Equilibrium, Kinetic and Thermodynamic Assessment of the Adsorption of Copper (Cu^{2+}) Ion using *Luffa Cylindrica* Seed Shell Biomass

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ABSTRACT

The adsorption of copper (ii) ions from aqueous solution by Luffa cylindrica seed shell biomass was carried out with effects of initial metal ion concentration, solution pH, contact time, adsorbent dose and temperature of the process investigated. An optimum adsorbent dosage of 3.0g showed maximum metal uptake capacity (qe) of 1.9229 mg/g (98.2%) for an initial metal ion concentration of 2.0 mg/L and pH 5.5. Sorption equilibrium time was observed in 30 minutes. The equilibrium adsorption data were analyzed using Langmuir, Freundlich, and Temkin adsorption isotherm models. Temkin isotherm yielded the best fit to the experimental equilibrium adsorption data with a correlation coefficient (R^2) *of 0.7027. Pseudo-first-order, pseudo-second-order, and intra-particle diffusion models were used to discuss the kinetics of the adsorption. It was discovered that the adsorption of copper (ii) ions could be described by the pseudo-second-order kinetic model. Thermodynamic parameters such as enthalpy* (ΔH^0) *and entropy change of the sorption* (ΔS^0) *evaluated showed that the process was spontaneous, feasible and exothermic in nature. The results indicated that L. Cylindrica seed shell biomass can be used as an effective and low-cost adsorbent to remove copper (ii) ions from aqueous solutions.*

Keywords: Adsorption, Biomass, Copper (ii) ion, Equilibrium, Kinetics, Thermodynamics

INTRODUCTION

Heavy metals are present in the environment through natural and artificial sources. Industrialization has led to the generation of large quantities of liquid effluents, most of which contain heavy metals such as cadmium, copper, lead, nickel, mercury, arsenic, chromium and zinc[1]. Heavy metals are threats to both flora and fauna due to their bioaccumulation tendency and toxicity in biological systems[2]. Copper is often released into waterways by natural weathering of soil and rocks. Records from case-study reports of gastrointestinal illness induced by copper from contaminated water or beverages plus public health department reports for 68 incidents indicate an acute onset of symptoms. Symptoms generally appear after 15-60 min of exposure; nausea and vomiting are more common than diarrhea[3]. The removal of copper from waste water before releasing into natural water bodies is important so as to safeguard the public from copper health related problems. Conventional treatment methods such as ion - exchange, reverse – osmosis, precipitation, flocculation, electro thermal treatment and solvent extraction all have their disadvantages like incomplete metal removal, high reagent and energy requirements, high cost and generation of toxic sludges to mention but few. The search for suitable environmental – friendly alternative techniques that are affordable, efficient and can complement or replace the existing methods has been in place for some time now and attention is been directed to adsorption based on metal binding capacities of various biological materials[4-5]. In this study, the potential of *L. Cylindrica* seed shell to adsorb copper (ii) ion from aqueous solutions is being studied and the equilibrium, kinetics and thermodynamic of the process elucidated.

MATERIALS AND METHODS

Preparation of Adsorbent

The samples of sponge gourd (*L. Cylindrica*) were collected in Jos, Plateau State prior to the experiment. The seeds were separated from the fruit, washed with tap water and then air dried, the seeds were then soaked for 24 hours and the shell peeled and dried. It was then crushed using a clean mortar and pestle, sieved with 1mm mesh size. This was stored in an airtight poly ethylene bag, ready for use.

Batch Adsorption Experiments

All glasswares were washed with 1M HNO_3 and subsequently rinsed severally with deionized water to remove all possible interferences. Batch adsorption studies were carried out in 250 ml Erlenmeyer flasks to study the effects of initial copper ion concentration (0.5 mg/l to 5.0 mg/l), pH (4.5 to 5.5), contact time (5 to 120 min), adsorbent dose (3.0g) and temperature (10^0C to 45^0C). The experimental flasks were agitated at 200rpm in a rotating shaker for a specified time period. The pH of the solution was adjusted with 0.1M NaOH and HNO_3 as the case may be. At the end of the experiments, the flasks were removed from the shaker and the solutions separated from the biomass by filtration using filter paper

(Whatman no.1) and the filtrate analyzed for residual copper (ii) ion concentration using atomic adsorption spectrophotometer (AAS), model DK420. The metal uptake capacity (qe) and the adsorption percentage (R) were calculated using the following equations:

$$\frac{qe=(Ci-Ce)v}{m} -(1)$$

Where q_e= copper uptake (adsorption capacity) in mg/L

C_i= initial copper concentration in mg/L

C_f= final copper concentration in mg/L

V = volume of the Cu^{2+} solution in liters

m = weight of the biomass in grams.

$$R = \left(\frac{Ci-Cf}{Ci}\right) \times 100\text{------------------------------------} \ (2)$$

Where R = metal adsorption percentage,

C_i = initial metal concentration (mg/L)

C_f = final metal concentration (mg/L).

RESULTS AND DISCUSSION

Effect of Initial copper (II) ion Concentration

The rate of adsorption is a function of the initial concentration of the adsorbate which makes it an important factor to be considered for effective adsorption. As shown in Figure 1, the adsorption capacity at equilibrium increased with increase in initial copper (ii) ion concentration. This is considered possible due to the fact that higher initial concentration provides an important driving force to overcome all mass transfer resistance between the metal solution and *L. Cylindrica* seed shell wall and the number of collision between metal ion and the adsorbent increased with increasing initial metal ion concentration, hence enhancing the adsorption process[6]. The increase in the efficiency of the biomass could be due to the availability of the unoccupied surface area of the adsorbent since adsorption depends on the surface area of adsorbent[7]. The metal uptake can be attributed to different mechanism of ion exchange and adsorption processes[8].

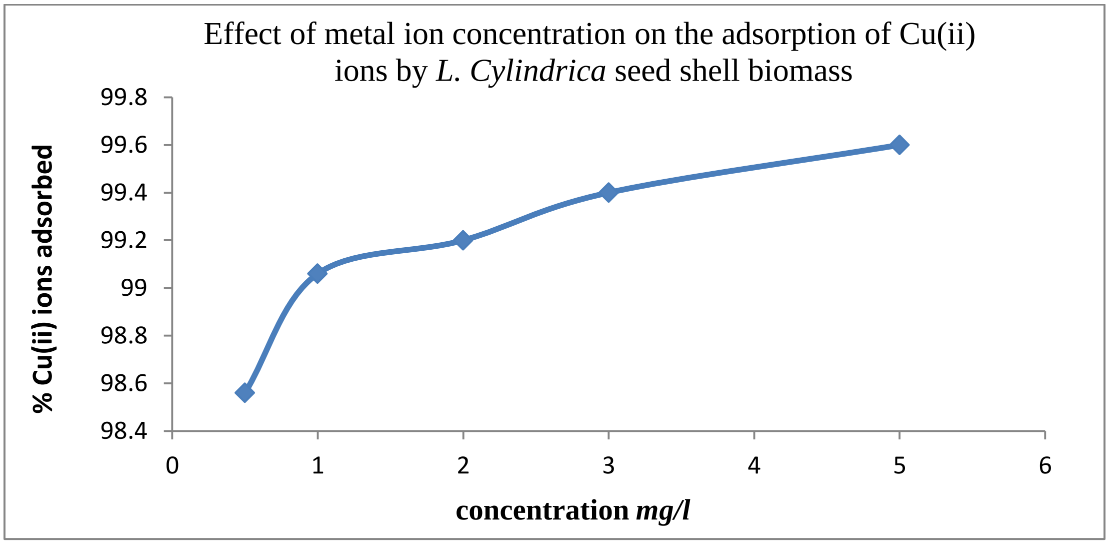


Figure 1: Effect of initial Cu^{2+} ion concentration

Effect of Contact Time on the Adsorption

The effect of contact time on the removal percentage of copper (ii) ions from aqueous solution using *L. Cylindrica* seed shell as shown in Figure 2. The rate of adsorption can be considered as one of the parameter for economical waste water treatment plant application[6, 9]. As a result, it is important to establish the time dependence of such system under various conditions. It was noticed that the Cu^{2+} uptake increased with increase in contact time. The adsorption of copper ions onto *L. Cylindrica* shell was more pronounced at 30 minutes with percentage Cu^{2+} adsorption of 99.9%. However, it can be seen from Figure 2. that the rate of Cu^{2+} ions removal decreased after 30 minutes with a contact time of 120 minutes and pH 5.5 having the least percentage adsorption of 96.1%. During the initial stage of adsorption, it is possible that a large number of uninhibited surface site are not occupied possibly due to repulsive force between the adsorbents molecules on the solid surface and the bulk phase[9].

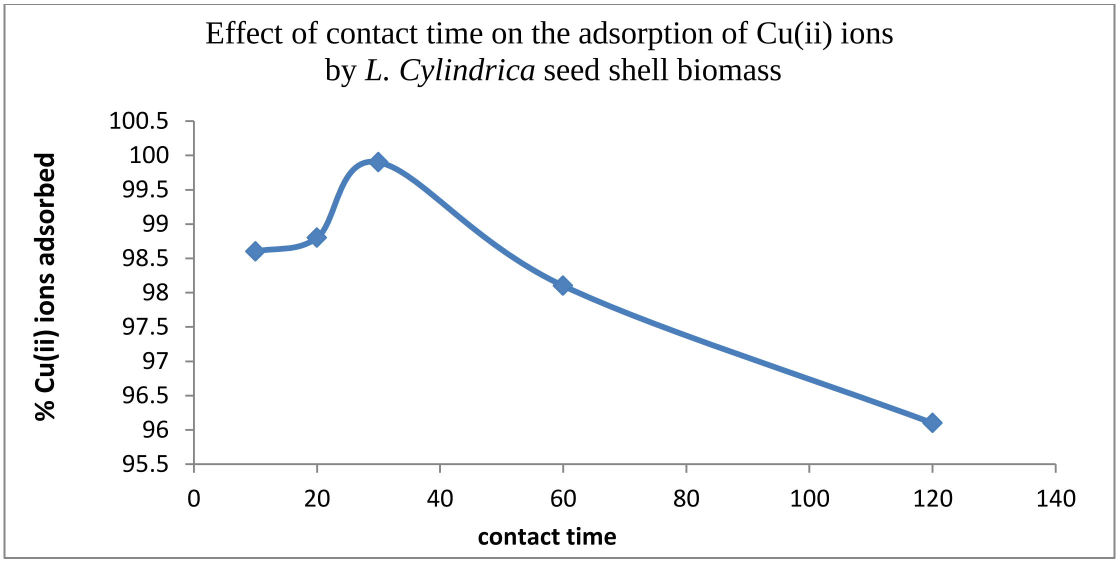


Figure 2: Effect of contact time on the adsorption of Cu^{2+} by *L. Cylindrica*

Effect of Temperature

The effect of temperature during the removal of Cu (ii) ions by *L. Cylindrica* seed shell was also investigated over the range of 10℃-45℃. The effect of different value of temperature on heavy metals uptakes using adsorbate initial concentration of 2mg/1, pH 5.5 and 3g of adsorbent in 30 minutes contact time is shown in Figure 3. It is shown that the effect of temperature on removal of Cu (II) ion is maximum at a temperature of 45 having 98.2%. The maximum heavy metal uptake recorded at a high temperature is attributed to increase kinetic energy and mass transfer of cautions[10]. At a high temperature due to rupture of functional group on adsorbent surface, there may be an increase in number of active sorption with the rise in temperature[11-12]

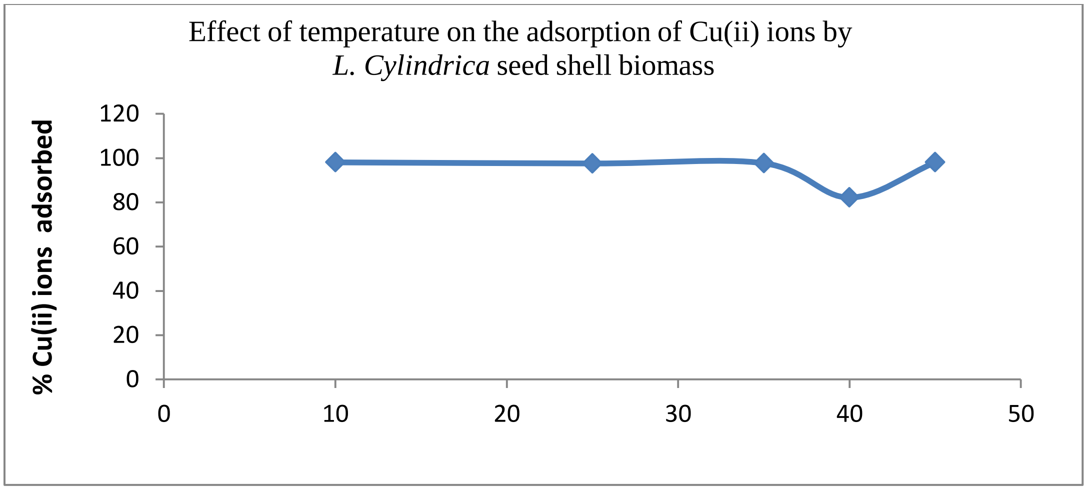


Figure 3: Effect of temperature on the adsorption of Cu^{2+} by *L. Cylindrica*

Adsorption Isotherm Modeling

Adsorption isotherm is the basic requirement for designing any adsorption system. Isotherm expresses the relation between the amounts of adsorbate removed from the liquid phase by a unit mass of adsorbent at constant temperature[13]. The extent of adsorption was estimated using the Langmuir, Freundlich and Temkin adsorption isotherms. The obtained experimental data are fitted with the Linearized form of these four two-parameter isotherm models.

Linearised Langmuir Isotherm:

$$\frac{1}{\text{qe}} = \frac{1}{qmax} + k_l C_e + \frac{1}{qmax} ------------ \quad (3)$$

Where C_e = is the equilibrium concentration of Cu (ii) ions (mg/L),

q_e= is the amount of metal adsorbed per specific amount of adsorbent(mg/g),

Qmax = is the maximum adsorption capacity (mg/g) and

K_L = is the Langmuir equilibrium constant (L/mg) related to energy of adsorption which quantitatively reflects the affinity between the adsorbent and adsorbate. Where $q_{max}K_L$ can be determined from the linear plot of q_e/C_e Vs q_e. The essential features of the isotherm were expressed in terms of dimentional constant; separation factor (R_L) defined by the relationship:

$$R_L = \frac{1}{1+KLCi} -------------- (4)$$

Where C_i — is the initial concentration (mg/L)

K_L = is the Langmuir equilibrium constant (L/mg).

The value of separation factor (R_L) provides important information about the nature of adsorption. The value of (R_L) indicates the type of Langmuir isotherm to be irreversible

($R_L = 0$), favourable($0<R_L<1$), linear ($R_L =1$) or unfavourable ($R_L >1$). Apparently when $K_L>1$), sorption is favourable[14]

The Freundlich isotherm, applicable to non-ideal heterogeneous surfaces was chosen to estimate the adsorption intensity of the adsorbent and the linear form of the isotherm can be represented as:

$$Inq_e = InK_f + {}^{I}/_{n} InC_e \text{-----------------------------} (5)$$

Where K_F = is the Freundlich constant related to sorption capacity (mg/g)

$(L/g)^{1/n}$ n = is related to the adsorption intensity of the adsorbent.

Where K_F and 1/n can be determined from the linear plot of $1nq_e$ versus $1nC_e$[15]. Temkin isotherm model takes into account the interactions between adsorbents and metal ions to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage[16].
Temkin isotherm: $q_e=RT/b_T(AC_e)$………………………………….(6)
Linearised form: $qe = BInA + BInC_e$...(7)

Where C_e = is the equilibrium concentration of the adsorbate (mg/L),
q_e= is the amount of adsorbate adsorbed at equilibrium (mg/g)
$RB/b_T = B$ where T is the temperature of (K)

R is the ideal gas constant ($8.314Jmo1^{-1}k^{-1}$), and A and B are constants. A plot of q_e Vs lnC_e enables the determination of A and B. The constant B_T is related to the heat of adsorption and A is the equilibrium binding constant (L/min) corresponding to the maximum binding energy.

Langmuir, Freundlich and Temkin plot adsorption isotherm linearized plot for Cu (ii) ions are given in Figure 4,5 and 6. Langmuir and Freundlich constants are evaluated from the isotherm with their correlation coefficient presented in Table 1.

It was found that the Langmuir model gave the best fit with experimental results for Cu (ii) ion based on R^2 value. Thus, indicating that *L. Cylindrica* seed shell would provide a monolayer and homogenous adsorption for Cu (II) ion. A similar observation was reported for adsorption of Cu (ii) ion on clay[17]. The value of separation factors R_L for all initial concentration are shown in Table 2. The values range from 0.0052-0.0487. The values are found to be less than one and greater than zero indicating favorable sorption of Cu (ii) ions onto the biomass[18].

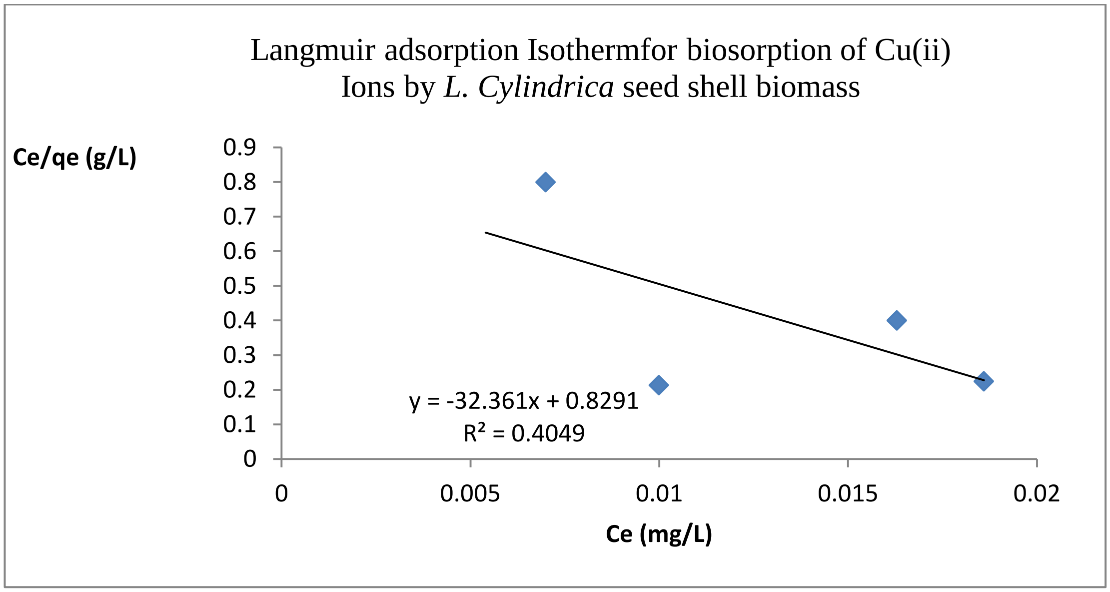


Figure 4. Langmuir isotherm model for copper (ii)adsorption.

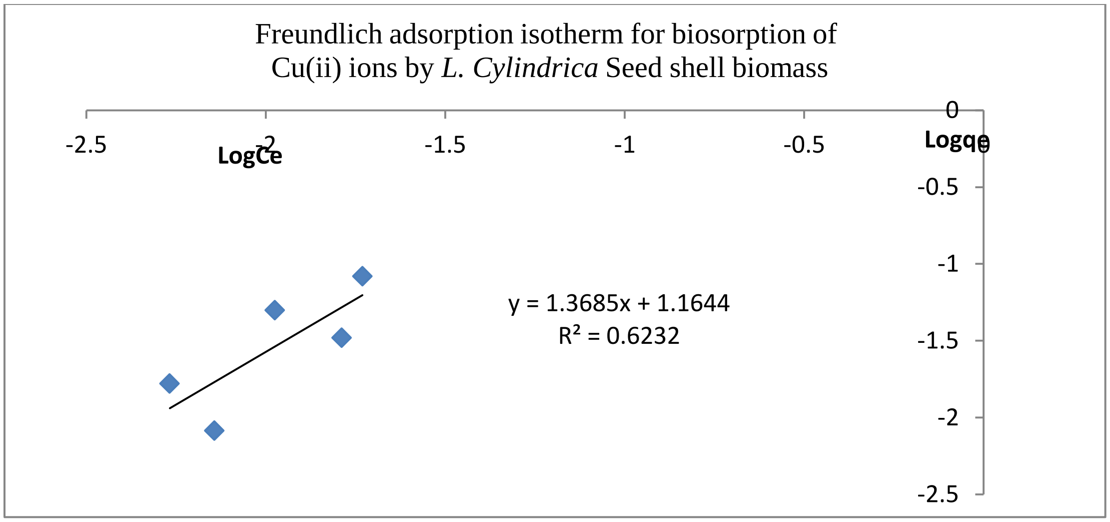


Figure 5. Freundlich isotherm model for copper (ii) adsorption.

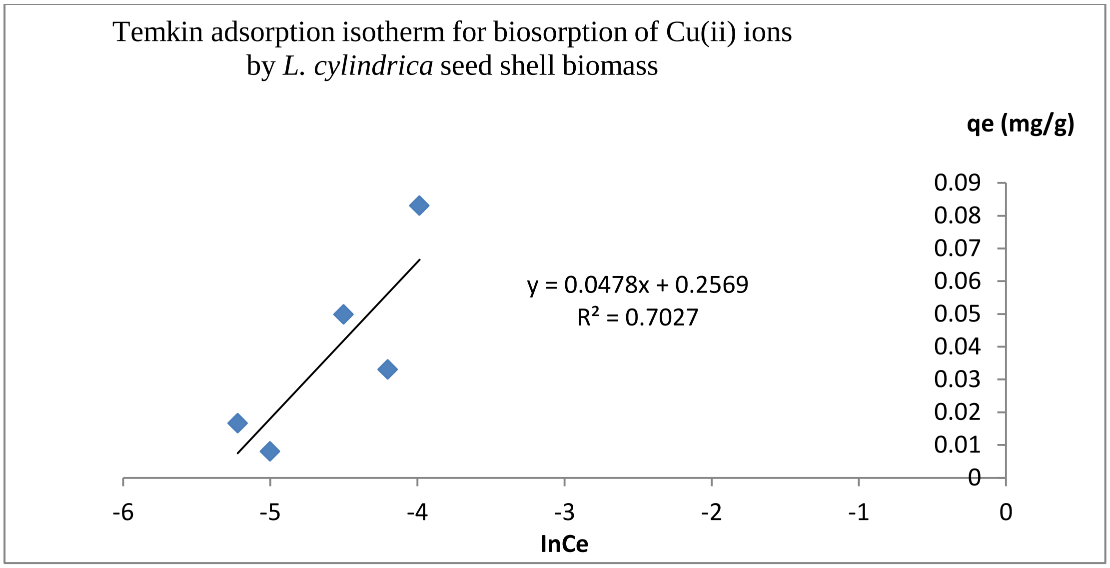


Figure 6. Temkin isotherm model for copper (ii) adsorption

Table 1: ***Summary of Adsorption Isotherm Constants for Copper (ii) ions Sorption onto Luffa Cylindrica seed shell biomas***

Langmuir	Freudlich	Temkin Isotherm
K_L =39.1 L/Mg	K_f =14.59	A = 601.8
R^2 = 0.4049	1/n = 1.368	B = 0.0047
	n = 0.7310	R^2= 0.7027
	R^2 = 0.6232	

Table 2: ***Dimensionless Langmuir separation factor concentration (mg/l)***

Concentration	0.5	1.0	2.0	3.0	5.0
RL	0.0487	0.0249	0.0126	0.0085	0.0052

Adsorption Kinetic Modeling

Kinetic data were fitted using Lagergren pseudo-first-order[19], and pseudo-second order[20] and an intra-particle diffusion[21] model to investigate the mechanism of the adsorption and potential rate controlling steps such as mass transport and chemical reaction processes. The first-order Lagergren equation is given as;

$$Log\ (logq_e) - \frac{kit}{2.303} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (8)$$

The pseudo-second order equation is,

$$\frac{t}{qt} = \frac{1}{k2qe^2} + \frac{t}{qe} - - - - - - - - - - - - - - - - -(9)$$

Where q_e=is the mass of metal adsorbed at equilibrium (mg/g),

q_t = the mass of metal adsorbed at time t (min),

k_1 = the pseudo-first order rate constant of adsorption (min$^{'1}$)

k_1 = the pseudo-second rate constant of adsorption (mg/g.min).

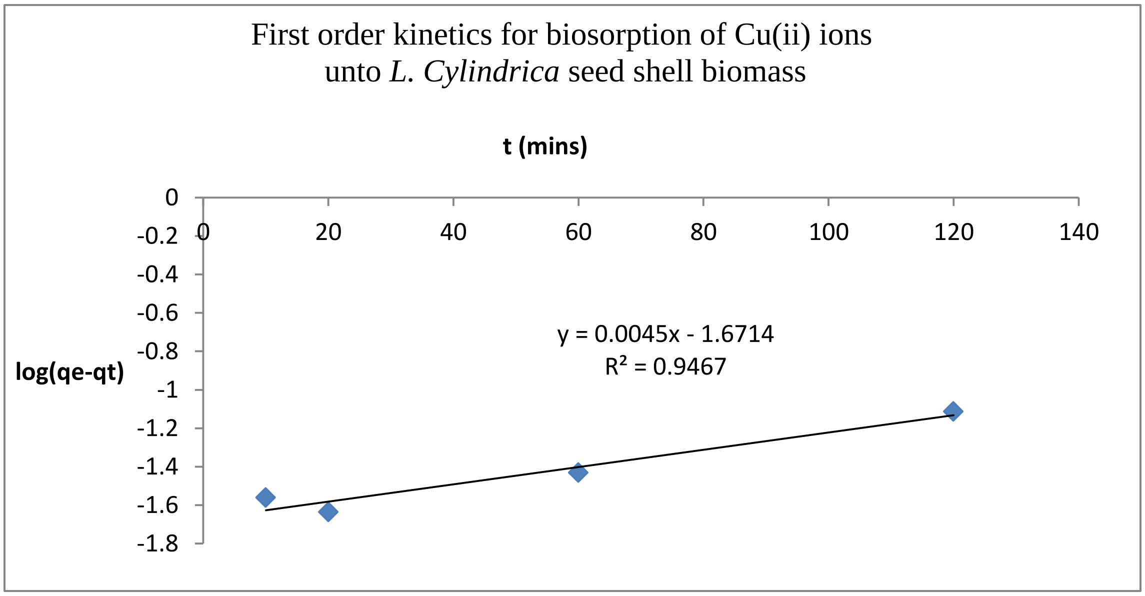
The intra-particle diffusion equation can be written as follows:

q_t=$K_d t$½ + *1* ……………………………..(10)

Where I = is the intercept which describes the boundary layer thickness

k_d(m*g/ g. min* ½)= is the rate constant of intra-particle diffusion.

The value obtained for K_1 and K_2 for correlation coefficient R^2 are K_1 R^2 = 0.9467 and K_2 = R^2 = 0.9999. It can be shown that the pseudo-second order model has excellent linearity with R^2 = 0.9999 in comparison to pseudo-first order. The value of rate constant K_2 suggests lower competition for the surface active sites by the metal ions and consequently high sorption rate[12].



First order kinetics for biosorption of Cu(ii) ions unto *L. Cylindrica* seed shell biomass

Figure 7. First order kinetics for copper (ii) adsorption

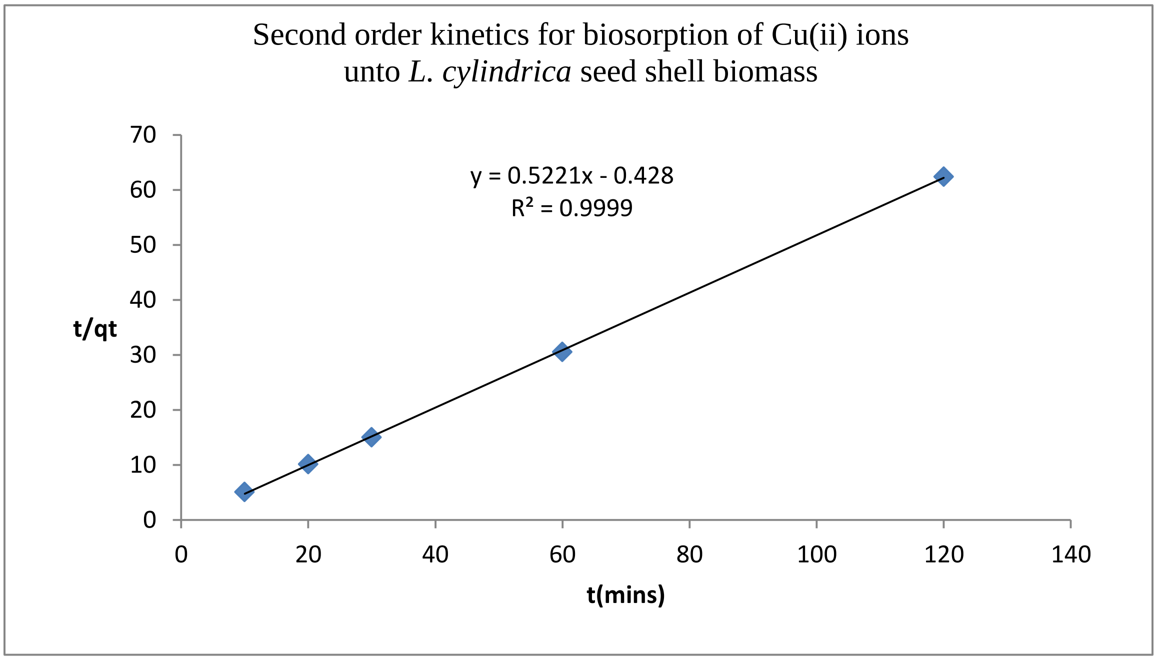

Second order kinetics for biosorption of Cu(ii) ions unto *L. cylindrica* seed shell biomass

Figure 8. Second order kinetics for copper (ii) adsorption.

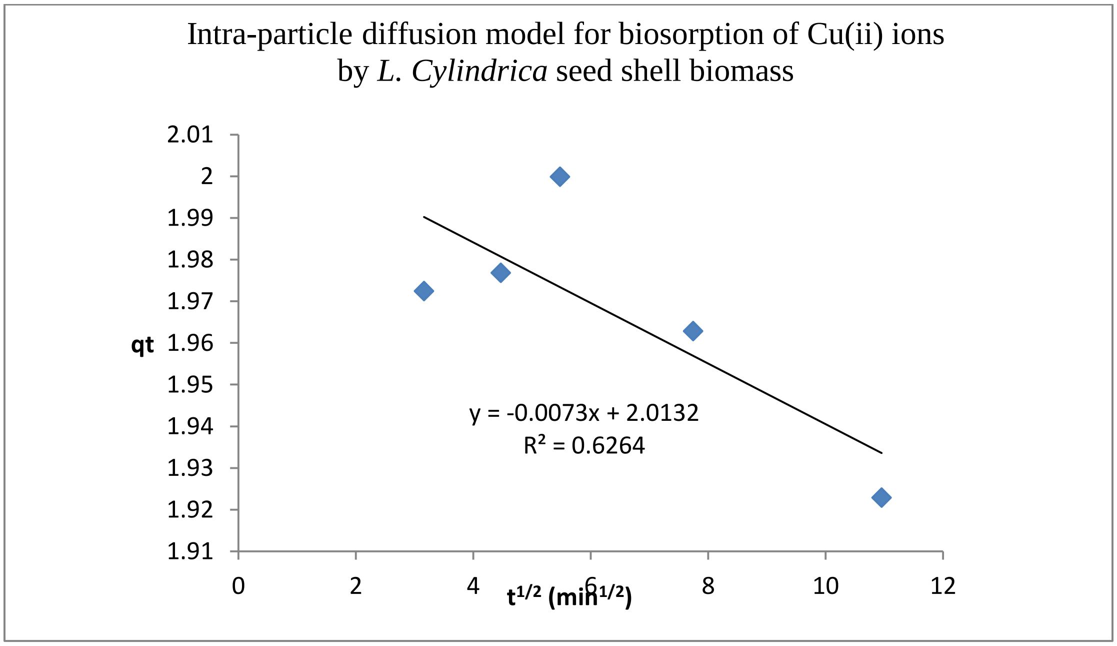

Intra-particle diffusion model for biosorption of Cu(ii) ions by *L. Cylindrica* seed shell biomass

Figure 9. Intra-particle diffusion model for copper (ii) adsorption

Table 3: ***Comparison between kinetic models for Copper (II) ions sorption onto L. Cylindrica seed shell biomass.***

Pseudo-first order	pseudo second	intra-particle
qe, exp = 1.9229mg/g	Order	Diffusion
qe, cal = 0.0213	K_2 = 0.6367	Kd = 0.007
K_1 = 0.0092	qe, cal = 1.916	I = 2.013
R^2 = 0.9467	R^2 = 0.9999	R^2 = 0.6264

Thermodynamic Treatment of the Sorption Process

In order to study the feasibility of the sorption process, the thermodynamic parameters such as free energy, enthalpy and entropy changes were estimated from the following equations.

$$K_c=\frac{CAe}{Ce}, ------------(11)$$

$$\Delta G^{o} = - RTInK_{C}\text{---------------------------------}\ (12)$$

$$Log\ K_C = \frac{\Delta S^{\circ}}{2.303\mathrm{R}} - \frac{\Delta H^{\circ}}{2.303\mathrm{RT}} ---------(13)$$

Where C_e= is the equilibrium concentration in solution in mg/L

C_{Ae} = is the equilibrium concentration on the sorbent in mg/L

K_C = is the thermodynamic equilibrium constant.

T = is the absolute temperature in Kelvin

R = is the universal gas constant (8.314JK^{-1} $mo1^{-1}$)

The potential sticking probability (S^*) was also calculated and used to deduce the activation energy (E_a) for the sorption process to ascertain whether the sorption process was of physisorption or chemisorption mechanism. They were calculated using the Arrhenius equation related to surface coverage (θ) as follows:

$$\theta = \left(\frac{1-Ce}{Ce}\right) \text{ and } S^{*}= (1-\theta)exp - \frac{Ea}{RT} ---------(14)$$

The sticking probability, S^*, is a function of the adsorbate/adsorbent system under consideration but must satisfy the condition $0<S^* <1$ and is dependent on the temperature of the system. The value of $E_a$and S^* can be calculated from slope and intercept of the plot of ln $(1-\theta)$ versus l/T respectively. $S^* >1$ indicates no sorption, S = 1 indicates mixture of physiosorption and chemisorption, S = 0 indicates that chemisorption is the predominant mechanism and $0 <S^* <1$ indicates that physiosorption is the predominant mechanism.

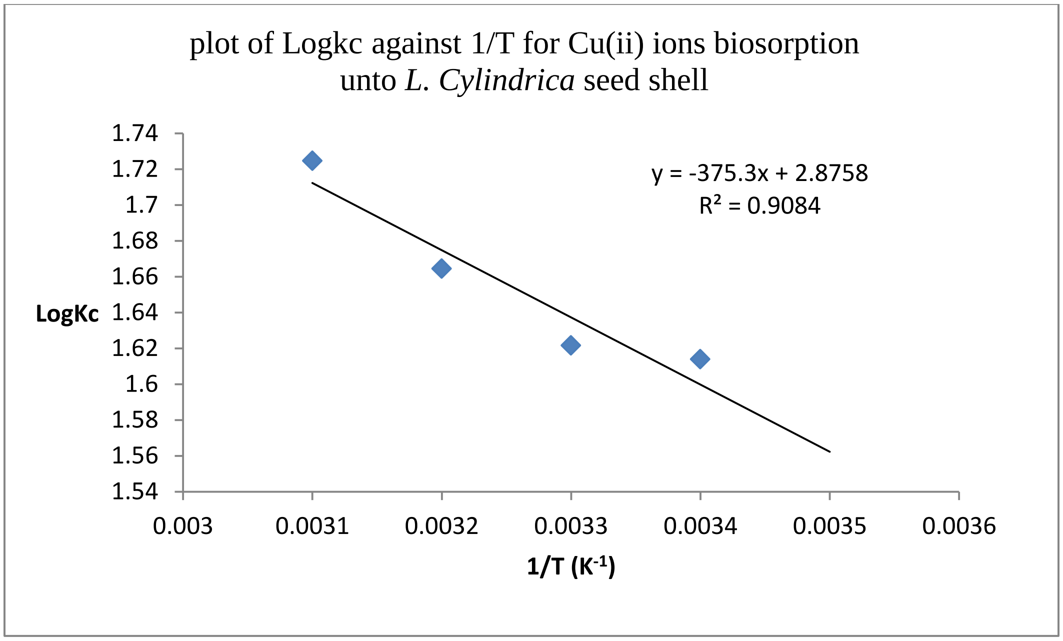


Figure 10. The plot of logKc against 1/T for Cu^{2+} (ii) ion adsorption

Table 4: ***Values for Gibb's Free Energy at Various Temperatures***

T^0K	283	298	308	313
ΔG^0*kj/mol*	-8.34	-9.20	-9.75	-10.03

Table 5: ***Thermodynamic Parameters for adsorption of Cd (II) ions onto Luffa Cylindrica seed shell Biomass.***

ΔS^0kj/mol	*ΔH^0kj/mol*	*S**	*Ea/kjmo*
0.055	7.19	8.01	0.0019

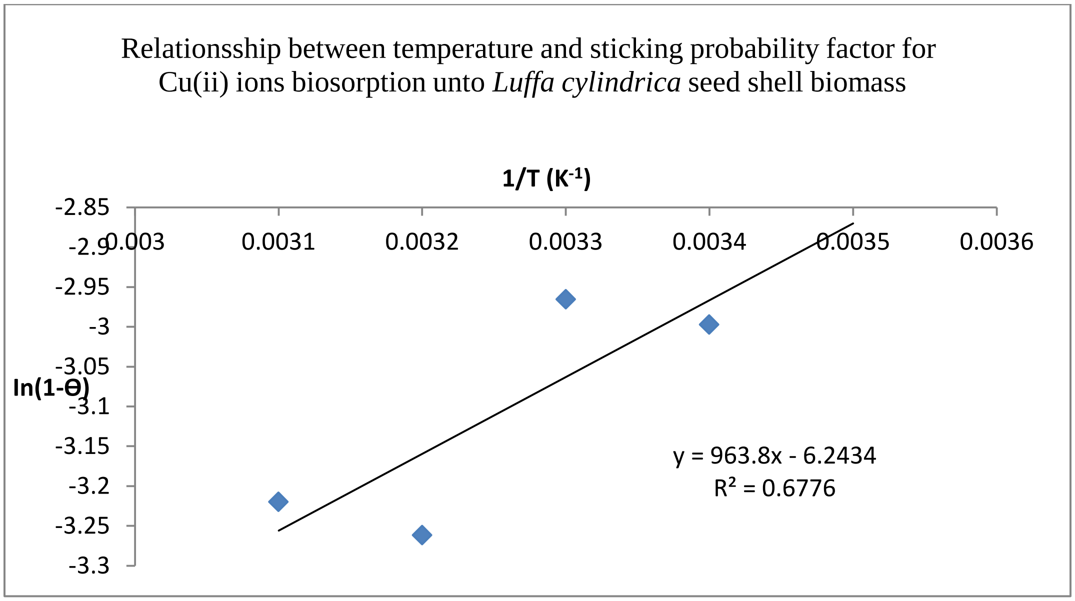


Figure 11. The relationship between temperature and sticking probability for Cu^{2+} adsorption

CONCLUSION

The removal of metal ions from aqueous solution is of paramount importance environmentally. The result of copper (ii) ion adsorption by *L. Cylindrica* seed shell showed that it is a good alternative adsorbent for Cu^{2+} ion removal from aqueous solution. The experimental parameters such as initial solution concentration, temperature and contact time adsorbent dosage was examined and proved to be important parameters in the description of the adsorption process.

The linear fitting of the Langmuir, Freundlich and Temkin isotherms batch data were used. The adsorption behaviour of Cu^{2+} ion fitted more in Temkin, judging from the correlation coefficient $R^2 = 0.7027$. For the three kinetic models used to adjust the sorption, the best filled was the pseudo-second order model (0.9999). The thermodynamic was described by linearized equation and revealed that the process was spontaneous with increased enthalpy and decreased entropy. Parameters obtained showed that *L. Cylindrica* seed shell could be a good adsorbent for for copper (ii) ion adsorption.

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