Vietnam Journal of Biotechnology **20**(3): 565-572, 2022

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

Hoang Thi Quynh[1,2], Duong Thi Thuy[1,2], Doan Thi Oanh[3,✉], Nguyen Thi Nhu Huong[1], Le Phuong Thu[4], Nguyen Mai Lan[3], Bui Nguyen Minh Thu[4], Nguyen Duc Dien[5]

[1]*Institute of Environmental Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Road, Cau Giay District, Hanoi, Vietnam*
[2]*Graduate University of Science and Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Road, Cau Giay District, Hanoi, Vietnam*
[3]*Hanoi University of Natural Resources and Environment, 41A Phu Dien Road, Bac Tu Liem District, Hanoi, Vietnam*
[4]*University of Science and Technology Hanoi, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Road, Cau Giay District, Hanoi, Vietnam*
[5]*Vinh University, 182 Le Duan Road, Vinh City, Nghe An Province, Vietnam*

✉To whom correspondence should be addressed. E-mail: doanoanh158@gmail.com

Received: 05.10.2021
Accepted: 11.01.2022

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 heavy 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 26ºC, 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 26ºC. 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 bioadsorbent 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 (Zinicovscaia *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). Bioadsorption 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 bioadsorbent 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 Obquus, 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 bioadsorption studies. The solution containing Zn^{2+} ions was prepared from $ZnSO_4.7H_2O$ 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_2HPO_4, 2.5 g/L $NaNO_3$, 1.0 g/L K_2SO_4, 1.0 g/L NaCl, 0.2 g/L $MgSO_4.7\ H_2O$, 0.04 g/L $CaCl_2.2H_2O$, and 1 mL trace elements solution A: 28.46 g/L $FeSO_4$, 30.2 g/L Na_2EDTA, and 1 mL trace elements solution B: 0.023 g/L NH_4VO_3, 0.096 g/L $KCr(SO_4)_2.12H_2O$, 0.0478 g/L $NiSO_4.6H_2O$, 0.0178 g/L $Na_2WO_4.2H_2O$, 0.04 g/L $Ti_2(SO_4)_3$, 0.044 g/L $Co(NO_3)_2.6H_2O$, and 1 mL trace elements solution C: 2.86 g/L H_3BO_3, 1.81 g/L $MnCl_2\ 4H_2O$, 0.222 g/L $ZnSO_4\ 7H_2O$, 0.39 g/L $Na_2MoO_4\ 2H_2O$, 0.079 g/L $CuSO_4\ 5H_2O$. 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 $NaHCO_3$. Domestic wastewater is settled, filtered, and autoclaved before entering the photobioreactor. *S. platensis* TH was batch cultivated under 30ºC, pH 9, with a light intensity of 5000 lux, a light-dark cycle of 12:12, and aerated 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 Zn^{2+} 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 Zn^{2+} ion adsorption was carried out by adding 1 g/L of cyanobacteria biomass to a medium containing Zn^{2+} 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 HNO_3 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 bioadsorbent 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 26ºC, material weight of 1.5 g/L and various Zn^{2+} 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 Zn^{2+} ions at the end of the adsorption process were determined by the AAS atomic absorption spectrometer (Thermo-UK).

The adsorption capacity formula*:*

$$q = \frac{(C_i - C_f).V}{m} \tag{1}$$

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 bioadsorbent (g).

Adsorption efficiency (H, %):

$$H = \frac{C_i - C_f}{C_i.100} \tag{2}$$

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

The Langmuir equation:

$$q = q_m.\frac{K_L.C}{1+K_L.C} \tag{3}$$

Where: q is the equilibrium adsorption load (mg/g); q_m is the maximum adsorption load (mg/g); K 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:

$$R_L = \frac{1}{1+K_L.C_o} \tag{4}$$

Where: $0 < R_L < 1$ indicates that the adsorption follows the Langmuir isotherm adsorption model.

Freundlich's equation:

$$log q_e = log k_f + \frac{1}{n}\, log C_e \tag{5}$$

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

RESULTS AND DISCUSSION

Effect of pH on the Zn^{2+} 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.

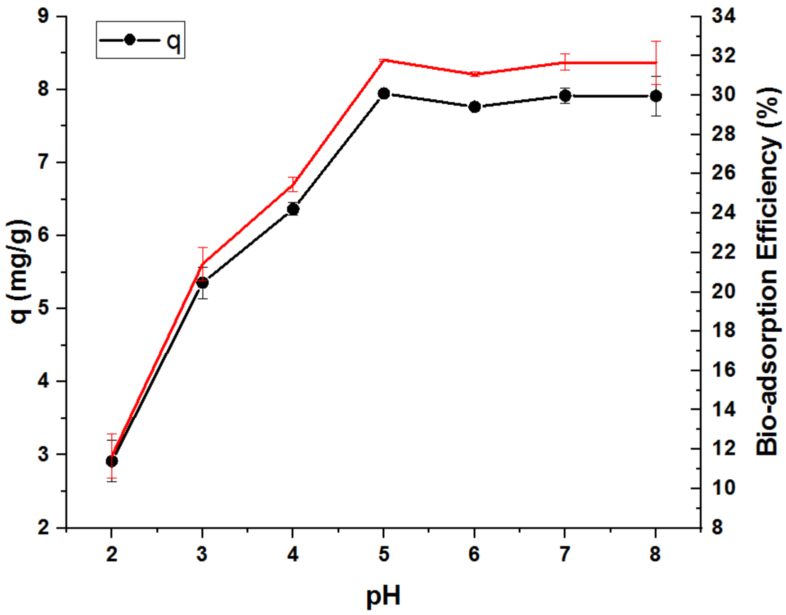


Figure 1. Effect of pH on the adsorption of Zn^{2+} ions of *S. platensis* TH biomass.

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.

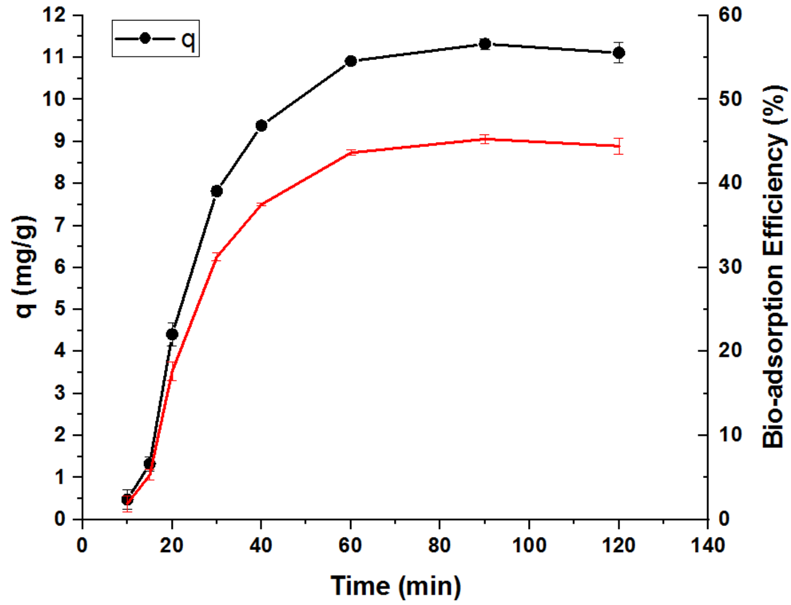


Figure 2. Effect of contact time on the adsorption of Zn^{2+} ions of *S. platensis* TH biomass.

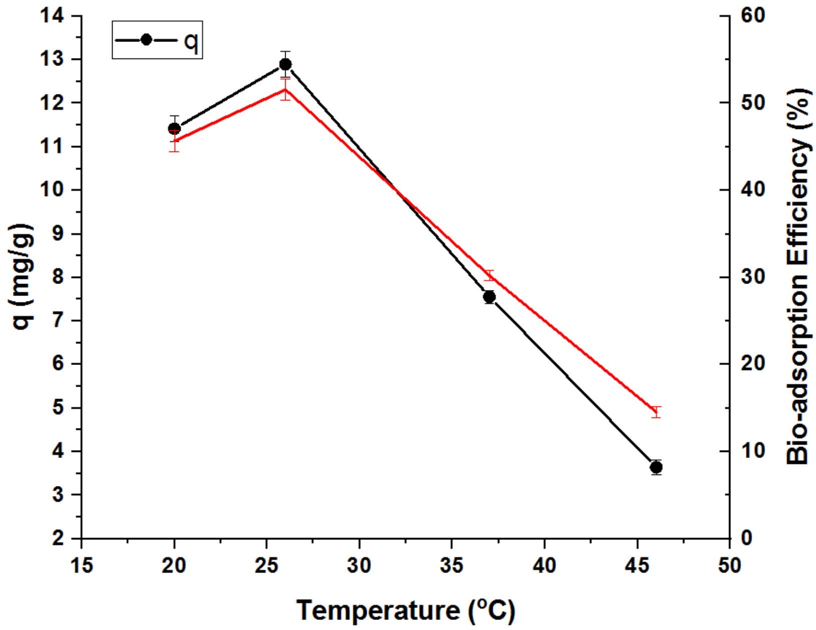


Figure 3. Effect of temperature on the adsorption of Zn^{2+} ions of *S. platensis* TH biomass.

Effect of temperature on the Zn^{2+} 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 Zn^{2+} ion adsorption from the aqueous solution of *S. platensis* TH biomass. The adsorption of Zn^{2+} ions in the solution of *S. platensis* TH adsorbent increased as the temperature was raised from 20 to 26ºC.

Experiment results demonstrated that a temperature of 26ºC is optimal for greatest Zn^{2+} 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 Zn^{2+} 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 Zn^{2+} 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 Zn^{2+} ion.

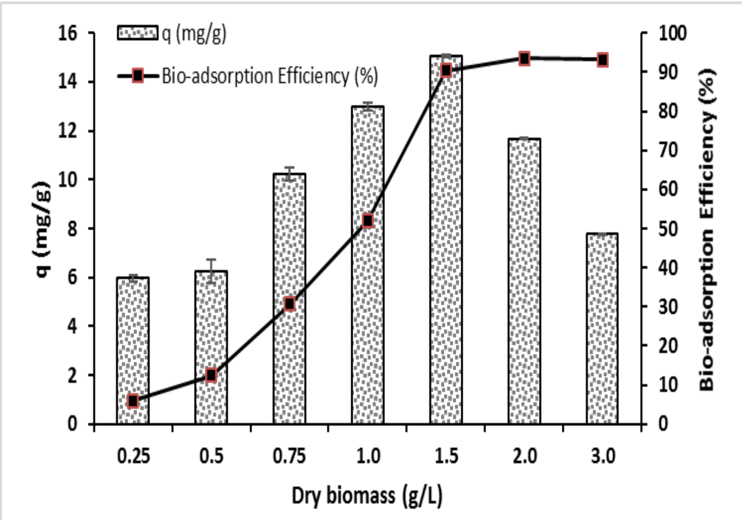


Figure 4. Effect of *S. platensis* TH biomass dosage on the Zn^{2+} ions adsorption.

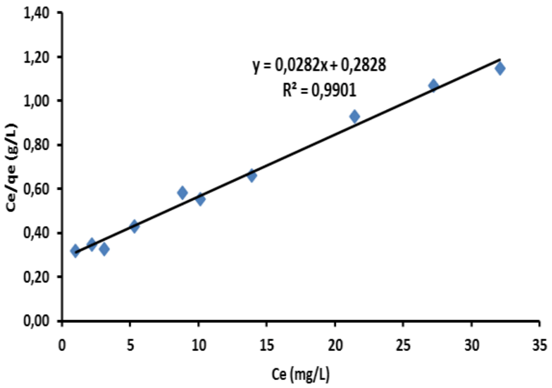
Figure 4 depicted the influence of bioadsorbent concentration on Zn^{2+} ion removal efficiency from solutions. The results revealed that the proportion of Zn^{2+} ions eliminated increased with adsorbent mass. As a result, as biosorbent concentrations increased from 0.25 to 1.5 g/L, the removal efficiency of Zn^{2+} 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 biosorbent, thereby increasing the number of available binding sites (Al-Homaidan *et al.*, 2015). There was no significant difference in Zn^{2+} 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 Zn^{2+} 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.

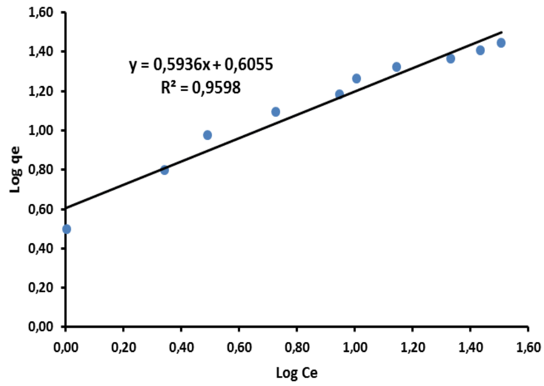
Biological adsorption isotherm

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.



(a)



(b)

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.

Langmuir model		Freundlich model	
R^2	0.9901	R^2	0.9598
q_m	35.46 mg/g	K_f	1.83
b	0.2828	1/n	0.79

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 26ºC. Results have revealed that *S. platensis* TH biomass is an easy, readily available, low-cost adsorbent and has a high bioadsorption capacity. Therefore, it could be used as a bioadsorbent in the treatment of wastewater containing Zn^{2+} ions.

Acknowledgment: *This research is funded by the Institute of Environmental Technology, Vietnam Academy of Science and Technology with project code: CSNU.01/21-21.*

REFERENCES

Ahluwalia SS, Goyal D (2007) Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresour Technol* 98: 2243-2257.

Al-Homaidan AA (2015) Adsorptive removal of cadmium ions by *Spirulina platensis* dry biomass. *Saudi J of Biol Sci* 22: 795-800.

Bai RS, Abraham TE (2002) Studies on enhancement of Cr(VI) biosorption by chemically modified biomass of *Rhizopus nigricans. Water Res* 36: 1224-1236.

Devlina Das, Basak G, Lakshmi V, Nilanjana Das (2012) Kinetics and equilibrium studies on removal of zinc(II) by untreated and anionic surfactant treated dead biomass of yeast: Batch and column mode. *Biochem Eng J* 64: 30-47.

Ferreira LS, Rodrigues MS, Monteiro de Carvalho JC, Lodi A, Finocchio E, Perego P, Converti A (2011) Adsorption of Ni^{2+}, Zn^{2+} and Pb^{2+} onto dry biomass of *Arthrospira (Spirulina) platensis* and *Chlorella vulgaris*. I. Single metal systems. *Chem Eng J* 173(2): 326-333.

Finocchio E, Lodi A, Solisio C, Converti A (2010) Chromium (VI) removal by methylated biomass of *Spirulina platensis*: the effect of methylation process. *Chem Eng J* 156(2): 264-269.

Hannachi Y, Dekhil BA, Taoufik B (2013) Biosorption potential of the red alga, *Gracilaria verrucosa* for the removal of Zn^{2+} ions from aqueous media: Equilibrium, kinetic and thermodynamic studies. *Inter J of Current Eng and Technol* 3(3): 1156-1163.

Incharoensakdi A, Kitjaharn P (2002) Zinc biosorption from aqueous solution by a halotolerant cyanobacterium *Aphanothece halophytica*. *Curr Microbiol* 45(4): 261-264.

Kumar YP, King P, Prasad VSRK (2006) Comparison for adsorption modeling of copper and zinc from aqueous solution by *Ulva fasciata* sp. *J Hazard Mater* 135: 1246-1251.

Lee JY, Kwon TS, Baek K, Yang JW (2009) Adsorption characteristics of metal ions by CO_2-fixing *Chlorella* sp. HA-1. *J Ind Eng Chem* 15: 354-358.

Linchuan F, Chen Z, Peng C, Wenli C, Xingmin R, Ke D, Wei L, Ji DG, Qiaoyun H (2011) Binding characteristics of copper and cadmium by cyanobacterium *Spirulina platensis*. *J Hazard Mater* 190: 810-815.

Monteiro CM, Castro PML (2012) Metal uptake by microalgae: underlying mechanisms and practical applications. *Biotechnol Progr* 28(2): 299-311.

Norton L, Baskaran K, McKenzie T (2004) Biosorption of zinc from aqueous solutions using biosolids. *Adv Environ Res* 8(3-4): 629-635.

Palaniswamy R, Veluchamy C (2017) Biosorption of heavy metals by *Spirulina platensis* from electroplating industrial effluent. *Environ Sci Ind J* 13(4): 139.

Rajiv K, Aneja U, Chaudhary G, Ahluwalia SS, Goyal D (2011) Biosorption of Pb^{2+} and Zn^{2+} by non-living biomass of *Spirulina* sp. *Indian J Microbiol* 50(4): 438-442.

Sarı A, Tuzen M, DoğanUluözlü Ö, Soylak M (2007) Biosorption of Pb(II) and Ni(II) from aqueous solution by lichen (*Cladonia furcata*) biomass. *Biochem Eng J* 37(2): 151-158.

Sun X, Huanga H, Zhua Y, Dua Y, Yao L, Jiangd X, Gao P (2019) Adsorption of Pb^{2+} and Cd^{2+} onto *Spirulina platensis* harvested by polyacrylamide in single and binary solution systems. *Colloids and Surfaces A* 583 123926.

Zarrouk C (1966) Contribution a L’etude D’une Cyanobacterie: Influence de Divers Facteurs Physiques et Chimiques sur la Croissance et la Photosynthese de *Spirulina maxima* (Setchell et Gardner) Geitler. *PhD Thesis*, University of Paris, France.

Zinicovscaia I, Duca G, Cepoi L, Chiriac T, Rudi L, Mitina T, Frontasyeva MV, Pavlov S, Gundorina SF (2015) Biotechnology of metal removal from industrial wastewater: zinc case study. *Clean-Soil Air Water* 42(1): 112-117.