

The Removal Of Copper From Aqueous Solution Using Modified Globimetula Oreophila

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The removal of copper from aqueous solution using modified *Globimetula oreophila*

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Abstract

The ability of adsorbent prepared from by-product of agriculture for the removal of dye was investigated. This study was aimed at the use of citric acid modified *Globimetula oreophila* to remove copper from aqueous solution. The adsorbent was characterized by Scanning electron microscope (SEM) and Fourier Transform Infrared (FTIR). The parameters investigated are the following: effect of pH, point of zero charge, initial copper concentration, contact time, kinetics and the effect of temperature. The optimum pH of adsorption was 5.2. Adsorption capacity increases gradually with increase in mass of biomass. The adsorption capacity decreased with increase in the initial copper concentration. 93% of the adsorption capacity was achieved in 15 minutes of contact time. The maximum adsorption capacity at equilibrium is 18.5 mg/g. The Dubinin–Radushkevich model was the most appropriate in describing the adsorption process. The Pseudo-second order kinetic model was suitable for explaining the adsorption of copper onto modified *Globimetula oreophila*. Thermodynamic properties related to the adsorption process were determined to be endothermic for the enthalpy change (36.3 kJmol⁻¹), spontaneous ($\Delta G = -ve$), and there was disorderliness at the adsorbent - adsorbate interface. The adsorption process was physisorption. Citric acid modified *Globimetula oreophila* is a promising adsorbent for the removal of copper from waste-water.

Keywords: Kinetics, *Globimetula oreophila*, copper, adsorption, pseudo-second order

Introduction

The increase in industrial activities has resulted in the elevation in the concentration of heavy metals introduced into the aquatic environment. Heavy metals in wastewater have become a source of worry to man as they have no benefit to the wellbeing of both man, animal and plants. The heavy metals introduced into the environment through anthropogenic sources include lead, arsenic, cadmium, zinc, copper, chromium, mercury, and nickel. Apart from the metal and mining related industries, other industries whose metal-laden effluents are discharged into water bodies are ceramic, paints, glassware, leather tanning, electroplating, battery, and photography (Brown and Welton 2008). These metals are very stable and persistent environmental contaminants since they are non-degradable, and therefore tend to aggregate in the soils, seawater, freshwater and sediments Chowdhury and Saha (2011). Copper becomes toxic to man if it exceeds 1.0 mg/L, the World Health Organization permissible level of copper in water (Siegel 2002). Industrial effluents usually contained high concentration of copper (Tong et al. 2011). Human intake of high concentration of copper has negative effect on the liver and kidney. It can also result in diarrhea, dizziness, depression, hepatic and renal damage, mucosal irritation, heart failure and brain damages (Ajaelu et al., 2017; Ajaelu et al. 2021; Ajmal et al. 1998; Larous et al. 2005; Zhu et al. 2009).

Different methods have been used to remove copper from water bodies. These include chemical precipitation Mishra and Devi (2011, Kitobo et al., 2012, Agrawal et al. 2008., Papadopoulos et al. 2004; Liquid – liquid extraction (Lee, 2011; Deep et al 2010; chelating or ion exchange resin (Janin et al. 2009); Bulai et al. 2009, electro dialysis and reverse osmosis (Kumar et al. 2019). Chemical precipitation enjoyed wide usage for copper

removal as hydroxide or sulfide. The demerit of chemical precipitation is the challenge involved in the disposal of the copper hydroxide. All the methods are not cost effective, and they lead to partial removal of copper, high usage of energy as well as the production of toxic sludge.

An alternative method known as biosorption process was developed for the elimination of heavy metals. The sorption procedure presents the effective and economical method for the remediation of metal-bearing wastewaters owing to its environmental friendly features, high uptake capacity, cost effectiveness, absence of toxicity constraints, less sludge, biosorbents availability and the possibility of biosorbent regeneration (Bhatnagar et al. 2012;). Some plant materials used as adsorbents for heavy metals include *Carica papaya* root powder (Alao et al. 2014), Orange peel (Gupta and Nayak, 2012), *Mangifera indica* (Ajaelu et al 2013, 2015), peanut (Tasar and Ozer 2020), periwinkle shell (2008), *Musa parasidiaca* (Emenike et al. 2017), groundnut seed, sesame seed coconut (Kumar et al. 2019) and Breadfruit leaf (2013). For that reason the possibility of using a biosorbent, *Globimetula oreophila*, to remove copper from industrial effluents was investigated.

Globimetula oreophila belongs to the *Loranthaceae* family. It has green leaves and can be found in every region of Nigeria. It grows on trees such as cocoa, rubber and orange among others. *Globimetula oreophila* is a parasitic plant that needs to be explored in the removal of metals. Its raw form had been used to remove copper from aqueous solution (Ajaelu and Faboro 2021) but its modified form has not been explored.

In the present study, citric acid modified *Globimetula oreophila* biosorbent (MGO) was produced and characterized using FT-IR and SEM. The Cu (II) adsorption kinetics was described by pseudo-first and pseudo-second order models. Adsorption isotherms were described by using Freundlich, Langmuir, Temkin and Dubinin–Radushkevich models. In addition, copper adsorption thermodynamics were also studied.

2. Material and methods

2.1 Material

Analytical grade chemicals were used. The modification of the *G. oreophila* was carried out using Citric acid monohydrate (CA) (Figure 1).

Preparation of the adsorbent

The *G. oreophila* leaves were washed with tap water to remove dust and extraneous material. It was then rinsed with distilled water and air dried and oven-dried at 105°C. It was then ground, screened with 1mm sieve and kept in a clean, air-tight container.

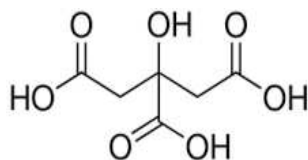


Fig. 1 Structure of citric acid

2.2 Adsorbent modification and adsorption process

We have previously reported the method used for the modification with little adjustments (Ajaelu et al. 2017, Ajaelu et al. 2019). In summary, raw *Globimetula oreophila* was mixed with 0.2 M citric acid and agitated for 60 min. The

acid/*Globimetula oreophila* mixture was dried in the oven at 80°C for 3 hours, and then elevated to 140°C for 3 hours. The cooled sample was washed with 0.15 M NaOH and then with distilled water to attain a neutral pH. The CA modified *Globimetula oreophila* was dried at 105°C until constant weight was achieved. It was stored in a clean dry bottle for further studies.

Surface structure characterization of MGO was done using Scanning electron microscope (Zeiss Auriga HRSEM) while the functional groups identifications were obtained using Fourier Transform Infrared Spectrophotometer, Agilent Technologies Cary 630FTIR spectrometer.

2.4 Adsorption of copper (II) ion

A solution of 1000 mg/L Cu (II) concentration was prepared by dissolving 24.96 g of hydrated copper salt in 100 mL beaker. The mixture prepared was then transferred into a 1L volumetric flask and was diluted with distilled water.

2.4. Batch Adsorption Method The adsorption experiments were carried out in batches. The effect of pH was carried out with 0.1 g of MGO at pH range of 1 – 8. Initial metal concentration was determined using 0.2 g of MGO and copper concentrations of 20, 40, 60 and 80 mg/L; mass of adsorbent from 0.1 -0.6 g. Adsorption kinetic studies was performed using 0.05 g of adsorbent from 0 to 120 minutes at varying copper concentrations (20, 40, 60 and 80 mg/L). Temperature studies was investigated from 303 -323 K using 0.2 g of MGO. These mixtures were then agitated for 2 hours. After adsorption, filter paper was employed for the separation of the residue from the filtrate and the level of Cu (II) ions in the filtrate was analyzed at a wavelength of 324.7 nm using atomic absorption spectrometer (Agilent Technologies Cary 630FTIR spectrometer).

The amount (q_e in mgg^{-1}) and percentage (%) of Cu^{2+} removed,) (eq. 1) and (eq. 2) respectively can be evaluated by the equations:

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

$$\% \text{ sorption capacity} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Where C_o (mgL^{-1}) and C_e (mgL^{-1}) are the starting concentrations of Cu^{2+} and the final concentration of Cu^{2+} in solution respectively. V (L) and w (g) represent the volume of Cu^{2+} and the weight of MGO respectively.

Experiment on the kinetics o adsorption was done by contacting 0.5 g each of the sorbent with 120 mL of 20 - 80 mg/L Cu^{2+} solutions at pH 7. The concentration of Cu^{2+} adsorbed q_t (mg/g) was obtained by the equation below:

$$q_t = \frac{C_o - C_t}{m} V \quad (3)$$

Where C_t (mg/L) represents the amount of Cu (II) ions adsorbed at time t .

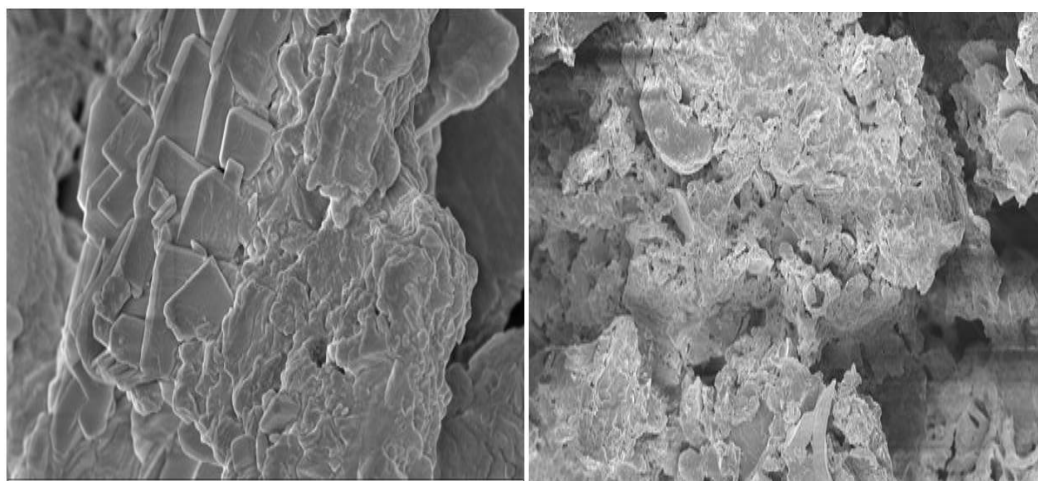
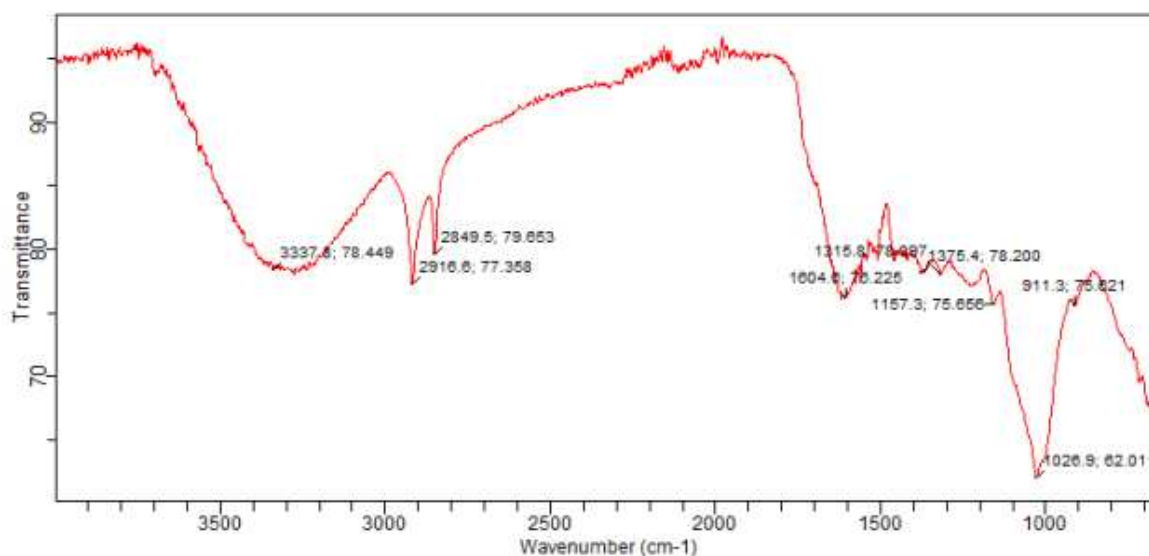


Fig. 2 Typical SEM of a. raw and b. citric acid modified *Globimetula oreophila*

Table 1 : Infrared Spectral Data of MGO pre- and post- sorption of Cu(II) ions

Adsorbent	$\nu(\text{OH})$ (cm^{-1})	$\nu(\text{CH})$ (cm^{-1})	$\nu(\text{C=O})$ (cm^{-1})	$\nu(\text{C=C})$ (cm^{-1})	$\nu(\text{C-O})$ (cm^{-1})
Modified <i>Globimetula oreophila</i> (MGO)	3342m	2919s 2851s	1731s 1636m		1165s 1034s
MGO after Cu (II) ions adsorption	3338m	2917m 2850m		1605m	1157s 1027m



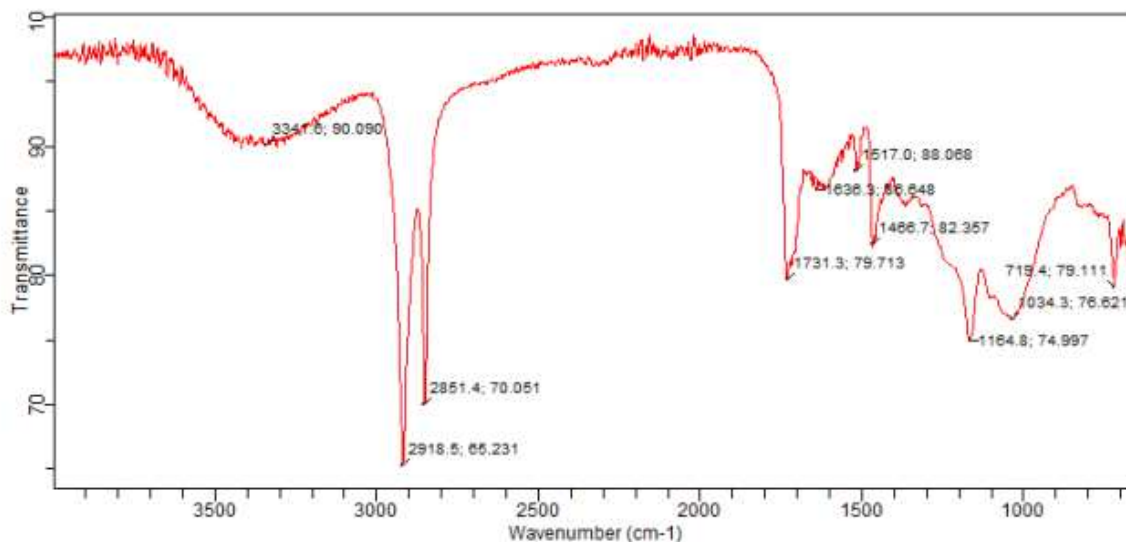


Fig. 3. FTIR of modified *Globimetula oreophila* a) pre- sorption b. post- sorption of copper (II) ions

Characterization of modified *Globimetula oreophila*

The SEM micrograph (Figure 2) of raw *Globimetula oreophila* was compared to the citric acid modified *Globimetula oreophila*. The raw *Globimetula oreophila* surface reveals irregular, flat and layered sheets containing some pores on its surface (Ajaelu and Faboro 2021). After treatment with citric acid, the surface looks like a fibrous, mushroom surface - like tissue containing uneven pores. Thus, the surface has enhanced microporous and mesoporous nature for adsorption.

FTIR analysis. Identification of functional groups through characteristic vibrational frequencies was done by comparing the spectra of the Cu (II) adsorbed citric acid modified *Globimetula oreophila* with that of the citric acid modified *Globimetula oreophila* (MGO) as presented in Figure 3 and Table 1. The infrared spectrum of the citric acid modified *Globimetula oreophila* revealed a broad and medium band around 3342 cm^{-1} , which is attributable to a $\nu(\text{OH})$ vibration band of an hydrogen bond due to the citric acid. This band has shifted slightly to 3338 cm^{-1} after adsorption with Cu (II) ions. The sharp and strong bands appearing at 2919 cm^{-1} and 2851 cm^{-1} are due to the $\nu(\text{CH})$ vibrational bands. These bands have remained almost unchanged at 2917 cm^{-1} and 2850 cm^{-1} after its adsorption with Cu (II) ions. The sharp and strong band appearing at 1731 cm^{-1} , as well as the sharp and medium band at 1636 cm^{-1} are attributable to $\nu(\text{C}=\text{O})$ stretching vibration bands appearing from the carboxylic acid. These bands disappeared in the spectrum of this adsorbed compound with Cu (II) ions. This indicates the coordination of the oxygen of the C=O bond to the Cu (II) ion during adsorption (Adetoye *et al.*, 2009). The appearance of a new sharp and medium band at 1605 cm^{-1} is attributable to the $\nu(\text{C}=\text{C})$ stretching vibrations. The medium and strong bands at 1165 cm^{-1} and 1034 cm^{-1} are attributable to the $\nu(\text{C}-\text{O})$ stretching vibration. These have shifted to lower frequencies of 1157 cm^{-1} and 1027 cm^{-1} after adsorption. This means that oxygen of the hydroxyl group is involve in Cu(II) ions adsorption (Adetoye *et al.*, 2009).

Effect of pH The pH for the sorption of copper on modified *Globimetula oreophila* was investigated from pH 2 to 8 (Figure 4). Optimum adsorption was at pH 5.2 while percentage adsorption increased from 5 to 35 %. This is lower compared to the already reported values for raw GO which has 95.6 % adsorption of copper. A reduction in the adsorption of copper by citric acid modified GO may be due to some reasons: Firstly, some of the pores in which adsorption will occur have been occupied by the citric acid, thereby reducing the number of pores available for adsorption. Secondly, the citric acid, being a weak acid, released only few hydrogen ions for exchange with copper. In addition, at higher pHs, formation of metal ions hydroxylated complexes may occur, limiting the activity by blocking the surface moieties (Singh et al. 2021, Wadhawan et al. 2020)

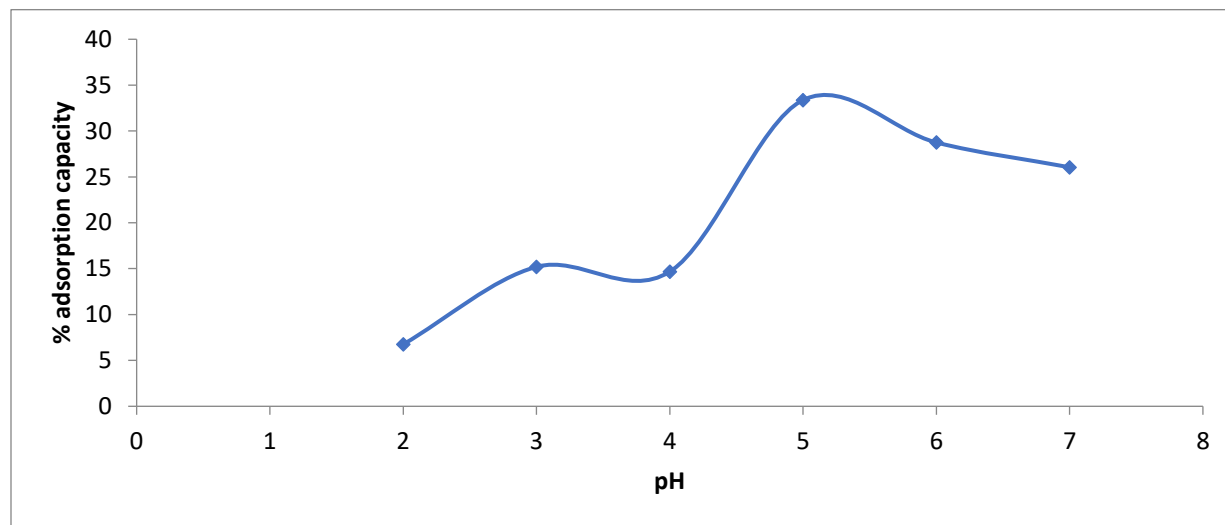


Fig. 4 The effect of pH on the sorption of copper on modified *Globimetula oreophila*

The point of zero charge (PZC) of *MGO* obtained was 2.0 as reflected in Figure 5. The point of zero charge explains the reason why the surface of adsorbents has a net zero charge density. It is the pH at which the net charge on the surface of the adsorbent is zero. When the pH is lower than the PZC, the *MGO* surface is positively charged, and at pH higher than PZC the surface is negatively charged. Optimum adsorption took place at pH 5, a value higher than the PZC. At very low pHs the surface of the adsorbent has functional groups that are protonated leading to electrostatic repulsion. Thus, as the pH increases the competition for the negative adsorption sites by H^+ ions decrease, thereby increasing the number of available site for sorption of $Cu(II)$ ions. The negative charges on the surface of the adsorbent due to the pH greater than the PZC enhanced the adsorption of copper.

Table 2. The results for pseudo-first and pseudo-second order kinetic models for the sorption of copper on modified *Globimetula oreophila*

conc(mg/L)	PSEUDO-FIRST ORDER				PSEUDO SECOND ORDER			
	$q_e(\text{exp})(\text{mg/g})$	$q_e(\text{calc})(\text{mg/g})$	k_1/min	Δq	$q_e(\text{calc})$	$k_2(\text{gmg}^{-1}\text{min})$	Δq	R^2
20	6.84	1.60	0.00006	3.71	7.63	3.74E-01	0.558	0.999
40	7.42	2.44	0.001	3.52	3.44	4.15E-02	2.82	0.998
60	10.8	1.19	0.177	6.77	11.1	1.72E+00	0.242	0.996
80	14.8	2.33	0.848	8.84	15.2	2.06E-01	0.221	1

Effect of initial metal concentration

The initial metal concentration effect on the adsorption process cannot be over-emphasized. Figure 6 reflects the impact of the initial copper concentration on the adsorption capacity of MGO. There was a decrease in adsorption capacity from 94.5 % to 92.1% as the initial concentration of copper increases from 20 - 40 mg/L. This is because the adsorption sites adsorbed the metal ion at a faster rate at reduced concentration due to the few sites available on the surface of the adsorbent. At higher amount of metal in solution vacant sites free for adsorption are few due to saturation of the vacant sites by copper ions. Adsorption can be enhanced by diluting the solution at higher concentration. Similar result was obtained by Zhang et al. 2021 and Cherono et al. 2021.

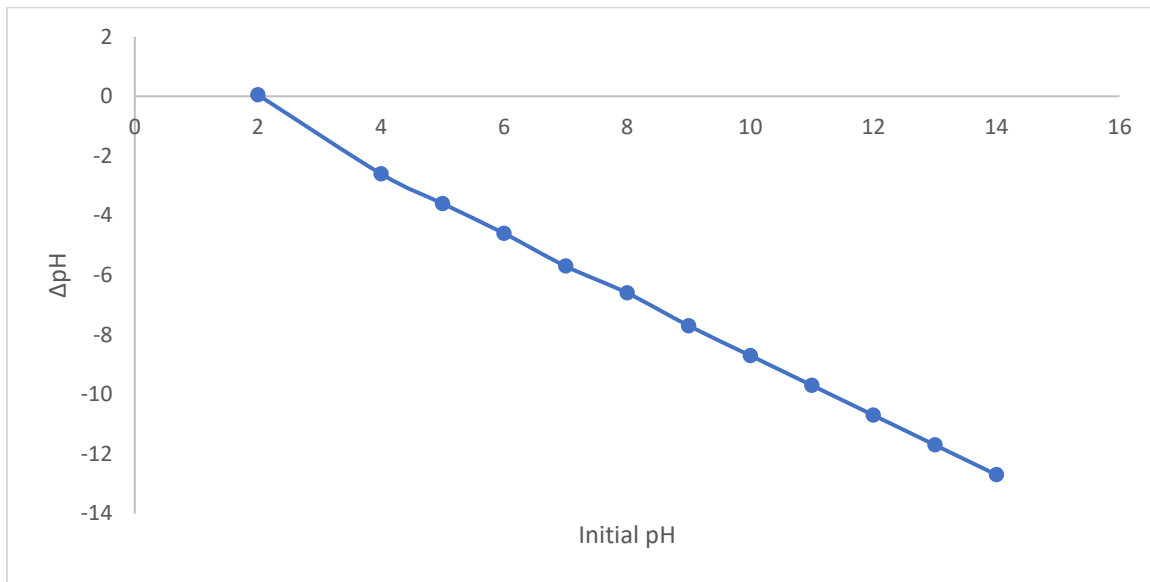


Fig. 5 The impact of point of zero charge on the adsorption of copper on modified *G. oreophila*

Effect of adsorbent dosage

Effect of adsorbent dosage on copper removal was investigated at room temperature and results obtained are depicted in Figure 7. There is a gradual rise in the percentage adsorption capacity as the adsorbent dosage increased for each of the concentrations (20 – 100 mg/L) studied. At a concentration of 100 mg/L and a sorbent dosage of 0.5 g, the percentage adsorption capacity was 98.8 %. This high adsorption capacity may be due to the large surface area of modified *Globimetula oreophila*.

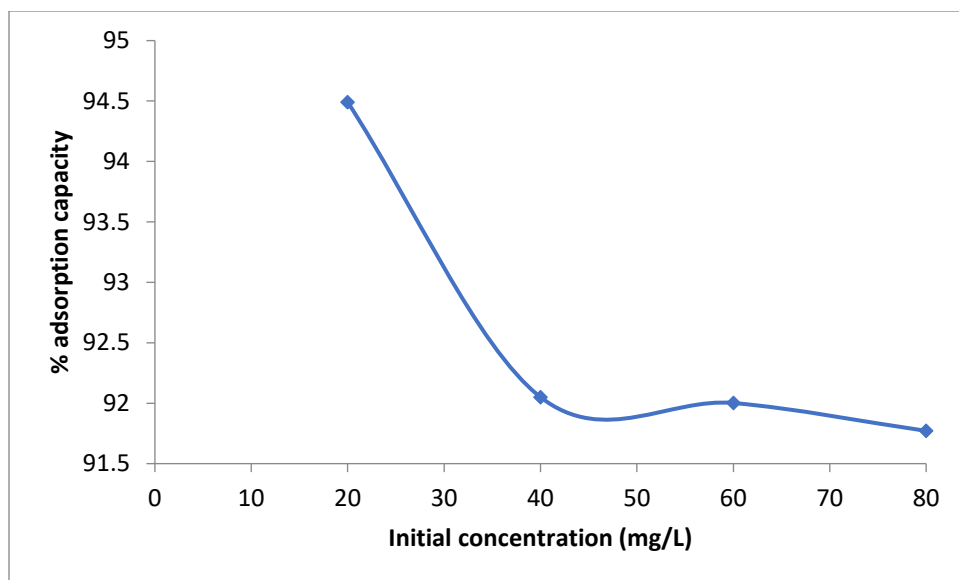


Fig. 6 The effect of initial metal concentration on the sorption of copper on modified *Globimetula oreophila*

Effect of contact time

Figure 8 presents the plot of the adsorption capacity of copper against time at various initial concentrations (20 - 80 mg/L). At the beginning of the adsorption process, the rate was rapid for the different concentrations attaining over 93 % of the sorption capacity at equilibrium within the first 15 minutes. This behavior was achieved because of the high number of available unoccupied adsorption sites at the early stage, in addition to the presence of high concentration gradient between the adsorbent and the adsorbate. Similar contact time result was obtained by Jung et al., 2017, Ajaelu and Faboro 2021.

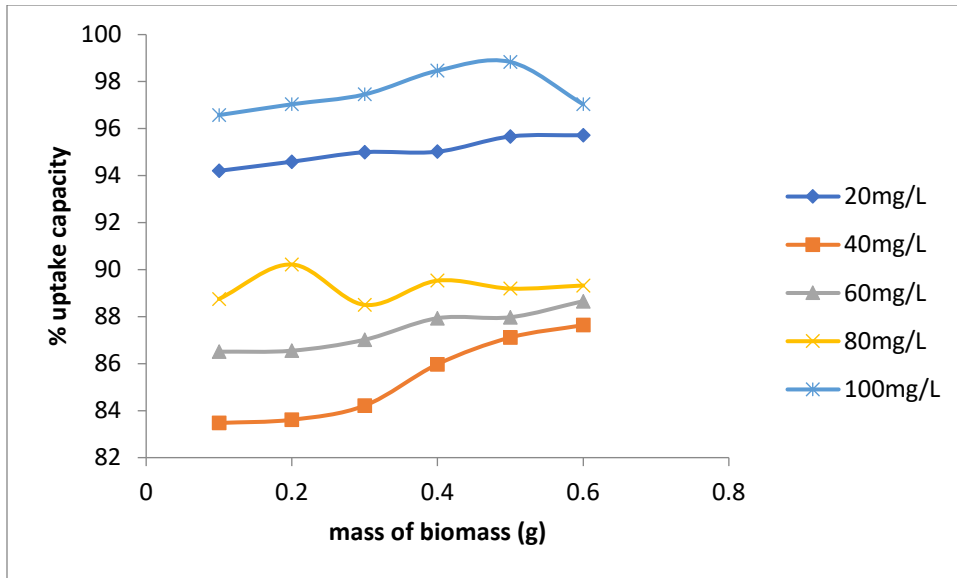


Fig. 7 The effect of mass of biomass on the sorption of copper on citric acid modified *Globimetula oreophila*

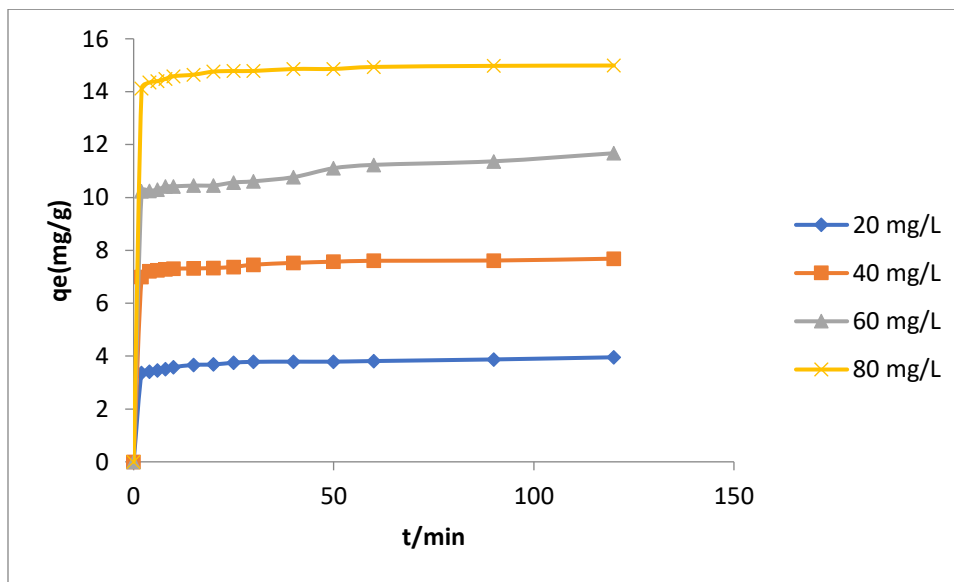


Fig. 8 Effect of contact time on the sorption of copper onto modified *Globimetula oreophila*

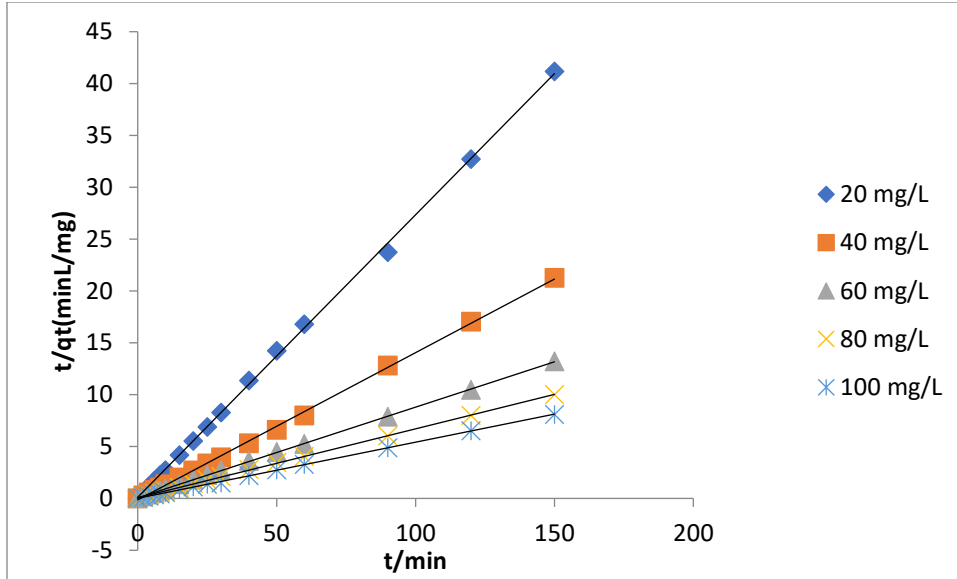


Fig. 9 Pseudo- second order kinetics for the sorption of copper on modified *Globimetula oreophila*

Adsorption kinetics

The kinetics of the sorption processes were explained using two isotherms, Pseudo- first order (eq. 13) and pseudo-second order (eq. 14) in their linear form.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (13)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_t} t \quad (14)$$

Where q_e (mg/g) and q_t (mg/g) represent the biosorption capacities of modified *Globimetula oreophila* at equilibrium and at any time t , respectively ; k_1 and k_2 are the rate constants of the pseudo- first and pseudo- second order biosorption as reflected in Table 2. The sorption of copper unto MGO follows the pseudo-second-order kinetic model (Figure 9) as compared to the pseudo-first-order model since its calculated and experimental values are quite close and its R^2 values are close to unity ($R^2 \approx 1$). The pseudo-second-order kinetic model indicates that Cu (II) sorption by MGO was as a result of chemical reaction that involves electrons exchange between the sorbent and metal (Chowdhury and Saha 2011). Moreover, the validity of the isotherms can be ascertained with the normalized standard deviation obtained from the equation below:

$$\Delta q = \sqrt{\frac{\sum [(q_{\text{exp}} - q_{\text{cal}}) / q_{\text{exp}}]^2}{n - 1}} \times 100 \quad (15)$$

Where q_{cal} and q_{exp} are the calculated and experimental amounts of copper ions adsorbed on the *MGO* and n is the number of experiments. The low values of Δq are indications that the pseudo-second order model is preferred for describing the kinetics of adsorption of copper on *MGO*.

Table 3 Isotherm parameters for the sorption of copper unto modified *Globimetula oreophila*

Langmuir	Temkin	D-R	Freundlich
$X_o = 18.5 \text{ mg/g}$	$f = 677.4$	$q_m = 8.78$	$K_F = 1.69$
$c = 0.0912$	$A = 1.06$	$\beta = 0.001$	$n = 1.33$
$R_H = 0.0988$	$R^2 = 0.96$	$E = 22.4$	$R^2 = 0.99$
$R^2 = 0.73$		$R^2 = 0.98$	

Equilibrium isotherms for describing adsorption**Langmuir model**

The Langmuir isotherms surmises that sorption occurs at definite homogeneous positions on the sorbent surface, meaning once a dye molecule fills a binding site, further sorption cannot take place at that site. Langmuir isotherm is widely used to explain the adsorption process and is mathematically given as

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \quad (4)$$

where q_e is the equilibrium concentration of copper per unit mass of sorbent (mgg^{-1}), Q_o is the highest amount of copper adsorbed per unit mass of sorbent, (mgg^{-1}), b is Langmuir constant (L/ mg).

The appropriateness of the sorbent for the adsorbate can be presented using the Hall separation factor (R_H , dimensionless) (Webber and Chakkravorti, 1974)

$$R_H = \frac{1}{(1 + C_o)} \quad (5)$$

R_H value determined as expressed in Table 3 indicates that the sorption of copper unto *MGO* was favourable since its value ($R_L = 0.0988$) is between 0 and 1.

The Temkin isotherm model (Temkin, 1940) assumes that the reduction in the heat of sorption as a function of temperature is linear and is expressed as:

$$q_e = U \ln A + U \ln C_e \quad (6)$$

$$\text{and } U = \frac{RT}{f} \quad (7)$$

The temperature is T in K while R is the gas constant in $\text{Jmol}^{-1}\text{K}^{-1}$. The constant f is related to the heat of sorption, A (Lmol^{-1}) is a constant related to the highest binding energy (Tong *et al.* 2011). The graph of q_e against $\ln C_e$ (Figure 10b) enabled the determination of the constants A as presented in Table 3.

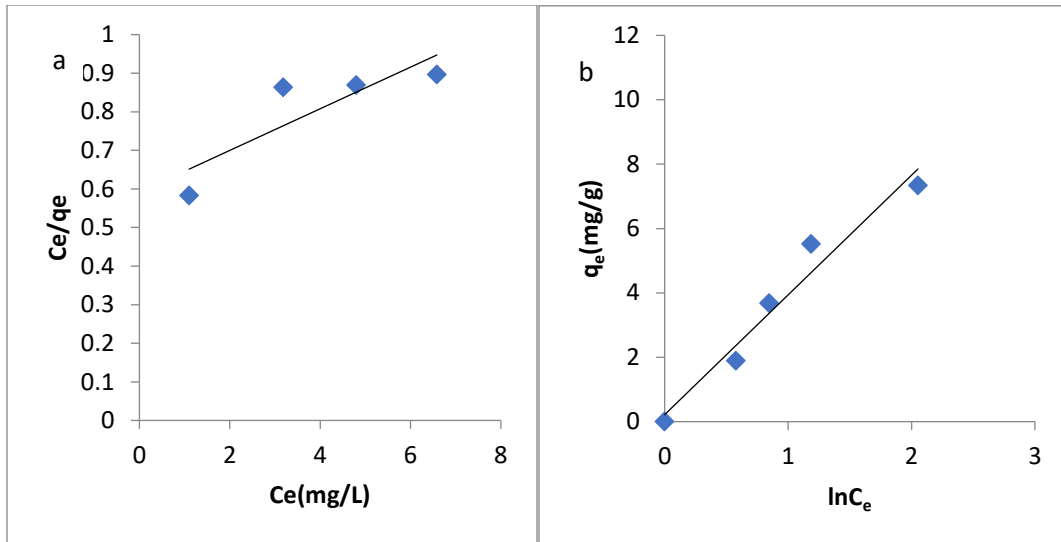


Fig. 10 (a) Langmuir and (b) Temkin isotherms for the sorption of copper onto modified *Globimetula oreophila*

The Dubinin–Radushkevich (D–R) isotherm is employed to evaluate the characteristic porosity of adsorbent especially of carbonaceous material and the mean free energy of adsorption. The equation is given by

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

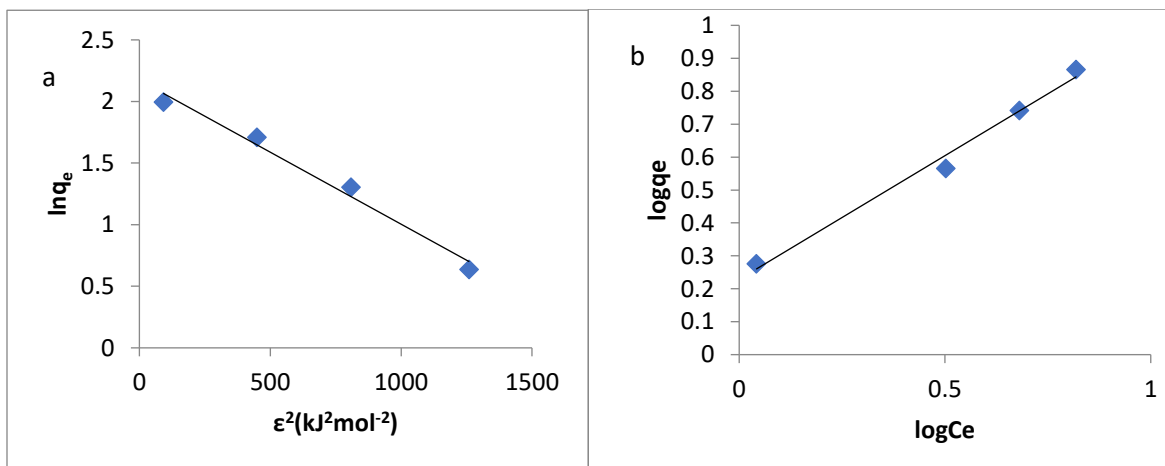


Fig. 11 (a) Dubinin–Radushkevich (D–R) and (b) Freundlich isotherms for the sorption of copper onto modified *Globimetula oreophila*

Where q_e is the concentration of copper adsorbed at equilibrium, β is a constant representing the adsorption energy, q_x is the maximum sorption capacity, ε is the Polanyi potential, and is given as

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

The straight line expression for eq. (8) is,

$$\ln q_e = \ln q_x - \beta \varepsilon^2 \quad (10)$$

Table 3 presents the values of q , β and R^2 for the graph of q_e against ε^2 . The β and q values were determined from the intercept and slope of the plots respectively (Figure 11a).

The mean free energy of sorption, E , was obtained from the expression

$$E = 1 / \sqrt{2\beta} \quad (11)$$

The value of E obtained was 22.4 kJ/mol. This value of the free energy of adsorption of copper onto MGO suggests that the mechanism of the adsorption was physisorption process.

Freundlich expression is based on adsorption onto a heterogeneous surface and comprises multilayer formation. The linear expression for the Freundlich isotherm is given as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (12)$$

Where K_F and n are Freundlich constants which measure the relative uptake capacity of the adsorbent and indicates the favorability of the adsorption process respectively. The Freundlich constant ($n = 1.33$) is greater than 1 which indicates the adsorption process was favorable while the correlation factor ($R^2 = 0.99$ obtained from Figure 11b) shows a good fit. Freundlich isotherm ($R^2 = 0.99$) was the best of the four in describing the adsorption process of copper onto MGO followed by the Dubinin–Radushkevich ($R^2 = 0.98$).

Temperature effect

Temperature has significant effect on the sorption process. Temperature effect shows that a rise in temperature resulted in the lowering of the adsorption capacity of *Globimetula oreophila* as presented in Figure 12. As the temperature becomes higher, the adsorption capacity slightly decreases. This is because the active sites on the surface of the sorbent is altered and reduced leading to the copper being leached into the solution. In addition at higher temperature, the copper molecule is separated from the surface of the adsorbent (Bermudez et al. 2012).

Thermodynamic effect

Thermodynamic parameters related to the sorption process can be derived by the calculation of the core thermodynamic characteristics such as Gibbs free energy (ΔG , kJmol⁻¹), enthalpy change (ΔH , kJmol⁻¹), and entropy change (ΔS , Jmol⁻¹K⁻¹) (Jung et al. 2017) using the equations below:

$$\Delta G = -RT \ln K \quad (16)$$

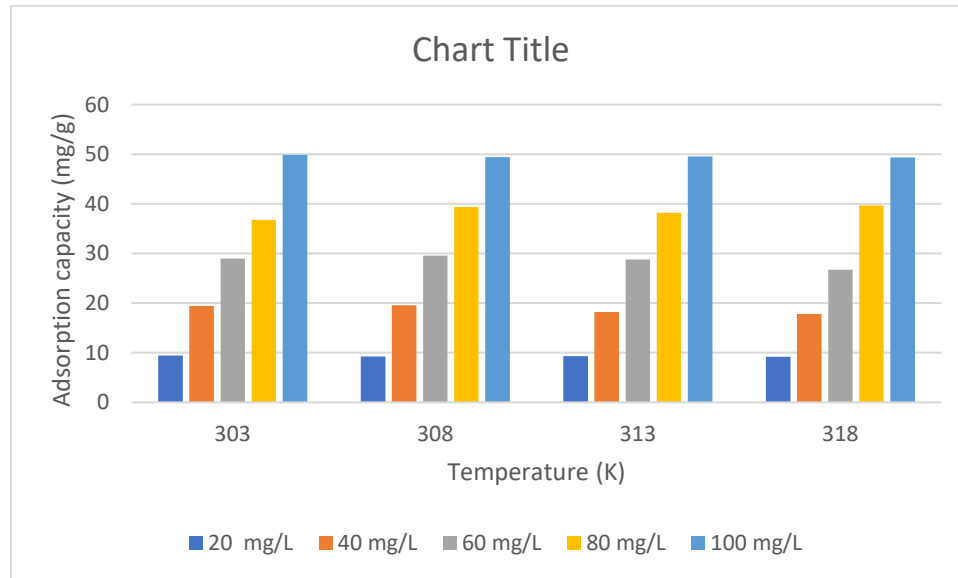
$$\ln K = \frac{C_e}{q_e} \quad (17)$$

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (18)$$

Table 4 Thermodynamic parameters for the sorption of copper on RGO

Temperature (K)	$\Delta G(\text{kJ/mol})$	$\Delta S(\text{J/molK})$	$\Delta H(\text{kJ/mol})$
303	-1.66	150.5	44.0
308	-2.41		
313	-3.17		
323	-4.67		

The change in free energy, ΔG , at different temperatures was obtained from equation 16 while the change in enthalpy ΔH and the entropy change ΔS were obtained from the van't Hoff plot of $\ln K$ against $1/T$ (Figure 13). It is clear from Table 4 that the adsorption of copper on MGO is endothermic, feasible and spontaneous as reported in the positive values of ΔH and the negative values of ΔG respectively. In addition, entropy positive values ΔS indicate increase in entropy during the adsorption process.

**Fig. 12** Effect of temperature on the sorption of copper by modified *Globimetula oreophila***Table 5 Sorption capacities of diverse adsorbents for copper**

Adsorbent	Adsorption capacity (mg/g)	Reference
Untreated <i>Senna alata</i>	2.44	[4]Ajaelu et al. 2017
Citric acid modified <i>Senna alata</i>	23.8	[4]Ajaelu et al. 2017
Rubber leave powder	9.07	[35]Obanla et al. 2021
Natural Mouka smectite	26.6	Langama et al. 2021
Kolanut shell activated carbon	36.6	Langama et al. 2021
Waste rubber tyres	12.4	[30]Cherono et al. 2021
Chemically modified <i>G. oreophila</i>	18.5	This study

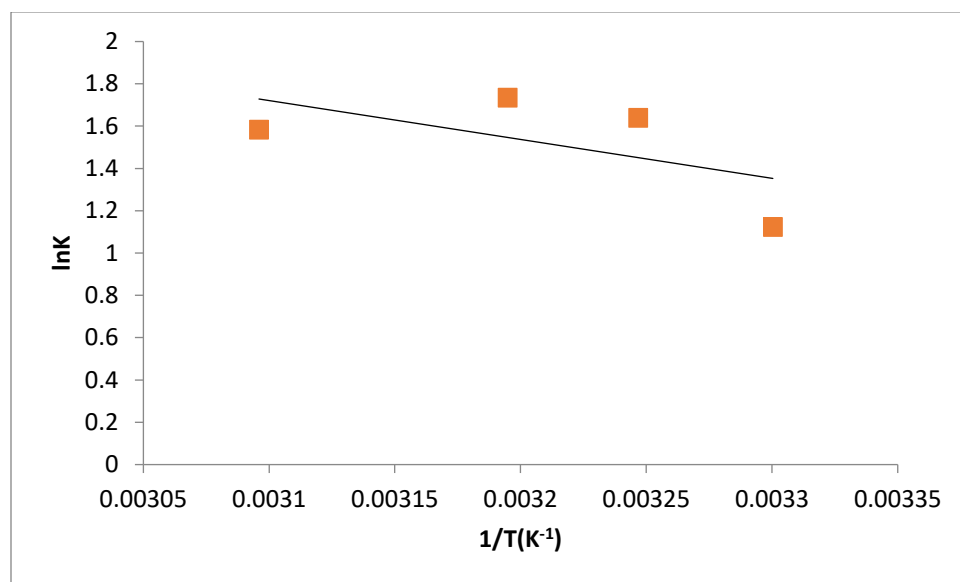


Fig. 13 Thermodynamic fitting for the sorption of copper by modified *Globimetula oreophila*

Sorption capacities of diverse adsorbents

The sorption capacities of diverse adsorbents for copper are presented in Table 5. The sorption capacities of some adsorbents such as Citric acid modified *Senna alata*, Natural Mouka smectite and Kolanut shell activated carbon have higher adsorption capacity than that of modified *Globimetula oreophila*. Rubber leave powder, untreated *Senna alata* as well as Waste rubber tyres have lower adsorption capacity compared to modified *Globimetula oreophila*. Modified *Globimetula oreophila* is a good adsorbent for adsorbing copper.

Conclusion

This study presented the adsorption of copper using citric acid modified *Globimetula oreophila*. The adsorption was dependent on pH, point of zero charge, initial metal concentration, sorbent dose, contact time and temperature effect. The optimum pH was 5.2. The sorption capacity reduced with elevation of the initial copper concentration. The percentage sorption capacity is elevated with increase in adsorbent dosage. Effect of contact time revealed that in 15 minutes, 93% of the adsorption capacity was achieved. Kinetic studies shows that the sorption process was second order. Thermodynamic parameters obtained for the adsorbents are responsible for the feasibility, spontaneity, and endothermic nature of the adsorption process at each concentration. This study revealed that citric acid modified *Globimetula oreophila* is a potential adsorbent for the removal of copper from aqueous solution.

REFERENCES

- Adetoye AA, Egharevba GO, Obafemi CA, Kelly DR (2009) Synthesis and physicochemical properties of Co(II), Cu(II), Fe(III), Mn(II) and Ni(II) complexes of the isatin derivative of sulphanilamide. *Toxicol and Environ Chem* 91(5):837-846

Agrawal A, Manoj MK, Kumari S, Bagchi D, Kumar V, Pandey BD (2008) Extractive separation of copper and nickel from copper bleed stream by solvent extraction route, *Minerals Eng.* 21: 1126–1130. <https://doi.org/10.1016/j.mineng.2008.02.016>

Ajaelu CJ, Atolaiye B, Ibronke OL, Alao OA (2015). Kinetics, Equilibrium and Thermodynamic of heavy metal sequestration unto mango seed biomass (*Mangifera indica*). *Journal of Chemical and Pharmaceutical Research.* 7(12): 605-617.

Ajaelu, CJ, Dawodu, MO. 2013. Sequestration of Cadmium onto mango (*Mangifera indica*) seed biomass: Kinetics and Equilibrium studies. *Journal of Chemical and Pharmaceutical Research.* 5(8): 174-180.

Ajaelu CJ, Dawodu MO, Faboro EO, Ayanda OS (2017) Copper Biosorption by Untreated and Citric Acid Modified *Senna alata* Leaf Biomass in a Batch System: Kinetics, Equilibrium and Thermodynamics Studies. *Phy Chem* 7(2):31

Ajaelu, CJ, Dawodu, MO, Abogunrin O, Otolurin, JA (2013) Kinetics and Equilibrium Studies of the Biosorption of Heavy metal ions from Simulated Wastewater using Breadfruit leaf (*Artocarpus artilis*). *European Journal of Scientific Research.* 98(1): 85-97.

Ajaelu CJ, Faboro EO (2021) Adsorption of copper (II) ions onto raw *Globimetula oreophila* (Afomo ori koko) leaves. *Afr J Biotechn* 20(3):122-133 <http://www.academicjournals.org/AJB>

- Ajaelu CJ, Ibronke L, Oladinni AB (2019) Copper (II) ions adsorption by Untreated and Chemically Modified *Tectona grandis* (Teak bark): Kinetics, Equilibrium and thermodynamic Studies. *African Journal of Biotechnology.* 18(14): 296-306. <https://doi.org/10.5897/AJB2018.16740>

Ajmal M, Khan AH, Ahmad S, Ahmad A (1998) Role of sawdust in the removal of copper (II) from industrial wastes. *Water Research* 32(10):3085-3091 [https://doi.org/10.1016/S0043-1354\(98\)00067-0](https://doi.org/10.1016/S0043-1354(98)00067-0)

- Bello SO, Adeogun, IA, Ajaelu JC, Fehintola EO (2008) Adsorption of methylene blue onto activated carbon derived from periwinkle shell: kinetics and equilibrium studies *Chemistry and Ecology* 24(4):285-295 <https://doi.org/10.1080/02757540802238341>

Bermúdez YG, Rico ILR, Guibal E, Hocesc MC, Martín-Lara MA (2012) Biosorption of hexavalent chromium from aqueous solution by *Sargassum muticum* brown alga. Application of statistical design for process optimization. *Chem Eng J* 183: 68– 76

Brown SE, Welton WC (2008) *Heavy Metal Pollution*, Nova Science Pub Inc.

Bulai P, Balan C, Bilba D, Macoveanu D. (2009) Study of the Copper (II) removal from aqueous solutions by Chelating Resin Purolite S930. *Environ Eng Manag J* 8: 213–218

Deep A, Kumar P, Carvalho JMR (2010) Recovery of copper from zinc leaching liquor using ACORGA M5640 Sep Purif Technol 76: 21–25

Cherono F, Njenga Mburu N, Kakoi B (2021) Adsorption of lead, copper and zinc in a multi-metal aqueous solution by waste rubber tires for the design of single batch adsorber *Heliyon* 7: e08254 <https://doi.org/10.1016/j.heliyon.2021.e08254>

El Azazi M, Shafie AS, Issa AA, Alsulaiti M, Al Yafie J, Shomer B, Al- saad K (2019) Potato peel as an adsorbent for heavy metals from aqueous solutions: Eco- structuring of a green adsorbent operating Plakett-Burman design. *Journal of Chemistry* <https://doi.org/10.1155/2019/4926240>

Emenike P.C, Omole D. O, Ngene B. U, Tenebe I. T, Maxwell O. 2017 Experimental investigation of copper removal from aqueous solution using *Musa paradisiaca* as a novel adsorbent. *WIT Transactions on Ecology and the Environment*. 216:1 73- 179

Gupta VK, Nayak A (2012). Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe₂O₃ nanoparticles. *Chemical Engineering Journal* 180 (2012). 81– 90.

Hoang LL, Jeong J, Lee JC, Pandey BD, Yoo JM, Trung HH (2011) Hydrometallurgical process for copper recovery from waste printed circuit boards (PCBs). *Miner Process Extr Metal Rev* 32:90–104.

Janin A, Blais JF, Mercier G, Drogui P, Selective recovery of Cr and Cu in leachate from chromated copper arsenate treated wood using chelating and acidic ion exchange resins. *J Hazard Mater* 169: 1099–1105

Jung KW, Choi BH, Hwang MJ, Choi JW, Lee SH, Chang JS, Ahn KH (2017) Adsorptive removal of anionic azo dye from aqueous solution using activated carbon derived from extracted coffee residues. *Journal of Cleaner Production* 166:360- 368.

Kitobo W, Gaydardzhiev S, Frenay J, Bastin D, Ndala I (2010) Separation of copper and zinc by solvent extraction during reprocessing of flotation tailings. *Sep Sci Technol* 45: 535–540

Kumar GVSR, Malla KA, Yerra B, Rao KS (2019) Removal of Cu (II) using three low-cost adsorbents and prediction of adsorption using artificial neural networks. *Applied Water Science* 9:44

Langama PLM*, Jean Jacques Anguile, Albert Novy Messi Me Ndong, Adam Bouraima, Crislain Bissielou 2021. Adsorption of Copper (II) Ions in Aqueous Solution by a Natural Mouka Smectite and an Activated Carbon Prepared from Kola Nut Shells by Chemical Activation with Zinc Chloride (ZnCl₂). *Open Journal of Inorganic Chemistry*, 2021, 11, 131-144

Larous S, Meniai AH, Lehocine MB (2005) Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust *Desalination* 185(1-3):483-490

Lee M (2011) Production of nickel metal powder from a spent etching solution by solvent extraction and chemical reduction. *J Nanosci Nanotechnol* 11: 1621–1624

Mehta SK, Gaur JP (2005) Use of Algae for Removing Heavy Metal Ions from Wastewater: Progress and Prospects. *Critical Rev in Biotechnol* 25:113-152 <https://doi.org/10.1080/07388550500248571>

Mishra S, Devi N (2011) Extraction of copper (II) from hydrochloric acid solution by Cyanex 921. *Hydrometallurgy* 107: 29–33

Misra RK, Jain SK, Khatri PK (2011) Ion exchange recovery of nickel(II) on macroporous weak acid resin (D151 resin). *Indian J Chem Technol* 18:13–20

Papadopoulos A, Fatta D, Parperis K, Mentzis A, Haralambous JK, Loizidou M (2004) Nickel uptake from a wastewater stream produced in a metal finishing industry by combination of ion-exchange and precipitation methods, *Sep Purif Technol* 39 :181–188

Siegel FR 2002 Contaminant/natural background values: timing and processes. *Environmental geochemistry of potentially toxic metals*. Springer: 77–101

Singh S, Kapoor D, Khasnabis S, Singh J, Ramamurth PC (2021) Mechanism and kinetics of adsorption and removal of heavy metals from wastewater using nanomaterials *Environmental Chemistry Letters* <https://doi.org/10.1007/s10311-021-01196-w>

Tasar S, Ozer A (2020) A thermodynamic and kinetic evaluation of the adsorption of Pb (II) ions using peanut (*Arachis hypogaea*) shell-based biochar from aqueous media. Polish J of Environ studies 29(1):293 – 305

Temkin MI, Pyzhev V (1940) Kinetics of ammonia synthesis on promoted iron catalyst, *Acta Phys. Chim. USSR*, 327–356.

Tong TS, Kassim MJ, Azraa A (2011) Adsorption of copper ion from its aqueous solution by a novel biosorbent, *Uncaria gambir*: Equilibrium, kinetics, and thermodynamic studies. *Chemical Engineering Journal* 170:145-153

Wadhawan S, Jain A, Nayyar J, Mehta SK (2020) Role of nanomaterials as adsorbents in heavy metal ion removal from wastewater: a review. *J Water Process Eng* 33:101038

Weber TW, Chakkravort RK. (1974). Pore and solid diffusion models for fixed bed adsorbers, *AIChE J* 20: 228

Zhang X, Liu H, Jang J, Zhang L, Cao B, Liu L, Gong W (2021) Removal of cadmium and lead from aqueous solutions using iron phosphate-modified pollen microspheres as adsorbents. *Reviews on Advanced Materials Science* 2021; 60: 365–376

Zhu SZ, Wang LP, Chen W (2009) Removal of Cu (II) from aqueous solution by agricultural by product: peanut hull, *Journal of Hazard Mat* 168:739-746

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The datasets generated during and/or analysed during the current study are included in the manuscript. Any other data needed are available from the corresponding authors on reasonable request.

Author's contribution

Chijioke John Ajaelu conceived and designed the experiments. Material preparation and data collection were done by Bukola Adegeye and Chijioke John Ajaelu, analysis was done by Chijioke John Ajaelu. The first draft of the manuscript was written by Chijioke John Ajaelu, Adebomi Ikotun took part in writing the second version of the manuscript. All authors read and approved the final manuscript