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Equilibrium and Kinetics Studies for the Adsorption of Aqueous Cu (II) ions onto Mangroves Biomass

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Abstract: ***In this study, adsorption of copper from aqueous solutions was investigated using mangrove biomass from the Kenyan Coast. The efficacy of mangrove biomass on the removal of copper (II) ions from aqueous solutions was investigated in single state in batch mode with respect to effects of initial pH, temperature, initial concentration of the metal ion, adsorbent dosage and contact time on metal ions adsorption. The roots showed highest ability for the uptake of the metal ions from aqueous solutions, therefore were used for all subsequent sorption studies in this research. The adsorption of the copper metal ions increased with increase in the ratio of the sample dose of the adsorbent and decreased with increasing adsorbent particle size. Increase in shaking speed was observed to increase the amount of ions that adsorbed on the adsorbent. However, agitation rate beyond 500 rpm led to a decrease in percentage adsorption. Langmuir and Freundlich adsorption models were used for mathematical description of adsorption equilibrium and after evaluating the correlation coefficients, Langmuir isotherm described the data appropriable (R^2=0.989) with the adsorption capacity (Q_{max}) of 11.36mg/g than Freundlich isotherm (R^2=0.928).The data was also subjected to kinetic models and pseudo second order model was more suitable than the pseudo first order model. These results indicated that mangrove roots can be used as low cost adsorbent for the removal of heavy metals from aqueous solutions.***

Keywords: Adsorption, Batch technique, Mangroves, Kinetics.

1. Introduction

Environmental pollution is currently one of the most important issues facing humanity. It has increased exponentially in the past few years and reached alarming levels in terms of its effects on living creatures [1].The most unique feature that distinguishes heavy metals with other forms of pollution is that they are toxic even at low concentrations. They are also non biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms which could lead to series of health problems to man [2]. Copper is one of the most toxic metals apart from mercury and cadmium. It has been known to cause Wilsons disease, hepatic cirrhosis, brain damage, demyelization and renal diseases. Conventional technologies for the removal of metal ions from industrial effluents are less efficient, very costly and generate toxic sludge [3].Among these processes include chemical precipitation, membrane filtration, adsorption, ion exchange, reverse osmosis and coagulation. The search for new techniques for the removal of toxic metals directed attention towards adsorption. Due to the presence of surface functional groups such as acetamido, alcoholic, carbonyl, phenolic, amido, amino, and sulfhydryl groups, cellulosic agricultural waste materials act as an important source for metal biosorption [3]. In addition adsorption has gained a lot of credibility currently because of its eco- friendly nature, excellent performance and cost- effectiveness [4].

The aim objective of this study was to investigate the effectiveness of mangroves for removal of Cu (II) ions from aqueous solutions. The adsorption kinetics and isotherms were also evaluated. The study also investigated the effect of varying temperature, pH and adsorbent dose on adsorption of copper from aqueous solutions using mangroves biomass.

2. Materials and Methods

2.1 Biomass Preparation

Mangrove samples (leaves, bark and roots) were collected from Dongo Kundu area in Mombasa County, Kenya. The samples were washed with distilled water to remove soil and soluble particles. Cleaned samples were then oven dried at 70^0C for 24 hours in order to obtain biomass in completely dried form. The dried mangrove samples were then ground into fine powder using mechanical grinder after which the powder was soaked and washed severally with both cold and hot tap water until clean. Clean mangroves powder were then soaked for 24 hours in cold distilled water, washed thoroughly and then dried in an oven at 60^0 C for 24 hours. Dried sample were finally sieved into different particle sizes of < 300µm, > 300 < 425µm and >425µm and samples stored in plastic containers awaiting adsorption experiments.

2.2 Chemicals

All reagents used were of analytical grade. Working solutions were prepared by appropriate dilutions of the stock solutions from Copper (II) sulphate ($CuSO_4.5H_2O$) which was supplied by Sigma Aldrich. Stock solutions of 1000 mgL^{-1} were prepared by dissolving appropriate masses in double distilled deionised water. Adjustments of pH were made using 0.1molesL^{-1} hydrochloric acid and 0.1 molesL^{-1} sodium hydroxide.

2.3 Analysis of Metal ions

The residue concentration of copper (II) ions was determined using Atomic Absorption Spectrophotometer (AAS) using air acetylene fuel at a flow rate of 3.5 L/min and a lamp current of 3.5mA. The operating wavelength was 324.2nm.

2.4 Biosorption Experiments

Batch experiments were conducted using 60mL propylene vials to which copper (II) ions solution and mangroves biomasses were added. These vials were agitated in an orbital shaker at a speed of 200rpm to study the parameters that affect adsorption like pH, contact time, adsorbent dosage, temperature and initial metal ion concentration. The effect of pH on metal ions removal was studied over a pH range of 2-8 where the pH was adjusted by addition of 0.1molesL^{-1} HCl and 0.1molesL^{-1} NaOH. In addition, the effect of temperature on sorption characteristics was investigated by varying the temperature from 25 to 70^{0}C using a thermo stated oven with temperature controls. After the adsorbate has had the desired contact time with the adsorbent, the samples were withdrawn at appropriate time and filtered using Whatman no. 42 filter paper and the residue metal ion concentration determined using Atomic Absorption Spectrophotometer (AAS). The amount of copper (II) ions adsorbed (q) was calculated by using the equation below.

$$q = \left(\frac{c_{0\,-}\,c_e}{m}\right) v \qquad (1)$$

While the percentage metal ions removal by mangroves was calculated using the equation below.

$$\%\ \text{Removal} = \frac{c_{0\,-}\,c_e}{c_0} \times 100 \qquad (2)$$

Where: C_0 and C_e are the initial and final metal ion concentrations (mg L^{-1}) respectively. V is the volume of the solution (L) and m is the amount of adsorbent used (g).

3. Results and Discussion

3.1 Effect of Initial Cu (II) Ion Concentration and Biomass

The initial concentration of Cu (II) solution was varied from 50ppm to 600ppm.The results obtained clearly depict the effect of initial concentration of Cu (II) solution on copper removal using mangrove roots. The results were presented in a graphical form as percentage removal versus initial copper concentration.

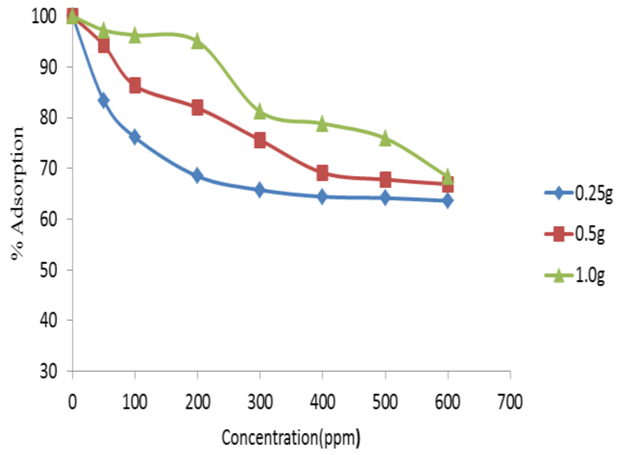

Figure 1: Effect of Initial Cu (II) Ions Concentration on Adsorption by Mangrove Roots

It is evident from Figures 1 that increases in initial concentration of Cu^{2+} ions, resulted in decrease in % adsorption. At lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption of the heavy metals ions. Therefore, functional adsorption is independent of initial metal ion concentration. However, at higher concentrations the numbers of heavy metal ions are relatively higher compared to availability of adsorption sites [5]. This sorption characteristic indicated that surface saturation was dependent on the initial metal ion concentrations. The initial concentration provides an important driving force to overcome all mass transfer resistance of metal ion between the aqueous and solid phases.

3.2 Effect of pH on Cu (II) ions Adsorption

Effect of pH on the removal of Cu (II) ions was evaluated at a pH range of 2-8. Figure 2 below shows the removal of Cu (II) ion by mangrove roots as a function of pH. The percentage removal was found to increase with increasing hydroxide ions. The solution pH affects the surface charge of the adsorbent, the degree of ionization and speciation of the surface functional groups [6].

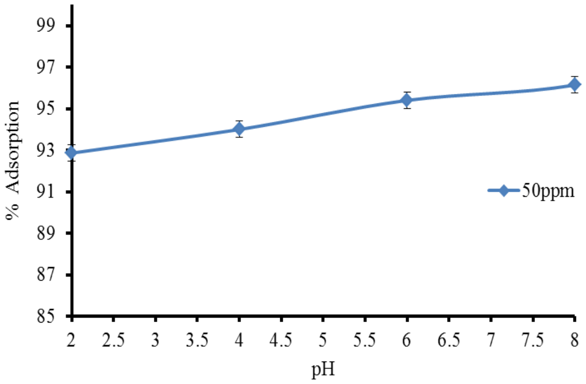

Figure 2: Effect of pH on the % Adsorption of 50ppm Cu^{2+} Ions by 0.5g of Mangrove Roots Biomass.

The low removal efficiency at low pH is apparently due to the presence of higher concentration of H$^+$ in the solution which compete with the Cu (II) ions for the adsorption sites of the mangrove roots.With the pH increasing, the H$^+$ concentration decreases leading to increased Cu (II) uptake. There is a strong relation between the adsorption and the number of negative charges at the biomass surface which is itself related to the functional groups. Therefore, Figure 2 above shows that the adsorption behavior of metal ions is more sensitive to pH changes. In addition, the increase in the metal removal as the pH increases (i.e. as the solution becomes more basic) can be explained on the basis of a decrease in competition between proton and metal species for the surface sites, and by the decrease in positive surface charge, which results in a lower columbic repulsion of the adsorbing metal ions [7]. This is in agreement with the results obtained by [3].

3.3 Effect of Particle Size and Weight of Mangroves Roots on Adsorption of 50 ppm Cu (II) Ions

The contact surface between any sorbent and the liquid phase plays an important role in sorption phenomena. For this reason, the effect of particle size of mangrove roots on removal of Cu^{2+} ions was studied using three different sizes (<300 µm, >300 µm and > 425 µm) while the effect of adsorbent dosage on adsorption of Cu (II) ions was studied at initial Cu (II) ion concentration of 50m/L and constant agitation speed of 200rpm for 20 minutes.

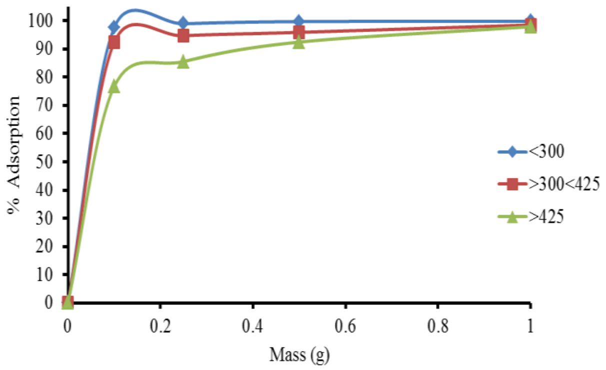

Figure 3: Effect of Particle Size and Weight of Mangrove Roots on Adsorption of 50 ppm Cu (II) ions.

From Figure 3, it is evident that there is an increase in the % adsorption with increase in mass for all the particle sizes. The increase in the adsorption is due to the availability of more binding sites for metal ions. Results also shown above revealed that maximum adsorption was attained at 1.0g for 30ml Cu^{2+} solution. This suggests that after a certain weight of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of adsorbent [8]. For smaller amounts of adsorbent, the metal ions were competing for adsorption at limiting adsorption sites. However, as the quantity of the adsorbent increased, the availability of adsorption sites increased, resulting in greater % adsorption of the metal ion.

3.4 Effect of Equilibration Time and Concentration on Adsorption of Copper (II) Ions

Removal of Cu (II) ions depends on its contact time with the mangrove roots adsorbent. Adsorption of copper at different contact time was studied for initial copper concentration of 50ppm and 1000ppm at their natural pH. The experiment was conducted by varying the contact time from 0 to 60 minutes at 5 minutes interval.

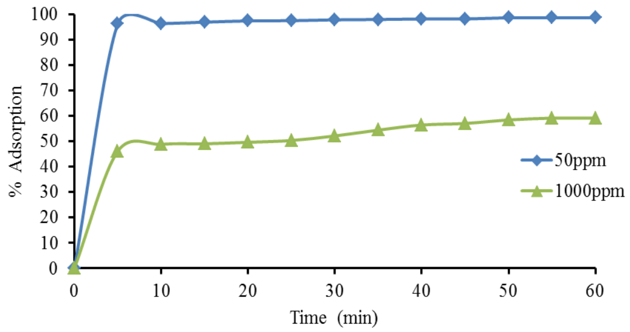

Figure 4: Effect of Contact Time on Adsorption of Cu (II) onto 0.5g of Mangrove Roots.

From Figure 4, it is clear that more than 96% removal for 50ppm copper solution and 46% removal for 1000ppm were established within the first 5 minutes. The Increase in the percentage removal with increase in contact time might be due to the fact that initially all adsorbents sites were vacant and the solute concentration gradient was high so the rate of adsorption was also high. Later, the copper uptake by the adsorbent was decreased due to the decrease in the number of adsorption sites as well as copper concentration. It is also clear that percentage adsorption decreased with increase in metal ion concentration. At lower concentration, the adsorption sites take up the available metal ions much quickly due to less competition among the metal ions for the available binding sites which are fixed in this case. However, as the concentration increases, the competition for the limited binding sites sets in as the binding sites [4]. At equilibrium, the rate of adsorption is equal to the rate of desorption .So after equilibrium it is found that there isn’t significant increase in % removal with increase in contact time.

3.5 Effect of Temperature on Cu (II) Ions Adsorption

Temperature is known to affect the adsorption rate by altering the molecular interaction and the solubility of the adsorbate. Adsorption studies were carried out at varying temperatures (25 to 70^0C) and the results were presented as percentage removal of copper versus temperature.

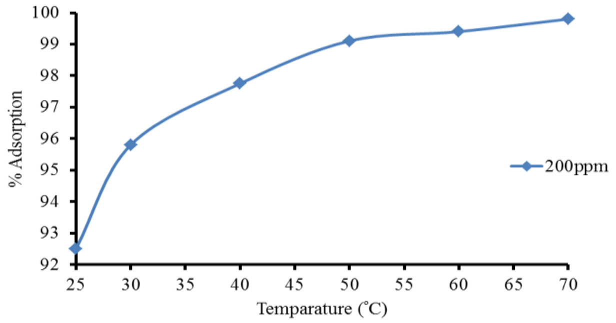

Figure 5: The Effect of Temperature on Adsorption of 200ppm Cu^{2+} ions by 0.5g Mangrove roots.

The percentage removal of copper with initial concentration 200ppm increased from 92.5% to 99.8% for 25^0 C to 70^0 C temperatures. It can clearly be seen from Figure 5 that the percentage adsorption increased with increase in temperature. The increase in percentage removal of the metal ions with temperature increase indicates that the adsorption process is an endothermic process. The enhanced adsorption of copper (II) ions may be due to change in pore size and enhanced rate of intra-particle diffusion. It could also be due to dissociation of some compounds available in the adsorbent which may provide more sites for adsorption.

3.6 Adsorption Isotherm Studies for Cu (II) Ions

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium. Adsorption isotherms are characterized by certain constants whose values express the surface properties and affinity of the adsorbent. In this study, the distribution of adsorbate Cu (II) between the adsorbent and the bulk of the solution when the system is in equilibrium is important to establish the capacity of the adsorbent for adsorbing the adsorbate. The Cu (II) ions adsorption data was fitted with the Langmuir and Freundlich isotherms. The Langmuir isotherm model is expressed as:

$$\frac{c_e}{q_e}=\frac{1}{Q_{\max}\,b}+\frac{1}{Q_{\max}}c_e \qquad (linear\ \ form) \qquad (3)$$

Where:q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e the equilibrium concentration of solute in the bulk solution (mg/L), Q_{max} the monolayer adsorption capacity (mg/g) and b is the Langmuir constant which reflects the binding strength between metal ions and adsorbent surface (L/mg). b is the reciprocal of the concentration at which half saturation of the adsorbent is reached.The Freundlich isotherm model equation is expressed as:

$$\log q_e = K_F + \frac{1}{n}\log c_e \qquad (4)$$

Where:q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e the equilibrium concentration of solute in the bulk solution (mg/L), K_F a constant indicative of the relative adsorption capacity of the adsorbent (mg/g) and the constant $1/n$ indicates the intensity of the adsorption. A higher value of n (or a smaller value of 1/n) indicates a stonger bond between the adsorbate and the adsorbent.

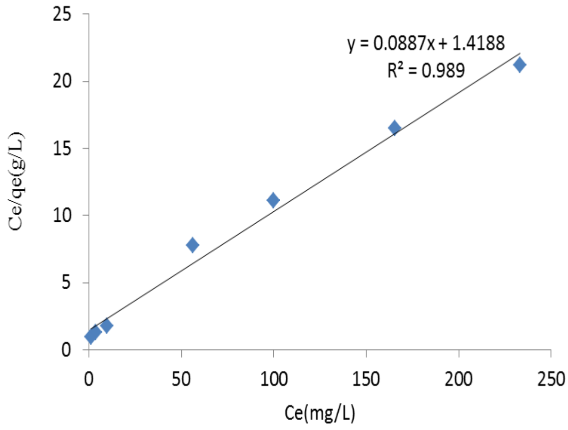

Figure 6: Langmuir Linearized Isotherm for Cu (II) Adsorption onto 1.0g Mangrove Roots

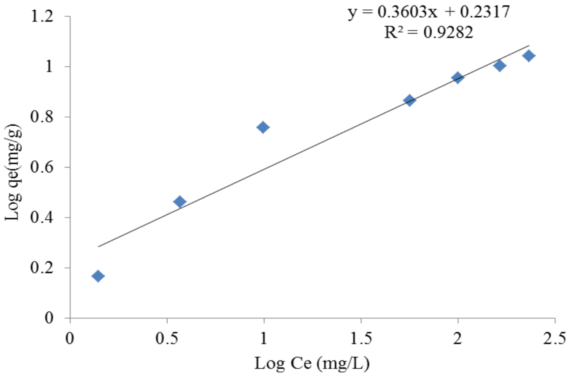

Figure 7: Freundlich Plot for Adsorption of Cu (II) onto 1.0g Mangrove Roots

Comparing the correlation coefficients values of Freundlich adsorption isotherm with that of Langmuir adsorption isotherm it is clear that the adsorption of copper onto the mangrove roots biomass was correlated well with Langmuir (R^2=0.989) equation as compared to Freundlich (R^2=0.928) equation under the concentration range studied. This is also confirmed by the low n value. The table below shows the Langmuir and Freundlich isotherm constants and the correlation coefficients.

Table 1: A Summary of Langmuir and Freundlich Parameters for Cu (II) Ions Adsorbed by 1.0g Mangroves Roots.

Langmuir			Freundlich		
Q_{max}(mg/g)	b(L/mg)	R^2	K_F	n	R^2
11.3636	0.0621	0.989	1.702	2.778	0.928

The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the mangrove roots surface. The sorption capacity, Q_{max}, which is a measure of the maximum sorption capacity corresponding to complete monolayer coverage, showed that the mangrove roots had a mass capacity of (11.36gm/g) for Cu (II) ions.

3.7 Adsorption Kinetics of Cu (II) ions Adsorption

A study of kinetics of solute uptake is desirable as it provides information about the mechanisms of adsorption, which is important for efficiency of the process. In addition Information on the kinetics of adsorption is required for selecting optimum operating conditions for full-scale batch process. In order to evaluate the kinetic mechanism that controls the adsorption process of Cu (II) ions on the Mangroves, the kinetic data was analyzed using two kinetic models, pseudo-first-order model and pseudo-second-order model. Pseudo- first –order rate model is represented by the equation:

$$\log\left(q_e - q_t\right)=\log c_e - \frac{K_1}{2.303}t \qquad (5)$$

Where: q_e and q_t are the amounts of heavy metal adsorbed (mg/g) at equilibrium and at the time (t min) respectively and k_1 is the rate constant of the pseudo-first-order adsorption process (min^{-1}). Linear plots of log(qe-qt) versus t was used to predict the rate constant (k_1) and adsorption at equilibrium (mg/g), which are obtained from the slope and intercept respectively. The pseudo-second-order equation assumes that the rate limiting step might be due to chemical adsorption . According to this model metal cations can bind to two binding sites on the adsorbent surface.The equation can be expressed as shown below.

$$\frac{t}{q_t}=\frac{1}{k_2 q^2{}_e}+\frac{1}{q_e}t \qquad (6)$$

Where: k_2 is the rate constant of the pseudo –second- order adsorption (g/mg/min).If the adsorption kinetics obeys the pseudo-second-order model ,a linear plot of t/q_t versus t can be observed .The slope of the plot will give the value of calculated adsorption at equilibrium (q_e,calc),while the intercept gives the value of the rate contant (k_2).

The results of the kinetic modelling are displayed below in Figures 8-12.

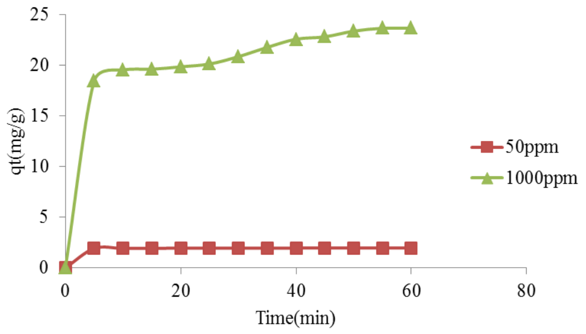

Figure 8: Effect of Contact Time on Uptake of Cu (II) Ions by Mangrove Roots.

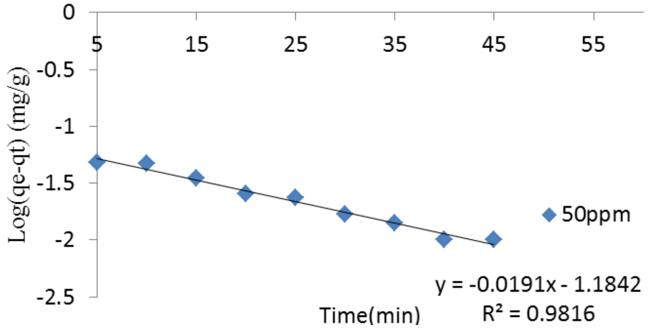

Figure 9: Pseudo –First Order Plot of 50ppm Cu (II) ions Adsorption onto 0.5g Mangrove Roots.

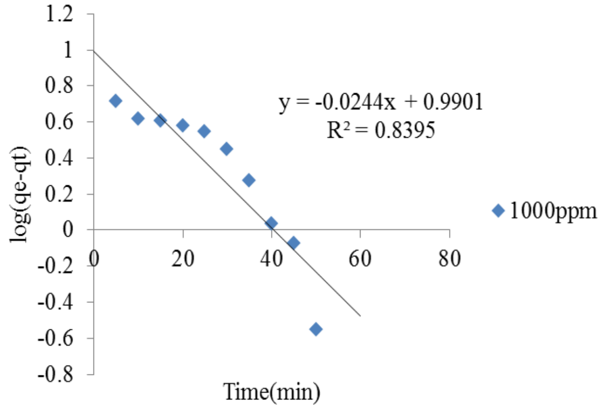

Figure10: Pseudo-First -Order Plot for Adsorption of 1000ppm Cu (II) onto 0.5g Mangrove Roots.

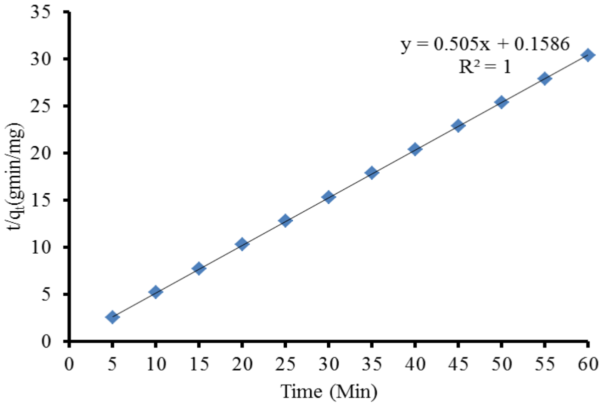

Figure 11: Pseudo-Second-Order Plots for 50ppm Cu (II) Ions Adsorption onto 0.5g Mangrove Roots.

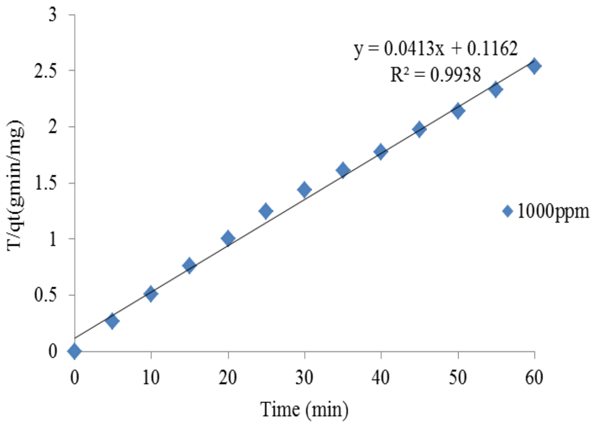

Figure 12: Pseudo-Second-Order Plots for 1000ppm Cu (II) ions Adsorption onto 0.5g Mangrove Roots.

Table 2: Pseudo-First-Order and Pseudo–Second-Order Rate Constants for Adsorption of Cu (II) ions on 0.5g Mangrove Roots

Pseudo-first-order				**Pseudo-second -order**		
[Cu] mg/L	**$Q_{e(mg/g)}$**	**Constant (min^{-1})**	**R^2**	**Q_e (mg/g)**	**Constant (g/mg/min)**	**R^2**
50	0.0654	0.0438	0.981	1.98	1.614	1.00
1000	9.772	0.0553	0.839	24.39	0.0145	0.993

The results obtained suggests that the adsorption of copper onto mangrove roots fits the pseudo-second -order model which is based on the assumption that the rate limiting step may be chemisorption. This is due to a higher correlation coefficient (R^2) value of 1.00 compared to a value of 0.981 based on a concentration of 50 mg/L and 1000mg/L respectively. This gives an idea that adsorption process followed second order kinetics. The results of this study agree well with the results obtained in the adsorption of Cu (II) using activated phosphates [9].

4. Conclusions

From the adsorption studies done on Mangroves, it can be concluded that:

- Mangrove roots can effectively be used as adsorbents for the removal of Cu (II) ions from aqueous solutions.
- The removal of metal ions is affected by temperature, pH, biomass dosage, contact time and initial concentration of metal ions.
- The removal of metal ions increased with increase in pH values. The lower pH solutions hampered the adsorption process by tending to change the charge on the surface of the adsorbent.
- The equilibrium metal ion removal was attained in 5 minutes for lower concentrations
- The adsorption should be carried out at temperature above 25^0C since the adsorption process is exothermic.
- For a high % adsorption to be obtained, the shaking speed should not exceed 500rpm.
- The removal of metal ions is affected by particle size. Finely divided adsorbent (<300µm) gave the highest % adsorption because of an increase in the surface area which in turn increases the number of the binding sites.
- The data obtained in the study was described by Langmuir and Freundlich isotherm but Langmuir adsorption

isotherm fitted best implying that there was monolayer coverage of the metal ions on the surface of the adsorbent, homogenous distribution and that the surface was uniform.

- The adsorption data fitted well for pseudo-second-order model and the sorption capacity of mangrove roots for copper was found to be 11.36mg/g.

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Fidelis Ngugi is 29 years old. She has completed Master of Science in Analytical Chemistry at the University of Nairobi, Kenya. She hold a Bachelor of Sciences in Chemistry from Egerton University, Kenya. Her postgraduate and undergraduate studies are all concerned with research work and analytical issues. My thesis has strong laboratory component since it proposes innovative, scientific research and cost-effective approaches of reducing contaminants from the environment and safety precaution measures.