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Equilibrium and Kinetics studies for the biosorption of aqueous Cd (II) ions onto *Eichhornia crasippes* biomass

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Abstract: *Batch experiments were carried out to determine the capacity of E. crasippes biomass to adsorb Cd (II) ions from aqueous solutions with respect to contact time and initial concentration of Cd (II) ions, adsorbent dosage, pH and temperature. The experimental data were modeled by Langmuir and Freundlich isotherm models. The data fitted well with the Freundlich model which implies that the adsorption was multilayer. The data was also subjected to Kinetic models and the pseudo-second-order model found to fit the data. The macrophyte biomass used in this study did not undergo any chemical modification or pretreatment, which when added to its abundance and its low cost make it a green alternative for the removal of Cd (II) ions from water and waste water.*

Key words: *Biosorption, Water hyacinth (E. crassipes), Heavy metal ions, Isotherms, Kinetics*

I. Introduction

Water pollution is a major environmental problem faced by modern society (Chojnacka, 2010). Contamination of water by heavy metals is one of the most challenging environmental issues currently. Cadmium is one of the most toxic metals apart from lead and mercury. It has been reported to cause renal dysfunction, hypertension, lung insufficiency, bone lesions and cancer (Feng *et al*, 2010) which is a leading cause of death in Kenya. The cadmium drinking water guidelines value recommended by WHO is 0.005 mg L^{-1} (UNEP, 2008).

The principal sources of Cd into the environment are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes. Once released into the environment cadmium is toxic to plants animals and microorganisms. The metal is non-biodegradable, persistent and bioaccumulate mainly in the kidneys and liver of vertebrates, invertebrates and also in algae (Waseem *et al*., 2012)

A number of methods have been employed to remove Cd (II) ions from the environment including, ion exchange, reverse osmosis, membrane filtration, electrochemical treatment, and adsorption. Adsorption is the most versatile technique but activated carbon which is the most common adsorbent used is expensive. Therefore there is need to come up with other alternative low cost adsorbents especially those of biological origin commonly referred to as biosorbents.

Biosorption has gained a lot of credibility currently because of its eco- friendly nature, excellent performance and cost- effectiveness (Foo and Hameed, 2010, Volesky, 2007).

The aim of this study was to investigate Cd (II) ions removal from aqueous solutions using *E.crasippes* biomass in order to optimize the efficiency of the biosorption process. Equilibrium isotherm models and kinetic models were applied to the data obtained for a better understanding of the adsorption process.

II. Materials and methods

2.1 Biomass preparation

E. crassipes plants were harvested from Winam Gulf, Kisumu bay at Kisat and Hippo point of L. Victoria, Kenya. The collected biomass was washed several times with tap water to remove adhering dirt. The washed biomass was then cut into roots, shoots and stems and the parts dried separately for 2 weeks .The dried brown plant biomass were then transported to the University of Nairobi laboratories were they were further dried and later ground and sieved to various particle sizes(<75µm, >75< 300 µm, >300< 425 µm and > 425 µm). The material was washed again using distilled water, then dried in an oven for 48 hours at 70ºC then stored in plastic containers awaiting biosorption experiments.

2.2 Chemicals

All chemicals used in the present work were of analytical grade. The stock solution of Cd^{2+} was prepared in 1.0 g L^{-1} concentration using $3CdSO_4.8H_2O$ (Sigma Aldrich) then diluted to appropriate concentrations . 0.1 mol L^{-1} HCl and 0.05 mol L^{-1} NaOH was used for pH adjustment.

2.3 Analysis of metal ions

The concentration of Cadmium ions in the biosorption media was determined using Atomic absorption Spectrophotometer (Varian Spectr AA), equipped with air acetylene burner. The Hollow cathode lamp was operating at 5 mA. Analytical wavelength was set at 228.8 nm.

2.4 Biosorption Experiments

Biosorption experiments were conducted at room temperature (26 ºC) by agitating a given mass of biosorbent with 20 mL of metal ions solution of desired concentration in 100 ml polypropylene containers using an orbital shaker at a speed of 200 rpm for 20 min except for contact time experiments. The effect of solution pH on equilibrium biosorption of metal ions was investigated under similar experimental conditions between 2.0 and 7.0.

After the adsorbate has had the desired contact time of interaction with the adsorbent, the samples were filtered using Whatman no. 42 filter paper and the residual concentration analyzed using CTA- 2000 AAS. However experiments involving effect of contact time used filter paper no 2.For studies on effect of temperature the adsorption studies were carried out at 25, 30, 40, 50, 60 and 70 ºC.

The amount of biosorption (q) was calculated by using the equation below.

$$q = \frac{(Co-Ce)V}{m} \quad \ldots\ldots (1)$$

The biosorption efficiency, A %, of the metal ion was calculated from:

$$A\,\% = \frac{(Co - Ce)}{Co} \times 100 \quad \ldots\ldots (2)$$

Where **Co** and **Ce** 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 biosorbent used (g).

III. Results and discussion

3.1 Effect of pH on metal biosorption

Hydrogen ion concentration is one of the important factors that influence the adsorption behavior of metal ions in aqueous solutions. It affects the solubility of metal ions in solution, replaces some of the positive ions found in active sites and affects the degree of ionization of the adsorbate during the process of biosorption (Wan Ngah and Hanafia, 2008c). This is because it affects solution chemistry and also the speciation of the metal ions.

The effect of initial pH on biosorption of Cd (II) ions onto *E.crasippes* was evaluated in the pH range of 2.0 to 7.0. Studies in pH range above 7.0 were not attempted as there is precipitation of cadmium (II) hydroxides. From the figure 1 it could be seen that Cd (II) adsorption increased as the pH increased. At low pH values, protons occupy the biosorption sites on the biosorbent surface and therefore less Cd (II) ions can be adsorbed because of electrostatic repulsion between the metal cations and the protons occupying the binding sites.

When the pH was increased, the biosorbent surface became more negatively charged and the biosorption of the metal cations increased drastically until equilibrium was reached at pH 5.0 - 6.0. At pH of >6 .0 there is formation of hydroxylated complexes of the metal ions and these complexes compete with the metal cations for the adsorption sites hence a reduction in the effective metal cations removal. Therefore adsorption experiments at pH above this were not considered.

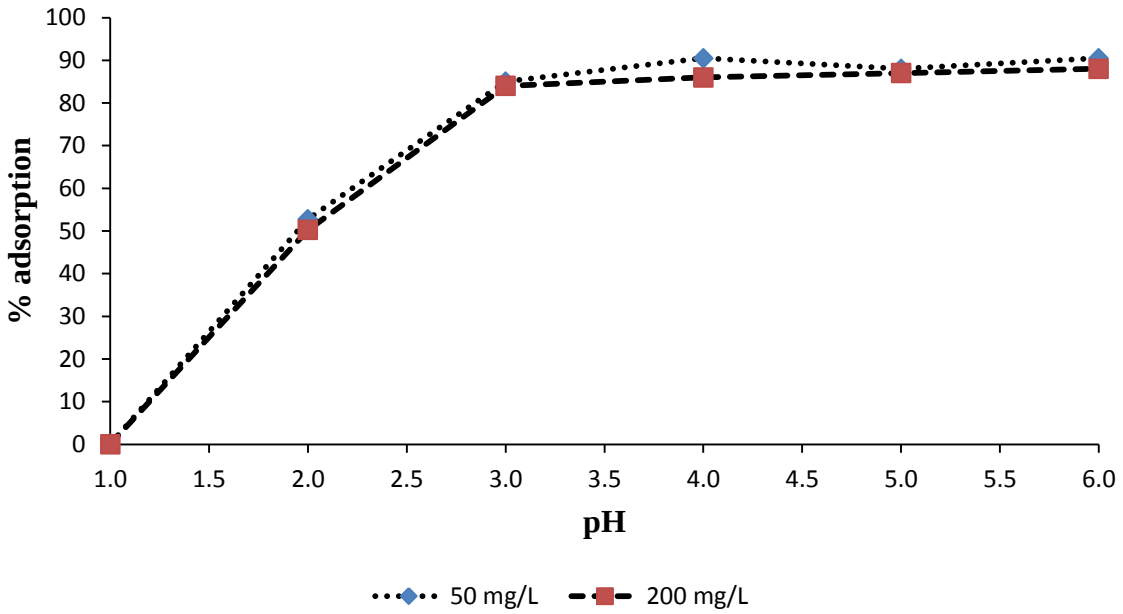

Figure 1: *Effect of pH on % adsorption of Cd (II) ions by 0.5 g of E.crassipes*

3.2 Effect of biosorbent dosage

The number of available binding sites and exchanging ions for the biosorption depends upon the amount of biosorbent in the biosorption system. This is attributed to the fact that it determines the number of binding sites available to remove the metal ions at a given concentration. The dosage also determines the adsorption capacity of the biosorbent with an increase in mass reducing the biosorption capacity as the mass increase from 0.125 g to 2.5 g per 20 mL of adsorbate. The effect of biomass dosage on adsorption of Cd (II) ions is indicated in figure 2. An increase in the % adsorption is attributable to an increase in the number of binding sites for the metal cations .Similar results were recorded in the literature for other adsorbents. However the mass could not be increased infinitely as at some point all the solution is sequestered leaving no residual solution for concentration determination.

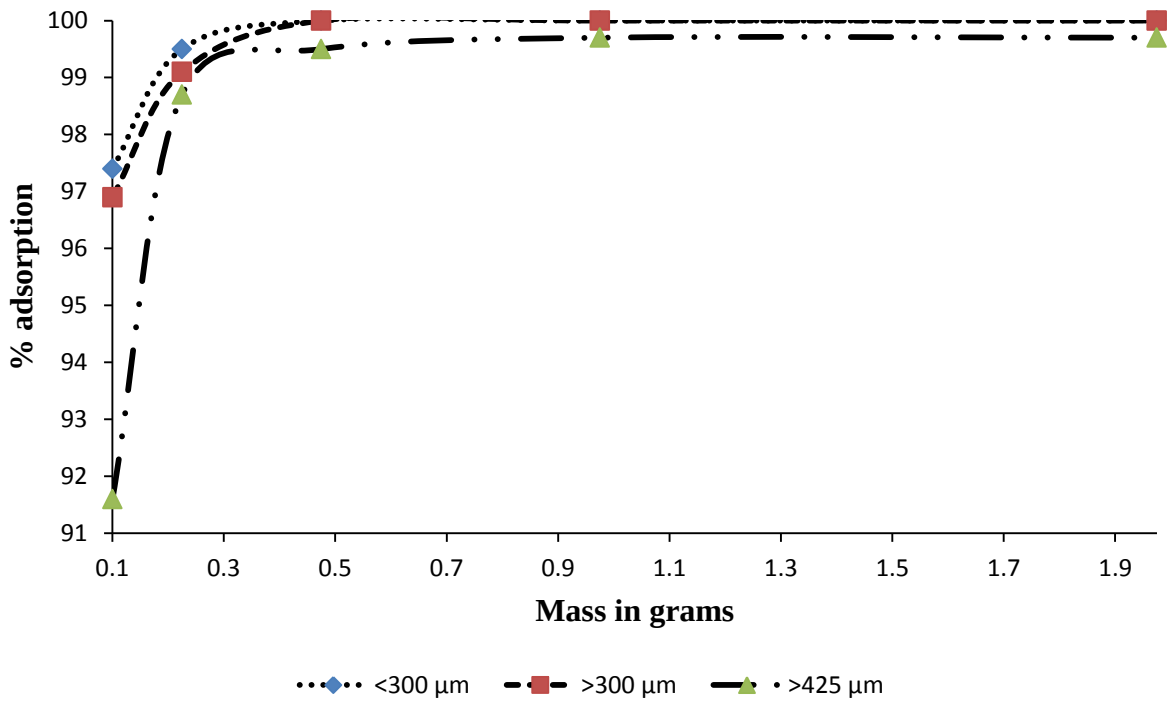

Figure 2: *Effect of weight and particle size on Cd (II) ions adsorption by E.crasippes.*

3.3 Effect of initial metal concentration.

The initial concentration remarkably affected the uptake of Cd (II) ions in solution. The efficiency of Cd (II) ions adsorption by *E.crasippes* at different initial concentrations (20-600 mg L^{-1}) was investigated as shown in figure 3. At a 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 become saturated.

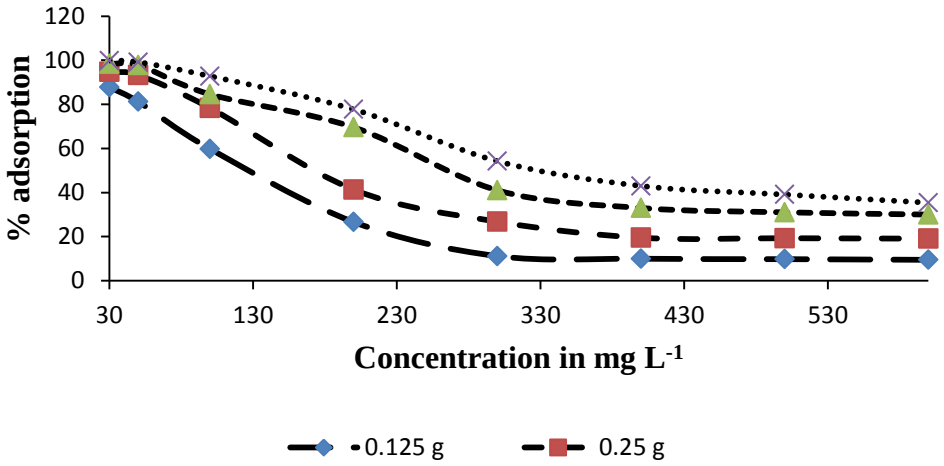

***Figure 3**: Effect of initial concentration of Cd (II) ions on adsorption by E. crassipes.*

3.4 Effect of contact time

Contact time is an important parameter for any successful use of the biosorbents for practical purposes (Sari *et. al.*, 2007). Effect of contact time on adsorption of Cd (II) ions was investigated keeping the biomass in contact with the metal ion solution for different time periods between 0 to 60 minutes. It was noted that as adsorption proceeds, the sorbent reaches saturation state, at this point the sorbed solute tends to desorb back into solution (figure 4).Eventually, the rate of adsorption and desorption are equal at equilibrium. When the system attains equilibrium, no further net adsorption occurs. The time taken to attain equilibrium is very important for process optimization. The rate of adsorption is very fast at first and over 95 % of total biosorption of Cd (II) ions occurs in the first 5 minutes and thereafter it proceeds at a slower rate and finally no further significant adsorption is noted beyond 20 minutes of contact time. The very fast adsorption makes the material suitable for continuous flow water treatment systems.

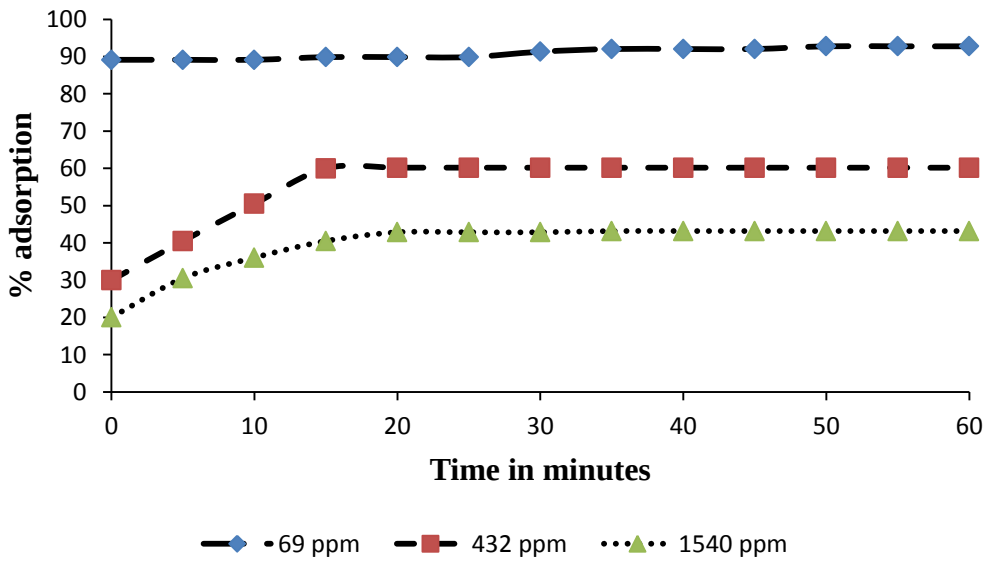

***Figure 4:** Effect of contact time on adsorption of Cd (II) ions by E. crassipes*

3.5 Effect of Temperature

Temperature of the medium affects the removal efficiency of pollutants in aqueous solutions. This is because a change in temperature in turn affects the solubility of pollutants and also the kinetic energy of the adsorbing ions. Therefore the effect of temperature on adsorption of Cd (II) ions was investigated and the data is shown in figure 5.The results indicate that the % adsorption increases with increase in temperature up to 40 ºC , after that any increase in temperature is accompanied by a reduction in % adsorption. This can be attributed to the fact that with increase in temperature of the solution, the attractive forces between the biomass surface and Cd (II) ions are weakened thus decreasing the sorption efficiency. This could be due to increase in the tendency for the Cd (II) ions to escape from the solid phase of the biosorbent to the liquid phase with increase in temperature. Finally increased temperature beyond 40 ºC could have destroyed some of the binding sites on the biosorbent surface due to bond rupture. (Meena et al., 2005).

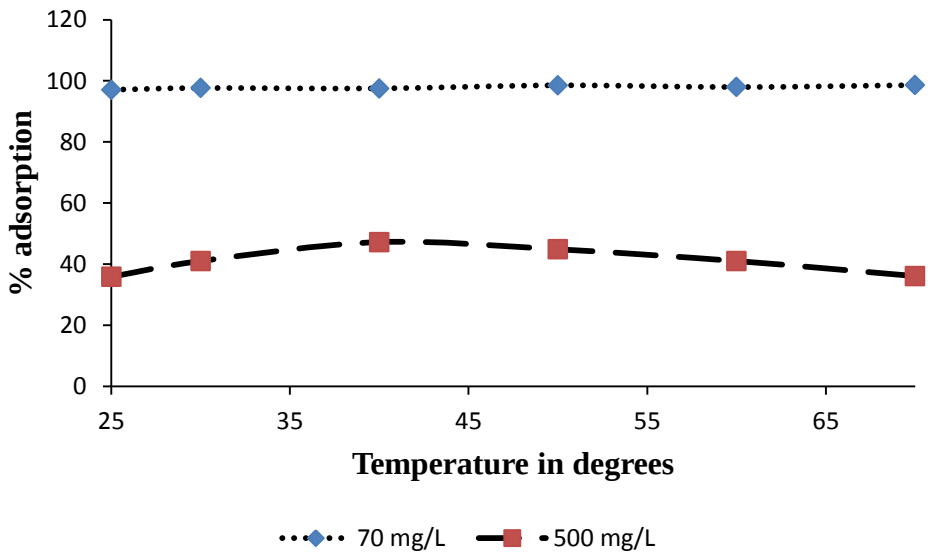

Figure 5: *Effect of temperature on % adsorption of Cd (II) ions by E.crassipes.*

3.6 Biosorption kinetics

Kinetic study provides useful information about the mechanism of adsorption and subsequently investigation of the controlling mechanism of biosorption as either mass transfer or chemisorption. This helps in obtaining the optimum operating conditions for industrial-scale batch processes.

A good correlation of the kinetic data explains the biosorption mechanism of the metal ion on the solid phase. In order to evaluate the kinetic mechanism that controls the biosorption process, the pseudo-first-order models were applied for biosorption of Cd (II) ions on the biosorbent. The Lagergren pseudo- first –order rate model is represented by the equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \ldots\ldots (3)$$

Where $\mathbf{q_e}$ and $\mathbf{q_t}$ are the amounts of metal adsorbed (mg g^{-1}) at equilibrium and at time t respectively, and k_1 is the rate constant of pseudo-first-order biosorption (min $^{-1}$).The $\mathbf{q_e}$ and rate constant were calculated from the slope and intercept of plot of $\log(q_e - q_t)$ against time t.

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \ldots\ldots (4)$$

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 as shown in figure 6.

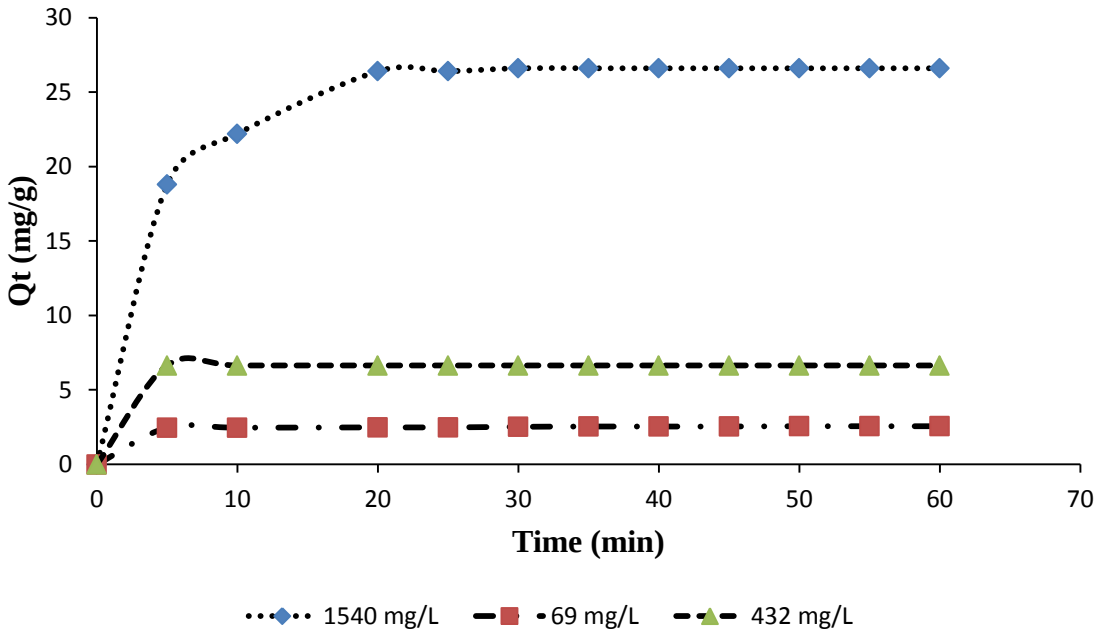

Figure 6(a) : Effect of contact time on Cd (II) ions uptake by E.crasippes biomass.

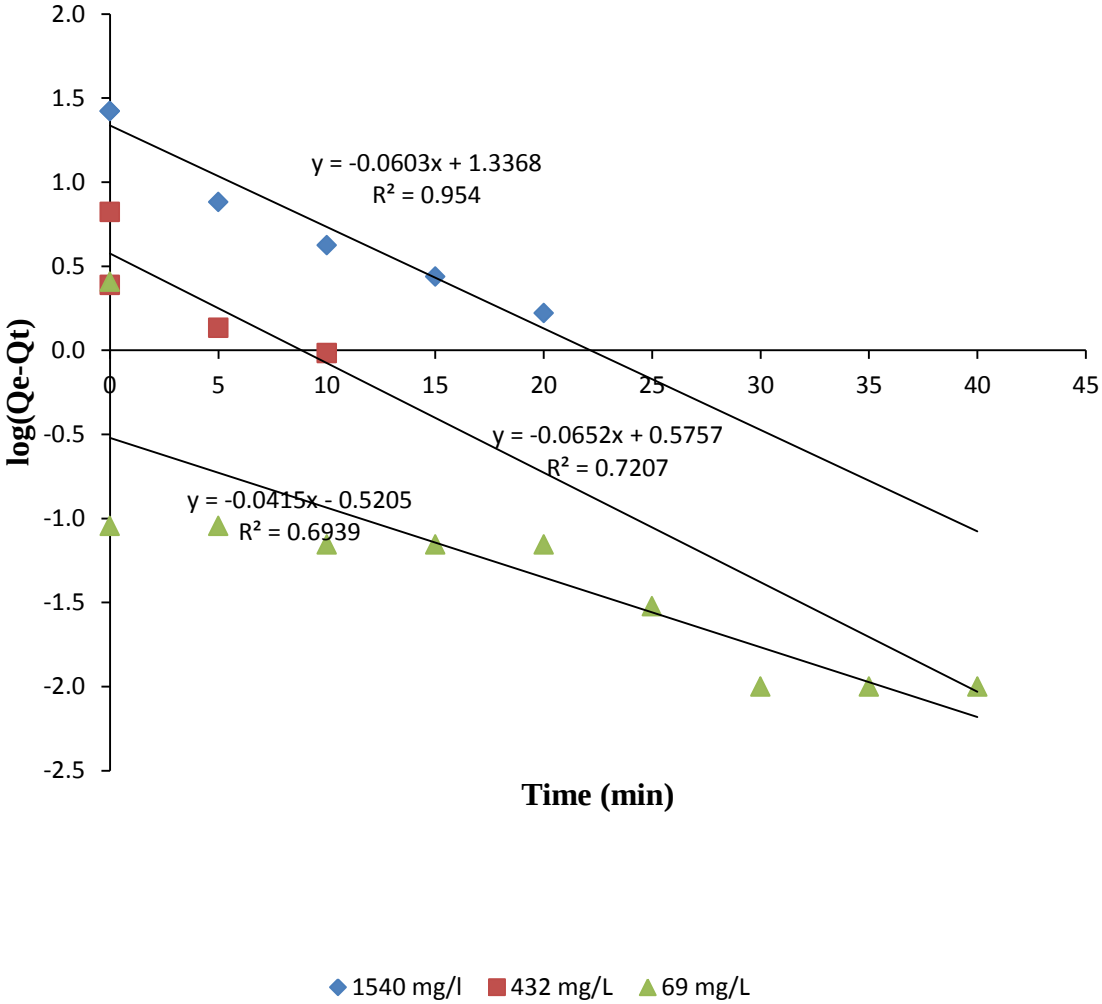

***Figure 6(b)**: Pseudo-first-order plots of Cd (II) ions adsorption onto E.crasippes*

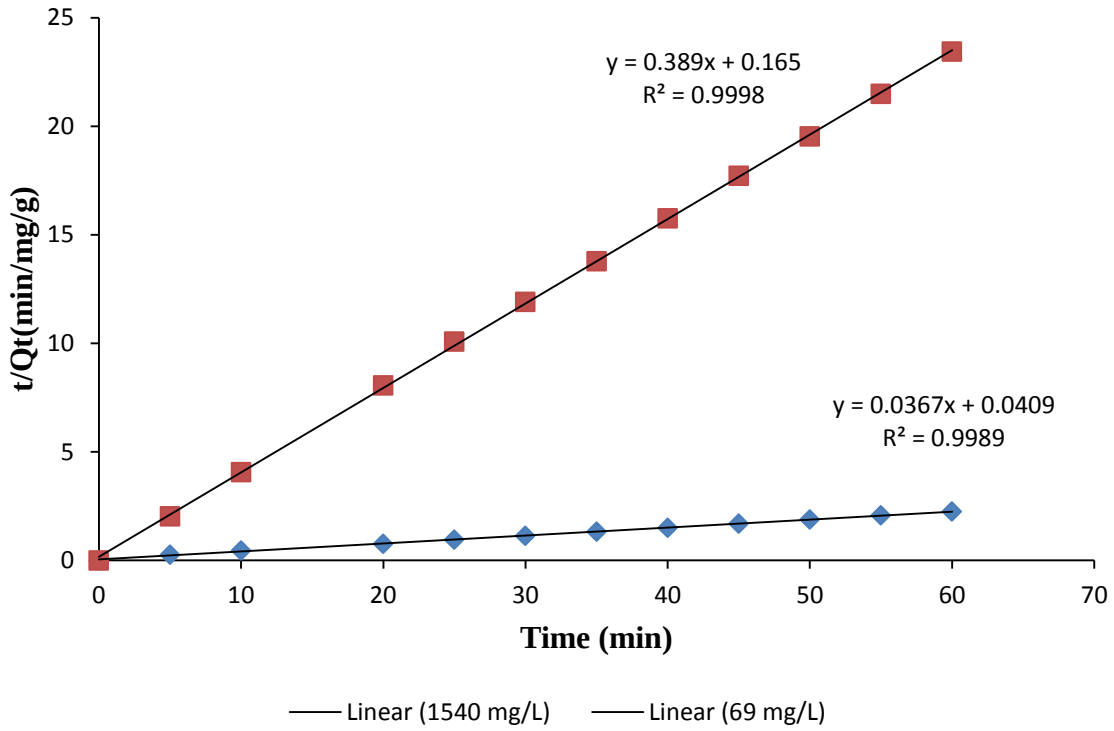

Figure 6(c): *Pseudo-second -order- plots of Cd (II) adsorption onto E. crassipes.*

3.7 Biosorption isotherms

For optimization of the biosorption process design, its imperative to obtain the appropriate correlation for the equilibrium data.biosorption isotherms describe how adsorbate interacts with the biosorbent and the residual metal ions in solution during the surface biosorption.The isotherms also help in determination of adsorption capacityof the biosorbent for the metal ions.The data on Cd (II) ions biosorption was fitted with the Langmuir and Freundlich isotherms.

The Langmuir isotherm assumes monolayer coverage of the adsorbate onto a homogeneous adsorbent surface and the biosorption of each cation onto the surface has equal activation energy. The Langmuir isotherm can be exppressed as :

$$\frac{Ce}{qe} = \frac{1}{qmax\ b} + \frac{Ce}{qmax} \quad \text{.....(5)}$$

Where q_{max} is the monolayer capacity of the biosorbent (mg g^{-1}), and b is the biosorption constant (L mg $^{-1}$).The plot of ce/qe versus ce should be a straight line with a slope of $1/q_{max}$ and intercept of $1/q_{max}$ b when the biosorption follows Langmuir equation.

The Freundlich equation can be expressed as :

$$\log q_e = \log K_F + \frac{1}{n}\log Ce \quad \text{.....(6)}$$

where K_F and 1/n are the Freundlich isotherm constants related to biosorption capacity and biosorption intensity respectively.If the equation applies then a plot of log qe versus log Ce will give a straight line of slope 1/n and intercept as K_F.

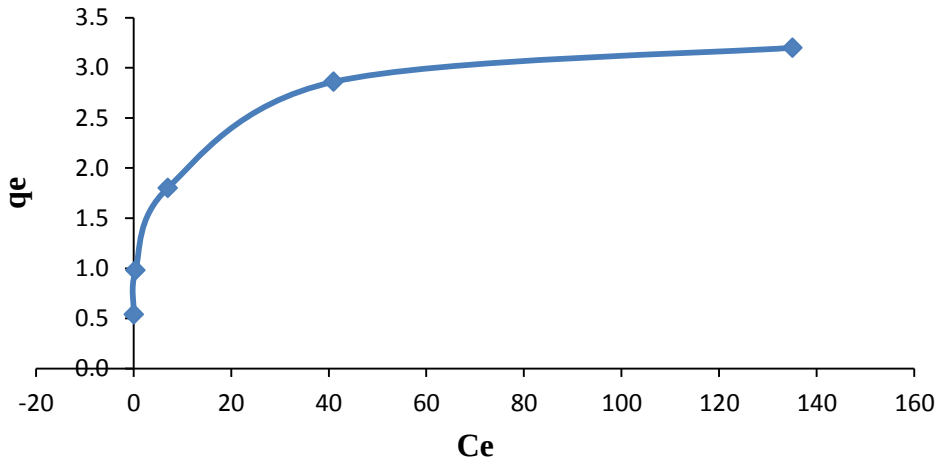

Figure 7(a) *: Langmuir isotherm for Cd (II) ions using E. crassipes at room temperature.*

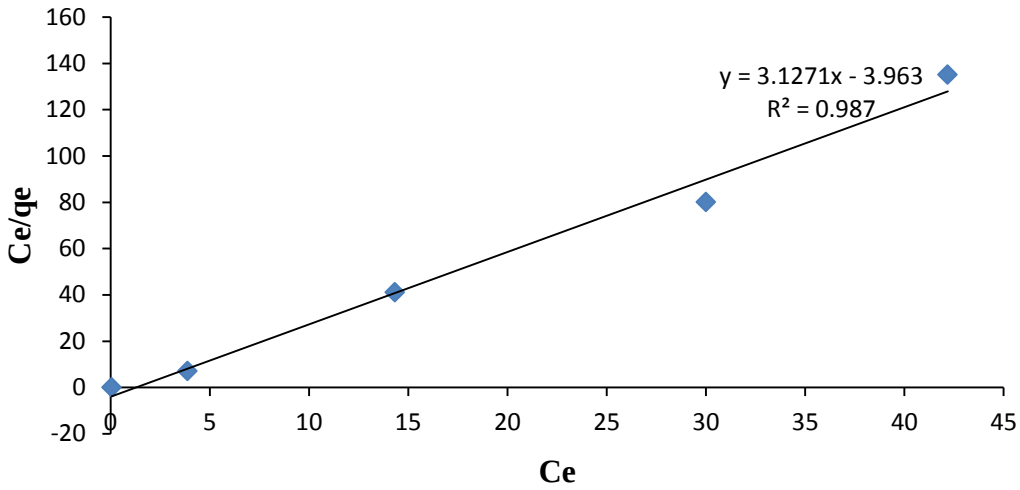

Figure 7(b) *: Linearized Langmuir isotherm plot for adsorption of Cd (II) by E.crasippes.*

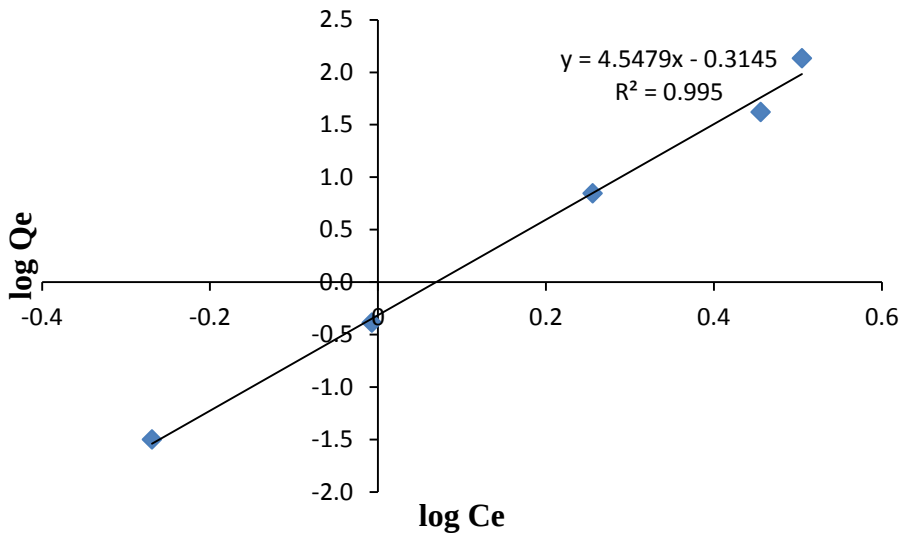

Figure 7(c)*: Freundlich isotherm plot for adsorption of Cd (II) by E. crassipes*

IV. Conclusion

This study demonstrates that E.crasippes is a promising adsorbent for the removal of Cd(II) ions from aqueous solutions. The adsorption process was affected by various physico chemical parameters such as contact time, pH, initial concentration of the metal ions, shaking speed and temperature.The kinetic study revealed that the adsorption data obeyed the pseudo-second-order model better than the pseudo-first-order model given the higher correlation coefficient(R^2). The FTIR spectra revealed that the interaction between Cd (II) ions and adsorbent surface takes place at the hydroxyl amine and carboxyl functional groups.It can therefore be concluded that *E.crasippes* is an effective alternative biomass for the removal of Cd(II) ions from wastewater because the material has a high adsorption capacity, naturally available , abundandly available at a low cost.

Acknowledgements

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