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Biosorption of Zn (II) ions from aqueous solutions by water hyacinth (*Eichhornia crasippes*): Equilibrium and Kinetic studies

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ABSTRACT: The biosorption characteristics of Zn (II) ions were investigated. Experimental parameters affecting the biosorption process such as pH, contact time, biomass dosage, initial metal ion concentration, and temperature were studied in batch adsorption experiments. Langmuir and Freundlich isotherm models were applied to the adsorption data .The biosorption capacity for *E. crasippes* was found to be 16.50 mg g^{-1}. The data was also subjected to pseudo-first-order and the pseudo-second-order kinetic models.

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

1 INTRODUCTION

The need to immobilize the heavy metals released into the environment by and partially lost trough anthropogenic activities must be top on our research agenda now. This is because it is well established that dissolved metals in the environment pose a serious threat to human and environmental health. Heavy metals in water have been a major preoccupation for researchers for many years due to their toxicity towards aquatic life, human beings and environment (Ibrahim *et al*, 2010).The heavy metals have a wide range of effects on fauna and flora, some of which are life threatening as they lead to damage of the essential body systems. Zinc though essential in low concentrations is known to have negative effects such as depression, lethargy, neurologic signs such as seizures and ataxia and increased thirst in humans (Barakat, 2011).

There is therefore urgent need to remove the heavy metals already immobilized and if possible recover them for recycling purposes. This is because they do not biodegrade unlike organic pollutants, making their presence in industrial effluents and drinking water a public health concern. The conventional techniques of heavy metal removal which include chemical precipitation, reverse osmosis, ion exchange are not only expensive but also easily subject to fouling. They also lead to generation of secondary sludge which is sometimes more problematic to treat apart from the inability to remove high volume low concentrations of heavy metals. Adsorption has come out strongly as an alternative technique with activated carbon being the main adsorbent for the removal of heavy metal ions from water and waste waters is costly (Gautam *et al.,* 2014).

In order to meet the ever stringent regulations and to protect and preserve the integrity of our environment there is therefore need to come up with effective and cheap technologies that will help in mitigation of the effects of these heavy metals in the environment.

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The objective of this study was to investigate the application of *E. crasippes* an invasive weed species which has potential to successfully colonize, spread, and subsequently displace vegetation and disrupt ecosystems (Holm, 1977) (Hohm et al, 1977) as an adsorbent for Zn (II) ions removal from aqueous solutions.

The effects of several physico-chemical parameters such as pH, adsorbent dosage, contact time, initial metal ion concentration and temperature that affect adsorption were investigated. Equilibrium isotherm models and kinetic models were applied to the data obtained for a better understanding of the adsorption process.

2 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 Zn (II) ions was prepared in 1.0 g L^{-1} concentration using 4.4200 g of ZnSO4.7H_2O (Sigma Aldrich) then diluted to appropriate concentrations .The pH of the solutions was adjusted using 0.1 mol L^{-1} HCl and 0.05 mol L^{-1} NaOH solutions.

2.3 ANALYSIS OF METAL IONS

The concentration of Zn (II) ions in the biosorption media was determined using Atomic absorption Spectrophotometer (CTA 2000 and Varian Spectr AA), equipped with air acetylene burner. The hollow cathode lamp was operating at 4 mA. Analytical wavelength was set at 213.5 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.

$$q = (\frac{C_o - C_e}{m})V \quad (1)$$

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

$$A\% = (\frac{C_o - C_e}{C_o}) \times 100 \quad (2)$$

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).

3 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 (Volesky, 2007). This is because it affects solution chemistry and also the speciation of the metal ions.

The effect of initial pH on biosorption of Pb (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 lead (II) hydroxides. From the figure 1 it could be seen that Pb (II) ions adsorption increased as the pH increased. At low pH values, protons occupy the biosorption sites on the biosorbent surface and therefore less Pb (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. Similar results were reported (Amboga *et al,* 2014).

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 Zn (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.

3.3 EFFECT OF INITIAL METAL CONCENTRATION.

The initial concentration remarkably affected the uptake of Zn (II) ions in solution. The efficiency of Zn (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 Zn (II) 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.

3.4 EFFECT OF CONTACT TIME

Contact time is an important parameter for any successful use of the biosorbents for practical purposes. Effect of contact time on adsorption of Zn (II) ions was investigated keeping the biomass in contact with the metal ion solution for different time periods between 0 to 60 minutes. The adsorption of Zn (II) displayed a triphasic pattern with rapid initial uptake in the first 5 minutes, then a slowed down followed by a plateau.

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 Zn (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.

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 Zn (II) ions was investigated and the data is shown in figure 5.The results indicate that the % adsorption is not affected by temperature changes. However when the concentration is increased the reaction is slightly affected by temperature changes hence a reduction in the % adsorption. This can be attributed to the fact that with increase in temperature of the solution, some binding sites are damaged, the attractive forces between the biomass surface and Zn (II) ions are weakened thus decreasing the sorption efficiency. This could be due to increase in the tendency for the Zn (II) ions to escape from the solid phase of the biosorbent to the liquid phase with increase in temperature.

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 (Anayurt *et al*, 2009).

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 Zn (II) ions on the biosorbent. The Lagergren pseudo- first –order rate model is represented by the equation:

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

Where q_e and 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 qe 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

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

Where k_2 is the rate constant of the pseudo-second- order adsorption (g $mg^{-1}min^{-1}$).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 (a) and 6 (b).

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((Foo and Hameed, 2010). The data on Zn (II) 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 :

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \qquad (5)$$

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 :

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (6)$$

where K_F and 1/n are the Freundlich isotherm constants related to biosorption capacity and biosorption intensity respectively.n describes the heterogeneity of the adsorbent surface and its affinity for the adsorbate(Chen et al., 2003).A higher value of n (or a smaller value of 1/n) indicates a stronger bond between the adsorbate and the adsorbent thus values of n larger than unity indicate a strong bond which implies favourable adsorption(Sari et al., 2009). If the equation applies then a plot of log q_e versus log C_e will give a straight line of slope *1/n* and intercept as K_F.The experimental data was evaluated using Langmuir and Freundlich isotherms and results are displayed in 7 ((a) and 7 (b).

4 FIGURES

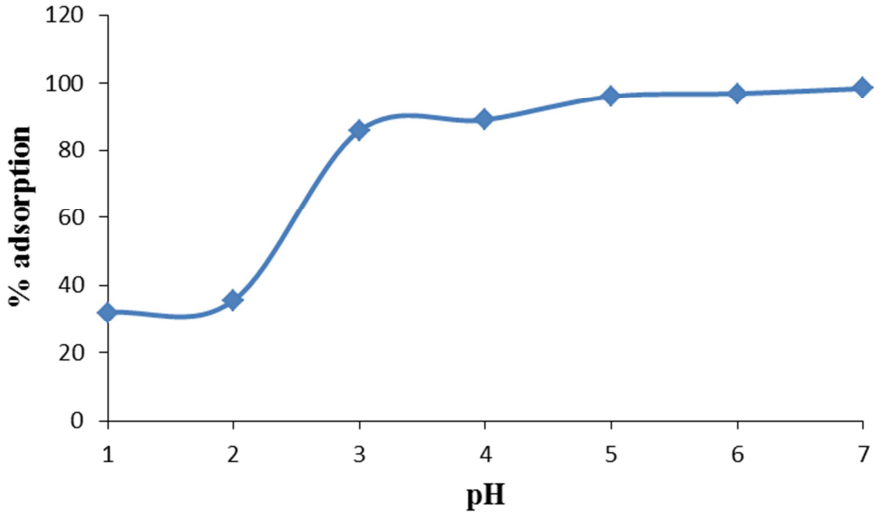

Figure 1 : Effect of pH on adsorption of Cu(II) ions onto E.crassippes

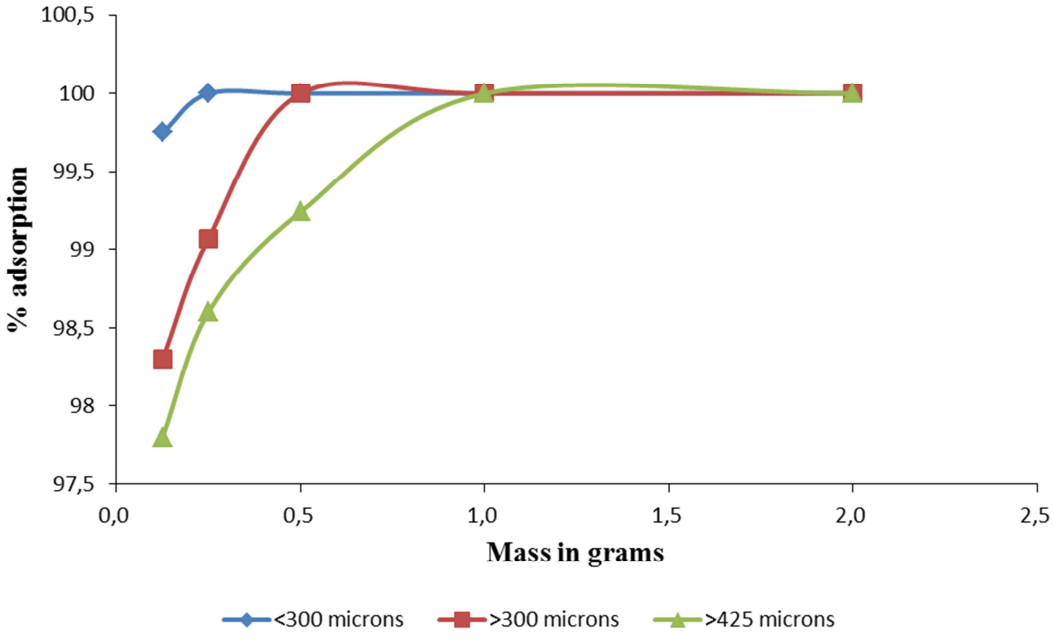

Figure 2: Effect of biomass dosage and particle size on adsorption of Cu (II) ions

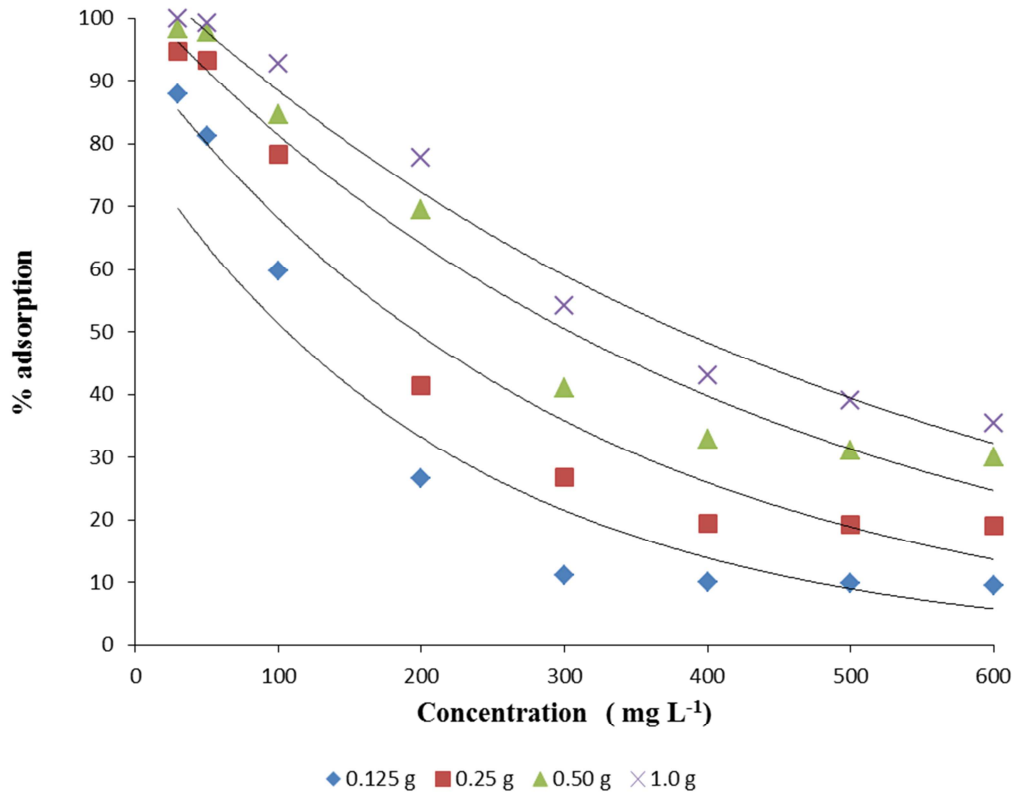

Figure 3: Effect of initial concentration of Zn (II) ions on adsorption by E. crassipes

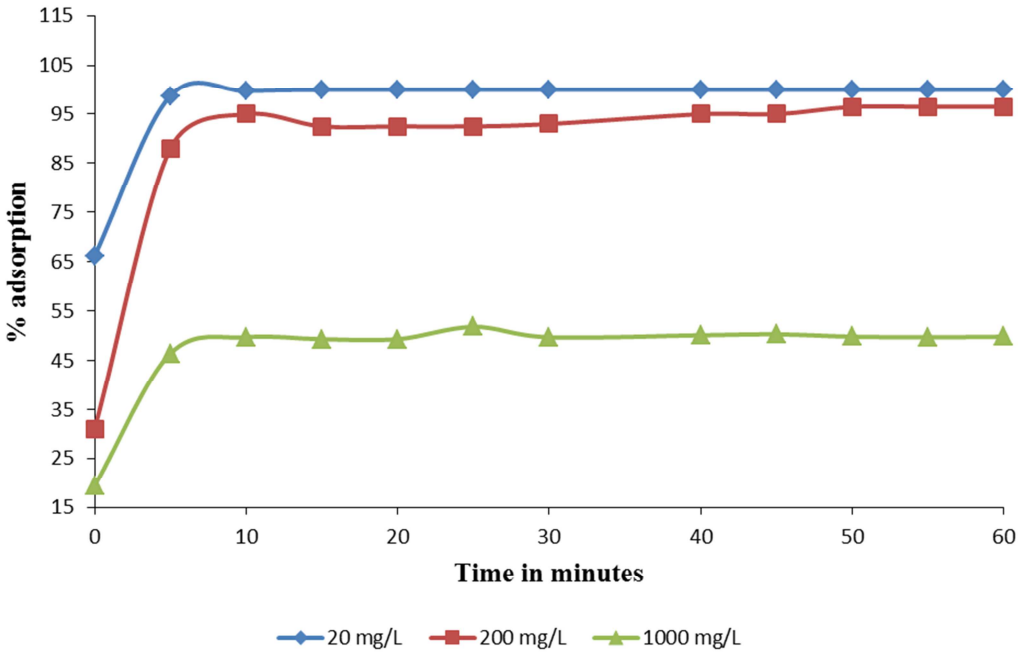

Figure 4: Effect of concentration and contact time on adsorption of Zn (II) ions by 0.5 g of E. crassipes

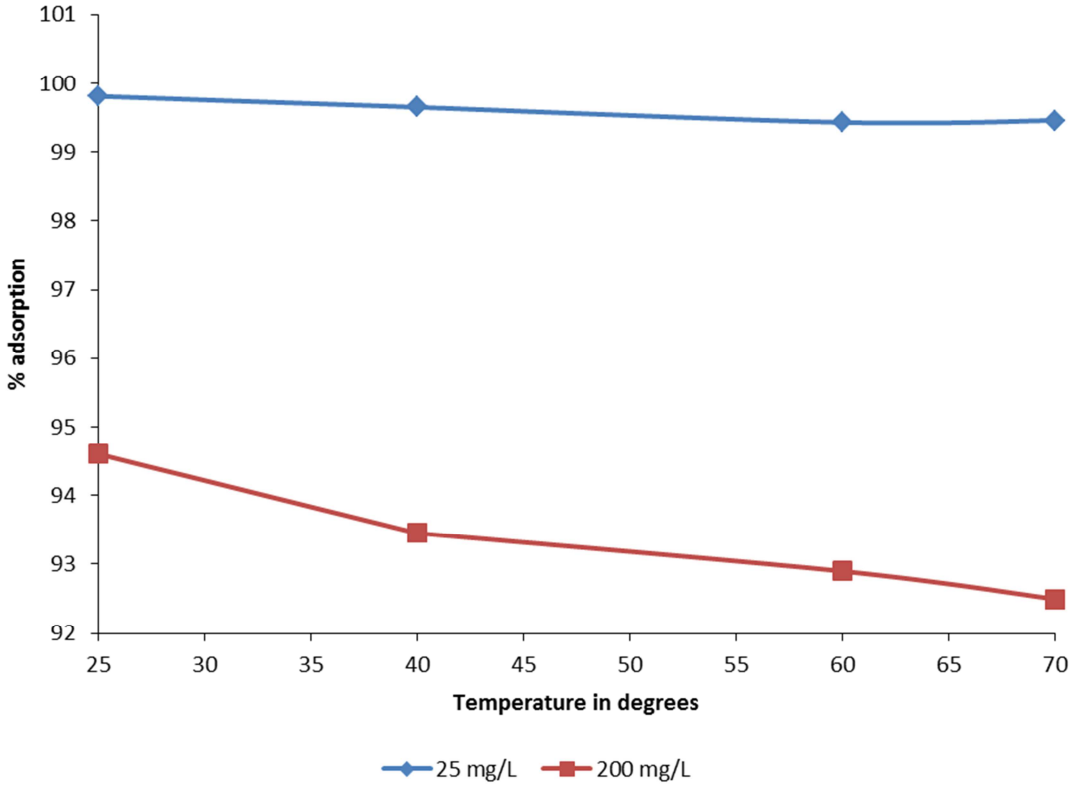

Figure 5: Effect of temperature on % adsorption of Zn (II) ions by 0.5 g of E. crassipes

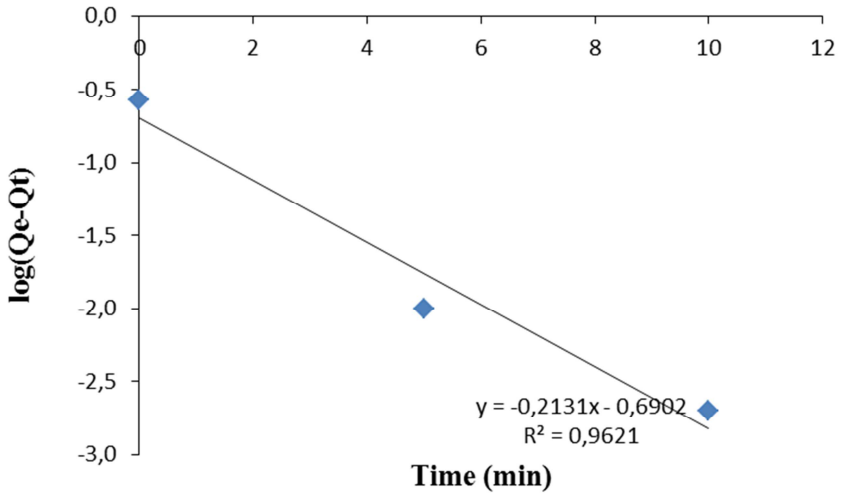

Figure 6(a): Pseudo-first-order plot for adsorption of 20 mg/L of Zn (II) onto E. crassipes

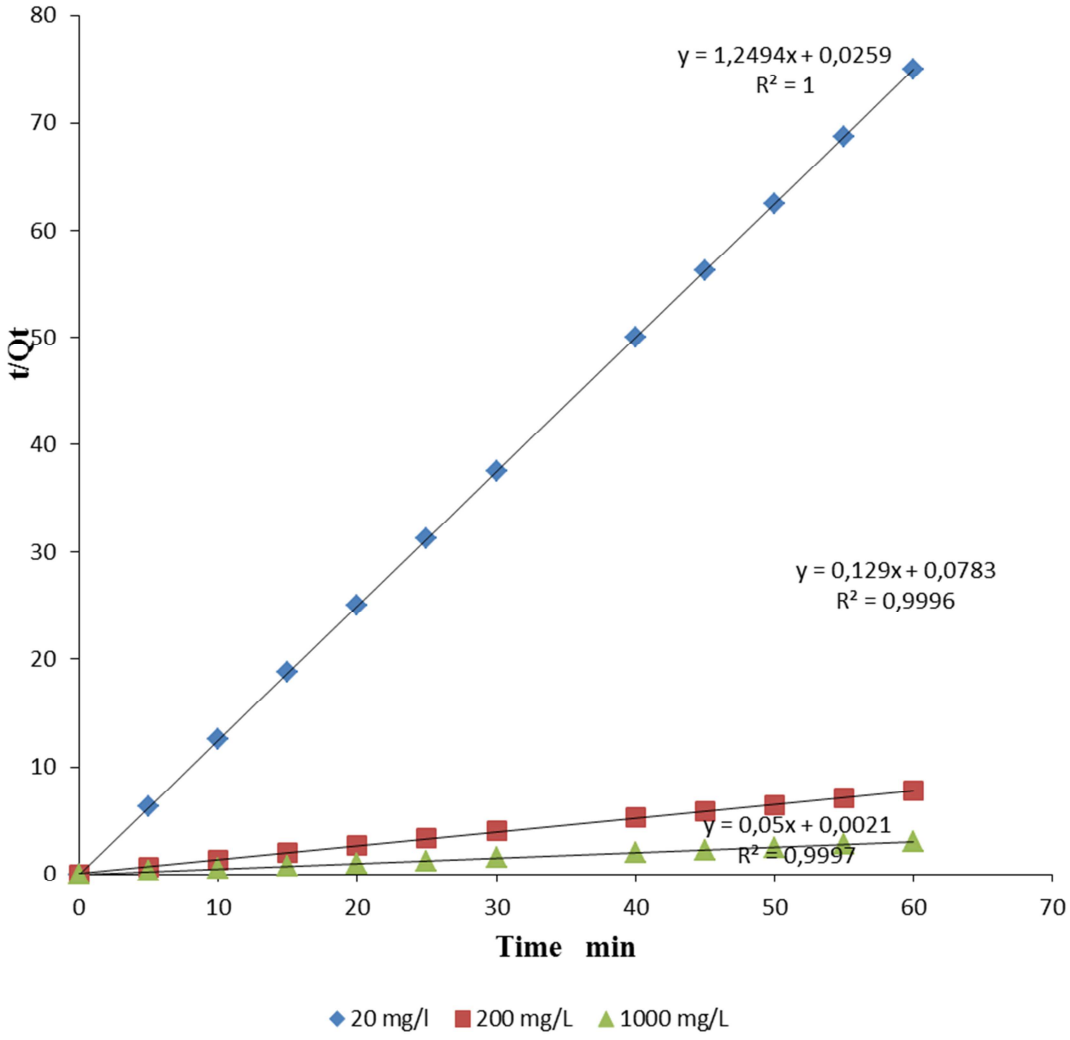

Figure 6(b): Pseudo-second- order plots for Zn (II) ions adsorption by E.crassipes.

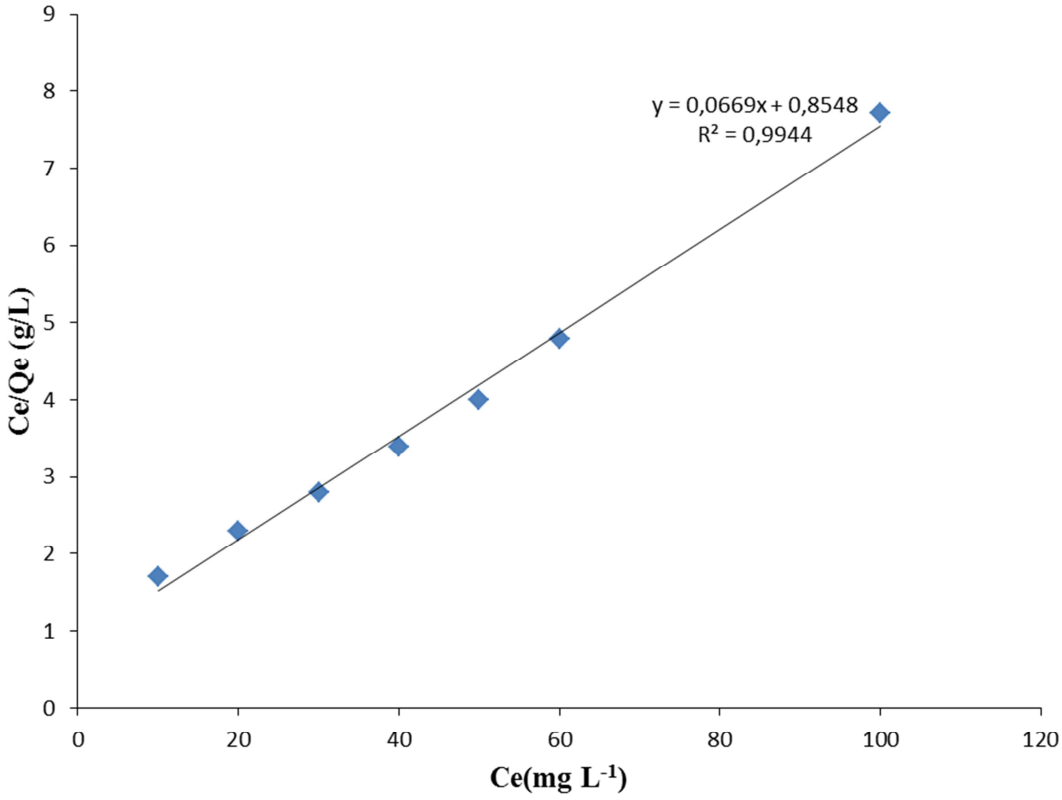

Figure 7(a): Linearized Langmuir isotherm for adsorption of Zn (II) ions by E.crasippes

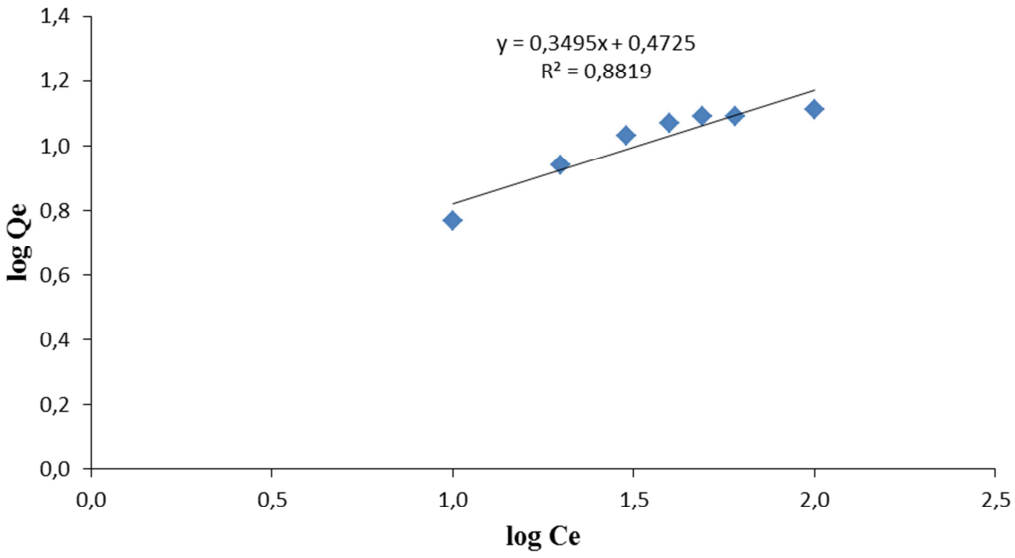

Figure 7 (b) : Freundlich isotherm for adsorption of Zn(II) onto E. crassipes

5 CONCLUSION

This study demonstrates that *E.crasippes* is a promising adsorbent for the removal of Zn(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). It can therefore be

concluded that *E.crasippes* is an effective alternative biomass for the removal of Zn (II) ions from wastewater because the material has a high adsorption capacity, naturally and abundantly available at a low cost.

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