. The percent biosorption decreased with increase in temperature as optimum biosorption was maintained at 303 K. However, modified cocoa pod husk (MCPH) showed higher biosorption of Cd^{2+} than unmodified cocoa pod husk (UCPH). Thermodynamic considerations showed that the biosorption process was feasible, spontaneous, exothermic, irreversible, diffusion controlled and predominantly physisorption mechanism. The values of the parameters and high biosorption capacity obtained therefore demonstrate cocoa pod husk as an efficient biosorbent for the removal of heavy metals from aqueous solutions/wastewaters.

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