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Kinetics, Isotherm and Thermodynamic Studies of the Reclusion of Cu (II) from Aqueous Solution by Maize Cob and Sugarcane Pulp

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Abstract:
Over the years, heavy metal contamination of the environment, through industrial waste had been a perennial problem to which biosorption is being proposed as solution in recent studies. The biosorption characteristics of Cu (II) ion using maize and saccharumofficinarum (sugarcane pulp) were investigated by contacting 0.5g of the biomass with 10ml of 100mg/L solution of the metal ions. Experimental parameters affecting the biosorption process such as pH, contact time, concentration and temperature were studied. Langmuir and Freundlich models were applied to describe the biosorption isotherms. The biosorption capacities of maize cob and saccharumofficinarum were found to be sufficiently high to consider the biomasses used as substances that could be employed in the removal of Cu (II) ions from waste water. The calculated thermodynamic parameters, ΔG^0, for biosorption of Cu (II) on to cob and bagasse determine at pH 5.0 and 301k, are -1.5KJmol^{-1} and -2.505KJmol^{-1} respectively. This showed that the biosorption of Cu (II) ions onto maize cob and saccharumofficinarum was feasible and spontaneous at 301K.

Keywords: *Reclusion, biosorption, isotherm, efficiency, bagasse, maize cob, biomasses*

1. Introduction

In many countries world over, one challenge faced as a result of industrial revolution, is how to control heavy metal contamination of the environment through industrial waste from mining operation, tanneries petrochemical industries, electroplating and chemical industries. These metals have been indicted in the causes of certain deceases and malfunctioning of parts of human system such as renal dysfunction and failure, hypertension, hepatic injury, lung damage and teratogenic effects to mention a few (Matheical *et al*, 1990; Lodeiro *et al*., 2006; Kaewsarn *et al*., 2001); therefore, the level of these heavy metals, such as Cu in waste water, drinking water and water used for agriculture should be reduced to the maximum permissible concentration. Several methods have been employed over the years on the elimination of heavy metals present in industrial waste waters and soil. These include chemical precipitation, ion exchange, solvent extraction, phytoextraction, ultrafiltration, reverse osmosis, electrolysis and adsorption (Patterson J. W. 1985; Bhattacharya *et al*., 2006). It is important to note, however, that economic and technical factors limit the feasibility of such processes.

Biosorption, an emerging technology, has been considered to be an alternate technique for the uptake of toxic metal ions from waste water. The major advantages of the biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of cheap, readily available materials such as maize cob (cob) and saccharumofficinarum (baggase). This work is to investigate the potential of cob and bagasse biomasses for removal of Cu (II) ions from aqueous solution. Experimental parameters affecting the biosorption process such as pH, contact time, concentration and temperature were studied. The equilibrium biosorption data were evaluated by Langmuir and Freundlich isotherm models and also investigated is the mechanism in terms of thermodynamics and kinetics.

2. Experimentals

2.1. Preparation of Biomass

The *Zea mays* cob (cob) supplied by a local farm, used as the biosorbent were obtained as dry cobs. The dry cobs were rinsed with distilled water, dried in an oven and cut into pieces. Saccharumofficinarum (bagasse), that is harvested, was crushed to extract the juice while the left over called bagasse were also washed with distilled water and dried in an oven. The biomasses were kept in a dry place till the time of usage.

2.2. Reagents and Equipment

The chemicals used for the study were analytical grades of copper (II) tetraoxosulphat vi ($CuSO_2$) manufactured by M & B, UK, Trioxonitrate V acid (HNO_2) and sodium hydroxide (NaOH). All chemicals and reagents used for the experiments and analysis were of analytical grade. Stock solution of 100mg/L of Ni (II) ion was prepared from $CuSO_2$ in distilled, deionized water that contained a few drop of 0.1 mo1/L HNO_2/NaOH to prevent the precipitation of Cu (II) ion by hydrolysis. The solutions were diluted as required to obtain working solutions. The initial pH of the working solution was adjusted to 5.0 by drop-wise addition of HNO_2 or NaOH except for the experiment examining the effect of pH. Fresh dilutions were used for each sorption study.

2.3. Batch Biosorption Procedure

Each of the batch biosorption studies was carried out by contacting 0.5g of the biomass with 10ml of 100mg/L solution of the metal ions under different conditions for a period of time in a glass tube, except for experiments involving varying the initial or stating concentration where solutions with concentration range of 0.2g/L to 1.8g/L was used. Studies were conducted at 28^0C to determine the effect of pH, initial ion concentration and contact time on the biosorption of Cu (II) ions and at a temperature range of 28^0C to 50^0C, the effect of temperature was observed. The pH was varied between 2 and 7 with the drop-wise addition of 0.1 Molar sodium hydroxide solution and or 0.1 molar trioxonitrate V acid to study the effect of pH. The experiments were conducted in a thermo stated water bath and the cob and bagasse were removed from the mixture by decantation. The residual metal ions in the solution were determined using Atomic Adsorption spectrophotometer (Buck scientific 210 VGP). The amount of metal ions biosorbed from the solution was determined by difference and the mean value was calculated for each set of experiment.

The biosorption capacity q_e of the sludge is expressed as milligrams of biosorbed ions per gram of dry mass of the biomass (mg g-1) and the removal efficiency of metallic ion (%E) were calculated by equation 1 and 2 respectively.

$$q_e = v\left(\frac{C_i - C_e}{m}\right) \text{ -- (1)}$$

$$\%E = 100\frac{C_i - C_e}{C_i} \text{ -- (2)}$$

Where, q_e is the amount of metal ions adsorbed per unit weight of cob and bagasse in mg/g, v is the volume of solution treated in L, C_i is the initial metal ion concentration in mg/L, C_e is the equilibrium metal ion concentration in mg/L and m is the dry weight of biomass in g.

The results obtained were analyzed using both Freundlich (Freundlich, 1906) and Langmuir (Langmuir, 1918) isotherms. The Freundlich isotherm in linearized form is

$$\log q_e = \frac{1}{n}\log C_e + logK_F \text{ ------------------------------------ (3)}$$

Where n and K are Freundlich constants. While the Langmuir isotherm (T. Cassey, 2011) in linearized form is

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b_m}\frac{1}{C_e} \text{ --- (4)}$$

Where b_m is a coefficient related to the affinity between the sorbent and the sorbate, and q_m is the maximum sorbate uptake under the given condition and

$$b_m = K_L q_m \text{ ------------------------------------ (5)}$$

3. Result and Discussion

The effect of pH on biosorption

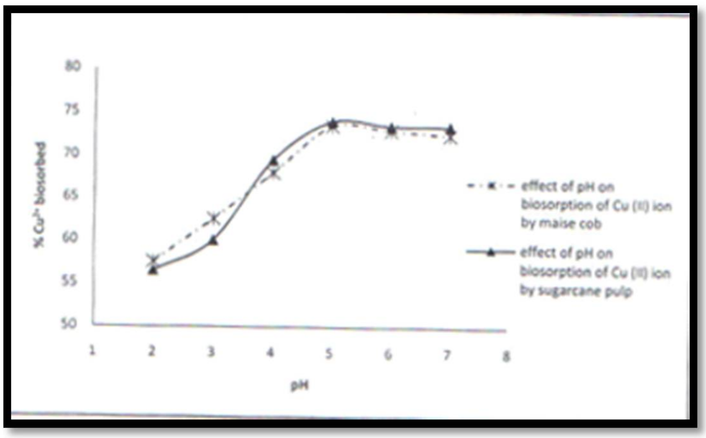

Figure 1: Plot of pH vs % of Cu Adsorbed

To examine the effect of pH on the Cu (II) ion removal efficiency, several experiments were performed at different pH ranges from 2 to 7 as shown in figure 1 for both cob and bagasse. The high biosorption efficiency was obtained around pH 5. At higher pH values, the biosorption yield for Cu (II) decreases. At pH range 2 to 4, the low biosorption of Cu (II) in the low pH range could be due to competition with H^+ ions for metal sites on the biomasses.

3.1. The Effect of Initial Concentration on the Biosorption of Cu (Ii) by Cob and Bagasse

The effect of initial Cu (II) ion concentration on its biosorption was studied at a concentration range of 0.2g/L to 1.8g/L (figure 2). The result showed that the capacity of uptake by the two biomasses varies directly with initial Cu (II) ion concentration. However, from the efficiency plot in figure 3, it was discovered that there is a maximum equilibrium point at initial concentration of 0.6g/L beyond which the efficiency of biosorption begins to decrease. This is because at higher starting concentration of the metal ion, the number of Cu (II) ions competing for biding sites on the biomass increases, leading to an increase in the number of the ions that will be left in solution, un-adsorbed.

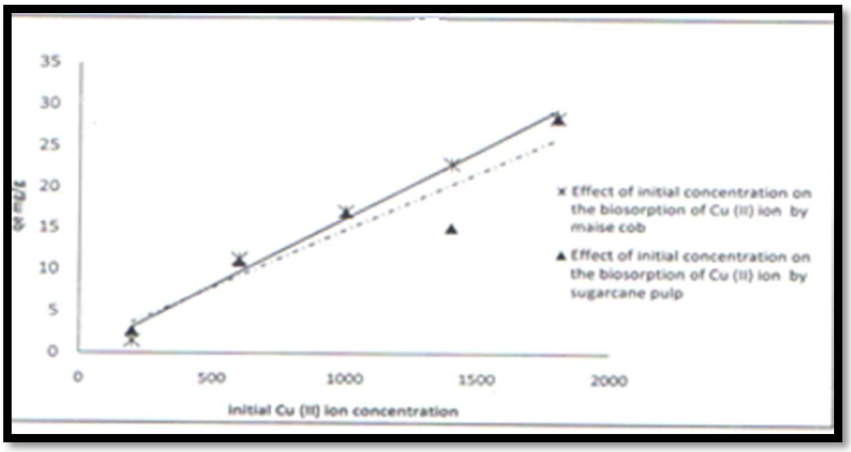

Figure 2: Plots of Initial Cu(II) ion vs qt

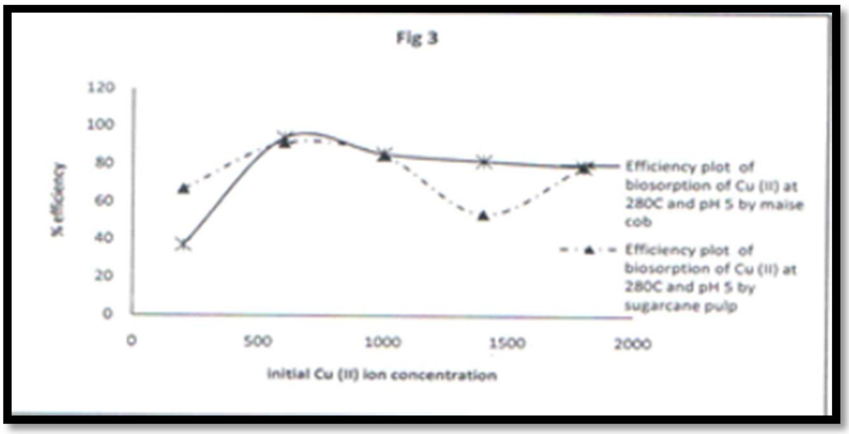

Figure 3: Plots of Initial Cu (II) ion vs % Efficiency

3.2. Effect of Contact Time and Temperature

The contact time was also evaluated as one of the most important factors affecting the biosorption efficiency of copper II ion by cob and bagasse. Figure 4 shows the time course for the biosorption of Cu (II) ion by cob and bagasse. The biosorption efficiency increases with increase in contact time up to 20 mins and after that it was almost constant. The reaction involved the biosorption of metal ion from the liquid phase to the solid phase. It is considered as a reversible reaction with equilibrium being made between the two phases.

The biosorption ability of both the maize cob and bagasse can be seen from figure 5 to be supported by increase in temperature. The percentage of Cu (II) ion biosorbed increased with increase in temperature. Using Le Charterliers principle if we consider the biosorption process of Cu (II) as a reversible reaction then the forward reaction of adsorbing the metal ion will be an endothermic process.

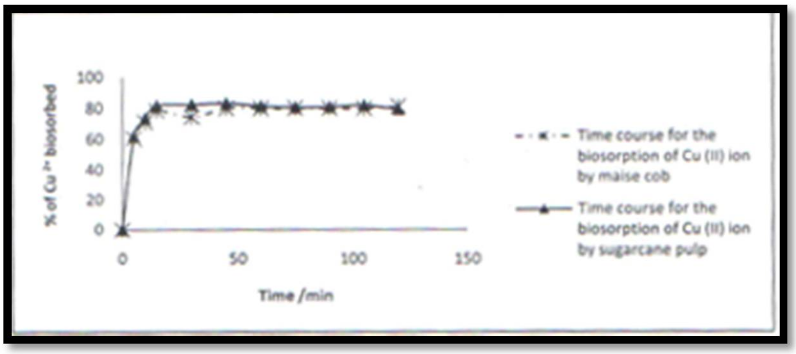

Figure 4: Plots of Time vs. % Cu2+ Adsorbed

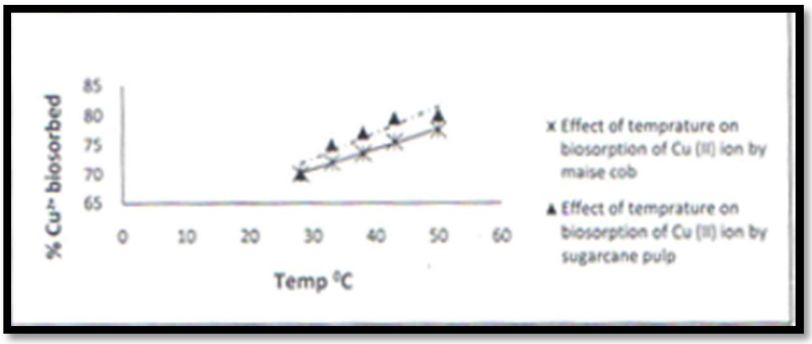

Figure 5: Plots of Temperature vs % Cu2+ Adsorbed

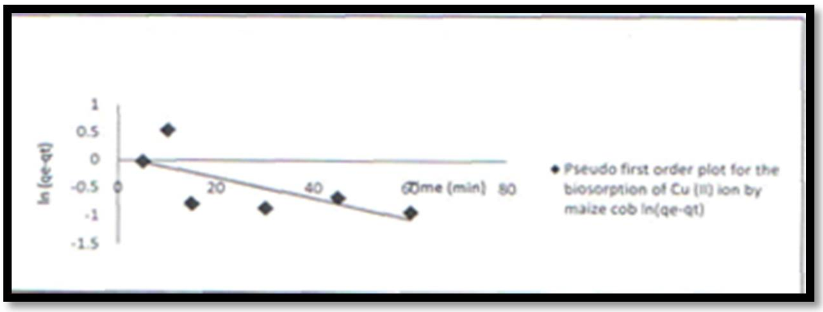

Figure 6: Pseudo First Order Plot for Biosorption of Cu (II) ion by Maize Cob

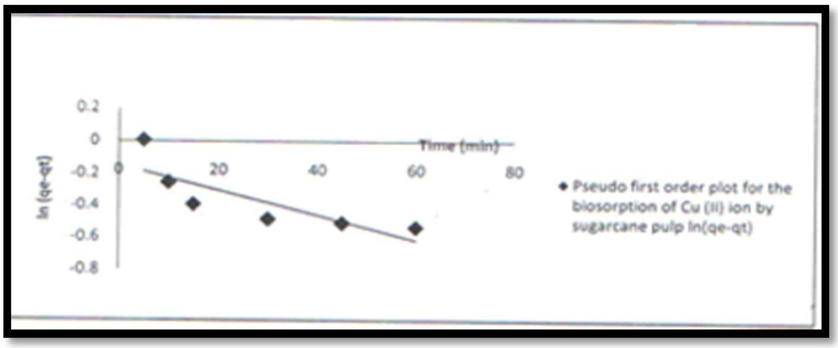

Figure 7: Pseudo First Order Plot for Biosorption of Cu (II) Ion Bagasse

3.3. Adsorption Isotherms

A biosorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the biosorbent and can also be used to compare the biosorptive capacities of the biosorbent for different pollutants (Dorsun *et al.*, 2005). In this study, two important sorption isotherms were selected to fit the experimental data which are Langmuir and Freundlich isotherm models.

These isotherms follow the typical Langmuir adsorption pattern as shown by the linear transformation in equation 4. The Langmuir model is based on the assumption of a single layer adsorption on a complete homogeneous surface. The equilibrium established between the adsorbed metal ions q_e and ions remaining free in the solution (C_e) were also represented by the Freundlich adsorption isotherms (equation 3).

The equilibrium data of Cu (II) ion adsorption by cob and bagasse obtained at 301k was applied to Langmuir and Freundlich models. The related parameters and correlation coefficients (R) and residual standard deviation (S.D) were listed in table 1. From the Langmuir constant K_1, the relative affinity of biosorbent to the investigated metals is as follows; Cu on cob > Cu on pulp.

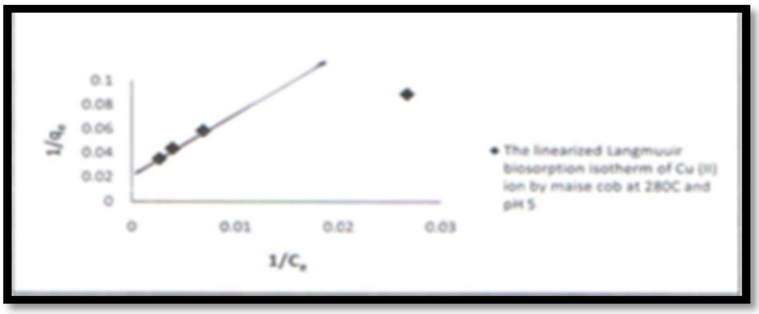

Figure 8: The Linearized Langmuir Biosorption Isotherm of Cu (II) Ion by Maize Cob at 28^{0}C and pH 5

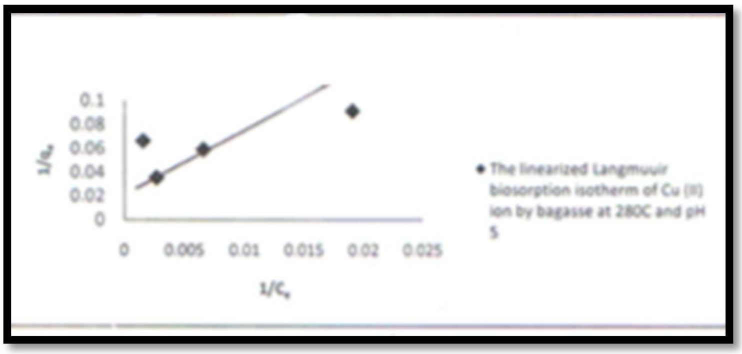

Figure 9: The Linearized Langmuir Biosorption Isotherm of Cu (II) Ion by Cane Pulp at 28^{0}C and pH 5

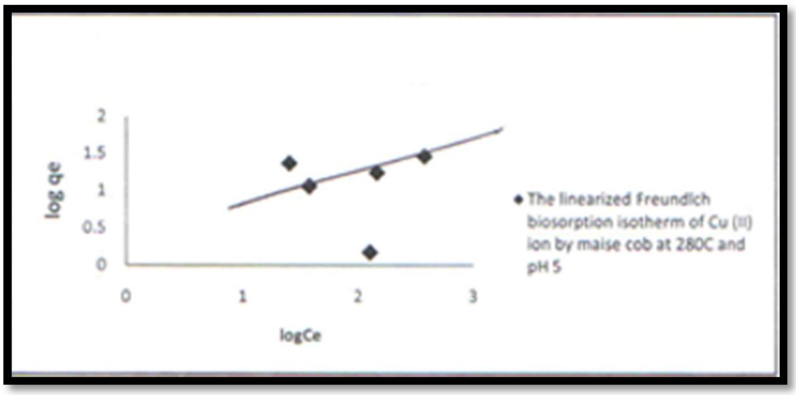

Figure 10: The Linearized Freundlich Biosorption Isotherm of Cu (II) Ion by Maize Cob at 28^{0}C and pH 5

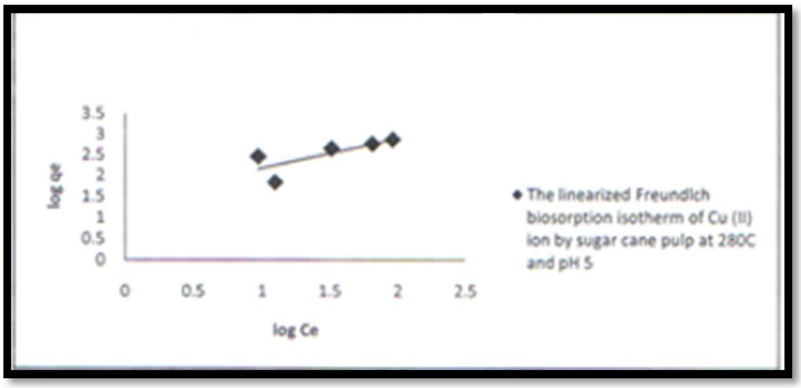

Figure 11: The Linearized Freundlich Biosorption Isotherm of Cu (II) Ion by Sugar Cane Pulp at 28^{0}C and pH 5

Metal/Biomass	Freundlich Constants		Langmuir Constants		
	K_1	n	K1(l/mg)		
Cu (II) ion on maize cob	2.512	0.41	0.0031	0.172	55.56
Cu (II) ion on sugarcane bagasse	63.096	0.537	0.0025	0.156	62.5

Table 1: Parameters for the Application of Langmuir and Freundlich Model to the Biosorption of Cu (II) Ion on Maize Cob and Sugarcane Bagasse

3.3.1. Biosorption Kinetics

In order to examine the controlling mechanism of the biosorption process, kinetic model was used to test the experimental data. The equilibrium data was analysed using the pseudo first order model as given by Lagergren. The linear form of the pseudo first order rate equation by Lagergren 1898, is given as

$\ln (q_e - q_t) = \ln q_e - k_1 t$ -------------------------------- (6)

Where q_e and q_t (mg/g) are the amounts of the metal ions biosorbed at equilibrium (mg/g) and t (min), respectively and k_1 is the rate constant of the first-order equation (min^{-1}).

The plot of In ($q_e - q_t$) versus t for the biosorption of Cu (II) ion by maize cob and bagasse at initial concentration of 100mg/L obeys the pseudo-first order reversible kinetics. The overall rate constant of the biosorption (k_1) was calculated from the slope of the curves. As could be seen in figures 6 & 7, the Lagergren first order rate constant obtained for this study are 0.0168 min^{-1} and 0.00841 min^{-1} for maize cob and bagasse respectively.

3.3.2. Biosorption Thermodynamics

Thermodynamics parameter ΔG^0 was used to describe thermodynamic behaviour of biosorption of Cu (II) ion on cob and bagasse using the following equation.

$\Delta G^0 = - RT\ln K_0$ ------------------------------------ (7)

Where, $k_0 = q_e/C_e$, the distribution coefficient obtained from the slope of the graph of q_e versus C_e as shown in figures 12 and 13, is the universal gas constant (8.341/mol K) and T is the absolute temperature.

The free energy changes for biosorption of Cu (II) onto cob and bagasse determined at pH 5.0 and 301k, are -1.5KJmol^{-1} and -2.505KJmol^{-1} respectively. The negative values of ΔG^0 validate the feasibility of the biosorption process, and the spontaneity of biosorption.

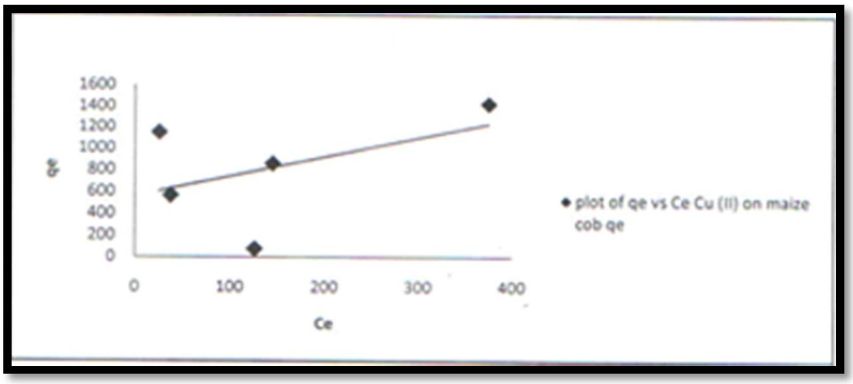

Figure 12: Plot of qevs Ce for Cu (II) on Maize Cob

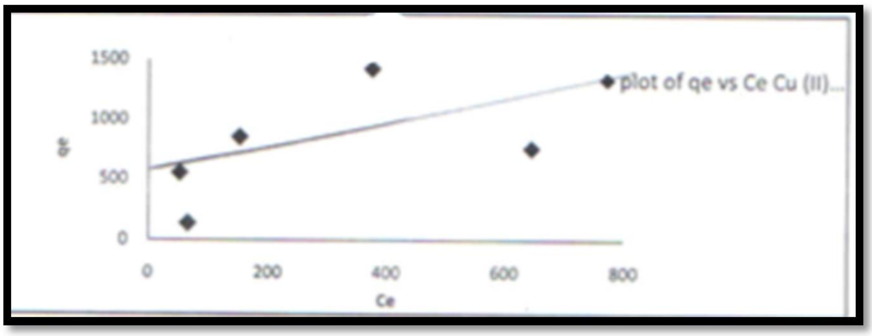

Figure 13: Plot of quvs Ce for Cu (II) on Bagasse

4. Conclusion

The study focused on the biosorption of Cu (II) ions onto maize cob and sugar cane bagasse (saccharumofficinarum) from aqueous solution. The operating parameters such as, pH of solution, initial concentration of solution, contract time and temperature, were effective on the biosorption efficiency of Cu (II) ion. Biosorption equilibrium was described by the Langmuir isotherm model with monolayer biosorption capacity of 55.56mg/g and 62.5mg/g onto cob and bagasse respectively. Kinetic examination of the equilibrium data showed that the biosorption of Cu (II) ion on to maize cob and sugar cane bagasse follow well the pseudo first order model and the thermodynamic calculations indicted the feasibility, endothermic and spontaneous nature of the process at 301k. It is, therefore, safe to conclude that maize cob and saccharum bagasse are effective and alternative biomass for the removal of Cu (II) from aqueous solution.

5. Acknowledgement

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