Comparative Studies of Copper (II) Biosorption by Streptomyces Species Using Existing and Proposed Equilibrium Models

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Abstract

The pollution of soils and water bodies by heavy metals is a serious concern because of its wide spectrum of negative impacts on environmental and human health. Due to urbanization and expansion of industrial activities, a large amount of metals are released into the environment, thereby, tampering with eco-balance. Conventional methods of remediation of heavy metal-polluted soil and water are expensive and not very eco-friendly. This necessitates the search for techniques to provide environmentally friendly remediation at low cost. The use of microbial biosorbents; Streptomyces chartreusis, Streptomyces aureoverticillatus and Streptomyces subrutilus for the removal of copper ions (Cu (II)) from aqueous solution was studied. Batch sorption experiments were conducted using the method of Khodaverdiloo and Samadi (2011) and the experimental data were analyzed with four isotherm models; Langmuir, Freundlich, Harkins–Jura and Halsey isotherms and a newly proposed isotherm. The lowest equilibrium uptake (Qe) of 205 mg/g to 216 mg/g was obtained at an equilibrium concentration (Ce) of 205 mg/l, while Ce of 1295 mg/l gave the maximum uptake (704 to 856 mg/g). The values of the correlation coefficient (R^2) of the isotherms gave the best fit (>0.9) with the proposed and Freundlich isotherms. Based on the values of sum of square error and standard error, Harkins-Jura isotherm gave the best fit (<0.005). It can be concluded that Streptomyces chartreusis, Streptomyces aureoverticillatus and Streptomyces subrutilus are effective biosorbents for the removal of Cu (II) from aqueous solutions based on the proposed biosorption isotherm.

Keywords: copper (II) removal; Equilibrium uptake; Equilibrium concentration; Error parameters; Streptomyces.

INTRODUCTION

Copper is an environmental pollutant, particularly in areas with high anthropogenic activities as considerable amount is released as byproduct of numerous manufacturing, industrial, refining and mining processes, inducing toxicity (Oves et al., 2016).

Copper toxicity affects all forms of life negatively. For instance, in plants, the normal physiological activities including respiration, photosynthesis, electron transport chain and cell division are hampered (Jadia and Fulekar, 2009; Pourrut*et al*., 2011). Furthermore, inhibition of cytoplasmic enzymes in plant cells occur which consequently affects growth and metabolism (Chibuike and Obiora, 2014; Gaur et al., 2014).

In humans, various health problems such as copperiedus, cirrhosis, autism, hypothyroidism, fibromyalgia, Alzheimer's disease etc have been linked to copper toxicity (Squitti et al., 2009). In microorganism, growth, morphology and metabolism are inhibited or terminated through functional disturbance, protein denaturation or destruction of the integrity of the cell membrane. However, prolonged exposure to heavy metal pollution results in selective pressure leading to the emergence of resistant microbial strains with bioremediation potentials (Anyanwu et al., 2011).

Microbial bioremediation of heavy metals have been attributed to a number of processes such as oxidation-reduction, complexation, methylation and biosorption.

Biosorption is rapidly gaining attention as a cost effective and eco-friendly technique for toxic metal removal owing to the metal binding capacities of various biological materials. It is based on the inherent ability of different biomaterials to bind and concentrate metal ions on the cell surface via functional groups such as phosphates, sulf-hydryl, hydroxyl and carboxyl groups (Nwidi and Aguwamba, 2015; Ayangbenro and Babalola, 2017).

Biosorption offer some advantages over conventional metal removal methods such as; cheaper production of biomass (adsorbents), multiple heavy metals uptake at a time, highly selective and specific for metal adsorption, functional over wide range of; temperature, pH and presence of other metal ions, easy desorption of adsorbed metals and less production of toxic by-products (Abbas et al., 2014; Abdi and Kazemi, 2015). However, challenges like saturation of active sites of metal binding ligands and reversible nature of metal sorption may limit its use in bioremediation.Biosorption systems, pathways and mechanisms are better understood and interpreted using biosorption or adsorption isotherms. Adsorption isotherms or equilibriums are used to represent solute sorption at solid/solution interface and used to describe the amount of adsorbate on the adsorbent at a constant temperature (Subramanyam and Das, 2014). In predictive microbiology, adsorption models are employed to ensure that the appropriate sorbent is used to remove the target pollutant at the right under appropriate environmental conditions (Tang *et al*., 2012; Salman *et al*., 2018). Typically, an adsorption isotherm is the plot of uptake of metal (q) versus equilibrium or final solute concentration in the solution (C_f). For studying the isotherm plots, parameters including temperature, pH and ionic strength are kept constant while varying metal concentration (Aichour et al., 2018; Kajjumba et al., 2018).

The aim of this work is to derive a novel adsorption isotherm from proportionality equations and compare its suitability with other existing isotherms in the biosorptionof copper (II) using Streptomyces biosorbents.

MATERIALS AND METHODS

Biosorbents collection: The biosorbents used in this study were Streptomyces strains namely; *Streptomyces chartreusis*, *Streptomyces aureoveticillatus* and *Streptomyces subrutilus.* They were collected from the Department of Microbiology University of Nigeria, Nsukka, resuscitated in mineral salt nutrient medium and stocked in bijou bottles slant at 4°C for further use.

Simulationof copper (II) pollution: Mineral salt medium in 250 ml Erlenmeyer flask containing; 0.2g $MnSO_4$. $5H_2O$, 0.2 g tryptone, 1.0 g KH_2PO_4, 1.0 g K_2HPO_4 and 10g soluble starch was artificially polluted with 0.5 g $CuSO_4$ in 1000 ml of distilled water and autoclaved at 121°C for 15 minutes.

Biosorption studies: Batch sorption experiments were carried out according to the method of Khodaverdiloo and Samadi (2011) with slight modification. Streptomyces biosorbents were grown in Erlenmeyer flasks (100 ml) containing 25 ml of the metal ion solution at varying metal ion concentrations of 100, 250, 500, 750, 900 and 1500 mg/l by agitation at 120 rpm in a rotary shakerfor 72h. Exactly 5ml of each sample was withdrawn and centrifuged at 10, 000 g for 2 min and the supernatant transferred into vials. Residual metal ion concentration was determined via flame atomic absorption spectrophotometer (AA-7000) at 324.8 nm. Metallic ion adsorption (Q_e) and biosorption efficiency (B.E) werecalculated as;

$$Q_e = (Co - Cf)V/M \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (I)$$

$$B.E = \frac{(Co-Ce)}{Co} \times 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots......(II)$$

Where: Co (in mg/l) is the initial metal ion concentration;Cf (mg/l)is the final or equilibriummetal ion concentrations; V is the solution volume (l) and M is the mass of biosorbent (g)

Adsorption isotherms: For the determination of the metal ion uptake at equilibrium, sorption experiment was performed in 100 ml Erlenmeyer flasks containing 25 ml of the metal ion solution at constant reaction temperature (30°C) and reaction pH (6.7). Constant temperature and pH were attained via a temperature controlled rotary shaker and 0.1m HNO_3/NaoH respectively while metal ion concentration was varied. Equilibrium data obtained were modeled using the following isotherms; Langmuir, Freundlich, Harkins-Jura, Halsey as well as a newly derived isotherm.

Model fitting: Coefficient of correlation (R^2), sum of squared error (SSE) and standard error ($SE_{\bar{X}}$) of each isotherm given in the equations below were comparatively assessed to determine the best fit for the experimental data

$$R^2 = \frac{\sum_{i=1}^{n}[q_{cal}-\overline{q_{exp}}]^2}{\sum_{i=1}^{n}[q_{cal}-\overline{q_{exp}}]^2 + \sum_{i=1}^{n}[q_{cal}-q_{exp}]^2} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (III)$$

$$SSE = \sum_{i=1}^{n} X_i - \bar{X}^2 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. \quad (IV)$$

$$SE_{\bar{X}} = \frac{S}{\sqrt{n}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..... \quad (V)$$

where; q_{cal} is the calculated amount of adsorbate adsorbed onto adsorbent, q_{exp} is the experimental amount of adsorbate adsorbed, s is the standard deviation of the mean and n is the number of data points (Hameed et al., 2007).

RESULT/ DISCUSSION

Result obtained for the biosorption of copper (II) ion by the biosorbents is shown in Table 1. At equilibrium concentration (Ce), it was observed that the lowest Cu (II) uptake (Qe) by *S. chartreusis*was216 mg/g and the highest was 704 mg/g. With *S. aureoverticillatus* as biosorbent, lowest and highest uptakes recorded were 205 mg/g and 831 mg/g respectively. Also, *S. subrutilus*gave a Qe value range of 227 mg/g to 856 mg/g. Except for a slight difference observed at 205 mg/l, adecrease in biosorpion efficiency (B.E) was seen with increase in metal ion concentration. This is comparable to the result of Kulkarni et al. (2019) that reported a decline in percentage biosorption from 86% to 73% as Cd (II) ion concentration was increased from 10 mg/L to 50 mg/L in a biosorption study. The decrease in biosorption is

due to the increased number of metal ions competing for the available active sites on biosorbent.

An adsorption isotherm model was derived and related to four other existing adsorption isotherms; Langmuir, Freundlich, Harkins-Jura and Halsey to determine which best described adsorption at the adsorbent-adsorbate surface. Three error parameters namely; coefficient of correlation, sum of squared error and standard error were employed in the comparative analysis of the proposed and the four existing models.

Table 1: Biosorption of Cu (II) by *S. chartreusis*, *S. aureoverticillatus* and *S. subrutilus*

Ce (mg/l)	B.E (%)	Qe (mg/g)		
		S. chartreusis	*S. aureoverticillatus*	*S. subrutilus*
34	66	370	350	412
130	48	420	399	522
205	59	216	205	227
579	23	545	448	493
752	16	578	548	672
1295	14	704	831	856

Harkins-Jura isotherm: the representation of the experimental data for the three biosorbents using the non-linear form of this isotherm is shown in Fig. 1. Harkins-Jura isotherm assumes the possibility of multilayer adsorption on the surface of adsorbents with heterogeneous pore distribution and expressed as;

$$\frac{1}{q_e^2} = \frac{B}{A} - \left(\frac{1}{A}\right) logC_e \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(VI)}$$

Where B and A are Harkin-Jura constants calculated from plotting $1/q_e^2$ against $logCe$ (Akmil, 2006).
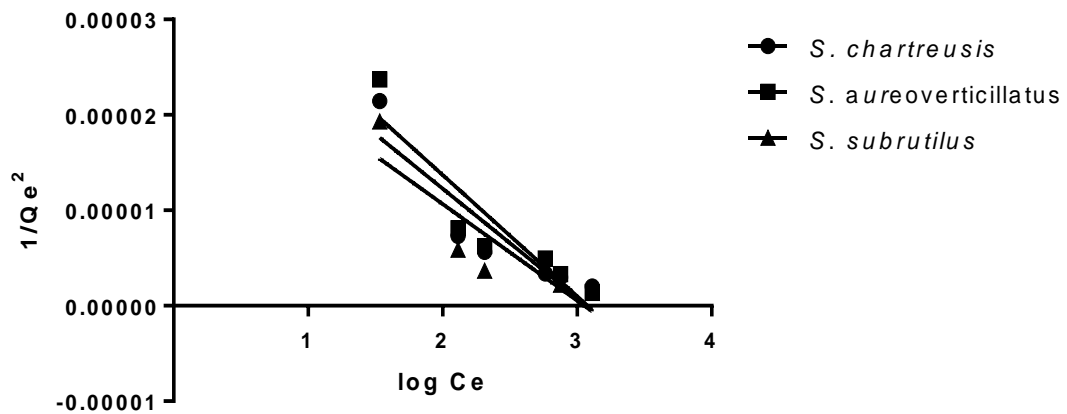

Fig. 1: Showing Harkins-Jura isotherm plot for *S. chartreusis*, *S. aureoverticillatus* and *S. subrutilus*

Foo and Hameed (2010) in their investigation on the uptake of reactive black 5 from wastewater using bentonite clay reported that; Harkin-Jura isotherm gave a better fit to the adsorption data than Halsey, Temkin and Freundlich isotherms. However, fitting experimental data from copper (II) adsorption into Harkins-Jura model yielded a very poor R^2 (-0.836) compared to other tested models as reported by Benzaoui et al. (2017).

Freundlich isotherm: adopted to describe the adsorption occurring onto heterogeneous surface (Ayawei et al., 2015) given by;

$$LogQe = Logk + \frac{1}{n}LogC_e \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (VII)$$

Where Qe is the metal uptake (mg metal per g biosorbent), C_e is the equilibrium concentration of the metal in the solution (mg/L), k and n are Freundlich constants indicative of biosorption capacity and biosorption affinity respectively in (mg/g (mg/L)$^{1/n}$). Fig.2 shows the Freundlich isotherm plot of the experimental data.
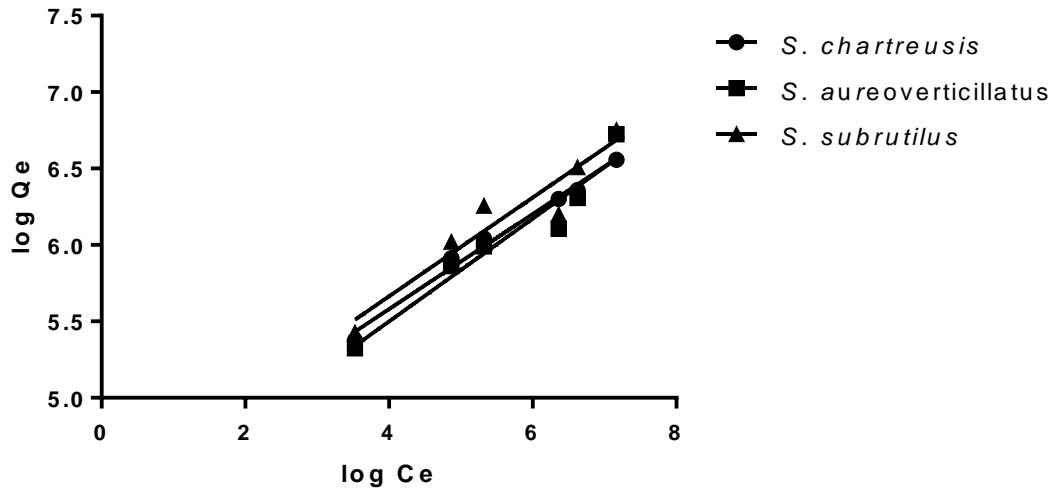

Fig. 2: Showing Freundlich isotherm plot for *S. chartreusis*, *S. aureoverticillatus* and *S. subrutilus*

Langmuir isotherm: first derived by Langmuir. Langmuir isotherm suggests that adsorption occur through monolayer sorption onto a surface with a finite number of identical sites given as;

$$\frac{1}{Qe} = \frac{1}{Qmax} \cdot \frac{1}{bCe} + \frac{1}{Qmax} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (VIII)$$

Where in both cases, Qmax (mg/g) is the maximum biosorption capacity of the biosorbent, b (mg/l) is the langmuir constant related to the affinity between the biosorbent and sorbate.
The linear Langmuir plot of the experimental data obtained for the three bisorbents is shown in Fig.3.
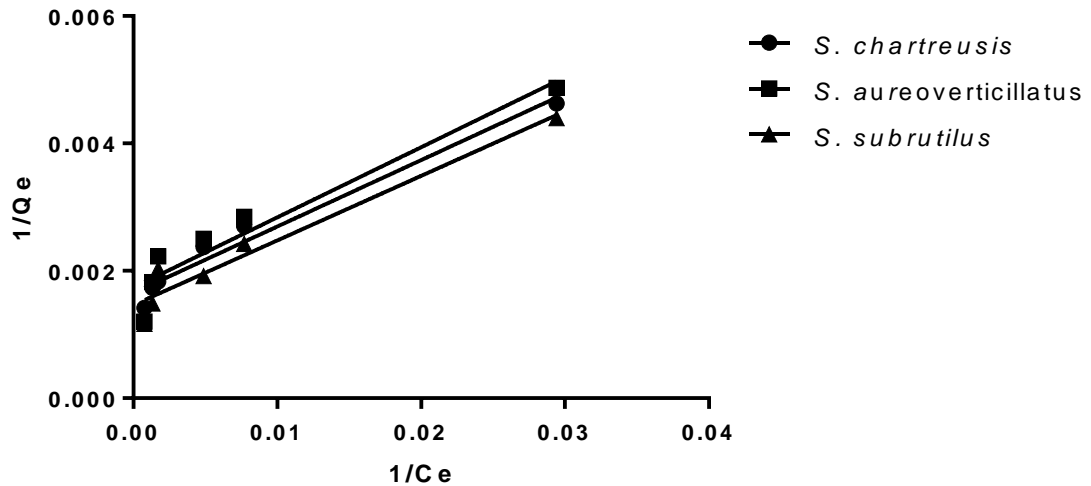
Fig. 3: Showing Langmuir isotherm plot for *S. chartreusis*, *S. aureoverticillatus* and *S. subrutilus*

Halsey isotherm: used to evaluate multilayer sorption at a relatively large distance from the surface. Songet al. (2014) applied the Halsey isotherm in the study of Pb^{2+} removal from aqueous solutions. On fitting the experimental data, a high R^2 value attributed to heterogeneous distribution of the active sites and multilayer adsorption was obtained. However, Benzaoui et al. (2017) modeled the use of bottom ash of expired drugs incineration for copper (II) ions adsorption and concluded that Halsey isotherm was not the most satisfactory fit for the experimental data since it yielded R^2 value of 0.907 (i.e.<0.99).

Halsey equation is given as follows;

$$Qe = Exp\left[\frac{lnK_H - lnCe}{n}\right]\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..(IX)$$

Where; K_H and n_H are Halsey isotherm constants obtained respectively from the slope and intercept of the plot of lnQe against lnCe (Ayawei et al. 2015). Fig. 4 is the graphical representation of the experimental data obtained for the three biosorbents using Halsey's isotherm.
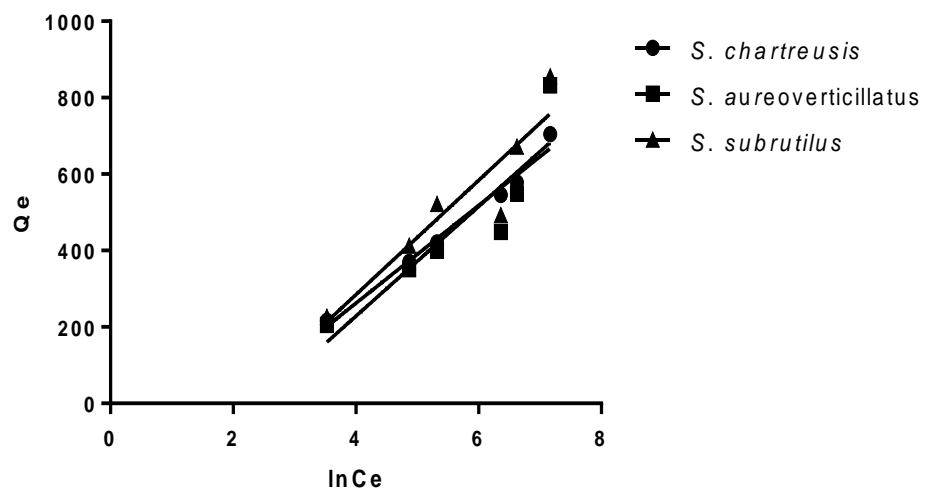

Fig. 4: Showing Halsey isotherm plot for *S. chartreusis*, *S. aureoverticillatus* and *S. subrutilus*

The proposed model: The proposed bisorption isotherm was based on Freundlich model but in addition to the possibility of a mechanical interaction at adsorbent-adsorbate surface that influence binding affinity of the adsorbate for the active sites. The model is given as;

$$\log Qe = 1/b \, (\log Ce) + 1/b \, (\log n) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(X)$$

where Ce (mg/l) and Qe (mg/g) refer to metal ion concentration and uptake at equilibrium respectively, b (mg/g $(mg/L)^{1/n}$) is the factor by which uptake increases while n is the biosorption affinity.The plot of loq Qe against logCe is shown in Fig.5 below.
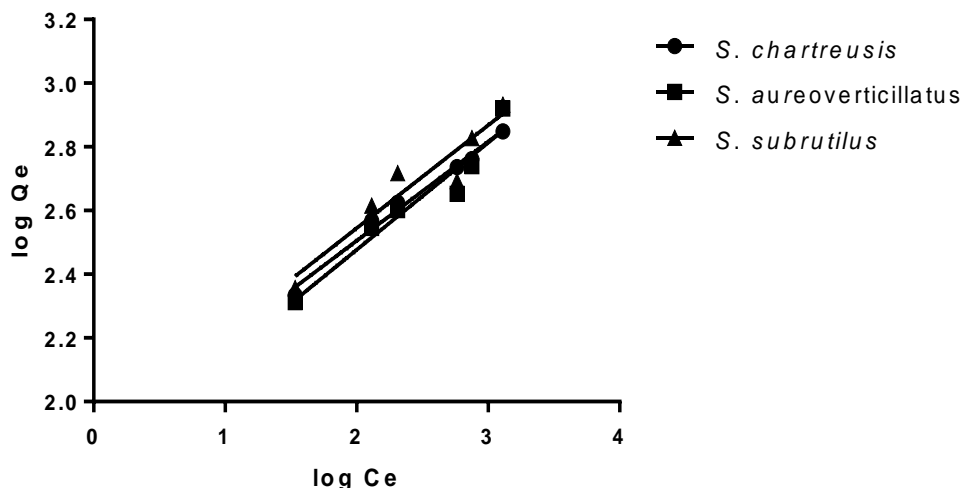

Fig. 5: Showing plot of the proposed isotherm for *S.chartreusis*, *S. aureoverticillatus* and *S. subrutilus*

Adsorption isotherms error parameters
Tables 2, 3 and 3, contain the values for sum of squared error, standard error and linear regression coefficient of correlation for bisorbents;*S. chartreusis*, *S. aureoverticillatus* and *S. subrutilus*respectively.

Table 2:Adsoption isotherm error parameters for copper (II) biosorption onto*S. chartreusis*

Error parameters/Adsorption isotherms	Harkins-Jura	Freundlich	Langmuir	Halsey	Proposed model
R^2	0.834	0.987	0.968	0.983	0.987
SSE	4.39×10^{-11}	1.15×10^{-2}	2.18×10^{-7}	251	2.17×10^{-3}
$SE_{\bar{X}}$	1.35×10^{-6}	2.19×10^{-2}	9.54×10^{-5}	10.2	9.51×10^{-3}

NB: values were given in 3 significant figures

Table 3: Adsoption isotherm error parameters for copper (II) biosorption onto *S. aureoverticillatus*

Error parameters/Adsorption isotherms	Harkins-Jura	Freundlich	Langmuir	Halsey	Proposed model
R^2	0.843	0.933	0.923	0.816	0.933
SSE	5.08×10^{-11}	7.29×10^{-2}	6.11×10^{-7}	417	1.38×10^{-2}
$SE_{\overline{X}}$	1.46×10^{-6}	5.51×10^{-2}	1.6×10^{-4}	41.7	2.39×10^{-2}

NB: values were given in 3 significant figures

Table 4: Adsorption isotherm error parameters for copper (II) biosorption onto *S. subrutilus*

Error parameters/Adsorption isotherms	Harkins-Jura	Freundlich	Langmuir	Halsey	Proposed model
R^2	0.781	0.907	0.948	0.862	0.907
SSE	4.87×10^{-11}	9.63×10^{-2}	3.404×10^{-7}	353	1.82×10^{-2}
$SE_{\overline{X}}$	1.42×10^{-6}	6.33×10^{-2}	1.19×10^{-4}	36.7	2.75×10^{-2}

NB: values were given in 3 significant figures

Langmuir Isotherm model is adopted to describe the adsorption properties of metal ions on the interface of a solid material which is typical of monolayer adsorption (Vasudevan et al., 2013). The plot of 1/Qe versus 1/Ce (Fig.3) yielded a linear graph, indicating the applicability of classical Langmuir adsorption isotherm to single metal ion solution. The value of linear regression coefficient R^2 was highest for *S. chartreusis* ($R^2>0.96$) and lowest for *S. aureoverticillatus* ($R^2<0.93$).

Freundlich Isotherm model is used to describe adsorption on a heterogeneous surface with uniform energy phases (Ramesh et al., 2007; Atia et al., 2008). Similar to the proposed model, Freundlich yielded very high R^2 values for the three bisorbents. However, the error values obtained for SSE and $SE_{\overline{X}}$were high (> 0.05).

The Harkins-Jura isotherm equation which accounts for multilayer adsorption and the existence of a heterogeneous pore distribution yielded low R^2 values between 0.781 to 0.843 (Tables 2-4). This was similar to reports by Dada et al. (2012), Fakhri (2013) and Erdogan (2018).This result could have initially indicated homogenous nature of the adsorbent surface for copper ions as opposed heterogeneous adsorption proposed by Harkins-Jura. However, a look at the SSE and $SE_{\overline{X}}$values suggested otherwise.

Halsey isotherm gave good R^2 value for *S. chartreusis* but the SSE and $SE_{\overline{X}}$ values for all the three biosorbents were extremely high.

A comparative analysis was done on the four cited bisorption isotherms and the proposed model. In this comparative analysis, three parameters; coefficient of correlation (R^2), sum of square error (SSE) and standard error ($SE_{\overline{X}}$) were employed.

Tables 2, 3 and 4, each contains the values for the error parameters determined for each of the biosorbent. Judging by the R^2 values from Table 2, the proposed model and Freundlich best described the biosorption of Cu (II) by *S. chartreusis*. This was followed closely by Halsey's and Langmuir's isotherms. However, in terms of sum of square and standard error values, Harkins-Jura isotherm best described biosorption for *S. chartreusis*, followed by Langmuir model and the proposed model. From table 3, judging biosorption equilibrium using the error

parameters shows that; R^2value of 0.933, 0.933 and 0.923 were obtained for the proposed model, Freundlich model and Langmuir model respectively. SSE value was as low as $4.39\times10^{-11}$for Harkins-Jura, followed by 2.184×10^{-7} for Langmuir and 2.17×10^{-3} for the proposed model. Also, $SE_{\overline{X}}$value was lowest for Harkins-Jura (1.46×10^{-6}), Langmuir (0.00016) and the proposed model (0.0239).

Finally from table 4, considering values of R^2, the proposed isotherm model best described the mechanism for the biosorption of Cu (II) by *S. subrutilus* while in terms of SSE and$SE_{\overline{X}}$, biosorption was best described by Harkins-Jura model.
The above results show that biosorption mechanisms are complex. For instance, while the proposed biosorption model produced the highest value of coefficient of correlation (R^2) for biosorption of Cu (II) by the three biosorbents, Harkins-Jura gave the highest of SSE and $SE_{\overline{X}}$ values, showing that a single parameter alone is not sufficient to determine the mechanism of biosorption.

CONCLUSION
In this study, tests were performed to evaluate the use of microbial cells as biosorbents for copper ions. It was found that the microbial cells were capable of Cu (II) uptake at optimum reaction concentration, temperature and pH. Adsorption equilibra described by Langmuir, Harkins-Jura, Freundlich and Halsey isotherms were used to model the experimental alongside a proposed model based specifically on binding affinity of the adsorbate for the adsorption site. It can be concluded that biosorption followed a heterogeneous process and theproposed model is best suited for the removal of the copper ions in this regardas it yielded both high R^2values and considerably low SSE and $SE_{\overline{X}}$values. For further studies, this proposed model can be calibrated and verified to reduce error values to the barest minimum.

CONFLICT OF INTERESTS
The authors declare that there is no conflict of interests in this study

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