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Biosorption of nickel from model solutions and electroplating industrial effluent using cyanobacterium *Arthrospira platensis*

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ABSTRACT

The biosorption of nickel from batch solutions and electroplating industrial effluent using cyanobacterium *Arthrospira platensis* was investigated. The maximum biosorption capacity of nickel was 13.4 mg/g at pH of 4.0, sorbent dosage of 6 g/L during 30 min of contact. The Langmuir and Freundlich adsorption isotherm models fit well the sorption equilibrium of the experimental data (R^2 0.99), while the kinetic data were best described using the pseudo second-order kinetic model ($R^2 > 0.99$). According to the thermodynamic parameters, the biosorption process was a spontaneous, endothermic process. Fourier transform infrared analysis was carried out to identify the role of different functional groups on cyanobacterium surface in nickel ions binding. According to the data obtained by neutron activation analysis, it has been shown that ion-exchange is one of the mechanism of nickel interaction with biomass. In addition, the effectiveness of the biomass was investigated in three sorption-desorption cycles using HCl, HNO_3, CH_3COOH and NaOH. In the case of industrial effluent, 68% of nickel was removed from effluent at a sorbent dosage of 20 g/L and interaction time 30 min. The study demonstrates the potential of *Arthrospira platensis* as biosorbent to remove nickel from batch solutions as well as from industrial effluents.

Keywords: Biosorption; Nickel; Arthrospira platensis; Atomic absorption spectrometry; Neutron activation analysis; FT-IR spectroscopy

1. Introduction

Wastewater generated by electroplating process, mining and metallurgy, battery and accumulator manufacturing often contains high concentrations of nickel ions. Exposure to nickel can cause allergic contact dermatitis and allergic sensitization [1]. According to regulations, its concentration in effluents discharged in natural water bodies should not exceed 2 ppm [2]. Thus, wastewater containing nickel ions must be properly treated before their discharge [2–4]. Techniques traditionally used for nickel removal from wastewater, precipitation, adsorption, ion-exchange, membrane processing, *etc.*, have been proved to be limited, since they often involve high capital and operational costs and may cause generation of secondary wastes, which present treat-

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ment problems [3]. Thus, cost-effective alternative technologies for treatment of metal contaminated wastewater are needed. Application of biological objects for metal removal has several advantages: the process does not produce chemical sludge, it could be highly selective, more efficient, easy to operate and hence cost-effective for treatment of large volumes of waste waters containing low pollutant concentrations [5].

Cyanobacteria is a group of microorganisms which are widely used in removal of metal ions such as lead [6,7], cadmium [8], chromium [9–12], zinc [6,7,13,14], silver [15], *etc*. from batch solution and industrial effluents. However, nickel biosorption has not received as much attention in the literature as biosorptive removal of other metals, probably, because of the relatively low uptake capacities achieved. Wong and co-authors [16] compared the efficiency of two unicellular green algae, *Chlorella vulgaris* and *Chlorella miniata* in removing nickel ions. The removal efficiency of *Chlorella vulgaris* (641.76 µg/g) was significantly lower than that of *Chlorella miniata* (1367.62 µg/g). Micheletti et al. [17] tested nine extracellular polymeric substances producing cyanobacteria for their ability to remove chromium, copper and nickel from single- and multiple-metal solutions. In the single ion solutions all tested cyanobacteria showed the lowest affinity for nickel. Chan et al. [18] investigated the potential of *Chlorella pyrenoidosa* and *Chlorella* HKBC-C3 for copper and nickel removal from an electroplating sewage effluent. Both microalgae showed a high rate of copper biosorption. On the contrary, the rate of nickel biosorption was very low. Ferreira et al. [19] and Rodrigues et al. [7] studied nickel adsorption from single, binary and ternary systems using *Arthrospira platensis* and *Chlorella vulgaris* as biosorbents. Dry biomass of *Chlorella vulgaris* behaved as better biosorbent than *Arthrospira platensis,* however both biomasses showed low affinity for nickel. Corder and Reeves [20] tested several strains of algae and cyanobacteria for the same purpose. However, none of them was able to bind nickel efficiently in the studied effluent samples.

The aim of the present study is to examine the efficiency of *Spirulina platensis* biomass as a biosorbent for removal of nickel ions from batch solution and industrial effluent. Equilibrium and kinetic studies are performed to describe the adsorption process. To determine the best biosorption conditions, factors, such as pH, temperature, adsorption time, initial metal concentration, and sorbent dosage are examined. Functional groups responsible for metal binding are determined by Fourier transform infrared spectroscopy.

2. Materials and methods

2.1. Reagents and materials

All the chemicals used for biosorption experiments were purchased from Sigma-Aldrich and were of analytical grade.

2.2. Industrial effluent

The industrial effluent containing nickel in concentration of 117 mg/L (pH 6) was taken from electroplating unit directly after the electroplating process. Current treatment scheme of industrial effluent for nickel removal include its chemical precipitation in the form of nickel hydroxide using lime or caustic.

2.3. Biosorbent

Arthrospira platensis (*A. platensis*) biomass purchased from "Biosolar MSU" company (Moscow, Russia) was dried in an oven at 80°C for 24 h. Then the biomass was homogenized in a homogenizer at 600 rpm for 10 min and afterwards used in the experiments.

2.3.1. Batch experiments in synthetic solutions

The experiments were conducted in 100 mL Erlenmeyer flasks containing 50 mL of nickel synthetic solutions. The flasks were shaken on a shaker incubator at a constant rate of 120 rpm. To investigate the effect of pH, sorbent dosage, initial metal concentration, temperature and contact time, different pH (2–6), sorbent dosage (2, 4, 6, 8, 10, 14, 20 g/L) of initial metal concentrations (5–100 mg/L), time (5, 7, 10, 15, 30, 45, 60, 120 min) and temperature (20, 30, 40, 50°C) were used. After experiment biomass was removed by filtration, and obtained solution were used for further analysis. All experiments were carried out in triplicate and the average value of obtained experimental values for used.

The metal uptake q (mgNi/g biosorbent) was calculated from the mass balance using the following equation:

$$q = \frac{V\left(C_i - C_f\right)}{m} \tag{1}$$

where V is the volume of solution, ml; C_i is the initial concentration of metal in mg/L, C_f is the final metal concentration in the solution, mg/L, and m is the mass of sorbent, g.

2.4. Desorption study

The nickel-loaded biosorbent which was exposed to 10 mg Ni/L at pH 4, was separated from solution by centrifugation. The biosorbent was then contacted with different eluents: HCl, HNO_3, NaOH and CH_3COOH for 1 h in a rotary shaker at 200 rpm. The remaining procedure was the same as that employed in the biosorption equilibrium experiments. The elution efficiency was determined from the ratio of the metal mass in the solution after desorption to the metal mass initially bound to the biosorbent.

2.5. Industrial effluent experiment

The effect of biosorbent dosage on nickel removal from industrial effluent was examined by varying its weight from 6 to 40 g/L at a contact time 30 min. The working volume was 50 mL.

3. Methods

Nickel concentration in solution was determined in propane flame on atomic absorption spectrophotometer KVANT-2a (Kortek company, Moscow, Russia) at a resonance line of 232.0 nm. The strength of the current was 16 mA. To determine the elemental composition of *A. platensis* biomass, neutron activation analysis (NAA) at the pulsed fast reactor IBR-2 (Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia) was applied. The description of the irradiation channels and the pneumatic transport system REGATA of the IBR 2 is given in [21].

Fourier-transform infrared spectroscopy was used to confirm the presence of the functional groups in the samples of *A. platensis* and to observe the chemical modification after nickel biosorption. Infrared spectra were recorded in the range of 4,000–400 cm^{-1} using a Bruker Alpha Platinum-ATR spectrometer (Bruker Optics, Ettingen, Germany).

4. Results and discussion

4.1. Effect of pH and sorbent dosage on biosorption

pH is one of the most important parameters for controlling the biosorption process. It affects the chemistry of the cell wall as well as chemistry of the metal. Therefore, preliminary experiments have been performed to find out the optimum pH for maximum metal removal before investigating the kinetic and thermodynamic aspects of the process. As it can be seen from Fig. 1, the nickel sorption reached the maximum (760 µg/g) at pH 4. At pH 2 due to competition of nickel ions with protons, the efficiency of nickel removal was very low (29%). Slight decrease of nickel biosoption at pH higher than 4 can be connected with the formation of anionic hydroxide [3]. In Bermúdez et al. study [22], it was shown than nickel precipitation begins at pH 7–7.3.

Seker et al. [23] performed experiments on nickel biosorption by *A.platensis* biomass, the process was studied at pH values 2, 4 and 6, and optimal pH in contrast to the present study was found to be 6. Aksu [7] showed that maximum nickel biosoprtion by microalga *Chlorella vulgaris* occurs at pH 4.5. The removal efficiency of nickel ions from batch solution by *Nostoc linkia* biomass showed the same value (95%) at pH 4.5 and 5.5 [24].

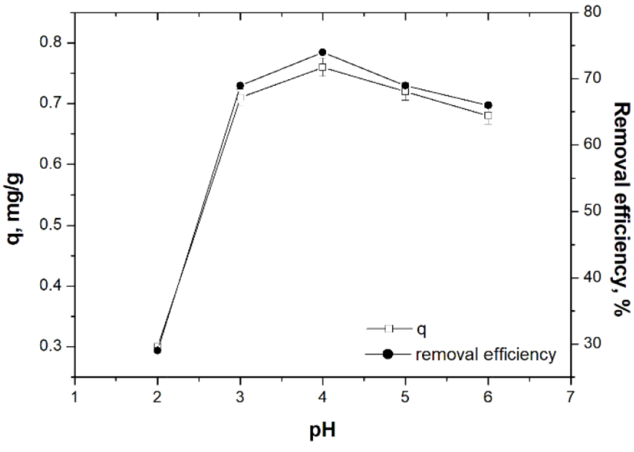

Fig. 1. Removal of nickel ions at different initial pH (at T 20°C; C_i 10 mg/L; sorbent dosage 10 g/L; adsorption time 1 h).

Fig. 2 illustrates the effect of the biosorbent dosage on the nickel biosorption from solutions. As it can be seen from the presented data, nickel removal efficiency varied from 61% to 67% at biosorbent dosage increase from 2 to 20 g/L. It should be mentioned that nickel removal efficiency was the same at the sorbent dosage in the range of 6–20 g/L. Thus, dosage 6 g/L was used for further experiments.

4.2. Effect of time and kinetics of sorption

Kinetic information of metal uptake by biosorbent is required for selecting optimum operating conditions for industrial scale metal removal process According to the data presented in Fig. 3, nickel biosorption was fast in the first 30 min (68%) of contact followed by slow biosorption till equilibrium was achieved. During 3 min 52% of nickel was sorbed by spirulina biomass from solution. Seker et al. [23] studying Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption by *A. platensis* showed that time required to reach equilibrium for each metal was in less than 1 h. Wong et al. [16] demonstrated that nearly 50% of the total amount

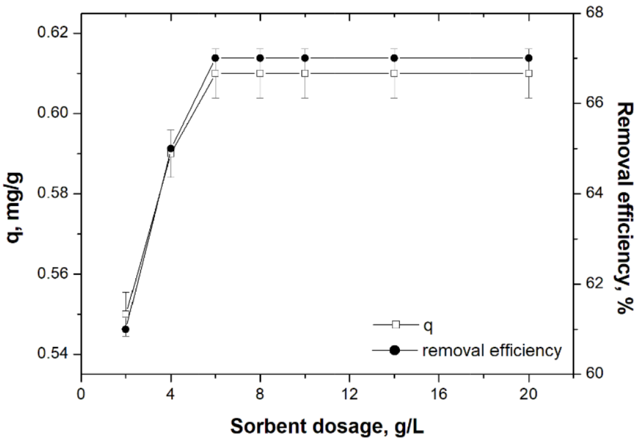

Fig. 2. Effect of biosorbent dose on biosorption capacity and removal efficiency of nickel ions by *A. platensis* biomass (at T 20°C; C_0 10 mg/L; pH 4; adsorption time 1 h).

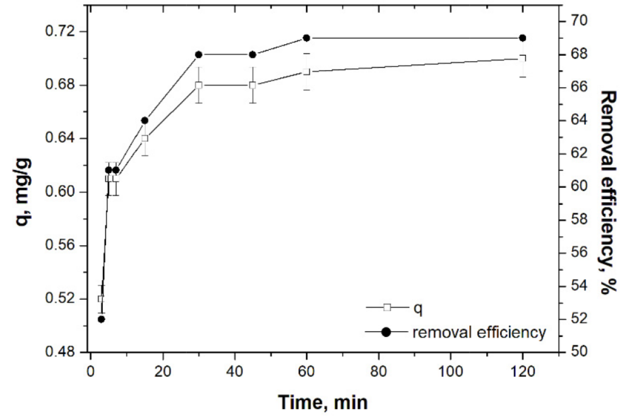

Fig. 3. Effect of contact time on the sorption of nickel ions by *A. platensis* biomass (at T 20°C; C0 10 mg/L; pH 4; sorbent dosage 6 g/L).

of nickel was adsorbed by *Chlorella vulgaris* after 1-min biosorption.

Lagergren's pseudo-first-order model and pseudo second-order model of Ho and McKay were used to fit the experimental data. These models are expressed as follows:

Lagergren's pseudo-first-order model:

$$\log\left(q_e - q\right) = log q_e - \frac{K_a}{2.303}t \tag{2}$$

where q and q_e are the adsorbed amounts (mg/g) at time (t) (min) and at equilibrium time, respectively, k_a (min^{-1}) is the rate constant of the first-order biosorption.

Pseudo-second-order model of Ho and McKay [25]:

$$\frac{t}{q} = \frac{1}{K_b q_e^2} + \frac{t}{q_e} \tag{3}$$

where q and q_e are the adsorbed amounts (µg/g) at time (t) (min) and at equilibrium time, respectively, k_b (g/mg*min) is the rate constant of the second-order biosorption.

The slope and intercept of plot of log $(q_e - q_t)$ vs. t were used to obtain the first-order rate constant k_a and equilibrium uptake q_e. The pseudo second-order biosorption rate constant (K_b) and q_e values were determined from the slope and intercept of the plot of t/q_t against time, t (Fig. 4).

As it can be seen from Table 1, the correlation coefficient for the pseudo-first-order is 0.944. The low correlation coefficient values obtained for the pseudo-first-order model indicate that sorption does not occur exclusively onto one site per ion [26]. The correlation coefficient for the pseudo-second-order rate equation is 0.999.

The applicability of pseudo second order kinetics model suggested that the overall rate of nickel sorption processes appears to be controlled by chemical processes, through sharing of electrons between biosorbent and sorbate, or covalent forces, through the exchange of electrons between the particles involved [26]. Pseudo-second order model is more applicable for nickel biosorption by different types of biosorbents [3,23].

4.3. Thermodynamic study

The solution temperature was varied in the range of 20–50°C. Increase of temperature from 20 to 50°C led to decrease of biomass biosorption capacity from 883 µg/g to 762 µg/g.

The thermodynamic constants, namely, free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process. The values of enthalpy (ΔH°) and entropy (ΔS°) were evaluated from the slope and intercept of ln K_d vs. 1/T plots (Fig. 5).

$$lnK_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{4}$$

where (ΔH°), (ΔS°), T (in Kelvin) and R are the enthalpy, the entropy, the temperature and the gas constant, respectively.

The ΔG° was calculated from the equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{5}$$

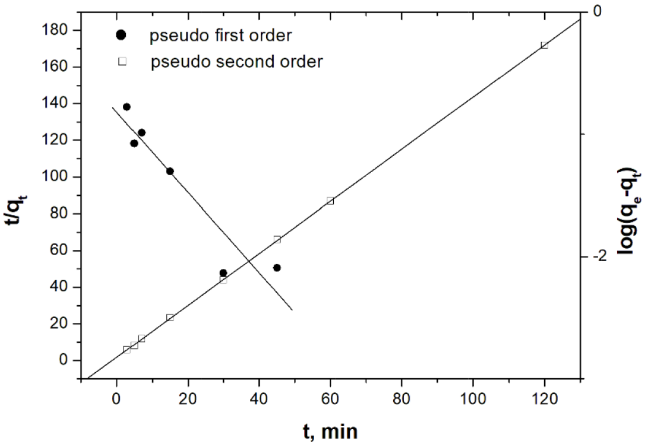

Fig. 4. The pseudo-first- and pseudo second order plots of kinetic study of nickel biosorption on *A. platensis.*

Table 1
Kinetic's models parameters

Pseudo-first-order model				
C_e, mg/L	$q_{e\ (exp)}$, mg/g	$q_{e\ (cal)}$, mg/g	k_a, (min^{-1})	R^2
10	0.70	0.41	0.07	0.944
Pseudo-second-order				
C_e, mg/L	$q_{e\ (exp)}$, mg/g	$q_{e\ (cal)}$, mg/g	K_b, g/mg*min	R^2
10	0.70	0.71	1.18	0.999

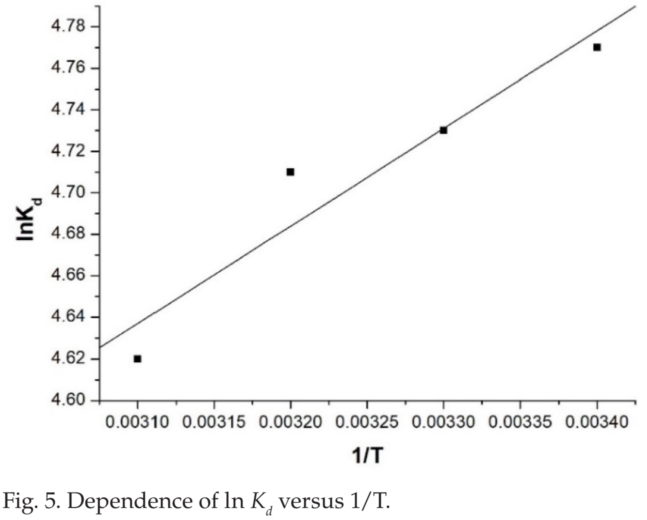

Fig. 5. Dependence of ln K_d versus 1/T.

The values of ΔH°, ΔS° and ΔG° are given in Table 2.

As it is seen from Table 2 all the Gibbs free energy change values are negative. A negative value of ΔG° indicates the feasibility of the process and spontaneous nature of the biosorption. It also depicts that the sorption reaction is largely driven towards the product [23]. The positive value of ΔH° suggests the endothermic nature of biosorption. This result is in agreement with the biosorption of Ni(II) using *Chlorella vulgaris* [5], and lead (II), cadmium (II) and nickel(II) using *A. platensis* [23]. The positive value of ΔS° confirms the increased randomness at the solid–solution interface during biosorption [3,5].

4.4. Effect of concentration and isotherm modeling

It is well know that biological sorbents are effective at metal concentration in solution lower than 100 mg/L. Thus, the effect of initial nickel concentration on biomass biosorption capacity was studied in the concentration range of 5–100 mg/L. Two types of experiments were performed: experiments with dry biomass and with living one. Initial nickel concentration as well as time of incubation in both experiments were the same. The adsorption capacity of Arthrospira biomass was proportional to the initial nickel concentration in the solution: the higher the initial concentration, the more the nickel ions bound by cyanobacterim cells. The maximum adsorption capacity was 4.2 mg/g and 4.9 mg/g for dry and living biomass, respectively.

The Langmuir and Freundlich models are used to describe the linear equilibrium between the nickel ions sorbed onto biomass and those ions in solution:

The Langmuir model is expressed as:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{bq_{max}C_e} \qquad (6)$$

where q_e is the amount of metal adsorbed per unit weight of adsorbent at equilibrium (mg/g), q_{max} is the maximum metal uptake per unit mass of the adsorbent (mg/g), *b* is the Langmuir constant (L/mg), related to the energy of sorption, which quantitatively reflects the affinity between the sorbent and the sorbate and C_e is the equilibrium concentration of adsorbate (mg/ L).

Table 2
Thermodynamic parameters for nickel biosorption on A. platensis

Temperature, K	ΔG°, kJ/mol	ΔH°, kJ/mol	ΔS°, J/mol·K
293	–3.83	3.9	26.4
303	–4.09		
313	–4.35		
323	–4.62		

The general Freundlich equation is written as follows:

$$lnq_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (7)$$

where K_F and *1/n* are Freundlich constants, associated with adsorption capacity and adsorption intensity, respectively.

The isotherm parameters have been calculated from linearized plots corresponding to each isotherm model Fig. 6 displays isotherms for dry biomass and Fig. 7 for living biomass, respectively. The obtained values are summarized in Table 3.

According to Langmuir model, binding to the surface primarily is due to physical forces and implicit in its deviation was an assumption that all sites possess equal affinity for the sorbate. The Langmuir model served to estimate the maximum uptake values, which could not be reached in the experiments [27]. High correlation coefficients obtained for both models for dry as well as living biomass point up the fact that applied models are suitable for describing the biosorption equilibrium of nickel ions in the studied concentration range. The applicability of Langmuir and Freundlich isotherm suggests that nickel biosorption by *Arthrospira* biomass involves several mechanisms. According to Langmuir adsorption isotherms, the maximum nickel adsorption capacity of dry spirulina biomass was two times higher than that of the living one.

Seker et al. [23] showed the applicability of Freundlich model to describe nickel biosorption by *Chlorella vulgaris.* According to Ferreira et al. [19] study the maximum values of sorption capacity of *A. platensis* and *Chlorella vulgaris* were 0.740 and 0.823 mmol/g for nickel. Maximum adsorption capacities obtained in the present work are higher than those found by Wong et al. [16] (2.98 mg/g for *Chlorella miniata* and 1.28 mg/g for *Chlorella vulgaris*), Micheletti et al. [17] (1.9 mg/g for Nostoc PCC 7936) and

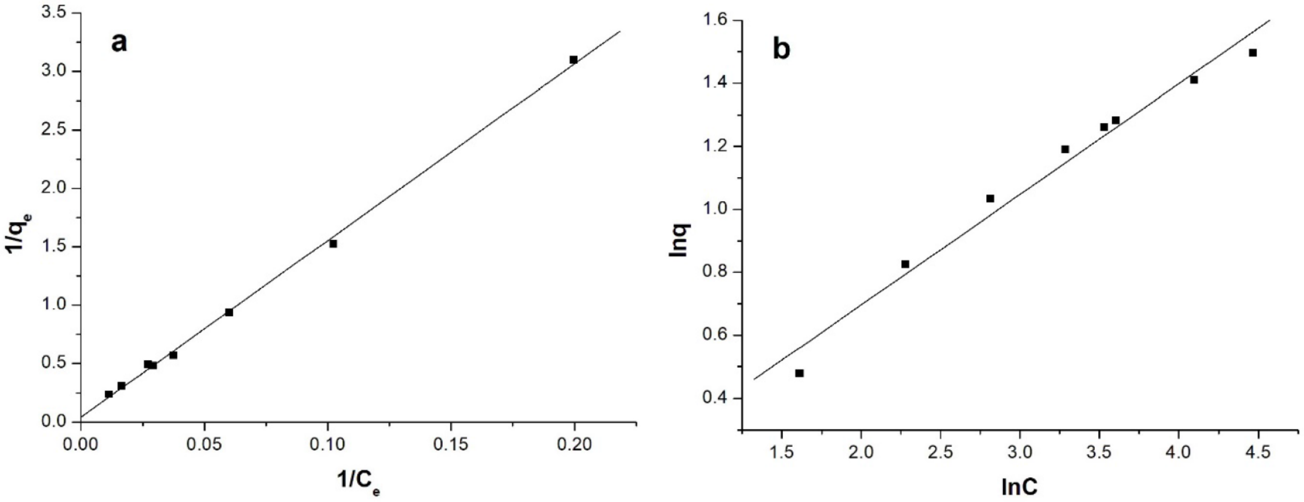

Fig. 6. Langmuir (a) and Freundlich (b) isotherm models for dry biomass.

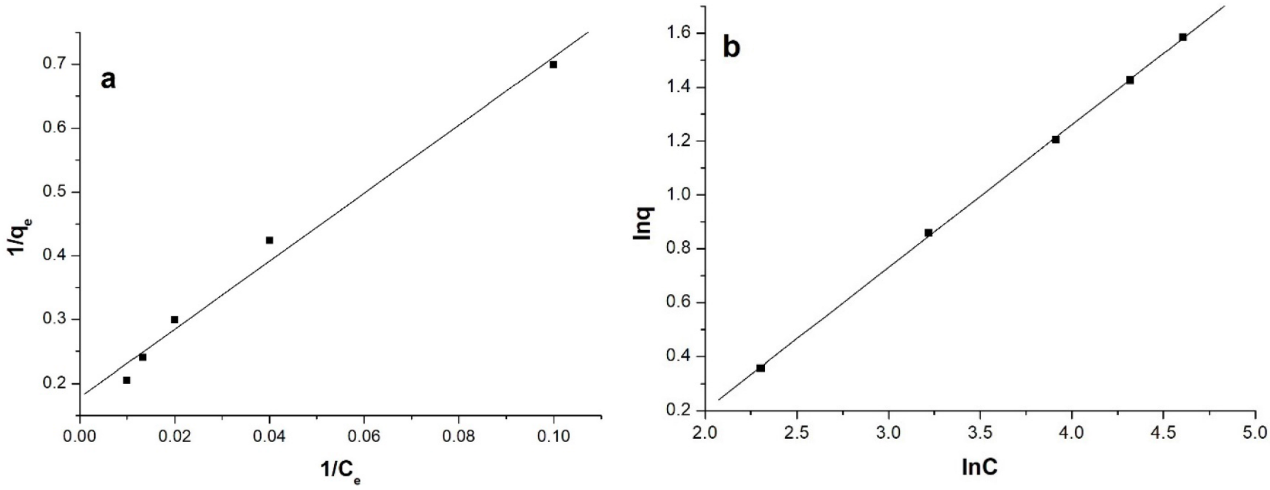

Fig. 7. Langmuir (a) and Freundlich (b) isotherm models for living biomass

Table 3
Isotherm parameters for the biosorption of nickel ions on *A. platensis* biomass

Langmuir model		Freundlich model	
Dry biomass			
R^2	0.99	R^2	0.988
Q_{max}	13.4 mg/g	ln K_f	0.99
b	0.006 L/mg	n	2.86
Living biomass			
R^2	0.99	R^2	0.999
Q_{max}	5.9 mg/g	ln K_f	0.42
b	0.03 L/mg	n	2.0

Tam et al. [28] (1.71 mg/g for *Chlorella vulgaris*). However, the obtained data are lower than data presented in Aksu [5] (48.1–60.2 mg/g for *Chlorella vulgaris*) and Tam et al. [28] (9.1 mg/g for *Chlorella miniata*) studies.

Relatively low nickel biosorption by microbial biomass may be due to its electronic configurations, when the number of electrons lying in very diffused and distant orbitals (d and f), which are notoriously more available than those closer to the nucleus, is lower [19]. It can be also explained by the fact that nickel in water generates very stable aqueous complexes and thus it probably becomes poorly exchangeable with the protons bound to the active sites of the biosorbent [17].

4.5. Mechanisms of biomass interaction with nickel ions

Biosorption of metal includes several processes: metal binding to functional groups, ion-exchange and microprecipation. Data obtained by NAA (Table 4) show the decrease of Na, K, Fe, As, Br and Sr content in biomass during the process of nickel biosorption. Thus, ion-exchange can be considered as one of the mechanisms of nickel biosorption.

In order to better understand and confirm the nature of active sites on biosorbent surfaces, the biomass was analyzed by FTIR spectroscopy. The FTIR spectrum of *A. platensis* control biomass showed several intense bands at wave numbers 3282, 2926, 1634, 1538, 1454, 1392, and 1056 cm^{-1} (Fig. 7). The strong boarded peak at wavenumber 3282 cm^{-1} could be attributed to hydroxyl (–OH) and a mine (–NH) functional groups. The presence of methyl (–CH) stretching vibrations could be confirmed by the adsorption peak at wavenumber 2926 cm^{-1}. The adsorption peaks in the region 1750–1350 cm^{-1} could be assigned to –CO groups. In addition, –C–O, –C–C, and –C–OH stretching vibrations could be found at the adsorption peaks in the region 1250–1000 cm^{-1}. The strong bands at wave numbers 3282; 1634; 1538; and 1242 cm^{-1} could correspond to the amide I–III bands of polypeptides or proteins, respectively. The insignificant deformations in the region 900–500 cm^{-1} could be attributed to –P–O, –S–O, and aromatic –CH stretching vibrations.

In the IR spectra of the Ni-loaded biomass the peaks positions of a mine (3282 cm^{-1}), carboxyl (1750–1350, 1250–1000 cm^{-1}), hydroxyl (3282, 1250–1000 cm^{-1}), phosphate and sulphate (900–500 cm^{-1}) groups were slightly shifted indicating their involvement in nickel ions binding.

4.6. Desorption study

The desorption analysis of *A. platensis* biomass for the nickel ions removal was performed using four different eluent solutions: HCl, HNO_3, CH_3COOH and NaOH (0.1 M). The acidic eluents were used because of their potential to dissolve nickel and nickel compounds: hydrogen ions can replace nickel ions in the biosorbent, thus functioning as an ion exchanger. The basic solution was used as desorbent because ion exchange was suspected of playing an important role in the biosorption process [2]. The obtained data (Table 5) show that mineral acids were efficient as desorbent agent (cycle I) with nickel recoveries of 70% by HNO_3 and 78% by HCl. However, once the biomass was reused in the next two biosorption cycles, the elution efficiency significantly decreased. As it was shown in Vijayaraghavan et al. study [27], acid eluates can dissolve some types of biomolecules that may contain nickel binding sites. CH_3COOH

Table 4
Change of the elemental content of biomass during nickel biosorption

Ni concentration in solution, mg/L	Element content in biomass, µg/g					
	Na	K	Fe	As	Br	Sr
0	5830 ± 300	14700 ± 730	4900 ± 340	1.93 ± 0.08	2.26 ± 0.09	107 ± 11
10	1380 ± 70	10800 ± 540	1420 ± 100	1.22 ± 0.05	1.31 ± 0.05	38.6 ± 3.9
25	1080 ± 50	9150 ± 450	970 ± 65	1.22 ± 0.05	1.37 ± 0.05	33.5 ± 3.3
50	920 ± 45	9840 ± 490	925 ± 65	1.19 ± 0.05	1.32 ± 0.04	30.5 ± 3.0
75	841 ± 40	8600 ± 430	899 ± 65	0.989 ± 0.04	1.14 ± 0.04	48.5 ± 4.9
100	866 ± 40	8520 ± 430	927 ± 65	0.96 ± 0.04	1.13 ± 0.04	59.8 ± 6.0

Table 5
Elution efficiency of different type of desorbing agents

Cycle	Effluent			
	CH_3COOH	HNO_3	HCl	NaOH
I	71%	70%	78%	25%
II	81%	8.6%	19%	6.1%
III	20%	4.1%	14%	1.9%

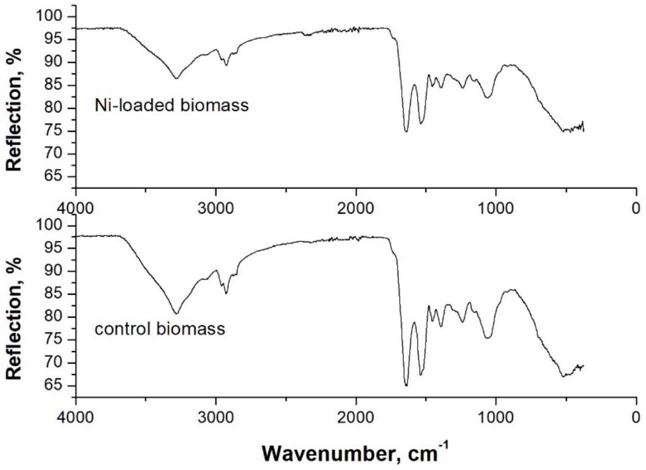

Fig. 8. FT-IR spectra of *A. platensis* biomass: control and Ni-loaded.

showed good desorption capacity during two sorption-desorption cycles. The lowest elution efficiency was obtained for NaOH.

4.7. Nickel biosorption from industrial effluent

In our previous study [12] it was shown that wet *A. platensis* biomass was able to remove 66% of nickel ions from effluent containing nickel in concentration of 14.1 mg/L at sorbent dosage of 0.5 g. In the present study due to higher nickel concentration in effluent the process of its removal was studied at the dosage range of 6–40 g/L. The time of biomass interaction with effluent was 30 min. Data presented in Fig. 8 shows that with the increase of sorbent dosage from 6 to 40 g/L nickel removal efficiency increased from 42 to 68%. The difference in biomass removal efficiency at sorbent dosage of 20 and 40 g/L was only 2%. One can conclude that optimal dosage of *Arthrospira* biomass for nickel removal is 20 g/L.

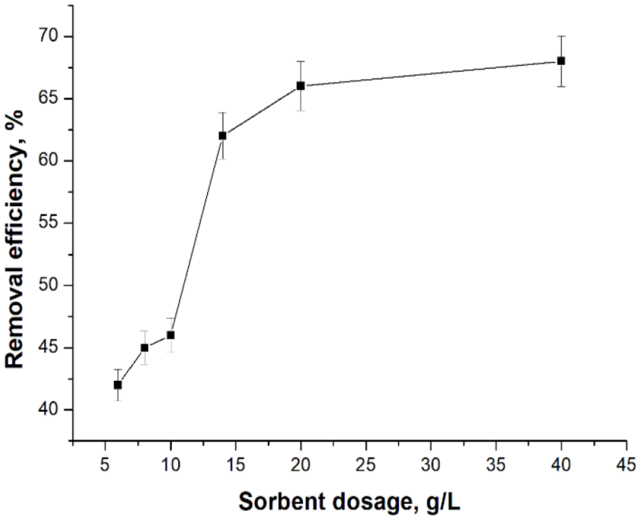

Fig. 9. Effect of biosorbent dose on biosorption capacity and removal efficiency of nickel ions from industrial effluent by *A. platensis* biomass (T 200 C; C_i 117 mg/L; pH 6; adsorption time 30 min).

As nickel concentration in effluent was relatively high, it is reasonable to treat firstly the effluent in a chemical way to reduce nickel concentration and after that to apply Arthrospira biomass for effluent post-treatment.

In Corder and Reeves [20] study from eight studied microorganisms' cyanobacteria *Anabaena flos-aquae* demonstrated the highest binding capacity for nickel from a batch solution. However, only 28% of nickel was removed from wastewater contained 7.1 mg/L of nickel. Chan et al. [18] showed that the rate of nickel biosorption by *Chlorella pyrenoidosa* and *Chlorella* HKBC-C3 was very low (< 20% removal in 72 h).

5. Conclusion

The results of the present study show that *Arthrospira platensis* can be beneficially used as an effective biosorbent for nickel removal from batch solutions and industrial effluents. The maximum biosorption capacity of nickel 13.4 mg/g was achieved at pH 4.0, sorbent dosage 6 g/L. Biosorption equilibrium data for dry as well as living biomass fit well the Langmuir and Freundlich models. Kinetic studies reveal that nickel biosorption by Arthrospira biomass could be described more favorably by the pseudo-second-order kinetic model. The process of nickel biosorption was spontaneous and endothermic. Mechanisms of nickel biosoption include ion-exchange and metal binding to –NH, –OH, –COOH groups. From four tested eluents CH_3COOH can be considered as the more efficient one. Nickel sorption from industrial effluent constituted 68% at initial nickel concentration of 117 mg/L, pH 6 and sorbent dosage 1.0 g.

References

[1] A. Antico, R. Soana, Nickel sensitization and dietary nickel are a substantial cause of symptoms provocation in patients with chronic allergic-like dermatitis syndromes, Allergy Rhinol (Providence)., 6(1) (2015) e56–e63.

[2] I.P. Suhasini, G. Sriram, S.R. Asolekar, G.K. Sureshkumar, Nickel biosorption from aqueous systems: studies on single and multi metal equilibria, kinetics, and recovery, Sep. Sci. Technol., 34(14) (1999) 2761–2779.

[3] H. Pahlavanzadeh, A.R. Keshtkar, J. Safdari, Z. Abadi, Biosorption of nickel(II) from aqueous solution by brown algae: Equilibrium, dynamic and thermodynamic studies, J. Hazard. Mater., 175 (2010) 304–310.

[4] M. Tsezos, E. Remoudaki, V. Angelatou, A systematic study on equilibrium and kinetics of biosorptive accumulation. The case of Ag and Ni, Int. Biodeter. Biodegr., 35 (1995) 129–l53.

[5] Z. Aksu, Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel(II) ions onto Chlorella vulgaris, Process Biochem, 38 (2002) 89–99.

[6] R.K. Aneja, G. Chaudhary, S.S. Ahluwalia, D. Goyal, Biosorption of Pb and Zn by non-living biomass of Spirulina sp., Indian. J. Microbiol., 50 (2010) 438–442.

[7] M.S. Rodrigues, L.S. Ferreira, J.C. de Carvalho, A. Lodi, E. Finocchio, A. Converti, Metal biosorption onto dry biomass of *Arthrospira (Spirulina) platensis* and *Chlorella vulgaris*: multimetal systems, J. Hazard. Mater., 30 (2012) 217–218.

[8] C. Solisio, A. Lodi, D. Soletto, A. Converti, Cadmium biosorption on *Spirulina platensis* biomass, Biores. Technol., 99 (2008) 5933–5937.

[9] E. Finocchio, A. Lodi, C. Solisio, A. Converti, Chromium (VI) removal by methylated biomass of *Spirulina platensis*: The effect of methylation process, Chem. Eng. J., 156 (2010) 264–269.

[10] A. Lodi, D. Soletto, C. Solisio, A. Converti, Chromium(III) removal by *Spirulina platensis* biomass, Chem. Eng. J., 136 (2008) 151–155.

[11] I. Michalak, A. Zielinska, K. Chojnacka, J. Matula, Biosorption of Cr(III) by microalgae and macroalgae: equilibrium of the process, Am. J. Agric. Biol. Sci., 2 (2007) 284–290.

[12] I. Zinicovscaia, L. Cepoi, T. Chiriac, L. Rudi, O.A. Culicov, M.V. Frontasyeva, S. Pavlov, E. Kirkesali, S. Gundorina, T. Mitina, A. Akshintsev, E. Rodlovskaya, *Spirulina platensis* as biosorbent of chromium and nickel from waste waters, Desal. Water, Treat., 57(24) (2016) 11103–11110.

[13] I. Zinicovscaia, Gh. Duca, V. Rudic, L. Cepoi, T. Chiriac, M.V. Frontasyeva, S.S. Pavlov, S.F. Gundorina, *Spirulina platensis* as biosorbent of zinc in water, Environ. Eng. Manag. J., 12 (2013) 1079–1084.

[14] I. Zinicovscaia, Gh. Duca, L. Cepoi, T. Chiriac, L. Rudi, T. Mitina, M.V. Frontasyeva, S. Pavlov, S.F. Gundorina, Biotechnology of metal removal from industrial wastewater: zinc case study, Clean-Soil Air Water, 42 (2015) 112–117.

[15] I. Zinicovscaia, L. Cepoi, T. Chiriac, T. Mitina, D. Grozdov, N. Yushin, O. Culicov, Application of *Arthrospira (spirulina) platensis* biomass for silver removal from aqueous solutions, Int. J. Phytoremediat., 19(11) (2017) 1053–1058.

[16] J.P.K. Wong, Y.S. Wong, N.F.Y. Tam, Nickel biosorption by two chlorella species, *C. Vulgaris* (a commercial species) and *C. Miniata* (a local isolate), Biores. Technol., 73 (2000) 133–137.

[17] E. Micheletti, G. Colica, C. Viti, P. Tamagnini, R. de Philippis, Selectivity in the heavy metal removal by exopolysaccharide-producing cyanobacteria, J. Appl. Microbiol., 105 (2008) 88–94.

[18] S.S. Chan, H. Chow, M.H. Wong, Microalgae as bioabsorbents for treating mixture of electroplating and sewage effluent, Biomed. Environ. Sci., 4(3) (1991) 250–261.

[19] L.S. Ferreira, M.S. Rodrigues, J.C. Monteiro deCarvalho, A. Lodi, E. Finocchio, P. Perego, A. Converti, Adsorption of Ni^{2+}, Zn^{2+} and Pb^{2+} onto dry biomass of *Arthrospira (Spirulina) platensis* and *Chlorella vulgaris*. I. Single metal systems, Chem. Eng. J., 173 (2011) 326–333.

[20] S.L. Corder, M. Reeves, Biosorption of nickel in complex aqueous waste streams by cyanobacteria, Appl. Biochem. Biotech., 45 (1994) 847–859.

[21] M. Frontasyeva, Neutron activation analysis for the life sciences. A review, Phys. Part. Nuclei., 42 (2011) 322–378.

[22] Y.G. Bermudez, I.L.R. Rico, O.G. Bermudez, E. Guibal, Nickel biosorption using *Gracilaria caudata* and *Sargassum muticum*, Chem. Eng. J., 166(1) (2011) 122–131.

[23] A. Seker, T. Shahwan, A.E. Eroglu, S. Yılmaz, Z. Demirel, M.C. Dalay, Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead (II), cadmium (II) and nickel (II) ions on *Spirulina platensis*, J. Hazard. Mater., 154 (2008) 973–980.

[24] I. Zinicovscaia, L. Cepoi, A. Valuta, L. Rudi, O.A. Culicov, M.V. Frontasyeva, E.I. Kirkesali, S.S. Pavlov, T. Mitina, *Nostoc linckia* as biosorbent of chromium and nickel from electroplating industry waste waters, J. Mater. Sci. Eng. B., 4(8) (2014) 242–247.

[25] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[26] R. Alfaro-Cuevas-Villanueva, A.R. Hidalgo-Vázquez, C.D.J. Cortés Penagos, R. Cortés-Martínez, Thermodynamic, kinetic, and equilibrium parameters for the removal of lead and cadmium from aqueous solutions with calcium alginate beads, Sci. World J., 2014 (2014).

[27] K. Vijayaraghavan, Biosorption of nickel from synthetic and electroplating industrial solutions using a green marine algae Ulva reticulate, Clean-Soil Air Water, 36(3) (2008) 299–305.

[28] N.F.Y. Tam, J.P.K. Wong, Y.S. Wong, Repeated use of two Chlorella species, *C. vulgaris* and WW1 for cyclic nickel biosorption, Environ. Pollut., 114 (2001) 85–92.