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Dynamic biosorption characteristics and mechanisms of dried activated sludge and *Spirulina platensis* for the removal of Cu^{2+} ions from aqueous solutions

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ABSTRACT

During biosorption, removal is ensured by several mechanisms that occurred between living or nonliving microorganisms and transporting metal ions. In this study, the kinetics, equilibrium, and thermodynamics of the biosorption of Cu^{2+} onto dried activated sludge and *Spirulina platensis* from aqueous solution were investigated at different experimental conditions. The biosorption characteristics were investigated with respect to some of the significant parameters including the effect of pH, biosorbent dosage, and temperature. The Langmuir, Freundlich, and Temkin equilibrium adsorption models were studied. Results showed that Langmuir isotherm model fitted well the experimental data followed by the other isotherm models used. In order to determine the mechanism of the biosorption, kinetic models were applied. The results of the kinetic studies indicated that the biosorption processes fitted the pseudo-second-order model. The thermodynamic parameters were also calculated, and the values indicated that the biosorption process was spontaneous, exothermic, and more ordered in nature.

Keywords: Biosorption; Copper removal; Dried activated sludge; *Spirulina platensis*; Thermodynamics

1. Introduction

Development in electroplating, manufacturing, mining, metallurgy, electronics, automotive, and renewable energy sectors has an adverse effect on the heavy metal pollution in aquatic environment, if necessary precautions are not taken. Different physicochemical methods, such as precipitation, adsorption, ion exchange, solvent extraction, and membrane filtration were implemented for the removal of heavy metals from waters [1–5]. As known, metals have distinguished characteristics from other toxic pollutants. Although metals are not biodegradable, they can be accumulated in living or nonliving biomass. Biosorption is defined as passive uptake of dissolved contaminants from aqueous solutions using living or nonliving biomass, as well as their derived products [6].

During biosorption, metal ions are taken up by microorganisms intracellularly either by adsorption of the heavy metal onto the cell wall of the microorganism, or by biodegradation with exopolysaccharides produced by the cell [7]. Metal uptake is generally attributed to electrostatic attractions between metal

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cations and negatively charged sites of the cell surface [7].

Spirulina platensis is a phytoplanktonic microorganism in the shape of a perfect spiral coil living both in sea and fresh water [8]. The cell wall of *S. platensis* possess functional groups, such as aminic, carboxylic, thiolic, sulfhydrylic, and phosphoric groups which are responsible for metal binding [9,10].

Waste activated sludge is a by-product of municipal wastewater treated by activated sludge process. Most of the microorganisms in waste activated sludge have functional groups, such as amine, methyl, hydroxyl, and carboxyl groups [11]. Therefore, activated sludge can be an attractive biosorbent for heavy metals, dyes, and organic compounds present in wastewaters. Since it eliminates the problem of heavy metal toxicity, nonliving biomass is generally used for biosorption studies [12–14].

Removal of copper from waters by biosorption, using waste activated sludge, or dead biomass of *S. platensis* can be a promising process. Large quantities of waste activated sludge and *S. platensis* are generated and can be reused before final disposal. Many different biosorbents have shown potential for heavy metals removal, such as waste sludge, algae, yeast, and fungi [12,13,15] but only low cost biomaterials with satisfactory metal binding capacities can be exploited in full-scale processes [10,15]. Among these, waste activated sludge and algal biomass are of important biomaterials due to availability in large quantities, large cultivation worldwide, being much cheaper than other commercially available adsorbents [10].

2. Materials and methods

2.1. Materials

Two different biosorbents, namely, *S. platensis* and dried activated sludge were used in this study. The *S. platensis* harvest was carried out in Ege University. *S. platensis* was grown in outdoor cultivation ponds under constant light and temperature. The culture was then filtered using plankton net and washed with deionized water to remove the impurities. Harvested cells were then dried at 40°C in an air oven.

Activated sludge samples were obtained from the aeration tank of a municipal wastewater treatment plant. Activated sludge biomass was harvested by centrifugation at 7,000 rpm for 15 min and washed three times with distilled water and then centrifuged at 7,000 rpm for 15 min. The samples were dried at 60°C until constant weight. Dried activated sludge was pestled using a mortar and then was separated into certain particle sizes by a 60 mesh sieve before use in adsorption experiments.

Analytical grade $CuSO_4{\cdot}5H_2O$ was used as an adsorbate. The stock solution of Cu^{2+} was prepared by dissolving in distilled water to obtain initial concentrations of 500 mg/L. The pH of the Cu^{2+} solutions was adjusted by using dilute NaOH or H_2SO_4.

2.2. Fourier transform infrared (FT-IR) analysis

FT-IR spectra of *S. platensis* and dried activated sludge were recorded with a FT-IR (Bio-Rad Tropical Option for FTS 175°C) spectrometer. The potassium bromide pellets were prepared and the samples were analyzed in transmittance and absorbance.

2.3. Equilibrium studies

The biosorption of Cu^{2+} on *S. platensis* and dried activated sludge was studied by batch technique. Biosorption studies were conducted in polypropylene conical flasks of 100 mL using 50 mL of metal solution. The equilibrium isotherms were obtained measured by contacting 0.1 g biosorbent with a range of different initial concentrations (40–400 mg/L) of Cu^{2+} solution. The effect of solution pH on the biosorption rate of *S. platensis* and dried activated sludge was investigated in the range of 2–5 which was not controlled during experimentation. The experiments were carried out at pH values without any further adjustment during the sorption process. The solution pH was kept at original pH varying between 4.10 and 4.30 according to the concentration range (400–40 mg Cu^{2+}/L), since pH values lower than 5 were reported to be the optimum pH for copper biosorption [12,13]. Thus, Cu^{2+} precipitation in the form of $Cu(OH)_2$ at pH levels above 5 was avoided [16]. The flasks were incubated in an orbital shaker (Heidolph Unimax 1010) at 25°C. The contact time and biomass concentration was determined with respect to preliminary experiments.

Effects of temperature on biosorption were also studied at temperatures of 25–40°C. Additionally, the effects of biosorbent amount and agitation rate on biosorption were also investigated at 0.05–0.2 g and 150–300 rpm, respectively. These experiments were carried out at 80 mg/L initial metal concentration and 240 min. A control flask free of the biomass with 80 mg/L Cu^{2+} ions was used to determine Cu^{2+} removal in the absence of the adsorbents used. Since polypropylene conical flasks were used throughout the experiments, no adsorption of Cu^{2+} was observed. The metal uptake capacity, q_e, was calculated from Eq. (1):

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

where q_e (mg/g) is the adsorption capacity of the biosorbent at a given time, m (g) is the adsorbent dosage, and V (L) is the volume of the solution. The removal percentage ($R\%$) is given as:

$$R(\%) = 100 \times \frac{C_i - C_e}{C_i} \tag{2}$$

C_i and C_e (mg/L) are initial and equilibrium metal concentrations, respectively.

The equilibrium between adsorbed ions on the biosorbents and unadsorbed Cu^{2+} ions in solution can be represented by adsorption isotherms, which are widely used to analyze data for water and wastewater treatment applications. There are a number of different isotherm models that can be applied. In this study, three different models, namely the Langmuir, Freundlich, and Temkin models were used.

The most widely used isotherm equation for modeling equilibrium is the Langmuir equation which is based on the assumption that there is a finite number of binding sites which are homogeneously distributed over the adsorbent surface [17]. The mathematical description of this model for a single component adsorption is represented as in Eq. (3):

$$q_e = \frac{Q^{\circ} b C_e}{1 + bC_e} \tag{3}$$

where, Q° is the monolayer adsorption saturation capacity which is a useful parameter in the comparison of adsorption performance, and b is a constant related to the affinity of the binding sites. Q° and b can be determined from the linear plot of $1/q_e$ vs. $1/C_e$.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (R_L), which is defined as in Eq. (4):

$$R_L = \frac{1}{1 + bC_0} \tag{4}$$

The value of R_L indicates the type of isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [18].

The empirical Freundlich model is suitable for a highly heterogeneous surface suggesting that binding sites are not equivalent and/or independent and is expressed as in Eq. (5) [19]:

$$q_e = K_f C_e^{1/n} \tag{5}$$

where K_f and n are the Freundlich constants denoting the adsorption capacity and adsorption intensity of the sorbent, respectively. The Freundlich model is a widely used model; however, it should be noted that it provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model. The adsorption isotherm constants express the surface properties and affinity of the sorbent. These values can also be used to compare the biosorptive capacity of biosorbents used for the same sorbate [20].

The Temkin isotherm model assumes that the fall in the heat of adsorption is linear rather than logarithmic, as in the Freundlich isotherm model and is expressed as in Eq. (6) [21]:

$$q_e = \left(\frac{RT}{K_T}\right) \ln(a_T C_e) \tag{6}$$

where a_T is the Toth constant and K_T is the Temkin constant, T is the absolute temperature in Kelvin, and R is the universal gas constant, 8.314 J/mol.K.

2.4. Biosorption kinetics

Kinetic models provide important information on the mechanism between the adsorbate and adsorbent used. In an agitated system, the binding sites of the biomass cell wall are made readily available for adsorbate uptake, and the effect of external film diffusion on biosorption rate can be ignored. Pseudo-first (Lagergren), pseudo-second-order and Elovich kinetic models were used for the experimental data.

The pseudo-first-order reaction equation of Lagergren [22] is widely used for the adsorption of liquid/solid system on the basis of solid capacity. The mathematical description of this model is given in Eq. (7):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{7}$$

For the boundary conditions $t = 0$ to $t = \mathrm{t}$ and $q_t = 0$ to $q_t = q_e$ the integrated and linear form of Eq. (7) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2,303} t \tag{8}$$

where q_e and q_t are the adsorption amount at equilibrium and time t, respectively. K_{ad} is the rate constant in the pseudo-first-order adsorption process. The constants were determined by plotting of log $(q_e - q_t)$ vs. t.

The pseudo-second-order kinetic model based on the sorption capacity of the solid phase can be used in cases where the adsorption follows second-order chemisorption [23]. The pseudo-second-order kinetic rate equation is expressed as in Eq. (9):

$$\frac{dqt}{dt} = k_2(q_e - q_t)^2 \tag{9}$$

where, k is the second-order biosorption rate constant. For the boundary conditions $t = 0$ to $t = \mathrm{t}$ and $q_t = 0$ to $q_t = q_e$ the integrated and linear form of Eq. (9) becomes

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{10}$$

If second-order kinetics is applicable, the plot of t/q_t vs. t of Eq. (10) should give a linear relationship, from which q_e and k can be determined from the slope, and intercept of the plot.

The Elovich model is generally expressed as in Eq. (11) [24]:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{11}$$

In the Elovich model, the expression was simplified with the assumption of $\alpha\beta t \gg \mathrm{t}$ and for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$ the integrated and linear form of Eq. (11) becomes

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{12}$$

where q_t is the initial adsorption rate and $\alpha\beta$ is the desorption constant. A plot of q_t vs. ln(t) should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $1/\beta \ln(\alpha\beta)$.

2.5. Biosorption thermodynamics

Both energy and entropy factors must be considered in biosorption studies, to determine whether a process will occur spontaneously or not. The process of metal ion biosorption is assumed to be a reversible process, which represents a heterogeneous equilibrium. For such equilibrium reactions, the Gibbs free energy (ΔG°) was determined by Eq. (13):

$$\Delta G^o = -RT\ln(K_c) \tag{13}$$

where, R is the universal gas constant, 8.314 J/mol.K and T is the absolute temperature in K and K_c is the equilibrium constant.

The thermodynamic constant of the biosorption K_c, can be obtained from the plot of $\ln(q_e/C_e)$ vs. q_e. The intercept of the plot gives the K_c value and can be expressed as in Eq. (14) [25]:

$$K_c = \frac{q_e}{C_e} \tag{14}$$

The Gibbs free energy indicates the degree of spontaneity of the adsorption process, where more negative values reflect a more energetically favorable adsorption process. The relationship between the equilibrium constant, K_c and the temperature is given by the van't Hoff equation (Eq. (15)):

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{15}$$

where ΔH° is enthalpy change, ΔS° entropy change. According to thermodynamics, the Gibbs free energy change is also related to the entropy change and heat of adsorption at constant temperature by Eq. (16):

$$\Delta G^\circ = \Delta H^\circ - T(\Delta S^\circ) \tag{16}$$

2.6. Analytical methods

At the end of each experiment, the biomass was removed by centrifugation at 5,000 rpm for 5 min. The supernatant was then filtered through filter paper and the filtrate was analyzed using a flame atomic absorption spectrometer (Perkin Elmer).

3. Results and discussion

Bacteria-utilized biosorption depends largely on pH, biomass amount, culture conditions, the presence of metal ions in solution, and, to a more limited extent, temperature. The effects of some of these parameters were tested and presented in this study.

3.1. Characterization

FT-IR spectra of the *S. platensis* and dried activated sludge in the range of 4,000–650 cm^{-1} are shown in Fig. 1. The spectral features deriving from different functional groups serve as a characteristic "finger-

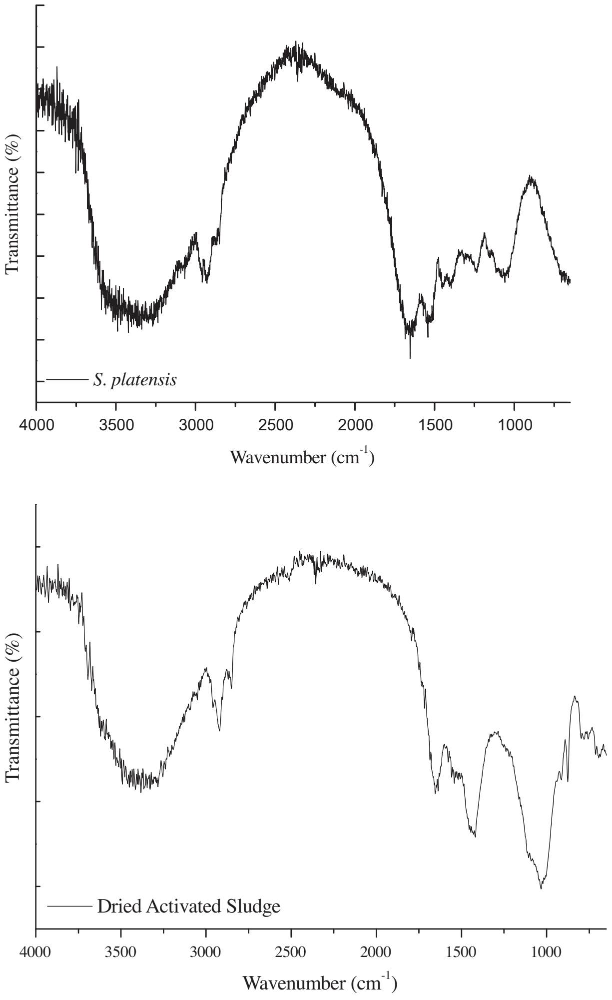

Fig. 1. FT-IR spectra of *S. platensis* and dried activated sludge.

print" of the biosorbents studied [26]. The FT-IR spectrum of the biosorbents showed that their surfaces have different functional groups which can capture metal ions from aqueous solution. The main detected peaks were quite similar to each other for both *S. platensis* and dried activated sludge. The FT-IR spectral analysis demonstrated the existence negatively charged functional groups (carbohydrate, carboxyl, hydroxyl, and amine residues) on the surface of biosorbents used in this study. The broad and strong bands in the high frequency region around 3,500 cm^{-1} could be attributed to the stretching modes of –OH and –NH groups [27]. The existence of –C = O stretches could be confirmed by the sharp peaks in the region 1,645–1,400 cm^{-1}. In addition, the sharp peaks appeared at the range of 1,300–1,000 cm^{-1} are ascribed generally to the C–O and C–C stretching vibration [28].

3.2. Effect of pH

It is well known that pH has a significant effect on the solubility of the metal ions in solution and on the concentration of negatively charged functional groups of the cell wall. That is to say, pH could affect the protonation of the functional groups on the biomass as well as the metal chemistry [29,30]. Under acidic conditions, functional groups on cell wall are protonated, and consequently metal cations cannot reach cell wall, as repulsive forces are in effect. However, with a rise in pH, more functional groups such as amino, phosphate, and carboxylic groups with negative charges would be exposed to metal ions due to attractive forces, resulting in an increase in the degree of ionization [31,32]. When pH is increased, metals are not present in solution as alkaline cations (copper ions in the form of $Cu(OH)_2$, but not as free metal cations (Cu^{2+}), prior to precipitation of the corresponding soluble hydroxide. The alkaline cations, which are bulkier and less charged, have less affinity for the functional groups [33]. Therefore, the selection of optimum pH value is of important significance.

Considering these issues and the precipitation pH value of metal ion used in this study, the values of pH tested were 2, 3, 4, and 5. In this study, the metal sorption uptake increased with pH and this effect was observed for both biosorbents, as expected (Fig. 2). It was observed that a pH value of 5 was deemed to be favorable. However, during the study, the original pH value of 4.17 was chosen in order not to use additional chemicals for pH adjustment.

3.3. Effect of temperature

The influence of temperature on the equilibrium uptake of Cu^{2+} ions on the biosorbents for an initial

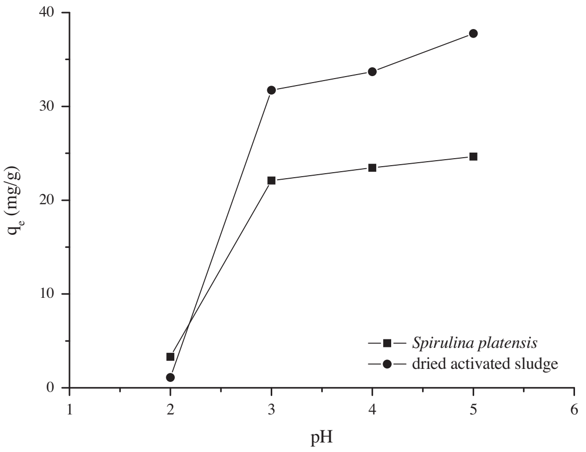

Fig. 2. The effect of pH on Cu^{2+} biosorption ($C_o = 80$ mg/L, $T = 25$°C, AG = 250 rpm, $m = 0.1$ g).

Cu^{2+} ion concentration of 80 mg/L is presented in Fig. 3. The experiments were carried out at four different temperature values ranging from 25 to 40°C. Increasing temperature resulted in a decrease in sorption capacity for *S. platensis*. This showed that the adsorption of Cu^{2+} ion onto *S. platensis* was controlled by an exothermic process. With the change of temperature from 25 to 40°C, the Cu^{2+} ion uptake capacity decreased from 30.38 to 25.58 mg/g, respectively. The decrease in sorption capacity at higher temperatures was attributed to the damage of active binding sites in the protonated biomass [18]. On the other hand, it has been observed that there was no significant effect of temperature on Cu^{2+} ion sorption onto dried activated sludge. Increasing temperature resulted in a slight increase for dried activated sludge. With the increase of temperature from 25 to 40°C, the Cu^{2+} ion uptake capacity increased from 35.06 to 37.75 mg/g, respectively. This suggested that biosorption between dried activated sludge and Cu^{2+} ions could involve a combination of chemical interaction and physical adsorption.

Although it was reported in previous studies, that with an increase in temperature, pores in biosorbent enlarge, resulting in larger surface area available for the sorption, diffusion, and penetration of metal ions within the pores causing increased sorption [34,35], but in this study, the obtained results indicated that increasing temperature did not have a significant effect on sorption for dried activated sludge.

3.4. Effect of biomass concentration

The effect of the biomass concentration on the metal sorption uptake is shown in Fig. 4(a) for *S. platensis* and Fig. 4(b) for dried activated sludge. For this purpose, three different biomass concentrations of 1, 2, and 4 g/L were tested. The highest sorption specific uptake was achieved with the lowest concentration (1 g/L) for the Cu^{2+} ion, which was in accordance with the literature. The amount of Cu^{2+} adsorbed on per unit weight of biosorbent decreases with the adsorbent dosage. When the adsorbent dosage is increased, adsorption onto the adsorbent surface is faster, which then results in a lower adsorbate concentration in the solution. This is due to the concentration gradient between the solute concentration in the solution and the solute concentration on the surface of the adsorbent [33]. It is obvious that the number of active sites increases with biomass concentration and that has a positive effect on the percentage of metal removal. Both the adsorption amount and removal percentage of Cu^{2+} reach relatively high values, when the biosorbent concentration was adjusted to be 2 g/L.

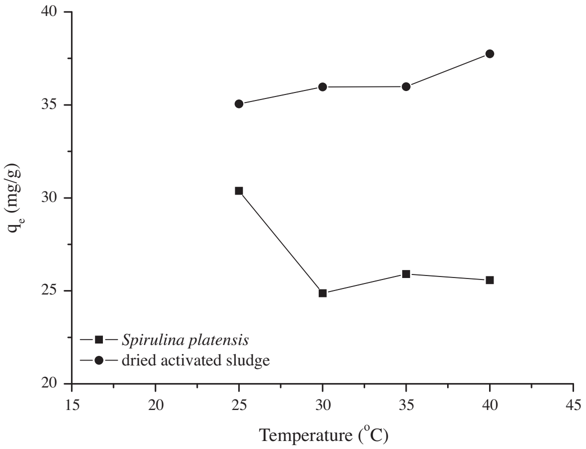

Fig. 3. The effect of temperature on Cu^{2+} biosorption (C_o = 80 mg/L, AG = 250 rpm, pH_{in} = 4.17, m = 0.1 g).

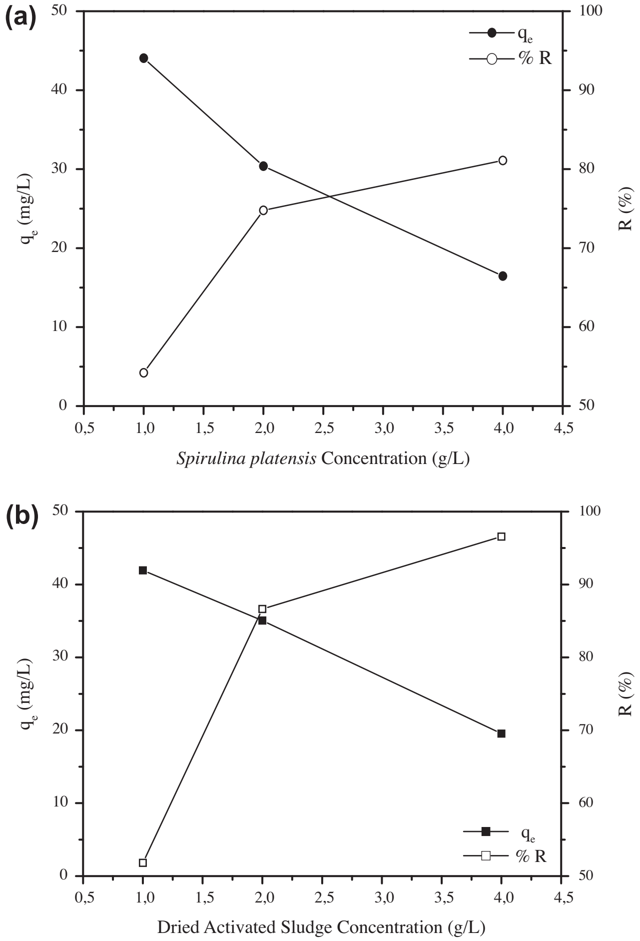

Fig. 4. The effect of biosorbent concentration on Cu^{2+} biosorption (a) *S. platensis*, (b) dried activated sludge (C_o = 80 mg/L, AG = 250 rpm, pH_{in} = 4.17, T = 25°C).

Therefore, the isotherm studies were performed with an adsorbent dosage of 2 g/L.

3.5. Equilibrium studies

During biosorption, a rapid equilibrium is established between adsorbed Cu^{2+} ions on the biosorbents (q_e) and unadsorbed Cu^{2+} ions in solution (C_e) (Fig. 5).

The equilibrium isotherm plots obtained using Langmuir (Fig. 6(a)), Freundlich (Fig. 6(b)) and Temkin (Fig. 6(c)) models are given in Fig. 6(a)–(c) and the constants calculated are presented in Table 1. The results showed that the Langmuir isotherm model fitted well with the experimental data followed by Freundlich and Temkin models. The value of the correlation coefficient, R^2, for dried activated sludge is 0.998, indicating a good fit of the monolayer Langmuir model to the biosorption of Cu^{2+}. However, the model fitting was somewhat weaker for *S. platensis* as reflected by the R^2 value of 0.865. As shown in Table 1, the value of Q° for *S. platensis* was 37.45 mg/g, which was slightly lower than that for dried activated sludge (39.37 mg/g), showing a lower biosorption capacity for Cu^{2+}. High values of b implied the strong bonding of Cu^{2+} onto the biosorbents. In a recent study, using methylated *S. platensis*, the Q° value was obtained 16.7 mg/g for the initial Cr^{+6} ion concentration of 8–50 mg/L and biosorbent concentration of 1 g/L at room temperature [36]. In an other recent study for the removal of Cu^{2+} ions with *S. platensis*, the Q° value was found to be 52.41 mg/g at pH 4 with initial Cu^{2+} ion concentration of 25–250 mg/L and 1 g/L biosorbent concentration [37]. Hammaini and colleagues (2007) [14] found that the Q° value for Cu^{2+} biosorption using dried activated sludge was 0.30 mmol/g, which was lower than the findings of the current study. Comparison of maximum capacities of Cu^{2+} on some adsorbents is given in Table 2.

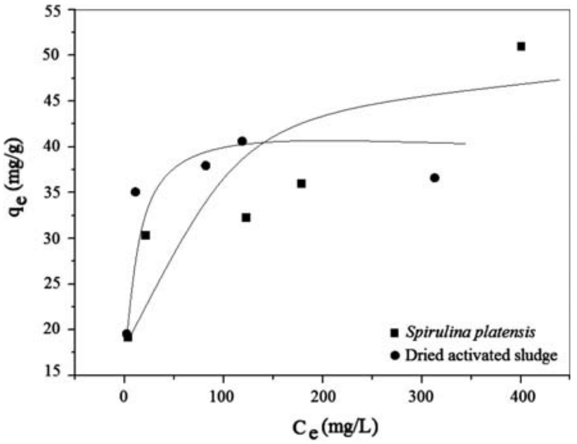

Fig. 5. Equilibrium isotherms of Cu^{2+} adsorption by *S. platensis* and dried activated sludge at *T*: 25˚C; initial pH: 4,17; agitation rate: 250 rpm; adsorbent dosage: 0.1 g.

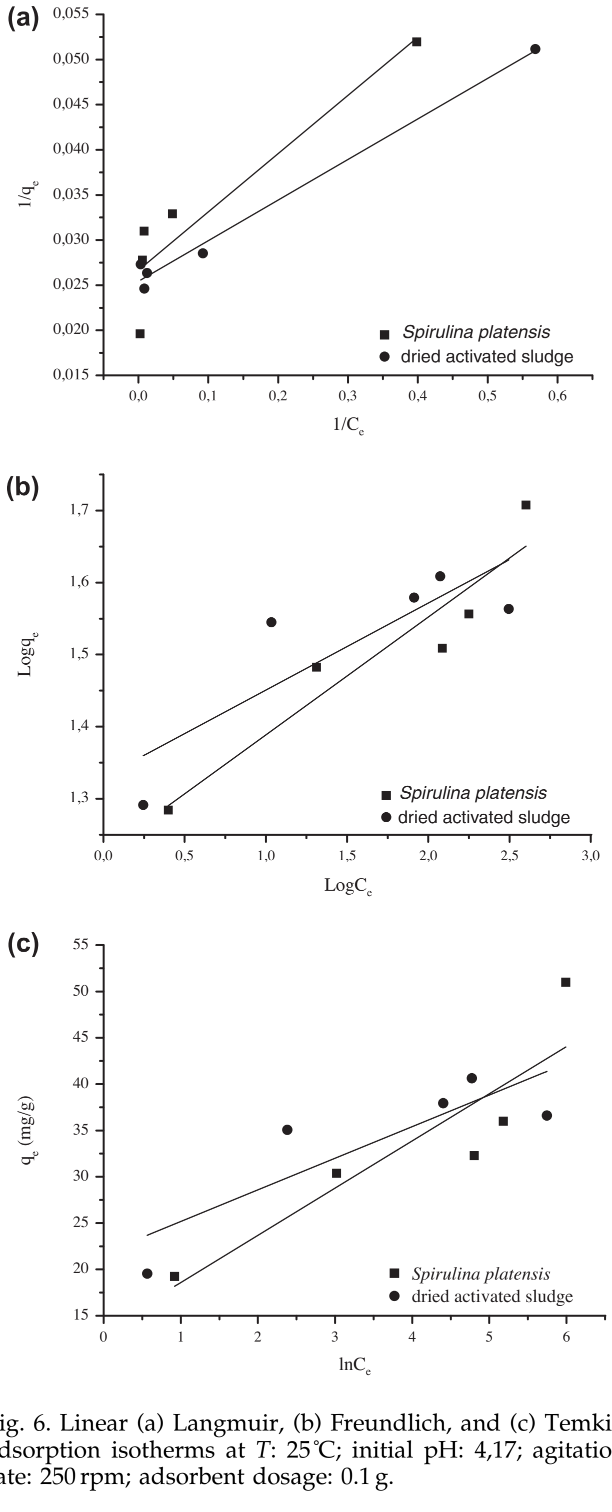

Fig. 6. Linear (a) Langmuir, (b) Freundlich, and (c) Temkin adsorption isotherms at *T*: 25˚C; initial pH: 4,17; agitation rate: 250 rpm; adsorbent dosage: 0.1 g.

The maximum adsorption capacities of *S. platensis* and dried activated sludge for Cu^{2+} biosorption were

Table 1
Biosorption equilibrium constant obtained from Langmuir, Freundlich and Temkin isotherm models for the biosorption of Cu^{2+} ions onto *S. platensis* and dried activated sludge

Biosorbent	Langmuir			Freundlich			Temkin		
	Q° (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n	R^2	a_T (L/g)	K_T (J/mol)	R^2
S. platensis	37.45	0.41	0.865	16.78	6.11	0.895	14.15	5.09	0.811
Dried activated sludge	39.37	0.56	0.998	21.37	8.28	0.720	590	3.41	0.730

Table 2
Comparison of maximum capacities of Cu^{2+} on some adsorbents

Biosorbent	Max. capacity (mg/g)	Refs.
Pseudomonas syringae	25.40	[38]
Sphaerotilus natans	57.47	[39]
Rhizopus arrhizus	10.75	[40]
Rhizopus arrhizus	35.24	[41]
Sphaerotilus natans	37.47	[42]
Thiobacillus thiooxidants	31.00	[43]
Thuja orientalis	11.80	[44]
Chlorella vulgaris	81.97	[45]
Cladonia rangiformis	68.63	[46]
S. platensis	37.45	This study
Dried activated sludge	39.37	

37.45 and 39.37 mg/g, respectively. Table 2 illustrates several other biosorbents reported in the literature for the removal of Cu^{2+} from aqueous solutions. However, it should be noted that comparison among these biosorbents is difficult due to various experimental conditions used in these studies. From Table 2, it is evident that the biosorbents used in this study can be used for Cu^{2+} removal and were competitive to some of the adsorbents. Differences were expected due to the characteristics of each biosorbent such as, functional groups, and surface area.

The values of R_L at different temperatures for both biosorbents were given in Table 3. The R_L values indicated that the sorption is more favorable for the low initial Cu^{2+} ion concentrations than for the higher ones. However, the sorption is more favorable at higher temperatures. Although it should be noted that for dried activated sludge the R_L values were higher for 35℃ compared to 40℃. It can be concluded that the biosorption of Cu^{2+} ions on both biosorbents studied is favorable within the experimental conditions studied.

High K_f values indicated ready uptake of sorbate from aqueous medium (Table 1). Even though the correlation coefficient values, R^2 were less than 0.9, the n values obtained are greater than 1.0, indicating that the Cu^{2+} ions were favorably adsorbed by both of the biosorbents used.

The Toth and Temkin constants, a_T and K_T were determined from the slope and intercept of the plot of q_e vs. $\ln C_e$. Temkin constants, a_T and K_T were determined from the slope and intercepts of the plots obtained by plotting q_e vs. $\ln C_e$. Based on the linear regression correlation coefficient, R^2, it can be concluded that the equilibrium data could not be well interpreted by the Temkin isotherm.

Table 3
The values of R_L at different temperatures for *S. platensis* and dried activated sludge

C_o (mg/L)	R_L							
	S. platensis				Dried activated sludge			
	25°C	30°C	35°C	40°C	25°C	30°C	35°C	40°C
40	0.057	0.238	0.238	0.255	0.042	0.044	0.072	0.068
80	0.030	0.135	0.135	0.146	0.022	0.023	0.038	0.035
160	0.016	0.077	0.077	0.084	0.012	0.012	0.020	0.019
200	0.012	0.059	0.059	0.064	0.009	0.009	0.015	0.014
400	0.006	0.030	0.030	0.033	0.004	0.005	0.008	0.007

Table 4
Comparison of the kinetic constants used in this study

Biosorbent	Initial conc. (mg/L)	Experimental q_e values (mg/g)	Pseudo-first order			Pseudo-second order			Elovich		
			k_1 (1/min)	R^2	Calculated q_e values (mg/g)	k_2 (g/mg.min)	R^2	Calculated q_e values (mg/g)	α (mg/g.min)	β (g/mg)	R^2
S. platensis	40	18.225	0.018	0.934	8.872	0.005	0.999	18.657	438.63	0.632	0.965
	80	27.830	0.025	0.967	20.184	0.013	0.997	26.178	49.37	0.295	0.967
	160	41.420	0.016	0.944	10.351	0.019	0.999	39.841	10×10^3	0.328	0.954
Dried activated sludge	40	19.645	0.012	0.922	2.524	0.021	0.999	19.512	23×10^5	1.034	0.950
	80	35.570	0.007	0.933	12.303	0.002	0.999	35.486	90.27	0.264	0.983
	160	44.050	0.009	0.916	19.499	0.001	0.998	44.445	508.67	0.258	0.976

3.6. Kinetic studies

The kinetic studies were carried out at three different initial Cu^{2+} ion concentrations of 40, 80, and 160 mg/L. Pseudo-first-order (Lagergren), pseudo-second-order and Elovich kinetic models were applied to the experimental data and the results of kinetic constants were given in Table 4.

The correlation coefficients of both the pseudo-first-order and Elovich kinetic models were found to be very low. In addition, the theoretical q_e values, which were calculated using the k_1 values obtained from the linearized pseudo-first-order equation, were not reasonable. This suggested that the biosorption of Cu^{2+} on *S. platensis* and dried activated sludge was not a first-order reaction. Although the Elovich coefficients were slightly higher than the Lagergren ones, they too were lower than those obtained with the second-order model, and therefore were disconsidered. The correlation coefficients of pseudo-second-order model equation were between 0.997 and 0.999. The calculated q_e values also agree very well with the experimental data. This strongly suggested that the biosorption of Cu^{2+} onto *S. platensis* and dried activated sludge can be most appropriately represented by a pseudo-second-order rate process.

3.7. Biosorption thermodynamics

Temperature changes affect the stability of the metal ion species, algal–metal complex, and others [47]. The influence of temperature on the adsorption process depends on the type of the material. In some studies, increasing temperature increased the uptake capacity showing endothermic nature of the process

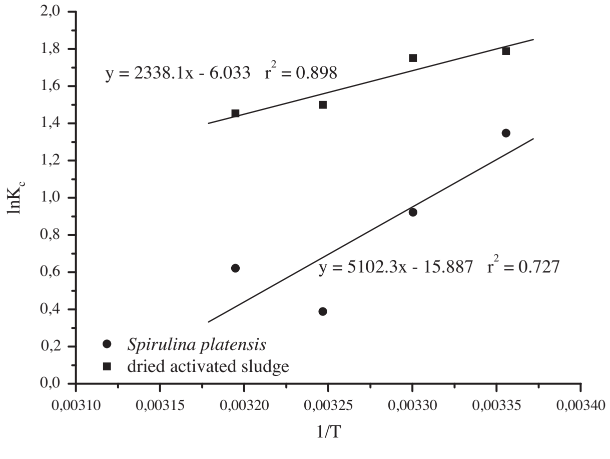

Fig. 7. Plot of lnK_c vs. $1/T$ for the estimation of thermodynamic parameters.

Table 5
Thermodynamic parameters for the biosorption of Cu^{2+} ions by *S. platensis* and dried activated sludge at various temperatures

Biosorbent	T (°C)	$\Delta G°$ (kJ/mol)		$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/molK)
		$\Delta G° = \Delta H° - T.\Delta S°$	$\Delta G° = -RT \ln K_c$		
S. platensis	25	−3.07	−3.33	−42.42	−0.13
	30	−2.41	−2.32		
	35	−1.75	−1.00		
	40	−1.09	−1.61		
Dried activated sludge	25	−4.49	−4.43	−19.44	−0.05
	30	−4.24	−4.41		
	35	−3.99	−3.84		
	40	−3.74	−3.78		

[48,49]. However, in other studies it was shown increasing temperature decreased the uptake capacity showing an exothermic character of biosorption [50,51].

The biosorption equilibrium constants (K_c) for the biosorption of Cu^{2+} ions by *S. platensis* and dried activated sludge were calculated from the plot of $\ln(q_e/C_e)$ vs. q_e [25]. The calculated K_c values were then used to obtain the thermodynamic parameters (the entropy change of biosorption, ΔS°, and the enthalpy change of biosorption, ΔH°) by plotting $\ln K_c$ vs. $1/T$ (Fig. 7). The thermodynamic parameters for the biosorption of Cu^{2+} ions by *S. platensis* and dried activated sludge at various temperatures were presented in Table 5. The ΔG° values were calculated by two different equations as seen in Table 5, in order to examine the calculated K_c values. The results for ΔG° values indicated that the calculated K_c values were very close to the real equilibrium constant. The negative ΔG° values for Cu^{2+} ions indicated that the sorption of this metal on the biosorbents used was a spontaneous process. However, it should be noted that the value of ΔG° increased with an increase in temperature, indicating that the spontaneous nature of adsorption was proportional to the temperature. The negative value of ΔH° confirmed the exothermic nature of the process. The value of entropy, ΔS° was also negative which suggested a more ordered behavior or affinity of the metal ion on the sorbent at the solid–solution interface during the adsorption process.

4. Conclusions

Equilibrium, kinetic and thermodynamic studies of the biosorption of Cu^{2+} ions onto *S. platensis* and dried activated sludge revealed that these biosorbents could be effectively used. The effects of pH, biomass dosage, and temperature were investigated. The adsorption equilibrium data fitted the Langmuir model better compared to the Freundlich and Temkin models in the concentration range of 40–400 mg/L. Pseudo-second-order kinetics explained the biosorption of the metal ion better than the pseudo-first-order and Elovich kinetic models. The thermodynamic parameters indicated that the biosorption processes were spontaneous, exothermic, and more ordered in nature.

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