Online Journal of Chemistry, 2022, 2, 23-38
www.scipublications.org/journal/index.php/ojc
DOI: 10.31586/ojc.2022.263

Article

Kinetic, Equilibrium and Thermodynamic Study of the Adsorption of Pb (II) and Cd (II) Ions from Aqueous Solution by the Leaves Biomass of Guava and Cashew Plants

Nasiru Yahaya Pindiga [1,*], Abubakar Haruna Walid [1], Abdullateef Olalekan Abdullahi [1], Adamu Baba Mohammad [1]

[1] Department of Chemistry, Faculty of Science, Gombe State University Gombe, Gombe State. PMB 127, Nigeria

*Correspondence: Nasiru Yahaya Pindiga (npy500@yahoo.com)

Abstract: The plant leaves used as adsorbent in this study were Guava plant leaves (GPL) and Cashew plant leaves (CPL). The samples were collected within Gombe State. Batch adsorption method was used in determining the adsorption process. Fourier Transform Spectroscopy (FT-IR), Scan-ning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) were used for the characterization. The results show promising signs as they were in agreement with most literatures; various per-centage removals were obtained from Pb^{2+} and Cd^{2+} (GPL and CPL) at optimum conditions. The equilibrium data fitted well with both Langmuir and Freundlich isotherm models. Langmuir mod-el fitted well for Pb^{2+} (CPL) with R^2 value (0.9855) and Cd^{2+} for (GPL and CPL) with R^2 values (0.9945 and 0.9948) while Pb^{2+} (GPL) with correlation coefficient at 0.9116 best fits well with Freundlich isotherm model. Pseudo first order and second order were used in testing the kinetics study from which pseudo second order best fitted better than that of the first order kinetics. The thermodynamic study shows that ΔG is negative in most cases except for Cd^{2+} (GPL) where ΔG is positive. Whereas ΔH and ΔS are positive in some cases showing an endothermic and spontane-ous adsorption processes respectively, as well as negative in some. Based on this study, GPL and CPL could be used as a natural adsorbent to remove Pb^{2+} and Cd^{2+} heavy metals from wastewater and environment due to their high removal efficiencies.

Keywords: Adsorption; Kinetic, Equilibrium and Thermodynamic Study; Leaves Biomass of Guava and Cashew plants

How to cite this paper : Pindiga , N. Y., Walid, A. H., Abdullahi, A. O., & Mohammad, A. B. (2022). Kinetic, Equilibrium and Thermodynamic Study of the Adsorption of Pb (II) and Cd (II) Ions from Aqueous Solution by the Leaves Biomass of Guava and Cashew Plants. *Online Journal of Chemistry*, 2(1), 23–38. Retrieved from https://www.scipublications.com/journal/index.php/ojc/article/view/263

Received: March 31, 2022
Accepted: May 13, 2022
Published: May 15, 2022

1. Introduction

Heavy metals are important environmental pollutants and have toxic effects on humans which are unfavorable to ecological, evolutionary, nutritional and environmental balances. These heavy metals are discharged into the environment through industrial, agricultural and domestic processes. Several natural and human day to day activity sources of heavy metals include erosion of soil, natural weathering of the earth's crust, industrial effluents, mining, urban runoff, sewage discharge, insect or disease controlling agents, which are applied to crops [1]. In waste water, commonly found heavy metals include cadmium, arsenic, chromium, lead, copper, zinc and nickel, all of these are causing risks to human health and the environmental balance by entering the surroundings *via* natural means and through human activities [2]. Cadmium (Cd) is a highly toxic and carcinogenic heavy metal discharged into water from mining, smelting, electroplating, and alloy manufacturing, among various industries [3]. Unlike various pollutants, Cd cannot be degraded and constantly accumulate in the environment, causing a serious threat to aquatic ecosystems and human health [4-6]. Acute inhalation of cadmium can result in flu with symptoms like (chills, fever, and muscle pain) and as well damage the lungs. Chronic exposure can result in kidney, bone and lung disease, the maximum contamination level of Cd in drinking water is 0.003 mg/L.

Lead on the other hand is one of the most toxic metals from the dangerous heavy metals list. It is used in many industrial purposes, including storage battery manufacturing, painting pigment, fuels, photographic materials, coatings, automotive industries and hundreds of other products [7]. Acute lead poisoning usually affects the gastrointestinal tract or the nervous system, and sometimes both. The World Health Organization (WHO) has set the maximum contaminant level of lead in drinking water at 0.01mg $^{L-1}$. There are so many methods of removing heavy metals away from the environment such as reverse osmosis, ion exchange, electrochemical degeneration, adsorption etc. most of this methods seems to be expensive, unfriendly to the environment (ecosystem) and may sometimes led to environmental pollution expect for adsorption which is inexpensive, eco-friendly and also effective.

Adsorption is one of the most favorable techniques applied for water treatment, mainly because it is suitable for low concentration of metal ions and cost effective [8-10]. Adsorption is a physico-chemical process where the substance called adsorbate accumulates at the interface of solid called adsorbent [9,11]. Activated carbon is commonly used as an adsorbent for water treatment because it has porous structure and large surface area [11-13]. In spite of its great physical properties, the use of activated carbon is restricted to its high cost [11-13]. Therefore, alternative adsorbents derived from low-cost materials should be introduced to minimize the operating cost particularly in developing countries.

Low-cost adsorbents can be defined as materials that are abundant in nature and waste from industries [9,11,16]. In this study, plants leaves will be used as low cost adsorbents in removing heavy metals from the environment.

2. Experimental

2.1. Materials

The leaves biomass of GPL and CPL were collected within Gombe metropolis, Gombe State. All chemicals used were of analytical grade. Stock solution (1000mg/L) was prepared from which the experiment was conducted by dissolving the salts $Pb(NO_3)_2$ and $CdCl_2$ in distilled water, HCl and NaOH solution were for pH adjustments. From the stock solution prepared, initial concentration of each metal was prepared and concentrations were analyzed using Atomic Adsorption Spectrophotometer (AAS).

2.2. Adsorbent Preparation

The leaf biomass were washed with ordinary water thoroughly and with distilled water in order to remove impurities and debris present, after which the samples were allowed to dry for about 8 days to completely remove moisture content. These dried samples were then grounded to a fine powder and then sieve with a micrometer sieve of 150μm. The sieved powder was stored and used for batch experiments.

2.3. Characterization of the Sample

2.3.1. Fourier Transform Infra-Red Spectroscopy (FT-IR)

FT-IR was used to give a qualitative analysis of the main chemical functional groups present on the biomass and responsible for the adsorption processes which was adopted by Wassila *et al.* [17]. The analyses were carried out using Perkin Elmer Spectrophotometer with model number 10.03.09.

2.3.2. Scanning Electron Microscopy (SEM)

The Scanning electron microscopy (SEM) was implemented to examine the physical structure change using SEM model Phenom ProX, by phenom World Einhoven, Netherland. Samples were placed on double adhesive which was on a sample stub, coated with a sputter coater by quorum technologies model Q150R, with 5nm of gold. Thereafter it was taken to the chamber of the SEM machine where it was viewed via NaVCaM for focusing and little adjustment, it was then transferred to SEM mode where the focused and brightness contrasting was automatically adjusted.

2.3.3. X-Ray Diffraction (XRD)

XRD was used for the characterization crystalline materials and also provides information on structural elucidation, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, strain, and crystal defects. The analyzed materials were finely grounded, homogenized, and average bulk compositions were determined. The powdered samples were then prepared using the sample preparation block and compressed in the flat sample holder to create a flat, smooth surface that waslater mounted on the sample stage in the XRD cabinet. The samples were analyzed using the reflection transmission spinner stage using the Theta-Theta settings. The 2θ starting position is 4 degrees and ends at 75 degrees with a θ step of 0.026261 at 8.67 seconds per step.

2.4. Batch adsorption experiment

Batch adsorption experiments were carried out by varying contact time, initial concentration, pH, temperature and adsorbent dose. Batch adsorption experiment process carried out in contact with the aqueous solution containing Pb^{2+} and Cd^{2+} in a 250ml conical flask. The flask was agitated in an orbital shaker at a constant speed of 150 rpm. The adsorption process was conducted under the following conditions; initial concentration (50-1000mg/L), contact time (15-60mins), adsorbent dose (0.2-1g), pH (2-10) and temperature (25-60 ^{o}c) which were then varied to study their effects on metal ion.

After equilibrium was reached, each sample was filtered using Whatman 41 filter paper and analyzed using Atomic Adsorption Spectrophotometer (AAS). Percentage removal and amount of metal ion adsorbed at equilibrium were calculated using the formulas below;

Percentage Removal: $E\% = (Ci - Ce)/Ci \times 100$

Amount Adsorbed: $qe = (Co - Ce)\ v/w$
Where; Ci = the initial concentration of the metal solution (mg/L),
Ce = the equilibrium concentration of the metal solution (mg/L),
C_0 = the initial concentration of the sorbate.
W = the mass of adsorbent (g)
V = the volume of the solution (L)

2.5. Adsorption Isotherm

Isotherms curves in expressing the difference in amount of gas adsorbed by adsorbent with pressure at constant temperature, most commonly used isotherms are Freundlich and Langmuir Isotherm. The Freundlich isotherm model deals with adsorption at multilayer heterogeneous surfaces [10] while the Langmuir isotherm model assumes all sites on adsorbents have equal energy [12,18]. Linear form of Freundlich isotherm model is expressed as:

$$\log q_e = \log K_F + 1/n \log C_e$$

Where K_F (mg/g) and n are the Freundlich constants related to adsorption capacity and intensity, respectively. A linear plot of q_e against log C_e will give K_F and n values while that of Langmuir Isotherm can be written in the following linear form

$$Ce/qe = 1/\ (q_mK_L) + Ce/q_m$$

Where Ce (mg/l) is the concentration of adsorbent at equilibrium, K_L (mg/l) is the Langmuir constant related to the adsorption energy and qm (mg/g) is the adsorption capacity. The adsorption capacity can be correlated with the variation of the surface area and porosity of the adsorbent. Higher surface area and pore volume resulted in higher adsorption capacity [19]. The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the equilibrium parameter, R_L [20].

2.6. Adsorption Kinetics

Is the measure of adsorption with respect to time at constant pressure and concentration.

Pseudo First order equation of Lagergren [21] is given as follows:

$$\ln (qe - qt) = \ln qe - k_1t$$

Where qt and qe are the amounts adsorbed at time t and equilibrium (mg/g), respectively, and k1 is the pseudo first-order rate constant for the adsorption process (1/min). The linear graph of ln (qe – qt) vs. t shows the applicability of first order kinetic.

For Pseudo Second Order Kinetics the chemisorption kinetic rate equation is expressed as follows:

$$t / qt = (1/ k_2qe_2) + (1/qe)\ t$$

Where k_2 is the equilibrium rate constant of pseudo-second order equation (g/mg min). The linearity of t / qt vs t suggests the best fitted with pseudo-second order kinetic [22].

2.7. Thermodynamic Study

The free energy of adsorption (ΔG°) can be related with Langmuir adsorption constant [23] by the following equation:

$$\Delta G° = -RT \ln K_L$$

Thus, a plot of $\ln K_L$ versus 1/T should be a straight line. ΔH° and ΔS° values were obtained from the slope and intercept of this plot, respectively.

3. Results and Discussion

3.1. Characterization of the Adsorbent

The FT-IR spectra of GPL and CPL adsorbent are shown in Figure 1 and 2 respectively. Figure 1, FT-IR spectra shows abroad bend at 3444.06cm^{-1} corresponding to O-H stretch, due to the adsorbed water and the presence of hydroxyl group (OH) of alcohol, carboxylic acids and phenols, widely found in lignocellulosic materials [24]. 2923 cm^{-1} is attributed to C-H stretch, stretch at 1633.74cm^{-1} corresponding to C=C group. Peak at 1456.98 cm^{-1} is attributed to C-C band. The band at 1032.94 cm^{-1} is assigned to C-O stretch [25].

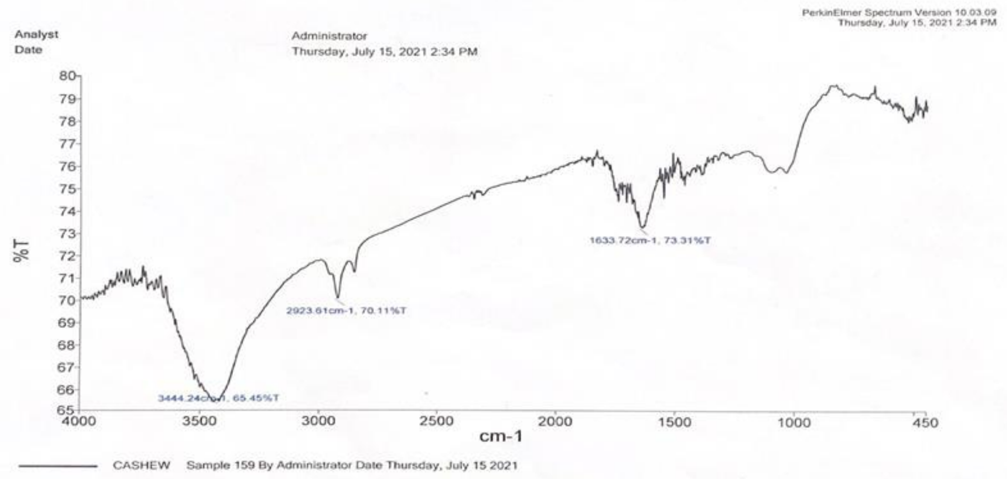

Figure 1. FT-IR spectrum of GPL

FT-IR spectrums of Figure 2 for CPL shows a strong and broad peak which were originated from O-H stretch is at 3444 cm^{-1}. Other bends are 2924 cm^{-1} and 1634 cm^{-1} which were found to be at C-H and C=C stretches respectively. Similar work was carried out by Navid *et al*. [26] where the results were in agreement with the current study.

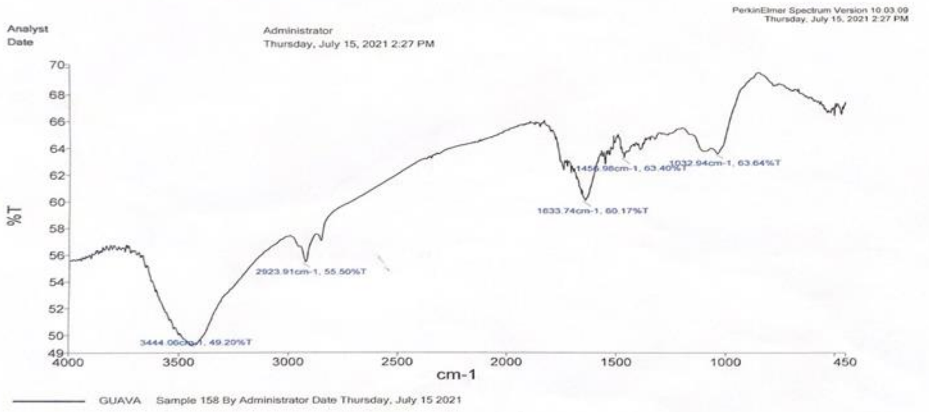

Figure 2. FT-IR spectrum of CPL

3.2. SEM

SEM analysis results in Figure 3 show the surface morphology of GPL with scattered layer, porous surface and some particles have irregular sharp which makes GPL suitable for adsorption process. Similar work has been done by Himanshu and Vashi [27]. While for CPL in Figure 4, the surface morphology appears to have a rough surface with irregular sharps.

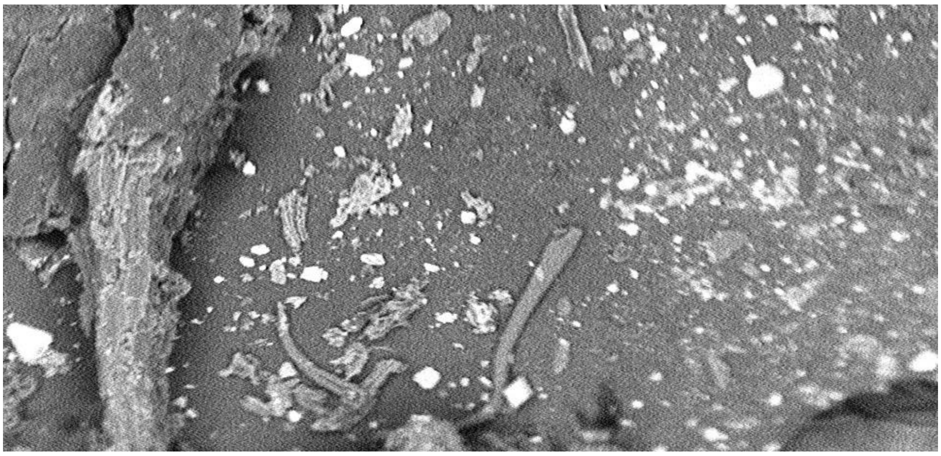

Figure 3. SEM image of GPL

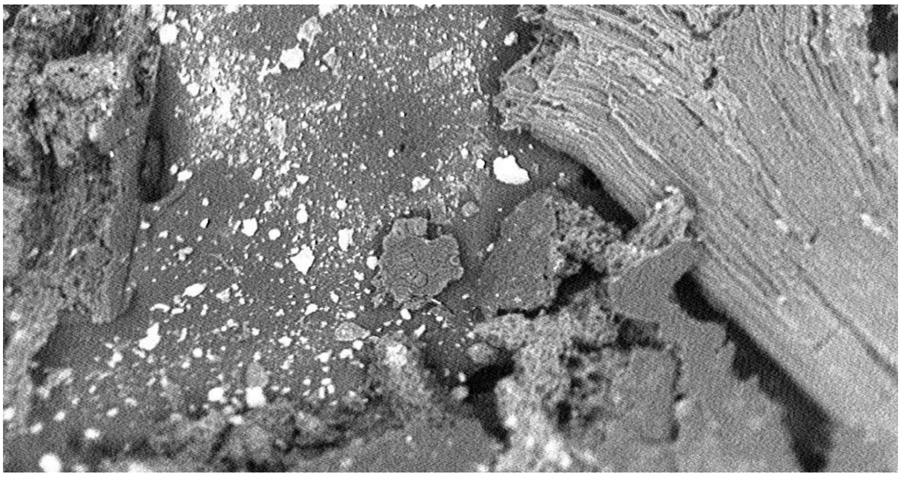

Figure 4. SEM image of CPL

3.3. XRD

Figures 5 and 6 below displayed XRD spectra of GPL and CPL, respectively. The XRD specturm, of GPL shows pattern at 2θ = 14.96, average crystal size was calculated to be 35.54nm while for CPL in Figure 6 shows adsorbent peak at 22.48 from which average crystal size was calculated to be 35.76nm.

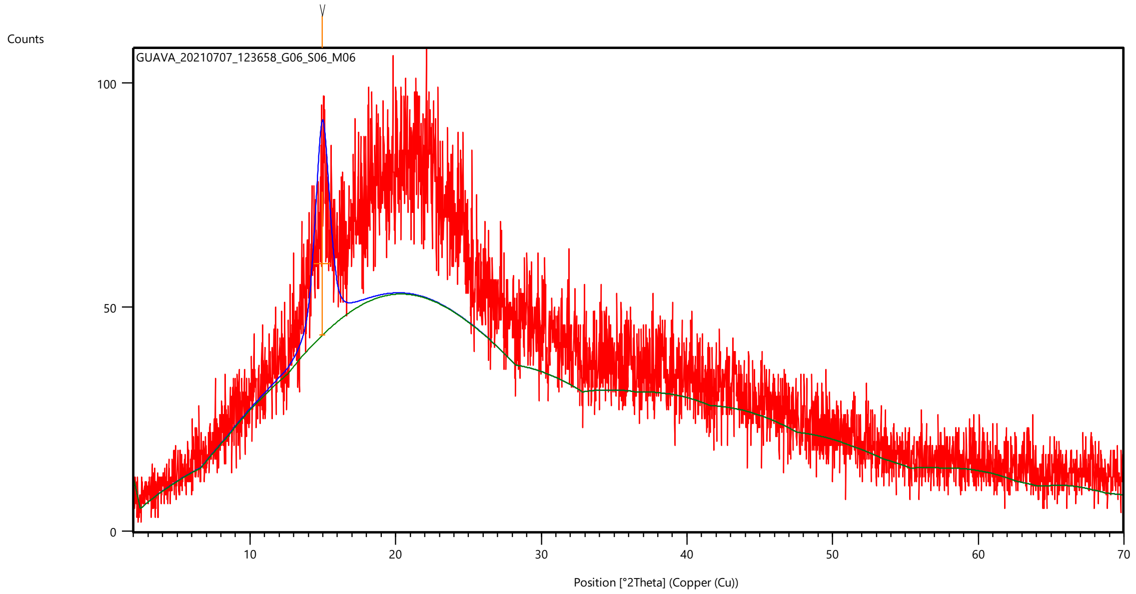

Figure 5. XRD image of GPL

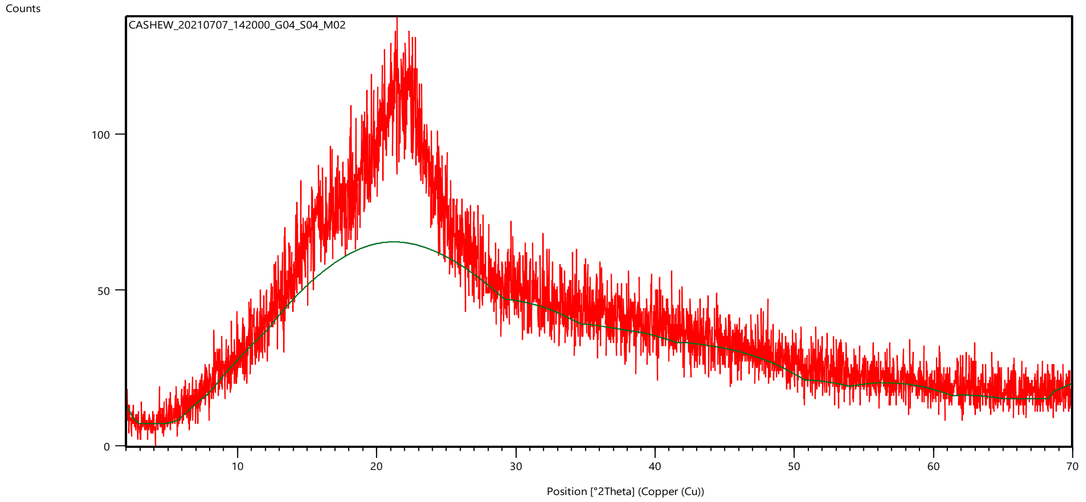

Figure 6. XRD image of CPL

3.4. Effect of Adsorbent Dose

The effect of adsorbent dose of GPL and CPL were investigated from the range of 0.2 – 1g where initial concentration (50 – 1000mg/L) and other parameters were kept constant, as shown in Figures 7 and 8, percentage removal of Pb^{2+} for GPL and Cd^{2+} for GPL and CPL increases as adsorbent dose also increase until it reaches optimum condition at 1g. While for Pb^{2+} CPL which equilibrium was attended at 0.8g. This could be due to the increased adsorbent surface area, pore size and volume, and the availability of vacant sites. The higher adsorbent dosage gave rise to higher removal of metal ions providing an important driving force to overcome all mass transfer resistance of the metal ions between the aqueous and solid phase [28]. Optimum dose reached will be used during the experiment.

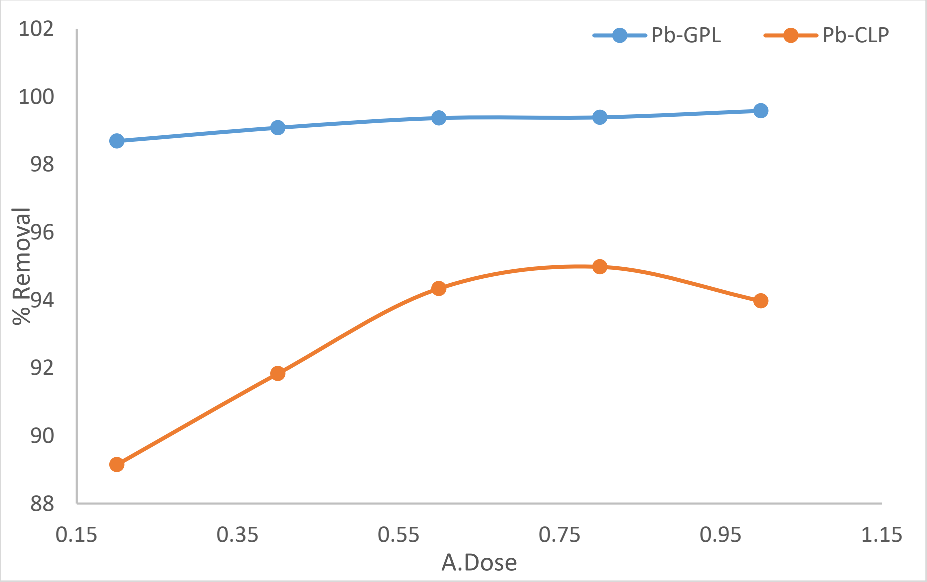

Figure 7. Effect of adsorbent dose on the adsorption of Pb^{2+} on GPL and CPL

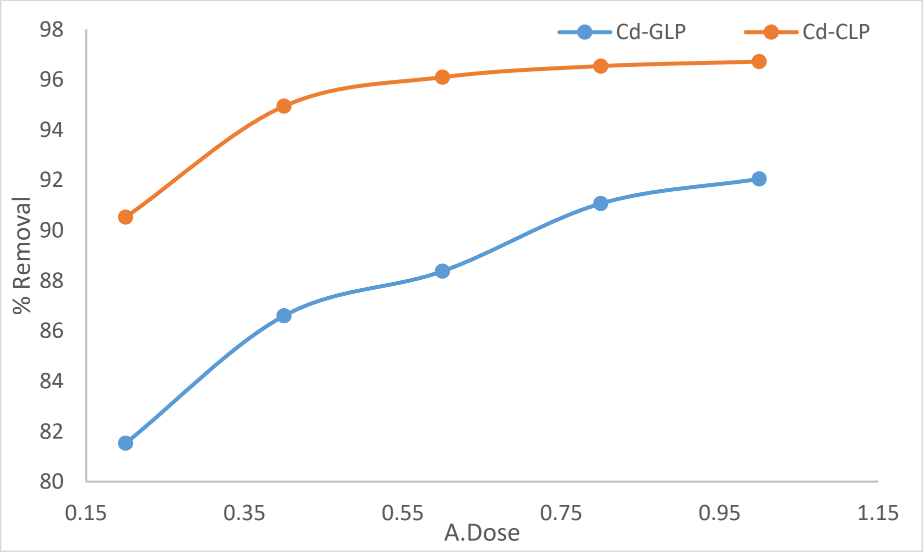

Figure 8. Effect of adsorbent dose on the adsorption of Cd^{2+} on GPL and CPL

3.5. Effect of Initial Concentration

The effect of initial metal concentration (50 – 1000 mg/L) is shown on Figures 9-10 below, where adsorbent dose is at 1g while other parameters were kept constant. From the results obtained percentage removal increases from 89.78 to 99.48 as initial concentration also increases. At low initial concentrations (50 mg/l) most of the metal ions have been removed from aqueous solution. High adsorption at low initial metal concentrations can be attributed to availability of vacant sites for metal binding [10,29,30].which suggests that increase in adsorbate concentration increase number of available molecules per binding site.

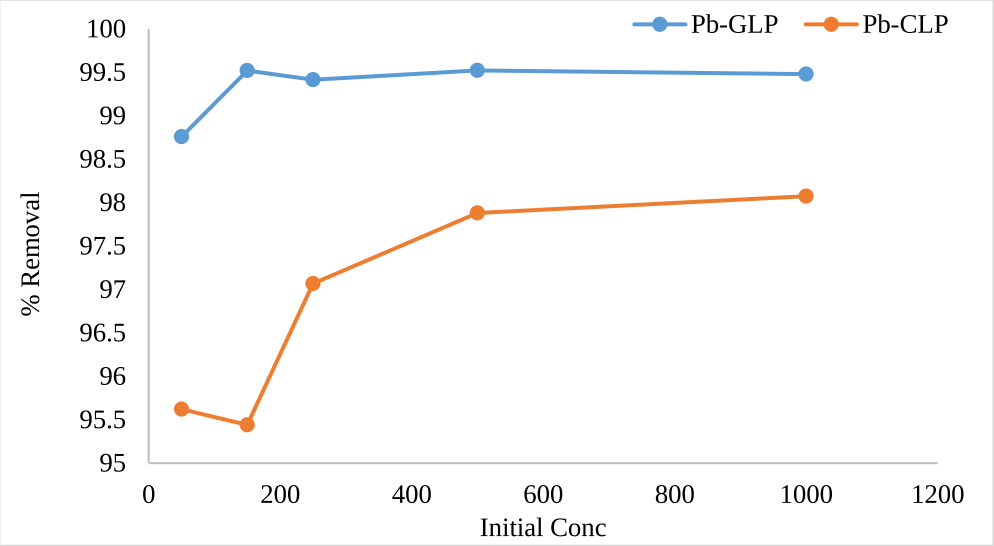

Figure 9. Effect of initial concentration on the adsorption of Pb^{2+} on GPL and CPL

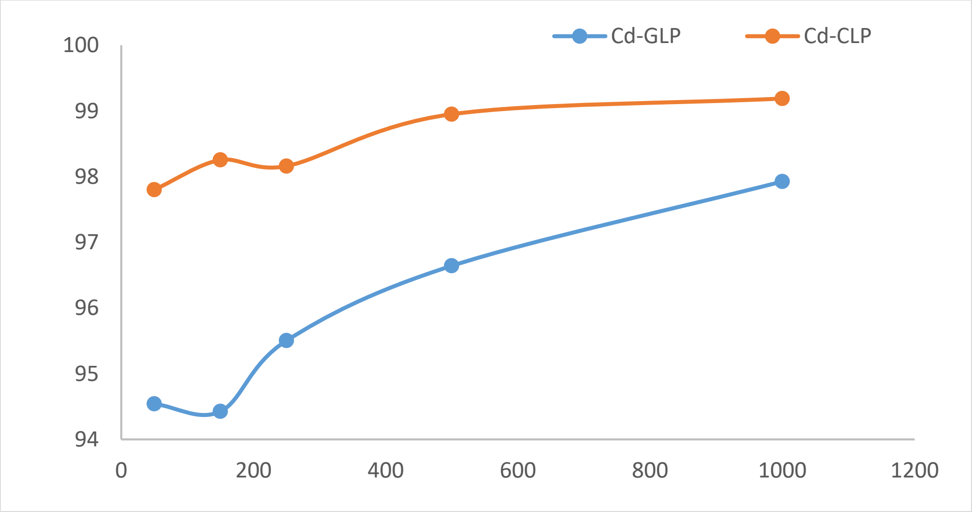

Figure 10. Effect of initial concentration on the adsorption of Cd^{2+} on GPL and CPL

3.6. Effect of pH

Effect of pH on adsorption capacity of GPL and CPL on Pb^{2+} and Cd^{2+} were investigated with pH range of 2 – 10 while the contact time and other parameters were kept constant. The results are shown in figures 11 and 12 below indicate that the amount of metal ion adsorbed for Pb^{2+} (GPL) and Cd^{2+} (GPL and CPL) increases until it reaches equilibrium at pH 7 and for Pb^{2+} (CPL) which reaches it optimum level at pH 8. This observation can be explained by the fact that the concentration of H_3O^+ ion was high at low pH. The scenario will cause completion between H_3O^+ and metal ions for active sites on the surface of biosorbents [29].

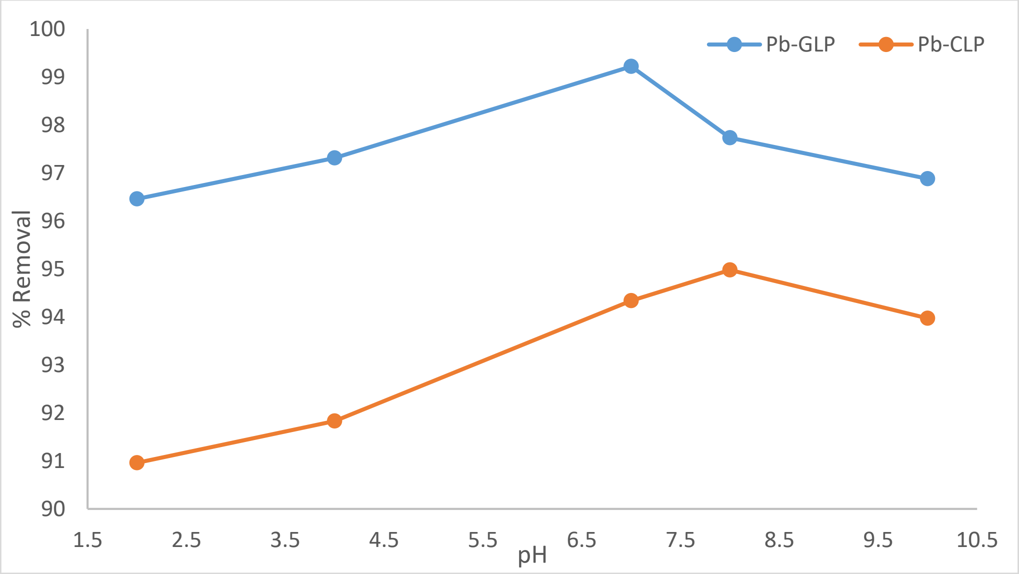

Figure 11. Effect of pH on the adsorption of Pb^{2+} on GPL and CPL

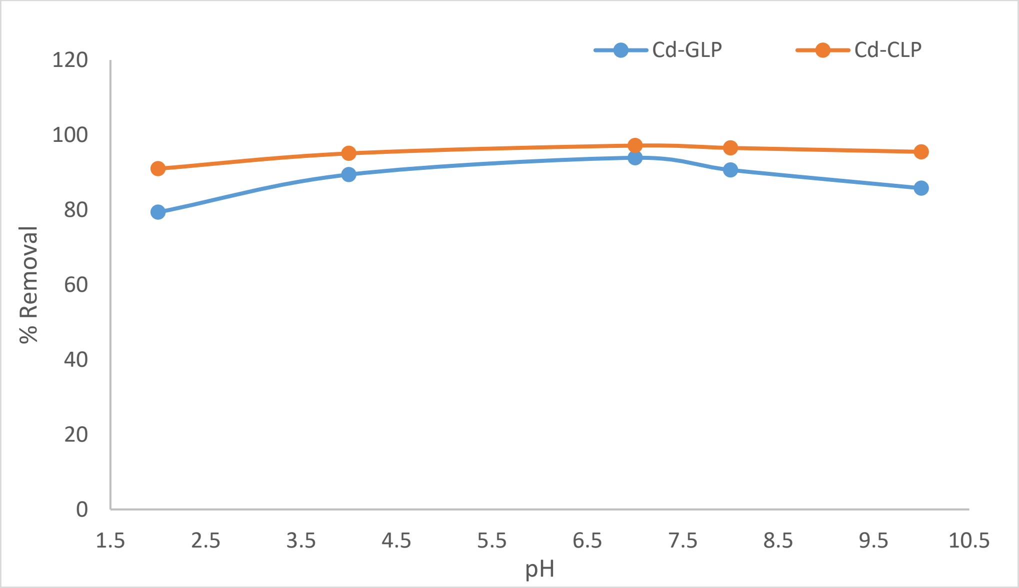

Figure 12. Effect of pH on the adsorption of Cd^{2+} on GPL and CPL

3.7. Effect of Contact Time

The effect of contact time on the percentage removal of Pb2+ and Cd2+ from aqueous solution is shown in Figures 13 and 14 below. Percentage removal increases as time tend to increase until it reaches equilibrium at 60mins, increase in time increases, and the number of sites adsorbed to the metal ions, which becomes difficult for the metal ions to search for the very few remaining sites.

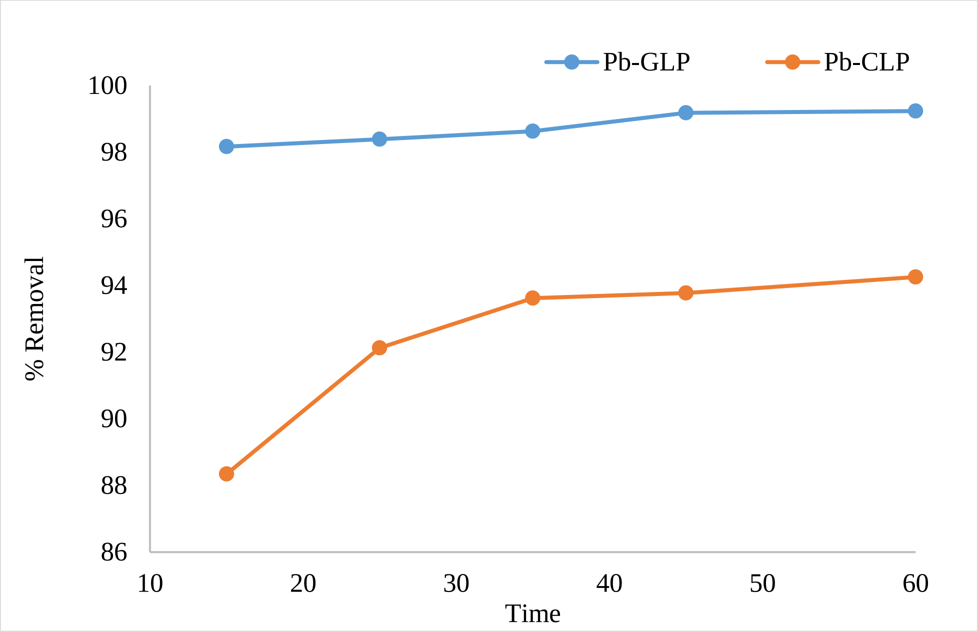

Figure 13. Effect of contact time on the adsorption of Pb^{2+} on GPL and CPL

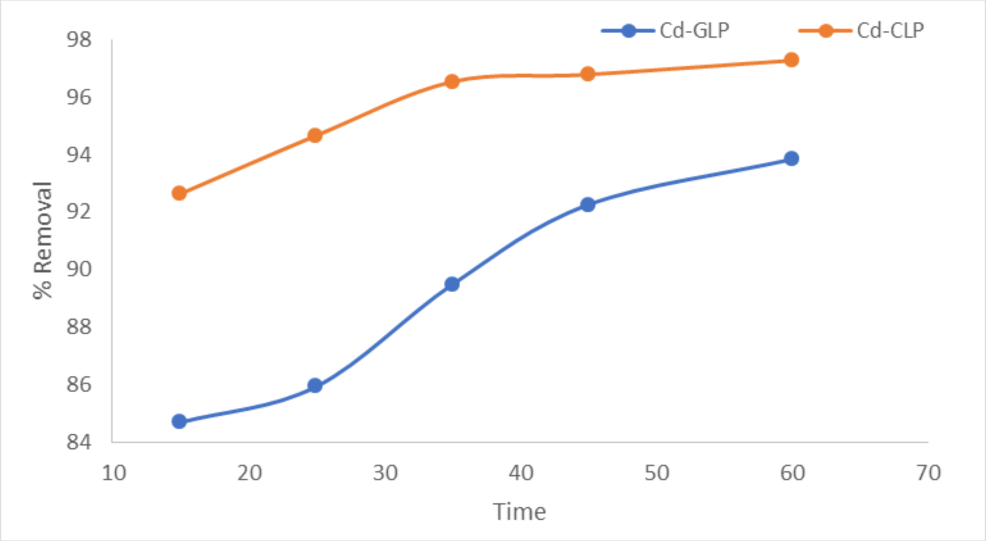

Figure 14. Effect of contact time on the adsorption of Cd^{2+} on GPL and CPL

3.8. Effect of Temperature

Effect of temperature was studied by conducting the experiment at different temperatures stating from 25 to 60^0 C while other parameters were at equilibrium. As illustrated in Figures 15 and 16 below, percentage removal increases as temperature also increases at 55^{0}C which is the optimum level before decreasing. This may be due to the endothermic nature of the adsorption; also the increase of metal ions could be as a result of increase in mobility of the metal ions acquired in the system [28].

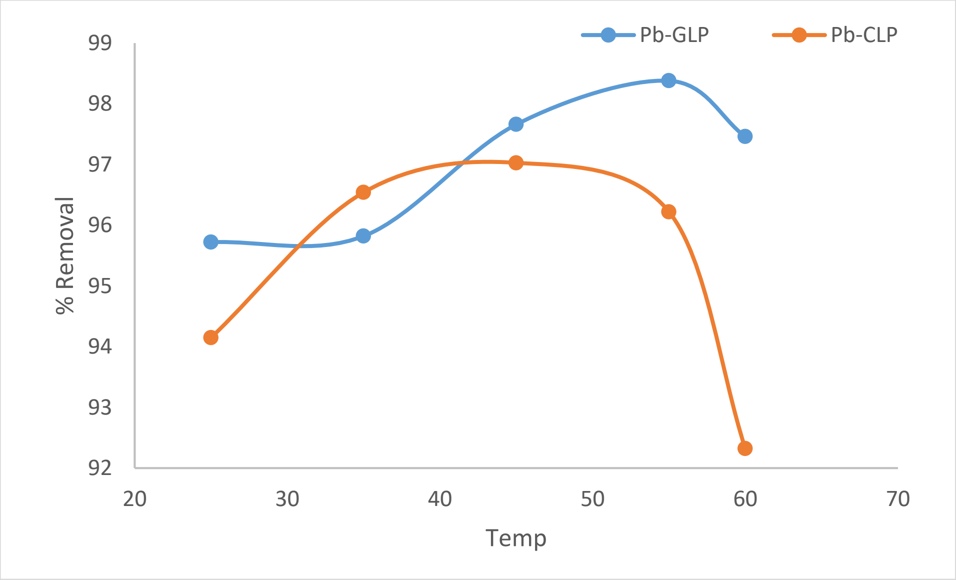

Figure 15. Effect of temperature on the adsorption of Pb^{2+} on GPL and CPL

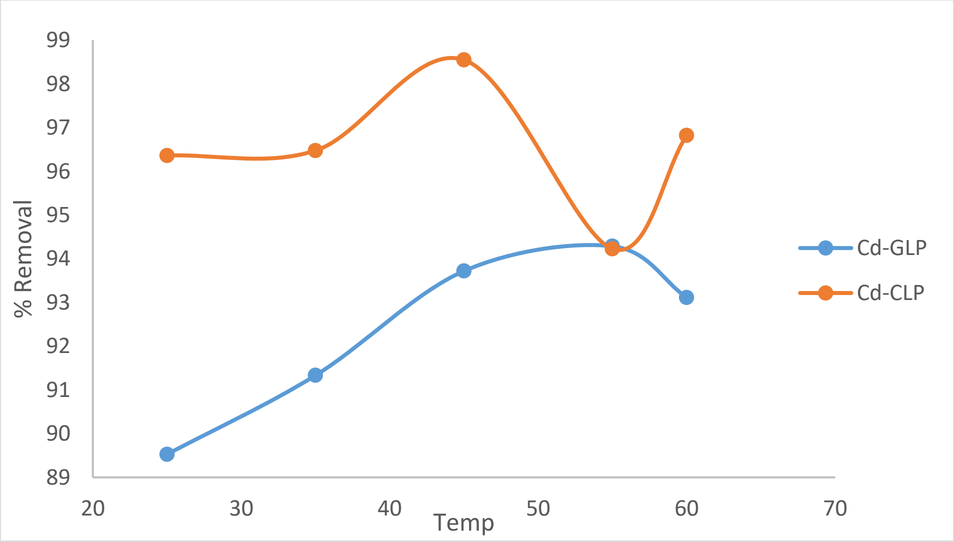

Figure 16. Effect of temperature on the adsorption of Cd^{2+} on GPL and CPL

3.9. Adsorption Isotherm

The experimental data were analyzed using Langmuir and Freundlich as the two most commonly used isotherm models. Table 1 and 2 give the overall summaries of both Langmuir and Freundlich models. For Pb^{2+} (GPL) with high R^2 values of (0.9116) which show that the experimental data fits well with Freundlich model. The value of K_F obtained was 7.3029 while that of n was 1.2494. This indicates that the value of n was favorable as it lies between 1 and 10. While, Pb^{2+} (CPL) obeys Langmuir model with R^2 value at 0.9855 and K_L value of -0.0368.

For Cd^{2+} (GPL and CPL), the values of R^2 (0.9945 and 0.9948) indicated that Langmuir have better fitted model than Freundlich isotherm. The Langmuir model obtained the adsorbent has a limit number of binding sites with all sites having binding power and the adsorption of each site is non-aligned of each other. As a result, monolayer formation of large ion or molecule between heavy metal ions and the adsorption substrate is the dominant coverage in the untreated control sample [31].

Table 1. Isotherm Parameters for Guava Plant Leave (GPL)

Isotherm Models	Adsorbates (metal ions)		
	Pb^{2+}	Cd^{2+}	Zn^{2+}
Langmuir			
R^2	0.7354	0.9945	0.9584
Q_m	-19.4553	-36.1011	109.8901
K_L	-0.2357	-0.0222	0.0172
Freunlich			
R^2	0.9116	0.9467	0.8628
N	1.2494	1.4194	1.1691
K_f	7.3029	0.4668	1.4424

Table 2. Isotherm Parameters for Cashew Plant Leave (CPL)

Isotherm Models	Adsorbates (Metal Ions)		
	Pb^{2+}	Cd^{2+}	Zn^{2+}
Langmuir			
R^2	0.9855	0.9948	0.9583
Q_m	-33.8983	-23.3645	32.3624
K_L	-0.0368	-0.0865	0.1740
Freunlich			
R^2	0.9587	0.9604	0.8791
N	1.4240	1.6502	0.9614
K_f	0.8651	29.2954	4.0794

3.10. Kinetic Study

Tables 3 and 4 below show a summary of both kinetic models. The adsorption kinetics of each heavy metal ion determine under precise time condition was performed. The kind of adsorption process depends on physio-chemical characteristic of the adsorbent and system status like temperature [31]. The linear graph of pseudo-first order was plotted from ln (qe-qt) against t (mins) and the graph of pseudo-second order was plotted from t/qt against t (min). From the results obtained, pseudo-second order correlated well with the experimental data better than pseudo-first order. The R^2 from pseudo-second order were much higher than that of pseudo first order and also the theoretical and experimental values are in a good correlation with each other. By contrast, in the pseudo second order model, the calculated qe(cal) values are very close to qe (exp), and the R^2 values converge to 1, indicating the validity of the pseudo second order [32], With this we can say that pseudo second order is best fitted for the adsorption.

Table 3. Kinetic Parameters of Guava Plant Leave (GPL)

Absorbates	Pseudo first Order			Pseudo Second Order		
	K_1	q_e	R^2	K_2	q_e	R^2
Pb^{2+}	0.0003	7.5950	0.9221	0.4525	7.4794	1
Cd^{2+}	0.0648	2.6960	0.9461	1.2336	5.9691	0.9992
Zn^{2+}	0.0313	0.3399	0.9235	0.2571	7.1633	1

Table 4. Kinetic Parameters of Cashew Plant Leave (CPL)

Absorbates	Pseudo first Order			Pseudo Second Order		
	K_1	q_e	R^2	K_2	q_e	R^2
Pb^{2+}	0.0019	6.053884	0.7346	0.093146	9.025271	0.9999
Cd^{2+}	0.1732	0.956284	0.9609	0.128948	7.429421	1
Zn^{2+}	0.0429	0.637118	0.8880	-0.08364	5.379236	0.9999

3.11. Thermodynamic Study

Thermodynamic parameters are properly assessed; they provide in-depth information regarding the inherent energy and structural changes after adsorption [33]. ΔG is the change in free Gibbs energy ($kJmol^{-1}$), R is the universal gas constant (8.314 $Jmol^{-1}K^{-1}$), Ke is the thermodynamic equilibrium constant and T is the absolute temperature (K).

The values of ΔH and ΔS were determined from the slope and the intercept from the plot of lnKe against 1/T (K^{-1}) in Tables 5 and 6 below which show the summary. For Pb^{2+} (GPL), ΔG value is negative which implies that the processes was spontaneous, a positive ΔH indicated that adsorption is endothermic while a positive ΔS indicated an increased randomness at solid-liquid interface. A similar study was reported by Ahmaruzzaman and Gupta [34] for the adsorption of heavy metals by rice husk ash, and the positive entropy ΔS° confirms the increased randomness at the solid liquid interface [17]. Pb^{2+} (CPL), ΔG was negative while ΔS and ΔH were also negative. Negative value in ΔH and ΔS means that both ΔH and ΔS are exothermic. Cd^{2+} (GPL), ΔG was positive indicating that the adsorption took place, but non spontaneous at lower temperature and ΔH and ΔS were both positive as well. Cd^{2+} (CPL), adsorption showed that ΔG is negative, while negative ΔH indicated that the adsorption was exothermic. Positive value of ΔS showed that affinity of the adsorbent for the solid-liquid interface [28].

Table 5. Thermodynamic Parameter for Guava Plant Leave (GPL)

Parameters	**ΔH (KJ/mol)**	**ΔS (KJ/mol/K)**			**ΔG**			**R^2**
Temperature(K)			298	308	318	328	333	
Pb^{2+}	0.0202	68.6927	-276.84	-349.35	-1944.8	-3028.8	-1803.8	0.6854
Cd^{2+}	13.5222	38.7922	2106.0	1640.6	774.09	524.1	1083.8	0.7625
Zn^{2+}	-7.3252	-26.5640	1587.3	392.20	-726.23	1466.8	2763.6	0.0679

Table 6. Thermodynamic Parameter for Cashew Plant Leave (CPL)

Parameters	**ΔH (KJ/mol)**	**ΔS (KJ/mol/K)**			**ΔG**			**R^2**
Temperature(K)			298	308	318	328	333	
Pb^{2+}	-3192.9	-9.5295	539.837	-852.60	-129.3	-657.69	140.45	0.017
Cd^{2+}	-0.3699	1.5197	-694.65	-801.96	-322.9	554.33	-116.4	0.029
Zn^{2+}	1635.9	55.796	-272.82	54.8535	-252.4	-3380.7	-548.34	0.2531

4. Conclusion

This study provides a simple, economical and effective adsorption process for removal of adsorbent from wastewater and environment. Instrumental analysis of FTIR, SEM AND XRD results showed promising signs as they were in agreement with most literatures, various percentage removals were obtained for Pb^{2+} and Cd^{2+} using (GPL and CPL) at optimum conditions. The equilibrium data fitted well with Langmuir isotherm model for Pb^{2+} (CLP) with R^2 value 0.9855, Cd^{2+} for (GPL and CPL) with R^2 values (0.9945 and 0.9948) while Pb^{2+} (GPL) with correlation coefficient at 0.9116 best fitted well with Freundlich isotherm model. Pseudo second order best fitted well than that of the first order kinetics in this study. The thermodynamic study shows that ΔG is negative in most cases expect for Cd^{2+} (GPL) were ΔG is positive. Whereas ΔH and ΔS are positive in some cases showing an endothermic and spontaneous adsorption processes respectively, as well as negative in some. Based on this study, GPL and CPL could be used as a natural adsorbent to remove Pb^{2+} and Cd^{2+} from wastewater and environment due to their high removal efficiencies.

References

[1] Arruti, A., Fernández-Olmo, I. and Irabien, A. "Evaluation of the contribution of local sources to trace metals levels in urban PM2.5 and PM10 in the Cantabria region (Northern Spain)." *J Environ Monit,* 2010, 12(7) :1451–1458.

[2] Beyersmann, D. Hartwig, A. "Carcinogenic metal compounds: recent insight into molecular and cellular mechanisms." *Arch Toxicol*. 2008, 82 (8): 493–512.

[3] Fu, F. and Wang, Q. "Removal of heavy metal ions from wastewaters." *Journal of Environmental Management*. 2011, 92 (3): 407–418.

[4] He, B., Yun, Z., Shi, J. and Jiang, G. "Research progress of heavy metal pollution in China: Sources, analytical methods status and toxicity." *Chinese Science Bulletin*. 2013, 58 (2): 134–140.

[5] Mishra, S., Dwivedi, S. P. and Singh, R. K. "A review on epigenetic effect of heavy metal carcinogens on human health. "*The Open Nutraceuticals Journal* 2010, 3(1): 188–193.

[6] Huang, Z., Pan, X. D., Wu, P.G., Han, J. L. and Chen, Q. "Heavy metals in vegetables and the health risk to population in Zhejiang, China." *PLoS ONE* 2014, 36 (1): 248–252. DOI: 10.1371/journal.pone.0075007.

[7] Lalhruaitluanga, H., Jayaram, K., Prasad, M. and Kumar, K. "Lead (II) adsorption from aqueous solutions by raw and activated charcoals of MelocannabacciferaRoxburgh (bamboo), A comparative study." *Journal of Hazardous Materials,* 2010, 175: 311–318.

[8] Demirbas, A. "Heavy Metal Adsorption onto Agro-Based Waste Materials: A Review." *Journal of Hazardous Materials*, 2008, 157: 220-229.

[9] Ngah, W.S.W. and Hanafiah, M.A.K.M. "Removal of Heavy Metal Ions from Wastewater by Chemically Modified Plant Wastes as Adsorbents: A Review." Bioresource Technology 2008, 99: 3935-3948.

[10] Heidari, A., Younesi, H., Mehraban, Z. and Heikkinen, H. "Selective Adsorption of Pb (II), Cd(II), and Ni(II) Ions from Aqueous Solution Using Chitosan-MAA Nanoparticles." *International Journal of Biological Macromolecules*, 2013, 61: 251-263.

[11] Bhatnagar, A. and Sillanpää, M. "Utilization of Agro-Industrial and Municipal Waste Materials as Potential Adsorbents for Water Treatment-A Review." *Chemical Engineering Journal* 2010, 157: 277-296.

[12] Liang, S., Guo, X. and Tian, Q. "Adsorption of Pb2+ and Zn2+ from Aqueous Solutions by Sulfured Orange Peel." *Desalination* 2011, 275: 212-216.

[13] Guo, S., Li, W., Zhang, L., Peng, J., Xia, H. and Zhang, S. "Kinetics and Equilibrium Adsorption Study of Lead (II) onto the Low Cost Adsorbent-Eupatorium adenophorum Spreng." *Process Safety and Environmental Protection*, 2009, 87: 343-351.

[14] Kaur, R., Singh, J., Khare, R., Cameotra, S.S. and Ali, A. "Batch Sorption Dynamics, Kinetics and Equilibrium Studies of Cr(VI), Ni(II) and Cu(II) from Aqueous Phase Using Agricultural Residues." *J. Applied Water Science*, 2013, 3: 207- 218.

[15] Banerjee, K., Ramesh, S.T., Gandhimathi, R., Nidheesh, P.V. and Bharathi, K.S. "A Novel Agricultural Waste Adsorbent, Watermelon Shell for the Removal of Copper from Aqueous Solutions." *Iranica Journal of Energy and Environment*, 2012, 3: 143-156.

[16] Benaissa, H. and Elouchdi, M.A. "Removal of Copper Ions from Aqueous Solutions by Dried Sunflower Leaver." *Chemical Engineering and Processing* 2007, 46:614-622.

[17] Wassila, B., Badreddine, B., Boualem, H. and Mohamed, T. "Kinetic and Equilibrium Studies of Biosorption of M(II) (M = Cu, Pb, Ni, Zn and Cd) onto Seaweed Posidonia oceanica fibers." *Applied Water Science*, 2019, 9(173).

[18] Kwon, J.S., Yun, S.T., Lee, J.H., Kim, S.O. and Jo, H.Y. "Removal of Divalent Heavy Metals (Cd, Cu, Pb, and Zn) and Arsenic (III) from Aqueous Solutions Using Scoria: Kinetics and Equilibria of Sorption." *Journal of Hazardous Materials*, 2010, **174**, 307-313.

[19] Kavitha, D. and Namasivayam, C. "Experimental and kinetic studies on methylene blue adsorption by coir pith carbon." *Biores. Tech*. 2007, 98: 14–21.

[20] Weber, T. W. and Chakkravorti, R. K. "Pore and Solid Diffusion Models for Fixed Bed Adsorbers." *Amer. Inst. Chem. J*, 1974, 20: 228.

[21] Hashemian, S. "Utilization of Modified Sawdust for Removal of Methyl Violet (Basic Dye) From Aqueous Solutions." *Asian J. Chem*, 2009, 21(4): 3622-3630.

[22] Bulut, Y. and Baysal, Z. "Removal of Pb(II) from wastewater using wheat bran. *J. Environ. Manage* 2006, 78 (2): 107–113.

[23] Ponnusami, V., Vikram, S. and Srivastava, S.N. "Guava (Psidium guajava) Leaf Powder: Novel Adsorbent for Removal of Methylene Blue from Aqueous Solutions." *J. Hazard. Mater*, 2008, 152 (1): 276–286.

[24] Guimarães, B., Silva, J. T. T., Santos, K. G., Vieira Neto, J. L. "Sequencing of unit operations for integral and sustainable peanut processing." *Research, Society and Development*. 2020

[25] Mohrig, J.R., Hammond, C.N. and Schatz, P.F. "Techniques in Organic Chemistry." 2nd Edition, W. H. Freeman, New York. 2006

[26] Navid, N.H., Zavvar, M., Eskandar, K., Aisan, K. "Orange tree Leaves, A Perfect Adsorbent for the Removal of Cd(II), Co(II) and Zn(II) from Wastewater." Department of Chemistry, Semnan University, Semnan, Iran. *Chem. Ind. Chem. Eng.* Q. 2019, 25(2): 107−117.

[27] Himanshu, P. and Vashi, R. T. "Equilibrium, Kinetic and Thermodynamic Studies on Adsorption of Reactive Dyes onto Activated Guava Leaf Powder." *J. Fresenius Environmental Bulletin* 2011, 20(3).

[28] Mustapha, S., Shuaib, D. T., Ndamitso, M. M., Etsuyankpa, M. B., Sumaila, A., Mohammed, U. M., Nasirudeen, M. B. "Adsorption Isotherm, Kinetic and Thermodynamic Studies for the Removal of Pb(II), Cd(II), Zn(II) and Cu(II) ions from Aqueous Solutions Using Albizia lebbeck Pods." *Applied Water Science*, 2019, 9(142).

[29] Reddy, D.H.K., Seshaiah, K., Reddy, A.V.R., Rao, M.M. and Wang, M.C. "Biosorption of Pb2+ from Aqueous Solutions by Moringa oleifera Bark: Equilibrium and Kinetic Studies." *Journal of Hazardous Materials*. 2010, 174: 831-838.

[30] Etim, U.J., Umoren, S.A. and Eduok, U.M "Coconut Coir Dust as a Low Cost Adsorbent for the Removal of Cationic Dye from Aqueous Solution." *Journal of Saudi Chemical Society*. 2012

[31] Navid, N., Hassan, Z. M., Eskandar, K., Aisan, K. "Orange Tree Leaves, a Perfect Adsorbent to the Remove Cd (II), Co (II), Zn (II) from Wastewater." Department of Chemistry, Semnan University, Iran. Iran. *Chem. Ind. Chem.* 2018

[32] Ncibi, M., Mahjoub, B., Hamissa, A. B., Mansour, R. B., Seffen, M. "Biosorption of Textile Metal Complexed dye from Aqueous Medium using Posidonia Oceanica (L.) Leaf sheaths: Mathematical modelling." *Desalination* 2009. 243:109–121.

[33] Liangcheng, X., Kangle, D., Yan, L., Mei, Z., Chao, H. "Experimental, Thermodynamic and Kinetic Studies for the Adsorption of Phenolic Compounds Derived from Oilfield Wastewater by the Corncob Hydrochar." *Open Journal of Yangtze Gas and Oil*, 2019, 4: 285-300.

[34] Ahmaruzzaman, M. and Gupta, V.K. “Rice husk and its ash as low-cost adsorbents in water and wastewater treatment.” *Ind Eng Chem Res,* 2011, 50:13589–13613.