Isothermal and Thermodynamic Studies of the Biosorption of Zinc(II) Ions by Calymperes erosum

N.A. Adesola Babarinde, O.O. Oyesiku, J. Oyebamiji Babalola and Janet O. Olatunji

Department of Chemical Sciences, Olabisi Onabanjo University, Ago-Iwoye, Nigeria.
Department of Plant Science and Applied Zoology, Olabisi Onabanjo University, Ago-Iwoye, Nigeria.
Department of Chemistry, University of Ibadan, Ibadan, Nigeria.

Abstract: Varying the parameters such as pH, contact time, initial metal ion concentration and temperature carried out the potential feasibility of Calymperes erosum for the removal of Zn(II). The residual Zn(II) in solution was determined using atomic absorption spectrophotometer (AAS). The study on pH shows that the biosorption is pH dependent. The optimum pH range for the biosorption is pH 2-7. The study shows that the biosorption is also time dependent. The maximum biosorption was obtained after 60min of the process. Equilibrium isotherms were analysed by Freundlich and Langmuir isotherms. The Freundlich equation obtained is \( \log \Gamma = 0.4522 \log \text{Ce} + 0.9283 \) while the Langmuir equation obtained is \( \frac{1}{\text{Ã}} = 0.0041/\text{Ce} + 0.0005 \). The correlation factors are 0.9997 and 0.9934, respectively. The changes in entropy (\( \Delta S^o \)) and the heat of biosorption (\( \Delta H^o \)) of Calymperes erosum were estimated as 78.6258 Jmol K\(^{-1}\) and 8.2466 kJ mol\(^{-1}\), respectively. The free energy change (\( \Delta G^o \)) obtained for the biosorption process at 27°C, initial Zn(II) concentration of 100mgL\(^{-1}\) and pH 7 is –26.99 kJmol\(^{-1}\). The high negative value of change in Gibbs free energy indicates the spontaneity and feasibility of the biosorption of Zn(II) by Calymperes erosum. These results indicate that Calymperes erosum has potential for the uptake of Zn(II) from industrial effluents.

Key words: Biosorption, Zn(II), Freundlich isotherm, Langmuir isotherm, Calymperes erosum

INTRODUCTION

The conventional processes such as precipitation, electrolysis and crystallization for treating effluents contaminated by heavy metals are expensive. They generate new products or transfer from one medium to another without propitiating the definite solution of the problem\(^{[1]}\). However, the search for inexpensive methods has led to the development of new technologies based on the utilization of biomasses of plant and animal origin, which serve as biosorbents for the removal of heavy metals from industrial effluents. Biosorption is the removal of heavy metal ions, radionuclides and dyes from aqueous solutions by biological materials\(^{[2]}\). Biosorption utilizes the ability of biological materials to accumulate heavy metals from waste streams by either metabolically mediated or purely physico-chemical pathways of uptake\(^{[3]}\). Microorganisms, including algae, bacteria, yeast, fungi, plant leaves have been used as biosorbents for detoxification and recovery of heavy metals from aqueous solutions\(^{[4,5]}\). Cell walls of organisms possess various mechanisms for metal biosorption such as complexation, coordination, chelation, ion exchange, inorganic precipitation and /or a combination of these\(^{[12]}\). The adsorption process is influenced by the nature of the adsorbate and its substituent groups\(^{[13]}\). It is believed that the predominant mechanism is the exchange of ions on the biomass. Anionic groups are responsible for the biosorption and chelation of a number of cations. Consequently, the cell walls of algae, cyanobacteria, fungi and bacteria have been studied extensively. The purpose of this work was to evaluate the biosorption capacity of the dried moss, Calymperes erosum, which is a nonvascular green plant that produces spores instead of seed, for removal of Zn(II) from aqueous solution.

MATERIALS AND METHODS

Preparation of Biomass: The plant (Calymperes erosum) used as the biosorbent was obtained on a palm tree trunk in dry form from a farm settlement in Apoje, Ogun State, Nigeria. It was kept in a dry place till the time of usage.

Corresponding Author: N.A. Adesola Babarinde, Department of Chemical Sciences, Olabisi Onabanjo University, Ago-Iwoye, Nigeria. E-mail: solababarinde@yahoo.com
Preparation of Metal Solution: The zinc salt used for this study was analytical grade of \( \text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \). Stock solution of 1000 mg L\(^{-1}\) of Zn\(^{2+}\) was prepared from the salt. The initial pH of each solution was adjusted to the desired pH by drop wise addition of 0.1M HNO\(_3\) and/or 0.1M NaOH solution. Fresh dilution of the stock solution was done for each biosorption study.

Biosorption Studies: Each of the batch biosorption studies was carried out by contacting 0.2g of the *Calymperes erosum* with 25ml of 100mgL\(^{-1}\) Zn(II) solution in a glass tube. The pH of each of the solutions had been adjusted to the desired value with concentrated HNO\(_3\) and/or concentration NaOH. Each tube was placed in a thermostated water bath and agitated at 27°C. The studies were conducted at pH values of 1-7. The glass tubes containing the mixture were maintained in the water bath for 24h. The biomass was removed from the solution after centrifuging. The residual Zn(II) concentration in the solution was analyzed using AAS. Each of the studies was conducted in triplicates and the mean value was determined for each pH. Subsequent biosorption studies were performed at pH 7.

Effect of pH on Biosorption: The effect of pH on the biosorption of Zn(II) was carried out within the range that would not be influenced by the metal precipitated\(^{[2]}\). It has been reported that the suitable pH ranges for the sorption of different metal ions were slightly different. Consequently, the suitable pH ranges for Cu(II), Cd(II), Zn(II) and Pb(II) should be 1 – 6, 1 – 8, 1 – 7 and 1 – 7.5, respectively. The procedure used is similar to those earlier reported\(^{[14,16]}\).

The study on the effect of initial solution pH on the biosorption of Zn(II) was carried out by contacting 0.2g of the *Calymperes erosum* with 25ml of 100mgL\(^{-1}\) Zn(II) solution in a glass tube.

The studies were conducted at pH 1-7. The glass tubes containing the mixture were left in the water bath for 24h. The biomass was removed from the solution after centrifuging. The residual Zn(II) concentration in the solution was analyzed. All studies were conducted in triplicates and the mean value was calculated for each pH. Subsequent biosorption experiments were performed at pH 7.

Effect of Contact Time on Biosorption: The biosorption of Zn(II) by *Calymperes erosum* plant was studied at various time intervals (5 – 300 min). A constant concentration of 100 mgL\(^{-1}\) was used. 0.2g of *Calymperes erosum* (biomass) was weighed into each glass tube and 25ml of Zn (II) solution at pH 7 was introduced into it.

Effect of Initial Zn(II) Concentration on Biosorption: Batch biosorption study was carried out using a concentration range of 10 – 100 mg L\(^{-1}\). 0.2g of the *Calymperes erosum* was introduced into each of the glass tube employed and 25ml of Zn(II) solution at pH 7 was added to the tubes. The biosorption mixture was then maintained in a thermostated water bath in order to maintain the temperature at 27°C for optimum contact time required to reach equilibrium time. The biosorbent was removed from the solution and the concentration of residual Zn(II) ion in each solution was determined.

Effect of Temperature on Biosorption: The biosorption of Zn(II) by *Calymperes erosum* was studied at temperatures of 21°C, 24°C, 27°C, 34°C and 37°C with a constant concentration of 100mg L\(^{-1}\) of the Zn (II) solution used. 0.2g of the *Calymperes erosum* was introduced into each of the glass tubes employed and 25ml of Zn(II) solution at pH 7 was added to the tubes. The biosorption mixture was then left in a thermostated water bath to maintain the temperature for optimum time. The biosorbent was removed from the solution by centrifuging and the concentration of residual Zn(II) ion in each solution was determined.

RESULTS AND DISCUSSIONS

Effect of Initial pH on the Biosorption: The pH of the solution is perhaps the most important parameter in the biosorption of Zn\(^{2+}\). The charge of the adsorbate and the adsorbent often depends on the pH of the solution\(^{[17]}\). To understand the adsorption mechanism, the biosorption of Zn\(^{2+}\) as a function of pH was measured and the result is shown Fig.1. It is observed that there was an increase in the biosorption capacity of the biomass with increase in pH from 1 to 2. As a result of net negative charge on the cell wall of the biosorbent above the isoelectric point the ionic state of the ligands such as carbonyl, phosphate and amino groups favours reaction with Zn\(^{2+}\). On the other hand, on decreasing pH, the net charge on the cell wall of the moss is positive thereby inhibiting the approach of positively charge ions\(^{[19]}\). As the pH increased, the ligands in *Calymperes erosum* would be exposed, increasing the attraction of metal ions with positive charge and allowing the biosorption on the cell wall surface. The result suggests that optimum biosorption is obtained from pH 2-7 and that initial pH would play a vital role in the removal of Zn\(^{2+}\) from aqueous solutions using *Calymperes erosum*.

Effect of Contact Time on Biosorption: The effect of contact time on the biosorption of Zn\(^{2+}\) by *Calymperes erosum* was studied and the result shown in Fig 2.
From Fig. 2, it is observed that the biosorption capacity of *Calymperes erosum* for Zn$^{2+}$ increased as the contact time increased. The biosorption process was rapid for the first 30 min and equilibrium was nearly reached in 60 min. Hence, in the present study, 60 min was chosen as the equilibrium time.

Biosorption of metal ions has been reported to be biphasic$^{[19]}$. The initial fast phase occurs due to surface adsorption on the biomass. The subsequent slow phase occurs due to diffusion of the metal ions into the inner part of the biomass. It is observed in Fig. 2 that the Zn$^{2+}$ biosorption rate was high at the beginning but plateau values were obtained in 60 min, similar to what was reported earlier$^{[19]}$.

**Effect of Initial Zn$^{2+}$ Concentration on Biosorption:** The effect of initial Zn$^{2+}$ concentration on the biosorption capacity is shown in Figs. 3 and 4.

The results obtained were analysed using both Freundlich$^{[20]}$ and Langmuir$^{[21]}$ isotherms. The Freundlich isotherm in linearised form is

$$\log \Gamma = \frac{1}{n} \log C_e + \log K$$  \hspace{1cm} (1)

Where $n$ and $K$ are Freundlich constants:

The linearised form of the Langmuir isotherm is

$$\frac{1}{\Gamma} = \frac{1}{b_m} C_e + \frac{1}{\Gamma_m}$$  \hspace{1cm} (2)

Where $b_m$ is a coefficient related to the affinity between the sorbent and sorbate, and $\Gamma_m$ is the maximum sorbate uptake under the given condition.
Table 1: Freundlich and Langmuir isotherm biosorption parameters for the biosorption of Zn (II) at 27°C and pH 7 using Calymperes erosum.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Freundlich parameters</th>
<th>Langmuir parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>2.21</td>
<td>2.21</td>
</tr>
<tr>
<td>K</td>
<td>8.48</td>
<td>246.91</td>
</tr>
<tr>
<td>R</td>
<td>0.9997</td>
<td>2222.22</td>
</tr>
<tr>
<td>S.D.</td>
<td>0.0048</td>
<td>0.9934</td>
</tr>
</tbody>
</table>

The data fitted well into both isotherms. The isothermal biosorption parameters for these isotherms are shown in Table 1. These Freundlich and Langmuir isothermal parameters compare well with those of other biosorbents that have been reported\(^1\). The Freundlich equation obtained is \( \log \Gamma = 0.4522 \log C_e + 0.9283 \) while the Langmuir equation obtained is \( \frac{1}{\Gamma} = 0.0041/C_e + 0.0005 \). The correlation factors are 0.9997 and 0.9934, respectively. The standard deviation values are 0.0048 and 0.0093, respectively. The values of the parameters show that *Calymperes erosum* is a good biosorbent for the uptake of Zn\(^{2+}\) from wastewaters. The removal efficiency of the biosorption process was equally determined using the same data as shown in Fig. 5. The removal efficiency of the Zn\(^{2+}\) was calculated as follows:

\[ \% \text{Removal} = 100 \left( \frac{C_i - C_e}{C_i} \right) \]  

Where \( C_i \) is initial metal ion concentration (mgL\(^{-1}\)), \( C_e \) the equilibrium metal ion concentration (mgL\(^{-1}\)).

The result shows that up to 100 % of the metal ions was biosorbed at the initial metal ion concentration of 20 mgL\(^{-1}\). The efficiency slightly decreased as the initial Zn\(^{2+}\) concentration increased. The slight decrease in the efficiency of the biomass shows nearness to saturation of the available binding sites on it.

**Thermodynamics of biosorption of Zn\(^{2+}\) by Calymperes Erosum:** In the present study, the biosorption experiments were carried out in the temperature range 21-37°C. Thermodynamic parameters were obtained by varying temperature conditions over the range 21-37°C by keeping other variables constant. The values of the thermodynamic parameters such as \( \Delta G^o \), \( \Delta H^o \) and \( \Delta S^o \), describing zinc uptake by *Calymperes erosum*, were calculated using the thermodynamic equations described below\(^2\)\(^2\)\(^2\). The biosorption process can be regarded as a heterogeneous and reversible process at equilibrium. The apparent equilibrium constant for the process has been shown\(^2\)\(^2\)\(^2\)\(^2\)\(^2\) to be

\[ K_e = \frac{C_a}{C_c} \]  

The change in Gibbs free energy of the biosorption process is thus given as

\[ \Delta G^o = -RT \ln K_e \]  

The free energy change in the biosorption of Zn\(^{2+}\) using *Calymperes erosum* at 27°C, pH 7 and initial Zn\(^{2+}\) concentration of 100 mg L\(^{-1}\).

\[ \Delta G = -\Delta S^o (T) + \Delta H^o \]  

A plot of \( T \) against \( \Delta G^o \) gives a straight line with slope \( -\Delta S^o \) and an intercept of \( \Delta H^o \).
In Fig. 6, the slope is -78.6258 J mol\(^{-1}\)K\(^{-1}\) while the intercept is 8.2466 kJ mol\(^{-1}\). Therefore, the values of the entropy and enthalpy are 78.6258 J mol\(^{-1}\)K\(^{-1}\) and 8.2466 kJ mol\(^{-1}\), respectively. The decrease in the value of the free energy with increase in temperature indicates that the biosorption process is endothermic and it is thereby favoured with increase in temperature. It is observed in Fig. 6 that the free energy values decrease with increase in temperature. This implies that the spontaneity of the biosorption process increased with increase in temperature. The free energy change \((\Delta G^{0})\) obtained for the biosorption of Zn\(^{2+}\) at 310K, initial Zn\(^{2+}\) concentration of 100mg L\(^{-1}\) and pH 7 is -16.141 kJ mol\(^{-1}\). The large negative value of \(\Delta G^{0}\) obtained for the biosorption of Zn\(^{2+}\) shows spontaneity of the biosorption process at that temperature.

The large positive value of \(\Delta S^{0}\) (78.6258 J mol\(^{-1}\)K\(^{-1}\)) suggested the increase in randomness at the solid/solution interphase during the biosorption of Zn(II) on the moss. The value of \(\Delta S^{0}\) obtained in this study is more than twice the value obtained for the adsorption of 2,4-dichlorophenol by palm pitch carbon\(^{[25]}\).

**Conclusions:** A suitable indigenous dried moss has been identified as an effective biosorbent to remove Zn(II) ions from aqueous solution. The adsorption capacity is related to the pH of solution, and pH 5-7 is optimal. The biosorption of Zn(II) was found to be time dependent and optimum time for the uptake was 60 min. Furthermore, the equilibrium data of adsorption are in good agreement with the models of Freundlich and Langmuir. The large negative value of change in free energy obtained for the biosorption of Zn\(^{2+}\) shows spontaneity of the biosorption process at that temperature. The large positive value of the change in entropy suggested the increase in randomness at the solid/solution interphase during the biosorption of Zn(II) on the moss. The dried moss, *Calymperes erosum*, is an inexpensive effective biosorbent for the removal of Zn(II) from aqueous solution. The process is environment friendly and reduces the huge amount of indiscriminate effluent discharges around the industry concerned in the treatment of industrial wastewater containing Zn (II).

**ACKNOWLEDGEMENT**

The authors are grateful for the technical assistance rendered by Mr J. Adegoke of the Department of Chemical Sciences, Olabisi Onabanjo University, Ago-Iwoye, Nigeria.

**REFERENCES**


