Isotherm Study Of The Biosorption Of Cu (II) From Aqueous Solution By *Vigna Subterranea* (L.) *Verdc* Hull.

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Abstract: - The removal of Cu(II) ions from aqueous solutions is critical to minimize its toxicity to both plants and animals. *Vigna subterranea* (l.) *Verdc* hull (VSVH) was investigated for its potential to remove Cu(II) ions from wastewaters. Batch equilibrium studies were carried out to optimize pH, contact time, and dosage at constant temperature (25 ± 1 ^{o}C) and agitation rate (180 rpm). The effect of initial Cu(II) ion concentration was investigated under optimized conditions (pH, 6; contact time of 60 minutes and dosage of 6 g/L) and the equilibrium data were analyzed using two parameter isotherms; Temkin, Langmuir and Freundlich models. The equilibrium data fitted the isotherms in the order; Langmuir > Freundlich > Temkin, all with R^2 > 0.98. The biosorption of Cu(II) ions by *VSVH* was found to be favorable (0 < R_L< 1 and 1/n < 1), endothermic, spontaneous (ΔG^o = -11.11 kJ/mol) and chemisorption in nature. Very high removal efficiency and maximum sorption capacity were realized indicating the viability of the removal of Cu(II) ions by the novel biosorbent. The use of *VSVH* for the removal of Cu(II) ions from wastewaters can be implemented as a standalone technology or coupled with the conventional methods in order to complement their wastewater cleaning potentials.

Keywords: - Biosorption, Cu(II) ions, Equilibrium, Temkin, *Vigna subterranea* (L.) *Verdc.*

1 INTRODUCTION

The proliferation of small scale farmers, small scale industries and small scale mining activities in Zimbabwe has to be accompanied by cheap, readily available wastewater treatment methods to clean the effluents of heavy metal ions to meet the Standard Association of Zimbabwe (SAZ) and the World Health Organization (WHO) regulations. Copper is one of the most used metal and gets into the environment through wastewaters from copper wire mills, coal burning industries, electroplating, tanning, smelting and refining, insecticides, fungicides and iron and steel industries [1]. Copper is an essential micronutrient that is incorporated into a number of metallo-enzymes involved in hemoglobin formation, drug metabolism, carbohydrate metabolism, catecholamine biosynthesis, the cross-linking of collagen and the antioxidant defense mechanism [2].

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However if present in drinking water at concentrations higher than 5 mg/L, copper causes nausea, vomiting, abdominal pain and diarrhea immediately following ingestion. At very high concentrations in drinking water, it damages the immune system. Araya et al.[3] reported decrease in fetal growth in rats, mice and mink that were exposed to Cu(II) ions. It was against this background that the removal of Cu (II) ions from wastewater was prioritized. The conventional methods of metal-ion removal that include chemical precipitation, membrane technologies, filtration, evaporation recovery, chemical oxidation or reduction, ion exchange and electrochemical treatment require extremely high initial capital investment, generate chemical sludge whose disposal is problematic and have been reported to be ineffective when the metal ion concentration is less than 100 mg/L [4]. Recent developments are focusing on biosorption that has the following advantages: reusability of biomaterial, low initial and operating costs, selectivity for specific metal ion, short operation time and minimization of chemical sludge [5]. Several biomaterials have been investigated for their ability to remove metal ions from aqueous solutions. These include; river green algae [6], water hyacinth roots [7], [8], maize tassels [9], *Caesalpinia bonducella* seed [10], Nile rose plant [11], bael tree leaf [12], *Canna indica* roots [13], *Sphagnum* moss [4], groundnut hull [5] and fluted pumpkin waste [14]. These materials were able to biomine different metal ions from wastewaters. Bambara groundnut, *Vigna Subterranea* (L.) *Verdc* (*VSV*), is an important African legume that is grown across all farming regions in Zimbabwe [15]. The kernels can be boiled and eaten as a soft porridge; the dry seeds are eaten after being boiled, either on their own or mixed with maize grain or can be used as a relish during dry season [16]. The literature search done indicated that *Vigna Subterranea* (L.) *Verdc* hull has not been used as a biosorbent for metal-ion sorption. Investigating its potential for metal ion sorption is therefore important. The study was carried out to investigate the use of *Vigna Subterranea* (L.) *Verdc* hull for the sorption of Cu(II) ions from wastewater. Two parameter equilibrium adsorption isotherms were used to describe the sorption process under optimized conditions of pH, contact time and dosage.

2 METHODOLOGY

2.1 Sampling and sample treatment

About 50 kg of *Vigna Subterranea* (L.) *Verdc hull* (*VSVH*) was purchased from Kudzanai market place, Gweru, Zimbabwe, from four suppliers. The composite mixture of the nuts was hand shelled and 2 kg of the hulls was collected and washed four times with tap water thrice with distilled water. The hulls were sun dried for 6 hours and then further dried in a laboratory oven (DHG-9070, India) set at 105 ^{o}C to constant mass. The dry *VSVH* was ground into powder using pestle and mortar and then sieved through a 250 µm aperture sieve. The powder was sealed in polythene containers awaiting subsequent use.

2.2 Preparation of solutions.

Spectroscopic grade chemicals were used in preparing all the solutions that were used in the study. Synthetic stock solution of Cu (II) effluent (1000 mg/L) was prepared by dissolving 3.772 g of $CuSO_4.5H_2O$ (Skylabs, South Africa) in 1000 mL of deionized water. Calibration standards and all other concentrations of Cu (II) ions were prepared by serial dilution of the stock solution. Sodium hydroxide (0.1 M NaOH) was prepared by dissolving 0.4001 g of analytical grade NaOH (Glassworld) in 100 mL of distilled water. Hydrochloric acid (Skylabs, South Africa), 0.1 M and 0.1 M NaOH were used for pH adjustment of the aqueous solution.

2.3 Batch experiments.

Batch experiments were carried out in stopper Erlenmeyer flasks to investigate how the critical parameters affect the sorption process. The critical parameters included pH, contact time, dosage and initial metal ion concentration [17]. Solution temperature, volume of synthetic effluent and rate of agitation were maintained constant throughout the study at 25 ± 1 ^{o}C, 100 mL and 180 rpm respectively.

2.3.1 Effect of pH.

The effect of pH was investigated using Cu(II) ion solutions of initial concentration of 20 mg/L. A volume of 100 mL of 20 mg/L of Cu(II) ions was transferred into separate 250 mL Erlenmeyer flasks. The pH was adjusted to 2, 3, 4, 5, 6 and 7 using 0.1 M HCl and 0.1 M NaOH solutions [18]. *VSVH* dosage of mass, 0.3 g, was added to each Erlenmeyer flask and the mixtures were placed on the rotary shaker (RS-R12) operated at 180 rpm at a temperature of 25 ± 1 ^{o}C for 24 h. The samples were vacuum filtered and analyzed by a Shimadzu (AA-680) flame atomic absorption spectrophotometer (FAAS).

2.3.2 Effect of contact time

Batch adsorption studies were conducted at different contact times in the range from 5 to 150 minutes, by contacting 100 mL of 20 mg/L of Cu(II) ions with 0.3 g adsorbent dose of *VSVH* at the optimum pH of 6, flask shaking rate of 180 rpm and a temperature of 25 ± 1 ^{o}C. Replicate analysis of the residual Cu(II) ions was done at each predetermined time by FAAS. The equilibrium time was found to be 50 minutes and 60 minutes was used for subsequent experiments to ensure that equilibrium was achieved.

2.3.3 Effect of adsorbent dosage

To each of 100 mL portion of 20 mg/L of Cu(II) ions in Erlenmeyer flasks, varying amounts of biomass ranging from 0.1 to 1 g were separately added. The mixtures were agitated over a shaker at 180 rpm for 60 minutes at a temperature of 25 ± 1 ^{o}C and a pH of 6. The mixtures were vacuum filtrated and analyzed for residual Cu(II) ions by FAAS.

2.3.4 Effect of initial concentration

The effect of initial concentration of Cu(II) ions was examined under optimum conditions by contacting 0.6 g samples of *Vigna Subterranea* (L.) *Verdc hull* powder with 100 mL of Cu(II) ion solutions of different initial concentrations ranging from 20 to 150 mg/L at pH 6. The experiments were conducted at a temperature of 25 ± 1 ℃ , a constant flask shaking rate of 180 rpm for a contact time of 60 minutes. The samples were vacuum-filtered and appropriately diluted before analysis by FAAS [19], [20].

3 TREATMENT OF RESULTS.

The lower limit of correlation of determination (R^2) of 0.9 was used as the lower limit to accept the fitness of the adsorption models in describing the experimental data. The initial and equilibrium concentrations of Cu(II) ions in solution were measured and the amount adsorbed was calculated from the mass balance equation 1 given below:

$$Q_e = \frac{V(C_i - C_e)}{m} \quad (1)$$

The percentage removal was calculated using equation 2.

$$\% \, Removal = \frac{C_i - C_e}{C_i} \quad (2)$$

Where C_i and C_e are the initial and equilibrium concentrations of Cu(II) ions in mg/L respectively, Q_e is the amount of Cu(II) ions adsorbed at equilibrium in mg/g, V is the volume of the Cu(II) solution (L) and m is the mass of *VSVH* in grams.

RESULTS AND DISCUSSION

Effect of pH

Fig. 1 shows that as the pH is increased from 2 to 5, there is a gradual increase in the biosorption of Cu(II) ions by VSVH biomass. Both metal ion sorbed, Qe and % removal gradually increased from pH 2 to 5. No significant change in sorption was observed above pH 5. At low pH, H^+ ions competed effectively with the Cu(II) ions to occupy sorption sites on the biosorbent surface resulting in minimum sorption of Cu(II) ion. As the pH of the system increases to pH 6, the number of negatively charged sites on biomass surface increased and the number of positively charged sites decreases. This results in greater electrostatic attraction of the Cu(II) ions by the VSVH sorbent surface [21].

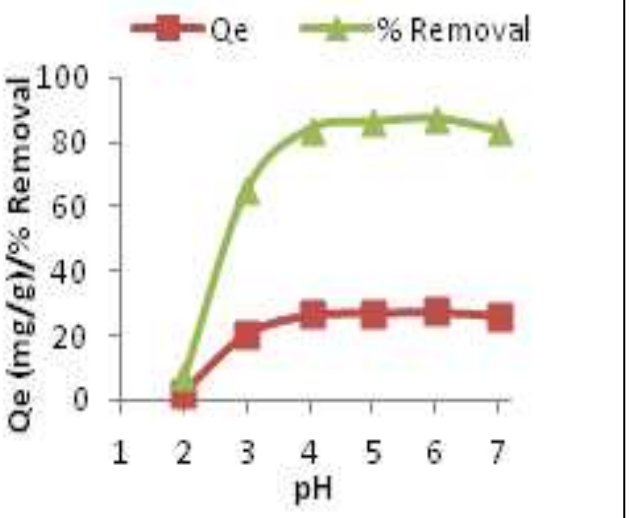


Fig. 1. Effect of pH on Cu(II) ion sorption.

Bishnoi et al [1] attributed the increase in Cu(II) ions uptake by Spirogyra algal biomass to the increase in negative charge on the surface of the biomass that promotes ionic interaction between adsorbent and the sorbate.

4.2 Effect of contact time

The effect of contact time was investigated using initial Cu(II) ion concentration of 20 mg/L with a sorbent dosage of 0.3 g at pH 6, a temperature of 25 ±1 ^{o}C and an agitation rate of 180 rpm over a time range from 5 to 150 minutes.

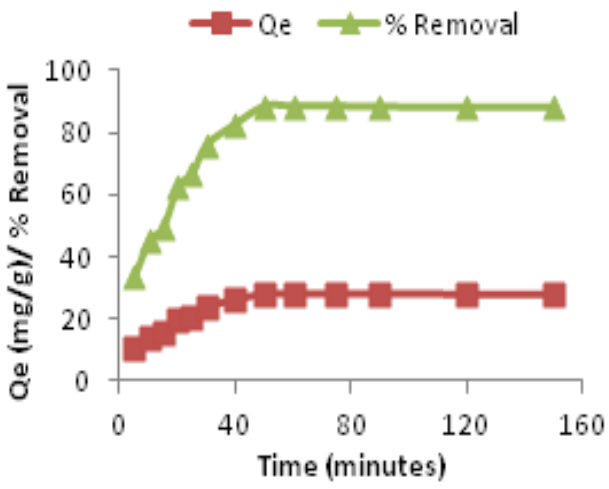


Fig. 2. Effect of contact time on Cu(II) ion sorption.

Fig. 2 shows that the adsorption is rapid at the initial stages and gradually decreases with time until it becomes constant after 50 minutes. This is attributed to the instantaneous utilization of the readily available sorbing sites on the surface of the *VSVH* [22]. The biosorption sites progressively diminish with time as they get occupied resulting in reduced diffusion gradient and hence the rate of sorption decreases with time until it reaches zero (equilibrium point) at 50 minutes. The contact time of 60 minutes was used throughout the study to ensure equilibration.

4.3 Effect of biomass dosage

The effect of biomass dosage on the sorption of Cu(II) ions is shown in Fig. 3. The amount of Cu(II) sorbed at equilibrium, Q_e, decreases with *VSVH* dosage. Rajamohan [23] argued that the decrease in Q_e may be due to solute transfer rate to the adsorbent surface getting splitted as the adsorbent dosage increased. This was echoed by Bishnoi et al [1] who attributed the decrease in Qe at higher biomass doses to the screen effect of dense outer layer of cells that block the binding sites from metal ions. Chirenje et al [22] got similar trends when wood ash was used for the retention of Cd, Cu, Pb and Zn. Percentage removal was also used to evaluate the effect of dosage. Fig. 3 shows that % removal increases with *VSVH* dosage up to a biomass dosage of 0.6 g (90.64%). After this optimum dosage, the Cu(II) % removal becomes constant. The results indicate that the optimum *VSVH* dosage for the sorption of Cu(II) ions from solution is 6 g/L.

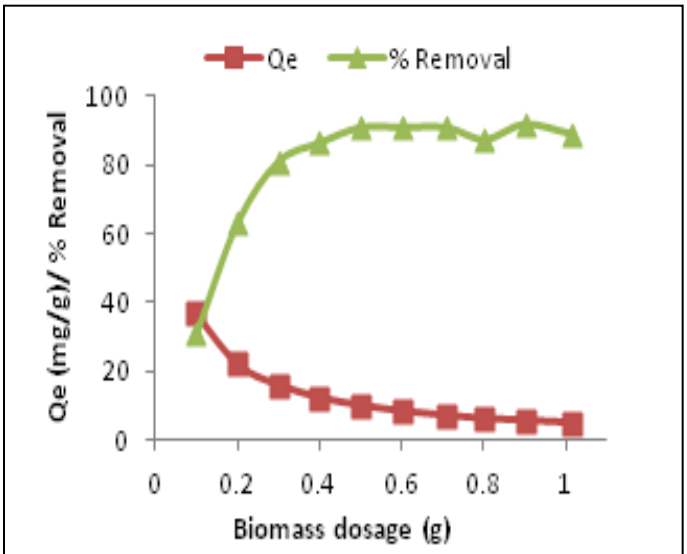


Fig. 3. Effect of adsorbent dosage on Cu(II) ion sorption.

4.4 Effect of initial Cu(II) ion concentration

The effect of initial Cu(II) ion concentration was investigated under optimum conditions of pH 6, 60 minute contact time, and VSVH dosage of 0.6 g/ 100 mL solution at a temperature of 25 ± 1 ^{o}C and agitation rate of 180 rpm.

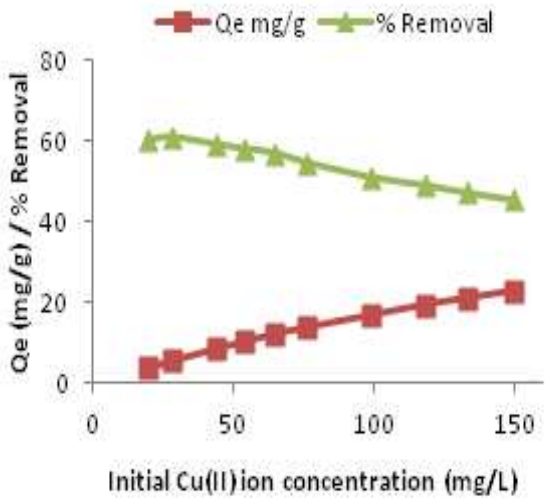


Fig. 4. Effect of initial concentration on Cu(II) ion sorption.

Fig. 4 shows that the amount of Cu(II) ion sorbed, Q_e, increases almost linearly over the concentration range investigated. The linearity between Q_e and C_i implied that significant removal of Cu(II) ions would occur beyond the 150 mg/L limit that was set in the research [24]. However, the % removal increases from 60.4 to 61.1 % at initial Cu(II) ion concentration of 20 to 30 mg/L respectively and gradually decreases to 45.8 % at initial Cu(II) ion concentration of 150 mg/L. This was the case when rice hulls were used to remove methylene blue from aqueous solution [25] and [11] also obtained similar trends during the adsorption of Cu, Zn, Cd and Pb ions from wastewater by Nile rose plant.

5 ADSORPTION ISOTHERMS

The interaction between the adsorbate molecules and the adsorbent can be inferred by the use of equilibrium adsorption isotherms. The isotherms are the presentation of the amount of solute adsorbed per unit mass of adsorbent (Q_e), as a function of equilibrium concentration (C_e) in bulk solution at constant optimum conditions [26]. The equilibrium data was generated by carrying out replicate adsorption experiments with varying initial concentration of Cu(II) ions in the range from 20 to 150 mg/L at constant solution temperature of 25 ± 1 ^{o}C, pH 6, *VSVH* dosage of 6 g/L, agitation rate of 180 rpm and a contact time of 60 minutes. The Temkin, Langmuir, Freundlich and Halsey isotherms were used to test the equilibrium data.

5.1 Temkin isotherm.

The isotherm assumes the adsorption process to be characterized by a uniform distribution of binding energies up to some maximum energy and that the heat of adsorption of all the molecules in the layer decreases linearly with surface coverage [27]. Boparai et al [28] reported that the Temkin isotherm considers chemisorption of an adsorbate onto the adsorbent. Therefore fitting of the model ($R^2 \geq 0.97$) to equilibrium data is confirmation of the chemisorption process. The model was chosen to estimate the adsorption potential and the heat of adsorption between the sorbate and sorbent [29]. The Temkin isotherm was used in its linearized form:

$$Q_e = RT/b_T \ lnK_T + RT/b_T \ lnC_e \qquad [3]$$

Where, T is the absolute temperature (K), R is the universal gas constant (8.314 J/mol.K), K_T is the equilibrium binding constant (L/mg), and b_T is the variation of adsorption energy (kJ/mol). Fig 5 shows the linear plot of Q_e against lnC_e. The correlation of determination (R^2 = 0.9835) shows that the Temkin isotherm fits the equilibrium data well implying that the Cu(II) ion adsorption on *VSVH* biomass was a chemisorption process.

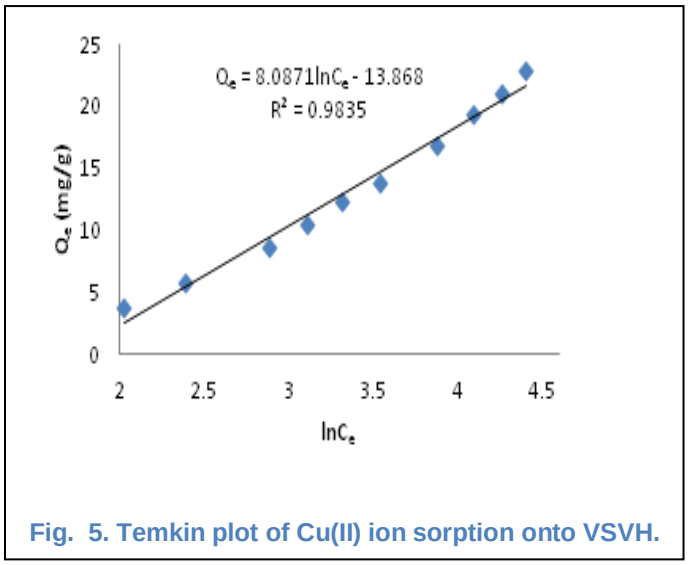


Fig. 5. Temkin plot of Cu(II) ion sorption onto VSVH.

The Temkin adsorption parameters in Table 1 show that the variation in adsorption energy, b_T, was positive (0.3065 kJ/mol) characteristic of an endothermic interaction between sorbate and sorbent. The low b_T value in this study, is similar to those obtained by [29] during the removal of Pb, Zn and Cu by Kaolinite. They concluded that ion-exchange mechanism was involved in the removal process. Kumar and Kirthika [12] came to a similar conclusion, based on low magnitude of b_T, when they used Bael tree leaf powder to remove Ni(II) ions from aqueous solution.

Table 1. Isotherm parameters for Cu(II) ion sorption onto VSVH.

Temkin parameters			Langmuir parameters			Freundlich parameters		
K_T	b_T	R^2	Q_m	b	R^2	Kf	1/n	R^2
0.1800	0.3065	0.9835	50.25	0.0113	0.9965	1.0043	0.7283	0.9847

5.2 Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption at a finite number localized sites that are equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites. Homogeneous adsorption occurs with each molecule possessing constant

enthalpies and sorption activation energy without transmigration of the adsorbate in the plane of the surface [26]. The linearized form of the isotherm was used in this study [30].

$$1/Q_e = 1/(bQ_m C_e) + 1/Q_m \quad (4)$$

Where C_e (mg/L) is the equilibrium concentration of the sorbate, Q_e is the amount of Cu(II) ions adsorbed at equilibrium (mg/g), b is the adsorption energy of the sorbent surface and Q_m is the maximum sorption capacity (mg/g). The plot of $1/Q_e$ against 1/Ce gives $1/Q_m$ as the y-intercept and $1/bQ_m$ as the gradient.

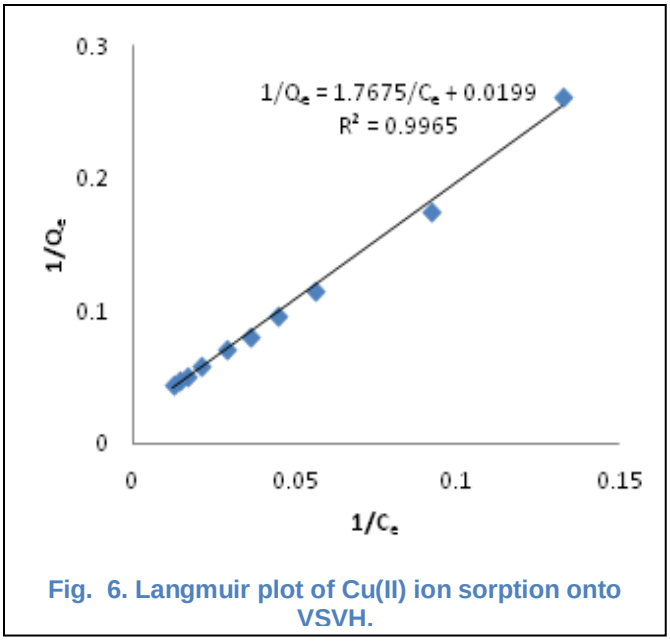


Fig. 6. Langmuir plot of Cu(II) ion sorption onto VSVH.

Fig. 6 and Table 1 show the Langmuir plot and parameters of the equilibrium data of Cu(II) ion sorption onto *Vigna Subterranea* (L.) *Verdc hull*. The correlation of determination (R^2 = 0.9965) was close to unit portraying the fitness of the model in describing the equilibrium data. A very high Q_m of 50.2513 mg/g was obtained that pointed to the high potential of the biomass in removing Cu(II) ions from aqueous solutions. This is much higher than the adsorption capacity of other adsorbents reported in the literature, namely; kaolite (4.42 mg/g) [29], acid treated *Canna indica* roots (19.4 mg/g) [13], garlic treated *Canna indica* roots (27.9 mg/g) [13], polyurethane immobilized *sphagnum moss* (13.2 mg/g) [4] and saw dust (7.8678 mg/g) [31]. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is expressed as:

$$R_L = 1/(1 + bC_i) \quad (5)$$

Where b is the Langmuir constant related to the apparent energy of sorption and C_i is the initial dye concentration [16]. The computed R_L values ranged from 0.823 to 0.3713 as the initial Cu(II) ion concentration was increased from 19.0295 to 149.826 mg/L. The R_L values were in the range $0 < R_L < 1$ that indicated sorption favorability. However as the initial concentration increased the separation factor approached zero indicating that the removal of Cu(II) ions by the *VSVH* biomass becomes less favorable [32].

5.3 Freundlich isotherm

Freundlich isotherm describes the non-ideal and reversible multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface [26]. The stronger binding sites are occupied first, until adsorption energies are exponentially decreased upon the completion of adsorption process. The slope ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value below one implies chemisorption process whereas 1/n above one is indicative of cooperative adsorption [33].

The linearized form of the isotherm can be expressed as:

$$lnQ_e = lnK_f + {}^1/_n \, lnC_e \quad (6)$$

Where K_f and n are constants indicating adsorption capacity and adsorption intensity respectively [34]. K_f and 1/n are obtained from the plot of lnQ_e against lnC_e shown in Fig. 7. The Freundlich isotherm fitted the adsorption data very well as shown by a high correlation of determination (R^2 = 0.9847). This evidences that adsorption process occurred on a heterogeneous surface with non-uniform distribution of adsorption heat and affinities. The parameter, 1/n (0.7283), is close to one implying that the surface is less heterogeneous hence the fitting of the equilibrium data to the Langmuir isotherm more than the Freundlich isotherm.

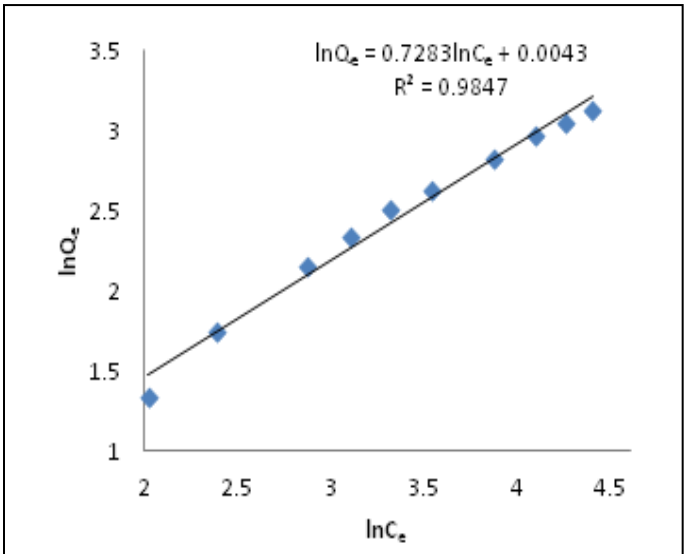


Fig. 7. Freundlich plot of Cu(II) sorption onto VSVH.

The value of 1/n < 1 further confirms the interaction between Cu(II) ions and *VSVH* biomass as a chemisorption process. The K_f and 1/n values (Table 1) show easy separation of Cu(II) ions from aqueous solution and indicate favorable adsorption [12]. Similar magnitude of 1/n were obtained by Charles and Odoemelam [35] during Hg(II), Pb(II) and Cd(II) ions' removal from aqueous solutions using unmodified and ester modified *Senilia senilus* and *Thais coronata* biomass. They concluded that the

adsorption of the metal ions were favorable.

5.4 Sorption spontaneity

Chemical changes occur spontaneously at a given temperature if the Gibbs free energy is negative. The Gibbs free energy of adsorption (ΔG) can be related with the equilibrium constant K (L/mol) corresponding to the reciprocal of the Langmuir constant b [36].

$$-\Delta G^{o}_{ads} = RT\ln K \quad [7]$$

Where ΔG^{o}_{ads} is the free energy change of adsorption (kJ/mol), T is the absolute temperature (K), R is the universal gas constant (8.314 J mol/K) and K is the Langmuir constant equal to 1/b (b = 0.0113). The negative value of ΔG°_{ads} (-11.11kJ/mol) associated with the biosorption of Cu(II) ions onto *Vigna Subterranea* (L.) *Verdc hull* proved the feasibility and spontaneity nature of the sorption process.

6.0 Conclusions

The batch studies were performed in Erlenmeyer flasks to determine the optimum sorption conditions between Cu(II) ions and *Vigna Subterranea* (L.) *Verdc hull* biomass at constant temperature and agitation rate. The optimum conditions were determined as pH of 6, contact time of 60 minutes and a biomass dose of 0.6 g per 100 mL of synthetic effluent of Cu(II) ions. The equilibrium data generated by varying initial Cu(II) ion concentration under optimum conditions was found to fit the Temkin, Langmuir and Freundlich adsorption isotherms. Based on the correlation of determination (R^2), all the isotherms were able to describe the equilibrium data in the order; Langmuir (0.9965) > Freundlich (0.9847) > Temkin (0.9835). The sorption of Cu(II) ions on *VSVH* was more of monolayer sorption than sorption on a surface having heterogeneous energy distribution. *Vigna Subterranea* (L.) *Verdc hull* proved to be a very good biosorbent of Cu(II) ions with a very high sorption capacity and sorption favorability. The adsorption process is a spontaneous chemisorption process that increase with solution temperature.

6.1 Further research

The adsorption kinetics, sorption of other cations, effects of the presence of other cations and anions, column studies, acid and base activation and modification of the *Vigna Subterranea* (L.) *Verdc hull* biomass needs to be investigated in order to fully realize the capabilities of the biomass prior to the implementation of the technology.

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