EVALUATION ON THE Zn$^{2+}$ ION ADSORPTION CAPACITY IN WATER OF SPIRULINA PLATENSIS BIOMATERIAL

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SUMMARY

Due to its rising accumulation in the food chain and ongoing presence in ecosystems, metal contamination has piqued the curiosity of experts from all over the world. Environmentally hazardous metal removal is being pursued utilizing a variety of techniques, such as ion exchange and precipitation, as well as chemical oxidation or reduction, electrochemistry, and filtration. However, these methods require high investment and operating costs, and generate toxic sludge. Spirulina platensis, a filamentous cyanobacteria species, has been reported as a potential bioadsorbent for the removal of some heavy metals from industrial wastewater. In this study, the bioadsorption of Zn$^{2+}$ ions in an assumed aqueous solution by the dry biomass of S. platensis TH was investigated. The Zn$^{2+}$ ion adsorption of biomaterials was evaluated under different conditions, including pH, contact time, temperature, and adsorbent mass. The optimal Zn$^{2+}$ ion removal efficiency reached 90.32 ± 0.29% at Zn$^{2+}$ ion concentration of 100 mg/L, pH 5.0, a temperature of 26°C, and a dry biomass dose of 1.5 g/L for 90 min. Langmuir and Freundlich's isothermal models were used to describe the adsorption isotherm of Zn$^{2+}$ ions on S. platensis TH. Equilibrium data fitted well with the Langmuir model as well as the Freundlich model, with a maximum adsorption capacity of 34.56 mg Zn$^{2+}$/g S. platensis TH under the reaction conditions of 1.5 g/L biomass dosage, the contact time of 90 min, pH 5.0, at 26°C. Research results have shown that S. platensis TH biomass is an easy, readily available, low-cost adsorbent and has a high bioadsorption capacity. Therefore, it can be treated as a biosorbent in the treatment of wastewater containing Zn$^{2+}$ ions. This process is not only environmentally friendly but also versatile as an alternative to conventional heavy metal treatment methods.

Keywords: Adsorption, biomass, biosorbent, Spirulina platensis, zinc.

INTRODUCTION

Metal pollution has caught the attention of scientists worldwide due to its increasing accumulation in food chains and persistence in ecosystems (Ahluwalia, Goyal, 2007). Zinc plays an important role in a number of biological processes in organisms. However, an excess of
zinc in water can cause stress, alter DNA, and/or even impair the growth and reproduction of organisms (Zmicovicova et al., 2015). Therefore, the presence of zinc ions in particular and metal ions in general in wastewater is a threat to humans and organisms (Finocchio et al., 2010).

Zinc is commonly found in wastewater from the galvanizing, electroplating, and alloy manufacturing industries, acid mine drainage, natural ores, and wastewater treatment plants (Palaniswamy, Veluchamy, 2017). At present, there are many heavy metal treatment methods such as ion exchange, precipitation, chemical oxidation or reduction, electrochemistry, and filtration. However, these methods require high investment and operating costs. In addition, the generation of toxic sludge adds a burden to the economic feasibility of the treatment processes (Ahluwalia, Goyal, 2007). Biosorption is a cost-effective alternative to conventional methods, based on a favorable combination of features such as reducing chemicals, low operating costs, and being effective with low pollution. Moreover, this approach can help recover metals and regenerate used materials (Monteiro, Castro, 2012). Microbial biomass has been used as a biosorbent and has been shown to be very efficient in removing heavy metals from wastewater due to its large surface area and high binding affinity (Monteiro, Castro, 2012). The cell surface of microorganisms carries a negative charge due to the presence of functional groups such as hydroxides, carboxylic acids, phosphates, etc., which have a high binding affinity for metal cations (Bai, Abraham, 2012). Studies using microalgae and cyanobacteria such as Chlorella vulgaris, Aphanothece halophytica, Scenedesmus Obliquus, Spirulina platensis, etc as biomaterials adsorbing heavy metals in water showed the potential for the application of inexpensive biomaterials in industrial wastewater treatment (Incharoensakdi, Kitjaharn, 2002; Lee et al., 2009; Linchuan et al., 2011; Monteiro, Castro, 2012).

In this study, the dry biomass of S. platensis TH was used as an adsorbent for Zn$^{2+}$ ion removal. The effects of the adsorption reaction parameters such as pH, contact time, temperature, biomass dose, and initial metal concentration on the biological material adsorption capacity were investigated. The relationship between the quantity of Zn$^{2+}$ adsorbed by a unit weight of adsorbent and the remaining amount of adsorbate in the solution at equilibrium is described by using adsorption isotherm models. The adsorption isotherms of the Freundlich and Langmuir models for the adsorption of Zn$^{2+}$ ions onto the dry biomass of S. platensis TH were studied.

MATERIALS AND METHODS

Materials

The cyanobacteria strain S. platensis TH was provided by the Department of Environmental Hydrobiology, Institute of Environmental Technology, Vietnam Academy of Science and Technology. The biomass of S. platensis TH was used for biosorption studies. The solution containing Zn$^{2+}$ ions was prepared from ZnSO$_4$.7H$_2$O salt (Merck, Germany).

Methods

S. platensis TH was grown in the standard Zarrouk medium for biomass production. The standard Zarrouk liquid medium (Zarrouk et al., 1966) contains: 16.8 g/L NaHCO$_3$, 0.5 g/L K$_2$HPO$_4$, 2.5 g/L NaNO$_3$, 1.0 g/L K$_2$SO$_4$, 1.0 g/L NaCl, 0.2 g/L MgSO$_4$.7 H$_2$O, 0.04 g/L CaCl$_2$.2H$_2$O, and 1 mL trace elements solution A: 28.46 g/L FeSO$_4$. 30.2 g/L Na$_2$EDTA, and 1 mL trace elements solution B: 0.023 g/L NH$_4$VO$_3$, 0.096 g/L KCr(SO$_4$)$_2$.12H$_2$O, 0.0478 g/L NiSO$_4$.6H$_2$O, 0.0178 g/L Na$_2$WO$_4$.2H$_2$O, 0.04 g/L Ti$_2$(SO$_4$)$_3$, 0.044 g/L Co(NO$_3$)$_2$.6H$_2$O, and 1 mL trace elements solution C: 2.86 g/L H$_2$BO$_3$, 1.81 g/L MnCl$_2$.4H$_2$O, 0.222 g/L ZnSO$_4$.7H$_2$O, 0.39 g/L Na$_2$MoO$_4$.2H$_2$O, 0.079 g/L CuSO$_4$.5H$_2$O. The cyanobacterial suspension was then employed as an inoculant in the following stage, which was the formation of cyanobacterial biomass in a laboratory-scale photobioreactor (PBR) system containing domestic wastewater. The PBR system was comprised of one bubble bioreactor with a
working volume of 8 L of domestic wastewater and 8.4 g/L NaHCO₃. Domestic wastewater is settled, filtered, and autoclaved before entering the photobioreactor. *S. platensis* TH was batch cultivated under 30°C, pH 9, with a light intensity of 5000 lux, a light-dark cycle of 12:12, and aeration for 8 h/day by an aquarium pump for 20 days. The biomass was dried and processed into an adsorbent according to Al-Homaidan's process (Al-Homaidan, 2015). To evaluate the Zn²⁺ ion adsorption capacity of the *S. platensis* TH material, experiments on the influence of parameters such as pH, contact time, temperature, biomass dosage, and metal concentrations were performed.

The effect of pH on Zn²⁺ ion adsorption was carried out by adding 1 g/L of cyanobacteria biomass to a medium containing Zn²⁺ ions (100 mg/L) with a pH varying between 2 and 8. The initial solution was adjusted to the desired pH by the addition of diluted or concentrated HNO₃ and NaOH solutions before adding the biosorbent. To determine adsorption equilibrium, the contact times (10, 15, 20, 30, 40, 60, 90, and 120 min) were performed at optimum pH conditions. All of the above experiments were performed at 20 °C (Hannachi et al., 2013), except for the temperature effect studies at 20, 26, 37, and 46 °C, respectively. The effect of the biosorbent material amount was carried out with dosages of 0.25, 0.5, 0.75, 1, 1.5, and 2 g/L (Sun et al., 2019). To investigate the biosorption equilibrium, kinetic experiments were performed at pH 5 with the contact time of 90 min at 26°C, material weight of 1.5 g/L and various Zn²⁺ ion concentrations (20, 40, 60, 80, 100, 120, 140, 160, 180, and 200 mg/L) (Al-Homaidan et al., 2015). All experiments were repeated 3 times with the working volume of 250 mL (Rajiv et al., 2010). The initial and remaining concentrations of Zn²⁺ ions at the end of the adsorption process were determined by the AAS atomic absorption spectrometer (Thermo-UK).

The adsorption capacity formula:

\[ q = \frac{(C_i - C_f)V}{m} \quad (1) \]

Where: \( q \) is the equilibrium adsorption capacity (mg/g); \( C_i \) is the initial solution concentration (mg/L); \( C_f \) is solution concentration when reaching adsorption equilibrium (mg/L); \( V \) is the volume of adsorbent solution (L); \( m \) is the mass of biosorbent (g).

**Adsorption efficiency (H, %):**

\[ H = \frac{C_i - C_f}{C_i} \times 100 \quad (2) \]

Investigate the parameters of the adsorption isotherm equation according to the Langmuir and Freundlich adsorption isotherm models.

**The Langmuir equation:**

\[ q = q_m \cdot \frac{K_L \cdot C}{1 + K_L \cdot C} \quad (3) \]

Where: \( q \) is the equilibrium adsorption load (mg/g); \( q_m \) is the maximum adsorption load (mg/g); \( K_L \) is the Langmuir adsorption (equilibrium) constant; \( C \) is the adsorbent solution concentration.

From the \( K_L \) value, it is possible to determine the equilibrium parameter \( R_L \):

\[ R_L = \frac{1}{1 + K_L \cdot C_o} \quad (4) \]

Where: \( 0 < R_L < 1 \) indicates that the adsorption follows the Langmuir isotherm adsorption model.

**Freundlich’s equation:**

\[ log q_e = log k_f + \frac{1}{n} log C_e \quad (5) \]

Where: \( k_f \) is the Freundlich adsorption constant and \( n \) is an experimental parameter.

**RESULTS AND DISCUSSION**

**Effect of pH on the Zn²⁺ ion adsorption of *S. platensis* TH**

The pH of the biosorption process is an essential factor for the adsorption of metal ions, as it affects the solubility of the metal or the degree of dissociation of functional groups.
located on the surface of the adsorbent. In this study, the pH values varied from 2 to 8. The Zn$^{2+}$ ion adsorption capacity of the $S. $platensis TH material is shown in figure 1.

The results demonstrated that the removal efficiency of Zn$^{2+}$ ions was lowest at pH 2 (about 11.66 ± 1.13%). The poor adsorption might be due to competitive adsorption between hydrogen ions, hydronium ions, and Zn$^{2+}$ ions for the active sites on the biomass surface at low pH (Norton et al., 2004). When the pH increased from 2 to 5, the Zn$^{2+}$ ion adsorption capacity augmented from about 2.92 ± 0.28 mg/g to 7.95 ± 0.01 mg/g. The effect of pH on adsorption efficiency could be explained by the relationship between surface functional groups and metal ions in the aqueous solution. When the initial pH is increased, the negative charge on the surface of the bioadsorbent also increases. The bioadsorbent surface becomes more negatively charged and the adsorption of Zn$^{2+}$ ions increases, reaching equilibrium at pH 5 and 6 (Devlina Das et al., 2012).

No difference was detected in the bioadsorption of Zn$^{2+}$ ions (range 7.77 ± 0.03 – 7.95 ± 0.01 mg/g) when increasing the pH from 5 to 8, corresponding to the removal efficiency of about 30–32%. Several investigations have indicated that at pH levels over 7, the phenomena of hydroxide precipitation will take place, and pH tests are most trustworthy when this phenomenon does not occur (Monteiro, Castro, 2012). Some research also revealed that the optimal pH for Zn$^{2+}$ adsorption by dry biomass of $S. $platensis, Chlorella vulgaris, and Gracilaria verrucosa was in the range of 5.0 to 6.0 (Hannachi et al., 2013; Ferreira et al., 2011). Therefore, pH 5.0 was selected in subsequent studies.

![Figure 1](image)

**Figure 1.** Effect of pH on the adsorption of Zn$^{2+}$ ions of $S. $platensis TH biomass.

**Effect of contact time on the Zn$^{2+}$ ion adsorption of $S. $platensis TH**

The obtained results in figure 2 indicated that the Zn$^{2+}$ ion adsorption capacity of the material increases with the increase of contact time in this study.

The material adsorption effectiveness was relatively low in experiments with contact times of 10 min, 15 min, and 20 min, with only 1.90 ± 0.95%; 5.32 ± 0.65% and 17.64 ± 1.12%, respectively. When the contact duration was prolonged to 60 min, the adsorption efficiency improved to 43.67 ± 0.32% and achieved the adsorption saturation state at the contact time of 90 min. At the
saturation time, the Zn$^{2+}$ ion maximum removal efficiency of the adsorbent was 45.30 ± 0.50%. Kumar et al. (2006) demonstrated that in the early stage, there are many vacancies (adsorption centers) on the surface of the material that have not been occupied, so the adsorption process usually occurs faster than in the later stage, when metal ions are unlikely to contact the remaining voids on the surface of the material or penetrate deeply into the cell membrane. According to these findings, the interaction duration between the Zn$^{2+}$ ions and the S. platensis TH bioadsorbent could not exceed 90 min.

![Figure 2](image_url). Effect of contact time on the adsorption of Zn$^{2+}$ ions of S. platensis TH biomass.

![Figure 3](image_url). Effect of temperature on the adsorption of Zn$^{2+}$ ions of S. platensis TH biomass.
Effect of temperature on the Zn²⁺ ion adsorption of *S. platensis* TH

Temperature is a vital parameter in the adsorption process. The findings of this investigation revealed that temperature variation impacted Zn²⁺ ion adsorption from the aqueous solution of *S. platensis* TH biomass. The adsorption of Zn²⁺ ions in the solution of *S. platensis* TH adsorbent increased as the temperature was raised from 20 to 26°C.

Experiment results demonstrated that a temperature of 26°C is optimal for greatest Zn²⁺ adsorption into the dry biomass of *S. platensis* TH, with 12.90 ± 0.29 mg/g corresponding to the treatment efficiency of 51.59 ± 1.17% (Figure 3). On the other hand, the biosorption percentage declined from 51.59 ± 1.17% to 14.57 ± 0.65% as temperature was increased from 20 to 46°C. The reduction of Zn²⁺ ion biosorption with increasing temperature might be attributable to either damage to active binding sites in the biomass (Hannachi *et al.*, 2013). Sari *et al.* (2007) hypothesized that when temperature rises, the adsorption of metal ions in the material reduces, presumably due to the desorption of metal on the material's surface into solution. These results suggest that the electrostatic force between the metal ions and the active binding sites could be weakened by the elevated temperature.

Effect of biomass dosage on the Zn²⁺ ion adsorption of *S. platensis* TH

The dose of adsorbent in the solution has a significant impact on the metal adsorption process. Figure 4 illustrates the relationship between the biomass weight of *S. platensis* TH and the treatment effectiveness of Zn²⁺ ion.

![Figure 4. Effect of *S. platensis* TH biomass dosage on the Zn²⁺ ions adsorption.](image)

Figure 4 depicted the influence of bioadsorbent concentration on Zn²⁺ ion removal efficiency from solutions. The results revealed that the proportion of Zn²⁺ ions eliminated increased with adsorbent mass. As a result, as biosorbert concentrations increased from 0.25 to 1.5 g/L, the removal efficiency of Zn²⁺ ions from a solution with an initial concentration of 100 mg/L rose from 5.96 to 90.32%. This increase may be due to an increase in the total surface area of the biosorbert, thereby increasing the number of available binding sites (Al-Homaidan *et al.*, 2015). There was no significant difference in Zn²⁺ ion removal as the adsorbent mass increased from 1.5 to 3 g/L (90.32–93.45%). In the study using a material weight of 1.5 g/L, the highest Zn²⁺ ion adsorption capacity was 15.05 ± 0.05 mg/g, corresponding to a treatment efficiency of
90.32 ± 0.29%. After this dosage, the adsorption efficiency was reduced due to partial aggregation of the biomass at higher concentrations, which resulted in a decrease in the effective surface area for adsorption (Palaniswamy, Veluchamy, 2017). Therefore, the optimal biomass concentration of 1.5 g/L was selected for the subsequent experiments.

**Biological adsorption isotherm**

To optimize the design of the bioadsorption process, it is necessary to obtain the appropriate correlation for the equilibrium curve. In this study, Zn$^{2+}$ ion adsorption isotherm data on S. platensis TH bioadsorbent was evaluated by the Langmuir and Freundlich models (Figure 5). The correlation coefficient ($R^2 = 0.9901$) in figure 5A and Table 1 showed that the bioadsorption of Zn$^{2+}$ ions into the S. platensis TH biomass is consistent with the Langmuir model, indicating the formation of a monolayer of the heavy metal ions on the surface of the bioadsorbent. The obtained maximum bioadsorption capacity ($q_m$) was 35.46 mg/g. Figure 5B and Table 1 displayed that the values of $k_f$ and $1/n$ are 1.83 and 0.59, respectively. Values of $1/n$ ranging from 0 to 1 implied that the bioadsorption of Zn$^{2+}$ ions into S. platensis TH biomass was favorable under the studied conditions. However, compared with the $R^2$ value of 0.9901 achieved from the Langmuir model, it could be significantly noted that the Langmuir isotherm model fits the equilibrium data.

**Figure 5.** Langmuir (a) and Freundlich (b) isotherm plots for Zn$^{2+}$ ion bioadsorption on S. platensis TH (mass of biomass material: 1.5 g/L; contact time: 90 min.; pH: 5; temperature: 26°C).

**Table 1.** Isotherm parameters for the Zn$^{2+}$ ion bioadsorption on S. platensis TH dry biomass.

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<th>Freundlich model</th>
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**CONCLUSION**

The potential of the cyanobacteria S. platensis TH to remove Zn$^{2+}$ ions from aqueous solution depends on the bioadsorption process such as pH, contact time, temperature, and material mass. The Langmuir bioadsorption isotherm was shown to provide the best correlation for the bioabsorption of Zn$^{2+}$ ions on S. platensis TH material. The maximum adsorption capacity was 35.46 mg Zn$^{2+}$/g S. platensis TH in the reaction conditions of 1.5 g/L.
material for 90 min at pH 5.0 and 26°C. Results have revealed that S. platensis TH biomass is an easy, readily available, low-cost adsorbent and has a high biosorption capacity. Therefore, it could be used as a biosorbent in the treatment of wastewater containing Zn\(^{2+}\) ions.

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**REFERENCES**


