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Adsorption Characteristics of *Chrysophyllum albidum* (African Star Apple) Peels Towards Heavy Metal Ions

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ABSTRACT

Currently the use of agricultural waste as a low-cost adsorbent has attracted much attention of researchers. The removal of cadmium (II), copper (II) and lead (II) ions from aqueous solution using peels of *Chrysophyllum albidum* (African Star Apple) was studied. The sorption studies were carried out by varying adsorbent dose, contact time and temperature. The experimental results showed that the adsorption removal efficiency of *Chrysophyllum albidum* peels on cadmium (II), copper (II) and lead(II) ions had a direct relationship with adsorbent dose and contact time while the Temperature study showed an inverse relationship. The maximum adsorption efficiencies of the adsorbent were 95.30, 93.22 and 92.78 % for Cd^{2+}, Cu^{2+} and Pb^{2+} respectively. Sorption kinetic data fitted well with the pseudo second order kinetic model. The experimental data were analyzed using Freundlich, Langmuir and Temkin isotherm equations. The best fit was obtained by Temkin isotherm for Cd^{2+} and Freundlich isotherm for Cu^{2+} and Pb^{2+} ions. The Arrhenius and Eyring activation energy showed that rate of Cd^{2+} adsorption is more rapid than rate of Cu^{2+} and Pb^{2+} adsorption. The thermodynamic data revealed that the Cd(II) and Pb(II) ion uptake was exothermic while Cu(II) ion was endothermic and they were all spontaneous in nature. From these results, *Chrysophyllum albidum* peel could be recommended as an adsorbent for metal ion removal from aqueous solution.

1. Introduction

In recent years, increasing awareness about the environmental impact of heavy metals has prompted a demand for the purification of industrial wastewater prior to discharge into natural water [1]. The removal of heavy metals via adsorption over solid adsorbents, e.g., activated carbons and others is one of the most convenient methods used. However, most of these techniques do not lead to a satisfactory purification of industrial wastewater considering the operational costs. Precipitation methods are particularly reliable, but require large settling tanks for the precipitation of voluminous alkaline sludge and subsequent treatment are needed. Ion exchange has the advantage of allowing the recovery of metallic ions, but it is expensive and sophisticated.

These have encouraged research into discovering materials that are both efficient and cheap. Interest has recently arisen in the investigation of some unconventional methods and low-cost materials for scavenging heavy metal ions from industrial wastewaters. A number of adsorbents from agricultural waste materials have been used in the removal of heavy metals from wastewater because agricultural materials are rich in cellulose and lignin which can bind metal ions [2,3]. The cell wall of agricultural biomass essentially consists of various organic compounds such as chitin, lipids, amino acids and other cellular compounds that could provide a passive uptake of

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metal ions through surface adsorption, ion exchange, complexation, chelation and micro-precipitation [4]. This present work investigated the efficiency of *Chysophyllum albidum* (African Star Apple) peels on the removal of Cd(II), Cu(II) and Pb(II) ions from aqueous solutions. The effects of contact time, adsorbent dosage and temperature were investigated. The equilibrium data were analyzed using Langmuir, Freundlich, Temkin isotherms, pseudo first order and pseudo second order kinetics.

2. Materials and methods

2.1 Preparation of Adsorbent

Chrysophyllum albidum fruit was bought at the Relief market in Owerri North local government Area of Imo state, Nigeria. The peels were separated from the pulp. The sample (peels) was washed with distilled water, sun dried and ground. The ground sample was sieved and particle size of 0.4mm was obtained through standard steel sieve of 400µm mesh size. The ground sample was then used for experiments without further washing or any physical or chemical treatment.

2.2 Preparation of Synthetic Wastewater

Synthetic wastewater samples were prepared by using analytical grade lead nitrate, copper chloride and cadmium chloride. The chemicals were products of BDH with 98 % purity. The batch sorption test was done at known initial metal ion concentration of 100 mg/l cadmium, copper and lead. Firstly, a stock solution of metals (1000 ppm) was prepared from lead nitrate ($Pb(NO_3)_2$) and cadmium chloride ($CdCl_2.H_2O$) and copper chloride ($CuCl_2.2H_2O$). Secondly, serial dilution was made from the stock solution to the needed concentration of 100ppm using distilled water.

2.3 Sorption Experiments

Batch experiments for cadmium (II), copper (II) and lead (II) ions were carried out using a series of reagent bottles. Batch experiments were conducted to investigate the effects of contact time, adsorbent dose, and temperature on sorption of metal ions from its solutions. All the sorption experiments were carried out at room temperature (28 ± 2 ℃) except where the effect of temperature was being investigated.

2.3.1. The Effect of Contact Time on the Removal of Metal ions

The batch biosorption test was done at different contact time of 20 min, 40 min, 60 min, 80 min and 100 min intervals and at a known concentration of 100 ppm for cadmium(II), copper(II) and lead (II) ions. The sorbent dose used was 2.0 g/100 ml at a temperature of 28 ± 2 ℃. The samples were agitated for the different contact period, after which the mixtures were filtered using filter paper, and the Cd(II), Cu(II) and Pb(II) ion concentration were determined using Atomic Absorption Spectrometer (AAS).

2.3.2. The Effect of Biosorbent Dose on the Removal of Metal ion

Biosorbent dose experiments were also performed with 100ml of 100 ppm Cd^{2+}, Cu^{2+} and Pb^{2+} solution with the following biosorbent masses; 1.0, 2.0, 3.0, 4.0, 5.0 g at 28 ± 2 ℃. After the established contact time (60 min) was reached, the suspension was filtered and filtrate analyzed for unadsorbed metal ion concentrations using Atomic Absorption Spectrometer (AAS).

2.3.3 The Effect of Temperature on the Removal of Metal ion

Lastly, experiments for the reaction temperature were also performed following the same procedure, with all other parameters fixed (biosorbent dose; 2.0g/100ml, contact time; 60 min), but at different temperature ranges, 30, 40, 50, 60, and 70 ℃ respectively.

2.4 Determination of Metal Content on the Removal of Metal ion

The unadsorbed metal ion concentration was determined with Atomic Absorption Spectrometer model, Solaar 950A. Analytical grade standards were used to calibrate the instrument, which was checked periodically throughout the analysis of the instrument's response. The batch experiments were performed in triplicates and the average values were computed for each set of experiments.

2.5 Determination of Adsorption Efficiency and Capacity

The adsorption capacity and removal percentage were determined using equation 1 and 2, taking into account the concentration difference of the solution at the beginning and equilibrium [5].

$$q_e = \frac{C_o - C_e}{m} \quad (1)$$

$$\text{Removal percentage} = \frac{(C_o - C_e)V}{m} \times 100 \quad (2)$$

Where C_O and C_e are the initial and the equilibrium metal concentration (mg/L), respectively, V is the volume of solution (ml) and m is the mass (g) of the adsorbent.

3. Results and Discussion

3.1 Effect of Contact Time

The effect of time on the rate of adsorption of heavy metal by *Chysophyllum albidum* peels was studied. The effect of contact time on the adsorption capacity of Cd(II), Cu(II) and Pb(II) ions on *Chysophyllum albidum* (CA) is shown in Figure 1 and Figure 2 shows the effect of contact time on the removal efficiency of Cd(II), Cu(II) and Pb(II) ions onto CA. The plot of adsorption capacity reveals high sorption uptake at initial stage and slows down after 60 min due to the saturation of the surface of the adsorbent. The net adsorption capacities were 3.82 mg/g, 3.52 mg/g and 3.35 mg/g for Cd, Cu and Pb ions respectively. From the result obtained, cadmium and copper reached an adsorption maximum at 60min while lead reached at 100 min which can be attributed to the specificity of the interaction of the metal ions with the adsorbent. At the initial stage, there were a large number of vacant sites on the surface of the biosorbents which enhanced its sorption capacity, but as the reaction progressed, the vacant sites became filled by the sorbate and this reduces the sorption capacity of the adsorbent [6].

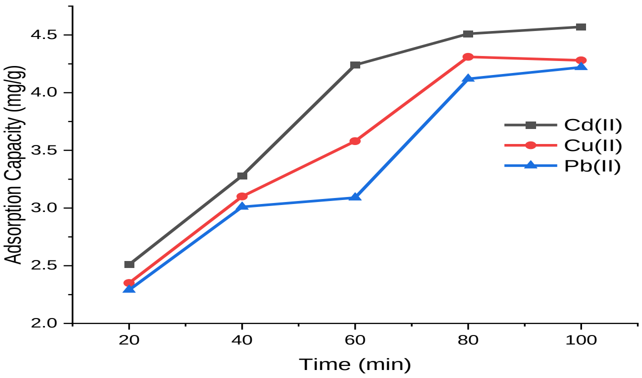

Figure 1: Effect of contact time on adsorption capacity of CA for Cd, Cu and Pb (II) ions

The removal percentage efficiency result shows high rate of metal removal at the initial stage as the highest Percentage removal efficiency of cadmium (II), copper (II) and lead (II) were 91.32%, 88.21% and 84.30% respectively at equilibrium. Other researchers have reported that the high rate of removal at the beginning was probably due to the larger surface area of the adsorbent being available at the beginning for the adsorption of metals [7]. The results show, interaction between the metal ion and the site of organic matter was responsible for metal ions uptake, and the fast initial uptake was due to the accumulation of metal ions in the surface of adsorbent at a rapid rate. These can be attributed to the highly porous structure of the adsorbent and particle size, which provide a large surface area for the sorption of metals on the binding sites.

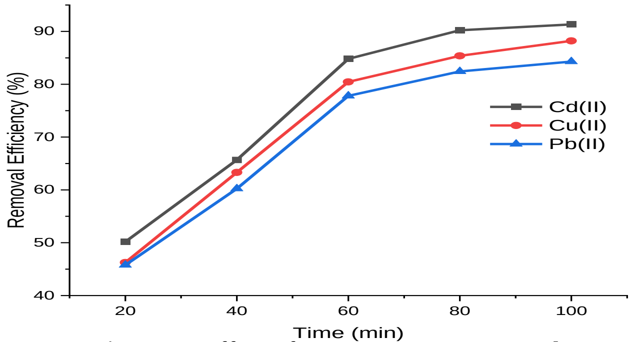

Figure 2: Effect of contact time on removal efficiency of CA for Cd, Cu and Pb (II) ions

3.2 Effect of Adsorbent Dose on Heavy Metal Removal

The effect of adsorbent dose on removal of cadmium, copper and lead (II) ions were studied in the range of 1-5g/100ml. Figure 3 shows the effect of adsorbent dose on the adsorption capacity of Cd(II), Cu(II) and Pb(II) ions on CA peels. The adsorption capacity decreases from 7.24 – 1.91 mg/g, 6.85- 1.88 mg/g and 6.37 – 1.86 mg/g for Cd, Cu and Pb ions respectively. The result shows increase in adsorbent dose have insignificant uptake of the metal ions. Figure 4 shows the removal efficiency of metal ions onto CA peels. The result revealed that, the removal efficiency, increased from 72.40 – 95.30%, 68.55 – 93.22% and 63.68 – 92.78% for cadmium, copper and lead ions respectively as adsorbent dose increased from 1 – 5g.

This trend is attributed to an increase in the adsorptive surface area and the availability of more binding sites due to the mass increase of the adsorbent [8-10]. Based on figure 4, the adsorption of Cd(II), Cu(II) and Pb(II) ions was observed to increase rapidly from adsorbent dose 1-2g and further increase from 3-5g did not show a significant increase in the removal efficiency of the adsorbent. It has been reported that electrostatic interactions between the adsorbent can be a significant factor in the relationship between adsorbent and metal sorption [11]. Banerjee *et al*,[12], have earlier reported that an insignificant increase in the percentage sorption removal from an increase in adsorbent dose is due to a very fast superficial adsorption on the adsorbent surface that produces a lower solute concentration in the solution than when adsorbent dose is low. Furthermore, the difference on the removal efficiency of the studied metal ions may be due to the chemical nature of the heavy metals and their affinity to the biosorbents [13].

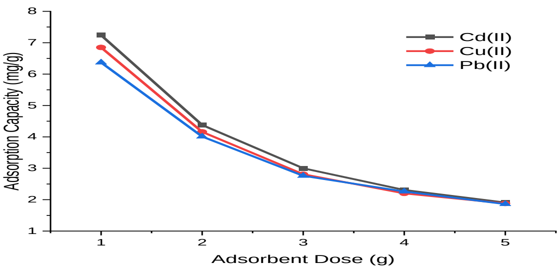

Figure 3: Effect of adsorbent dose on adsorption capacity of CA for Cd, Cu and Pb

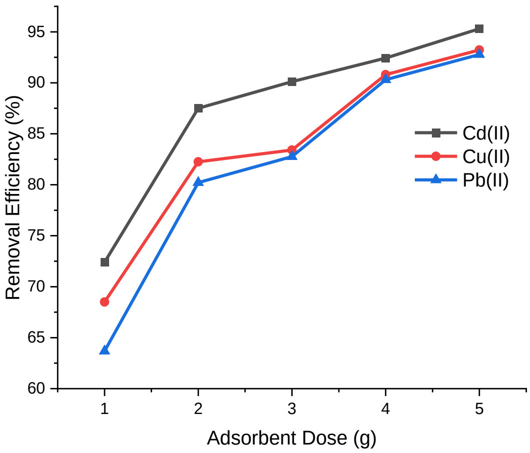

Figure 4: Effect of adsorbent dose on removal efficiency of CA for Cd, Cu and Pb (II) ions

3.3 Effect of Temperature

Temperature affects the adsorption behaviour of metallic ion in solution as an increase in temperature probably may weaken the bond formed between the metal ions and the adsorption sites or create a wider surface area for adsorption, thereby resulting to decrease or increase in the amount of metal ions adsorbed [1]. The effect of temperature on the adsorbent was also studied at different temperature of 30-70℃ on the removal of cadmium and lead ions from the aqueous solution (Figs. 5 and 6). Temperature of adsorption medium could be important for energy dependent mechanisms in metal adsorption by adsorbent [12]. Fig. 5 shows the effect of temperature on the adsorption capacity of Cd(II), Cu(II) and Pb(II) on CA peels.

The adsorption capacity and adsorption efficiency, increased from 30-40℃, but decreases after 40℃. The decrease in adsorption after 40℃ may be due to favourable interaction between the adsorbent surface and the metal ions in solution at the lower temperature.The biosorption efficiency deceased from 80.76 – 66.06% for Cd, 80.15 – 65.25% for Cu and 78.23 – 61.23% for Pb(II) ions as the temperature increased from 30 – 70℃ for the equilibrium time of 60min. The result indicated the exothermic nature of cadmium and lead (II) ions sorption onto *Chrysophyllum albidum*. A decrease in metal ion sorption with the rise in temperature may be due to either the damage of the active binding sites in the biomass [14] or increasing tendency to metal desorption from the interface to the solution by weakening of adsorptive forces between the active sites of the adsorbent [15-19]. El-Sayed et al [15] conducted zinc (II), cadmium (II) and manganese (II) removal experiments using maize stalks and observed the maximum removal efficiency decreases from 52 % to 28 % for Zn(II) ions, from 34 to 16 % for Cd(II) ions and from 39 to 13 % for Mn(II) ions as the temperature increased from 25 ℃ to 55 ℃. A similar trend was observed by Kumar et al [20] in the case of Cd(II) ions onto cashew nut shell, they found that the biosorption removal efficiency decreased from 80.13 % to 74.32 % with the rise in temperature from 30 to 60 ℃. They attributed their observation to the decrease in the surface activity of the adsorbent.Researchers have explained this trend to the damage of active adsorption sites of agricultural waste biosorbents or the increasing number of metal ions mobility from the agricultural waste biosorbents surface to the solution [15,20,21].

Several agricultural byproducts have been evaluated as promising adsorbents for the removal of heavy metals from wastewater [22]. A comparison of adsorption efficiency of agricultural byproducts was established between literature data as compared to the present results (Table 1). It is evident from the tabulated data that the used adsorbent is effective and efficient in the removal of heavy metals from aqueous solution.

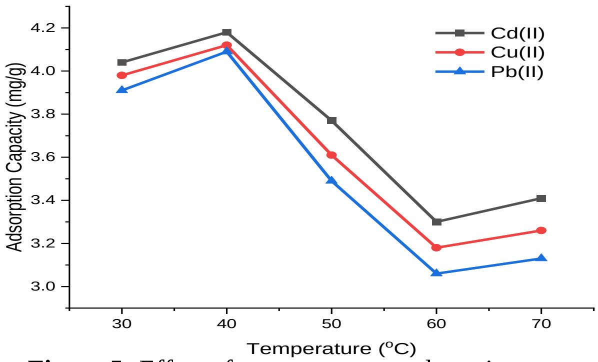

Figure 5: Effect of temperature on adsorption capacity of CA for Cd, Cu and Pb (II) ions

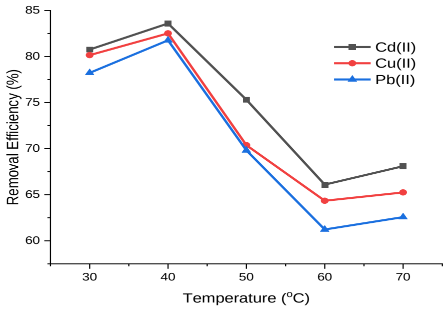

Figure 6: Effect of temperature on removal efficiency of CA for Cd, Cu and Pb (II) ions

Table 1: Comparative effectiveness of various used agricultural adsorbents in the removal of heavy metals.

Biosorbent	Pollutants	Conc. (mg/l)	Dose (g/l)	Removal efficiency	q_{max}	Ref.
Orange peel	Cd(II)	0.001	0.025	93.72		23
Orange peel	Cu(II)	5	0.01	93.70	70.73	24
Orange peel	Pb(II)	50	0.01	99.40	209.8	24
Pomegranate peel	Cu(II)	20	0.25		55	25
Pomegranate peel	Pb(II)	50	0.25		64	25
Banana peel	Cd(II)	10	0.1	97	35.52	26
Tea waste	Cu(II)	100	1.5	64	48	27
Tea waste	Pb(II)	200	1.5	92	65	27

3.4 Adsorption Isotherms

The most information on the efficiency of a given adsorption is provided by the study of equilibrium between the solid phase and the liquid phase [28]. The equilibrium study in this system (metal ions – biosorbent) determines the distribution of substances that are dissolved in the solution and the capacity of its own biosorbents. The equilibrium adsorption isotherms are important in the design of adsorption systems. The equilibrium data were analyzed by the most commonly used isotherms such as Langmuir, Freundlich and Temkin isotherms.

3.4.1 Langmuir Isotherm

The Langmuir equation, which is valid for monolayer adsorption onto a completely homogenous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules, is represented in the linear form as follows [12]:

$$\frac{1}{q_e} = \frac{1}{bq_{max}}\frac{1}{C_e} + \frac{1}{q_{max}} \qquad (3)$$

Where q_e(mg/g) and C_e(mg/L) are the amount of adsorbed metal per unit mass of adsorbent and metal concentration at equilibrium respectively. q_{max} is the maximum amount per unit mass of adsorbent to form a complete monolayer on the surface bound at high C_e and b is the Langmuir constant (l/mg) related to the energy of adsorption.

The Langmuir constants q_{max} and b were determined from the slope and intercept of the plot and are presented in Table 2. The results reveal that the amount of metal ions adsorbed per unit mass of the adsorbent was higher in cadmium ion than lead ion. The estimated model parameters with a correlation coefficient (R^2) for the different metal are shown in Table 2. The values of R^2 are regarded as a measure of the goodness of fit of experimental data on the isotherm model. The correlation coefficients are 0.9330, 0.9366 and 0.9046 for Cd(II), Cu(II) and Pb(II) ions respectively. The correlation values indicated that the adsorption data for Cu(II) ion onto *Chrysophyllum albidum* peels fitted well with the Langmuir isotherm, suggesting the formation of monolayer coverage of the adsorbate on the surface of adsorbent for copper ion [15].

The effect of isotherm shape can be used to predict whether an adsorption system is favourable or unfavourable both in fixed bed systems as well as in batch process [29]. The essential features of the Langmuir dimensionless constant are referred to separation factor or equilibrium parameter R_L, which is given by the following equation [30]:

$$R_L = \frac{1}{1+bC_o} \qquad (4)$$

Where C_o is the initial concentration of adsorbate (mg/L), R_L is a dimensionless separation factor and b is Langmuir constant (L/mg). The parameter R_L indicates the shape of the isotherm accordingly:

Values of R_L	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The dimensionless separation factor R_L values between 0 and 1 indicate favourable adsorption. The calculated R_L values for Cd(II), Cu(II) and Pb(II) at 303K as presented in Table 2, shows that the value of R_L in the present investigation was found to be 0.233, 0.059 and 0.250 for cadmium, copper and lead ions respectively, indicating favourable adsorption of the three metals onto *Chrysophyllum albidum* peels [9,15]. The maximum adsorption capacity (q_{max}) of adsorbent calculated for Langmuir isotherm in this work was found to be comparable with other adsorbents reported in literature for Cd, Cu and Pb(II) ions.

Table 2: Langmuir isotherm model constants and correlation coefficients for adsorption of Cd, Cu and Pb(II) ions on peels of *Chrysophyllum albidum*.

Isotherm model	**Parameters**		
Langmuir isotherm	**Cd**	**Cu**	**Pb**
q_{max}(mg/g)	12.99	8.33	10.00
b_L (L/mg)	0.033	0.16	0.030
R_L (L/mg)	0.233	0.059	0.250
R^2	0.9330	0.9366	0.9046

3.4.2 Freundlich Isotherm

The Freundlich isotherm assumes a heterogeneous sorption surface with sites that have different energies of sorption. The Freundlich model can be represented as stated in eqn 5 [15]:

$$\log q_e = logK_f + \frac{1}{n}logC_e \quad (5)$$

Where K_f is the relative adsorption capacity of adsorbent and n_f is a constant related to adsorption intensity.

The linear plot indicated the applicability of the Freundlich model in the study of adsorption properties of *Chrysophyllum albidum* on Cd(II), Cu(II) and Pb(II) ion removal from aqueous solution. The Freundlich parameters and results are tabulated in Table 3. Then values indicating adsorption intensity of the adsorbent was 1.250, 1.943 and 1.333 for cadmium, copper and lead ions, respectively and was greater than one, indicating that the adsorption was favourable. It can be observed from the correlation coefficient values (R^2) in Table 3 that Freundlich isotherm model exhibited good fit to the sorption of Cd(II), Cu(II) and Pb(II) than the Langmuir isotherm model by the adsorbent. Studies have shown that the Langmuir isotherm corresponds to a dominant ion exchange mechanism while the Freundlich isotherm shows adsorption complexation reactions taking place in the adsorption process [2,31].

Table 3: Freundlich isotherm model constants and correlation coefficients for adsorption of Cd, Cu and Pb(II) ions on peels of *Chrysophyllum albidum*.

Isotherm model	**Parameters**		
Freundlich isotherm			
	Cd	**Cu**	**Pb**
K_f(mg/g)	0.513	1.623	0.398
n_f	1.250	1.943	1.333
R^2	0.9631	0.9885	0.9419

3.4.3 Temkin Isotherm

The Temkin adsorption isotherm model was used to evaluate the adsorption potentials of *Chrysophyllum albidum* peels on cadmium, copper and lead ions. It is based on the assumption that the heat of adsorption decreases linearly with the increase of coverage of adsorbent [32]. The Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic as implied in the Freundlich equation [9]. The Temkin isotherm has commonly been applied in the following form:

$$q_e = a + blnC_e \quad (6)$$

Where a(L/g) is Temkin adsorption capacity and b (kJ/mol) is heat of sorption. The constant values of a_T and b_T were determined from the intercept and slope of the straight line plot. From Table 4, examination of the data shows that *Chrysophyllum albidum peels* have adsorption capacity (a_T) of 5.6, 0.8 and 4.0(l/g) while the heat of adsorption (b_T) was 3.79, 5.88 and 3.11(kJ/mol) for cadmium, copper and lead ions respectively. Comparing the correlation coefficient obtained from the three isotherm as shown in Table 2, 3 and 4, the correlation value indicates that Temkin model can be applied successfully to Cd(II) adsorption study while Freundlich model appears to be favourable for fitness to Cu(II) ion adsorption by the adsorbent. The applicability of the three isotherm models for the present data approximately follows the order: Freundlich>Temkin> Langmuir in case of copper and lead, Temkin>Freundlich> Langmuir in case of cadmium.

Table 4: Temkin isotherm model constants and correlation coefficients for adsorption of Cd, Cu and Pb(II) ions on peels of *Chrysophyllum albidum*.

Isotherm model	**Parameters**		
Temkin isotherm	**Cd**	**Cu**	**Pb**
a_T (l/g)	5.6	0.8	4.0
b_T(kJ/mol)	3.7915	5.88	3.1136
R^2	0.9694	0.9675	0.9381

3.5 Adsorption Kinetics

The kinetic studies provide useful data regarding the efficiency of adsorption process and feasibility of scale-up operations. To evaluate the performance of unit process utilizing adsorption, it is necessary to have an understanding of the time dependence of the concentration distribution of the solute in both the bulk solution and solid adsorbent phases to identify the rate determining step [33]. Several kinetic models are available to describe the adsorption kinetics. The kinetics of Cd, Cu and Pb(II) ions adsorption onto the peels of *Chrysophyllum albidum* were investigated using pseudo first order, pseudo second order kinetics and power function model. The best fit model was selected based on the correlation coefficient (R^2) values.

3.5.1 Pseudo first order kinetics.

The pseudo first order kinetic considers the rate of occupation of adsorption sites to be proportional to the number of unoccupied sites [10]. The pseudo first order equation is generally expressed as:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \qquad (7)$$

Where q_e and q_t are the adsorption capacity at equilibrium and time t, respectively (mg/g), k_1 is the rate constant of pseudo first order adsorption (min^{-1}). The linear plot of log (q_e- q_t) against t, gives values of k_1 and q_e as shown in Table 5 which were determined from the slope and intercept respectively. The application of this model to the study of Cd, Cu and Pb(II) ions on *Chrysophyllum albidum* peels indicated inapplicability of the model compared to other model studied due to low correlation coefficient (R^2) value.

Table 5: Pseudo first order models constants and correlation coefficients for adsorption of Cd, Cu and Pb(II) ions on peels of *C. albidum*.

Kinetics model	Parameters		
Pseudo first order	Cd	Cu	Pb
q_e (mg/g)	3.89	0.89	3.55
K_1 (g/mg.min)	0.023	0.123	0.017
R^2	0.9514	0.9859	0.9495

3.5.2 Pseudo Second Order Kinetic

The pseudo second order equation is based on adsorption equilibrium capacity and is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{t}{q_e}\right) \qquad (8)$$

Where k_2 is the rate constant for the pseudo second order kinetic (g/mg.min). The linear plot of t/q_t against t was used to evaluate the pseudo second rate constant for cadmium, copper and lead ions adsorption onto *Chrysophyllum albidum* peels. The initial sorption rate was calculated using the relation.

$$k_0 = k_2 q_e^2 \qquad (9)$$

The parameters calculated for the pseudo second order kinetic model are shown in Table 6. The results revealed that the pseudo second order is a predominant kinetic model due to its high correlation coefficient (R^2) value for the metal adsorption by peels of *Chrysophyllum albidum*. Similar kinetic results have been reported on the removal of heavy metal from aqueous solution using pomegranate peels and sawdust [7,10]. The present work shows the applicability of pseudo second order kinetic model in the adsorption process of cadmium and lead ions onto peels of *Chrysophyllum albidum*. The model is based on the assumption that the rate limiting step may be a chemical adsorption involving valence forces through sharing or exchanging of electrons between adsorbent and adsorbate [9].

Table 6: Pseudo second order constants and correlation coefficients for adsorption of Cd, Cu and Pb(II) ions on peels of *C. albidum*.

Kinetics model	Parameters		
Pseudo second order	Cd	Cu	Pb
q_e (mg/g)	5.88	2.98	5.56
k_2 (g/mg.min)	0.0061	0.056	0.0061
k_o(min^{-1})	0.2109	0.50	0.1886
R^2	0.9884	0.9958	0.9896

3.5.3 Power Function Model

Power function kinetic model develops a relation between metal uptake onto the adsorbent and time [34]. The equation is given as:

$$\log q_t = \log a + b\log t \qquad (10)$$

The linear plot between log q_t and log t gives the constants of power function a and b. the constant a represents the initial rate and refers to the intercept of the straight-line plot of log q_t against log t, while b is the rate constant of the reaction and is given by the slope of the plot. The detailed results of power function constants are tabulated in Table 7.

Table 7: Power function models constants and correlation coefficients for adsorption of Cd, Cu and Pb(II) ions on peels of *Chrysophyllum albidum*.

Kinetics model	Parameters		
Power function model	Cd	Cu	Pb
a	1.7378	1.5136	1.4791
B	0.3560	0.3231	0.3793
R^2	0.9822	-0.8624	0.9843

The correlation coefficient in Table 6 shows that the experimental data gave a negative correlation for copper ion adsorption while cadmium and lead ions gave a high positive correlation. The negative correlation of Cu(II) ion may represent the adsorbent inability to hold the metal ion. On the other hand, a high positive correlation can be an indication of adequate

Table 8: Fitted isothermal and kinetic models used in various studies for removal of heavy metals.

Biosorbent	Pollutants	Fitted isotherm model	Fitted kinetics model	Ref.
Orange peel	Cu(II), Pb(II), Zn(II)	Langmuir		24
Pomegranate peel	Cu(II)	Freundlich	Pseudo second order	25
Pomegranate peel	Pb(II)	Langmuir	Pseudo second order	25
Banana peel	Cd(II)	Langmuir	Pseudo second order	26
Tea waste	Cu(II), Pb(II)	Langmuir, Freundlich	Pseudo second order	27

metal adsorption from the medium. The kinetic study shows that the applicability of the adsorption process in wastewater treatment is in the order of pseudo second order >power function> pseudo first order for cadmium and lead (II) ions while copper ion was in the order of pseudo second order > pseudo first order > power function for adsorption onto the peels of *Chrysophyllum albidum* respectively. Table 8 shows a summary of the studies performed on the utilization of fitted kinetics and isothermal models for the removal of heavy metals using agricultural waste.

3.6 Activation Energy

The Arrhenius equation continues to play a dominant role in classical studies of chemical kinetics. It shows the dependence of the rate constant over a wide range of temperature in terms of experimental activation energy (E_a) and pre-exponential factor (A). The values of the pseudo second order constant k_2 at different temperature of 30 ˚C, 40 ˚C, 50 ˚C, 60 ˚C, and 70 ˚C were deployed to estimate the activation onto *Chrysophyllum albidum* peels by the Arrhenius equation as follows:

$$lnk_2 = \ln A_0 - \frac{E_a}{RT} \quad (11)$$

Where A_o is the Arrhenius factor and R is gas constant. Straight-line plots were obtained by plotting lnk_2 constants of pseudo second order kinetics against the reciprocal of the absolute temperature in Kelvin. The activation energy of the reaction as shown in Table 9, were 12.86 kJ, 7.48 kJ and 17.14 kJ for cadmium, copper and lead ions respectively. The low activation energy indicates that the adsorption of cadmium, copper and lead ions on the adsorbent surface were rapid. The correlation coefficient and Arrhenius factor are provided in Table 9. The result shows that the removal at above ambient temperature is cost ineffective.

3.5 Erying model

Erying model explain the rates of a reaction at the transition state. The equation can be expressed as:

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R}\ln\left(\frac{k_b}{h}\right) \quad (12)$$

Where $\Delta H^{\ddagger}$ is the activation enthalpy and $\Delta S^{\ddagger}$ is the activation entropy. The plot of $ln\frac{k}{T}$ against $\ln\frac{1}{T}$ gives a straight-line graph in which slope is $\frac{\Delta H^{\ddagger}}{RT}$, intercept is $\frac{\Delta S^{\ddagger}}{R}$ + $\ln(\frac{k_b}{h})$ and $\ln(\frac{k_b}{h})$ is 23.7600.

The Erying constants are shown in Table 10. The activation energies ($E_a^{\ddagger}$) are 14.98, 20.47 and 17.17 kJ for cadmium, copper and lead ions respectively. The activation energy of Erying plot was higher than the activation energy of Arrhenius plot. The large negative values of entropy change ($\Delta S^{\ddagger}$) at the transitional state shows that the adsorbent is more ordered or rigid structured than the reactants in the ground state. The negative value of the enthalpy change ($\Delta H^{\ddagger}$) shows the exothermic nature of the adsorption and the low values show the fast rate of adsorption at the transitional state.

Table 9: Arrhenius models constants and correlation coefficients for of Cd, Cu and Pb(II) ions on peels of *C. albidum.*

Model	Parameters		
Arrhenius constants	**Cd**	**Cu**	**Pb**
A_o (g/mg.min)	5.5×10^{-6}	0.051	3.95×10^{-6}
E_a (kJ)	12.86	7.48	17.14
R^2	0.8762	-0.8364	0.8778

Table 10: Erying models constants and correlation coefficients for of Cd, Cu and Pb(II) ions on peels of *Chrysophyllum albidum*.

Model	Parameters		
Erying constants	**Cd**	**Cu**	**Pb**
Ea (kJ)	14.98	20.47	17.17
$\Delta S^{\ddagger}$ (J/mol/K)	-197.50	-93.59	-197.51
$\Delta H^{\ddagger}$ (kJ/mol)	-17.50	-20.78	-19.69
$\Delta G^{\ddagger}$ (kJ/mol)	-42.34	7.57	-40.15
R^2	0.8987	-0.7164	0.8970

3.8 Thermodynamic Studies

Thermodynamic parameters such as change in free energy (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) gives information on the amount of heat transferred during the adsorption process. The free energy change can be obtained from the temperature variation of equilibrium of the biosorption process from the equation below:

$$\Delta G^o = -RTlnk \quad (13)$$

Where ΔG is the Gibb's free energy change and determines the spontaneity and feasibility of the adsorption process, R is the molar gas constant, T is temperature in kelvin and K is the equilibrium constant. The Gibb's energy can be represented as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

Where ΔH^o is the standard enthalpy change and determines whether the process is endothermic or exothermic and ΔS^o is the standard entropy change and determines the randomness of the adsorption process. Vant' Hoff type equation shown below is applied to the computation of ΔH^o and ΔS^o.

$$lnk = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (15)$$

The Vant' Hoff plot of lnK against 1/T was plotted for cadmium, lead and copper ion and The enthalpy change and entropy change were obtained from the slope and intercept of the plot and are tabled in Table 11. The values of ΔG^o for all the studied temperatures are given in Table 11. The values of Gibb's free energy change (ΔG^o) of cadmium, copper and lead ions adsorption for all the studied temperature were found to be negative. The negative values of free energy are the indicative of spontaneous process with a high affinity of the adsorbate to the surface of adsorbent. The result shows that the adsorption process for the three metal ions are feasible and spontaneous. This might be due to the weakening of adsorptive forces between the active sites of the adsorbents and the adsorbate species and also between the adjacent molecules of the adsorbed phase [35].

The values of ΔG^o at higher temperature were more negative than in the lower temperature, showing the high efficiency of adsorption at high temperature [36]. Ghaffer [35] reported that at high temperature, the aggregation of metal ion at the surface of sorbents increases, which results in an exchange reaction with the already adsorbed species. Adsorption of cadmium and lead shows negative values of enthalpy change (ΔH^o) indicating the exothermic nature of the adsorption while copper gave a positive enthalpy change indicating the endothermic nature of adsorption. The positive values of ΔS^o show increased randomness at the solid/solution interface during the adsorption process [37]. The adsorbed water molecules, which are displaced by the adsorbate species gain more translational energy than is lost by the adsorbate ions, thus allowing the prevalence of randomness in the system [30].

Table 11: Thermodynamics constants of Cd, Cu and Pb(II) ions on peels of *Chrysophyllum albidum*.

Elements	T(K)	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol/K)
Cadmium	303	-3.6276	-14.8779	15.7675
	313	-4241.7		
	323	-3007.7		
	333	-1854.9		
	343	-2167.3		
Lead	303	-3224.5	-16.8467	11.9165
	313	-3903.4		
	323	-2255.8		
	333	-1273.5		
	343	-1454.4		
Copper	303	-4419.68	31.1775	14.22
	313	-4277.48		
	323	-4561.88		
	333	-4704.08		
	343	-4846.28		

3.9 Mechanism of Adsorption

Based on FT-IR results of *Chysophyllum albidum* reported in our previous work which displayed a number of functional groups on the surface indicating the complex nature of the studied adsorbent [3]. The spectrum shows the following functional group. −OH group of lignocellulose structures, C−H group of aliphatic compounds, C=O group of carbonyl compounds, aromatic C−H groups of methyl, methylene and methoxy groups and C−O group of alcohol or carboxylic acid. The adsorption mechanism may be proposed based on the stated functional groups to be complexation reaction.

4. Conclusion

In this study, the biosorption of cadmium, copper and lead (II) ions on *Chrysophyllum albidum* peels as a low cost and natural adsorbent was investigated. The equilibrium sorption data fitted in the order: Temkin>Freundlich> Langmuir model for cadmium ions, Freundlich>Temkin> Langmuir model for copper and lead ions while the adsorption kinetics fitted pseudo second order in the three metals studied. Arrhenius and Eyring plot indicated that cadmium ions are easily adsorbed on the adsorbent. The thermodynamic data shows that the adsorption process was exothermic in cadmium and lead removal while copper shows endothermic process in the adsorption process and Gibb's free energy shows the process was spontaneous in nature. The results would be useful for the design of wastewater treatment plant for the removal of cadmium and lead ions.

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