Efficiency of extremophilic microbial mats for removing Pb(II), Cu(II), and Ni(II) ions from aqueous solutions

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Abstract
Two different extremophilic films were used as natural biosorbents to remove Cu(II), Ni(II), and Pb(II) from aqueous solutions. Surface area, scanning electron microscopy imaging, and Fourier transformation infrared spectroscopy were used to characterize the surfaces of the biosorbents. The results indicated high affinity of the biosorbents to remove Pb(II), Cu(II), and Ni(II), with adsorption rates ranging from 73.6 to 100% for both biosorbents. The biosorbents succeed in removing the metal ions from aqueous mixtures in the following order: Pb(II) > Cu(II) > Ni(II). The maximum removal rates of metal ions were achieved at pH 6, contact time of 150 min, biosorbent dose of 2.5 g/L, and metal ion concentration of 50 mg/L. The isothermal studies showed that both Langmuir and Freundlich models well expressed the adsorption process. Kinetically, the pseudo-second-order reaction better expressed the type of reaction than the pseudo-first-order reaction.

Keywords Biosorption · Cyanobacterial mat · Extreme habitat · Nickel · Lead · Copper

Introduction
In recent decades, humanity has increasingly understood the need to conserve the environment and different habitats. Pollution, especially with heavy metals, affects life on the planet either directly or indirectly. Toxic pollutants are generated during different stages of industrial processes (Land-Acúa et al. 2020) and mining (Beltrán-Pineda and Gómez-Rodríguez 2016). These pollutants tend to accumulate or be transported into the environment, raising alarm about toxic products (Rai and Tripathi 2007). Some heavy metals, such as Cd, Pb, Hg, As, Ni, and Cr, are found in industrial waste and cause serious problems to aquatic environments due to their accumulation, non-degradability, and their long persistence in the tissues (Gupta et al. 2016). Owing to exacerbation of the problem of toxic metals in the environment, researchers have stepped up their efforts to develop eco-friendly, low-cost, and clean techniques to overcome this issue. Bioremediation is considered one of the most promising biotechniques to clean up contaminated environments (Ali et al. 2019; Kumar 2017).

Biological treatment is carried out through bioaccumulation by living cells (Ali et al. 2016; Churchill et al. 1995) or biosorption using dry dead cells (Davis et al. 2003; Singh 2020). In biosorption, the adsorption process involves dry dead cells (solid phase) and metal ion solution (liquid phase) (Farooq et al. 2010). The high affinity between the biosorbent (dry cell biomass) and the sorbate (metal ions) leads to high attraction and binding of the sorbate onto the surface of the biosorbent (Das et al. 2008). In contrast, bioremediation involves a biological treatment through a series of steps to achieve the recovery of polluted environments using living organisms, such as plants and microorganisms (fungi, bacteria, and algae) to remove, adsorb, and degrade different dangerous pollutants (Maeir et al. 2009). Cyanobacteria and bacteria are the adsorbents most widely used to bioremediate and degrade dyes, hydrocarbons, and heavy metals (Kumar and Kundu 2020) due to their high growth rates that confer a large surface area, which permits high adsorptive capacity for heavy metal binding (Ahad et al. 2017). Jia et al. (2018) suggested that Microcystis aeruginosa may be used in the removal of toxic metal ions from eutrophic lakes. Furthermore, Sun et al. (2018) largely focused on the bioaccumulative and...
biosorptive mechanisms of metallic ion uptake by *M. aeruginosa*. Moreover, Deng et al. (2020) investigated the physiological responses of live *M. aeruginosa* to bioremove Zn and Cd. They revealed that *M. aeruginosa* has considerable potential for the remediation of heavy metal ions.

Cyanobacterial–bacterial films are widely distributed in different normal habitats (e.g., terrestrial, freshwater, and marine) as well as being found in extreme habitats such as hot springs, Antarctic ponds, and hypersaline waters (Madigan et al. 2000; Nakagawa and Fukui 2002; Singh 2014). Siwa Oasis is characterized as an extreme habitat with a high temperature of >50°C, very arid climate, and highly radioactive media with a radionuclide concentration 100 times higher than the permissible level (Misak et al. 1997; Masoud and Koike 2006). These cyanobacterial–bacterial films are composed of different fundamental bio-functional classes, such as cyanobacteria, oxygenic photosynthetic bacteria, aerobic heterotrophs and anaerobes, sulfate-reducing bacteria, and sulfur-oxidizing bacteria (Elsaid et al. 2017). Cyanobacterial–bacterial films have several advantages in comparison with other living organisms; they have a cell wall with a unique composition, high binding capacity, large surface area, low need for nutrients for growth, and greater polysaccharide volume ( Micheletti et al. 2008a; Pathak et al. 2018).

Many scientists have reported excellent biosorption removal efficiency for several cyanobacterial strains. *Oscillatoria angustissima* had high removal efficiency for Zn (dry weight of 641 mg/g) (Ahuja et al. 1999). In addition, high biosorption capacity of Cu has been reported (240, 143, and 67.93 mg/g) for *Cyanospira capsulata*, *Cyanothece* sp., and *Arthrospira platensis*, respectively (Celekli and Bozkurt 2011; Micheletti et al. 2008b; Papert et al. 2006). Abdel-Aty et al. (2013) also reported that the maximum biosorption efficiencies of *Anabaena sphearea* live cells were 121.95 and 111.1 mg/g for Cd and Pb, respectively. Ahad et al. (2017) additionally reported that *Nostoc muscorum* removed 71.4 mg/g of Cd. Moreover, high removal capacities for 1.47 and 0.65 mmol for Pb and Ni were achieved using *Lyngbya taylorii* Klimmek et al. (2001).

Both living and dead bacterial biomass can effectively be used as a biosorbent for removing toxic metals from aqueous media, even at low concentrations (Mohapatra et al. 2019; Todorova et al. 2019). Bacterial removal of heavy metals has previously been reported. For example, *Arthrobacter viscosus* has been utilized for removing Cr(VI) from aqueous solutions (Lameiras et al. 2008). The removal efficiency of *A. viscosus* was optimized by applying an *Escherichia coli* biofilm supported on granulated activated carbon (Quintelas et al. 2009). In addition, Khanafari et al. (2008) used *Bacillus circulans* to remove Pb(II) and Cr(VI) from aqueous solutions. *Pseudomonas aeruginosa* biofilm over a flexible polyvinyl conduit was also efficiently able to eliminate 85% of Cu(II) from a solution (Qureshi et al. 2001). Moreover, *E. coli* biofilm supported on kaolin had metal removal ability in the following order: Fe(III) > Cd(II) > Ni(II) > Cr(VI) (Quintelas et al. 2009).

Despite the above studies, very few studies used microbial consortia of cyanobacteria and bacteria in bioremediation treatments. Therefore, the main aim of this study was to fill the gap in the literature on such examinations of whole cyanobacterial biofilms. Another aim was to determine the adsorption efficiency of two different cyanobacterial–bacterial consortia for removing Cu, Ni, and Pb ions from mixed aqueous solutions. A further aim was to describe the different factors affecting the biosorption process, such as pH, contact duration, and adsorbent dosage.

### Materials and methods

#### Cyanobacterial samples

Microbial mats were collected from a hot spring (biosorbent 1) and a cold spring (biosorbent 2) located in Siwa Oasis in the Western Desert, Egypt. The collected samples were packed in dry clean polyethylene bags. After reaching the laboratory, the samples were washed several times with deionized water. Microbial biomass was dried at 105°C in a circulated-air oven (Binder ED 115) for 48 h, after which it was ground in an electric mill (model Kz II; Wuhan, China) and passed through a 63 μm sieve.

#### Characterization

The surface area of both biosorbents was determined according to the Brunauer–Emmett–Teller (BET) method using a Coulter SA3100 with outgas of 15 min at 150 °C (Brunauer et al. 1938). Pore diameter, pore volume, and micropore surface area were determined by the Barrett–Joyner–Halenda (BJH) method (Barrett et al. 1951). A scanning electron microscope (JEM-2100; JEOL, Tokyo Japan) at an acceleration voltage of 200 kV was used for scanning electron microscopy (SEM) imaging and energy-dispersive X-ray spectroscopy (EDX). The Fourier transform infrared (FT-IR) spectra were measured before and after metal adsorption using a spectrometer (6700 FTIR; Nicolet, USA). The samples were ground with KBr (1:100), and measurements were undertaken within the range of 400–4000 cm⁻¹.

#### Preparation of metal ion standard solutions

Analar-grade standard metal ion solutions at 1000 mg/L Cu(II), Ni(II), and Pb(II) were purchased from Sigma Company. After that, serial dilutions were prepared using...
Batch biosorption studies

Biosorption of Cu(II), Ni(II), and Pb(II) from mixed aqueous solutions is affected by several factors, such as solution pH, dose of biosorbent, contact time, and initial metal ion concentration. The optimal conditions for the biosorption process were chosen through studying the effect of solution pH at different pHs (2–9) under a contact time of 150 min and 50 mg/L metal ions concentration. The effect of biosorbent dose was studied using different dry biosorbent weights (0.5–4 g/L). The effect of contact time was investigated with different times in the range of 15–180 min, at pH 6, biosorbent dosage of 2.5 g/L, and initial metal ion concentration of 50 mg/L. Finally, the effect of the initial metal ion concentration was determined by varying this characteristic (5–50 mg/L) at constant pH 6, biosorbent dose of 2.5 g, and contact time of 150 min. Experiments were carried out in triplicate in 250 ml glass flasks for each treatment; each flask contained 100 ml of metal mixture solution with continuous stirring at 300 rpm for 150 min. Metal mixtures were centrifuged at 5000 rpm for 7 min to separate the biosorbents. The supernatants were analyzed by Perkin Elmer inductively coupled Plasma Model Optima 3000XL ICP-OES. The adsorption capacity of heavy metal ions by different microbial mat could be expressed as follows:

\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{bq_{\text{max}}} \cdot \frac{1}{c_e}
\]

where \( q_{\text{max}} \) (mg/g) is the maximum adsorption capacity, \( q_e \) is the metal ion concentration adsorbed at equilibrium (mg/g), and \( b \) (L/mg) is the Langmuir constant. The Langmuir separation constant (\( R_L \)) was calculated as follows:

\[
R_L = \frac{1}{1 + bC_i}
\]

where \( C_i \) is the initial metal ion concentration (mg/L) and \( b \) is the Langmuir constant. Separation factor (\( R_L \)) value determines the Langmuir isotherm type; if \( R_L = 0 \) (irreversible), \( R_L = 1 \) (linear), \( R_L > 1 \) (unfavorable), or \( 0 < R_L < 1 \) (favorable) (McKay et al. 1982).

Freundlich isotherm model

The Freundlich isotherm model is mainly used to describe heterogeneous adsorption on an adsorbent surface by adsorbate molecules. This model is described by the following equation:

\[
q_e = K_f C_e^{1/n}
\]

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

where \( q_e \) is the adsorbed metal amount (mg/g), \( C_e \) is the equilibrium adsorbate concentration in mg/L, \( K_f \) is the adsorbent capacity, and \( n \) is the adsorption intensity.

Kinetic study models

The pseudo-first-order model

This model supposes that the uptake of metal ions is directly proportional to the difference between saturation levels and is expressed as follows:

\[
\log(q_e - q_i) = \log(q_e) - \frac{k_1}{0.203} t
\]

where \( q_e \) is the adsorbed metal amount (mg/g), \( C_e \) is the equilibrium adsorbate concentration in mg/L, \( K_f \) is the adsorbent capacity, and \( n \) is the adsorption intensity.
where \( q_t \) is the concentration of adsorbed metal ions (mg/g) at time \( t \), \( q_e \) is the amount of adsorbed metal ions (mg/g) at equilibrium, and \( k_1 \) (min\(^{-1}\)) is the constant of the pseudo-first-order reaction.

The pseudo-second-order model

This model assumes the occurrence of chemical adsorption, involving chemical bonds forming between the biosorbent surface and adsorbate (Bernard et al. 2013). The pseudo-second-order model equation is expressed as follows:

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

where \( q_t \) is adsorbed metal ions (mg/g) at time \( t \), \( q_e \) is the amount of adsorbed metal ions (mg/g) at equilibrium, and \( k_2 \) (mg/g.min\(^{-1}\)) is the constant of the pseudo-second-order reaction.

Results and discussion

Surface area

The surface areas of biosorbents were measured to illustrate their capacity to adsorb metals (Table 1). Biosorbent 2 has larger surface area than microbial film from biosorbent 1.

Scanning electron microscope (SEM)

The morphological differences between the surfaces of biosorbents before and after the adsorption of Cu(II), Ni(II), and Pb(II) ions were detected using SEM. Figure 1a and c present SEM micrographs of biosorbent 1 and biosorbent 2 biomasses before the adsorption of metal ions, while Fig. 1b and d present SEM micrographs after the adsorption of metal ions. A relative difference of surface morphology of biosorbents between before and after the adsorption of metal ions was clearly observed. The surfaces of biosorbents consisted of several very fine particles with irregular sizes and shapes and a coarse nature, making it feasible to visualize small pores. After the complete adsorption of metal ions, the biosorbent surface exhibited an irregular structure, fragile walls, and the appearance of bright dots on the surface, which provided good evidence of the occurrence of absorption of metal ions (Fig. 1b and d). These results are supported by the findings of El-Naggar et al. (2018) on the removal of Pb\(^{2+}\) using Gelidium amansii biomass.

Electron-dispersive spectroscopy (EDX)

Elemental analysis of biosorbents was carried out using EDX spectra, which is useful for the chemical characterization and determination of the elemental composition of biosorbents (Dmytryk et al. 2014). The EDX results before and after the adsorption of metal ions are shown in Fig. 2a–d. Before adsorption, three peaks belonging to O, Ca, and C were observed in the biosorbent 1 biomass, with abundances of 50.55%, 33.8%, and 12.92%, respectively. Meanwhile, biosorbent 2 biomass showed slight differences in elemental composition, where O, Fe, and Si were observed with abundances of 43.98%, 23.0%, and 17.45%, respectively (Fig. 2a and c). After the biosorption of metal ions, peaks of Cu, Pb, and Ni appeared on the surface of biosorbent 1 with ratios of 6.61%, 3.3%, and 2.95%, respectively (Fig. 2b). Meanwhile, biosorbent 2 had the ratios of 2.28%, 1.83%, and 0.65 % for Cu, Pb and Ni, respectively (Fig. 2d) which revealed biosorption of the studied metal ions. Kim et al. (1995) and Shukla et al. (2012) found the appearance of Pb and Cr peaks in EDX spectra after the adsorption of Pb and Cr from aqueous solution.

FT-IR analysis

FT-IR spectrograms of biosorbents were measured before and after metal ion biosorption (Table 2 and Fig. 3). FT-IR detected the changes occurring on the surface of biosorbents as a result of the interaction between the different functional groups found on the biosorbent surfaces and metal ions after adsorption. FT-IR results showed several peaks for biosorbents’ functional groups before metal adsorption at 3430.7, 2922.6, 2519.5, 1800.2, 1630.5, 1422.2, 1032.7, and 874.5 cm\(^{-1}\). After adsorption, these peaks were shifted to 3415.3, 2926.5, 2510.5, 1810.2, 1620.5, 1411.3, 1020.77, and 863.6 cm\(^{-1}\), respectively (Table 2 and Fig. 3). The shifts of the peaks and the changes of their intensity depended on the interaction between metal ions and the persisting functional groups (Ali et al. 2019).

The appearance of a broad peak at 3430 cm\(^{-1}\) is attributed to O–H group stretching, revealing the presence of free hydroxyl groups of carboxylic acids (Iqbala et al. 2009). The peak appearing at 2922 cm\(^{-1}\) is assigned to the stretching vibration of C–H and =C–H of lipids (Li et al. 2007). A minor peak appearing at 2510 cm\(^{-1}\) corresponds to stretching acid O-
H. Stretching vibration of the carbonyl group C=O appeared at 1800 cm$^{-1}$ (Axson 2012). The peak at 1630 cm$^{-1}$ is attributed to stretching vibration of C=C (Gnanasambandam and Protor 2000). Weak stretching of -COO- of pectin or C=O. 

Fig. 1 SEM micrographs of biosorbent 1 a before and b after the adsorption of Cu, Ni, and Pb ions from aqueous solution and biosorbent 2 c before and d after the adsorption of Cu, Ni, and Pb ions from aqueous solution.

Fig. 2 Energy-dispersive spectra (EDX) of biosorbent 1 a before and b after the adsorption of Cu, Ni, and Pb ions and biosorbent 2 c before and d after the adsorption of Cu, Ni, and Pb ions.
of amide was observed at 1032 cm$^{-1}$ (Fig. 3). In general, FT-IR analysis indicated that carbonyl, carboxyl, free hydroxyl, methylene, and carbonate groups are responsible for metal biosorption.

The sorption of metal ions onto the biosorbent surface through the formation of a complex was associated with two or more metal ions (Kanamarlapudi et al. 2018). Monodentate and/or multidentate complexes are formed between the ligand

### Table 2

| Wavenumber (cm$^{-1}$) | Attribution | Before adsorption | After adsorption | Attribution |
|------------------------|-------------|-------------------|------------------|-------------|
| 3430.74                | Stretching O-H | 3415.31           | 3410.94          | O-H stretching of hydroxyl group |
| 2922.59                | -C-H and =C-H stretching vibration | 2926.45           | 2925.48          | =C-H and =C-H stretching vibration of methyl and methylene groups |
| 2519.54                | Stretching acid O-H | 2510.54           | 2510.54          | C=O carbonyl group |
| 1800.22                | C=O carbonyl group | 1810.19           | 1809.26          | C=O carbonyl group |
| 1630.52                | C=C stretching | 1620.55           | 1620.55          | C=C stretching |
| 1422.24                | Epoxy C-O groups | 1411.28           | 1411.28          | Epoxy C-O groups |
| 1032.69                | Weak stretching of -COO- of pectin, C=O amide | 1020.77           | 1020.77          | Weak stretching of -COO- of pectin, C=O amide |
| 874.56                 | Alkyl halide stretching C-Cl | 863.60           | 863.60           | Alkyl halide stretching C-Cl |
| 712.57                 | Alkyl halide stretching C-I | 712.57           | 712.57           | Alkyl halide stretching C-I |
| 609.40                 | Alkyl halide stretching C-I | 609.40           | 609.40           | Alkyl halide stretching C-I |
| 461.87                 | Alkyl halide stretching C-I | 461.87           | 461.87           | Alkyl halide stretching C-I |

**Fig. 3** FT-IR spectra of a biosorbent 1 biomass and b biosorbent 2 biomass before (black line) and after (red line) biosorption of metal ions from aqueous solution
and metal ion(s). The central metal ion carries a positive charge depending on the number of binding ligands involved. Furthermore, the activity of functional groups on the surface of the biosorbents and the competition of metal ions to form complexes with the available ligands play an important role in the biosorption process. The competition between metal ions and protons for binding sites means that the biosorption of metal ions is often decreased at low pH.

**Batch biosorption experiments**

**Effect of pH**

Biosorption results of Cu(II), Ni(II), and Pb(II) ions at different pH values of the solutions are shown in Fig. 4a and b. The results show decreases in the efficiency of removal of both biosorbents at low pH, especially < 4.5, because the biosorbents’ surfaces were protonated by excess H⁺ ions, which compete with the positive Cu⁺², Ni⁺², and Pb⁺² ions for active binding sites on the biosorbents’ surfaces. In contrast, H⁺ ions have low abundance at higher pH, and the active binding sites become negatively charged; thus, the functional groups are free and the biosorption of positively charged metal ions is increased (Singh 2020). The maximum removal percentages of Pb(II), Cu(II), and Ni(II) reached 100%, 93.2%, and 73.6% for biosorbent 1, which were achieved at pH 6. Biosorbent 2 shows slight increases of the removal percentages, which reached 100%, 94.2%, and 74.6% for Pb(II), Cu(II), and Ni(II), respectively (Fig. 4b). Slightly acidic pH (5–6.5) was reported as being optimal for metal removal (Table 3), while pH values of 6–6.5 were optimal for removing Cu(II), Ni(II), and Pb(II) using Sargassum sp. and Chaetoceros sp. as biosorbents, respectively (Molazadeh et al. 2015; Barquilha et al. 2019). Similarly, pH 6 was optimal for the biosorption of Cd(II) and Ni(II) using Cystoseira indica (Khajavian et al. 2019).

![Fig. 4](environ-sci-pollut-res-28-53365-53378_f4.png)
Effect of contact time

Contact time plays an important role in the biosorption of metal ions onto the surface of different biosorbents. The rate of biosorption is very rapid in the beginning of the reaction, as a result of the availability and vacancy of all active binding sites. With the passing of time, the biosorption rate decreases because of a decrease of active site availability (Michalak et al. 2013). The biosorption of Cu(II), Ni(II), and Pb(II) onto the surfaces of biosorbent 1 and biosorbent 2 is shown in Fig. 5 A and B). The results showed that the uptake of Cu and Pb by the two biosorbents rapidly reached about 70% during the first 30 min, while the rate for Ni was lower (45%). The rates became lower with the passing of time until the maximum removal efficiency was reached after 150 min; then, the rate tended to be steady (Fig. 5 A and B). Furthermore, the results indicated the complete removal of Pb(II) and Cu(II) onto the surface of biosorbent 1 after 150 min with qe of 49.8 and 48.8 mg/g, followed by Ni(II) with a removal percentage of 68.1% (qe = 33.9 mg/g). Biosorbent 2 showed lower efficiency for the removal of metal ions, with ratios of 93.2%, 91.2%, and 65% for Pb(II), Cu(II), and Ni(II), respectively. Some algal species, such as Chlorella sp., showed a low contact time (60 min) for the maximum adsorption of Cd at a pH of 7.5 (Leong and Chang 2020). Spirulina platensis showed maximum biosorption efficiency for removing Cd after 90 min (Al-Homaidan et al. 2015), while Synechococcus sp. reached its maximum removal percentage for Ni, Cu, and Pb after 80 min (Gardea-Torresdley et al. 1998) (Table 3).

Effect of biosorbent dose

In general, the increase of microbial biomass is accompanied by an increase of adsorption of metal ions due to the availability of a large surface area, providing an increasing number of active binding sites (Michalak et al. 2013). Therefore, variations of biosorbent doses are regarded as an important factor affecting the biosorption process (Dixit and Singh 2013). The effects of various biosorbent doses (0.5 to 5 g/L) for the removal of Cu(II), Ni(II), and Pb(II) were thus studied (Fig. 6 A and B). A significant rapid increase of biosorption rates was observed with increasing biosorbent dose from 0.5 to 2.5 g/L, while further increases of the dose did not cause a significant increase in the biosorption rate. The results revealed that the maximum removal ratios of biosorbent 1 reached 98.7%, 82.6%, and 72.9% for Pb, Cu, and Ni, respectively (Fig.
Slight decrease of biosorption efficiency of biosorbent 2 than of biosorbent 1 was observed. The maximum removal ratios of biosorbent 2 reached 95.9%, 80.3%, and 72.4% for Pb, Cu, and Ni, respectively (Fig. 6B). The obtained results are in agreement with several studies that used different algal species for metal ion adsorption. Dirbaz and Roosta (2018) reported 120 min as the optimal contact time for the maximum adsorption of Cd onto the surface of *Parachlorella* sp., while *Synechococcus* sp. needed 80 min for the maximum adsorption of Ni, Cu, and Pb (Gardea-Torresdey et al. 1998).

**Effect of initial metal concentration**

Biosorption capacity increased with increasing metal concentration due to the available free active binding sites for interaction. A further increase of metal concentration was shown due to active binding sites being occupied, stopping further biosorption (Michalak et al. 2013). The biosorption of Cu, Ni, and Pb increased with increases of their initial concentrations from 5 to 50 mg/L (Fig. 7 A and B), while further increases of their concentrations had insignificant effects on the biosorption rate, which means that the reaction had reached its saturation point (Ahad et al. 2017). The maximum removal ratios of biosorbents reached to 100%, 91.0% and 74.3% for Pb, Cu, and Ni, respectively, at a metal ion concentration of 50 mg/L, with corresponding adsorption capacity $q_e$ of 49.8, 44.5, and 38.5 mg/g (Fig. 6 A and B).

**Adsorption equilibrium isotherms**

Calculated Langmuir and Freundlich constants for the biosorption of Pb(II), Cu(II), and Ni(II) onto the surface of used biosorbents are shown in Table 4 and graphically presented in Figs. 8 and 9. The results showed that both Langmuir and Freundlich models are well suited to describe the isothermal biosorption type, with $R^2 > 0.95$. A narrow difference between the adsorption capacities of the two biosorbents was observed. At an $L$ range of $0 < L < 1$, favorable adsorption of Pb(II), Cu(II), and Ni(II) was achieved (Table 4). The lower values of $< 1$ for the studied metal ions revealed that the adsorption is a chemical adsorption process (Desta 2013).

**Kinetic studies**

Biosorption kinetics is an important factor to evaluate biosorption efficiency (Moghadam et al. 2013). Thus, pseudo-first-order and pseudo-second-order models were used to illustrate the kinetics of the biosorption of Pb(II), Cu(II), and Ni(II) onto the surfaces of the two cyanobacterial biosorbents. The kinetic constants and linear plots of the

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**Table 4** Langmuir and Freundlich isotherm constants for Pb, Cu, and Ni biosorption onto the surfaces of biosorbent 1 and biosorbent 2

|       | Langmuir | Freundlich |
|-------|----------|------------|
|       | Biosorbent 1 | Biosorbent 2 | Biosorbent 1 | Biosorbent 2 |
| Pb    | b | $Q_{max}$ | $R_L$ | $R^2$ | b | $Q_{max}$ | $R_L$ | $R^2$ | $K_f$ | n | $R^2$ | $K_f$ | n | $R^2$ |
|      | 0.46 | 11.29 | 0.04 | 0.98 | 0.35 | 17.51 | 0.05 | 0.97 | 11.21 | 0.52 | 10.51 | 0.60 | 0.97 |
| Cu    | 0.20 | 12.09 | 0.09 | 0.97 | 0.16 | 11.74 | 0.11 | 0.98 | 2.73 | 0.59 | 1.70 | 0.55 | 0.94 |
| Ni    | 0.04 | 1.63  | 0.33 | 1.00 | 0.22 | 2.78  | 0.08 | 0.98 | 1.29 | 0.66 | 7.52 | 0.62 | 0.99 |
pseudo-first- and pseudo-second-order reactions are given in Table 5 and presented graphically in Figs. 10 and 11. In accordance with the constants calculated for both biosorbents, we can conclude that biosorption of the studied metals followed the pseudo-second-order reaction. The recorded $q_e$ ranged between 19.72 and 26.3 and 18.97 and 24.1 mg/g for the two biosorbents, with $R^2$ exceeding 0.99.

**Conclusion**

Two different microbial mats inhabiting extreme habitats were collected from a hot spring (biosorbent 1) and a cold spring (biosorbent 2) and were used to remove Pb(II), Cu(II), and Ni(II) ions from aqueous solutions. The microbial mats showed excellent affinity for adsorbing and removing metal ions from mixed aqueous solutions. The maximum biosorption efficiency for Pb(II), Cu(II), and Ni(II) for two biosorbents was achieved at pH 6, contact time of 150 min, biosorbent dose of 2.5 g/L, and initial metal ion concentration of 50 mg/L. Biosorbent 1 achieved maximum adsorption capacity of 46.26, 44.5, and 38.5 mg/g, whereas biosorbent 2 showed slight increases reaching 47.26, 45.1, and 38.3 mg/g for Pb(II), Cu(II), and Ni(II), respectively. Isothermal data revealed good representation with both Langmuir and Freundlich models, and the results showed that biosorption capacity was in the following order: Pb > Cu > Ni ions. Kinetically, the biosorption reaction obeyed the pseudo-
Table 5  Constants of pseudo-first-order and pseudo-second-order reactions for biosorption of Pb(II), Cu(II), and Ni(II) onto the surface of cyanobacterial biosorbents

|      | Biosorbent 1 | Biosorbent 2 |      | Biosorbent 1 | Biosorbent 2 |
|------|--------------|--------------|------|--------------|--------------|
|      | qₑ             | K₁            | R²   | qₑ             | K₁            | R²   |
| Pb   | 5.35          | 0.011         | 0.845 | 4.44          | 0.011         | 0.876|
| Cu   | 6.22          | 0.012         | 0.855 | 10.74         | 0.032         | 0.948|
| Ni   | 8.80          | 0.020         | 0.890 | 6.25          | 0.014         | 0.860|
|      | qₑ             | K₂            | R²   | qₑ             | K₂            | R²   |
| Pb   | 26.11         | 0.005         | 0.994 | 24.10         | 0.006         | 0.999|
| Cu   | 26.32         | 0.004         | 0.999 | 23.64         | 0.006         | 0.999|
| Ni   | 19.72         | 0.004         | 0.995 | 18.97         | 0.006         | 0.993|

Fig. 10  Pseudo-first-order reaction plot for biosorption of Pb(II), Cu(II), and (Ni(II) ions by cyanobacterial biosorbents biomass.

Fig. 11  Pseudo-second-order reaction plot for biosorption of Pb(II), Cu(II), and (Ni(II) ions by cyanobacterial biosorbents biomass.
second-order reaction model, with $q_e$ ranging between 19.72 and 26.32 mg/g and $R^2 > 0.99$

**Availability of data and materials** All data generated or analyzed during this study are included in this published article.

**Author contribution** Khairia M. Al-Qahtani performed final revision and editing of the manuscript and supported the work through the allowed fund. Mohamed H.H. Ali conceived, designed, and performed the experiments and wrote the manuscript. Afify D.G. Al-Afify and Mohamed S. Abdelkarim contributed to the experiments and analyzed the data. All authors read and approved the final manuscript.

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**Declarations**

**Ethics approval and consent to participate** Not applicable

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