Orginal Article

Removal of Copper from Aqueous Solution using Triplochiton Scleroxylon Sawdust: Equilibrium and kinetic studies

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Abstract

Sawdust of Triplochiton Scleroxylon was evaluated as a new biosorbent of heavy metals. On contacting 100mgL−l copper (II) solutions with 20 g L−1 Sawdust, during shake flask contact time of 45 min, the metal removal was noted to be 69%. The influence of pH, sorbent dose, concentration, temperature, and contact time on the sorption of Cu(II) on sawdust has been studied by batch process. The optimum conditions of sorption were found to be: contact time of 45 min, pH and temperature 4.0 and 40°C respectively. The sorption kinetics was found to follow pseudo-second-order model. The sorption data perfectly fit the linear Langmuir isotherm model with 0.99 regression coefficient (R2) and 0.66 average percentage errors (ε%). The fit on Freundlich adsorption isotherm model was acceptable but not as good. Calculated thermodynamic parameters such as ΔHo, ΔSo and ΔGo indicated spontaneous and exothermic nature of the process. The study points out the potential use of sawdust; at present has no commercial value, for the treatment of wastewaters contaminated with heavy metals.

Keywords: *Sorption, Sawdust, Copper, Isotherms, Kinetics*

INTRODUCTION

The growth in industrial activities combined with urban development in recent years has led to the discharge of huge amount of wastewater which is a serious threat to the environment. Heavy metals contained in these discharges are of concern because they can be detrimental to various living species including humans. Since they are not biodegradable, they can be bioaccumulated, causing various diseases and disorders (Abu Al-Rub, et al, 2006). It is therefore necessary to remove these metals from industrial effluents, before their discharge into water bodies. Removal of heavy metals from wastewater is usually achieved by physical and chemical processes which include precipitation,coagulation/flocculation, sedimentation, filtration, reduction membrane process, ion exchange and adsorption biological process, electrochemical processes, and chemical reaction (Adouby,et al, 2007)

Technical as well as economic considerations limit the use of these techniques mostly in developing countries where financial resources are scarce. It is therefore important to find alternative for these purposes. In recent years, numerous low cost natural materials have been proposed as potential biosorbents, including peat, tree fern, Sawdust, beer yeast, sugar beet pulp, microalgae, seaweeds and vegetable wastes (Han Li, et al,2006). These sorbents, compared to others, have several advantages.

The aim of this study was to evaluate Sawdust, wood waste material as sorbent. Sawdust is a by-product of wood industry whose disposal is becoming more and more difficult because of the large amount produced each year by sawmills. The only disposal practice used in developing countries is burning but this can be detrimental to the environment because of the greenhouse effect.

The work here by reported concerns the use of sawdust of Triplchiton Scleroxylon for the removal Cu(II) from aqueous solution. Environmental parameters affecting the process such as pH, contact time, metal ion concentration, temperature, and adsorbent concentration were evaluated. The equilibrium adsorption data have

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been evaluated by Langmuir and Freundlich isotherm models.

MATERIAL & METHODS
Sorbent
Sawdust waste of *Triplochiton Scleroxylon* wood generated in local wood processing industries was collected from small sawmill *Tropical Bois* of Adzopé (in South-Eastern part Côte d'Ivoire).
The Sawdust was dried in sunlight for 15 days until constant weight. It was ground to a fine powder and sieved for a particle size of 0.5 mm then directly used without any pretreatment, as a sorbent for the removal of copper (II) ions from aqueous solutions.

Chemicals
All chemicals used in this study were analytical grade. Copper (II) solutions of desired concentration were prepared by dissolving the appropriate amount of its nitrate: $Cu(NO_3)_2.3H_2O$ (99.5% MERCK) in distilled water. Nitrate salt was selected as a possibly inhibiting anion because of its low tendency for complex formation with most metals. pH of solutions was adjusted by the addition of concentrated nitric acid: HNO_3 (67%Prolabo). The solutions are prepared at the experiment day.

Dynamic studies
Sorption studies were carried out by batch process. A desired Sawdust dose was placed in a 250mL conical flask with 100mL solution of metal ions of desired concentration and pH. Measurement of initial pH was performed using a pH meter Hannan HI-98150. The mixture was shaken in water bath with temperature controlled at 300 rpm.
The mixture was agitated on a shaker and samples were taken at specific times. Sawdust from the samples was separated by vacuum filtration using a 45 μm membrane filter to remove the particulates and the filtrate is used as sample. The metal content of the sample was analyzed using a Varian Atomic Absorption Spectrophotometer (AAS) Varian Model AA 20 in an air-acetylene flame. The concentrations of Cu(II) adsorbed were obtained from the difference between initial and final metal concentration in solution.
The amount of Cu(II) adsorbed in mg·g^{-1} at time t was computed by using the following equation:

$$q_t = \frac{(C_o - C_t)V}{m} \qquad (1)$$

Where C_o and C_t are the metal concentrations (in mg.L^{-1}) initially and at a given time t, respectively; and V is the volume of the metal

solutions in mL and m is the weight of Sawdust in g.

The copper percentage of removal was calculated using the following equation:

$$R(\%) = \frac{(C_o - C_t)}{C_o} x100 \qquad (2)$$

Where C_0 and C_t are the initial and final metal concentrations in solution, respectively.
For effect of time study, a series of conical flasks, each having 2 g sorbent and 100mL solution (100mg/L of metal concentration) were shaken at 300rpm and room temperature (30 ± 2°C). At the predetermined time intervals (1 to 90min) the solution of the specified flask was taken out and filtered. The concentration of metal in the filtrate was determined by AAS. The amount of metal sorbed in each case was then determined as described earlier.

Effect of pH
In order to investigate the effect of initial pH on Cu(II) sorption, 100mg.L^{-1} metal solutions of various initial pH values were prepared using 0.1mol.L^{-1} HNO_3. Initial pH within the range 2.0 to 6.0 in order to avoid metal hydroxide precipitation. 2g of Sawdust were added to 100 ml of Copper(II). Flasks were shaken for 45min at 300 rpm and room temperature. Samples were filtered and the filtrate was analysed via AAS.

Effect of temperature
In this work, a series of experiments were conducted at 30 to 60°C to investigate the effect of temperature on the sorption dynamics. Keeping the Sawdust 20g L^{-1}, pH 4.0, and the initial concentration of 100mg L^{-1} for Cu(II). The relative conical flasks was then shaken at a constant speed of 300 rpm in a shaking water bath with temperatures, 30, 40, 50 and 60°C respectively. Samples were filtered and the filtrate was analyzed via AAS.

Effect of metal ion concentration
All working solutions were prepared by diluting the stock solution with distilled water. For this purpose 50–400 mg L^{-1} of copper (II) were contacted with 20 g L^{-1} Sawdust at room temperature. After the contact times of 45 min, Samples were filtered and the filtrate was analyzed via AAS. The amount of metal sorbed in each case was then determined as described earlier.
Effect of sawdust mass on adsorption

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The influence of *Triplochiton Scleroxylon* Sawdust dosage on copper removal was examined by varying dosages from 2 to 25 g L^{-1} at pH 4, for a contact time (45 min). The initial concentrations of Cu(II) was 100 gL^{-1}. Batch sorption tests were done with different amount of sawdust. The samples were then filtered and the filtrate was analyzed for the remaining Cu(II) as previously described.

Sorption kinetics

The kinetics studies were carried out by conducting batch sorption experiments with different temperature (30 to 60°C). Samples were taken at different time periods and analyzed for their copper concentration.

Isotherm experiments

Sorption studies were carried out by batch process in 250mL conical flasks. The equilibrium isotherms were determined by contacting fixed copper concentration (100 mg/L) with different mass of sawdust (2 to 25g).

The Sawdust and copper solutions were agitated in a series of flasks with equal volumes of solution (100 ml) for a period of 45 minutes at desired temperature. The series of flasks was agitated at a constant speed of 300 rpm in a water bath at temperatures 20, 30 40 and 60°C, respectively. Sawdust from the samples was separated by vacuum filtration using 45 μm membrane filters to remove the particulates and the filtrate was analyzed using a Varian Atomic Absorption Spectrophotometer. The concentrations of Cu(II) adsorbed at each time were obtained from the difference between initial and final metal concentration in solution.

RESULTS & DISCUSSION

Effect of sawdust–metal ion contact time

The results reveal that the sawdust percentage of removal is higher at the beginning. We observed a two-stage sorption. The first step involves rapid metal uptake within the first 10 min of contact that is followed by the subsequent removal of the metal which continues for a period of time until equilibrium is reached. Therefore the contact time necessary to reach equilibrium is about 45 min. The rapid stage is probably due to the abundant availability of active sites on the biomass, and with the gradual occupancy of these sites, the sorption becomes less efficient in the slower stage (Ho, 1995). The fast metal uptake by this woody material may be attributed to its highly fine structure, which provides ready access and large surface area for the sorption of metals on the binding sites. The percentage of sorption at the equilibrium was 69% under the experimental conditions of the study.

Other authors using agriculture by-products and biomass wastes found similar sorption kinetics (Ho, Mckay, 2004). The rapid metal removal has significant practical importance, as this will facilitate the use of small sorbent volumes to ensure efficiency and economy.

Effect of pH

To understand the sorption mechanism, the sorption of Cu(II) as a function of pH was measured, and the result is shown in **Fig. 2**. This figure depicts that pH significantly affects the extent of sorption of copper by Sawdust. It was observed that sorption was low at the initial pH 2 (35%). The low metal adsorption at low pH may be explained on the basis of active sites being protonated, resulting in a competition between H$^+$ and Cu (II) for the occupation of the binding sites on Sawdust (Kempton, Sterritt, Lester, 1987). As the pH increases, there will be more exposed sorption sites on sawdust that carry negative charges which subsequently attract copper ions with positive charges leading to the sorption to the sorbent surface [33]. Maximum sorption capacity was obtained at pH 4, an increase or decrease in the pH from these optimum pH resulted in a reduction in the sorption of metal ions. The decrease of sorption after pH 4 is due to the complexation of copper (II) by OH$^-$ groups which would prevent the metal sorption (Kumar, King, Prasad, 2006).

Effect of metal ion concentration

The metal uptake mechanism is particularly dependent on the initial metal concentration C_i: as low concentrations metals are absorbed by specific sites, while with increasing metal concentrations the sites of sorption are saturated (Langmuir, 1918). As shown in Fig.3, Cu (II) uptake mechanism is particularly dependent on the initial heavy metal concentration (C_i). The data shows that the metal uptake increases and the percentage of sorption of copper generally decrease with increase in metal ion concentration. This copper uptake increase (1.58–8.49mg.g^{-1}) is a result of increase in the driving forces, i.e. concentration gradient (Lehmann, Hater, 1984). However, the Cu(II) percentage of sorption on Sawdust was increase (69%) with increasing sorbent dosage from 50 to 100 mg.L^{-1}, stabilized at 150 mg.L^{-1} then decreased as Cu(II) ions increased. The decrease in percentage of sorption may be attributed to lack of sufficient surface area

to accommodate much more metal available in the solution. Similar results were observed for copper removal using macroalgae *Fucus vesiculosus* as adsorbent (Li, et al, 2007).

Effect of sawdust dose

Figure 4 shows the effect of sorbent concentration on the removal of cupper ions at equilibrium conditions. The percentage of copper removal increased from 23 to 69% when the sawdust dose increased from 2 to 25g.L^{-1}. This can be explained by the availability of more binding sites for sorption of metal ions [38] which is in agreement with the observation of Schiewer and Volesky (Ozer, 2007).

Effect of temperature

The effect of temperature on sorption of Cu(II) by *Triplochiton Scleroxylon* Sawdust is shown in Fig. 5. The measurement of sorption at temperatures exhibits an increase in the Cu(II) removal with the increase in temperature in the interval 30–40°C and then the sorption decreased in the interval 40–60°C. Increasing the temperature is known to increase the rate of diffusion of the sorbate, due to the decrease in the viscosity of the solution.

The effect of temperature on the sorption process found in the literature presents different and opposite behaviors. Some of the authors have reported higher uptake capacities of metal in different sorbent as temperature increases (Pan, Lin, Tseng, 2003). On the other hand, few have reported temperature independent effect of metal uptake on sorption capacity. In contrast, there are also reports showing a decrease in the uptake capacity with temperature increase (Sabramanyam, Das, 2009).

The complex situation obtained in this study was also described for the sorption of cadmium by chitin where an initial increase in the capacity of sorption was followed by a subsequent reduction (Saeed, Akhter, Iqbal, 2005). Similar results were also observed for chromium removal using *Ficus religiosa* leaves as adsorbent (Ho, 2003).

Sorption kinetics

Sorption kinetics, expressed in terms of the rate of solute removal, that controls the residence time of the sorbate in the solid–solution interface, is one of the most important aspects of the operation defining the efficiency of the process. It is of vital importance from the standpoint of treatment plant design to predict the rate at which the pollutant is removed from the aqueous solution. Several kinetic models have described the reaction order in sorption systems. Traditionally, a first-order equation has been used to describe kinetics. However, over the past few years, a pseudo-

second-order kinetic model has been considered to be among the most appropriate (Saeed, Iqbal, Akhtar, 2002).

As a result, if a pseudo-second-order equation is allowed, which is consistent with many authors who have studied sorption kinetics in divalent metal ions using several different biosorbent materials [46-47], the rate equation for the reaction may be represented by the following expression:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \qquad (3)$$

where k is the sorption rate constant (g/mg min), q_e the amount of metal ions sorbed in the equilibrium (mg/g) and q_t is the amount of metal ion on the sorbent surface at any time t (mg/g).

By separating variables and integrating the equation for the limits, t = 0, q_t = 0 and t = t, q_t = q_t:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \qquad (4)$$

is obtained, which can be rearranged to obtain the following linear form,

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \qquad (5)$$

If pseudo-second order kinetics is applicable, the plot of t/q_t against *t* of Eq. 5 should give a linear relationship, from which q_e and k can be determined from the slope and intercept of the plot (Fig.6) and are shown in Table 1.

At all temperature, the linear regression correlation coefficient R^2 values were higher and ranged from 0.998 to 0.999. The higher R^2 values confirm that the sorption data are well represented by pseudo-second order kinetics and supports the assumption behind the model that the sorption is due to chemisorption (Slater, Ferrari, Wisniewski, 1987).

Equilibrium modeling

Isotherms studies provide information on the capacity of adsorbent which is a most important parameter for a sorption system. Sorption isotherms are characterized by certain constants and describe the mathematical relationship between the quantity of adsorbate and concentration of adsorbate remaining in the solution at equilibrium at a fixed temperature. There are several isotherm equations describing the equilibrium and the most common of them are

Langmuir and Freundlich (Soares, De Coninck, Duarte, Soares, 2002).

Langmuir sorption isotherm is most widely used model for the sorption process and based on monolayer coverage of sorbate on the surface of adsorbents.

According to Langmuir theory, it has been assumed that adsorption occurs at a specific homogenous site within adsorbent; each site is occupied only an adsorbate molecule, all sites are equivalent and there are no interactions between adsorbate molecules (Sud, Mahajan, Kaur, 2008). The non-linear form of Langmuir isotherm model can be represented by Eq.6:

$$q_e = \frac{bq_oCe}{1+bCe} \qquad (6)$$

Where:

C_e = the metal concentration in solution at equilibrium (mg.L^{-1}).

q_e = the amount metal ions adsorbed per unit mass of adsorbent at equilibrium (mg.g^{-1}),

q_o = Langmuir constant related to maximum adsorption capacity (mg.g^{-1}).

b = Langmuir isotherm constant related intensity of sorption.

The linear form of Langmuir isotherm is given by Eq. 7:

$$\frac{C_e}{q_e} = \frac{1}{bq_o} + \frac{1}{q_o}C_e \qquad (7)$$

The parameters were obtained by fitting the experimental data of the plot of C_e/q_e versus C_e. The values of q_o and b were calculated from the slopes and intercepts of Eq.7.

Figure 7 show the Comparison of experimental equilibrium data with the theoretical equilibrium data obtained from the non-linearized Langmuir sorption isotherms at various temperatures.

The Langmuir constants qo and b determined from the linear models (Eq. 7) are listed in Table 2 to compare the values of them to those of non-linear models.

The results of table 2 show that there is no remarkable difference between the values of q_o calculated for two models. The values of q_o calculated from linear and non-linear models were found to be 7.15and 7,27mg/mg for the experiments carried out at 40°C. The optimum temperature was found to be 40°C because the value of q_o was the largest.

The effect of isotherm shape can be used to predict whether a sorption system is "favourable" or "unfavourable". According to(Tobin, Cooper, Neufeld,1984), the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R which is given by the following expression:

$$K_R = \frac{1}{1+bC_0} \qquad (8)$$

Where b is the Langmuir constant (L.mg^{-1}) and C_0 is the initial concentration of copper (mg L^{-1}).

The parameter K_R indicated the shape of isotherm as follows: $K_R > 1$, unfavourable sorption; $K_R = 1$, linear; $0 < K_R < 1$, favourable sorption; $K_R = 0$, irreversible.

K_R values are 0.13; 0.17 0.22 and 0.18 while the temperatures are 30, 40, 50, and 60°C respectively. All K_R values obtained for Cu(II) sorption are greater than zero and less than unity showing favorable sorption of Cu(II) onto Sawdust biomass.

The empirical Freundlich isotherm is used to describe multi-side adsorption isotherm for heterogeneous surfaces [52] and expressed by the following equation:

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (9)$$

where K_F and *n* are the Freundlich constants and represent sorption capacity and intensity of sorption, respectively.

Figure 8 show the Comparison of experimental equilibrium data with the theoretical equilibrium data obtained from the non-linearized Freundlich sorption isotherms at various temperatures.

Eq.9 is generally used in the linear form, represented by following equation:

$$Lnq_e = LnK_F + \frac{1}{n}LnC_e \qquad (10)$$

Values of K_F and 1/n were determined from the intercepts and the slopes of the plot Lnq_e versus LnC_e. The isotherms constants related to linear and non-linear Freundlich models determined are listed in Table 2.

K_F, one of the Freundlich constants has been used as a relative measure of sorption capacity. High values of constant K_F indicate high sorption efficiency [21; 53]. The values of constant K_F, are quite close to each other for all temperatures except for 50°C which has also the smallest value. The values of *n* inform about the heterogeneity

degree of the sorption sites. As n approaches zero, the surface site heterogeneity increase (Fiol, 2006).The values of $0.1 < 1/n < 1$ indicate favorable sorption of Cu(II) by *Triplochiton Scleroxylon* sawdust at all the temperatures studied.

In order to verify the validity of the Langmuir or Freundlich models, in addition to the coefficients of correlation (R^2), it is essential to calculate the average percentage and chi-square values as shown in Table 3.

The chi-square (χ^2) and average percentage errors ($\varepsilon\%$) between the experimental and calculated values for the sorption isotherm models were evaluated using Eq. 11 and 12(Volesky, 2001).

$$\chi^2 = \sum \frac{(q_e - q_{em})^2}{q_e} \qquad (11)$$

$$\varepsilon^\% = \frac{\sum_1^N \left| \frac{q_{e,\exp} - q_{e,cal}}{q_{e,\exp}} \right|}{N} x100 \qquad (12)$$

It is clear from table 3 that the average percentage errors ($\varepsilon\%$), and the coefficients of correlation (R^2) values of the Langmuir models were better than Freundlich models. Moreover, Linear Langmuir model has higher correlation coefficients than those of non-linear Langmuir; also average percentage values of linear Langmuir model were lower (0.66-3.49) than those of non-linear Langmuir (1.19-5.05). Consequently, the linear Langmuir model is the most suitable model for this sorption system.

Thermodynamic parameters

For designing sorption systems, one should be able to understand the changes that can be expected to occur and how fast they take place. The fast reaction can be calculated from the knowledge of kinetic studies. But the changes in reaction that can be expected during the process require some ideas of thermodynamic parameters. In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process can occur spontaneously. The Gibbs free energy change (ΔG^o) is the basic criterion of spontaneity, and a negative value indicates the reaction as spontaneous. By using the equilibrium constant (b) obtained for each temperature from the Langmuir model using the linear method, ΔG^o can be calculated according to the following equations:

$$\Delta G^o = -RTLnb = \Delta H^\circ - T\Delta S^o \qquad (13)$$

where R the universal gas constant and T (K) the absolute temperature .

The equilibrium constant may be expressed in terms of enthalpy change of sorption (ΔH^o) and entropy change of sorption (ΔS^o) as a function of temperature. The relationship between the b and temperature is given by the Van't Hoff equation:

$$Lnb = \frac{\Delta S^o}{R} - \frac{\Delta H^0}{RT} \qquad (14)$$

The values of ΔH^o and ΔS^o were, respectively, determined from the slope and intercept of the plot of Lnb versus 1/T at different temperatures.

The plot of Eq. 12 is shown in Fig. 9 and the thermodynamic parameters ΔH^o, ΔS^o and ΔG^o are shown in Table 4.

For all temperature, ΔG^o is negative indicating that sorption of copper by sawdust is spontaneous. The negative value of ΔH^o indicates that the overall process of Cu(II) sorption is exothermic and the positive values of ΔS^o reflects the affinity of the Sawdust for Cu(II), confirms the increased randomness at the solid–solution interface during the sorption.

3.10: Comparison of Cu(II) removal with different sorbents reported in the literature

We hereby compared the sorption capacity of some agriculture by-products for the removal of Copper(II) reported by the literature to adsorption by *Triplochiton Scleroxylon* Sawdust. The values of sorption capacities have been summarized in Table 5.

The experimental data of the present investigation show that Sawdust exhibits a mild capacity for Cu(II) sorption from aqueous solutions. This result reveals that natural Sawdust is effective sorbent for copper (II) ions from wastewater. It should be noted that the values and comparisons reported for copper removal capacity have only a relative meaning because of different testing conditions (e.g., temperature, pH, and contact time), type of biomaterials and methods.

CONCLUSION

The aim of the present study is to evaluate the Sawdust of Triplochiton Scleroxylon as potential adsorbent for the removal of Cu(II) ions from aqueous solution. This study shows clearly that Sawdust which is a cheap and abundant material can be used as an effective sorbent for removal of copper from wastewater. The adsorption process

was fast enough, as maximum removal took place within 45 min of contact time, and the optimum pH is 4.0. Increasing the initial concentration of Cu(II) results in higher adsorptive quantity. The maximum uptake of Cu(II) at an initial pH of 4 is 7.15mg/g at 40°C. The optimum sorption capacity of Sawdust was compared with other sorbents reported in literature. The kinetics of sorption can be described by a model of a pseudo-second-order because of the strong correlation of the experimental results obtained with linearized pseudo-second-order equation. Langmuir isotherm is better fit for the equilibrium data compared to the Freundlich isotherm. The negative value of enthalpy and free energy reflect the exothermic and spontaneous nature of sorption respectively.

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Table 1. Adsorption kinetic parameters for Cu (II) adsorption by *Triplochiton Scleroxylon*

Temperature (°C)	q_e (mg/g)	K (g.mg^{-1} min^{-1})	R^2
30	3.54	0.157	0.99998
40	4.24	0.172	0.99997
50	3.26	0.127	0.99961
60	3.22	0.214	0.99999

Table 2. Non-linear and linear model isotherm parameters for Cu (II) adsorption by *Triplochiton Scleroxylon*

	Langmuir model			
Temperature (°C)	**Non-linear model**		**Linear model**	
	q_o(mg/g)	b(Lmg^{-1})	q_o(mg/g)	b(Lmg^{-1})
30	4.99	0.06578	5.09	0.0527
40	7.27	0.0390	7.15	0.0470
50	4.84	0.0410	4.93	0.0461
60	4.49	0.0493	4.51	0.0468

	Freundlich model			
Temperature (°C)	**Non-linear model**		**Linear model**	
	K_F(mg/g)	1/n	K_F(mg/g)	1/n
30	1.11	0.319	1.05	0.33
40	0.99	0.4216	0.92	0.42
50	0.63	0.4164	0.62	0.42
60	0.97	0.3165	1.08	0.28

Table 3. Comparison of Non-linear and linear model isotherm correlation coefficients for Cu (II) adsorption by *Triplochiton Scleroxylon*

	Langmuir			Freundlich		
Temperature(°C)	$\varepsilon\%$	χ^2	R^2	$\varepsilon\%$	χ^2	R^2
	Non-linear model					
30	1.19	0.40	0.996	2.01	0.10	0.953
40	3.25	0.21	0.985	4.10	0.41	0.928
50	5.05	0.31	0.983	5.59	0.42	0.889
60	1.62	0.10	0.976	3.47	0.22	0.937
	Linear model					
30	0.66	0.35	0.997	4.20	0.33	0.954
40	2.75	0.92	0.988	4.33	0.96	0.927
50	3.49	0.90	0.977	4.98	0.78	0.901
60	0.47	0.27	0.999	3.22	0.22	0.975

Table 4. Thermodynamic parameters of Cu(II) sorption by *Triplochiton Scleroxylon*
at different temperatures.

Temperature (K)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol/K)
303	-20.44		
313	-20.81	-3.44	55.81
323	-21.42		
333	-22.13		

Table 5. Copper sorption capacities of some sorbents reported in literature.

sorbents	q_{max} (mg/g)	References
Chlorella vulgaris	24.39	Al-Rub et *al.* [53]
Pterygota macrocarpa sawdust	23.02	Adouby et *al.* [23]
Papaya wood	18.88	Saeed et *al.*[29]
Tree fern	11.7	Ho Y.S. [19]
Teak wood sawdust	8.07	Shukla et *al.* [30]
Triplochiton Scleroxylon Sawdust	7.15	*Present study*
Sawdust of poplar trees	6.58	Li et *al.* [12]
Groundnut shells	4.46	Shukla et *al* [30]
Modified oak sawdust	3.22	Argun et *al.* [55]
Olive stone	3.19	Fiol et *al.* [56]
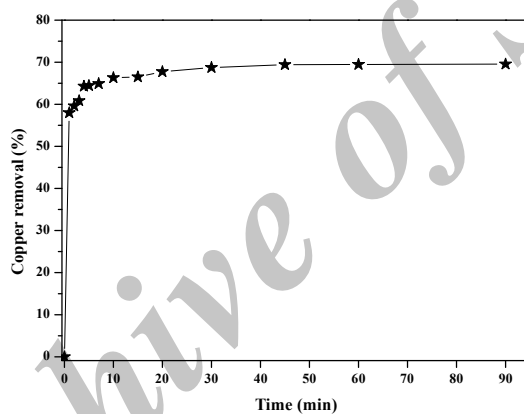
Fig1.Effect of contact time on Cu(II) removal) by *Triplochiton Scleroxylon* Sawdust for 100 mg/L of metal solution, 20g/L of biomass concentration and pH 4.at 30°C
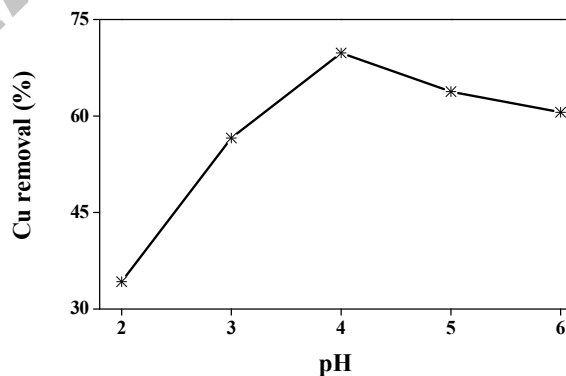
Fig2. Effect of pH on Cu(II) removal by *Triplochiton Scleroxylon* Sawdust for 100 mg/L of metal solution, 20g/L of biomass concentration at 30°C
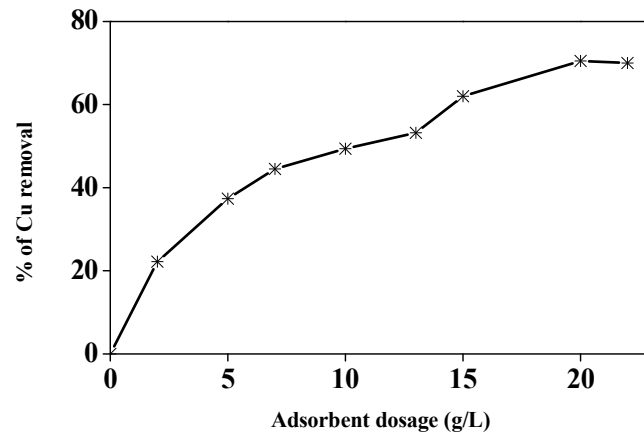
Fig3. Effect of metal concentration on Cu(II) removal by *Triplochiton Scleroxylon* Sawdust for 20g/L of biomass Concentration, pH 4 at 30°C
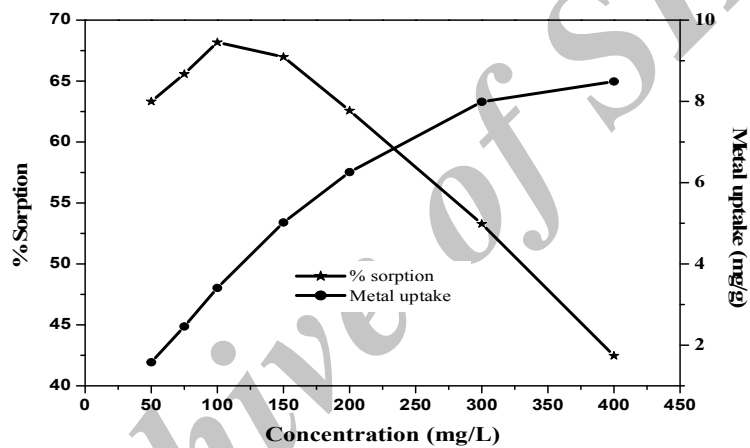

Fig4.Effect of *Triplochiton Scleroxylon* Sawdust dose on Cu(II) removal for 100 mg/L of metal solution , pH 4. at 30°C.
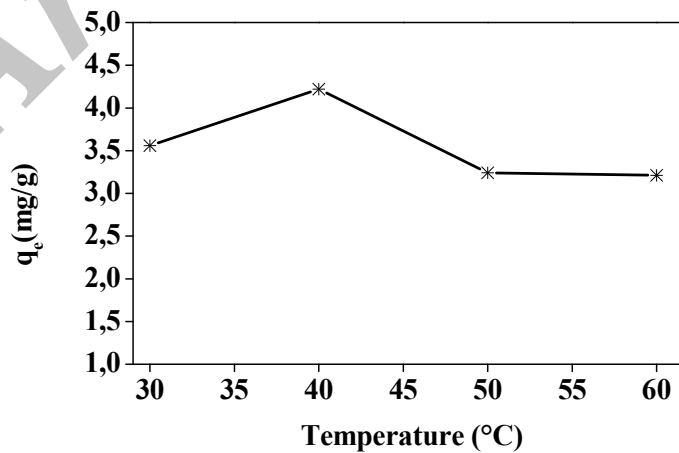

Fig5. Effect of temperature on Cu(II) removal by *Triplochiton Scleroxylon* Sawdust for 100 mg/L of metal solution, pH 4, and 20g/L of biomass concentration.
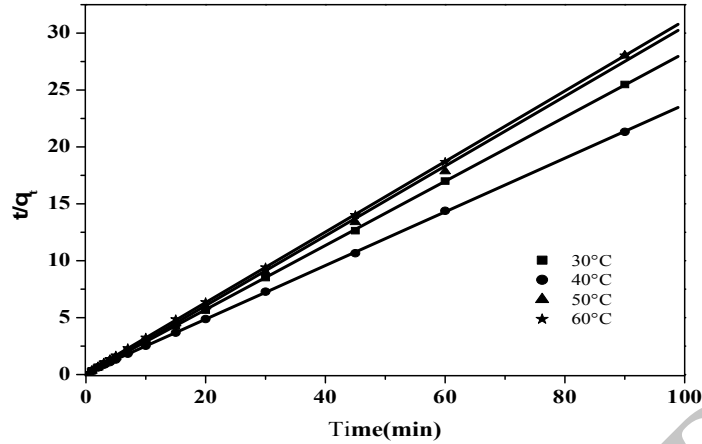
Fig6.Pseudo-second order kinetics for Cu(II) onto *Triplochiton Scleroxylon* Sawdust at various temperatures for100 mg/L of metal solution, 20g/L of biomass Concentration, pH 4.
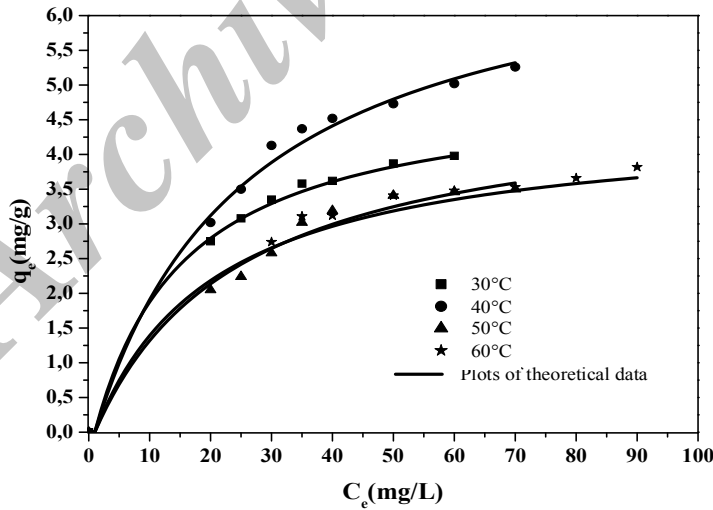
Fig 7. Comparison of the experimental equilibrium data with the theoretical equilibrium data obtained from the non-linearized Langmuir sorption isotherms at different temperatures. 100 mg/L of metal Concentration, 2 to 25g/L of biomass Concentration, pH 4.
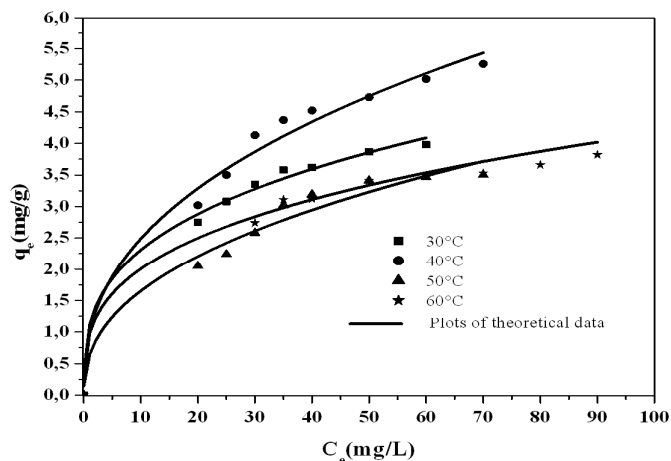
Fig8: Comparison of the experimental equilibrium data with the theoretical equilibrium data obtained from the non linearized Freundlich sorption isotherms at different temperatures.100 mg/L of metal Concentration, 2 to 25g/L of biomass concentration pH 4.
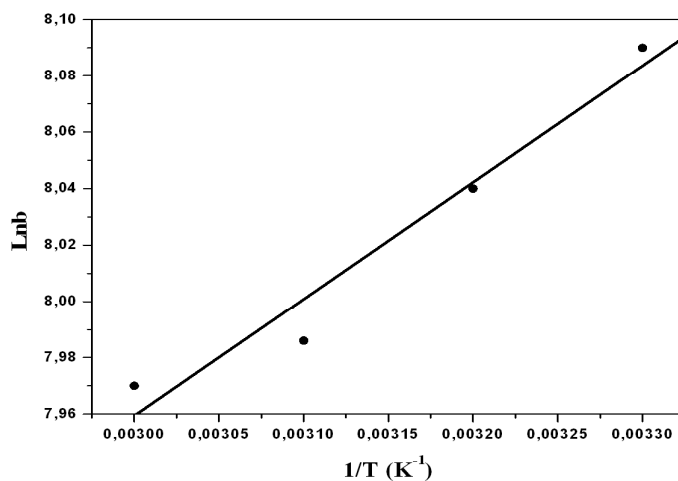

Fig9: Plot of Langmuir constant (Lnb) vs temperature (1/T), initial pH 4 and 20 g/L of biomass concentration

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