

## Competitive Sorption of Lead and Cadmium (II) Ions from Aqueous Media Using Carbon from Bamboo Culms and Periwinkle Shells

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**Abstract:** *The study assessed the potential application of periwinkle shells and bamboo culms carbon as biosorbents for the competitive sorption of cadmium and lead ions from aqueous solution. The bamboo culms and periwinkle shells were carbonized (pyrolyzed) at 500<sup>o</sup>c. These were milled, sieved with shaker sieve and some of the carbon (bamboo and periwinkle) were blended in a rotary blender in the ratio of 1:1. The bamboo and periwinkle carbon were characterized and used to determine the amount absorbed ( $q^1$ ) mg/g. The applicability of equilibrium isotherms models and equilibrium kinetics models were examined for the experimental data. The results from the competitive sorption systems shows that sorption maxima ( $mgg^{-1}$ ) for the Cd, and Pb ions followed the order  $Cd^{2+} > Pb^{2+}$  for the sorbents. In equilibrium kinetics, the experimental data fits pseudo second order equation.*

**Keywords:** *Competitive sorption, Carbon, Aqueous media Cadmium, Lead.*

### 1. INTRODUCTION

The pollution problem of industrial waste water is becoming negatively of great concern in the world today. Consequently, the treatment of polluted industrial waste water remains a topic of global concern since waste water collected from industries contaminates the ground water and must ultimately be returned to receiving waters or to the land (Mohsen, 2007).

Lead and other heavy metals are one of the major pollutants in the environment and they exhibit a potentially damaging effect on human physiology and other biological systems when the tolerance levels are exceeded (Joshi, 2003).

Metals like lead and cadmium are of special concern because they are not biodegradable and therefore persistent. Their presence in the streams and lakes ranges from beneficial through troublesome to dangerously toxic (ATSDR, 2001). Therefore, elimination of heavy metals from water and waste water is important to protect public health and wildlife (Elachia et.al, 2005).

A number of treatment methods for the removal of heavy metals ions from waste water have been reported in various literatures which include among others, ion exchange, adsorption, etc (Ahmedina et.al, 1997).

Most of these methods suffer from drawbacks such as high capital, operational cost, time consumption, equipment complexity and the disposal of the residual metal sludge (Amuda and Ibrahim, 2006). Adsorption is the process of collecting soluble substances (adsorbate) that are in solution, on a suitable interface (with adsorbent). The interface can be between the liquid and a gas, a solid, or another liquid. Adsorption offers the best solution since the process is cheap, fast and fewer complexes coupled with the fact that sophisticated items of equipment are not required to conduct the experiments (ASTM, D4607).

The use of sorbents produced from biomass to remove heavy metals because of its high chemical activity, reliability, low cost and availability has been discussed in several studies (Ahmed et.al, 2011).

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With this in mind, we have sought to explore the potential use of periwinkle shells and bamboo culms carbon as sorbents for the sorption of cadmium and lead ions from aqueous media. Periwinkle shells are a waste product generated from the consumption of periwinkle, a small greenish-blue marine snail found in many coastal communities within Nigeria (Olutoge et.al, 2012). The shells are typically disposed of after consuming the edible parts as sea food thereby contributing to environmental pollution. The reuse capacity of these shells can be improved by utilizing them for the development of value added products such as biosorbents. In the process, the environmental burden posed by their inappropriate disposal is also eliminated.

Bamboo is one of the oldest building materials used by mankind (Abd-Latif, and Abd-Razak, 1991). The bamboo culms, or stem, have been made into an extended diversity of products ranging from domestic household products to industrial applications. Examples of bamboo products are food containers, skewers, chopsticks, handicrafts, toys, furniture's, flooring, pulp and papers, boats, charcoal, musical instruments and weapons. In Asia, bamboo is quite common for bridges, scaffolding and housing, but it is usually a temporary exterior structural material. In many overly populated regions of the tropics, certain bamboos supply the one suitable material that is sufficiently cheap and plentiful to meet the extensive need for economical housing.

In this work, we study the potential application of periwinkle shells and bamboo culms carbon as biosorbents for the competitive sorption of cadmium and lead ions from aqueous solution through:

- i. Preparation of periwinkle shells and bamboo culms carbon.
- ii. Characterization of the periwinkle shells and bamboo culms carbon produced to determine their physiochemical properties.
- iii. Evaluation of the sorption potentials of the carbon for cadmium and lead from aqueous media,
- (iv) Evaluation of the adsorption equilibrium isotherm and kinetics using the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich and Lagergren pseudo first order, Pseudo second order, Elovich equation and intra-particle diffusion model.

## 2. MATERIALS AND METHOD

### 2.1 Materials

**Table 2.1.** *Materials, reagents source and grade*

Materials/Reagents	Supplier/Source	Grade
Periwinkle shells	Sourced locally from Rumolumini by sliverbird cinema in portharcourt, River state. (7.01 <sup>0</sup> E, 4.78 <sup>0</sup> N, 16m above sea level).	-
Bamboo culms	Sourced locally from Igieduma, Benin-Auchi Road, Ehor, Edo State. (5.37 <sup>0</sup> E, 6.20 <sup>0</sup> N, 88m above sea level.	-
Lead nitrate (Pb(NO <sub>3</sub> ) <sub>2</sub> ), Sodium hydroxide, hydrogen chloride, nitric acid and cadmium nitrate Cd(NO <sub>3</sub> ) <sub>2</sub>	Sigma Aldrich, Germany	Analar grade
Muffle furnace	Green lab, Palm House, Benin City	-
Atomic Absorption Spectrophotometer(AAS)	Integrated Lab at M.M. way, Benin City	-
Distilled water	Purchase from chemical sales outlet in Igbe road, Auchi	-

### 2.2 Preparation of the Cadmium and Lead Ions in Aqueous Media

Aqueous standard solutions of Cd(II) and Pb(II) were prepared by dissolving an accurately weighed amount of Cd(NO<sub>3</sub>)<sub>2</sub> and Pb(NO<sub>3</sub>)<sub>2</sub> salts in deionized water so as to yield a metal ion concentration of 1000 mgL<sup>-1</sup>. Appropriate aliquots were taken from these standards for subsequent dilution to the

desired concentration level. NaOH and HCl solutions, both  $0.10 \text{ molL}^{-1}$ , were used for pH adjustment. pH meter was used for the pH measurements. Polyethylene bottles were selected as containers. The bottles were first cleaned with a metal-free non-ionic detergent and washed with tap water. They were then soaked in 1:1  $\text{HNO}_3 + \text{H}_2\text{O}$  solution for 24 h at  $70^\circ \text{C}$  and subsequently rinsed thrice with de-ionized water. The total cadmium and lead concentrations in the solution samples were determined respectively using flame atomic absorption spectroscopy (AAS).

### **2.3 Adsorbent preparation and characterization**

The material used in this study was obtained by carbonization of periwinkle shells and bamboo culms respectively in order to prepare the desired biosorbents according to the method described by (Aisien et.al, 2014) with some modification. Thus, it was first washed with detergent solution and then with dilute HCl in order to remove soil debris. Then the clean and dry parts were taken in a porcelain crucible and carbonized completely at  $500^\circ \text{C}$  in a muffle furnace for 1 h. The cooled carbon was characterized by standard methods as described by (Ishak and Baker, 1995).

### **2.4 pH Determination**

The pH of the carbonized samples were determined using ASTM D 1512 method, 1983 by immersing 1.0g samples in 20.0ml of deionised water in a 250ml beaker. The mixture stirred for 15minutes and the pH measured using a pH meter and values were read. Samples were run as triplicates.

### **2.5 Bulk Density Determination**

Bulk Density of the carbon was determined by the tampering procedure described by (Ahmedina et.al, 1997). Accurately weighed samples were poured into a uniform cylinder of cross sectional area and were then tapped several times until there was no change in the volume occupied. This volume was then recorded and the bulk density calculated.

### **2.6 Determination of Surface Area**

Surface area was measured by adopting the method described by (Ahmedina et.al, 2000). The iodine adsorption method was used in the determination of surface area of the samples. 0.1 molar Sodium Thiosulphate solution was titrated against 20.0ml of 0.488M iodine solution containing 0.5g of samples using 5.0ml of freshly prepared Starch solution as indicator. Similarly, the thiosulphate was titrated with 20ml 0.488M iodine solution without samples (blank) and the quantity needed to titrate the blank was determined and procedure carried out in triplicate and the average of the values obtained in each case were calculated and recorded. The surface areas of the powdered samples were calculated using the inverse of the iodine value (I.V).

The iodine adsorption value in chemistry is the mass of iodine in grams that is consumed by 100 grams of a chemical substance, in this case the sample.



Calculation: The surface area of the RSSC was evaluated using the inverse of the iodine value (I.V.)

$$\text{IV} = \frac{Y-X}{y} \times \frac{V}{M} \times M \quad (126.9) \text{ mg iodine/100g sample} \quad (2.1)$$

Y = Volume of thiosulphate used for blank solution, M = molarity of iodine solution used.

X = Volume of thiosulphate used for the RSSC, W = weight of RSSC used, V = volume of iodine solution used for titration

### **2.7 Determination of the Loss on Ignition**

Loss on ignition (LOI) refers to the mass loss of a combustion residue whenever it is heated in an air or oxygen atmosphere to high temperatures. The loss on ignition of the samples was determined gravimetrically, in accordance to the procedure described in ASTM D7348, 1983 and expressed in terms of percentage. Loss on Ignition is a test used in inorganic analytical chemistry, particularly in the analysis of minerals. It consists of strongly heating ("igniting") a sample of the material at a specified temperature, allowing volatile substances to escape, until its mass ceases to change. This may be done in air, or in some other reactive or inert atmosphere. The simple test typically consists of placing a few grams of the material in a tared, pre-ignited crucible and determining its mass, placing it

in a temperature-controlled furnace for a set time, cooling it in a controlled (e.g. water-free, CO<sub>2</sub>-free) atmosphere, and predetermining the mass. The process may be repeated to show that mass-change is complete.

## 2.8 Determination of the Moisture Content

The moisture content of the sample was determined by method described in ASTM D 1509, 1983 at 125 ° C. This method was used to determine the percentage of water in a ‘percentage, by weight, of the dry sample. The moisture sample was determined by weighing the rubber seed shell and record as “wet weight of sample”; the wet sample was dried to a constant weight, at a temperature not exceeding 115°C using suitable drying equipment (drying oven). The sample was allowed to cool and then weighed again, and recorded as the “dry weight of sample”

### Calculation

The moisture content of the sample is calculated using the following equation:

$$\% W = \frac{A - B}{A} \times 100 \quad (2.2)$$

Where:

% W = Percentage of moisture in the sample,

A = Weight of wet sample (grams), and

B = Weight of dry sample (grams)

## 2.9 Determination of the Metal content of the carbon

The method adopted here for metal content analysis of carbon samples was that used by (Jones, 1990) 1g of the sample was weighed and ashed at 510 ° C, 10% nitric acid was used to digest the sample and made up to 100ml mark in a 100ml volumetric flask. Portions of the sample in the flask were used for the determination of metal contents. For Calcium and Magnesium determination, 10ml of the aliquot was titrated with 0.004molar concentration of Ethylenediaminetetra-acetic acid (EDTA) using Erichrome Black T as the indicator, Potassium Cyanide as the masking agent, Ammonia buffer and Hydroxylamine Hydrochloride. For Calcium determination, 10 ml of the aliquot was titrated with 0.004M EDTA, Cal-red was used as indicator, Potassium Cyanide as masking agent, 8M Potassium Hydroxide as buffer. Necessary calculations were done to determine the values of the calcium and Magnesium contents. The Sodium and the Potassium contents were determined using Flame Photometer.

## 2.10 Adsorption studies

Adsorption isotherms were determined using the batch equilibrium method. The adsorption of Cd(II) and Pb(II) were studied after adding 5g mg of adsorbent into an aqueous solution containing the desired Cd(II) and Pb (II) concentration (50– 500mgL<sup>-1</sup>) respectively, adjusting the pH of the solution to 6, shaking at 150 rpm for 2 h at 25 °C in a reciprocating shaker and then the samples were centrifuged at 5000 rpm for 5 min. The adsorbent particles were separated from the suspensions by filtration through a 75µm membrane filter. The residual concentrations of cadmium and lead ions were determined by atomic absorption spectrometry.

In addition to the adsorption tests, a set of blank tests with adsorbent was conducted in order to evaluate the removal by metal hydroxide precipitation at the pH of determination. The amount of Cd (II) and Pb (II) adsorbed on the adsorbents were calculated from the difference between the initial concentration and the equilibrium concentration of Cd(II) and Pb (II). The percent Cd(II) and Pb (II) removal, *Re*, was calculated using the following equation:

$$Re = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2.3)$$

where *C<sub>i</sub>* and *C<sub>f</sub>* are the initial and equilibrium concentrations of the adsorbate, respectively.

The reported value of Cd(II) and Pb (II) ions adsorbed by adsorbent in each test was the average of at least three measurements.

### 2.11 Batch mode adsorption studies

Batch mode adsorption studies for individual metal compounds were carried out to investigate the effect of adsorbate concentration. Solution containing adsorbate and adsorbent was taken in 250 mL capacity beakers and agitated at 150 rpm in a mechanical shaker at predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using Whatman No.1 filter paper. To avoid the adsorption of adsorbate on the container walls, the containers were pretreated with the respective adsorbate for 24 hours.

### 2.12 Desorption studies

After adsorption, the adsorbates – loaded adsorbent were separated from the solution by centrifugation and the supernatant was drained out. The adsorbent was gently washed with water to remove any unadsorbed adsorbate. Regeneration of adsorbate from the adsorbate – laden adsorbent was carried out using the desorbing media – distilled water at pH ranges 4.0 to 12.0 using dilute solutions of NaOH and HCl. Then they were agitated for the equilibrium time of respective adsorbate. The desorbed adsorbate in the solution was separated and analyzed for the residual heavy metals.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Characteristics of Bamboo culms carbon

**Table 3.1.** The characteristics of the powdered carbon prepared from Bamboo culms

Ash Content (%)	pH	Bulk Density (g/cm <sup>3</sup> )	Surface Area 10 <sup>2</sup> (g/mgI <sub>2</sub> )	Moisture Content (%)	Particle size μm
3.91±0.02	7.8±0.01	0.499±0.01	0.126± 0.15	4.98±0.01	75±0.00

The values of the pH of bamboo culms carbon are within the range of 6-8 which is the normal range for sorption by carbon because of the tendency towards alkalinity of the pH of 7.8. This signifies that the surface charges are negative, which shows an attraction towards heavy metals.

### 3.2 Characterization of Periwinkle shell carbon

**Table 3.2.** The characteristics of the powdered carbon prepared from periwinkle shells.

Ash Content (%)	pH	Bulk Density (g/cm <sup>3</sup> )	Surface Area 10 <sup>2</sup> (g/mgI <sub>2</sub> )	Moisture Content (%)	Particle size μm
4.58±0.02	6.8±0.01	0.148±0.01	0.086± 0.15	10.01±0.01	75±0.00

The value of the pH 6.8 obtained from periwinkle shells carbon is near neutrality which is within the range of sorption of heavy metals by carbon.

**Table 3.4.** Isotherm Constants of four Isotherm Models for the competitive sorption of Cd<sup>2+</sup> and Pb<sup>2+</sup> by Biosorbents. (C<sub>0</sub> = 2.0-50.0mg/l for Pb<sup>2+</sup> and Cd<sup>2+</sup>, Dosage = 0.5g, T = 25<sup>o</sup>C, t = 3hr)

Isotherm Model	Constants	Pb <sup>2+</sup>	Cd <sup>2+</sup>
		PSC, BCC, BPCB	PSC, BCC, BPCB
Langmuir Isotherm	q <sub>max</sub> (mg/g) K <sub>L</sub> x 10 <sup>-3</sup> (L/mg) R <sup>2</sup>	0.95, 0.97, 0.98 267.00,450.70,159.70 0.910, 0.220, 0.660	0.95, 1.00, 1.00 557.10,750.90,255.00 0.820, 0.380, 0.590
Freundlich Isotherm	K <sub>f</sub> n R <sup>2</sup>	1.44, 1.01, 1.14 1.01, 1.02, 1.08 0.998, 0.997, 0.999	1.31, 1.02, 1.08 1.01, 1.01, 1.05 0.990, 0.999 ,0.999
Temkin Isotherm	B <sub>1</sub> b K <sub>t</sub> R <sup>2</sup>	20.94, 20.67,19.62 118.4,120.0, 126.30 7.96, 6.96, 6.78 0.990, 0.980, 0.970	22.23,22.27,17.64 111.50,111.30,140.50 7.90, 7.16, 6.56 0.970,0.970,0.960
Dubinin Radushkevich	K <sub>ad</sub> x 10 <sup>-5</sup> q <sub>s</sub> R <sup>2</sup>	284, 280, 255 31.7, 35.3, 24.7 0.980, 0.980, 0.820	285, 261, 247 33.80,26.30,22.80 0.980, 0.820, 0.820

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Four models (Langmuir, Freundlich, Temkin and Dubinin-Radushkevich) were used. Freundlich isotherm equal fits the data based on the correlation coefficients for all the sorption process.

From the variable  $q_{\text{Max}}$ , the blended bamboo and periwinkle shells is higher compared to other sorbents for  $\text{Pb}^{2+}$  while also the blended bamboo and periwinkle shells and bamboo culms carbon are higher for  $\text{Cd}^{2+}$  sorption. Based on  $q_{\text{Max}}$  the  $\text{Cd}^{2+}$  is preferable to  $\text{Pb}^{2+}$  in sorption because of atomic radius or size of the  $\text{Cd}^{2+}$  compared to  $\text{Pb}^{2+}$ .

**Table 3.6.** Kinetic Parameters of the Kinetic Models for the Competitive Sorption of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ( $T = 298\text{K}$ , Initial  $\text{pH}=7$ , Dosage =  $0.5\text{g}/100\text{ml}$ ,  $C_e = 20\text{mg}/\text{l}$ )

Kinetics Model	Constants	$\text{Pb}^{2+}$ PSC, BCC, BPCB	$\text{Cd}^{2+}$ PSC, BCC, BPCB
Pseudo first order	$q_e$ calc.(mg/g) $K_1$ $R^2$	2.64,1.37, 1.22, 0.02, 0.10, 0.12 0.999, 0.540, 0.760	3.29, 1.92, 1.76  0.23, 0.15, 0.20 0.99, 0.79, 0.800
Pseudo Second order	$q_e$ calc $K_2$ $R^2$	9.02, 8.50, 9.24  0.43, 3.00, 0.91 0.999, 0.999, 0.999	9.76, 9.51, 9.77  0.30, 0.67, 1.66 0.999, 0.999, .999
Elovich Equation	$\alpha$ (mmol/g) x $10^5$  $\beta$ (g/mmol)  $R^2$	0.91, 0.52, 0.47  2635.8, 1642264.8, 39751696.9  0.810, 0.810,0.730	0.94, 0.75, 0.63  2420.4,46678.2, 531156.2  0.900,0.770, 0.910
Intraparticle Diffusion model	$K_{id}$ (mg/gin <sup>1/2</sup> ) Intercept $R^2$	0.93, 0.54, 0.58 6.02, 7.00, 7.49 0.830, 0.630, 0.750	1.07, 0.77, 0.67 6.23 ,7.16, 7.67 0.860, 0.740, 0.750

Four models were used to determine the mass of the metals per unit time. The study shows that pseudo second order fits the data most based on the correlation coefficients which shows that the rate of sorption of the metals is second order reaction.

#### 4. CONCLUSION

It has been shown that blended bamboo culms carbon and periwinkle shell carbon were successfully prepared with significant characteristics which make them suitable for use in sorption of lead and cadmium ions in aqueous media. The carbon produced for metal ions removal was technically feasible, eco-friendly and with high efficiency.

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## Competitive Sorption of Lead and Cadmium (II) Ions from Aqueous Media Using Carbon from Bamboo Culms and Periwinkle Shells

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