Adsorptive performance of a mixture of three nonliving algae classes for nickel remediation in synthesized wastewater

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Abstract

Purpose The present study provided a comprehensive description regarding the application of a mixture of three nonliving classes of algae as a promising and inexpensive biosorbent for removing toxic nickel (Ni(II)) ions from the aqueous medium.

Methods The biosorption process was tested by varying several experimental parameters such as pH (2–8), contaminant concentration (20–300 mg/L), biosorbent content (0.2–2 g/100 mL), and temperature (20–40 °C). In addition, the competition effects of the presence of Pb(II), Cu(II), and Zn(II) ions on the Ni(II) removal efficiency was studied by varying their concentrations from 30 to 40 mg/L.

Results The microscopic analysis of algae demonstrated that the used biosorbent consisted mainly of Chrysophyta (80%), Chlorophyte (14%), and Cyanophyta (6%). Results demonstrated that these environmental parameters influenced the removal efficiency with a different degree and there was no stable effects rank at conditions under examination. FT-IR and SEM analysis revealed that the biosorbent surface consists of many strong and active groups of negative valences such as hydroxyl and carboxyl groups, thus exhibiting several morphological properties of interest. Further, it was found that the Temkin model best fitted the isotherm biosorption data. The kinetic study showed that the Ni(II) biosorption was rapid within first 20 min of reaction time, thereby following a pseudo-second-order model, which in turn demonstrated a chemisorption process of Ni(II) ions reaction with the biosorbent binding sites. Also, the thermodynamic study suggested that the biosorption process of Ni(II) onto algal biomass was a spontaneous and endothermic in nature. The maximum uptake of Ni(II) was 9.848 mg/g under optimized conditions and neutral environment.

Conclusions Thus, this significant finding suggested a favorable and eco-friendly treatment mechanism for removal of Ni(II) ions from aqueous medium via biosorption onto the used mixture of nonliving algal biomass.

Keywords Algal biomass · Nickel · Biosorption · Isotherm, Kinetic · Thermodynamic

Introduction

Spurt and booming of urbanization and industrialization have led to rise in the concentration of several toxic contaminants sometimes over the acceptable limits in the aquatic environment [24, 46, 36]. Among these contaminants, heavy metals are the one which is often detected, in the water sources and drinking water [4, 51]. These hazardous elements can lead to extremely harmful effects to human and ecosystem organisms,

upon continuous exposure to even low concentrations of metals [21, 40]. Heavy metals that have a major worry in treatment systems include nickel, chromium, zinc, cadmium, arsenic, lead, copper, cobalt, and mercury. Nickel (Ni(II)), the metallic ion, which is picked up as model inorganic contaminant in the present study, is found at an elevated level in the effluents from several industries which includes mining, metallurgy of Ni(II), pigments, ceramic, zinc base casting, electroplating, and stainless steel production [8]. World health organization has classified Ni(II) as a humanoid carcinogenic element and prescribed it as toxic if consumed above 0.5 mg/L, which is the maximum permissible concentration in drinking water [49]. Though Ni(II) is prerequisite in small quantities for various biological metabolisms, nevertheless, this metal in high concentrations is considered as toxic for living organisms [26]. Additionally Ni(II) ions, like other metals, were

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characterized based on their non-biodegradability and persistence ability in the environment. Therefore, they are capable of accumulating in human's active tissues causing many carcinogenic diseases and mutations at birth levels [1]. Thus, it is imperative to enable monitoring of this metal during wastewater and industrial waste treatment before being discharged into water bodies [22].

Various advanced techniques for treatment and removal of heavy metal from wastewater underwent trial in many studies [21, 34]. Among them, ion-exchange, precipitation, evaporation, membrane separation, flotation, and adsorption have been well utilized for this purpose [7]. Indeed, the abovementioned treatment methods are effective only to a certain extent, thereby imparting one or more restrictions. Generally, these methods are (i) expensive, (ii) demonstrate low removal percentage, (iii) require sensitive operating conditions, (iv) produce a huge quantity of sludge, and (v) exhibit problems during extraction of sorbent from sorbate [38]. Thus, keeping in mind the above limitations, enormous efforts are invested by scientists to find an alternative treatment method. In this context, the biosorption process, which uses agricultural or natural wastes is a promising treatment method and is being suggested in the literature as an efficient technique for removal of harmful contaminants up to permissible level [48]. Evaluations of different low cost, efficient, nonhazardous, and abundant biosorbents for the eradication of different contaminants have been carried out [33]. Results showed that there is a possibility to reach up to 100% removal efficiency. From this perspective, nonliving algal biomass has occupied a prominent place in recent studies due to its remarkable adsorptive properties especially towards heavy metals. Further, this phenomenon occurred due to the surface properties of this biomass, which consists of several negatively charged active groups such as amino, hydroxyl, carboxyl, and sulfate. Therefore, it acts as a binding site for positively charged metals via both complexation and electrostatic attraction process [11, 44].

Mostly, the biosorption capacity of one species of algae in virgin or modified form has been studied, by various researchers such as Jaafari and Yaghmaeian [21]; Ratnasri and Hemalatha [39]; and Akbari et al. [1]. To the authors' knowledge, however, little research has been done regarding the use of algae mixture, belonging to three different classes, as a biosorbent material for Ni(II) ion removal. Therefore, the current investigation was carried out with the aim to fill the gap that exists in the research literature by examining the role of a mixture of three nonliving algal biomass, belonging to classes viz. Chrysophyta, Cyanophyta, and Chlorophyte, as an adsorbent toward Ni(II) ions, being sequestered from simulated wastewater. The mechanisms of interactions between the metal ions and the biosorbent in a solid-liquid couple along with the effects of different environmental parameters were also reported, in addition to, the detailed mechanism of isotherm, kinetic, and thermodynamic adsorption process.

Materials and methods

Biosorbent

The total amount of naturally available algal biomass was collected from selected location in the Tigris River in Baghdad (Iraq). Three samples of collected algae were analysed for their classes by using microscope. These analyses were achieved according to the standard methods [5] in laboratories of Iraqi Ministry of Sciences and Technology/ Water Treatment Directory. The weight percentage (wt.%) to major classes of the collected algae under examination, is given as 80% Chrysophyta, 14% Chlorophyte, and 6% Cyanophyta. The collected samples were washed, repeatedly with tap water to get rid of the impurities, dirt, and other unwanted materials. Further, the clean biomass obtained was washed twice with distilled water followed by filtration. Subsequently, the washed nonliving algal biomass was sun dried for 3.0 days, oven dried at 60 °C for 3.0 h, grounded in a mechanical grinder, and were finally passed through sieves to obtain particle size larger than 500 µm. The prepared nonliving algal biomass particles were stored in tight polyethylene container to ensure that the prepared particles do not get moistened until being fully used in the experiments. Functional groups analysis of nonliving algal biomass particles was performed using Fourier transform infrared (FT-IR) spectroscopy instrument in the wave number range of 400–4000 cm⁻¹. For this purpose, the nonliving algal biomass particles were crushed, mixed with KBr, and made into pellet samples, while Brunauer–Emmett–Teller (BET) analysis was performed using Belsorp mini II instrument. Moreover, to elucidate the fundamental morphological characteristics of the prepared dead algal biomass, SEM images before and after adsorption at a scale bar of 0.5 mm, were captured.

Chemicals

Powdered nickel nitrate of analytical grade was obtained from Merch Co. (chemical formula: Ni(NO₃)₂·6H₂O, molecular weight: 290.81 g/mol, solubility: 94.2 g/100 mL water, and purity: 99%). Further, to prepare and dilute the Ni(II) stock solution (1000 mg/L) as well as all working reagents used throughout the experiments stages, deionized water was employed. The prepared metal solutions were stored in a refrigerator under slightly acidic medium to prevent metal precipitation until further used for biosorption experiments. Additionally, the pH value was regulated, throughout the experimental work by using 1.0 N of HCl and NaOH solutions.

The pH of point zero charge (pH_{pzc})

The determination of pH_{pzc} of nonliving algal biomass was carried out according to the conventional method, which is

based on previous studies [32, 42]. Thus, nine flasks filled with 50 mL of 0.1 M NaCl solution were adjusted to the initial pH of 2.0 to 10 using 0.1 M NaOH or HCl solutions, followed by addition of 0.5 g of dried powdered biosorbent to each flask. To further equilibrate the condition, the mixture obtained undergoes vigorous shaking to for 24 h at a speed of 150 rpm. The final pH was noted and plotted versus initial pH, where the intersection point of the two curves determines the pH_{pzc} of the biomass.

Adsorption experiments

The experimental work was conducted in a batch mode using a series of 250 mL flasks containing 100 mL of Ni(II) solution. To optimize the adsorption conditions in the subsequent isotherm and kinetic experiments, the metal adsorption process onto used adsorbent were investigated by varying the pH (2–8), contact time (0–120 min), initial Ni(II) concentration (20–300 mg/L), biosorbent dose (0.2–2 g/100 mL), and temperature (20–40 °C). In addition, the effects of the expected competitor ions was studied regarding to the presence of Pb(II), Cu(II), and Zn(II) ions in concentration of 30, 35, and 40 mg/L. The flasks were shaken at a constant speed of 150 rpm using an incubator shaker and were allowed to equilibrate as determined from contact time experiment. At specific time interval of each test, aliquots of 0.1 mL from each solution was withdrawn, filtered, centrifuged, and then analyzed for Ni(II) concentration using the flame atomic absorption spectrophotometer (Model: 210 VGP, USA). Notably, the results obtained from the effects of the biosorbent dose, contact time, and the temperature, was subsequently applied for the isotherm, kinetic, and thermodynamic studies, respectively. The quantity of biosorbed Ni(II) onto nonliving algal biomass (q_e , mg/g) and the removal efficiency ($R\%$) were determined using Eqs. 1 and 2, respectively.

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (1)$$

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where C_0 and C_e are the initial and equilibrium Ni(II) concentrations (mg/L), respectively, the volume of Ni(II) solution in (L) is denoted by V , and M is the quantity of the used nonliving algal biomass (g).

Results and discussion

Biosorbent characterization

The BET analysis was measured by nitrogen adsorption isotherm, which is revealed that the surface area and pore volume

of the used biosorbent were found to be 3.24 m²/g and 0.101 cm³/g, respectively. FTIR spectra were conducted to indicate the nature of the cell wall active groups onto nonliving algal biomass that explains the biosorption of the Ni(II) ions (Fig. 1a). For FTIR analysis of nonliving algal biomass, prior Ni(II) biosorption (solid black line in Fig. 1a), strong peaks were detected in the range of 3471.61 to 3259.47 cm⁻¹, which belongs to hydroxyl (–OH) and amine (–NH) functional group [6], while the bands found between 2962.46–2516.93 cm⁻¹ are denoted to the presence of alkyl chains (C–H stretch) [45]. Bands found at 1799.48, 1637.45, and 1427.23 cm⁻¹ were corresponding to the carboxylates groups [25]. The intense band detected in the range of 1159.14 to 445.53 cm⁻¹ were related to the –C–O, C–C, –C–OH, and –C–H aromatic functional groups [3, 43]. After Ni(II) adsorption (dotted red line in Fig. 1b), the absorbency of all abovementioned peaks changed, which further explains the interaction between the active sites and the Ni(II) ions.

Clearly, some peaks were more intense after the adsorption process, such as peak at 3400, 2900, and 2500 cm⁻¹. This phenomenon can be represented as the first evidence of the adhering of the metal ions onto algal biomass. The shift in the intensity of these groups after biosorption signifies their role in the binding of Ni(II) ions in the liquid-solid phase. The degree of shifting is related to the active group participation either through precipitation or by developing some electrostatic bonds to sorb the contaminant molecules [47].

Figure 1b and c are the SEM images of the algal biomass corresponding to prior and post unloading with Ni(II), respectively. From the micrograph of unloaded algal biomass, it is evident that the surface of this biosorbent consists of several fine filaments of irregular sizes. Additionally, it seems that the surface of algal biomass is of coarse nature which in turn made feasible to visualize small pores. These significant features impart a favorable property onto the outer and inner surface of algal biomass, for Ni(II) reaction, since these characteristics increase the surface area of the contaminants reaction. After the Ni(II) reaction onto algal biomass, the surface morphology of this biosorbent appears to be unaffected by Ni(II) biosorption as shown in Fig. 1c.

Effect study

In the environmental engineering applications, the metal removal efficiency must be considered at different pH values since the metal ion sorption varies significantly by the pH of the solution. This parameter exhibits effects to a great extent on the sorption property and surface charge of the sorbent active sites [16]. Therefore for a particular use, determination of the optimum pH of Ni(II) ions biosorption onto nonliving algal biomass has become essential. Figure 2 depicts the variation of Ni(II) removal efficiency as a function of pH. Initially, the analysis revealed that the pH_{pzc} of nonliving algal

Fig. 1 **a** FTIR analysis and SEM of nonliving algal biomass **b** prior and **c** post Ni(II) biosorption

biomass was found to be approximately 5.8, which indicates that beyond this pH value the surface of this biomass will be negatively charged (inner figure in Fig. 2). The current investigation further highlights the effect of the pH solution in the range of 2 to 8. To prevent removal of Ni(II), by other mechanisms like precipitation pH > 8 was excluded from effect study. Thus, at pH 7, the maximum biosorption efficiency of 75% was observed. Alternatively, at pH less than 6, the Ni(II) removal efficiency gets hampered since the metal ions undergo repulsion by the positively charged surface of algal biomass which has

$\text{pH}_{\text{zpc}} = 5.8$. Indeed, at $\text{pH} < \text{pH}_{\text{zpc}}$, high H^+ concentration competes with the Ni(II) cations for the negatively charged sites of the biosorbent. In contrary, when the pH of the solution increases above pH_{zpc} , the negatively charged active sites, present on the surface, increases the metal removal efficiency [37], thereby enabling removal of metals in a sizeable amount. Thus, the occurrence of an insignificant variation in the Ni(II) removal efficiency at $\text{pH} > 6$ was evident.

Above pH 7, the removal efficiency was diminished slightly due to the reaction of Ni(II) cations with OH^- anions to

Fig. 2 Effects of solution pH on the Ni(II) removal efficiency and pHzpc determination of nonliving algal biomass (Ni(II) concentration = 35 mg/L; algal biomass dose = 0.5/100 mL, temperature = 25 °C, shaking speed = 150 rpm for 2 h)

form relatively stable ions in the bulk solution phase. Therefore, the number of available Ni(II) ions for adsorption decreases [16]. However, relatively high removal efficiencies between pH 6 and 7 were determined. This significant phenomenon established a favorable and eco-friendly treatment method of Ni(II) adsorption onto algal biomass since almost all natural water bodies are within near neutral pH. In summary, subsequent biosorption experiments will be carried out at pH 7. Similar results have been reported in various studies during the removal of different metals onto nonliving algal biomass [37, 45] and onto other sorbents (Samarghandi et al., 2015; Noorzi et al., 2018).

The effect of varying the biosorbent content on the contaminant biosorption was investigated, at algal quantities from 0.2 to 2 g/100 mL of solution (Fig. 3 a). From this figure, the percentage removal of Ni(II) biosorption increased from 40.82 to 90.63% by increasing algal biomass dosage from 0.2 to 1 g/100 mL and then plateaued was attended. The reason for this behavior is the rise in the adsorbent amount in the aqueous solution, which in turn increases the surface area or binding sites for pollutant sorption [31]. Furthermore, the agglomeration of some algae particles in the solution was behind

the reason of stability in the percentage removal by a further increase in the adsorbent dose above 1 g per 100 mL of Ni(II) solution [30].

The effects of the variation of initial Ni(II) concentration on its removal efficiency was examined, within range of 20–300 mg/L and contact time from the inception to 120 min (Fig. 3b). The adsorption process was rapid initially and subsequently reaches the equilibrium within 20 min. However, a further increase above 20 min in the experiment time, had a negligible improvement in Ni(II) adsorption rate. The fast adsorption in the first part of biosorption process can be attributed, to the availability of high number of uncovered active groups on the outer surface of the biosorbent having a high affinity for the metal ions. These active sites provide a high probability for the pollutant ions to adhere to them. Subsequently, the required sites for the sequestration of Ni(II) will lack, thereby reaching the saturation condition. Indeed, the fast adsorption process imparts a positive property to the non-living algal biomass to be an excellent agent for practical applications in the adsorption units. Moreover, the Ni(II) removal efficiency at equilibrium was markedly lowered from 96.75 to 62.20% with an increase in the initial Ni(II) concentration from 20 to 300 mg/L, respectively. It occurs due to the saturation of the adsorbent surface sites at high Ni(II) concentration, thus some metal ions are not adsorbed, which in turn decreases the metal removal efficiency. However, the amount of Ni(II) ions removed at equilibrium condition were increased with the increase of Ni(II) concentration from 20 to 300 mg/L. This is due to the fact that with increased Ni(II) concentration, the driving force for mass transfer also increases [13, 46].

Effect of temperature and thermodynamic study

Notably, the varying temperature exhibited a feeble effect on the removal efficiency as reported in Table 1. Further, an increase in the temperature from 20 (293) to 40 °C (313 K)

Fig. 3 Effect of **a** algal biomass dose using 35 mg/L initial Ni(II) concentration, and **b** initial Ni(II) concentration on the Ni(II) removal efficiency (pH = 7, temperature = 25 °C, shaking speed = 150 rpm for 2 h)

showed limited improvement in the Ni(II) removal efficiency ($R\%$) from 90.10 to 96.56%. This behavior of the enhancement of sorption reaction rate with the elevation of temperature is due to increase in diffusion rate of metal ions across the bulk and internal boundaries of the algal biomass particles [46]. Also, one can conclude that the biosorption process of Ni(II) onto used nonliving algal biomass is an endothermic process in nature. Eventually, the thermodynamic parameters of Gibbs free energy change (ΔG° , kJ/mol), enthalpy change (ΔH° , kJ/mol) and entropy change (ΔS° , kJ/mol.K), were determined for interpreting the spontaneous degree of the biosorption process. These parameters were calculated using the results obtained from the temperature effect experiment and the Eqs. 3 and 4 [29, 35], and the results obtained are tabulated in Table 1.

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3)$$

$$\Delta G^\circ = -RT \ln K_c \quad (4)$$

where K_c is the equilibrium constant defined by the ratio of the concentration of Ni(II) biosorbed (mg/L) and the equilibrium concentration (mg/L), R is the universal gas constant (8.314 J/mol. K), and T stands for the solution temperature (K).

The values of ΔG° were negative which further decreases with an increase in the temperature suggesting that the biosorption is a spontaneous process, being inversely proportional to the temperature. However, the positive numbers of both ΔH° and ΔS° demonstrated the endothermic nature of Ni(II) biosorption onto nonliving algal biomass and an increase in randomness during the interaction at the liquid-solid phase [14].

Effect of competitor ions

The wastewater effluents from industries have a high content of refractory pollutants such as metal ions. In the biosorption treatment systems, these ions interact among them with the sorbent used in different ways and different capacity, thus competing for the binding sites of the sorbent [25]. Therefore, the competing effect on Ni(II) biosorption, resulted from the present three competitor metals such as Pb(II),

Cu(II), and Zn(II), were examined at pH = 6, biosorbent dose 1 g/100 ml, and 25 °C. A series of experiments were conducted using 30, 35, and 40 mg/L of Pb(II), Cu(II), and Zn(II), respectively, while fixing the Ni(II) concentration at 35 mg/L in all solutions. The plotted results in Fig. 4 reveals that Pb(II) can significantly compete for the Ni(II) ion. Thus, the removal efficiency of Ni(II) ions decreases from 90.63% in absence of competitor ion solution to 70.09; 55.49; 45.33% in presence of 30, 35, and 40 mg/L of Pb(II) solutions, respectively. The other two metals also showed interference with the Ni(II) sorption but with a lesser degree than Pb(II). For all range of concentrations, the competitor effect can be ranked, based on the competitor effect, in the order of Pb(II), Cu(II), and Zn(II). This behavior can be explained by the strong valence of Pb(II) toward active sites of algal biomass in comparison to other metal ions.

Isotherm study

The equilibrium isotherm data (derived from Fig. 3a) were modeled using the Langmuir, Freundlich, and Temkin isotherm models given by Eqs. 5, 6 and 7, respectively [15, 17, 28]. For further information about the scientific backgrounds and the physical meaning of the parameters of these widely used models; the following references (i) [1]; (ii) [50]; and (iii) [15], have been referred. The parameters of each model as well as the statistical error parameters of sum square error (SSE) and chi-square test (X^2), were determined by nonlinear regression of Levenberg-Marquardt algorithm built in STATISTICA program, with the results being tabulated in Table 2. Moreover, Fig. 5 depicts the theoretical and experimental results of Ni(II) biosorption isotherm for nonliving algal biomass. Comparison among the statistical parameters of these models suggests that Temkin model parameters were predicted more precisely, which is further indicated

Table 1 Thermodynamic parameters for Ni(II) biosorption onto nonliving algal biomass

T (K)	R%	ΔG° (kJ/mol)	ΔS° (J/mol. K)	ΔH° (KJ/mol)
293	90.10	-5.084	172.640	45.499
298	90.63	-5.947		
303	93.40	-6.810		
308	95.30	-7.674		
313	96.56	-8.537

Fig. 4 Effect of increasing concentration of Pb(II), Cu(II), and Zn(II) on Ni(II) removal efficiency (pH = 7; biosorbent dose = 1 g/L; Ni(II) conc. = 35 mg/L; temperature = 25 °C, shaking speed = 150 rpm for 2 h)

Table 2 Isotherm models parameters and their associated statistical error parameters (pH = 7, temperature = 25 °C, shaking speed = 150 rpm for 2 h)

Langmuir		Freundlich		Temkin	
q_m (mg/g)	9.848	K_f	1.719	K_t (l/mg)	0.971
K_L (l/mg)	0.125	n	2.074	b_t (J/mole)	2.4011
R^2	0.950	R^2	0.916	R^2	0.957
SSE	1.242	SSE	2.081	SSE	1.063
X^2	0.672	X^2	1.069	X^2	0.533

by high R^2 and lower SSE and X^2 values. Thus, one can deduce that the Temkin model is more suitable for representing the isotherm data. According to the obtained R^2 value, the Langmuir model fitted in a better way. However, the values of statistical error (SSE and X^2), for the Langmuir model, were on the higher side than those calculated from the Temkin model. Additionally, the isotherm study enlightens that the Freundlich model failed to model the isothermal profile data of Ni(II) biosorption. Also, this model was statistically insignificant because of the prediction of high error parameters. Based on the Langmuir isotherm results, the K_L values for used algal biomass indicated that Ni(II) biosorption mechanism was favorable and the maximum uptake (q_m) of algal biomass for Ni(II) was found to be 9.848 mg/g under the conditions of the experiment. Thus, it indicates that the sorption mechanism of pollutant molecules onto active sites surface of sorbent, as represented by Temkin isotherm, is heterogeneous in nature [23].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

$$q_e = K_f C_e^{\frac{1}{n}} \quad (6)$$

$$q_e = \left(\frac{RT}{b_t} \right) \ln(K_t C_e) \quad (7)$$

Fig. 5 Plot of experimental and theoretical isothermal data of Ni(II) biosorption onto nonliving algal biomass (pH = 7, temperature = 25 °C, shaking speed = 150 rpm for 2 h)

Based on the Ni(II) uptake values, the present studied biosorbent exhibited relatively good ability to eliminate this metal ions compared with other similar biosorbents (Table 3). Although several biosorbents have demonstrated higher Ni(II) biosorption capacity than the current biosorbent, the biosorption process at neutral pH is considered as a favorable and environmental friendly treatment process since most of the wastewater effluents of neutral pH (Noorozi et al., 2018; [37]).

Regeneration of the biosorbent

Despite the availability of the collected nonliving algal biomass in huge quantities adds on several additional features with them such as they are (i) easy to collect, (ii) cost-effective and cheap, (iii) easy to prepare and operate, and (iv) can be used directly without preliminary treatment with acids or bases. The regeneration aspect of the biosorbent is also an important to be investigated in current study. To check the possibility of the removal and recovery process for Ni(II) from loaded algae biomass, several sequential cycles of biosorption/desorption were done. Afterward each desorption cycle, the algae was regenerated using 0.05 M HNO_3 as eluent agent, and then re-used in subsequent biosorption cycle. This process was tested by repeating desorption process in five cycles and the recovery percentage of Ni(II) was calculated per each cycle [20]. The regeneration process was carried out by separating the algal biomass from aqueous solution by filtration, washed several times with distilled water, and then dried in an oven at 90 °C until complete dryness. Moreover, this experiment was repeated using and 0.1 M HNO_3 and the results were plotted as Fig. 6. It can be seen, that the used algal biomass can be regenerated by different ratio according to the HNO_3 concentration. Clearly, the 81.43 removal efficiency percentage of Ni(II) was approximately realized with 0.1 M HNO_3 from loaded algal biomass of weight = 1 g. As can be seen, that the biosorption efficiency decreased gradually from 81.43% (first cycle) to 46.20% (fifth cycle), and this is due to losing in mass of algal biomass during washing and drying between each reusability cycle. Therefore, the utilized biosorbent can be regenerated and re-used in the Ni(II) biosorption process for five times with minor losses of this metal removal efficiency (biosorption-desorption).

Kinetic study

The understanding of the highly complex kinetic mechanism for monitoring the selectivity and performance of a sorbent, being utilized as a contaminant purification material, has become essential [10, 42]. Moreover, the accurate design of the continuous adsorption system in the tertiary treatment units depends extremely on the knowledge obtained from the

Table 3 The comparison of maximum uptake by current biosorbent with other studied similar biosorbents in published literatures

Biosorbent	q_m (mg/g)	pH	References
Chlorella vulgaris	60.20	4.2	Aksu [2]
Anaerobic granules	26.00	4.0–5.5	Hawari and Mulligan [18]
Codium vermilara	13.20	6	Romera et al. [41]
Spirogyra insignis	17.50	6	Romera et al. [41]
Asparagopsis armata	17.10	6	Romera et al. [41]
Chondrus crispus	37.20	6	Romera et al. [41]
Ascophyllum nodosum	43.30	6	Romera et al. [41]
Fucus spiralis	50.00	6	Romera et al. [41]
Mixture algae	9.84 mg/g	7	This study
Rhodococcus opacus bacteria strain	7.63	5	Cayllahua et al. [12]
Ficus Religiosa (Peepal) leaves	6.35	7	Aslam et al. [8]

interaction mechanism between the adsorbent–adsorbate complex [9]. In the current study, the assessment and validation of applicability of pseudo-first-order and pseudo-second-order kinetic models for the analysis of Ni(II) biosorption kinetic was carried out. These two formalisms are mostly used for modeling the experimental data and for the description of the kinetics of adsorption process. Equations (8) and (9) represent the pseudo-first-order and pseudo-second-order kinetic models, respectively [19, 27]. Further, for the kinetic study, the data of initial metal evolution experiment (Fig. 3b) will be employed (mentioned previously). Indeed, the pseudo-first-order-kinetic model was developed based on the assumption that (i) one pollutant molecule is adsorbed onto one active site on the adsorbent surface and (ii) the adsorption rate of adsorbate over time is directly proportional to the saturation concentration and the number of active sites, thus, following physisorption mechanism. Alternatively, the pseudo-second-order equation assumes that the pollutant molecule can occupy more than one sorption site, which indicates that it follows the chemisorption process. Further, in the Table 4 the nonlinear analysis results of these models with the experimental data are

reported. It reveals that the experimental data are in good agreement with the pseudo-second-order model, which is further confirmed by satisfactorily high R^2 , low SSE and X^2 values. Moreover, the experimentally observed uptake (q_e, exp) values are in close approximation with the calculated values. Thus, this kinetic model is consistent with the trend of adsorption rate at different concentrations of Ni(II) in the entire range studied. Furthermore, the uptake values calculated from the pseudo-second-order model were closer to the experimental values than values obtained from the pseudo-first-order model. Such trends suggested the chemisorption nature of adsorption of Ni(II) ions onto the surface active sites of algal biomass.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (8)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (9)$$

where q_t is the amount of uptake (mg/g) at time t (min); k_1 and k_2 are the rate constants of the first-order and second-order models (min^{-1}); respectively.

Fig. 6 Five cycle of adsorption-desorption with two different concentration of HNO_3 (initial Ni(II) concentration = 100 mg/L, biosorbent dose 1 g/100 mL, temperature = 25 °C, shaking speed = 150 rpm for 1 h)

Table 4 Parameters of the kinetic models for sorption of Ni(II) ions

Pseudo-first-order					Pseudo-second-order					q_e , exp (mg/g)	C_0 (mg/L)
q_e	k_1	R^2	SSE	X^2	q_e	k_2	R^2	SSE	X^2		
0.134	0.036	0.757	1.010	1.565	1.944	0.837	0.999	0.453	0.023	1.935	20
0.333	0.028	0.938	1.220	1.767	3.179	0.588	0.999	0.443	0.055	3.172	35
0.315	0.021	0.758	2.004	1.334	8.149	0.296	0.999	0.327	0.015	8.143	100
3.909	0.044	0.950	1.563	1.765	14.322	0.030	0.998	0.405	0.140	14.090	200
7.112	0.028	0.863	1.662	1.865	19.084	0.010	0.996	0.503	0.118	18.660	300

Conclusion

In the present study, a nonliving algal biomass prepared from three different classes of algae is being investigated regarding removal of Ni(II) ions from synthesis wastewater. The characterization investigation was carried out using SEM and FT-IR techniques, which indicated that the used algal biomass has good biosorption features related to the surface morphology and active groups. The biosorption performance of algal biomass for Ni(II) was remarkably affected by the changing the experimental conditions such as pH, biosorbent content, initial metal concentration, and temperature. Also, the biosorption rate was rapid and achieved more than 50% in the first 20 min of reaction time even under worst conditions. The isotherm study highlighted that the Temkin model can be accurately used to describe the isothermal data. The data of kinetics profiles could be best fitted with the pseudo-second-order model since this model had statistically significant parameters, suggesting chemisorption biosorption process. Moreover, the results indicated that the biosorption process was spontaneous and endothermic in nature, as suggested by the thermodynamic study. The competitor ions in term of Pb(II), Cu(II), and Zn(II) lowered the Ni(II) removal efficiency by different degree, where their effect trend can be ranked as Pb(II) > Cu(II) > Zn(II). The Ni(II)-biosorption capacity of algal biomass reached to 9.848 mg/g at pH near neutral and room temperature, demonstrating eco-friendly biosorbent made from algal biomass since almost all natural water bodies and wastewater are within near neutral environments. These results suggest that the used algal biomass was an attractive and good biosorbent for removal of Ni(II) from aquatic medium. In the future studies, the environmental effect of shaking speed should be considered.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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