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Adsorption of copper (II) ions onto raw *Globimetula oreophila* (Afomo ori koko) leaves

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This study examined the adsorption of copper onto raw *Globimetula oreophila* leaves. The adsorbent surface nature was examined using scanning electron microscopy and Fourier transform infrared spectroscopy. Adsorption parameters such as the $-\log_{10}[H^+]$, point of zero charge, initial metal concentration, mass of biomass and contact time were determined. Copper adsorption decreased gradually with pH. The point of zero charge (PZC) obtained was 4.5. The percentage adsorption capacity increased from 97.6 to 99.3% as the initial amount of copper rose from 20 to 100 mg/L. Temkin isotherm gave the best fit (R^2=0.99) in describing the adsorption equilibrium process. Contact time effect resulted in an equilibrium attained in 15 min due to the initial rapid increase in adsorption. Kinetic data were excellently fitted to the pseudo-second order model. Thermodynamic studies affirmed a spontaneous and endothermic adsorption process. The activation energy and the energy of adsorption obtained affirmed that the adsorption process was chemisorption. *G. oreophila* is a recommendable adsorbent for the remediation of copper contaminated soil.

Key words: *Globimetula oreophila*, kinetics, adsorption, isotherm, copper.

INTRODUCTION

Toxic metals availability in the environment are major problem to the world because of its adverse effect on human race. These metals even in trace amount are very harmful to man and his environment. They are persistent in the environment and cannot be degenerated or destroyed. They are found to aggregate in the soil, sediment, seawater and freshwater (Chowdhury and Saha, 2012). The effluents containing heavy metals are discharged into water bodies. Culpable industries are paints and pigments, refineries, metal cleaning and plating baths, fertilizer, paper board mills, wood preservatives, printed circuit board production, pulp, wood pulp production (Chowdhury and Saha, 2012; Zhu et al., 2009, Alao et al., 2014).

Copper is one of the most harmful metals to man and animals if it exceeds the permissible levels. The copper levels in drinking water based on the study from Europe, Canada and USA range from ≤0.005 to >30 mg/L, with the primary source most often being the corrosion of interior copper plumbing (US EPA, 1991; Health Canada, 1992; IPCS, 1998; US NRC, 2000; WHO, 2004). The effluents from industries mostly have high amount of copper (II) ion (Tong et al., 2011). Human ingestion of excess copper ions may lead to possible necrotic

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changes in the liver and kidney, gastrointestinal irritation, central nervous problems, hepatic and renal damage, mucosal irritation, severe liver and brain damages, widespread capillary damages and depression (Ajaelu et al., 2017a; Ajmal et al., 1998; Larous et al., 2005).

Several methods available for reducing or totally removing the heavy metal from industrial wastewater include chemical precipitation, evaporation, ion exchange, reverse osmosis, filtration, solvent extraction, oxidation and electro deposition (Tong et al., 2011; Wang and Qin, 2005). The constraint associated with these procedures include the difficulty in removing low amount of heavy metals, inability to apply this method to considerable range of pollutants, it is not cost effective and mostly used for ex-situ amelioration (Ahmada et al., 2014). The use of activated carbon for adsorption is seen as effective but it is quite costly.

Globimetula oreophila is a member of the Loranthaceae family of parasitic mistletoes. Their leaves are greenish. 1000 species and about 75 genera are present in the Loranthaceae *family. G. oreophila* are found in the South West, South- South and South East of Nigeria. They are also found in the North West of Cameroon. All mistletoes species are members of the Loranthaceae family except those of North America and Europ*e.* More than 60 species of the family have been located in West Africa. Some of the trees on which *G. oreophila* are found include cocoa tree, rubber tree and orange tree among others. It is acclaimed by the traditional health practitioners in Nigeria that the extracts of *G. oreophila* are employed in the prevention, treatment and management of cardiovascular related diseases and ailments (Faboro et al., 2018).

This study investigated the viability of *G. oreophila* for the adsorption of copper (II) ions from simulated waste water. Parameters studied included the effects of biomass, pH, point of zero charge and initial metal concentrations. Adsorption kinetics and effect of temperature were also studied.

MATERIALS AND METHODS

G. oreophila leaves were harvested from Cocoa tree in Ondo State, Nigeria. The chemicals used include $CuSO_4.5H_2O$, HCl and NaOH. All these chemicals are of analytical grade.

Biomass preparation

The *G. oreophila* leaves were washed with distilled water and air dried after which they were oven-dried at 105°C overnight. Pulverization of the dried leaves was carried out followed by the screening through a 1 mm sieve to obtain the geometric size and then stored in an air tight plastic bag.

Adsorption studies

Biosorption procedures were carried out by varying the amounts of solution pH, initial Cu (II) ions concentration (having a pH of 4.57), mass of adsorbent, contact time and temperature under batch experiments. Adjustment of the solution pH was done by adding either 0.1 M NaOH or 0.1 M HCl solutions before adsorption experiment. The experiments took place on a Stuart Orbital Shaker at 250 rpm. The amount of Cu (II) ions was obtained using Atomic Absorption spectrophotometer (PG 990, PG instruments, Britain). The studies were performed in duplicate and the average value was used for later calculation.

The amount of *G. oreophila* adsorbed was given by:

$$q = \frac{(C_o - C_e)}{W} xV \qquad (i)$$

$$\% \text{ adsorption capacity} = \frac{(C_o - C_e)}{C_o} x100 \qquad (ii)$$

Where q(mg/g) is the adsorption capacity, C_o (mg/L) and C_e (mg/L) are the initial Cu^{2+} ion concentration and equilibrium Cu^{2+} ion concentration respectively, V(L) is the volume while W (g) is the mass of the adsorbent.

RESULTS AND DISCUSSION

SEM and FTIR analysis

The surface structure was characterized by SEM as presented in Figure 1. The surface has irregular, flat sheets containing some pores. The irregular sheets are in layers. There may be the possibility of the adsorbent having a microporous and a mesoporous surface. Functional groups are possible adsorption sites for dyes. FTIR analyses of raw *G. oreophila* without and with copper as presented in Figure 2a and b reflect the following functional groups: Vibrational frequency appeared between 3514.9 and 3941.7 cm^{-1} attributed to the O-H stretching which shifted from 3520.5 to 3893.2 cm^{-1} for adsorbent with copper. The band at 3384.4-3514.9 cm^{-1} attributed to the N-H stretch shifted to 3230.7-3503.7 cm^{-1} in the *G. oreophila* with copper. The bands at 1636.3 - 1653.1 cm^{-1} corresponding to C=O of amide were shifted to 1638.2 - 1684.8 cm^{-1} for adsorbent with copper. The band at 1375.4 cm^{-1} for adsorbent without copper was shifted to 1319.5-1362.3 cm^{-1} for adsorbent with copper and is assigned to C-H rock of alkane. The band observed at 1164.8 - 1217.0 cm^{-1} for adsorbent without copper are attributed to -C-O stretch of alcohol was shifted to 1036.3 - 1217.0 cm^{-1} for adsorbent with copper. The band observed at 1164.8 - 1217.0 cm^{-1} for adsorbent without copper are attributed to -CN stretch aliphatic amine was shifted to 1036.3 - 1217.0 cm^{-1} for adsorbent with copper. These results show that the major functional groups responsible for the adsorption process are amide, amine and alcohol.

Effect of pH

The pH of solution has played a major role in the

Figure 1. SEM of raw *G. oreophila.*

Figure 2. FTIR of *G. oreophila* (a) before adsorption; (b) after adsorption of copper (II) ions.
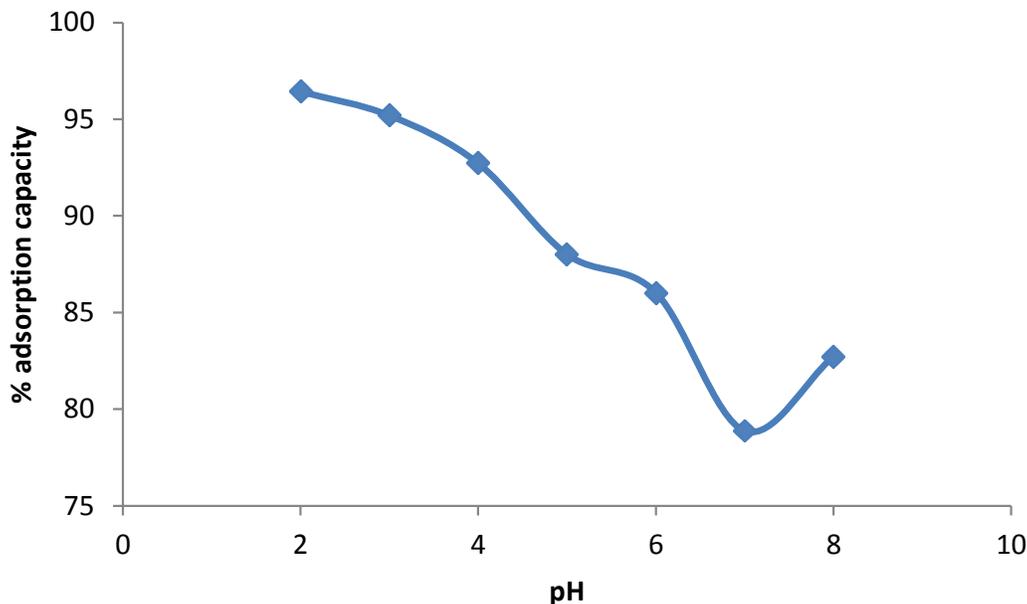
Figure 3. pH effect on the sorption of copper on *G. oreophila*.

adsorption of heavy metals from aqueous solution and consequently waste water. The effect of pH was considered in the range 2.0 to 8.0 as seen in Figure 3. The pH at which the net surface charge on an adsorbent is zero is referred to as the point of zero charge, PZC. When the pH value is lower than PZC the number of negatively charged sites on the adsorbent reduces which results in the increase in the number of positively charged sites which enhances the adsorption of anions. At pH values greater than PZC, there is increase in the number of negatively charged sites on the surface of the adsorbent such that the extent of adsorption of cations increases because of ionic attraction between the negatively charged surface and the cationic adsorbate. The result obtained is quite surprising. Percentage adsorption increases with decrease in pH. The PZC obtained for *Globimetula oroephila* is 4.5 as shown in Figure 4. Below that value, the surface of the adsorbent is expected to be positively charged and the adsorbate is also positively charged. Possible explanation is that there may be some negatively charged functional groups responsible for the attraction and increase.

Initial copper concentration

Initial metal concentration has significant effect on the adsorption of metals by adsorbents. Figure 5 shows that percentage adsorption capacity increased from 97.6 to 99.3% as the initial metal concentration increased from 20 to 100 mg/L. This can result from the fact that at higher initial copper concentrations more vacant sites are available for adsorption. The variant concentrations

enable the essential driving force to overwhelm the mass transfer of copper (II) ions between the solid and aqueous phases.

Effect of mass of biomass

Adsorbent mass is known to affect the capacity of adsorption of various adsorbents. Figure 6 reports the adsorptive removal of Cu(II) ions by *G. oreophila*. Adsorption capacity of *G. oreophila* reduces with a rise in the mass of biomass. The reduction in the amount of copper adsorbed at the surface of *G. oreophila* with increase in mass of biomass can be ascribed to the concentration gradient or split in the flux between the amount of copper in the solution and that on the surface. Therefore, the amount of copper adsorbed onto unit mass of adsorbent (*G. oreophila*) reduces as the adsorbent weight rises, thus leading to a reduction in the amount of Cu(II) ions adsorbed (q_e) as the weight of adsorbent rises. Similar findings had been described by Ajaelu et al. (2017a) and Zafar et al. (2006).

Adsorption isotherms

Equilibrium adsorption isotherms are vital in designing adsorption process for they strongly imply metal ions distribution between the phases that are liquid and the adsorbent at equilibrium with respect to the metal concentration. Each time an adsorbent contacts a solution of metal ion, the surface of the adsorbent experiences a sudden rise in the concentration of metal ions until a
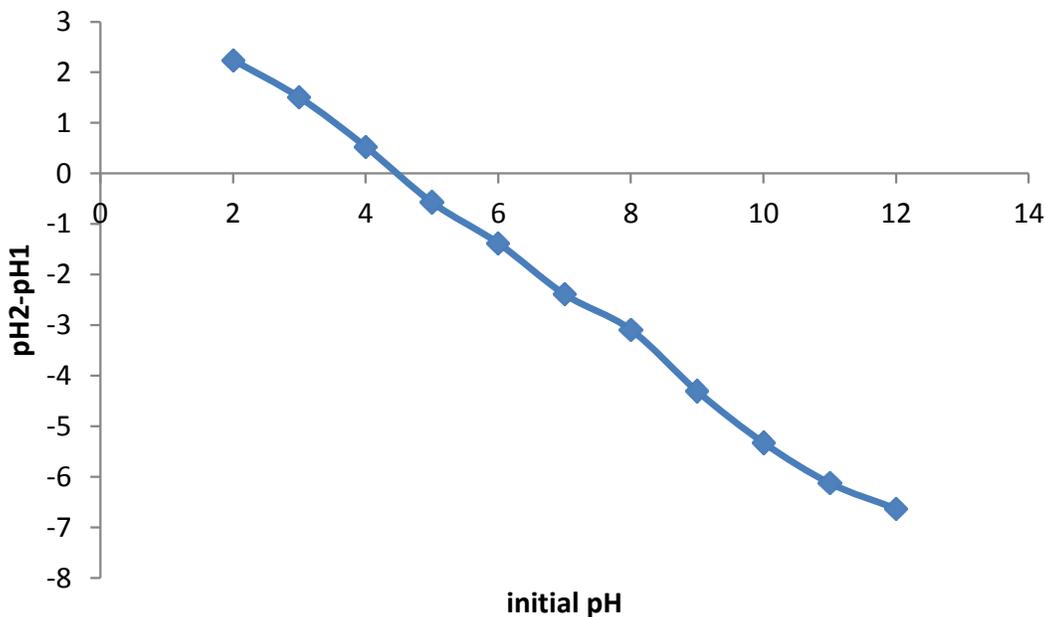
Figure 4. Point of zero charge effect on copper (II) ions biosorption onto *Globimetula oreophila.*
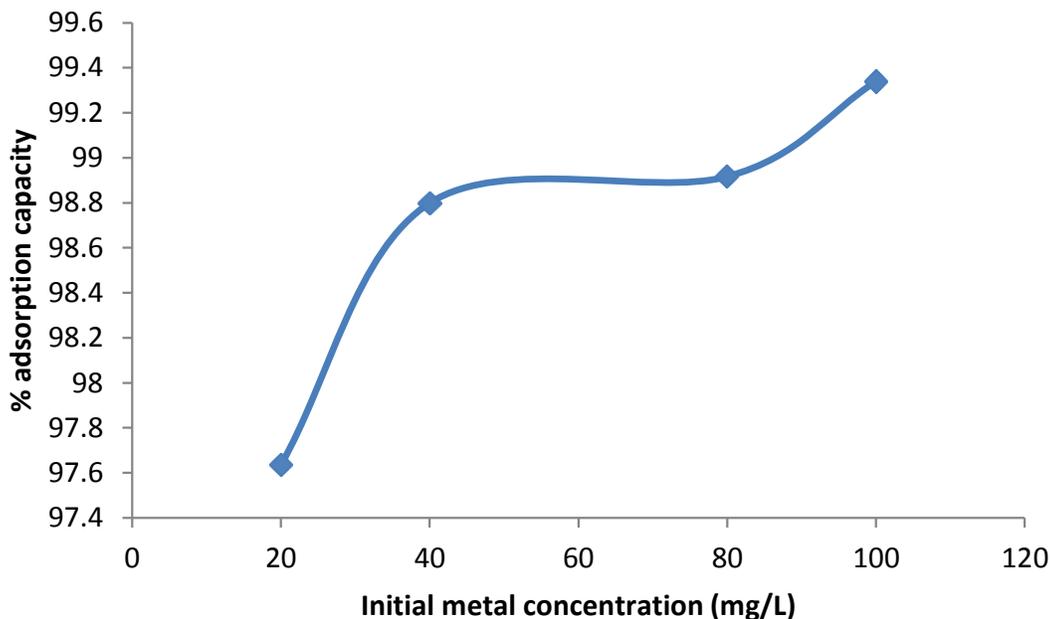
Figure 5. Initial metal concentration effect on the adsorption of copper on *Globimetula oreophila.*

dynamic equilibrium is attained. Four biosorption models specifically, Langmuir, Freundlich, Temkin and Dubini-Radushkevich were employed to describe the adsorption of copper on *G. oreophila.*   The Langmuir model surmises that adsorption sites are equivalent and adsorption at each site is not dependent on adsorption or desorption at adjacent sites. The linear expression of the Langmuir equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \qquad (3)$$

Where C_e and q_e are the amount of solute in the solution at equilibrium ((mg/L) and the amount of solute adsorbed per unit mass of adsorbent (mg/g), respectively. Q_o (mg/g) refers to the highest level of monolayer uptake
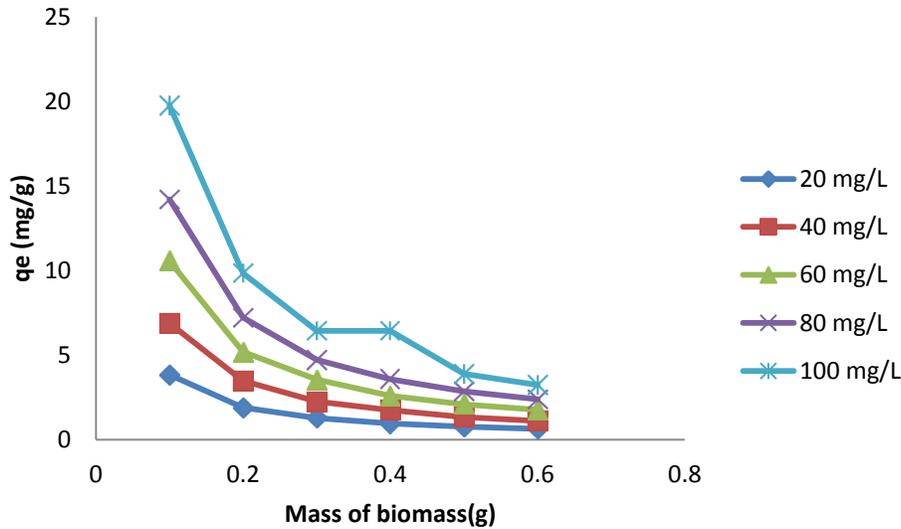
Figure 6. Mass of biomass effect on the adsorption of copper by *Globimetula oreophila.*
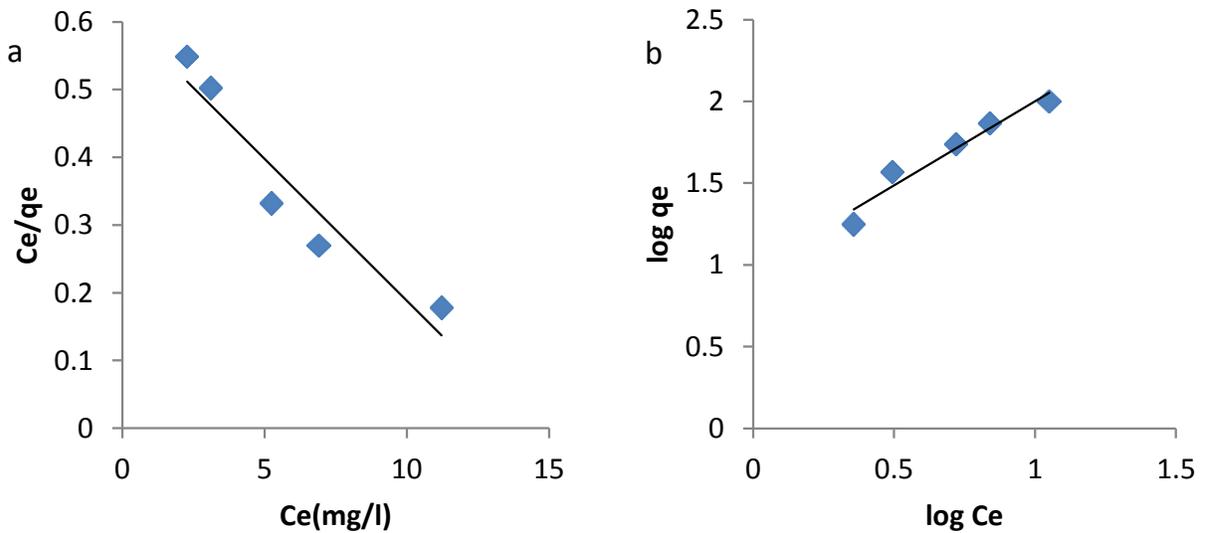
Figure 7. (a) Langmuir and (b) Freundlich isotherms for the adsorption of copper onto *G. oreophila.*

capacity and b (L/mg) is a constant associated with the free energy of adsorption. Figure 7a presents the graph of C_e/q_e and the amount at equilibrium (C_e). The slope and intercept from the plot were used to calculate the values of Q_o and b as presented in Table 1. A dimensionless equilibrium factor, R_L that describes the favourability of adsorption was obtained from the expression (Weber and Chakkravort, 1974).

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

R_L value calculated as reported in Table 1 shows that the

adsorption of copper by *G. oreophila* was favourable since its value is between 0 and 1. The Freundlich expression assumes a heterogeneous surface adsorption. The linear expression for the Freundlich isotherm is:

$$\log q_e = \log K_x + \frac{1}{v} \log C_e \qquad (5)$$

Where K_x is a constant which is a measure of the relative uptake capacity of the adsorbent and v' is a constant which is a measure of adsorption intensity as well as the heterogeneous nature of the surface of the adsorbent. Values of K_x and v, were obtained from the plot of log q_e

Table 1. Freundlich, Langmuir, Temkin and Dubinin–Radushkevich Isotherms for the adsorption of copper on *G. oreophila*.

Langmuir	Freundlich	Temkin	D-R
Q_o = 23.9 mg/g	K_x = 9.40	A = 0.65 mg/g	q_x = 1.05 mg/g
b = 0.069 L/mg	v = 1.00	B = 48.2	β = 2.8 x 10^{-3}
R^2 = 0.91	R^2 = 0.94	R^2 = 0.99	E = 20.4 kJ/mol
R_L = 0.127			R^2 = 0.95
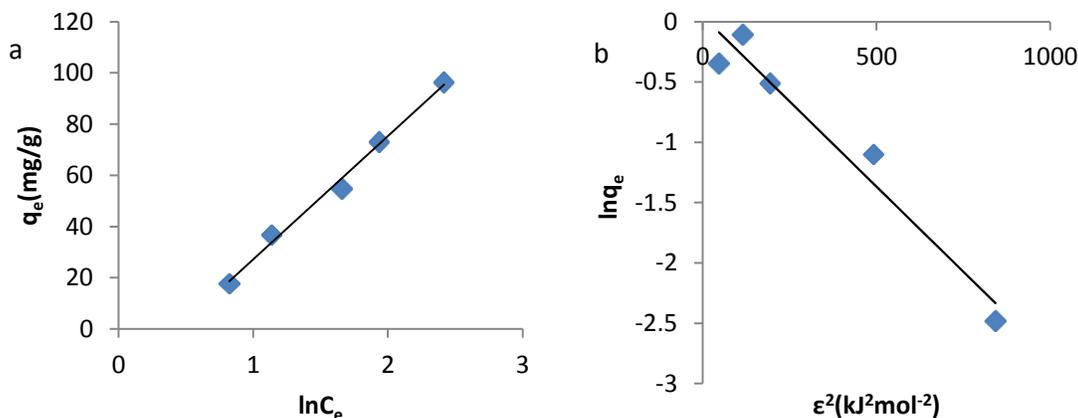
Figure 8. (a) Temkin and (b) Dubinin Rudishkevich isotherms for the adsorption of copper onto *Globimetula oreophila*.

and log C_e as presented in Figure 7b.

The Temkin isotherm (Temkin, 1941) considered the interaction between the adsorbate and the adsorbent. This isotherm assumes a reduction in the heat of biosorption of molecules in the layer. Temkin expression is given as:

$$q_e = B \ln A + B \ln C_e$$

Where $B = \dfrac{RT}{b}$

The temperature and the gas constant are represented by T(K) and R (Jmol^{-1}K^{-1}) respectively. The constant b is associated with the heat of adsorption, A (Lmol^{-1}) is the binding constant at equilibrium which is associated with the maximum binding energy (Tong et al., 2011). The plot of q_e versus $\ln C_e$ (Figure 8a) helps in the calculation of constants A and B as reported in Table 1.

The Dubinin–Radushkevich (D–R) expression is given by:

$$\ln q_e = \ln q_x - \beta \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \tag{8}$$

where q_e is the equilibrium amount of copper biosorbed,

β is a constant corresponding to the adsorption energy, q_x is the capacity at maximum adsorption, ε is the Polanyi potential, that is equal to:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \tag{9}$$

(6)

Equation 8 can be re-written as:

(7)

$$\ln q_e = \ln q - \beta \varepsilon^2 \tag{10}$$

Table 1 reports the value of R^2 for the plot of q_e against ε^2. The q and β values were obtained from the gradient and intercept of the plots (Figure 8b).

The mean free energy of biosorption, E, was calculated from the equation:

$$E = 1/\sqrt{2\beta} \tag{11}$$

The magnitude of *E* explains the ion-exchange, physical or chemical sorption of the adsorption process. As reported by Atkins and Paula (2006), physisorption, can be caused by weak van der Waal interactions between the adsorbent and the adsorbate. The energy of physisorption is in the region of less than 20 kJ/mol.
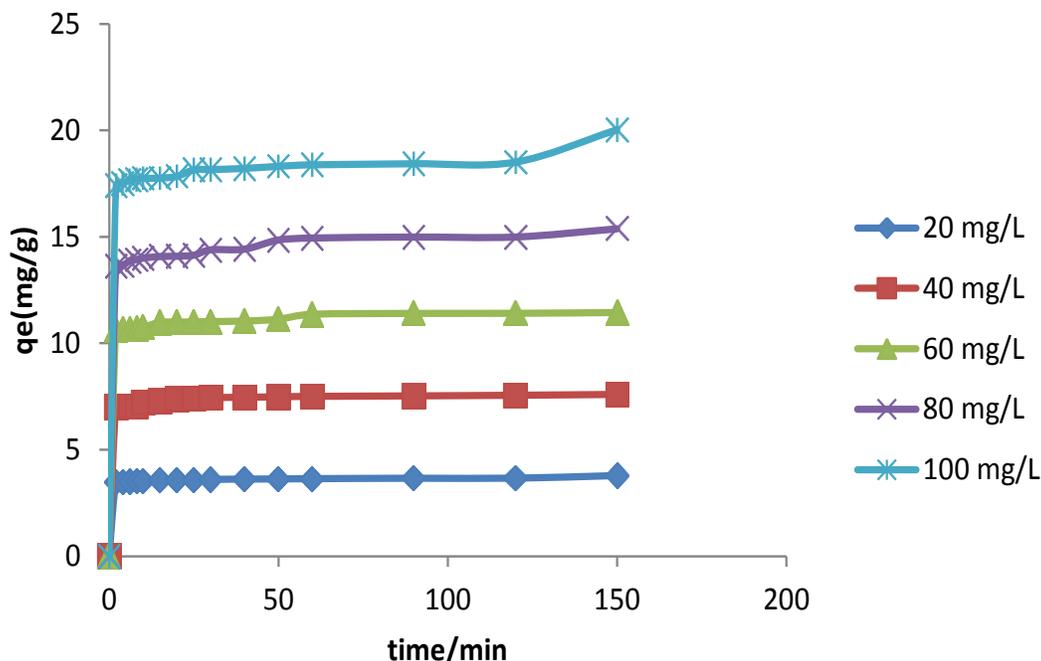
Figure 9. Effect of contact time on the adsorption of copper onto *G. oreophila*.

Atkins added that there is covalent bond between the adsorbate and the adsorbent in chemisorption in which the substrate (adsorbent) is limited to monolayer coverage. The value of E, the mean free energy of biosorption, determined from this study as reported in Table 1 was higher than 20 kJ/mol, thus chemisorption process predominates. Out of the four adsorption isotherms, Temkin isotherm gave the best fit.

Copper adsorption kinetics

Contact time effect

Figure 9 reports the contact time effect on the sorption of copper by *G. oreophila*. Adsorption increases rapidly initially and reached equilibrium in 15 min of mixing of *G. oreophila* with the copper solution. This occurred due to the numerous available active sites on the adsorbent surface and the electrostatic interaction between the positively charged copper (II) ions and the negatively charged surface of *G. oreophila*. As copper (II) ions occupy the sites, electrostatic repulsion gradually increases between the copper (II) ions present in the site and the copper (II) ions present in the solution. This consequently reduces the adsorption of copper (II) ions and thus equilibrium is established.

Kinetic effect on the process of adsorption is vital since it explains the rate of adsorption of the adsorbate which then regulates the contact time of the *G. oreophila* at the solid–solution interface. The kinetics of copper biosorption by *G. oreophila* was analyzed using the Pseudo- first and pseudo-second order models. The Langergren pseudo-first order expression is given below:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (12)$$

Where q_e and q_t refer to the equilibrium and time t biosorption capacities respectively, of *Globimetula oreophila*; k_1 is the pseudo- first order biosorption rate constant. The plots of log $(q_e$-$q_t)$ versus t (min) for different copper concentrations give straight lines (Figure 10a). From the plots, k_1 and q_e are obtained from the gradient and intercept respectively as presented in Table 2.

The linear expression of the pseudo-second order kinetic isotherm is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_t}t \qquad (13)$$

The graph of t/q_t against t is presented in Figure 10b while the parameters of these kinetic models were reported in Table 2. The pseudo-second-order isotherm is more suitable for describing copper adsorption unto *G. oreophila* than the pseudo-first-order isotherm, since it has higher R^2 values (R^2 = 1) and its calculated and experimental values are equivalent. In addition, the authenticity of the kinetic models can be verified by using the normalized standard deviation given by:
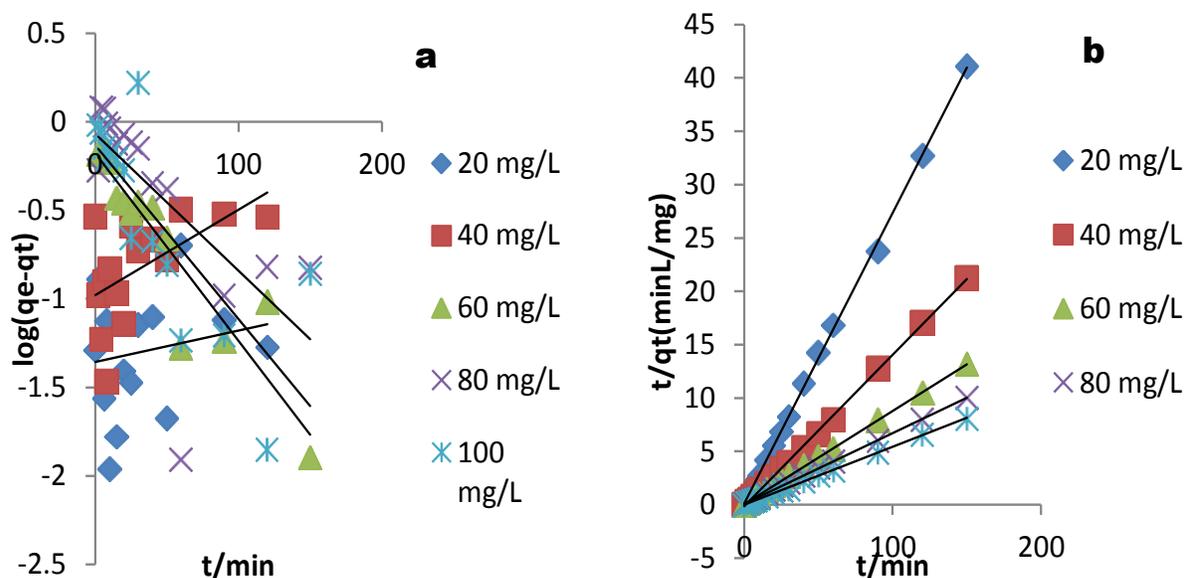
Figure 10. Kinetic plot showing a. Pseudo- first and b. pseudo- second order for copper adsorption onto G. *oreophila.*

Table 2. Pseudo-first and pseudo-second order isotherms for the biosorption of copper on *G. oreophila.*

	Pseudo-first order				Pseudo second order			
Conc (mg/L)	$q_{e(exp)}$ (mg/g)	$q_{e(calc)}$ (mg/g)	k_1/min	Δq	$q_{e\ (calc)}$	k_2 ($gmg^{-1}min$)	Δq	R^2
20	3.59	3.88	0.0018	7.49	3.67	0.704	0.583	1
40	7.34	2.66	0.0048	121	7.04	0.129	1.058	1
60	11.4	1.19	0.1775	262	11.4	0.149	0.178	1
80	14.8	1.07	0.0686	355	15.1	0.072	0.384	1
100	18.4	1.14	0.133	445	18.5	0.249	0.163	1

$$\Delta q = \sqrt{\frac{\sum\left[(q_{\exp} - q_{cal})/q_{\exp}\right]^2}{p-1}} x100 \qquad (14)$$

Where q_{exp} is the amount of copper (II) ions obtained by experiment and q_{cal} values are the amount of copper (II) ions obtained by calculation, and p is the number of determinations. The low value of Δq corroborates the study that the pseudo-second order kinetic isotherm is better explaining the adsorption kinetics of copper onto *G. oreophila*. Previous study on the adsorbent, *Tectona grandis,* reported similar result (Ajaelu et al., 2017b).

Thermodynamic effect

The temperature effects were investigated at 303, 308, 313 and 318 K. Figure 11 shows that there was a slight reduction in the adsorption capacity as the temperature decreases. This means that the adsorption process was chemisorptions, corroborating the earlier mentioned mean

free energy of biosorption obtained from Dubinin-Radushkevich model. The thermodynamic parameters determined were calculated as follows:

$$\Delta G = -RT\ln K \qquad (15)$$

$$\ln K = -\frac{\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (16)$$

The entropy change ΔS as well as the enthalpy change ΔH was calculated from the plot of lnK against 1/T as presented in Figure 12. The K_L values were calculated from the expression $K = q_e/C_e$ at different amounts of Cu (II) ions from 20 to 100 mg/L, and the data are reported in Table 3. The adsorption of copper on *G. oreophila* is spontaneous (ΔG is negative) and endothermic (ΔH is positive). Moreover, there is a rise in entropy (ΔS is positive) at the adsorbent-adsorbate interface and this positive value means that the adsorbate species displace the adsorbed solvent molecules to gain more translational entropy than was lost by the adsorbate, thus
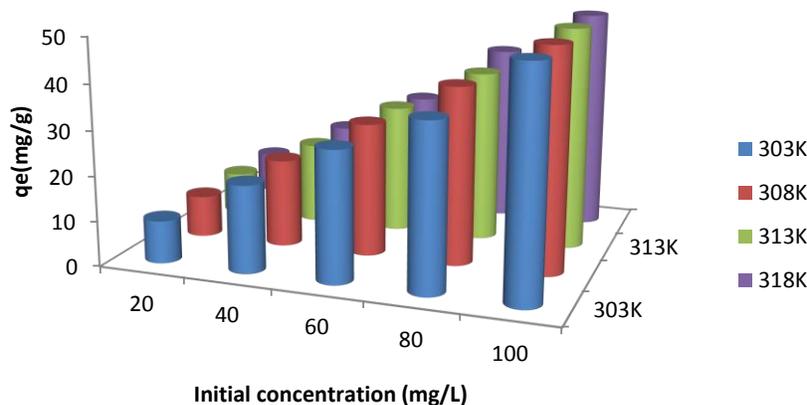
Figure 11. Effect of temperature and initial concentrations on the adsorption of copper by *G. oreophila.*
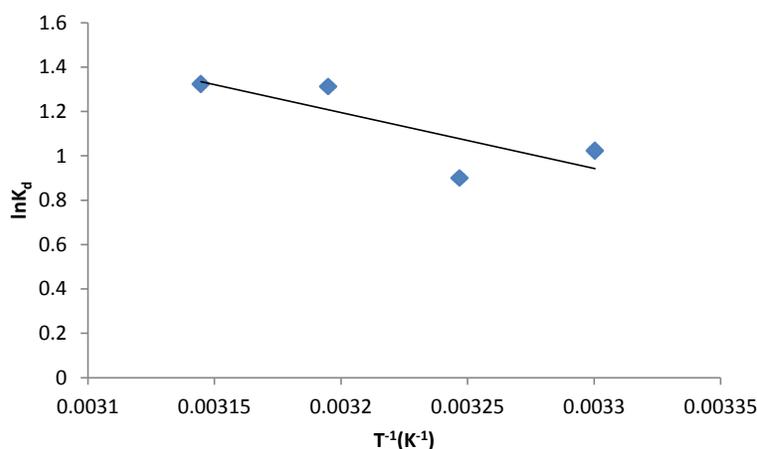
Figure 12. van't Hoff plot for the adsorption of copper by *G. oreophila.*

allowing randomness in the system (Baccar et al., 2013).

The adsorption activation energy was determined using the Arrhenius equation for it denotes the minimum energy required for the adsorption reaction to proceed. The equation is given by:

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (17)$$

The value of E_a (168.3 kJmol^{-1}) falls in the energy range of 40 to 800 kJ/mol, which means that chemisorption is the process of adsorption.

Ionic strength effect

Ionic strength has significant effect on the adsorption process. Figure 13 presents the influence of ionic strength on the adsorption capacity of copper unto *G. oreophila*. As the ionic strength increases from 0.02 to 0.08 moldm^{-3}, the capacity of adsorption increased from 231 to 1620 mg/g. This shows that adsorption increases with increase in ionic strength. This result is contrary to what was obtained by some researchers. These may be due to accessibility modification of the functional group sites that binds metals on the *G. oreophila* surface as well as the modification in the activity of the aqueous metal cations as a function of ionic strength (Borrok and Fein, 2005).

Conclusion

This study investigated the adsorption efficiency of raw *G. oreophila* on copper. Increase in initial copper concentration increases the adsorption capacity. Equilibrium isotherm shows that of the four isotherms, Temkin model is the most appropriate for explaining the

Table 3. Thermodynamic parameters for the adsorption of copper on *G. oreophila.*

| ΔS(J/molK) | ΔH(kJ/mol) | ΔG(kJ/mol) | | | | E_a(kJ/mol) |
		303K	308K	313K	318K	
77.7	20.9	-2.58	-2.31	-3.42	-3.50	168.3
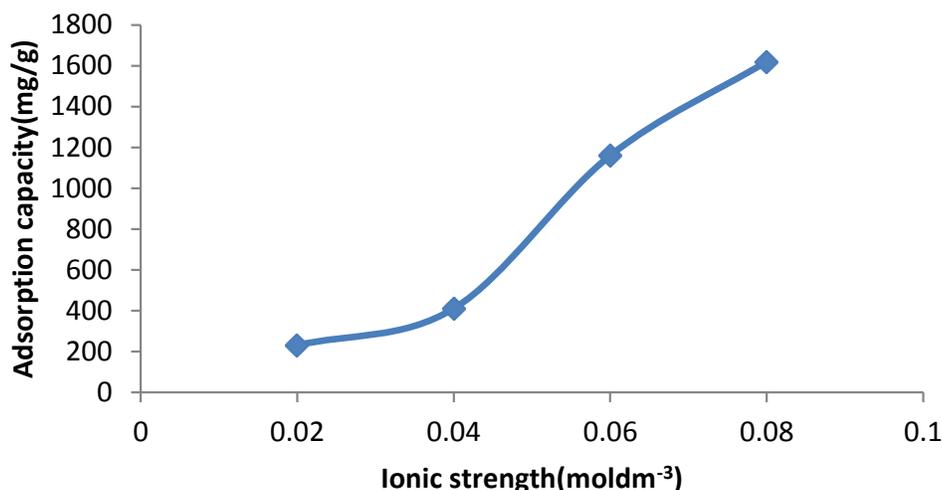
Figure 13. Impact of ionic strength on copper biosorption on *G. oreophila.*

adsorption process. D-R isotherm, as well as the activation energy, which is the minimum energy required for the adsorbent- adsorbate interaction, shows that the adsorption process is chemisorption. Increase in ionic strength significantly increased the capacity of *G. oreophila* in removing copper from solution. This study reports the usefulness of *G. oreophila* as an adsorbent for removing copper from aqueous solution.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

ACKNOWLEDGEMENT

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