Biosorption of zinc from aqueous solution by cyanobacterium *Fischerella ambigua* ISC67: optimization, kinetic, isotherm and thermodynamic studies
Moein Safari and Salman Ahmady-Asbchin

**ABSTRACT**

In this present study, biosorption of Zn(II) from aqueous solution by cyanobacterium *Fischerella ambigua* was investigated in batch experiments. The effects of pH, bacterial dosage, initial Zn(II) concentration, contact time and temperature were studied. Removal process was influenced significantly by the variation of pH, biosorbent concentration, initial Zn(II) ion concentration, temperature and contact time. Optimum biosorption conditions were found to be initial pH of 5, bacterial dosage of 0.2 g/l and initial Zn(II) ion concentration of 175 mg/l at room temperature and contact time of 90 min. The maximum uptake capacity of *F. ambigua* for Zn(II) ions was found to be 98.03 mg/g at optimum conditions. The correlation coefficient for the second-order kinetic model was 0.995. The Freundlich isotherm model showed better fit to the equilibrium of the system, compared with the Langmuir model. Fourier transform infrared analysis of bacterial biomass revealed the presence of carboxyl, hydroxyl, sulfite and amino groups, which are likely responsible for the biosorption of Zn(II). The negative values of Gibbs free energy, $\Delta G^\circ$, confirm the spontaneous nature of the biosorption process. Finally, *F. ambigua* adsorption capacity was compared with other biosorbents. Results showed that *F. ambigua* was an efficient biosorbent in the removal of Zn(II) ions from an aqueous solution.

**Key words** | biosorption, *Fischerella ambigua*, FTIR, heavy metals, isotherm, kinetic

**INTRODUCTION**

Environmental contamination with heavy metals is a serious problem due to their toxicity to humans, plants and animals. Wastewaters from a variety of industries are an important source of environmental pollution (Ahmady-Asbchin et al. 2008; Flores-Garnica et al. 2015). Heavy metals constitute dangerous environmental pollution due to their high toxicity and tendency to migrate and bioaccumulate in the food chain (Dutton & Fisher 2011; Takahashi et al. 2012). Zinc (Zn(II)) is a very common heavy metal which contaminates water from a variety of industrial activities like mining, manufacturing and products such as batteries, wood, ceramics, textiles, fertilizers, and paints (Katsou et al. 2010). If the untreated industrial wastewater were discharged into the aquatic ecosystem or directly into the sewerage system, it may pose risks and hazards to humans through contact with contaminated soil or drinking of contaminated water (Balintova et al. 2012). According to the World Health Organization (WHO) drinking water standards, the maximum acceptable concentration of Zn(II) ions is 3 mg/L (WHO 1996). Higher concentrations of Zn(II) may cause difficulties to respiratory activity such as breathing rate and coughing and problems like abdominal pain, vomiting and nausea (Plum et al. 2010). Therefore, the removal of Zn(II) ions from aqueous solutions is necessary and very important.

The ever lower limits for heavy metal levels in water and wastewater discharged into the environment require new and efficient methods to remove them. Today, various methods have been applied to remove dissolved metal ions from aqueous solutions and include chemical precipitation, ion exchange, filtration, electrochemical treatment and reverse osmosis (Tsekoa et al. 2010; Shanmugaparakash & Sivakumar 2015). The main disadvantages of these methods include the relatively low efficiency of treatment in wastewater with low concentrations of metal ions. In addition, their use is energy-intensive and leads to large quantities of sludge.
of secondary impurities. Alternative methods include biotechnological processes such as biosorption or bioaccumulation. Biosorption is an alternative technology employing low-cost filtration materials and high removal efficiency of different metal concentrations (Witek-Krowiak et al. 2011; Elwakeel et al. 2012; Oguz & Ersoy 2014; Elwakeel et al. 2015; Elwakeel et al. 2017). This method allows the use of cheaper and more efficient materials for sewage and wastewater with low concentrations of impurities. The mechanism of binding biomass may take place by biosorption on the biosorbent’s surface, bioaccumulation inside cells and chemical conversion of metal ions as a result of metabolic activity. Materials of biological origin are characterized by relatively large sorption capacities and are also much cheaper, especially when using waste materials from various industries (e.g. in food industry). Various biomaterials such as bacteria, fungi, algae, yeasts and agricultural by-products have been examined for their biosorptive properties (Sulaymon et al. 2013; Tabarak et al. 2014; Ahmady-Asbcchin et al. 2015a).

In recent years, cyanobacteria has become known as a biosorbent of heavy metals in sewage and wastewater (Hussain et al. 2009). Cyanobacteria, the photosynthetic prokaryotes, are oxygen-evolving organisms that react to stress conditions (Borbely et al. 1990). Cyanobacterial strains like Oscillatoria have been investigated for their potential as a bioremediation agent, although little information is available to support their use for bioremoval of heavy metals (Solisio et al. 2006; Das 2012). Several researchers reported that cyanobacterial strains contain a variety of functional groups such as carboxyl, hydroxyl, sulfate, and other charged groups which are responsible for metal binding and thus these strains are useful for low-cost industrial wastewater treatment (Vanella & Verma 2006; Ahmad et al. 2010). Studies confirmed that cyanobacteria can both adsorb and take up metal ions within cells (Sivakami et al. 2015). Also, cyanobacteria have some advantages over other microorganisms including their greater mucilage volume with high binding affinity, large surface area, and simple nutrient requirements (Davis et al. 2003). These microorganisms are easily cultivated in a large scale in laboratory cultures, providing a low-cost biomass for the biosorption process. Therefore, in the present study, biosorption capabilities of Fischerella ambigua ISC67 strain for removal of Zn(II) ions were investigated for the first time. Factors affecting biosorption and mechanisms of biosorption were also studied. Biosorption kinetic, isotherm and thermodynamic parameters were determined from biosorption measurements.

MATERIALS AND METHODS

Microorganism and its preparation for biosorption

Biosorbent for the removal of metal ions from aqueous solutions was prepared using the cyanobacterium Fischerella ambiguca ISC67 which was acquired from the Iranian Academic Center for Education, Culture and Research, Applied Science Center, Jahad Daneshgahi, Shahid Beheshti University, Tehran, Iran. The culture was sub-cultured and maintained on BG11 minimal medium (Stanier et al. 1971), supplemented with NaN03 at a concentration of 1.5% w/v as the nitrogen source at pH 7 ± 0.2 and incubated under fluorescent light (3,000 lux) at a temperature of 28 ± 2 °C for 18 days. The complete composition of BG11 medium is shown in Table 1. Biomass was then harvested by centrifugation at 5,000 rpm for 15 min. Thereafter, the biomass was washed thoroughly with deionized distilled water and was subsequently used for metal biosorption experiments. The dry weight of cells was determined by pelleting a known volume of cell suspension and drying the pellet at 60 °C for 48 h until constant weight was obtained. The dried sample powder was then used in further experiments for Zn(II) removal from aqueous solutions.

Preparation of metal solutions

A stock solution of 1,000 ppm zinc was prepared by dissolving the Zn(NO3)2.4H2O salt (Merck) in deionized water;

<table>
<thead>
<tr>
<th>Component</th>
<th>Addition per litre culture medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO3</td>
<td>15</td>
</tr>
<tr>
<td>MgSO4.7H2O</td>
<td>7.5</td>
</tr>
<tr>
<td>CaCl2.2H2O</td>
<td>3.6</td>
</tr>
<tr>
<td>K2HPO4.3H2O</td>
<td>4</td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.6</td>
</tr>
<tr>
<td>Ferric ammonium citrate</td>
<td>0.6</td>
</tr>
<tr>
<td>EDTA (Triple x III)</td>
<td>0.1</td>
</tr>
<tr>
<td>Na2CO3</td>
<td>2</td>
</tr>
<tr>
<td>H3BO3</td>
<td>2.86</td>
</tr>
<tr>
<td>MnCl2.4H2O</td>
<td>1.81</td>
</tr>
<tr>
<td>ZnSO4.7H2O</td>
<td>0.222</td>
</tr>
<tr>
<td>Na2MoO4.2H2O</td>
<td>0.39</td>
</tr>
<tr>
<td>CuSO4.5H2O</td>
<td>0.079</td>
</tr>
<tr>
<td>Co(NO3)3.6H2O</td>
<td>0.0494</td>
</tr>
</tbody>
</table>

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the working solutions were prepared by diluting the stock solutions to the desired concentrations in deionized water. Concentrations of solutions were determined using an atomic absorption spectrophotometer (Chem Tech Analytical model CTA2000). All chemicals used in this study were of analytical-reagent grade.

Metal biosorption experiments

Batch technique adsorption studies were carried out to investigate the effect of different parameters such as biomass, contact time, temperature, initial concentration of zinc, and pH on the rate of adsorption of zinc by biomass. NaNO₃ (0.01 M) as the background electrolyte to buffer ionic strength was added to the solutions. The experiments were conducted in 250 mL flasks containing Zn(II) solution and varying biomass with varying pH from 2 to 6. The pH value was adjusted to required value using 0.1 M HNO₃ and 0.1 M NaOH. Effect of initial Zn(II) concentration from 25 to 150 mg/l and the effect of bacterial dosage from 0.5 to 2.5 g/l were studied. The mixtures were transferred onto a shaker with 100 rpm for 90 min. The biosorbent was filtered through a Whatman paper filter, then centrifuged for 10 min at 4,000 rpm. The final concentration of Zn(II) was determined by an atomic absorption spectrophotometer. Amounts of Zn(II) adsorbed by the biomass were calculated using the following equation:

\[ q = \frac{V(C_i - C_e)}{M} \]  \hspace{1cm} (1)

where \( q \) is the amount of Zn(II) adsorbed by biomass (mg/g), \( C_i \) is the initial concentration of Zn(II) (mg/l), \( C_e \) is the concentration of Zn(II) (mg/l) at equilibrium, \( V \) is the volume of the metal solution (l), and \( M \) is the mass of adsorbent (g) (Farooq et al. 2010; Lee & Chang 2011). All the experiments were performed in triplicate and the results expressed as mean values.

RESULTS AND DISCUSSION

Effect of pH

This parameter is directly related to the competitive ability of hydrogen ions against metal ions for the active sites on the biosorbent surface. Biomass may contain many functional groups (e.g. hydroxyl (OH), carboxyl (COOH) and amine (NH)) which have many important functions such as involvement in the ion exchange of the metal ions during biosorption and interfering with the combining force between the functional groups on the biomass and metal ions in the solution (Huang & Liu 2013). The effect of pH on the biosorptive capacity of Zn(II) by F. ambigua is shown in Figure 1. It can be seen from Figure 1 that the biosorptive capacity of Zn(II) by bacteria is very low at low pH values and increases with pH until reaching an optimum at pH 5.0. However, at pH higher than 5.0, the Zn(II) begins to precipitate due to formation of Zn(OH)₂. It has been shown that the affinity of cationic species for the functional groups present on the cellular surface is strongly dependent on the pH of the solution. At low pH values, cell wall ligands are closely associated with hydronium ions and restrict the biosorption of Zn(II) as a result of competition between H₃O⁺ and Zn(II) with the bacterial biosorbent cell wall ligands. As the pH increases, more ligands, such as carboxyl, phosphate, imidazole, and amino groups, would be exposed and carry negative charges which attract Zn(II) and biosorb it onto the cell surface (Joo et al. 2013).

Effect of bacterial dosage

The effect of dose (concentration) of adsorbent on adsorption of zinc was studied using different concentrations, 0.2–2.5 g/l, at the same pH, initial Zn(II) concentration and room temperature, shown in Figure 2. The optimum bacterial dosage was 0.2 g/l. The dosage of a biosorbent strongly influences the extent of biosorption. In many instances, lower biosorbent dosages yield higher uptakes. An increase in the biomass concentration generally increases the amount of solute biosorbed, due to the increased surface area of the biosorbent, which in turn increases the number of binding sites; conversely, the
quantity of biosorbed solute per unit weight of biosorbent decreases with increasing biosorbent dosage, which may be due to the complex interaction of several factors. An important factor at high sorbent dosages is that the available solute is insufficient to completely cover the available exchangeable sites on the biosorbent, usually resulting in low solute uptake. Also, the interference between binding sites due to increased biosorbent dosages cannot be overruled, as this will result in a low specific uptake (Vijayaraghavan & Yun 2008).

**Effect of initial metal concentration**

The impact of initial concentration of zinc in test solution on adsorption by biosorbent was studied at different initial Zn(II) concentration, ranging from 25 to 225 mg/l, at the same pH and room temperature. The results in Figure 3 show that the biosorption capacity \( q \) increased with the increasing initial Zn(II) concentration at the same pH and temperature; the optimum metal concentration was 175 mg/l. The initial solute concentration seems to have an impact on biosorption, with a higher concentration resulting in a high solute uptake. This is because at lower initial solute concentrations, the ratio of the initial moles of solute to the available surface area is low; subsequently, the fractional sorption becomes independent of the initial concentration. However, at higher concentrations, the sites available for sorption become fewer compared to the moles of solute present; hence, the removal of solute is strongly dependent upon the initial solute concentration. It is always necessary to identify the maximum saturation potential of a biosorbent, for which experiments should be conducted at the highest possible initial solute concentration (Vijayaraghavan & Yun 2008).

**Effect of temperature and contact time**

Temperature seems to affect biosorption only to a lesser extent within the range from 25 to 45 °C. Higher temperatures usually enhance sorption due to the increased surface activity and kinetic energy of the solute; however, physical damage to the biosorbent can be expected at higher temperatures. It is always desirable to conduct/evaluate biosorption at room temperature, as this condition is easy to replicate (Vijayaraghavan & Yun 2008). Table 2 shows that the biosorption capacity \( q \) increased with the increasing temperature. Figure 4 shows that the removal rate of Zn(II) after 120 min was constant.

**Kinetic experiments**

In order to clarify the kinetics of biosorption of Zn(II) by the cyanobacterium *F. ambigua*, the experimental data have been described using two models to determine the mechanism of the adsorption process. The pseudo-first-order model assumes that metal ion binds only to one sorption site on the sorbent surface (Chojnacka 2010). In the Lagergren model (Perez Silva et al. 2009), the rate of occupation of

<table>
<thead>
<tr>
<th>( T (^\circ C) )</th>
<th>( q ) (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>77 ± 0.57</td>
</tr>
<tr>
<td>35</td>
<td>82 ± 0.28</td>
</tr>
<tr>
<td>45</td>
<td>89 ± 0.28</td>
</tr>
</tbody>
</table>

Table 2 | Effect of temperature (pH: 6, t: 90 min, bacterial dosage – 0.5 g/l, \( C_i = 100 \) mg/l)
biosorption sites is proportional to the number of unoccupied sites:

$$\log \left[ \frac{q_e}{q_e - q_t} \right] = \frac{k_1}{2.303} t$$

where $q_e$ and $q_t$ are the amounts of adsorbed Zn(II) ions on the biosorbent at equilibrium and at time $t$ (mg/g), respectively, and $k_1$ is the equilibrium rate constant of pseudo-first-order adsorption (1/min) (Perez Silva et al. 2009). The slopes and intercepts of the plot of $\log \left( \frac{q_e - q_t}{q_t} \right)$ versus $t$ were used to obtain the first-order rate constant $k_1$ and equilibrium adsorption density $q_e$. The adsorption kinetics may also be described by the pseudo-second-order model. Metal ions are bound to two binding sites on the sorbent surface (Chojnacka 2010):

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

where $k_2$ is the equilibrium rate constant of pseudo-second-order adsorption (Perez Silva et al. 2009). The slope and intercept of plot $t/q_t$ versus $t$ were used to calculate the second-order rate constants $k_2$ and $q_e$. The straight lines obtained from the plot of $t/q_t$ versus $t$ showed good fitness of experimental data with the second-order kinetic model (Figure 5). As shown in Table 3, the correlation coefficient for the pseudo-first-order and pseudo-second-order models were found to be 0.940 and 0.995 respectively. The amounts of adsorbed Zn(II) on the biosorbent at equilibrium calculated by first- and second-order models were 164 and 99 mg/g, respectively. Experimental value of $q_e$ was 56 mg/g. Hence, it was concluded that this sorption system was better described by the second-order rate equation than by the first.

Another technique used for identifying the mechanism involved in the adsorption process is by fitting the experimental data in an intraparticle diffusion plot. The intraparticle diffusion model used here refers to the theory proposed by Weber and Morris:

$$q = f \left( \frac{D t^{1/2}}{r_p^2} \right) = k_t t^{1/2}$$

where $r_p$ is particle radius, $D$ is the effective diffusivity of solutes within the particle, $q_t$ (mg/g) is the adsorbed metal ion amount at any time and $k_t$, the intraparticle rate constant (mg/(g min$^{1/2}$)). The slope of plot $q$ versus $t^{1/2}$ gives $k_t$, which was 4.65 mg/(g min$^{1/2}$) in optimum conditions. It was observed that the Zn(II) amounts biosorbed by $F. ambigua$ have multi-linearity in that two or more steps occur (Figure 6). The first, sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where the intraparticle diffusion is rate-controlled. The third portion is final equilibrium stage where the intraparticle diffusion starts to slow down due to extremely low solute concentrations in the solution (Özer et al. 2009).

### Determination of equilibrium models

The description of the equilibrium of Zn(II) biosorption by cyanobacterium $F. ambigua$ was based on the Langmuir
and Freundlich models. The Freundlich isotherm is a nonlinear sorption model. This model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules (Khodaverdiloo & Samadi 2011). The logarithmic form of this model is:

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  

(5)

where \( K_F \) (mg/g) and \( n \) are the Freundlich constants.

The Langmuir model represents one of the first theoretical treatments of nonlinear sorption and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate (Ahluwalia & Goya 2011). The general Langmuir equation is commonly presented in linearized form as follows:

\[ \frac{C_e}{q_e} = \frac{1}{q_{\text{max}} b} + \frac{C_e}{q_{\text{max}}} \]  

(6)

where \( q_e \) is the amount of metal ion removed (mg/g), \( C_e \) is the equilibrium concentration (mg/l), \( b \) is the Langmuir constant related to affinity, and \( q_{\text{max}} \) is the maximum metal uptake under the given conditions.

The Freundlich and Langmuir constants, along with the regression coefficients, have been calculated from the corresponding plots. The Freundlich constants \( (K_F \) and \( n \)) are shown in Table 4. The \( n \) value greater than 1.0 represents favorable biosorption conditions (El-Sikaily et al. 2011). The maximum metal uptake \( (q_{\text{max}}) \) under the optimal conditions and adsorption binding constant \( (b) \) in the Langmuir model are shown in Table 4. The correlation coefficient for the Freundlich and Langmuir adsorption isotherm was found to be 0.9776 and 0.9912, respectively. \( R^2 \) value was the same for the two models, but \( q_{\text{max}} \) Langmuir was not in good agreement with the experimental data. The Freundlich type adsorption isotherm is an indication of surface heterogeneity of the adsorbent while the Langmuir model hints at surface homogeneity of the adsorbent. The experimental data for the biosorption of Zn(II) on \( F. \) ambigua is given in Figure 7.

### Characterization of biosorbent using Fourier transform infrared spectroscopy

In order to determine the main functional groups of \( F. \) ambigua participating in Zn(II) biosorption, Fourier transform infrared (FTIR) spectra of natural and metal-loaded \( F. \) ambigua were recorded (Figure 8(a) and 8(b)). There were clear band shifts and intensity change in four bands. These bands are the functional groups of \( F. \) ambigua participating in Zn(II) biosorption (C–O, S–O, C–SO\(^{-}\), O–H, N–H, and –COO\(^{-}\)).

The peak at 3,350.35 cm\(^{-1}\) was due to O–H and N–H stretching vibrations indicating the presence of both surface free hydroxyl groups. The peak at 1,635.85 cm\(^{-1}\) and 1,551.13 cm\(^{-1}\) was attributed to a C–O stretching vibration of carboxylate (–COO\(^{-}\)) or an N–H deformation vibration of amide I groups. The wavenumber that appeared at 1,078.30 cm\(^{-1}\) was attributed to the S–O link of the (C–SO\(^{-}\)) groups. Some shifts in wavenumbers from 3,350.35 cm\(^{-1}\) to 3,380.35 cm\(^{-1}\), 1,635.85 cm\(^{-1}\) to 1,638.85 cm\(^{-1}\), and 1,078.30 cm\(^{-1}\) to 1,075.30 cm\(^{-1}\) were observed.

### Table 4 | Equilibrium models for biosorption of Zn(II)

<table>
<thead>
<tr>
<th>Model</th>
<th>( K_F ) (mg/g)</th>
<th>( n )</th>
<th>( R^2 )</th>
<th>( q_{\text{max}} ) (mg/g)</th>
<th>( b ) (mg/g)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>7.13</td>
<td>2.004</td>
<td>0.9776</td>
<td>98.03</td>
<td>0.026</td>
<td>0.9912</td>
</tr>
<tr>
<td>Langmuir</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 6 | Plot of the intraparticle diffusion (Weber–Morris model) for the biosorption kinetics of Zn(II) on \( F. \) ambigua (pH = 5, T = 25°C, bacterial dosage = 0.2 g/l, \( C_i = 175 \text{ mg/l} \)).

Figure 7 | Isotherm of Zn(II) biosorption on \( F. \) ambigua (pH = 5, T = 25°C, bacterial dosage = 0.2 g/l, contact time = 120 min).

Figure 8 | FTIR spectra of natural and metal-loaded \( F. \) ambigua showing band shifts and intensity change in four bands (A) and (B) respectively.
1,735.93 cm\(^{-1}\), and 1,078.30 cm\(^{-1}\) to 1,138.29 cm\(^{-1}\) were noticed in the spectra of dried \textit{F. ambigua} before and after use. The shifts in wavenumbers suggested that amide, hydroxyl, sulfonic, and carboxylate groups could participate in Zn(II) biosorption on the surface of dried \textit{F. ambigua}.

Figure 8 | (a) FTIR spectrum of dried \textit{F. ambigua}: before use. (b) FTIR spectrum of dried \textit{F. ambigua}: after use.
Comparison with other biosorbents

Table 5 compares the maximum adsorption capacities obtained from this study with some other values reported in the literature. The adsorption capacities for Zn(II) using F. ambiguus was found to be comparable with many of the reported literature values. However, a direct comparison of experimental data is not possible, due to different experimental conditions such as pH, temperature, equilibrium time, heavy metal concentration, and biomass dosage.

Sorption mechanism

In ion exchange modeling, the release of Ca²⁺, initially fixed onto the F. ambiguus, has been followed in the same time of Zn(II) adsorption. This release depends on the initial Zn(II) concentration of the solution, which could lead to a fixation mechanism by ion exchange.

Thermodynamic study

Thermodynamic considerations of a biosorption process are applied to determine whether the process is spontaneous or not. The changes in thermodynamic parameters, Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), of the biosorption process were calculated by using the following equations (Fontana et al. 2016), respectively:

\[ K_c = \frac{q_e}{C_e} \]  

\[ \Delta G^0 = -RT \ln K_c \]  

\[ \ln K_c = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \]

where \( q_e \) and \( C_e \) are defined as the concentration of adsorbed Zn(II) on the biosorbent and residual Zn(II) concentration at equilibrium, respectively. \( K_c \) is the thermodynamic equilibrium constant (l/mol), \( R \) is the universal gas constant (8.314 J/(mol K)) and \( T \) is the temperature (K).

In a Van’t Hoff plot of ln \( K_c \) as a function of 1/\( T \), a straight line is obtained, and \( \Delta H^0 \) and \( \Delta S^0 \) were determined by the slope and intercept equation. The values of \( \Delta G^0 \), \( \Delta H^0 \), and \( \Delta S^0 \) in all experimental conditions are shown in Table 6. The change in the standard free energy \( \Delta G^0 \) with negative values at all the experimental temperatures indicated the Zn(II) biosorption process is spontaneous. The standard enthalpy and entropy changes of biosorption were 36.99 kJ/mol and 0.128 kJ/(mol K), respectively. The positive value of \( \Delta H^0 \) indicated that Zn(II) biosorption is an endothermic process. The positive value of \( \Delta S^0 \) confirms the increased randomness at the biosorbent Zn(II) solution interface during the biosorption process.

CONCLUSIONS

Biosorption is a relatively new process that has been shown to have a considerable potential for the efficient removal of pollutants from aqueous effluents. The present study gives evidence of the possible benefits of using the dry biomass of cyanobacterium F. ambiguus for the removal of heavy metals from aqueous media. The biosorption performances

Table 6 | Thermodynamic parameters for the biosorption of Zn(II) on F. ambiguus at different temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>ΔG° (kJ/mol)</th>
<th>ΔH° (kJ/mol)</th>
<th>ΔS° (kJ/(mol K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>−2.987</td>
<td></td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>−3.879</td>
<td>36.99</td>
<td>0.128</td>
</tr>
<tr>
<td>313</td>
<td>−5.440</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
are strongly affected by parameters such as initial concentration, pH, temperature and contact time. The optimum biosorption conditions were determined as initial pH 5, at temperature 25 °C, biosorbent concentration 0.2 g/l and initial Zn(II) concentration 175 mg/l. The biosorption capacity of Zn(II) increased with the increasing temperature and decreased with the increasing bacterial dosage at the same initial concentration of Zn(II), and increased with the increasing initial concentration at the same pH. It was found that the Zn(II) biosorption attained equilibrium after 120 min and this contact time was taken as the equilibrium. The Langmuir and Freundlich isotherm models were applied to the equilibrium data. The maximum uptake capacity of *F. ambigua* for Zn(II) ions was found to be 98.05 mg/g at optimum conditions. The correlation coefficient for the second-order kinetic model was 0.995. The Langmuir and Freundlich isotherm models were also applied to the equilibrium of the system, and data were better fitted with the Freundlich isotherm. The properties of the biosorbent were determined and the nature of biomass–metal ion interactions were evaluated by FTIR analysis, which showed the participation of COOH, OH, SO₃ and NH₂ groups in the biosorption process. The results obtained through this study support that the cyanobacterium *F. ambigua*, is an effective and low-cost biosorbent for Zn(II) removal from aqueous solutions.

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