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# Biosorption isotherm for of Cu(II) and Zn(II) onto Calcined Limpet shells as a new biosorbent ions from aqueous solutions: Comparison of linear and non-linear methods

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**Abstract:** The ability of calcined limpet shells (CLS), to remove Cu(II) and Zn(II) from effluent solution by biosorption has been studied. All the studies were conducted by a batch method to determine equilibrium and kinetic studies. The effects of contact time, CLS dose, pH and temperature were studied for the biosorption of Cu(II) and Zn(II) on CLS. Biosorption kinetics data were tested using pseudo-first-order and pseudo-second-order models. Kinetic studies showed that the biosorption followed a pseudo-second-order reaction. From thermodynamic studies, it was seen that the biosorption was spontaneous and endothermic. Equilibrium biosorption isotherms were measured for the single component system and the experimental data were analyzed by using Langmuir and Freundlich isotherm equations, to determine the best-fit isotherm for each system, both linear and non-linear regressions were carried out.

**Keywords:** Calcined Limpet Shells, Biosorption, Cu(II), Zn(II), Non-Linear Regressions, Isotherms

## 1. Introduction

Copper and zinc are two typical widespread heavy metal pollutants in natural water environment. Due to application of fertilizers in agriculture, or through land disposal of metal-contaminated municipal and industrial waste discharge, the two kinds of metals can accumulate in sediment, be transferred to plants and fish, and even do harm to human's health. Copper contamination in streams occurs mainly because of metal cleaning and plating baths, paper, pulp, wood preservative-employing mills, fertilizer industry and so on [1,2]. Zinc is considered to enter the environments as the result of human activities such as mining, purifying, steel production and coal burning, etc [3]. Excessive human intake of Cu leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage, and central nervous system irritation followed by depression [1]. Severe gastrointestinal irritation and possible necrotic changes in the liver and kidney can also occur [4]. Trace amounts of zinc are essential for life. However, in large amounts zinc is a toxic element. Among the main symptoms of zinc toxicity, irritability, muscular stiffness, loss of appetite and nausea are to be mentioned [5,6]. A large excess of zinc may be carcinogenic [7]. The World Health Organization (WHO) recommends a level of zinc in drinking water below 5 mg/L [8].

Therefore, the removal of excess heavy metal ions from wastewater is essential to protect human and environmental health. As a result, the removal of toxic heavy metal ions from sewage and from industrial and mining effluents has been widely studied in recent years.

The most widely used methods for removing heavy metals are chemical or electrochemical precipitation, both of which pose a significant problem in terms of disposal of the precipitated wastes [9,10], and ion-exchange treatments, which do not appear to be economical [11]. It has been

reported that some aquatic plants [12,13], wood materials [14-16], agricultural by-products [17], clay [18], natural zeolite [19], turba (partially decomposed vegetable matter) [20,21], microorganisms [22-24], and other adsorbents [25] have the capacity to adsorb and accumulate heavy metals. In the last few decades alternative sorbents for the treatment of heavy metal contamination have been investigated. The most popular adsorbents among them are biomass. These are natural materials available in large quantities and, being waste products, have a low price. Examinations mentioned included determination of adsorbent capacity, kinetics of adsorption, thermodynamic parameters, presumption of bonding mechanisms, reusability, influence of other ions, etc. Despite the fact that single toxic metallic species rarely exist in natural water and wastewater, they are mostly scrutinized in a single model system, probably for the reason of better knowledge of adsorption phenomena.

In the present work, the biosorption kinetics of Cu(II) and Zn(II) onto calcined limpet shells were studied. The effect of solution pH, initial concentration and temperature on the kinetics of heavy metal biosorption were primarily investigated. Tow kinetic models are used to fit the experimental data and the associated parameters have been evaluated. The experimental data were fitted into Langmuir and Freundlich equations (form linear and non-linear).

# 2. Experimental

### *2.1. Instrumentation*

The elemental analysis was performed using a Panalytical analyzer. Scanning electron microscopy (SEM) was performed using a FEI Quanta 200 instrument. Infrared (IR) spectra was obtained with KBr pellets in the range of 4000–450cm$^{-1}$, using a FT/IR-Vertex 70 spectrometer. DRX analysis in the solid phase was performed using a X'Pert Pro MPD Panalytical with Cu anode as the source of X-rays at wavelength λ=1.54 Å. The specific surface area was measured by the BET method using a Pore Size Micrometric (9320 model, USA). The pH of the solutions was adjusted using a Ph Metre Basic 20+, CRISON. The concentration of Cu(II), and Zn(II) ions was determined by Atomic Absorption Spectroscopy (AAS) using a Perkinelmer 200 spectrometer equipped with an air-acetylene flame atomizer and a Hitachi hollow cathode lamp specific for each metal ion. The lamp was operated under the conditions recommended by the manufacture. Also, conventional values for the wavelength, slit width and burner height were applied.

### *2.2. Biosorbent*

The limpets used in this study were collected from a popular restaurant in Morocco. They were repeatedly washed several times with tap water followed by distilled water and then left in open air for several days after they were dried in oven at 100°C for 12 h.

The limpet shells are crushed, powdered to small grains and then calcined at 900°C for 2 h. The residue was washed with distilled water three times and dried at 105°C for 24 h. The residue was finely chopped and ground into small particles of different sizes in the range of 75-100 mm, milled in an agate mortar, washed with distilled water, dried overnight at 105°C, then calcined at a heating rate of 2°C/min to 400°C and maintained at this temperature for 4 h.

The resulting material was stored in a glass bottle for further use without any pretreatment and the resulting material of calcined limpet shells was abbreviated as CLS.

### *2.3. Biosrbate*

The stock solution of Cu(II) and Zn(II) was prepared in 1.0 g/L concentration using $Cu(NO_3)_2.3H_2O$ and $ZnSO_4.7H_2O$ respectively and then diluted to appropriate concentrations. HCL and NaOH were obtained from Merck and used for pH value adjustment.

### *2.4. Batch Experiments*

Biosorption of Cu(II) and Zn(II) from aqueous solutions was investigated in batch experiments. Effects of pH (3-8), kinetic experiments (0-180 min), effect of initial concentration of biosorbent (2-16 g/L) and temperature (293-323 K) on biosorption were studied.

The experiment conditions were modulated according to the requirement. All the biosorption experiments were carried out at 25°C, in which pH was maintained in a range of 4.5±0.1 units, biosorbent concentration was kept constant at 400 mg in 100 mL solution, initial Cu(II) and Zn(II) concentration was 100 mg/L, equilibrium time was kept as 3h, except stated otherwise.

After biosorption reached equilibrium, the solutions were then filtered to remove the biosorbent by a 0.45 µm filter (ALBET 400 B, 38-43 µm, EEC). The filtrate was determined for $Cu^{2+}$ and $Zn^{2+}$ concentration by using an Atomic Absorption Spectrophotometer.

The equilibrium metal uptake by the biosorbent and the percent of biosorption were calculated as follows [26]:

$$qe = \frac{(Co-Ceq)}{w} V \quad (1)$$

$$\text{percent of biosorption} = \frac{(Co-Ceq)}{Co} *100 \quad (2)$$

where, $q_e$ (mg/g) is the equilibrium metal uptake, $C_0$ and $C_e$ (mg/L) are the initial and equilibrium concentrations in solution of Cu(II) and Zn (II), w is the mass of the biosorbent (g) and V is the solution volume (L)

### *2.5. Biosorption Kinetics Models*

In order to analyse the biosorption kinetics of Cu(II) and Zn(II) ions, the pseudo-first order and pseudo-second order kinetic models were applied to data.

A simple pseudo-first order equation due to Lagergren was used by different researchers [27,28]:

$$\ln(q_e-q_t) = \ln(q_e)-K_1 t \quad (3)$$

where $q_e$ and $q_t$ are the amount of biosorption at equilibrium and at time t respectively, and $k_1$ (1/min)is the rate constant of the pseudo-first order biosorption process. Plot of ln ($q_e$-$q_t$) versus t gives a straight line for first order biosorption kinetics, which allows computation of the biosorption rate constant, $k_1$.

Ho's second-order rate equation which has been called pseudo-second order kinetic expression has also been applied widely [29,30]. The linear form of the kinetic rate equations can be written as follows:

$$\frac{1}{qt} = \left(\frac{1}{K_2 q_e^2}\right)\left(\frac{1}{t}\right) + \frac{1}{qe} \quad (4)$$

where $k_2$ is the rate constant of biosorption (g/mg min), $q_e$ the amount of metal ion biosorbed at equilibrium (mg/g), and $q_t$ is the amount of metal ion biosorbed at time t (mg/g). The constants can be determined experimentally by plotting of 1/qt against t.

### *2.6. Equilibrium Isotherms*

The experimental biosorption data were fitted according to the Langmuir and the Freundlich models, respectively.

#### *2.6.1. Langmuir Isotherm*

The Langmuir model assumes that the biosorbent surface has sites of identical energy and that each biosorbate molecule is located at a single site; hence, it predicts the formation of a monolayer of the biosorbate on the biosorbent surface [31].

The Langmuir isotherm model can be represented by the following equation [32]:

$$\frac{q_e}{q_m} = \frac{K_L C_e}{1 + K_L C_e} \quad (5)$$

Where $q_e$ and $C_e$ are the amount biosorbed (mg/g) and the biosorbate concentration in solution (mg/L), respectively, both at equilibrium. $K_L$ is the Langmuir constant (L/mg) and $q_m$ is the maximum biosorption capacity of the monolayer formed on the biosorbent (mg/g). It was observed that the Langmuir isotherm can be linearized into five different types and simple linear regression will result in different parameter estimates [33,34]:

$$\text{Linear Langmuir I} \quad \frac{1}{q_e} = \frac{1}{C_e}\frac{1}{q_m K_L} + \frac{1}{q_m} \quad (6)$$

$$\text{Linear Langmuir II} \quad \frac{C_e}{q_e} = C_e\frac{1}{q_m} + \frac{1}{q_m K_L} \quad (7)$$

$$\text{Linear Langmuir III} \quad q_e = -\frac{1}{K_L}\frac{q_e}{C_e} + q_m \quad (8)$$

$$\text{Linear Langmuir IV} \quad \frac{q_e}{C_e} = -K_L q_e + K_L q_m \quad (9)$$

$$\text{Linear Langmuir V} \quad \frac{1}{C_e} = K_L q_m \frac{1}{q_e} + K_L \quad (10)$$

To determine if biosorption process is favourable or unfavourable for the Langmuir type sorption process, the isotherm can be classified by the dimensionless constant separation factor (Hall parameter) $R_L$ [35]:

$$R_L = \frac{1}{1 + K_L C_O} \quad (11)$$

There are four probabilities for the $R_L$ value: for favorable biosorption, $0 < R_L < 1$; for unfavorable biosorption, $R_L > 1$; for linear biosorption, $R_L = 1$; for irreversible biosorption, RL = 0.

#### *2.6.2. Freundlich Isotherm*

The Freundlich isotherm is one of the most widely used isotherms for the description of biosorption equilibrium. This isotherm is an empirical equation employed to describe equilibrium on heterogeneous surfaces and hence does not assume monolayer capacity. Mathematically, it is expressed by [36]:

$$q_e = K C_e^{1/n} \quad (12)$$

Where $K_F$ ($mg^{1-n} L^n/g$ ) and n are the Freundlich isotherm constants indicating the biosorption capacity and biosorption intensity (unitless), respectively [37].

Eq.(12)can be expressed in linear form:

$$\log(q_e) = \log(K_F) + \left(1/n\right)\log(C_e) \quad (13)$$

### *2.7. Biosorption Thermodynamics*

Based on fundamental thermodynamic concept, it is assumed that in an isolated system, energy cannot be gained or lost and the entropy change is the only driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will occur spontaneously. The thermodynamic parameters change in Gibb's free energy (ΔG°), change in entropy (ΔS°) and change in enthalpy ΔH° for the biosorption of Cu(II) and Zn(II) over CLS has been determined by using the following equations [38-40]:

$$\Delta G = \Delta H - T\Delta S \quad (14)$$

$$K_d = \frac{q_e}{C_e} \quad (15)$$

$$\ln(K_d) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (16)$$

Where $q_e$ is the biosorption capacity of Cu(II) and Zn(II) per unit mass of CES (mg/g), $C_e$ is equilibrium concentration (mg/L) and T is temperature in (K). $K_d$ is called the Distribution coefficient. ΔS° and ΔH° are obtained from a plot of ln($K_d$) versus 1/T. Once these two parameters are obtained, ΔG° is determined from Eq. (14).

## 3. Results and Discussion

### *3.1. Characterization of CLS Biosorbent*

The chemical composition of CLS shows that CLS is rich in calcium (63.73%), which represents the main chemical species in the presence of other elements with small amounts, such as silicon (0.72%), magnesium (0.37%), phosphorus (0.26%) and traces of other elements such as iron, sodium,

chlorine, aluminum and cesium. The X-ray diffraction of our biosorbent is shown in Fig. 1. show a main peaks identified in the range 2θ = 25-50 are 2θ = 28.72, 29.43 °, 34.13, 36.03 °, 39.47 °, 48.55 ° and 50.85. These peaks are assigned to the plane of Miller following: (1 1 1), (2 0 0), (2 2 0), (3 1 1), (1 0 0), (2 2 2) and (2 0 2) respectively. These correspond to those of the calcite, syn and portlandite as deduced by comparison with the data file ICDD reference number structure. 84-1998.

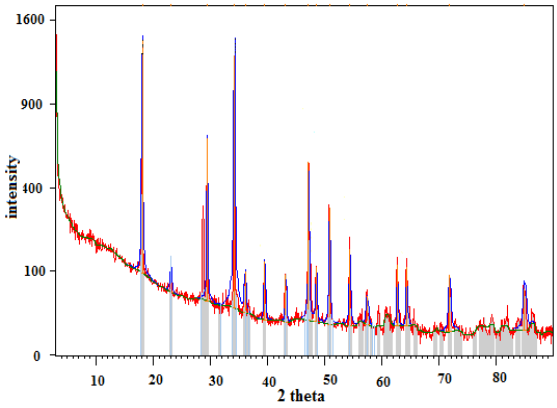


***Figure 1.*** *X-ray diffraction of CLS*

Analysis of FT-IR spectrum of CLS biosorbent is shown in Fig 2, spectral data indicate that the carbonate ion is present in CLS. The substitution of the carbonate ion is identified by characteristic peaks around υ3 = 1530 $cm^{-1}$ and υ3 = 1475 $cm^{-1}$, υ2 = 875 $cm^{-1}$ and υ4 = 725 $cm^{-1}$, wide band observed at about υ = 3480 $cm^{-1}$ indicates $H_2O$ adsorbed in the sample. The band around υ2 = 3650 $cm^{-1}$ is due to the OH group, the resulting frequency characteristics of $PO_4^{3-}$ mode are observed at about υ3 = 1100 $cm^{-1}$, υ3 = 1050 $cm^{-1}$ and υ4 = 550 $cm^{-1}$. The specific surface area of the CES calculated by the BET (Brunauer-Emmett-Teller) method is 63 $m^2/g$.

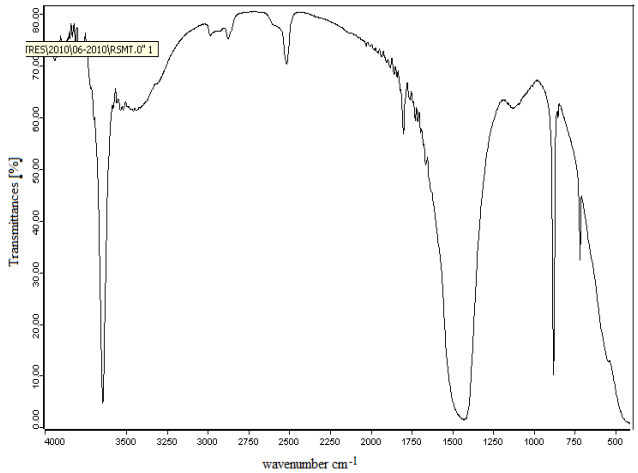


***Figure 2.*** *FT-IR spectra of CLS*

Scanning electron microscope has been widely used to study the morphological features of the biosorbent. Study of the SEM micrographs of CLS showed in Fig. 3 indicated that the biosorbent has a wide distribution of grains of different sizes.

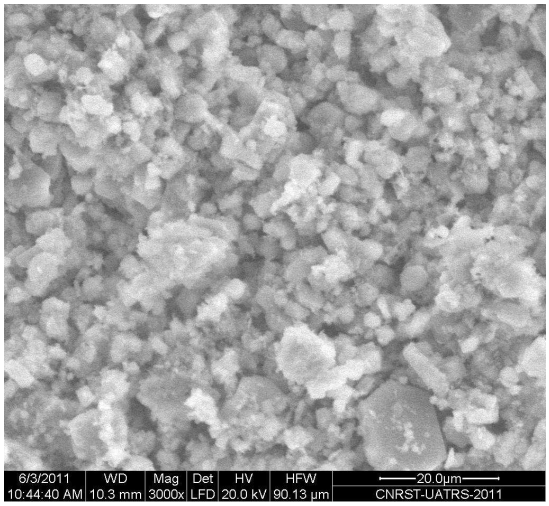


***Figure 3.*** *SEM photographs of CLS*

### *3.2. The pH Zero Point Charge Determination by Salt Addition Method*

The $pH_{zpc}$ of CES was determined by salt addition method as described by Chun and Muhammad [41,42], 100 mg of the sample was added to 95 ml of 0.01 M sodium chloride (NaCl) solution. The pH of the suspension was adjusted to 2.0-10.0 by adding HCl (1N) or NaOH (1N). The mixture was then kept in an end-to-end water shaker bath for 6 h at ambient temperature. The final pH value of each suspension was recorded after 6 h of equilibration by using a pH meter. The $pH_{zpc}$ of the sample was calculated by plotting ΔpH (final pH - initial pH) versus $pH_i$.

The value obtained at the intersection of the initial $pH_i$ with the ΔpH in Fig.4 gives the $pH_{zpc}$ of the suspended solid. From Fig.4 the $pH_{zpc}$ of CLS is found around 10.7.

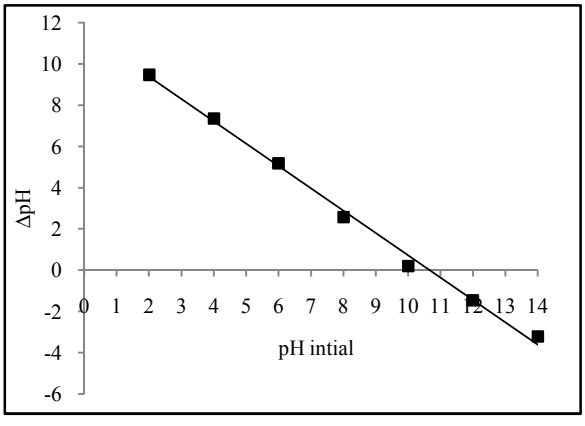


***Figure 4.*** *Determination of $pH_{ZPC}$ of the CLS*

### *3.3. Influence of pH*

It is well known that pH of the medium is most important factors that influence the biosorption process [43]. The pH level affects the network of negative charge on the surface of the biosorbent walls, as well as physicochemsitry and

hydrolysis of the metal. Therefore, preliminary experiments have been performed to find out the optimum pH for maximizing the metal removal. The amount removal of the metal ions as a function of pH is shown in Fig. 5. It has been observed that under highly acidic conditions (pH≈3.0) the amount of tow metals removal was very small, while the sorption had been increased with the increase in pH from 3.0 to 6.0 and is maintained in the range 6.0 and 8.0. The lower removal efficiency at low pH is apparently due to the presence of higher concentration of $H^+$ in the solution which compete Cu(II) and Zn(II) ions for the biosorption sites of the CLS. With increase in pH, the $H^+$ concentration decreases leading to increased Cu(II) and Zn(II) uptake.

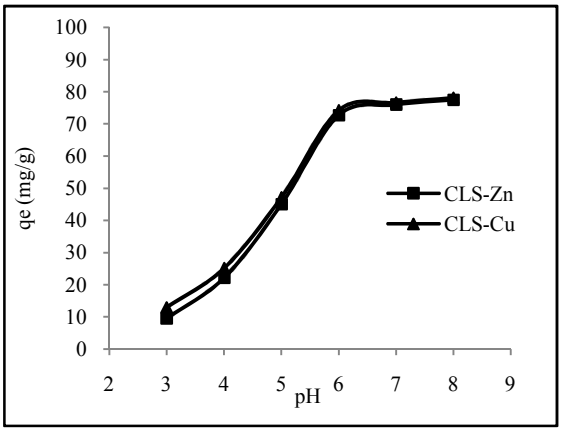


***Figure 5.*** *The effect of the pH on the biosorption of Cu(II) and Zn(II) on CLS*

On considering the point of zero charge of CLS another explanation for Cu(II) and Zn(II) has been provided. The pH of zero point of charge (ZPC) of biosorbent was determined. At pH below 10.7 (ZPC), the surface of CLS would positively charged due to protonation. This protonation effect was more pronounced at lower pH values due to the presence of higher concentration of $H^+$ ions in the solution which resulted in more unfavorable Cu(II) and Zn(II) ions biosorption. Increased of the amount biosorption at the alkaline pH (pH>6) was more to the precipitation in the form of hydroxide ions (Cu (OH) 2 and (Zn (OH) 2) or metal oxides (ZnO and CuO) that occur at alkaline pH [44-47].

Therefore, in the next stages of investigations, the optimal pH value was maintained at pH = 4.5. It should be mentioned that the precipitation of heavy metal ions was not observed.

### *3.4. Effect of Biosorption Time*

Fig. 6 illustrates the biosorption of Cu(II) and Zn(II) in the solution at T = 20°C and pH = 4.5 as a function of contact time. As shown in Fig. 6, the biosorption speed of Cu(II) and Zn (II) was rapid in the first 40 min, reached equilibrium after approximately 50 min, and remained constant for 1 h. About $q_e$ = 33.2 mg/g and 27 mg/g removal of Zn (II) and Cu(II) respectively were achieved within the first 40 min of contact, while only about $q_e$ = 2mg/g of additional removal occurred in the following biosorption time. It also can be found from Fig. 6 that the amount removable of Zn(II) is higher than Cu(II) at equilibrium time

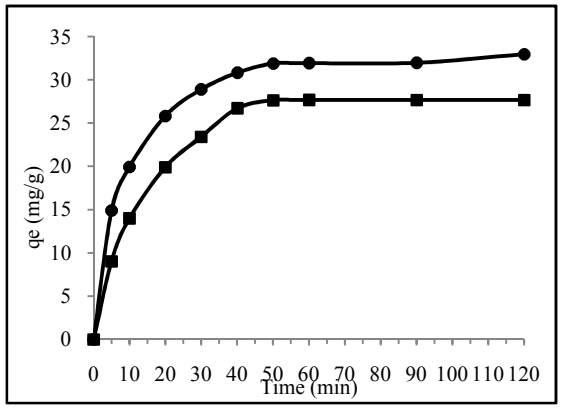


***Figure 6****. Effect the biosorption time of Cu(II) and Zn(II) on CLS*

### *3.5. Effect of Biosorbent Dose*

Biosorption of Cu(II) and Zn(II) onto CLS was studied by changing the quantity of sorbent from 2 to 16 g in the test solution while maintaining the initial concentration 100 mg/mL, pH = 4.5 and contact time 3h constant. Biosorption of Cu(II) and Zn(II) as a function of biomass shown in Fig. 7, indicates capacity decreases with the increase of biosorbent dose. However, the removal efficiency decreases from qe = 32mg/g and qe = 29 mg/g to qe = 12.5 mg/g and qe = 14 mg/g for Cu(II) and Zn(II) respectively, with the increase of the biosorbent dose. It is explained that the more the addition of biosorbent in the solution, the more the availability of active sites for the CLS.

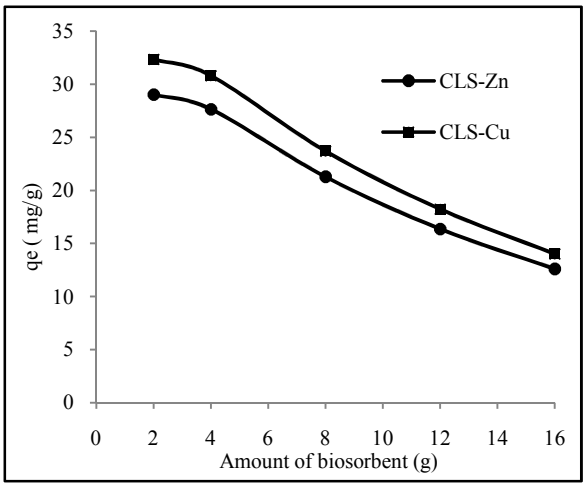


***Figure 7.*** *Effect of biosorbent dose on the biosorption of Cu(II) and Zn(II) by CLS*

### *3.6. Biosorption Kinetic Study*

The pseudo-first order model and the pseudo-second order model were used to analysis the experimental data of Cu(II) and Zn(II) biosorption by CLS.

#### *3.6.1. Pseudo-First-Order Kinetic Model*

Fig 8 show the plot of $\ln(q_e-q_t)$ vs t. The results are given

in Table 1.

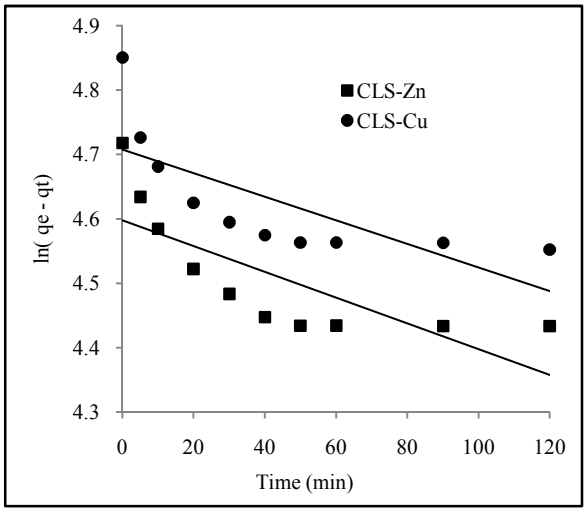


***Figure 8.*** *Pseudo first-order kinetic plots for Cu(II) and Zn(II) biosorption on CLS*

The theoretical values ($q_{e,cal}$) were far lower than those experimental data, $q_{e,exp}$ and low correlation coefficient values obtained for the pseudo first-order model indicate that concluded that the kinetics of Cu(II) and Zn(II) biosorption on CLS is not probably following the pseudo first order kinetic model.

### *3.6.2. Pseudo-Second-Order Kinetic Model*

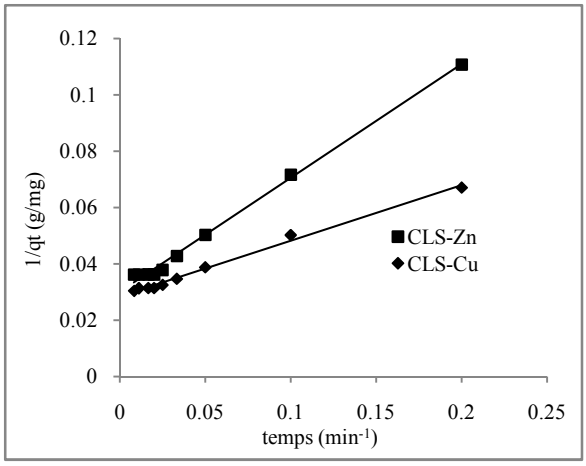


***Figure 9.*** *Pseudo second-order kinetic plots for Cu(II) and Zn(II) biosorption on CLS*

Fig. 9 shows that the plot of $t/q_t$ versus t is a straight line with slope of 1/qe and intercept $1/k_2q_e$. Using the value of $q_{e,cal}$ from the slope, the value of $k_2$ is determined from the intercept. The calculated value of $k_2$, $q_e$ and their corresponding regression coefficient ($R^2$) values are presented in Table 1.

From Table 1, the value of regression coefficient is nearly unity (0.99) for Cu(II) and Zn(II) ions biosorption on CES, which confirms that, the bisorption kinetics of Cu(II) and Zn(II) ions follows a pseudo-second-order process. It may also be found from Table 1 that the $q_{e,cal}$ values are very close to that of experimentally obtained $q_{e,exp}$. Thus, it may be concluded that the biosorption of Cu(II) and Zn(II) ions on CES can be better explained by pseudo-second-order kinetic model than that of first-order kinetic model.

### *3.7. Effect of Temperature*

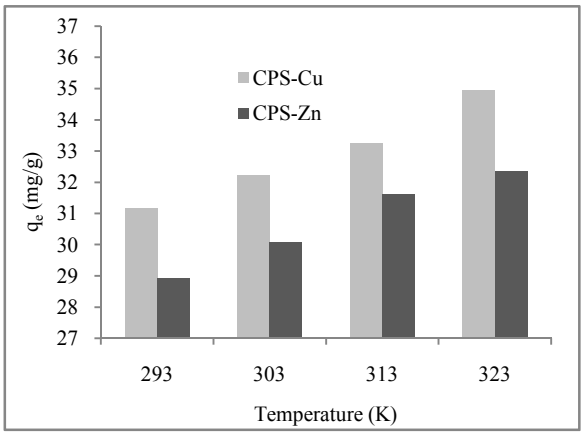


***Figure 10.*** *Effect of temperature on Cu(II) and Zn(II) removal by CLS*

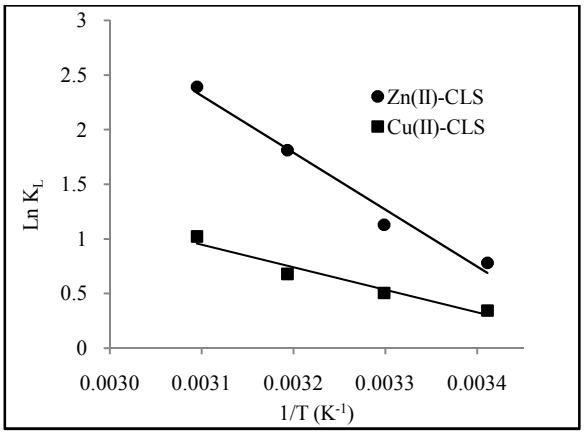


***Figure 11.*** *The plots of ln(Kd) vs. 1/T for Cu(II)-CLS and Zn(II)-CLS.*

The influence of temperature on biosorption of Cu(II) and Zn(II) on CES was studied and is shown in Fig. 10, It has been observed that with increase in temperature, biosorption capacity increases as shown in Fig. 10. This implies that for the initial dye concentration of each solution, the biosorption is endothermic in nature. Based on the obtained results the thermodynamic parameters for the sorption of Cu(II) and Zn(II) such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy(ΔS°) were determined. The values of ΔG° were calculated from Eq. (19). Reciprocal of temperature (1/T) was plotted against ln(k) and a straight line was obtained (figure 11). The values of ΔH° and ΔS° calculated from the slope and intercept of the straight line were summarized in Table2.

***Table 1.*** *Kinetics parameters for the biosorption of Cu(II) and Zn(II) onto CLS*

| | qe, exp (mg/g) | Pseudo-first-order model | | | Pseudo-second-order model | | |
|---|---|---|---|---|---|---|---|
| | | $k_1$ $10^2$ (1/min) | $q_{e,cal}$ (mg/g) | $R^2$ | $k_2$ $10^3$ (g/mg min) | $q_{e\ cal}$ (mg/g) | $R^2$ |
| CLS-Zn | 27.658 | 0.2 | 99.25 | 0.589 | 2.23 | 28.33 | 0.996 |
| CLS-Cu | 30.81 | 0.18 | 110.77 | 0.538 | 3.98 | 29.07 | 0.994 |

***Table 2.*** *Thermodynamic parameters for the biosorption of Cu(II) and Zn(II) onto CLS*

| T (K) | Cu(II) | | | Zn(II) | | |
|---|---|---|---|---|---|---|
| | H° (Kj/mol) | S° (j/mol.K) | G° (Kj/mol) | H° (Kj/mol) | S° (j/mol.K) | G° (Kj/mol) |
| 293 | 17.193 | 0.612 | -0.841 | 28.384 | 0.185 | -1.903 |
| 303 | | | -1.277 | | | -2.847 |
| 313 | | | -1.763 | | | -4.720 |
| 323 | | | -2.742 | | | -6.433 |

From Table 2, ΔG° varied from -0,841 to -2,742 KJ/mol and from -1,903 to -6,433 Kj/mol for the biosorption of Cu(II) and Zn(II) onto CLS, respectively. The negative values of ΔG° verifying that Cu(II) and Zn(II) biosorption were spontaneous and thermodynamically favourable. ΔG° decreased further with increase in temperature implies a greater driving force and more spontaneous adsorption at high temperature. by comparing the values of ΔG° between the biosorption of Cu(II) and Zn(II) show that the biosorption are more spontaneous and thermodynamically favorable for the biosorbtion of Zn ions metal. In addition, the positive values of ΔS° (0.612 and 0.185 j/mol.K for Cu(II) and Zn(II), respectively ) shows an affinity of biosorbent and the increasing randomness at the solid-solution interface during the biosorption of Cu(II) and Zn(II) on the CLS [48].

### *3.8. Biosorption Isotherm Modelling*

The successful representation of the dynamic biosorptive separation of solute from solution onto a biosorbent depends upon a good description of the equilibrium separation between the two phases. By plotting solid-phase concentration against residual liquid-phase concentration graphically it is possible to depict the equilibrium biosorption isotherm. In order to optimize the design of a sorption system to remove metals from aqueous solution, it is important to establish the most appropriate correlation for the equilibrium curve. There are many theories relating to biosorption equilibrium and among the used models are Freundlich and Langmuir. The mathematical equations of these models are illustrated in experimental paragraph and their associated parameters are given in Tables 3-4 for both linear and non-linear analysis. It can be seen that the $R_L$ values were in the range of 0-1, indicating that the bisorption of Cu(II) and Zn(II) ions onto CLS were favorable. The $q_m$ values from the Langmuir model could infer the potential maximum monolayer biosorption capacities of the biosorbent, which were 89 and 86 mg/g for Cu(II) and Zn (II), respectively.

***Table 3.*** *Isotherm parameters for the biosorption of Cu(II) on CLS*

| Models Langmuir | Parameters | | | |
|---|---|---|---|---|
| Form Linear Type 1 | $K_L$ = 0.080 L/mg | $q_m$ = 89.71 mg/g | $R_L$ = 0.112 | $R^2$ = 0.9891 |
| Form Linear Type 2 | $K_L$ = 0.082 L/mg | $q_m$ = 88.60 mg/g | $R_L$ = 0.122 | $R^2$ = 0.9780 |
| Form Linear Type 3 | $K_L$ = 0.088 L/mg | $q_m$ = 90.80 mg/g | $R_L$ = 0.114 | $R^2$ = 0.9367 |
| Form Linear Type 4 | $K_L$ = 0.083 L/mg | $q_m$ = 91.50 mg/g | $R_L$ = 0.121 | $R^2$ = 0.9376 |
| Form Linear Type 5 | $K_L$ = 0.087 L/mg | $q_m$ = 89.40 mg/g | $R_L$ = 0.115 | $R^2$ = 0.9891 |
| Form Non-Linear | $K_L$ =0.081±0.001 L/mg | $q_m$ = 90.93±3.95 mg/g | $R_L$ = 0.123 | $R^2$ = 0.9876 |
| Freundlich | | | | |
| Form Linear | $K_F$ = 9.36 $mg^{1-n}$ $L^n$ $g^{-1}$ | n = 0.5747 | | $R^2$ = 0.9821 |
| Form Non-Linear | $K_F$ = 10.43±1.58 $mg^{1-n}$ $L^n$ $g^{-1}$ | n = 0.573±0.031 | | $R^2$ = 0.9801 |

***Table.4.*** *Isotherm parameters for the biosorption of Zn(II) on CLS*

| Models Langmuir | Parameters | | | |
|---|---|---|---|---|
| Form Linear type 1 | $K_L$ = 0.064 L/mg | $q_m$ = 85.71 mg/g | $R_L$ = 0.136 | $R^2$ = 0.9881 |
| Form Linear type 2 | $K_L$ = 0.055 L/mg | $q_m$ = 86.50 mg/g | $R_L$ = 0.153 | $R^2$ = 0.9636 |
| Form Linear type 3 | $K_L$ = 0.061 L/mg | $q_m$ = 84.20 mg/g | $R_L$ = 0.140 | $R^2$ = 0.9134 |
| Form Linear type 4 | $K_L$ = 0.056 L/g | $q_m$ = 87.72 mg/g | $R_L$ = 0.151 | $R^2$ = 0.9145 |
| Form Linear type 5 | $K_L$ = 0.061 L/mg | $q_m$ = 85.11 mg/g | $R_L$ = 0.141 | $R^2$ = 0.9881 |
| Form Non - Linear | $K_L$ =0.053±0.001 L/mg | $q_m$ = 84.21±4.14 mg/g | $R_L$ = 0.157 | $R^2$ = 0.9831 |
| Freundlich | | | | |
| Form Linear | $K_F$ = 11.16 $mg^{1-n}$ $L^n$ $g^{-1}$ | n = 0.5921 | | $R^2$ = 0.9818 |
| Form Non - Linear | $K_F$ = 12.606±1.132 $mg^{1-n}$ $L^n$ $g^{-1}$ | n = 0.599±0.032 | | $R^2$ = 0.9801 |

#### *3.8.1. Linear Method*

The search for best-fit equation using the linear regression analysis was the most commonly used technique to determine the best-fit isotherm and the method of least squares has been used for finding the parameters of the isotherms. The tow isotherms, Langmuir and Freundlich and their corresponding linearized forms are studied. The calculated isotherm parameters were shown in Tables 3-4. From Tables 3-4, based on the $R^2$ values it was observed that the calculated isotherm parameters and their corresponding $R^2$ values varied for the five linearized types (types 1-5) of Langmuir isotherm and the linearized Freundlich isotherm. Types 1 and 5 forms of linearized Langmuir isotherm have same $R^2$ values, and showed a high $R^2$ values compared to the others linearized forms, followed by linearized Freundlich isotherms.

The present investigation suggests that the linear least squares method as a reasonable approach to determine the optimum isotherm and also for estimating the isotherm parameters. However, while comparing the $R^2$ values of the five types of linearized Langmuir isotherms with Freundlich isotherm alone will produce different outcomes. the higher $R^2$ value of type 1 or 5 Langmuir isotherm suggest that Langmuir isotherm was found to be the best-fitting isotherm followed Freundlich isotherm. The lower $R^2$ value of types 2,3 and 4 Langmuir isotherm suggest that the Freundlich isotherm is the best-fit isotherm followed by Langmuir isotherm for both systems CLS-Cu(II) and CLS-Zn(II). Two different outcomes were observed for the biosorption of Cu(II) and Zn(II) onto CLS. These different outcomes show the real complexities in estimating the isotherm parameters using the linearization technique. The different outcomes further suggest that the better fit of a set of experimental data in a particular isotherm model over another model alone is not sufficient to predict the sorption mechanism. The difference between the predicted and experimental equilibrium data by different linear expressions can be due to the problems with the transformation of non-linear to linear expression which will distort the experimental error and also the normality assumptions of the least squares method. Further linear method does not test whether the experimental data are linear. It assumes the experimental data were linear and predicts the slope and intercept that makes a straight line that predicts the best-fit of experimental equilibrium data. The linear method assumes that the scatter of points around the line follows a Gaussian distribution and the error distribution is the same at every value of X. But this is rarely true or practically impossible with equilibrium isotherm models (as most of the isotherm models are non-linear) as the error distribution gets altered after transforming the data to a linear form. The linear method just predicts the Y for the corresponding X. It considers only the error distribution along the Y-axis irrespective of the corresponding X-axis resulting in the different determined parameters (Tables 3-4) for the five different types of linearized Langmuir isotherms for the same experimental data. Thus, the experimental data were further fitted to the experimental equilibrium data of Cu(II) and Zn(II) onto CLS by non-linear method.

#### *3.8.2. Non-Linear Method*

The quality of the isotherm fit to the experimental data and hence the isotherm parameters obtained using linear regression are typically assessed based on the magnitude of the correlation coefficient for the regression, i.e. the isotherm with $R^2$ value nearer to unity is deemed to provide the best-fit. However, due to the inherent bias resulting from linearisation, non-linear regression was applied to determine alternative isotherm parameter sets.

For non-linear method, a trial and error procedure, which is applicable to computer operation, was used to determine the isotherm parameters by minimizing the respective the coefficient of determination between experimental data and isotherms using logiciel Satatistica version 10 (trial version). The calculated isotherm constants by non-linear method were shown in Tables 3-4. From Tables 3-4, based on the $R^2$ values it's clear that the form non-linear of Langmuir isotherm have a high $R^2$ values compared to form non-linear of Freundlich isotherms for both systems CLS-Cu(II) and CLS-Zn(II).

## 4. Conclusion

In this study, calcined limpet shells were selected as a local and cheaper biosorbent for the removal heavy metals from the aqueous solutions. biosorption of the Cu(II) and Zn(II) was studied by batch technique. Biosorption kinetics obeyed preferably the pseudo-second-order kinetics that provided the best correlation of the data. Thermodynamic parameters were also evaluated using equilibrium constants changing with temperature. The negative values of $\Delta G°$ indicated that the spontaneity and the positive values of $\Delta H°$ and $\Delta S°$ showed the endothermic nature and affinity of CLS for Cu(II) and Zn(II), respectively. The equilibrium biosorption of Cu(II) and Zn(II) by CLS was explained using the Freundlich and Langmuir isotherms.The present study shows non-linear regression method as a best way to obtain the isotherm parameters and also to select the optimum isotherm. The $R_L$ values showed that CLS was favourable for the biosorption of Cu(II) and Zn(II).

From the reported results, it would appear that CLS is a biosorbent offering greater wastewater treatment potential than other waste materials. However, further experiments with different heavy metals are now needed to fully investigate the potential of CLS waste in order to establish if it is an alternative to the other biosorbents.

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