

Kinetic Model for the Sorption of Cu (ii) and Zn (ii) Using Lady Fern (*Athyrium - Filix – Femina*) Leaf Waste Biomass from Aqueous Solution

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Abstract

This study presents the biosorption of two divalent metal ions, Cu(ii) and Zn(ii) onto lady fern (*Athyrium-filix-femina*) leaf waste biomass over a wide range of reaction conditions and equilibrium sorption kinetics. The rate of removal of Cu(ii) ions and Zn(ii) ions from aqueous solution by the lady fern leaf waste biomass was studied in batch conditions. The rate of sorption of copper and zinc was rapid within the initial time of 5-20 minutes and reached a maximum in 30 minutes. Kinetic modelling analysis of the pseudo-first order and pseudo-second order equation model using the linear coefficient of determination R^2 values showed that the pseudo-second order equation was the most appropriate model for the description of Cu(ii) and Zn(ii) ion sorption and can be said to follow a pseudo-second order model. The sorption process was examined by means of Langmuir and Freundlich isotherms. The Langmuir equation revealed a monolayer sorption capacity 0.09mg/g and 0.09mg/ for Cu(ii) and Zn(ii) respectively. The results from this present study indicates that lady fern leaf waste biomass could be employed for the removal of toxic and valuable metals from industrial effluents.

Keywords: Sorption Conditions, Adsorption isotherms and kinetics.

1. Introduction

The problems of our ecosystem are increasing with advancement in technology. Heavy metal pollution is one of these problems. Toxic heavy metal release into the environment has been increasing continuously as a result of man's industrial activities and technological development (Horsfall and Spiff, 2004). The release of heavy metals poses a significant threat to the environment and public health because of their toxicity, bioaccumulation in the food chain and persistence in nature (Ceribasi and Yeti, 2001). Industrial process for extracting metals or, more generally all processes involving metals in their productive cycle generate significant heavy metal cations (Fourest and Roux, 1992). Mine drainage, metal industries, refining, electroplating, dye and leather industries, domestic effluents, landfill leachate and agricultural runoff all generate wastewater that contain heavy metals (Abia et al, 2012). The presence of these heavy metals in the environment has led to a number of environmental problems. Since most of these heavy metals do not biodegradable into non-toxic end products (Augustine et al, 2009), their concentration in effluents must therefore be reduced to acceptable levels before discharging them into the environment. Otherwise, these metal ions could pose threat to public health or affect the aesthetic quality of potable water (Xu et al, 2006).

There are several physicochemical methods developed by scientists used in the removal of trace metal ions from industrial wastewater such as precipitation, ion exchange, membrane processes, solvent extraction, reverse osmosis, chemical oxidation/reduction, electrochemical treatment, evaporative recovery, lime coagulation and filtration (Suh and Song, 2009; Chong and Volesky, 1995; Horsfall and Spiff, 2005; Horsfall and Spiff, 2005). These processes however

may be ineffective or expensive and non-environment- friendly when the concentrations of the trace metal ions are high in the industrial effluent, say 1 – 100mg of trace metal ions per liter (Volesky,1990;Kapor and Viraraghavan,1995). These existing treatment processes also have disadvantages like high reagent and energy requirement, incomplete metal removal, generation of toxic sludge or other waste products which require careful disposal. All these have made it imperative for a cost-effective treatment method that is capable of removing trace metals from industrial effluents.

Biological methods such as biosorption/bioaccumulation are presented as alternative methods to traditional physicochemical methods for the removal of trace metal ions from effluents as they are more environment- friendly and economically feasible (Pagnanefi et al,2002). Adsorption as an alternative method to traditional physio-chemical methods is the physical adherence or bonding of ions and molecules onto the surface of another molecule. It is a process that uses special solids known as adsorbents to remove substances (pollutants) from either gaseous or liquid phase mixtures. It is a very common method in the form of sorption used in the treatment of wastewater. The adsorption process involves solid phase (adsorbent) and liquid phase (solvent) containing dissolved species (trace metal ions in this case) to be sorbed. Owing to the high affinity of the sorbent for the sorbate species, the latter is attracted and bound by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phase (Norton et al,2004).

The adsorbent material is usually a waste material or by product or even waste material from large scale industrial operations. For example, sorghum chaff, paper mill waste, cocoa-pod husks, coconut fibres, palm bunch wastes, tea waste and many others (Hussein et al,2004;Sudah and Abraham,2001).The major advantages of adsorption over other conventional treatment methods include: the treatment of large volumes of wastewater with high concentration of pollutants, high efficiency, low cost and minimization of chemical and/or biological sludge, regeneration of adsorbent and possibility of metal recovery (Abia et al,2005;Ho et al,1986,Ho et al,1996). The equilibrium of the adsorption process is often described by fitting the experimental data with models usually used for the description of equilibrium adsorption isotherm (Quek et al,1998). The isotherm models for single metal systems are the Langmuir and Freundlich isotherm models. This present study is therefore focused on the removal of Cu(ii) and Zn(ii) from wastewater via kinetic approach.

2. Materials and Method

2.1 Sample Collection

Fresh lady fern (*Athyrium- filix- femina*) leaves were collected from the river bank of River Ethiope in Abraka, Ethiope East Local Government Area of Delta State.

These were all hand-plucked from the bank, thoroughly washed with deionised water and allowed to air-dry for three days. The dried leaf samples were ground with mechanical grinder and then sieved through a British standard screen to obtain particles sizes ranging from 100µm to 400µm and stored in a plastic container for further analysis.

3. Experimental Procedures

3.1 *Activation and Purification of the Biomass*

The experiments on activation and purification of the biomass were carried out according to the previous works of (Horsfall and Spiff,2005). 600g of finely divided biomass was activated and at the same time, purified by soaking in excess 0.3M HNO₃ for 24 hours to remove any metals and debris that might be in the biomass prior to experimental metal ion exposure, followed by washing thoroughly with deionised water until a p^H of 7.1 ± 0.1 was attained and resuspended in 1.0M hydroxylamine to remove all O-acetyl groups. To remove all other soluble materials, the biomass was washed with deionised water and allowed to air-dry for 24 hours at room temperature. After this, the purified biomass cake obtained from the different particle sizes ranging from 100µm to 400µm were collected at room temperature.

3.2 *Effect of Metal Ion Concentration on Sorption*

The experiment on the effect of metal ion concentration on sorption was performed according to the previous works of (Horsfall and Spiff,2005). Several standard solutions of 10, 20, 30, 40, 50, 60 and 70mg/l were prepared for Cu(ii) from CuSO₄, and Zn(ii) from ZnSO₄.6H₂O.

The metal solutions made separately were adjusted to p^H of 5.0 (since most metals are soluble at this p^H) using concentrated HCl. 50ml of each metal ion solution was added to accurately weighed (250 ± 0.01mg) activated/purified biomass in different flasks and agitated for 2 hours to ensure that equilibrium was reached. At the end of the time, the suspension was filtered through Whatman No. 45 filter paper and centrifuged at 2500rpm for 5 minutes (this is to remove all traces of cloudiness). The supernatants were analyzed for metal ions by Atomic Absorption Spectrophotometer (AAS) machine(Horsfall and Spiff,2005).

3.3 *Effect of Contact Time on Sorption*

The experiment on the effect of contact time on the metal ion binding was performed according to the previous works of (Horsfall and Spiff,2005). Activated/purified biomasses (250 ± 0.01mg) were weighed into several flasks. Cu(ii) and Zn(ii) solutions (2.50mg in 50ml of water) were added to the biomasses. The flasks were then labelled for time intervals of 5, 10, 15, 20, 25, 30 and 35 minutes respectively. The p^H's of these suspensions were adjusted to 5.0. The flasks were tightly covered and shaken at the appropriate time intervals. At the end of each time interval, the suspensions were filtered using Whatman No. 45 filter paper and then centrifuged at 2800rpm for 5 minutes. The metal ion concentration was determined using the AAS machine(Horsfall and Spiff,2005).

3.4 *Analysis of Metal Content*

The Zn(ii) and Cu(ii) contents in all experiments were determined with an Atomic Absorption Spectrophotometer (AAS). Spectroscopic grade standards were used to calibrate the instruments, which were checked throughout the

analysis for instrument's response. The batch experiments were performed in triplicates and the means were computed for each set of values to maintain quality assurance.

4. Data Evaluation

4.1 Calculation of the Degree of Metal Ion Removal

The amount of Cu(ii) and Zn(ii) ions removed by the biomass during the series of the batch investigations were determined using a mass balance equation expressed as shown in Equation (1);

$$q_e = \frac{V}{M}(C_o - C_e) \dots\dots\dots(1)$$

Where;

q_e = metal-ion concentration on the biomass (mg/g) at equilibrium.

C_e = metal-ion concentration in solution (mg/l) at equilibrium.

C_o = initial metal-ion concentration in solution (mg/l)

V = volume of initial metal-ion solution used(L)

M = Mass of biomass used (g)

4.2 Kinetic Treatment of Experimental Data

In order to comprehensively investigate the mechanism of adsorption, pseudo-first order and the pseudo-second order kinetic mechanisms as have been used by some workers(Horsfall and Spiff,2005; Hu et al,1995), were applied to the experimental data.

The pseudo-first order expression earlier used by Horsfall and Spiff(2005), for the sorption system of divalent metal-ions using Aphagnum moss plant was adopted for this study.

The linear form of Langergren's pseudo first order model is given by Equation(2) ;

$$\ln(q_e - q_t) = \ln q_e - Kt \dots\dots\dots(2)$$

Where;

q_e = mass of metal adsorbed at equilibrium (mg/g)

q_t = mass of metal adsorbed at time t (mg/g)

K = equilibrium constant= K_1 for this pseudo first order analysis

A linear plot of $\ln(q_e - q_t)$ versus t confirms the model. From the plot

K_1 ,is the rate constant (lmin^{-1}) and can be determined from the slope, while q_e is the maximum sorption capacity at equilibrium (mg/g) and is obtained from the intercept of the plot.

The pseudo second order equation earlier used also by Horsfall and Spiff(2005) for the sorption system of divalent metal-ions using Aphagnum moss plant was adopted. The linear form of the pseudo-second order model is generally expressed in Equation (3);

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{t}{q_e} \dots\dots\dots(3)$$

Where

- q_t = the amount of divalent metal-ions on the biomass surface (mg/g) at anytime t.
- q_e = the amount of divalent metal-ions sorbed at equilibrium (mg/g)
- h_o = the initial sorption capacity (mg/g min)

The initial sorption rate, h_o , is defined as shown in Equation(4);

$$h_o = K_2 q_e^2 \dots\dots\dots(4)$$

Where;

K_2 is the Pseudo-second order rate constant (g/mg min), which indicates the rate constant of sorption (g/mg.min⁻¹) for the boundary conditions.

A linear plot of $\frac{t}{q_t}$ against t confirms the model. Having obtained the values of K_2 and q_e , the maximum

sorption capacity at any other time(q_t) can be obtained using Equation (5)

$$q_t = K_2 q_e \dots\dots\dots(5)$$

q_e , K_2 and h_o can be determined from the slope and intercept of the plot respectively [5].

5. Results and Discussions

5.1 Effect of Metal Ion Concentration on Adsorption

The experimental results of the uptake of Cu(ii) and Zn(ii) ions onto the fern leaf waste biomass at various initial metal-ion concentrations are shown in Table1. The sorption capacity increases from 0.078 – 0.089mg/g Cu(ii) and 0.082 – 0.091mg/g Zn(ii) with an increase in metal ion concentration from 10 – 70mg/l and a biomass dose of 5.0g. The two metals in the study were adsorbed in these order Zn(ii) > Cu(ii). However, the actual percentage removal of the metal ions from solution increased with increase in the initial metal-ion concentrations (Table 1). This may be due to the fact that at lower concentrations, adsorption of the metal-ions occurred slowly and further increase in initial metal-ion concentration led to a competition for available bonding sites on the biomass surface by the metal-ions and thus increased adsorption. Similar adsorption procedure have also been reported by other researchers (Abia etal,2002;Quek etal,1998;HorsfallandSpiff,1995).

5.2 Effect of Contact Time on Adsorption

Time-dependence experiments were conducted in order to obtain how long the fern leaf biomass would take to adsorb the metal-ions at optimum pH. The data from the time dependent experiments for the removal of trace metals is as presented in Table 2. As the contact time increased from 5 – 15 minutes, the amount of metal-ions removed by the biomass was observed to be relatively high until a contact time of 20 minutes was reached, after which the metal ion removed dropped and became fairly constant.

These data reveal that metal-ion removal by the biomass was initially rapid for the two metals investigated. Within the first 5 – 25 minutes, the biomass was capable of removing over 70% of each metal ion. Optimum adsorption of the two metals was achieved within 5 – 20 minutes and thereafter, dropped almost uniformly. The rapid adsorption of the metal ions by the biomass indicates that the adsorption might have taken place on the cell wall of the biomass, since most, soluble components were removed using washing. This relatively fast and early removal of metal-ions also indicates that physi-sorption as well as chem-sorption processes were involved in the reaction between the metal-ions and fern leaf biomass. Using differing biomasses, similar adsorption trends have been observed by other researchers(Queketal,1998; Horsfall and Spiff,1995).

6. Freundlich Isotherm

The Freundlich model was chosen to estimate the adsorption intensity of the solute (metal-ion) on the sorbent surface. The linear Freundlich isotherm for the sorption of the two divalent metals onto lady fern leaf waste biomass is shown in Figure 1. Examination of the plot ($\ln q_e$ VS $\ln C_e$) reveals that the Freundlich isotherm was not a very appropriate model for the sorption study of the metal-ions since the value of the coefficient R^2 for all the two metals were all less than 0.990. Table 3 shows the linear Freundlich sorption isotherm constants and the coefficient of determination (R^2). The k_f value of Zn(ii) (0.084) is greater than that of Cu(ii) (0.079), suggesting that Zn(ii) has the greater adsorption tendency towards the waste biomass than the other metal-ions. The Freundlich equation parameter, $1/n$, which is a measure of the adsorption intensity for Cu(ii) (0.073) is higher than that of Zn(ii) (0.051) indicating a preferential sorption of Cu(ii) by the waste biomass.

7. Langmuir Isotherm

The Langmuir isotherm was adopted for the estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface. The plots of specific sorption (C_e/q_e) against the equilibrium concentration (C_e) for Cu(ii) and Zn(ii) ion, is shown in Figure 2 while the linear isotherm parameters q_m, K_L and the coefficients of determination are presented in Table 4. The R^2 values suggests that the Langmuir isotherm provides a good model for the sorption system. The sorption capacity, q_m , which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage, showed that the fern leaf waste biomass had a high capacity for Cu(ii) (0.09mg/g) and Zn(ii) (0.09mg/g). The adsorption coefficient, K_L , which is related to the apparent energy of sorption was high for Zn(ii) ($7.71 \log^{-1}$) than that of Cu(ii) ($4.8461 \log^{-1}$). This observation shows that the energy of adsorption is not very favourable for Cu(ii), probably due to its large ionic radius hence, not all binding sites may have been available to Cu(ii). Similar capacity orders have also been reported by Horsfall and Spiff (1995),for different metal-ions onto fluted pumpkin waste biomass. The favourability of adsorption of the two metal-ions onto the fern leaf waste biomass was tested using the essential features of the Langmuir isotherm model, expressed in terms of a dimensionless constant called “separation factor” was also used by (Horsfall and Spiff,1995).The separation factor, S_F is defined by the following relationship in Equation(6).

$$S_F = \frac{1}{1 + K_L C_o} \dots\dots\dots(6)$$

Where:

K_L = Langmuir isotherm constant ; C_o = initial metal-ion concentration of 10mg/l

The parameter indicates the shape of isotherm as follows:

$S_F > 1$ Unfavourable isotherm; $S_F = 1$ Linear isotherm ; $S_F = 0$ Irreversible isotherm ; $0 < S_F < 1$ Favourable isotherm.

The separation parameters for the two metals are less than unity, indicating that the fern leaf waste biomass is an excellent adsorbent for the two metal-ions. And However, the S_F values (Table 4) of Cu(ii) > Zn(ii) indicates that in a single metal system, Zn(ii) will bind faster than Cu(ii) due to low S_F value of Cu. This observed separation factor also indicates that high concentration of Cu(ii) and Zn(ii) in an effluent will not be a limiting factor in the ability of the fern leaf waste biomass to sorb these metal-ions. Similar separation parameters have been reported by Horsfall and Spiff(1995). Based on the R^2 values, the linear form of the Langmuir isotherm appears to produce a reasonable model for the sorption of the two metals since the values are greater than 0.990, thus showing that lady fern leaf waste biomass is an excellent material for the removal of metal-ions from aqueous solution.

8. Kinetics of Sorption

This is the most important factor in determining the rate at which sorption takes place for a given system and is also very essential in understanding sorbent design, sorbate residence time and reactor dimensions (Horsfall,2004;Ceribas and Yeti,2001). However, according to (Horsfall and Spiff,1995), sorption kinetics shows a large range dependence on the physical and/or chemical characteristics of the sorbent materials, which also influences the sorption process and the mechanism.

8.1 Pseudo-first order model

A plot of $\ln(q_e - q_t)$ against t (Figure 3) gives the pseudo-first order kinetics. From the plot, it is observed that the relationship between the metal ion diffusivity, $\ln(q_e - q_e)$ and time, t , is non-linear; indicating that the diffusivity of the metal ion onto the biomass surface is film-diffusion controlled. The non-linearity of the diffusivity plot shows that this equation proposed was not adequate in describing the reactions among the two divalent metal ions onto the biomass surface. This trend has been reported by [21] on the kinetic study of different ions onto caladium bicolour biomass. It was also observed that the Langergren pseudo first order equation did not provide a very good description for the sorption of the two metal ions onto Athyrium- filix-femina biomass as the values of the coefficient of determination, R^2 , were all less than 0.990 for the two metals. Hence, no further consideration of this model was attempted.

8.2 Pseudo-second order model

The initial sorption rate, h_0 , the equilibrium sorption capacity, q_e , the pseudo-second order rate constant K_2 , and the coefficients of determination, R^2 , were determined experimentally from the slope and intercept of the plot of t/q_t against t (Figure 4) and are shown in Table 6. The data shows that Zn(ii) had a higher sorption rate than Cu(ii). This implies that in a single metal-ion system of the metals, Zn(ii) may be adsorbed better. The coefficient of determination, R^2 , for the pseudo-first order and second order rate models were used to confirm the sorption mechanism proposed. The R^2 values for the two rate constants are listed in Table 7. The data shows a good compliance with the pseudo-second order equation, as the coefficient of determination for metal ions on the biomass were all > 0.990 for the two divalent metal ions. The coefficients of determination for the pseudo-first order kinetic model were all smaller when compared to those of the pseudo-second order indicating that the pseudo-second order model was more appropriate in describing the sorption kinetics. Similar pattern of coefficients of determination have been reported by (Horsfall and Spiff, 2005) for the kinetics of sorption of different metal ions on the caladium bicolour biomass

9. CONCLUSION

This study shows that lady fern (*Athyrium-filix-femina*) leaf is a good and affordable adsorbent for the removal of Cu(ii) and Zn(ii) in aqueous. The fern leaf waste biomass adsorbed metal ions from solution, with an increment in sorption capacity, q_e , with increased metal ion concentration. The adsorption mechanism for these two metal is a stable, rapid process and occurred in less than 25 minutes, which indicates that adsorption was taken place on the cell wall surface of the lady fern leaf biomass. The Langmuir model showed a better fit than the Freundlich model when the equilibrium data was fit in both isotherms. The separation factor, S_f obtained from the Langmuir isotherm showed that adsorption of metal ions onto the lady fern leaf waste biomass was favourable. The kinetic data clearly established the pseudo-second order model to be a more appropriate model for the description of the metal ion sorption process of Cu(ii) and Zn(ii) onto *Athyrium-filix-femina* biomass than the pseudo-first order equation. The results got from this study shows that lady fern (*Athyrium-filix-femina*) leaf is a good and cheap biosorbent with the potential for the removal and recovery of metal ions from heavy metals contaminated wastewater.

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Table 1. Effect of Concentration on Metal-Ion Removal

Initial metal ion concentration (mg/l)	Amount of metal ion adsorbed (mg/g) q_e	
	Cu	Zn
10	0.078	0.082
20	0.087	0.089
30	0.089	0.091
40	0.089	0.092
50	0.090	0.092
60	0.089	0.091
70	0.089	0.091

(Mass of biomass 5g, p^H 5.0, temperature 25 °C, time 2 hours, volume 50ml)

Table 2. Effect of Contact Time on Metal Ion Removal

Initial metal ion concentration (mg/l)	Amount of metal ion adsorbed (mg/g) q_e	
	Cu	Zn
5	0.076	0.079
10	0.073	0.077
15	0.062	0.069
20	0.053	0.066
25	0.044	0.055
30	0.032	0.044
35	0.020	0.036

(Mass of biomass 5g, concentration 10mg/l, volume 50ml, p^H 5.0, temperature 25 °C)

Table 3. Linear Isotherm Freundlich Parameters

Metal ions	1/n	K_f	R^2
Cu(ii)	0.073	0.079	0.473
Zn(ii)	0.051	0.084	0.324

Table 4. Linear Langmuir Isotherm Parameters

Metal ions	q_m (mgg ⁻¹)	K_L (lg ⁻¹)	R^2	S_F
Cu(ii)	0.073	0.079	0.473	0.025
Zn(ii)	0.051	0.084	0.324	0.015

Table 5. Pseudo-first order rate kinetic values for the sorption of the two metal-ions

Metal ions	K_1	q_e (mgg ⁻¹)	R^2
Cu(ii)	0.104	0.0032	0.795
Zn(ii)	0.085	0.0038	0.847

Table 6. Pseudo-second order kinetic parameters values for the sorption of the two metal ions on the biomass

Metal ions	q_0 ($\text{mgg}^{-1} \text{min}^{-1}$)	K_2 ($\text{mgg}^{-1} \text{min}^{-1}$)	q_e (mgg^{-1})	R^2
Cu(ii)	0.0024	6.00	0.020	0.822
Zn(ii)	0.0056	4.48	0.034	0.925

Table 7. Comparison of coefficients of determination, R^2 , for the pseudo-first (K_1) and pseudo-second (K_2) order rate models

Metal ions	R^2 from K_1	R^2 from K_2
Cu(ii)	0.795	0.822
Zn(ii)	0.847	0.925

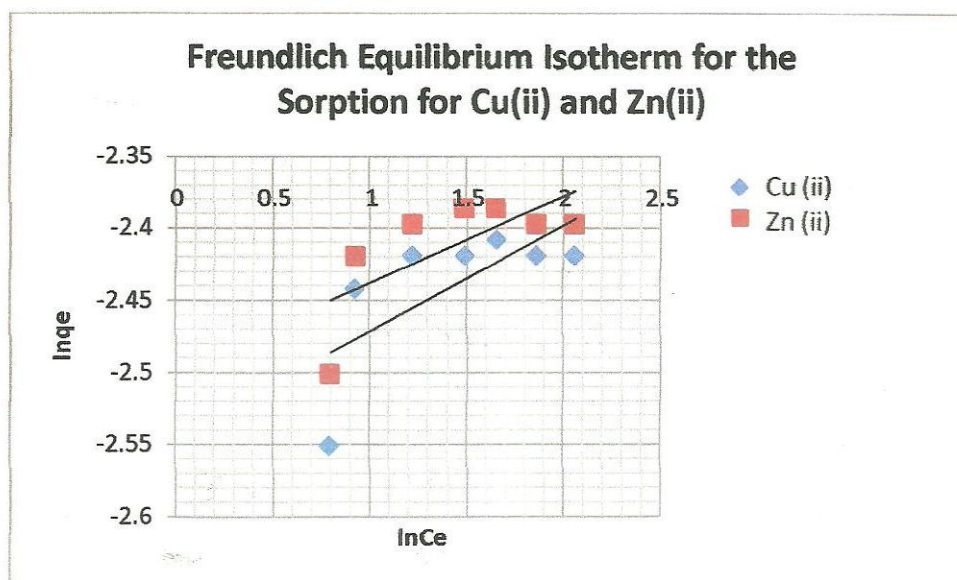


Figure 1: Freundlich Equilibrium Isotherm for the Sorption for Cu(ii) and Zn(ii) Ions

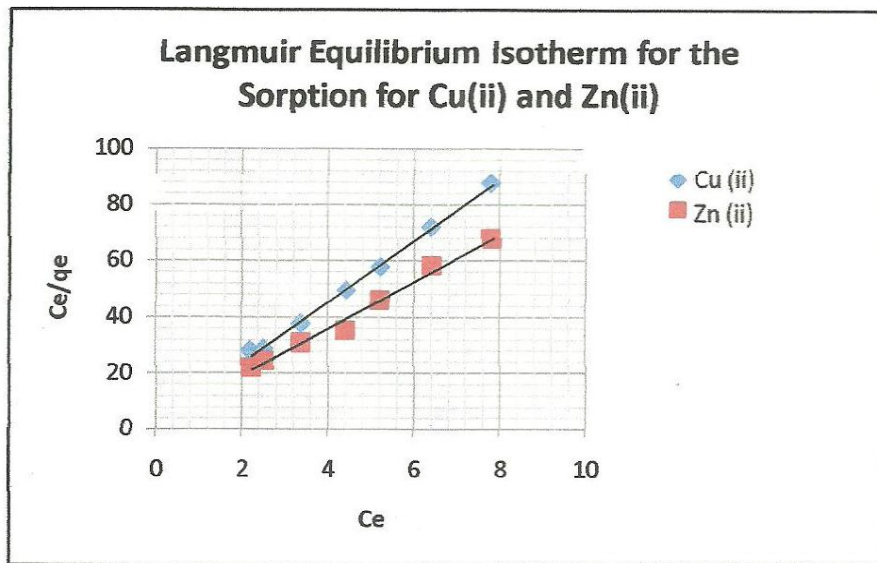


Figure 2:Langmuir Equilibrium Isotherm for the Sorption for Cu(ii) and Zn(ii)

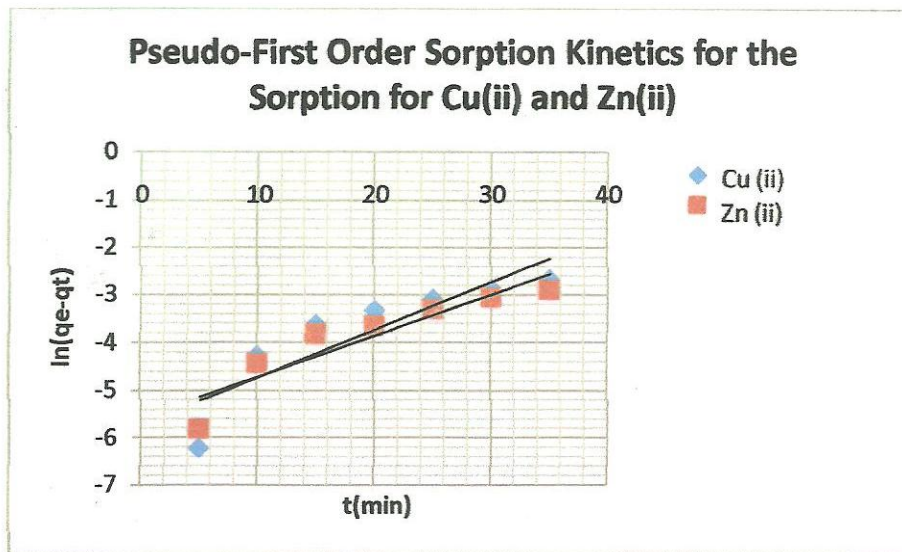


Figure 3. Pseudo-First Order Sorption Kinetics for the Sorption for Cu (ii) and Zn (ii) Ions

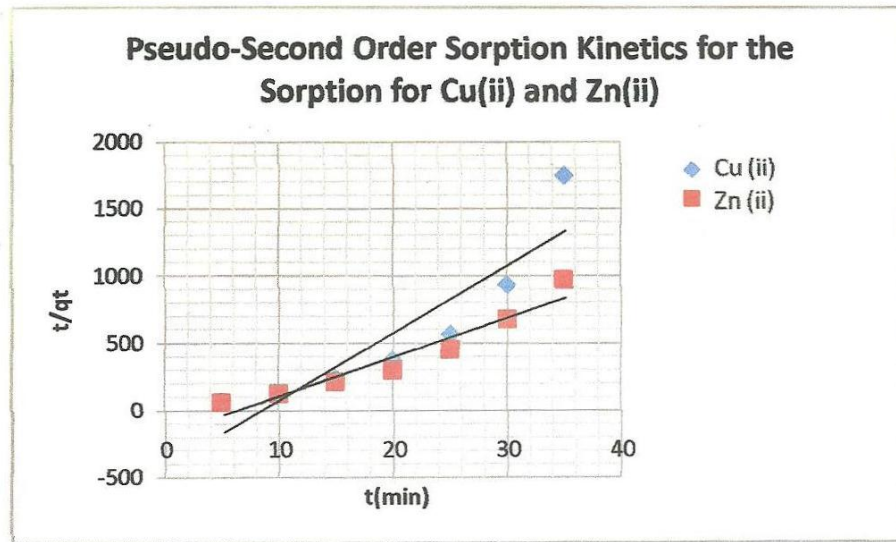


Figure 4: Pseudo-Second Order Sorption Kinetics for the Sorption for Cu (ii) and Zn (ii)

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