

Singapore Journal of
Scientific Research

ISSN: 2010-006x

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Research Article

Bio-adsorption of Heavy Metal Ions from Aqueous Solution Using Uziza (*Piper guineense*) Stem: Characterization, Equilibrium and Thermodynamic Studies

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Abstract

Background and Objective: Heavy metals are one of the contaminants that pose a major health risk to animals and humans on account of their high toxicity at both low and high concentration in water. The effectiveness of Ground *Piper guineense* Stem (GPGS) in the uptake of Cd^{2+} , Pb^{2+} and Cu^{2+} from aqueous solution was studied as a function of pH, adsorbent dose, initial metal ion solution concentration and temperature in a batch adsorption system. **Materials and Methods:** The GPGS adsorbent was characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) spectrophotometer and surface area was measured using methylene blue adsorption technique. Using non-linear regression curves, equilibrium data were fitted to Langmuir and Freundlich models and the thermodynamic parameters; entropy (ΔS°), enthalpy (ΔH°) and the Gibbs free energy (ΔG°), were also considered. **Results:** By both correlation coefficients and statistical error criteria, Freundlich Isotherm was found to best describe the uptake of the metal ions. Thermodynamically, the adsorption of heavy metal ions by GPGS was spontaneous and exothermic in nature. **Conclusion:** The GPGS adsorbent is a strong biosorbent for heavy metals uptake from aqueous solutions. The high biosorption ability, pH sensitivity and thermodynamic stability revealed that GPGS can be used as alternative sorbents for the removal of recalcitrant heavy metal ions in industrial wastewater.

Key words: Adsorption, *Piper guineense* stem, bio-sorbent, heavy metal ions, isotherm, thermodynamics, free energy, enthalpy, entropy

Citation: Chigbundu C. Emmanuel, Babayemi J. Olajire and Egbanu C. Paula, 2020. Bio-adsorption of heavy metal ions from aqueous solution using uziza (*Piper guineense*) stem: Characterization, equilibrium and thermodynamic studies. Singapore J. Sci. Res., 10: 282-292.

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Bio-adsorption is the ability of agricultural or biological or industrial organic waste materials to accumulate pollutants such as; heavy metals from wastewater through physicochemical pathways of uptake. The deterioration of water both in quality and quantity has resulted in increasing water stress and hence water scarcity due to human quest for urbanization and modern industrial development with technological advances had led to an increase in heavy metal burden in water¹.

These heavy metal pollutants are more pronounced in the effluents of some industries such as; metallurgical operating industries², surface coating and metal plating facilities³, electrolysis and battery manufacturing^{3,4}, metal-complexed dye production^{5,6} and paints industries^{7,8}. Heavy metals in the industrial wastewater are not visible to the naked eye, non-biodegradable and persistent in the environment; hence, their exposure and accumulation increase at an alarming rate as water demand and consumption increase⁹.

Changes in enzymatic activities, physiology, blood chemistry, tissue morphology and reproduction are the effects of aqueous heavy metal toxicity in aquatic organisms¹⁰. While in man, its bio-accumulation weakens the immune systems, leads to cancer, alteration of genetic material and dysfunction of vital organs⁹.

The most common aqueous heavy metal pollutants, especially in the aquatic organisms and its environment are copper, iron, zinc, lead, cadmium, arsenic (metalloid), manganese, cobalt, chromium, mercury and nickel¹¹. Several conventional techniques have been employed for removal and recovery of heavy metal ions from the aqueous environment. These include chemical precipitation, adsorption resins, ion exchange and electrochemical separation¹²⁻¹⁴. Other conventional techniques that have been used are membrane filtration processes such as; micro filtration, ultra filtration, nanofiltration, reverse osmosis and electrodialysis¹⁵⁻¹⁹. These conventional technologies involve high capital and operational costs; they are inefficient at low metal concentration and they are also associated with the production of secondary residues that present treatment problems. Bioremediation alternatives, however, have also been employed in the treatment of industrial wastewaters and groundwater contaminated with heavy metals; namely, the use of organisms such as microalga and bacteria. These organisms and others already used gave very good results but they have the disadvantage of the high cost when pure sorbents are employed²⁰. The focus has therefore, been shifted to the use of biological materials for biosorption in the same way as adsorption technology.

These agricultural or biological or industrial organic waste materials that are produced in large quantities as solid waste are easily accessible, abundantly available, inexpensive, eco-friendly and equally effective alternatives for water and wastewater treatment. Agricultural and industrial organic wastes such as; Groundnut shell²¹, orange and apple juice residues, seaweed, persimmon and grape wastes from fruit juice industry²², tea waste^{23,24}, coffee waste²⁴, watermelon seed hulls²⁵, kapok fibre²⁶, lam tree (*Cordia africana*) sawdust²⁷, *Ricinus communis*²⁸ and coir fibre^{23,29}. *Moringa oleiferabark*^{30,31} have been tested for metal ion biosorption. The mechanisms of the biosorption process followed the pathway of chemisorption, complexation, adsorption on the surface, diffusion through pores and ion exchange. The negatively charged sites like hydroxyl groups, phosphate, amino, carboxyl, phosphoryl, sulfate and acetamido on the biosorbent may give rise to the electrostatic attraction of metal cations³².

"Uziza" (*Piper guineense*) is an African plant. Its leaf and seed are used in popular local Nigerian dishes (especially in the eastern part of the country). Because there is no known use of the stem, it becomes agricultural waste. Instead of it turning to be an environmental nuisance, this study therefore, aimed at the utilization of ground *Piper guineense* stem (GPGS) as a low-cost biosorbent for the uptake of toxic heavy metal ions (Cd^{2+} , Pb^{2+} and Cu^{2+}) from aqueous solution, investigating the sorption capacity of the biosorbent and the effect of temperature on its adsorptivity.

MATERIALS AND METHODS

The study was carried out at Bells University of Technology, Chemical and Food Sciences Department, Industrial Chemistry Laboratory, from November, 2017-August, 2018.

Reagents and equipment: All chemicals used in this study were of analytical grade and used without further purification. Biosorption stock solutions used for this study were prepared from $CdCl_2$, $PbCl_2$ and $CuCl_2$, respectively. By appropriate dilutions of the stock, the working solutions of the metal ions were prepared and their initial pH was adjusted and read with a pH meter. Each 100 mL plastic bottle used for the biosorption was suspended in a thermostated water bath shaker (Uniscope SM101). The concentration before and after the biosorption of each metal ion was determined using Atomic Absorption Spectrophotometer (AAS). Fourier Transform Infrared (FTIR) spectroscopy was recorded at $500-4000\text{ cm}^{-1}$; Scanning Electron Microscope (SEM) was used

to determine the surface morphology of the adsorbent; X-Ray Diffraction (XRD) used to determine the crystallinity; Moisture analyzer (AND MF-50) used to determine moisture content and Muffle furnace (Uniscop SM9080) used to determine the ash content of the adsorbent.

Preparation of biosorbent: *Piper guineense* stem waste was obtained from local eateries at Sango Ota market, Ogun state. The stem was washed properly to remove all unwanted particles and dirt. It was cut into smaller pieces and sun-dried for 3-4 days. The dried *Piper guineense* stem was then pulverized with an electric blender, sieved and washed with 0.01 M NaOH to neutralize any acidity and remove completely the greenish dirty color. The sample was washed free of NaOH and confirmed using blue litmus paper. It was then dried in the oven at a temperature of 60°C for 6 h and stored in a dry container labeled Ground *Piper Guineense* stem (GPGS) sample.

Physicochemical characterization of GPGS

Determination of bulk density: About 2.0 g of GPGS was weighed into a 10 mL measuring cylinder and gently tapped on a hard surface for 10 min after which the volume mark of the compressed sample in the measuring cylinder was read³³. This was done in triplicate and the average value taken:

$$\text{Bulk density (g cm}^{-3}\text{)} = \frac{\text{Mass (g)}}{\text{Volume (cm}^3\text{)}} \quad (1)$$

Moisture content determination: About 5 g of GPGS sample was weighed into the moisture analyzer at a temperature of 105°C and the moisture content was read from the machine. This was done in duplicate.

Loss On Ignition (LOI) determination: Two gram each of GPGS samples were weighed in two oven-dried crucible dishes and transferred into a muffle furnace at 300°C for 5 h and percentage LOI was determined using the expression³⁴.

$$\text{LOI (\%)} = \left(\frac{W_A}{W_S} \right) \times 100 \quad (2)$$

where, W_A (g) and W_S (g) are the weights of the sample after and before ashing, respectively.

Point of zero charge determination: A solution of 0.01 M of NaCl was prepared, the pH was adjusted to 3, 4, 5, 6, 7, 8, 9 and 10 using a few drops of 0.1 M HCl and NaOH. Then 0.25 g

of GPGS sample was weighed into 8 different containers and 30 mL of the adjusted pH of 0.01 M of NaCl was measured into the sample containers, stirred for 1 h and left to stand for 24 h. The final change in pH was determined using the pH meter.

Cationic Exchange Capacity (CEC) determination: About 0.5 g of Methylene Blue (MB) dye was dispersed into 250 mL of distilled water in a standard flask. About 1 g of GPGS was weighed into a beaker and 8 mL of distilled water was added and stirred. Few drops of methylene dye solution were added to the GPGS sample in the beaker and stirred. With a glass rod, a drop of the mixture was intermittently placed on a filter paper to note the disappearance of a light blue halo. This process was repeated until the light blue halo persisted which indicated the endpoint. The CEC of the sample was then calculated using the expression³⁵:

$$\text{C.E.C. (meq 100 g}^{-1}\text{)} = \frac{100}{f'} \times V(\text{cm}^3) \times \text{Normality} \quad (3)$$

where, V (cm^3) is the volume of the methylene blue solution injected to get to the light blue halo endpoint in cm^3 , f' (g) is the dry weight of GPGS sample used.

The normality of the Methylene Blue dye (MB) was calculated using the following equation³⁶:

$$N_{\text{MB}} = \frac{\text{wt. of MB (g)}}{320} \times \frac{100 - X}{100} \quad (4)$$

where, X is the moisture content of methylene blue dye³⁶, which is 16.

Biosorption experiments: The effect of different operating conditions (pH, contact time, adsorbent dose, concentration and temperature) on adsorbate-adsorbent interaction was studied as shown in Table 1. The equilibrium of biosorption experiment of Cd^{2+} , Pb^{2+} and Cu^{2+} ions was carried out by contacting between 0.05-0.5 g of GPGS with 30 mL of different concentrations of the adsorbates from 5-100 ppm in 100 mL plastic bottles. After shaking the adsorbate-adsorbent mixtures properly, the suspensions were filtered and 0.25 mL of the filtrate was collected and transferred, using a micro pipette, into 5 mL distilled deionized water. The residual metal ion concentration in the filtrate was determined using Atomic Absorption Spectrophotometer (AAS). The amount (mg g^{-1}) and percentage (%) adsorbed was calculated using the expression³⁷⁻³⁹:

$$Q_{(\text{mg g}^{-1})} = \frac{(C_0 - C_e) \times v}{w} \quad (5)$$

$$\text{Sorption (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (6)$$

where, Q (mg g^{-1}) is the amount of metal ion adsorbed from solution, V (mL) is the volume of aqueous solution, C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and equilibrium concentration of metal ions before and after biosorption, respectively and w (g) is the weight of the biosorbent. The experimental data were fitted with Langmuir and Freundlich equilibrium isotherm models.

Studies of the effects of some operating variables on adsorption process

Effect of contact time: The adsorbent-adsorbate contact time for the adsorption of heavy metal ions unto GPGS biosorbent was performed at different contact times (1, 3, 5, 10, 15, 30, 45, 60, 90, 120 and 180 min). About 0.5 ± 0.02 g of the biosorbents was dispersed into 300 mL of the individual metal ions solution at $\text{pH} = 5 \pm 0.04$ and the suspension was agitated at 31°C . The above procedure was then performed at each different metal ion concentration; 30, 50 and 100 mg L^{-1} , respectively³⁷⁻³⁹.

Effect of pH: The effect of pH on the (percentage) adsorptivity of GPGS was performed using 200 mL suspension of 0.25 g GPGS, 50 mg L^{-1} of individual metal ion concentration and agitated for 2 h. This procedure was then carried out at each varied pH of 3, 4, 5, 6 and 7, respectively³⁷⁻³⁹.

Effect of biosorbent dosage variation: About 200 mL of 50 mg L^{-1} of individual metal ion concentration at $\text{pH} = 5 \pm 0.04$ was agitated with each different adsorbent dose of 0.05, 0.1, 0.15, 0.25 and 0.4 g respectively, in plastic bottles³⁷⁻³⁹.

Effect of metal ion concentration variation: 200 mL of 0.5 g GPGS at $\text{pH} = 5 \pm 0.04$ was agitated with each different individual metal ion concentration (5, 10, 20, 35, 55, 75 and 100 mg L^{-1}) in plastic bottles³⁷⁻⁴⁰.

Effect of temperature: The effect of temperatures were performed by adding 0.5 g of GPGS to 200 mL volume of the individual metal ions in solution at different concentrations (5, 10, 20, 35, 55, 75 and 100 mg L^{-1}) in a thermostated water bath with shaker and agitated at contact time of 120 min and

at $\text{pH} = 5 \pm 0.04$. Therefore, to evaluate the effect of temperature, the above procedure was performed at each different temperature 25, 30, 35 and 40°C , respectively. As a result, the thermodynamic parameters, such as change in standard free energy (ΔG^0), standard enthalpy (ΔH^0) and entropy (ΔS^0) for the adsorption process were calculated using the following equations^{38,40}:

$$\Delta G_0 = -Rt \ln K_c \quad (7)$$

$$\ln K_c = -\frac{\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

where, R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T (K) is the temperature in Kelvin and K_L (L g^{-1}) is the distribution coefficient of the metal ions between the solid and liquid phases. ΔH^0 and ΔS^0 were calculated from the slope and intercept of Vant Hoff plots of $\ln K_c$ versus $1/T$.

Error statistical analysis: The goodness of fit for these isotherm models was established by the following coefficient of determination (R^2) and the Chi-square (χ^2) test statistical functions.

Statistical analysis

Chi-square (χ^2): The statistical analysis of the data were carried out to further affirm the best fitted model to experimental data determined through the least values of chi-square test calculated. The advantage of using a chi-square test is to compare all isotherms on the same abscissa and ordinate. The equivalent mathematical statement was: if data from the model were similar to the experimental data, χ^2 would be a small number and would be acceptably best fitted isotherm model otherwise the model does not fit to the experimental data and will be reflected by the large values of χ^2 for such model⁴¹. This function expression is given as:

$$\chi^2 = \sum_{i=1}^N \frac{(q_{m,i} - q_{p,i})^2}{q_{p,i}} \quad (9)$$

where, N is the number of data points, q_m is the measured value and q_e or q_p expected or predicted values, respectively.

RESULTS

Physicochemical characteristics of GPGS: The studied physicochemical parameters are presented in Table 1 as determined by standard procedures.

Scanning electron microscope analysis of GPGS: Scanning Electron Microscope (SEM) image of GPGS is shown in Fig. 1. The SEM micrograph revealed a rough surface with small round uneven edges surrounded by dark area representing cavities or mass tiny pores.

Fourier transform infrared (FT-IR) spectroscopy analysis of GPGS: The stacked FTIR graph (Pristine and metal ions loaded) of GPGS is shown in Fig. 2. The peak at 3405 cm^{-1} is ascribed

Table 1: Physicochemical parameters of GPGS

Parameters	Values
Bulk density (g cm^{-3})	0.23
Loss on ignition (%)	96.03
MBA (specific surface area) ($\text{m}^2 \text{g}^{-1}$)	12.50
Moisture content (%)	11.10
Point of Zero Charge (pzc)	5.93
CEC (meq/100 g)	0.604

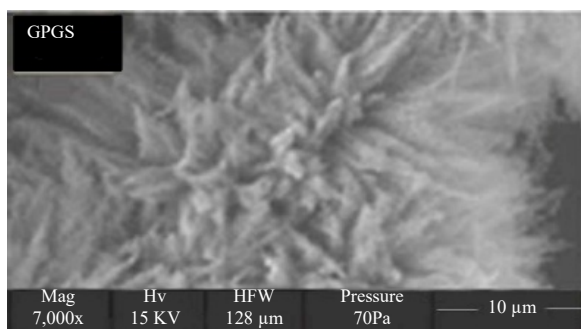


Fig. 1: Scanning electron microscope (SEM) image of GPGS

to O-H bond (stress) for molecular association. The band at $2925\text{--}2850\text{ cm}^{-1}$ is assigned to $-\text{CH}_2-$ which indicates the presence of a methyl group and a weak band at $2854\text{--}2800\text{ cm}^{-1}$ is assigned to $-\text{CH}-$ of the methylene group. The sharp peak observed at 1708 cm^{-1} is attributed to the bending vibration of the $\text{C}=\text{O}$ bond of a carboxylic acid that may be present in GPGS. In addition, the band of $1458\text{--}1420\text{ cm}^{-1}$ confirms the presence of $\text{C}=\text{C}$ of the aromatic ring of the phenolic compound. The band at $1258\text{--}1250\text{ cm}^{-1}$ indicates the C-O bonding of phenols. When GPGS was loaded with the metal ions (Cu^{2+} , Pb^{2+} and Cd^{2+}), the intensities of the percentage transmittance on the FTIR graph reduced (Fig. 2).

X-ray diffraction analysis of GPGS: The XRD graph of GPGS is given in Fig. 3. The XRD pattern shows many sharp peaks which were dispersed between $2\theta = 35\text{--}70^\circ$ aside the noise. The inverted concave broader peak are observed at $2\theta = 22^\circ$ of the XRD pattern of GPGS biosorbent sample.

Biosorption experimental studies

Effect of pH variation: The plot of pH against the metal ions removal (%) shown in Fig. 4 revealed a non-sensitivity to change in the pH of the solution for the uptake of Pb (II) ion, a sudden increase in percentage removal of Cd (II) ion and a gradual increase in the percentage removal of Cu (II) ion, respectively onto GPGS as the pH of the solution was increased (Fig. 4).

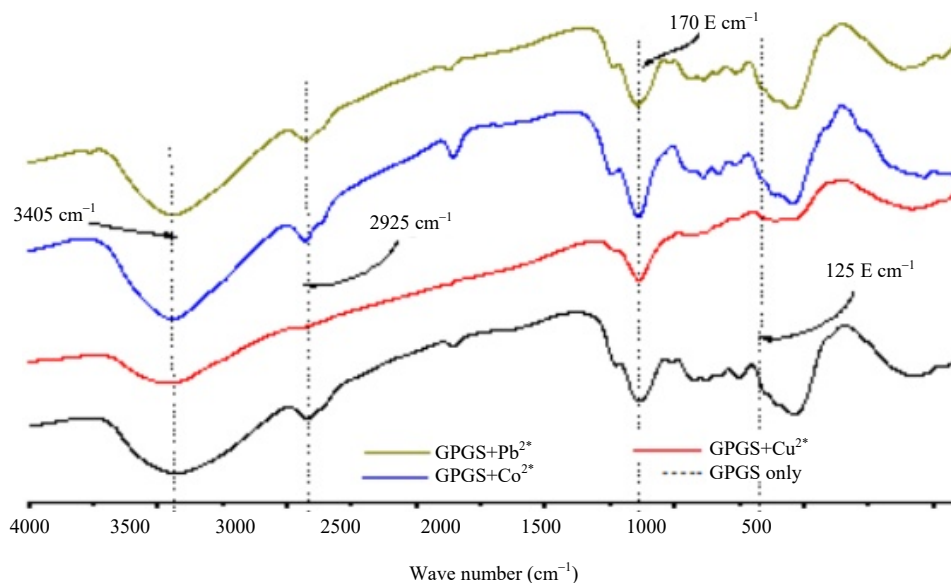


Fig. 2: Fourier transform infrared spectroscopy (FTIR) spectra of GPGS

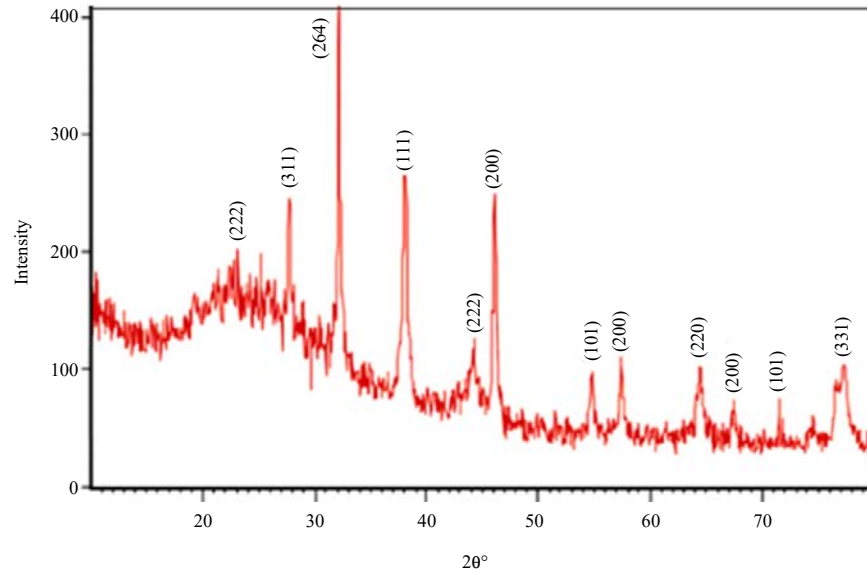


Fig. 3: X-ray diffractogram of GPGS

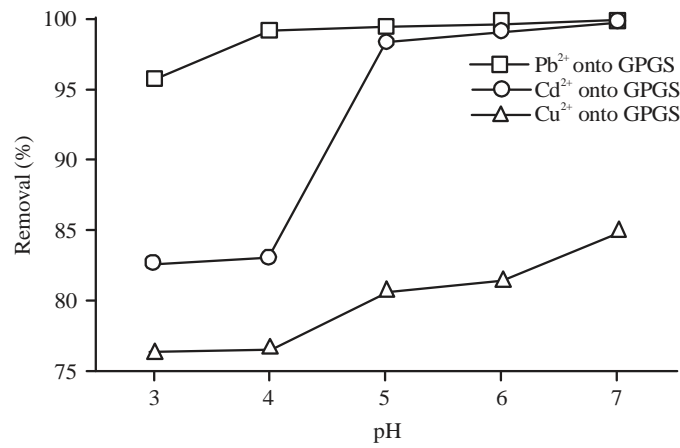


Fig. 4: Effect of pH on GPGS-metal ions system

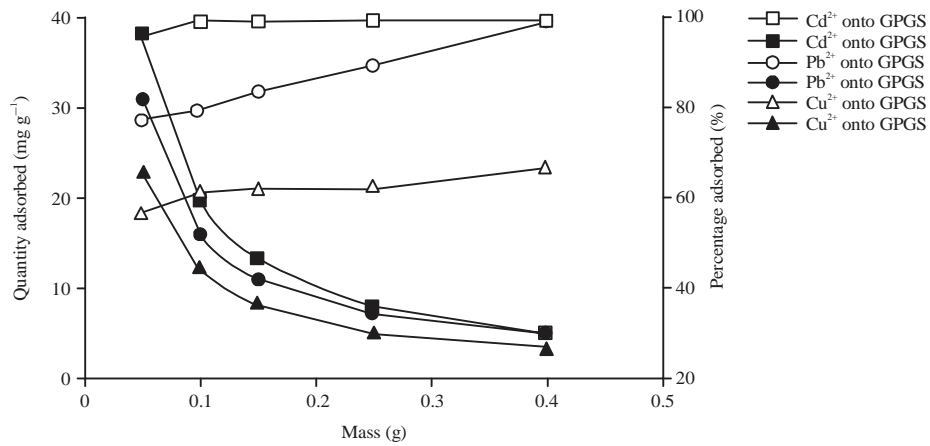


Fig. 5: Effect of biosorbent dosage on GPGS-metal ions system

Table 2: Adsorption isotherms parameters of GPGS-metal ions system

Metal ions	Langmuir isotherm				Freundlich isotherm			
	Q_m (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2	χ^2	K_F	1/n (mg g ⁻¹)	$R2$ (L g ⁻¹) ^{1/n}	χ^2 (L mg ⁻¹)
Cu ²⁺	11.99	0.01	0.9982	0.225	0.14	0.77	0.9986	0.002
Cd ²⁺	13.01	0.36	0.6841	2.368	3.54	0.44	0.7284	0.577
Pb ²⁺	11.12	0.19	0.9802	21.169	2.19	0.45	0.9919	-0.881

Q_m : Langmuir constants related to the maximum adsorption capacity (mg g⁻¹) adsorption (L mg⁻¹), K_L : Langmuir constants related to the maximum adsorption capacity (mg g⁻¹) and energy of adsorption (L mg⁻¹), K_F : Freundlich constant related to sorption capacity in (mg g⁻¹) (L g⁻¹)^{1/n}, n: Heterogeneity factor which is related to the capacity and intensity of the adsorption, R^2 : Coefficient of determination and χ^2 : Chi-square

Table 3: Thermodynamic parameters for adsorption of metal ions on GPGS

Metal	$\Delta G \times 10^2$ (J mol ⁻¹)				ΔH (KJ mol ⁻¹)	ΔS (KJ K ⁻¹ mol ⁻¹)
	298K	303K	308K	313K		
Cu (II)	-17.82	-21.19	-27.45	-33.31	-35.63 × 10 ²	12.645
Cd (II)	-24.01	-34.92	-56.26	-57.17	-84.08 × 10 ²	29.219
Pb (II)	-23.30	-21.88	-26.22	-26.61	-74.4 × 10 ¹	3.3991

Table 4: Previous metal ions biosorption compared with this study

Biosorbent	Metal ion adsorbate	Adsorption capacity (mg g ⁻¹)	References
<i>Fucus spiralis</i> (Brown Algae)	Pb (II)	0.98	Romera <i>et al.</i> ⁴²
<i>Caulerpa lentillifera</i> (Brown Algae)	Pb (II)	0.13	Kleinubing <i>et al.</i> ⁴³
<i>Fucus spiralis</i> (Brown Algae)	Cu (II)	1.10	Romera <i>et al.</i> ⁴²
<i>Spirogyra</i> sp.	Cu (II)	0.53	Rajfur <i>et al.</i> ⁴⁴
<i>Fucus spiralis</i> (Brown Algae)	Cd (II)	1.02	Romera <i>et al.</i> ⁴²
<i>Asparagopsis armata</i>	Cd (II)	0.28	Romera <i>et al.</i> ⁴²
<i>Hypnea valentiae</i> (Green algae)	Cd (II)	0.15	Rathinam <i>et al.</i> ⁴⁵
Maize stalks	Zn (II)	30.30	El-Sayed <i>et al.</i> ⁴⁶
Maize stalks	Cd (II)	18.05	El-Sayed <i>et al.</i> ⁴⁶
Maize stalks	Mn (II)	16.61	El-Sayed <i>et al.</i> ⁴⁶
Leaves of Araucaria cookii	Pb (II)	37.03	Deepa and Suresha ⁴⁷
Aloe barbadensis miller leaf powder ⁴⁸	Pb (II)	28.97	Gupta <i>et al.</i> ⁴⁸
<i>Piper guineense</i> stem (GPGS)	Pb (II)	11.12	
<i>Piper guineense</i> stem (GPGS)	Cu (II)	11.99	
<i>Piper guineense</i> stem (GPGS)	Cd (II)	13.01	

Effect of Biosorbent dose variation: Figure 5 shows a comparison of the effectiveness of removal of Cu²⁺, Pb²⁺ and Cd²⁺ ions from solutions as a function of adsorbent dosage variation. The percentage removal is in the order of Cd²⁺ > Pb²⁺ > Cu²⁺.

Adsorption isotherm: The experimental data obtained for the adsorption of Cd²⁺, Pb²⁺ and Cu²⁺ metal ions onto GPGS biosorbent were fitted to Langmuir and Freundlich isotherm models equations using non-linear regression curves is shown in Fig. 6 and 7 while the calculated values of these isotherm models parameters are given in Table 2. The highest values of the coefficient of determination (R^2) and the least value of chi-square (χ^2) test revealed the best fitted adsorption isotherm model (Table 2). By these criteria (R^2 and χ^2), it is obvious that Freundlich was a better fit than the Langmuir isotherm model equation (Table 2). Moreover, the value of n at equilibrium is above unity (Table 2).

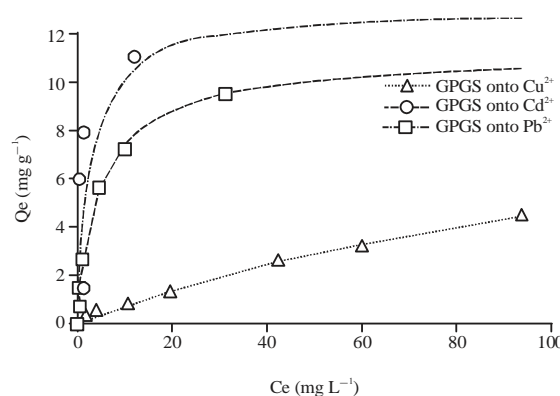


Fig. 6: Langmuir isotherms of GPGS-metal ion adsorption system

Thermodynamic parameter: The plot of ln Kc against 1/T for the determination of some thermodynamic parameters is shown in Fig. 8. The changes in standard Gibbs free energy (ΔH^0), standard enthalpy (ΔS^0) and standard

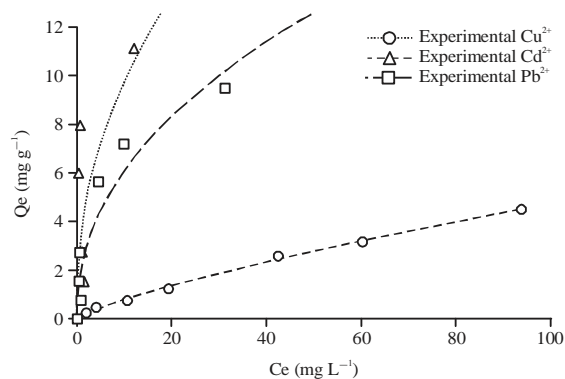


Fig. 7: Freundlich isotherm of GPGS-metal ion adsorption system

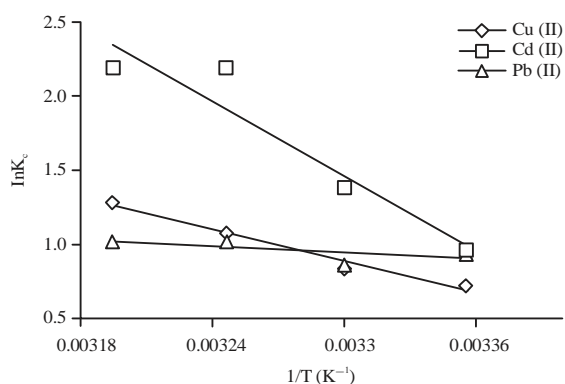


Fig. 8: Thermodynamics of adsorption metal ions onto GPGS

entropy (ΔG^0) for adsorption of Cd^{2+} , Pb^{2+} and Cu^{2+} onto GPGS are given Table 3.

Comparison of biosorption of different metal ions: The values of G^0 are negative at all the temperatures studied and decreases as the temperature increases for all the metal ion and also the value for the enthalpy change, ΔH^0 is negative for all the metal ion (Table 3). Furthermore, positive value was observed for the change in entropy, ΔS^0 of biosorption process (Table 3).

GPGS adsorbed the metal ions effectively in the following order $\text{Cd(II)} > \text{Cu(II)} > \text{Pb(II)}$ which has made GPGS comparable to other researched biosorbents as shown in Table 4. GPGS adsorptivity could greatly be further enhanced through surface modification.

DISCUSSION

The environmental and health challenges posed by toxic heavy metal pollution are increasing⁴⁹ and according to Groenberg and Lofts⁵⁰ and Kim *et al.*⁵¹, the rise in industrialization and advancement in technology of

developing countries has brought with it toxic heavy metal ion contaminants and other forms of water pollution. It is therefore, expedient to carry out more research by the use of low cost and available biosorbents to ameliorate heavy metal ion burden that are prevalent in these countries^{50,51}. The utilization of ground *Piper guineense* stem (GPGS) as a low-cost biosorbent for the uptake of toxic heavy metal ions namely; Cd^{2+} , Pb^{2+} and Cu^{2+} from aqueous solution was carried out and discussed.

The physicochemical properties of GPGS (Table 1) starting from its bulk density (at 0.23 g cm^{-3} dry weight per volume) revealed that the biosorbent had a good particle strength and stability in solution⁵². GPGS's value of pzc is an indication that its surface electrical density tends to zero at a pH of 5.93 and according to Bhatnagar *et al.*⁵³, the surface of this kind of biosorbents in a suspension at pH above this pzc value will present its surface with more negative charges to attract and bind strongly with cations (metal ion)⁵³. Additionally, as shown in Table 1, GPGS has a surface area of $12.5 \text{ m}^2 \text{ g}^{-1}$ which means that the biosorbent provide enough surface area per gram to expose its adsorption sites enough to interact with adsorbate and according to Farnane *et al.*⁵⁴, a large surface area make available enough active sites for adsorption.

The surface texture and morphology of GPGS biosorbents analyzed by SEM showed some irregular cavities. Varied changes in the external surface texture coupled with the evidences of the composition of anionic segments of functional group were revealed by FTIR; these characteristics indicate the GPGS surface will perform efficiently to a large extent in adsorption performance of heavy metals uptake⁵⁴.

The study of the effect of pH on GPGS for metal-ions uptake (Fig. 4) indicated that the dependence of the heavy metal biosorption on pH was different for each metal. This phenomenon was also recorded by Farnane *et al.*⁵⁴ during their work. In this study however, the percentage removal for all the metal ions, increased at pH values greater than the pH_{pzc} ($\text{pH} > \text{pH}_{\text{pzc}}$).

Biosorption isotherms of GPGS-metal ion adsorption system fitted to Freundlich isotherm, which is an indication that the adsorption of metal ion onto the biosorbent surface is heterogeneous with infinite numbers of none identical energy sites, distributed over the biosorbent surface resulting into physical sorption as a result of Van der Waals forces attraction between the adsorbates and GPGS. The values of the Freundlich constant n (Table 2) were higher than 1, which is an indication that relatively a strong bonding of the metal ions on the biosorbents exists⁵⁵. The Langmuir parameter (q_{max}) which is related to adsorption capacity, gives the information on the capacity of GPGS to adsorb the metal ions from aqueous solution as shown in Table 2.

CONCLUSION

The adsorption behavior of Cu (II), Cd (II) and Pb(II) ions onto ground *Piper guineense* stem (GPGS) through batch adsorption was successfully investigated. The mechanism of adsorption was by physical adsorption process. The high biosorption ability, pH sensitivity and thermodynamic stability revealed that GPGS can be used as alternative sorbents for the removal of recalcitrant heavy metal ions in industrial wastewater.

SIGNIFICANCE STATEMENT

This study discovered the use of the abundantly available piper guineense stem waste as a biosorbent that can be beneficial for toxic heavy metal ion bio-adsorption. The resultant effect of the use of this biosorbent will be to rid the water bodies, aquatic lives and human being of deleterious heavy metal ion water contaminants. This study will help the researchers to uncover the critical areas of biosorption utilizing piper guineense waste. Thus, a new theory may be derived on proportionating the adsorbent dosage to the metal ion uptake.

ACKNOWLEDGMENT

The authors gratefully acknowledge Bells University of Technology, Ota. Ogun state, Nigeria for granting us the privileged to use the laboratories and the instruments for this research work.

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