



Characterization of adsorption ability of *Spirulina platensis* for copper ions removal from aqueous solutions

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ABSTRACT

Among different techniques used to eliminate heavy metals pollution, biosorption using marine algae was found to be an effective method for cleaning aqueous solutions from heavy metals. Due to their low cost ratio and their effectiveness against a wide range of pollutants, marine algae are considered as potential alternative to common techniques used for environmental decontamination and for many industrial applications. Herein, the aim of this study was to highlight the importance of *Spirulina platensis* as naturally inspired biosorbent, where data obtained with scanning electron microscope detected considerable changes on the algal surface prior and following copper adsorption. Fourier-transform infrared spectroscopy determined a variety of functional groups available for copper binding. Freundlich isotherm model showed a spontaneous, endothermic as well as entropy favorable sorption behavior of copper ions represented by a linear plot. Maximal biosorption (90.6%) was obtained from a 100 mg copper/L and 0.050 g dry biomass solution, pH 7, at 37°C and following 90 min contact time. As such copper was considerably adsorbed on *Spirulina platensis* surface and hence could be used as an alternative, economic method for copper elimination from aqueous solutions.

Keywords: *Spirulina platensis*; Adsorption; Copper; Scanning electron microscope; Fourier-transform infrared spectroscopy analysis; Freundlich isotherm model; Thermodynamics

1. Introduction

Owing to the growing population and the rapid industrial expansion, environmental pollution became worse than ever, it is now considered as a fundamental concern not only to all environment researchers but also to eco-friends. Therefore, advanced methods nowadays called “green agenda” with new approaches are needed to meet the growing world population and follow the development of all modern societies [1]. Among the different techniques implemented to detect and remove heavy potentially toxic metals from aqueous environments listing fluorescent-based and electrochemical detector sensors for detection, enzyme

based and photocatalytic systems for degradation together with physico-chemical processes [1–3], biosorption remains the efficient, rapid, safe, and more economical method. In this context, the utilization of naturally inspired materials, for example, seaweeds as biosorbents, bio-materials with the ability to accumulate toxic wastes, has been successfully tested for various biotechnological and industrial applications mainly for the removal of many potentially toxic elements one of which is copper. Algae are the most employed biosorbents compared to any other material, the reason behind is that no treatment is required, they are low-cost biosorbents, and they possess high metal ion binding capacity on their cell wall.

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Although, heavy metals exist naturally on earth and some are important for both human and plant life; however, when present in very high concentrations or released into the environment they cause serious environmental pollution and hence they have to be eliminated [4]. Therefore, removal of non-biodegradable heavy metals is now a challenge for the marine organisms particularly algae to emphasize their ability to purify the aquatic environment [5]. In addition, the effectiveness of algal biomass biosorption depends on type and quality of the biosorbents: composition, chemical state, and surface functional group. Biosorption using *Spirulina* has been adapted in controlling many metal and industrial wastewater pollution in general for aquatic bioremediation [6–8]. *Spirulina platensis* is a blue green, filamentous alga, and it is readily available source of biomass for toxic metal removal. Herein the utilization of biosorption using *Spirulina* materials for potentially copper removal was the main aim and novelty of this study, along with revealing the biosorbent characteristics through different techniques listing: Fourier-transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) [9]. Equilibrium, and thermodynamic parameters were also determined to understand the biosorption mechanism as a continuation to the previous work [10] and thus to demonstrate the applicability of *Spirulina platensis* as an effective copper biosorption removal technique.

2. Materials and methods

2.1. Algal cultivation

The micro alga (cyanobacterium) (*Spirulina platensis* UTEX LB 2340) acquired from algae Culture Collection at the University of Texas was used as biosorbent for copper ions removal from an aqueous solution. The strain was cultivated in Zarrouk medium [11,12].

2.2. Adsorption experiment

In brief, *Spirulina platensis* biomass were dried at room temperature for 24 h and subsequently at 80°C for 12 h, then ground and sieved for further analysis. 10 g of the dried biomass were suspended in 100 mL deionized water and were incubated at ambient temperature for 60 min at 150 rpm in a rotary shaker. Following incubation, the biomass was filtered through 0.45 µm membrane filter (Millipore, USA) to be used for the adsorption study [10].

Biomass copper adsorption rate was carried out along with investigating the effect of different parameters such as: biomass, contact time, temperature, initial concentration of copper, and pH. Based on Al Homaidan et al. [10], for a maximal biosorption, a solution of was prepared in 250 mL Erlenmeyer flasks containing 100 mg copper and 0.050 g dry biomass/L respectively, the pH was adjusted to 7, and the solution was incubated in a rotary shaker (Model Comecta, Spain) at 150 rpm and 37°C for 90 min contact time.

The algal suspension was then decanted and separated from the adsorbent after centrifugation (6,000 rpm, for 30 min) followed by filtration using 0.45 µm membrane filters (Millipore Corporation, USA) and stored in sterile containers for further analysis.

2.3. Characterization of the biosorbent

2.3.1. Scanning electron microscopy

Biosorbent microscopic examination of the algal surface texture and morphology changes was performed before and after adsorption using SEM (JEOL, JSM, 3060LV, Japan). Briefly, the biosorbent was fixed with 2.5% glutaraldehyde, soaked on a clean filter paper, coated with gold and then attached on aluminium sample stub to be observed under the microscope.

2.3.2. Fourier-transform infrared spectrometer

2.3.2.1. FTIR analysis

The algal biosorbent surface was preliminary analyzed with FTIR for the detection of the main functional groups involved in metal binding, before and after metal adsorption. Detection of vibration wave number were observed indicating the changes in the sorbent surface since each group has a unique energy absorption band.

FTIR spectrum of the sample in study was performed using KBr (potassium bromide) pellet method, where 0.1 g of dried algal biomass was mixed and compacted in pellet form with KBr. FTIR spectra were then recorded within the wave range of 500–4,000 cm⁻¹ [13].

2.3.3. Freundlich adsorption isotherm

Algal biomass equilibrium state was tested with Langmuir and Freundlich (F type, for homogeneous surfaces) adsorption isotherm models [14]. Higher R^2 values were obtained with the Freundlich model compared to Langmuir, hence, Freundlich model was adopted in this study. The Freundlich model assumes that adsorption energy is variable and that according to the surface binding site, the adsorption heat varies too. The model considers the mutual interaction between adsorbate molecules. Hence an equilibrium state description between the two phases and the copper transfer behavior from the aqueous solution to algal biomass phases were calculated by the following Freundlich Eq. (1) non-linear and Eq. (2) linear and Langmuir equation [14]

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

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

$$\frac{1}{q_e} = \left(\frac{1}{C_e} \times \frac{1}{K_L q_{\max}} \right) + \frac{1}{q_{\max}} \quad (3)$$

where K_F and K_L : biosorption equilibrium constant representative of the sorption capacity for Freundlich and Langmuir models respectively. n : constant indicative of biosorption intensity $1/n$ values within 0 and 1 indicate favorable adsorption. n represents the intensity of adsorption. q_e is the amount of the solute adsorbed per unit weight of adsorbent (mg/g) and q_{\max} is the maximum amount of the solute absorbed;

C_e is the equilibrium concentration of the solute in the bulk solution (g/L).

3. Results

3.1. Scanning electron microscopy

Tested *Spirulina* samples were observed with SEM to analyze and identify their morphological structure pre and post adsorption.

3.2. FTIR analysis

FTIR analysis, in the present study, indicated the presence of different functional groups on the tested biosorbent cell wall surface.

Spectra for pre and post adsorption were determined within the wave range 4,000 to 500 cm^{-1} . Each peak corresponded to a specific functional group (Fig. 1), accordingly different functional groups were detailed and tabulated (Table 1) based on previous studies.

A: pre-copper adsorption
B: post-copper adsorption

The present FTIR data indicated that the algal surface was changed to more electronegative functional groups, which in turn may increase the biosorption.

3.3. Freundlich adsorption isotherm

Data for Freundlich plots with respect to copper biosorption by the non-living algal biomass are given in Fig. 2. The linear plots of $\ln C_e$ vs. $\ln q$ demonstrated a feasible Freundlich isotherm application.

The correlation coefficient, R^2 values and the constants obtained from the Freundlich isotherm model for copper adsorption on biomass algal are summarized in Table 2.

There was a moderate positive correlation (coefficient of determination $R^2 = 0.4532$ between the Cu concentration remaining in solution at equilibrium and the amount of Cu adsorbed per unit cell weight both in logarithmic form.

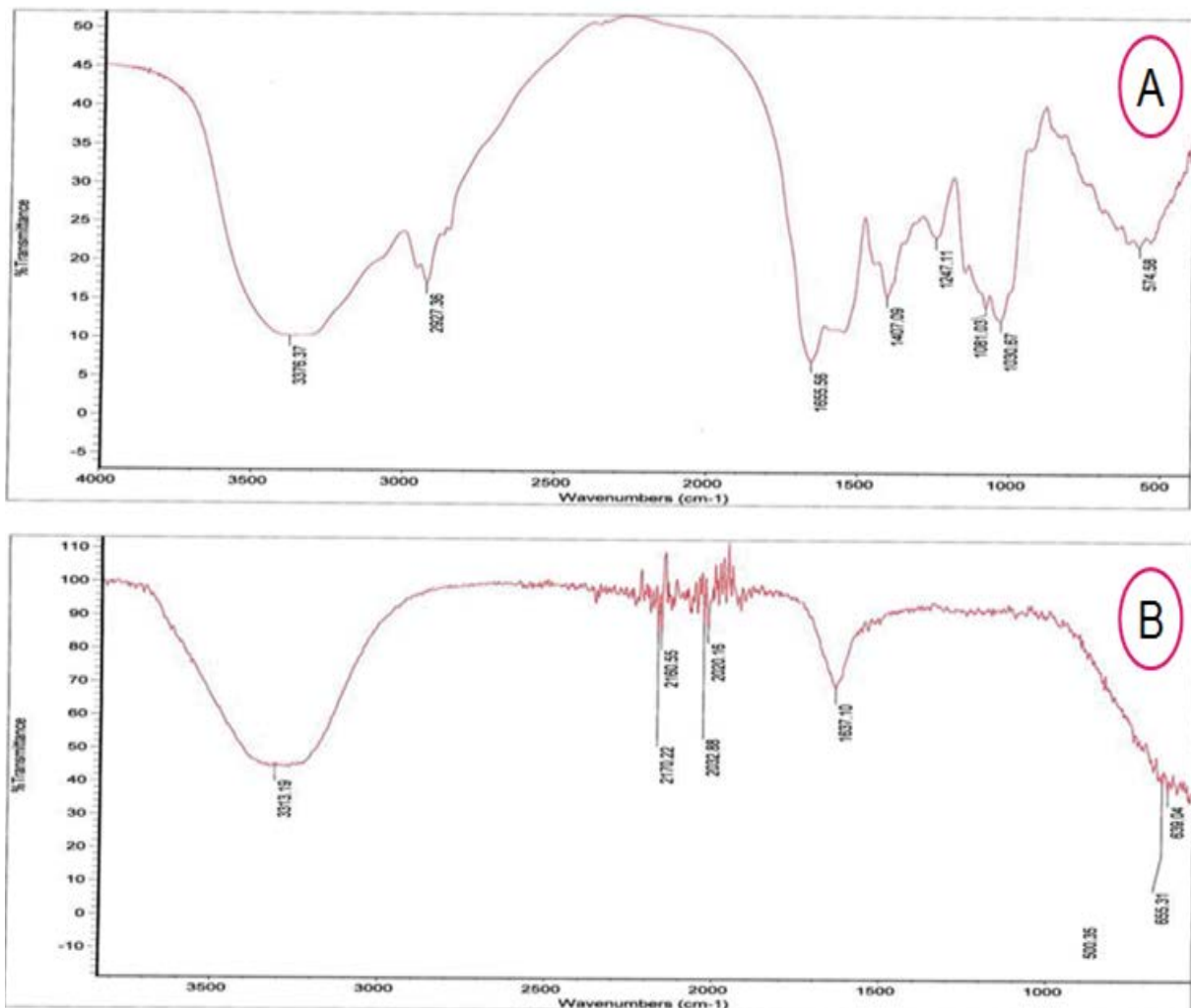


Fig. 1. FTIR spectrum of *Spirulina platensis* revealing the presence of different functional groups on the algal cell wall before and following copper intake.

Table 1
Infrared absorptions and functional group for *S. platensis*

Functional group	Characteristic absorption(s) wavenumber range (cm ⁻¹)	Peaks of <i>S. platensis</i> surface before and after adsorption
Alkyl C–H stretch	2,950–2,850 (m or s)	–
Alkenyl C–H stretch	3,100–3,010 (m)	–
Alkenyl C=C stretch	1,680–1,620 (v)	–
Alkynyl C–H stretch	~3,300 (s)	2,170.22
Alkynyl C=C stretch	2,260–2,100 (v)	–
Aromatic C–H stretch	~3,030 (v)	1,407.07
Aromatic C–H bending	860–680 (s)	–
Aromatic C=C bending	1,700–1,500 (m, m)	–
Alcohol/phenol O–H stretch	3,550–3,200 (broad, s)	3,376.37 3,313.19
Carboxylic acid O–H stretch	3,000–2,500 (broad, v)	2,927.36 2,332.58
Amine N–H stretch	3,500–3,300 (m)	–
Nitrile C=N stretch	2,260–2,220 (m)	–
Aldehyde C=O stretch	1,740–1,690 (s)	1,655.58
Ketone C=O stretch	1,750–1,680 (s)	1,637.10
Ester C=O stretch	1,750–1,735 (s)	–
Carboxylic acid C=O stretch	1,780–1,710 (s)	–
Amide C=O stretch	1,690–1,630 (s)	–
Amide N–H stretch	3,700–3,500 (m)	–

Based on Benning et al. [15], Giordano et al. [16], Keller [17], Naumann et al. [18], Stuart [19], Wong et al. [20], Dean et al. [21], Sigee et al. [22], Maquelin and Kirchner [23];
– no peaks were obtained in this range.

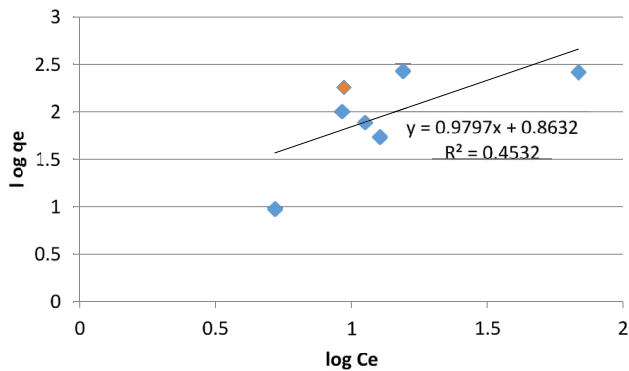


Fig. 2. Copper adsorption Freundlich isotherm model. Sorption isotherm constants and coefficients for metal ion adsorption determination revealed the approximate amount of copper absorbed by the dried algal biomass.

3.4. Biosorption thermodynamics

Adsorption thermodynamics were determined in this study by calculating the thermodynamic parameters ΔG° (kJ/mol) (Gibbs free energy change), ΔH° (adsorption enthalpy) (kJ/mol) and ΔS° (adsorption entropy) (J/mol K), considered as important parameters for the characterization of the adsorption process. These parameters were estimated using Eqs. (2)–(4). Data are represented in Table 2.

$$\Delta G^\circ = -RT \ln K_F \tag{4}$$

$$\ln K_F = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{5}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{6}$$

where K_F is the thermodynamic equilibrium constant (L g⁻¹), K_D obtained from the Freundlich model; T : temperature; R : the universal gas constant (8.314 J/mol K).

Gibbs free energy indicated the degree of spontaneity, the higher its negative values, the more energetically favorable adsorption process is reflected.

4. Discussion

The presence of different functional groups on the algal cell wall is highly affecting the degree of effectiveness of the biosorption mechanism. Adding to this, the secondary metabolites secreted by the algal sample may as well interfere in altering the biosorption mechanism. As reported by Vannela and Verma [7] that ion-exchange was the principle mechanism responsible for metal sorption on the biomass, where dried algal biomass functioned as natural ion-exchanger with the presence of specific presence of metal ion specific ligands/binding sites on the biomass, a strong attraction between the divalent cations and the pores on the

Table 2

Thermodynamic parameters for the biosorption of copper on algal biomass (*Spirulina platensis*) at different temperatures

Metal ion	Alga	Temperature (°C) (K)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹ K ⁻¹)	ΔS° (J mol ⁻¹ K)	
Cu(II)	<i>S. platensis</i>	26°C	299.15	-19.002	0.0599	
		37°C	310.15	-19.03	0.071	3.25
		45°C	318.15	-19.35	0.062	

surface of the dried biomass as well as to the presence of hydroxyl, carboxyl and sulfate groups [1] altering as such the morphological structure of the sorbent cell wall and hence the degree of toxic metal removal [1], this is in accordance with our findings, where FTIR spectrum indicated that the algal surface was changed to more electronegative functional groups, which in turn may increase the biosorption.

SEM data of the dried *Spirulina platensis* tested (Figs. 3 and 4) showed circular particles, the heavy metal ions, occupying the available free binding sites, in agreement with our findings [13] and indicated the strong attraction between the copper ions on the algal cell surface making it as such a natural bio-sorbent toxic metal removal of choice. Additionally, FTIR spectra obtained for pre and post copper adsorption (Fig. 1) indicated the alteration of the functional groups accordingly enhancing as such the binding mechanism [24–27] which in their turn are mainly dependent on the aqueous solution physical parameters precisely pH, temperature and the contact time. It was noted that at the highest wave number 3,300–3,310 cm⁻¹ amine bands were detected, pre and post copper ions exposure. However, stretching bands at 1,650 cm⁻¹ (asymmetrical) and 1,400 cm⁻¹ (symmetrical) corresponding to carbonyl groups (C=O) of primary amide protein and carboxylate ions were mainly detected following copper adsorption. The 1,540 cm⁻¹ band represented the stretching vibrations of protein secondary amides (-NH). Whereas 1,240 cm⁻¹ band was given by free -CO bound, while stretching vibrations at 1,150 and 1,050 cm⁻¹ corresponded to CC/CO mode

of polysaccharides ethers observed in both pre and post biosorption process. Within a wave number range of 1,240–1,050 cm⁻¹ hydroxyl bands were detected as well, they were observed before and after metal adsorption. The untreated dried *Spirulina* sample showed a peak around 3,376.37 cm related to O–H groups. The observed peaks at 2,927.36 cm can be assigned to stretching vibration of the C–H and O–H group. Additionally, peaks at 1,655.58 and 1,407.07 were associated with C=O, and C–O presence respectively [28,29].

Following Cu adsorption, significant changes in the wave numbers was observed as these shifted to 3,313.19 and 1,637.10 cm⁻¹, respectively suggesting the presence of amide and hydroxyl groups N–H, O–H able to interact with protons or metal ions. The above results indicated that functional groups present on the algal cell surfaces greatly affect adsorption. This could be related too to the high protein concentration naturally present in *Spirulina* sp. as reported too by Chauhan et al. [29].

An isotherm, on the other hand, describes the equilibrium relationship between the adsorbate concentration in the liquid phase and that of the adsorbent's surface at a given condition [30]. It is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH. Isotherms are a thermodynamic basic of separation processes and determine the extent to which a material can be adsorbed onto a particular surface [30].

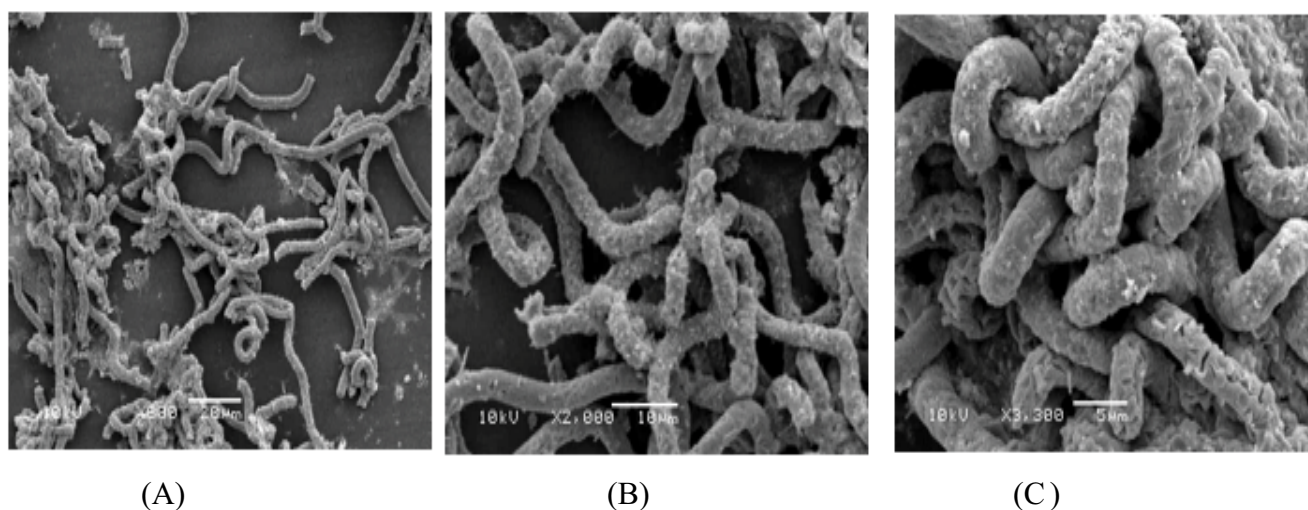


Fig. 3. Pre-adsorption scanning electron microscopic revealing the morphological identification and examination of crude *S. platensis* before adsorption at different magnifications (A, B, C).

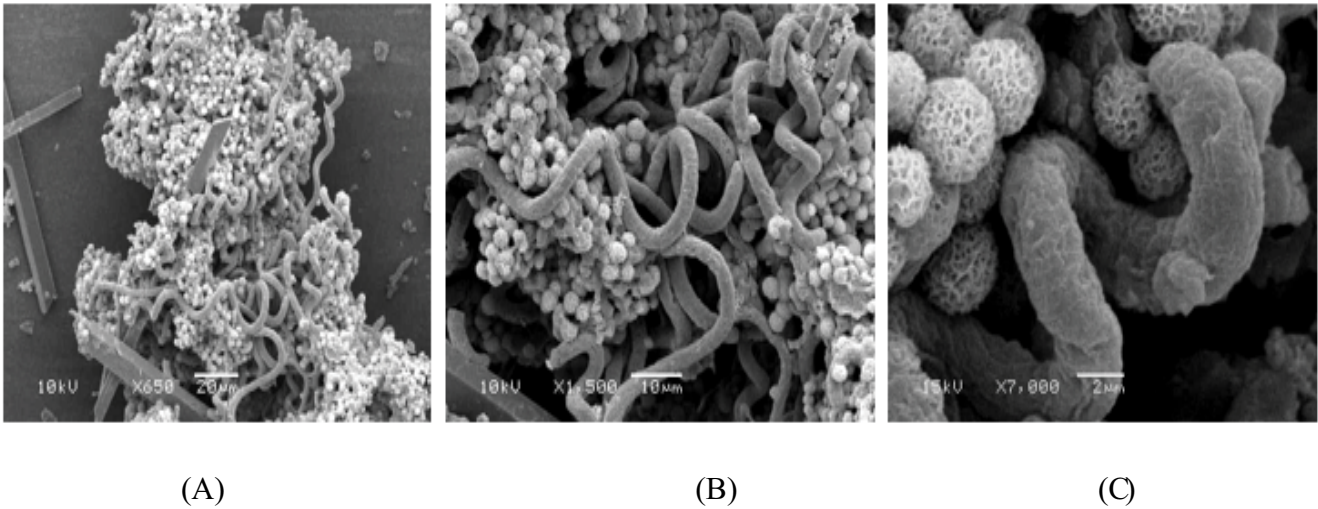


Fig. 4. Post adsorption scanning electron microscope image revealing the morphological identification and examination of *S. platensis*, and copper following adsorption. The surface morphological change can be linked to precipitation/complexation of Cu on the biosorbent surface at different magnifications (A, B, C).

A variety of isotherms have been developed to describe equilibrium relationships. However, no single model is universally applicable; all involve assumptions which may or may not be valid in particular cases.

The Freundlich isotherm model provides a more realistic description of adsorption by organic material because it accounts for different types of binding sites and their interactions, surface heterogeneity and the energy of the biosorbent surface [31]. Langmuir model, however, assumes uniform monolayer surface adsorption energies and no adsorbate interaction [31]. Therefore, the Freundlich model measured the short term Cu binding to a heterogeneous rather than a homogeneous assembly of binding sites at the cell surface of the algal sample. K_f values (Table 2) when compared to the Langmuir K values (Fig. 5 and Table 3) were consistent with the Cu binding sites on the whole dried non-living algal cell wall which was confirmed as well

by the SEM images demonstrated that >80% of *Spirulina platensis* was occupied by the cation (Fig. 4) showing as such high affinity of Cu on the *Spirulina* cell wall binding sites in agreement with Mubeen et al. [31] who reported that Red macroalgae *Gracilaria changii* had higher affinity to copper than lead; however, this affinity might differ from algal species to another, depending on the cell wall composition and hence the presence of binding sites, similar to other findings [32,33] which reported that potentially toxic element biosorption is hindered by the algal cell wall. For example, Romera et al. [33] suggested that brown algae are considered as the effective lead removal due to the presence of alginate in its cell wall.

In addition, as shown in Table 3, the enthalpy change ΔH° is positive (endothermic) due to adsorption increase with successive temperature increase. Further, negative ΔG°

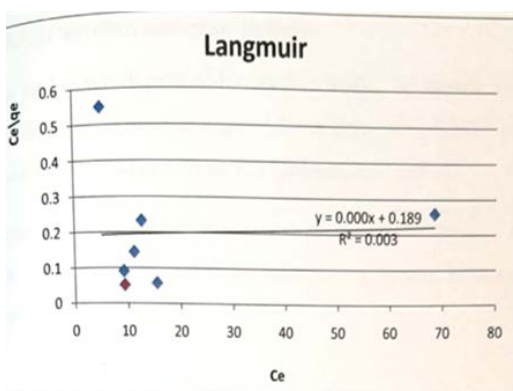


Fig. 5. Langmuir isotherm model. Langmuir model showed a non-significant correlation between the adsorbent and the copper ions due to $R^2 = 0.003$.

R^2 : coefficient of determination measuring the global fit to the Langmuir equation.

Table 3
Freundlich model calculation

Model	Parameters	Values	Calculation
Freundlich	Slope	0.9797	$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$
	Intercept	0.8632	
	K_f (mg/L)	-0.0638	
	R_f^2	0.4532	

R_f^2 : coefficient of determination measuring the global fit to the Freundlich equation.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

$1/n$ calculation:
 $1/n = \text{Slope}; 1/n = 0.9797; n = 1.0207$

$\ln K_f$ Calculation:
 $\ln K_f = \text{Intercept}; \ln K_f = 0.8632; K_f = -0.0638$

Table 4
Langmuir calculation

Models	Parameters	Values
Langmuir	Slope	0.0005
	Intercept	0.1895
	q_{\max} (mg/g)	2,000
	q_{\max} × intercept	379
	K_L (mg/L)	2.738
	R^2	0.0034

Langmuir equation:

$$\frac{1}{q_e} = \left(\frac{1}{C_e} \times \frac{1}{K_L q_{\max}} \right) + \frac{1}{q_{\max}}$$

values dictate spontaneous and feasibility of the adsorption process. The positive value of ΔS° reveals the increased randomness at the solid–solution interface during the fixation of the copper ion on the active sites of the biosorbent [34]. Since the adsorption process is endothermic, it follows that under these conditions the process becomes feasible and spontaneous [34,35].

5. Conclusion

Based on previous research and in this characterization study, biosorption of heavy metals is one of the promising technologies involved in the removal of heavy metals from waste waters. *S. platensis* is selected for studying biosorption due to its possibility of utilizing a waste biomass for the removal of toxic heavy metals. Characterization of adsorption by SEM and FTIR analysis results showed that *S. platensis* can be used as an adsorbent material for heavy metal adsorption. And equilibrium data of Cu(II) Freundlich isotherm model implying that heterogeneous energetic distribution of active sites on the surface of the biosorbent was possible. Thermodynamic study showed spontaneous and endothermic nature of the sorption process. However, the ability of the non-living biomass of the alga to adsorb multi-metals needs to be studied.

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Conflict of interest

Authors declare no conflict of interest

Data availability

Upon request from the corresponding author.

Authors contribution

NM: conceived the practical work, wrote and edited the manuscript.

HH: conceived the idea, the practical work and the data plotting.

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