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STUDY OF CHEMISTRY OF CR(VI)/Cr(III) BIOSORPTION FROM BATCH SOLUTIONS AND ELECTROPLATING INDUSTRIAL EFFLUENT USING CYANOBACTERIA *SPIRULINA PLATENSIS*

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The biosorption of Cr(III)-Cr(VI) from aqueous solutions on dry *Spirulina platensis* biomass was tested under laboratory conditions as a function of pH, initial metal ion concentration, biomass dosage, time and temperature. Optimum adsorption pH values of Cr(III) and Cr(VI) were determined as 3.0 and 2.0, respectively. The Langmuir adsorption isotherm model fit well the sorption equilibrium of the experimental data obtained for Cr(III), while Freundlich isotherm fit better data obtained for Cr(VI). The kinetic data were best described using the pseudo second-order kinetic model ($R^2 > 0.99$). The adsorption process was exothermic and the values of thermodynamic parameters of the process were calculated. *Spirulina platensis* biomass was also used as a biosorbent for the removal of Cr(VI) from electroplating industry effluent as a function of biosorbent dosage and contact time.

INTRODUCTION

Nowadays contamination of the environment by chromium has become a major area of concern. Chromium is present in the environment in several forms, the most common forms being Cr(III) and Cr (VI).[1] Cr(VI) and Cr(III) are characterized by different physiochemical behavior, mobility and toxicity.[2] Cr(III) is an important microelement and its deficiency causes disturbance to the glucose and lipids metabolism in humans and animals.[1] At the same time Cr(VI) is a known carcinogen, which can cause a number of noxious human health effects like skin rashes, upset stomachs, respiratory problems, weakened immune system.[2]

The large-scale use of chromium in metallurgical, pigment and dye, textiles, tanning, and electroplating operations make these industries potential sources of chromium pollution.[3] Chromium in industrial wastewaters is mainly in the form of the hexavalent form and the most practiced method of its removal involves reduction of Cr(VI) into Cr(III) followed by $Cr(OH)_3(s)$ precipitation.[2,3] However, there is evidence that $Cr(OH)_3$ may itself be oxidized to Cr(VI), leading to contamination of natural waters.[4] Other techniques for chromium ions removal from industrial effluents include adsorption, ion-exchange, flotation, electrolysis, etc.[2,5] High chemicals and energy consumption and large volume of sludge generation make such processes costly and ineffective.[2]

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Biosorption of metal ions by metabolically inactive microbial biomass is an innovative and alternative technology for removal of these pollutants from industrial effluents.[6] This technique has advantages over the conventional methods, among which are: no production of chemical sludge, high selectivity, easiness to operate and effectiveness in the treatment of large volumes of wastewaters containing pollutants in low concentrations.[3,4,7]

Among the organisms, cyanobacteria are gaining increasing attention in biosorption studies because of their low cost and high biosorption capacity. *Spirulina* biomass was extensively used in biosorption studies, including for chromium ions removal. For example, Jagiełło *et al.*[3] studied the effect of pH and Cr(III) concentration on Cr(III) biosorption by *Spirulina* sp. Chojnacka and co-authors[1] used four different morphological forms of *Spirulina* sp. biomass to study the process of Cr(III) biosorpion. Gagrai *et al.*[2] investigated the role of functional groups on the Spirulina sp. cell wall in Cr(VI) reduction to Cr(III) form. Finocchio *et al.*[4] studied the effect of biomass methylation on Cr(VI) adsorption by *Spirulina platensis* biomass.

The aim of the present study was to examine the efficiency of cyanobacteria *Spirulina platensis* biomass as a biosorbent for the removal of Cr(III)/Cr(VI) ions from batch solutions. Equilibrium and kinetic studies were 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 were examined. The process of Cr(VI) removal from industrial effluent was studied as well.

EXPERIMENTAL

Reagents and materials

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

Industrial effluent

The industrial effluent containing chromium(VI) in concentration 34 mg/L (pH 4) was taken from electroplating units. Industrial effluent was collected directly after the electroplating process. Current treatment schemes of industrial effluent for metal removal include a complex of chemical methods.

Biosorbent

Spirulina platensis (*S. platen*sis) biomass in a dried form was purchased from “Biosolar MSU” company (Moscow, Russia).

Batch experiment

The experiments were conducted in 100 mL Erlenmeyer flasks containing 50 mL of Cr(III)/Cr(VI) 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 (2.0–6.0), sorbent dosage (0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 1.0 g) initial metal concentration (10–200 mg/L), time (5, 7, 10, 15, 30, 45, 60, 120 min) and temperature (293, 303, 313, 323 K) were used. After the experiment the biomass was removed by filtration and the obtained solution was used for further analysis. All experiments were carried out in triplicate and the average value of obtained experimental values was used for calculations.

Industrial effluent experiment

The effect of biosorbent dosage (0.5–2.0 g) and contact time (5–60 min) on Cr(VI) removal from industrial effluent was examined. In all experiments the working volume was 50 mL.

Chromium concentration in the solution was determined by applying atomic absorption spectrometry (iCe 3000 series) with electrothermal atomization at a resonance line of 357.9 nm.

Data evaluation

The biosorption of Cr(III)/Cr(VI) by *Spirulina platensis* biomass was evaluated using the following parameters, which were calculated from experimental results:

(a) amount of heavy metals retained on mass unit of spirulina biomass (q, mg/g):

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

(b) efficiency of heavy metals removal (R, %):

$$R = \frac{C_i - C_f}{C_i} \cdot 100\% \tag{2}$$

where q is the amount of metal ions adsorbed on the biosorbent, mg/g; V is the volume of solution, L; 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.

The experimental equilibrium data were modelled using two isotherm models, namely Langmuir and Freundlich. According to the Langmuir isotherm model, the biosorption process occurs at specific homogeneous sites on the biosorbent surface, until a complete monolayer is formed. The linear form of equation of the Langmuir isotherm is expressed as follows:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{b q_{max} C_e} \tag{3}$$

where q_e (mg/g) is the amount adsorbed at the equilibrium concentration C_e, q_m (mg/g) is the Langmuir constant representing the maximum monolayer adsorption capacity and b (L/mol) is the Langmuir constant related to energy of adsorption.

The dimensionless separator factor (R_L) is the essential characteristic of this model, which is defined by:

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

where b is the Langmuir constant and C_i is the initial concentration of metal in solution. The value of R_L indicates the shape of the isotherms to be either irreversible (R_L=0), favorable (0<R_L<1) or unfavorable (R_L>1).

The Freundlich isotherm is an empirical equation, which assumes a heterogeneous biosorption system with different active sites. The liniar form of Freundlich equation is written as follows:

$$lnq_e = ln\, K_F + \frac{1}{n} ln\, C_e \qquad (5)$$

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

For the kinetic modelling, two kinetics models have been used to fit the experimental data. The pseudo-first-order Lagergren model expressed as:

$$log(q_e - q) = log\, q_e - \frac{K_a}{2.303} t \qquad (6)$$

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.

The pseudo-second-order kinetics can be expressed:

$$\frac{1}{q} = \frac{1}{K_b q_e^2} + \frac{t}{q_e} \qquad (7)$$

where q and q_e are the adsorbed amounts (mg/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 straight lines in the graphical representation of log (q_e-q) *vs.* t for the pseudo-first order kinetics model, and t/q *vs.* t for the pseudo-second order kinetics model highlight the applicability of these models in the describing of biosorption kinetics and will allow the calculation of characteristic kinetics parameters (K_a, K_b and q_e) from the slopes and intercepts of the linear plots.

The thermodynamic parameters, 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 obtained from the slope and intercept of lnK_d *vs.* 1/T plots, which are calculated by a curve-fitting program.

$$lnK_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (8)$$

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

The distribution coefficient (K_d) was calculated using the following formula:

$$K_d = \frac{(C_0 - C_e)V}{mC_e} \qquad (9)$$

where C_0 and Ce are initial and equilibrium chromium concentrations (mg/L), V is the volume of the solution (mL), and m is the mass of the biosorbent (g).

The Gibbs free energy, (ΔG°), of specific adsorption was calculated from the equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (10)$$

RESULTS AND DISCUSSION

Effect of pH and sorbent dosage

pH is the most important parameter affecting the solution chemistry of chromium as well as the distribution of functional groups of biomass species.[9] The effect of solution pH on Cr(III) and Cr(VI) sorption was evaluated within the pH range from 2.0 to 6.0. The process of chromium biosorption was studied till pH 6 as under alkaline conditions weakly soluble $Cr(OH)_3$ and $Cr(OH)_4^-$ forms are formed[3]. As it can be seen from Fig. 1 the Cr(III) uptake reached the maximum 74% at pH 3.0 and the decrease of metal removal capacity was observed at pH range 4.0-6.0. The high chromium biosorption can be explained by electric attractive interactions between the positive chromium ions $Cr(OH)^{2+}$, $Cr(OH)_2^+$ and Cr(III) and algal cell wall functional groups.[10]

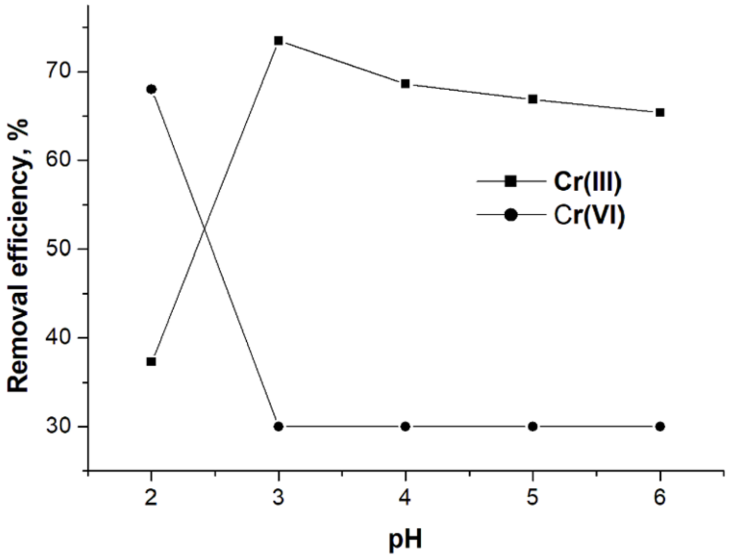

Fig. 1 – Removal of Cr(III) and Cr(VI) ions at different initial pH (T 293 K; C_i 10 mg/L; sorbent dosage 0.5 g; adsorption time 1 h).

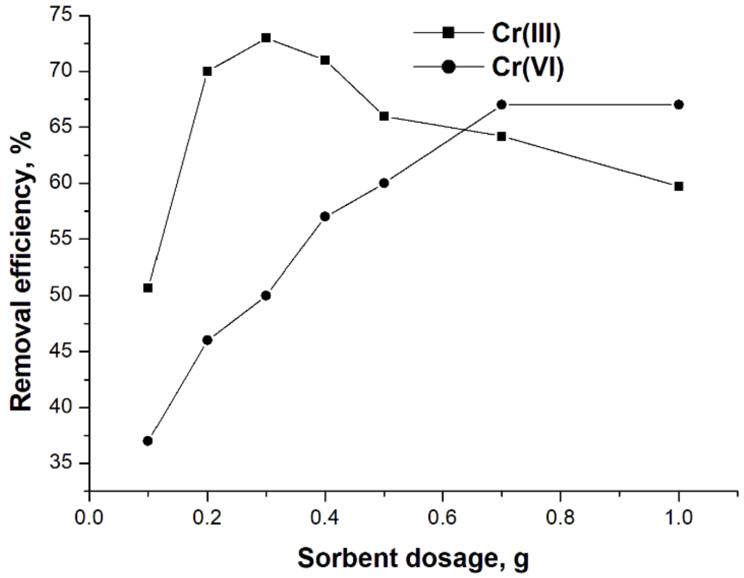

Fig. 2 – Effect of biosorbent dose on biosorption capacity and removal efficiency of chromium ions by *S. platensis* biomass (T 293 K; C_0 10 mg/L; adsorption time 1 h, pH 2 Cr(VI)/ pH 3 (Cr(III)).

Maximum Cr(III) sorption (74%) in Gagrai et al. study[2] was observed at initial pH 4.0. Jagiełło *et al.*[3] showed the pH 3.0 was optimal for Cr(III) removal by *Spirulina* sp.

The maximum Cr(VI) removal (0.73 mg/g) was achieved at pH 2.0, due to the protonation of functional groups on the cyanobacteria surface and presence of chromium in solution in anionic forms $HCrO_4^-$ and $Cr_2O_7^{2-}$.[12] At higher pH values, the overall surface charge on cell wall becomes negative and biosorption decreases.[13] Amine groups may play an important role in Cr(VI) ions binding.[2] Donmez and co-authors[9] performed experiments on Cr(VI) biosorption by *Chlorella vulgaris, Scenedesmus obliquus and Synechocystis sp* biomass and showed maximum Cr(VI) uptake at pH 2.0. The maximum biosorption of Cr(VI) (80%) from the medium occurs at pH 2.0 by *S. platensis* during 48 h experiment.[12]

Fig. 2 illustrates the effect of the biosorbent dose on the Cr(III)/Cr(VI) biosorption from solutions. The experiments were performed at optimal pH values determined in previous experiments. The dependence in Fig. 2 shows that Cr(VI) removal efficiency varied from 37% to 67% for an increase of the biosorbent dosage from 0.1 to 1.0 g. The biosorption was constant at sorbent dosage 0.7 and 1.0 g, that could be explained by the decrease of surface area for biosorption due to formation of aggregates of biomass at higher doses and competition of the ions for the available sites[13].

In case of Cr(III) maximum metal removal was achieved at sorbent dosage 0.3 g after some reduction was observed. The observed trend can be attributed to the fact that at higher sorbent quantities a partial aggregation of biomass occurs, which determined a decrease in the effective surface area for biosorption.[14] Therefore, the optimum sorbent dose for further experiments was selected as 0.3 g for Cr(III) and 0.7 g for Cr(VI).

Effect of time and kinetics of sorption

Contact time highly influences the biosorption process. Biosorption can be presented as a two-stage process, in which rapid sorption of metal ions to the surface groups of the biomass occurs at the first phase followed by diffusion of metal to internal binding sites on the biomass in the second phase.[13] Fig. 3 shows the effect of contact time on the biosorption of Cr(III) and Cr(VI) ions by *S. platensis* biomass.

The results indicated rapid sorption of Cr(III) in first 30 min of sorbent- sorbate interaction after that the equilibrium was reached. In 30 min 70% of chromium ions were removed from solution. The maximum amount of Cr(VI), which constitute 62% was removed in 45 min of interaction.

In order to investigate the process of Cr(III)/Cr(VI) ions biosorption by *S. platensis* biomass, two kinetic models, pseudo-first order and pseudo second order models, were used to analyze the experimental data. The slope and intercept of plot of $\log(q_e-–q_t)$ versus 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).

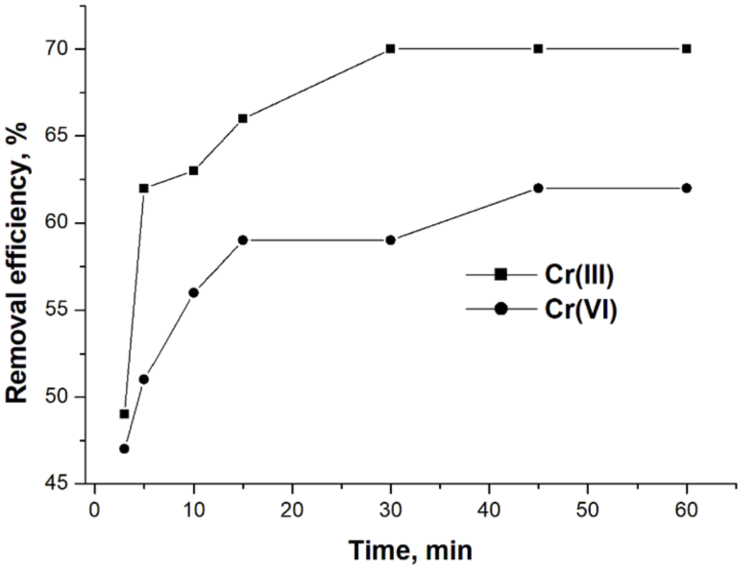

Fig. 3 – Effect of contact time on the sorption of chromium ions by *S. plat*ensis biomass (T 293 K; C_0 10 mg/L; pH 2 Cr(VI)/ pH 3 (Cr(III)).

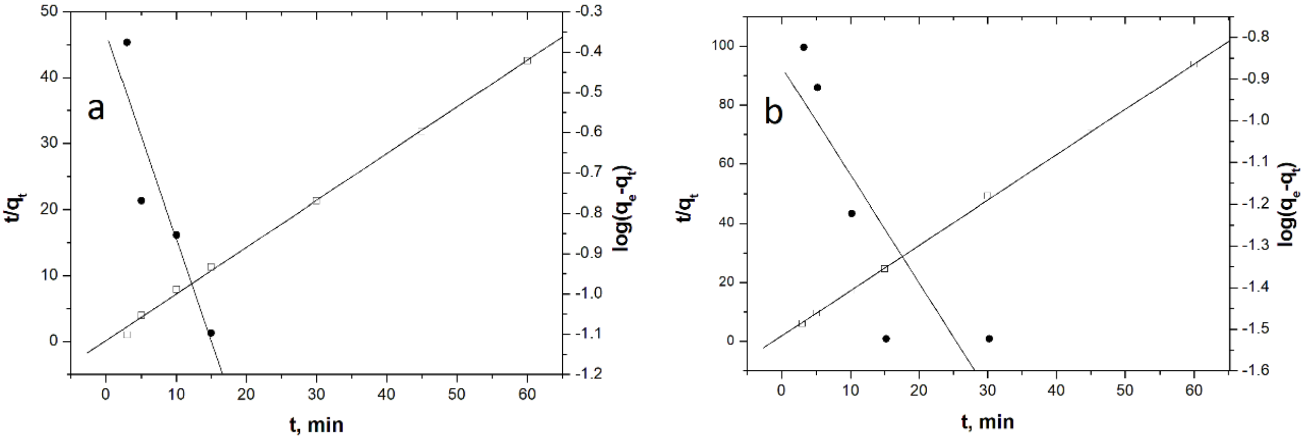

Fig. 4 – The pseudo-first- and pseudo second order plots of kinetic study of (a) Cr(III) and (b) Cr(VI) biosorption on *S. platensis*.

Table 1

Lagergren's pseudo-second-order model parameters

Cr(III)				
Ce, mg/L	$q_{e\,(exp)}$, mg/g	$q_{e\,(cal)}$, mg/g	k_b, g/mg*min	R^2
10	1.41	1.41	0.92	0.999
Cr(VI)				
Ce, mg/L	$q_{e\,(exp)}$, mg/g	$q_{e\,(cal)}$, mg/g	k_b, g/mg*min	R^2
10	0.64	0.65	1.56	0.999

The correlation coefficients for the pseudo-first-order model obtained for both forms of chromium show negative value. It can be concluded that pseudo-first-order model is not applicable to describe experimental data. The correlation coefficient, R^2, for the pseudo-second-order rate equation was 0.999 for both chromium species. Parameters calculated for pseudo-second-order model are presented in Table 1.

Applicability of second order model shows that the rate controlling step in the biosorption process is the chemical interaction between Cr(III)/Cr(VI) ions from aqueous solution and functional groups from cyanobacteria biomass surface.[14]

Effect of concentration and isotherm modeling

The initial metal ion concentration remarkably influenced the equilibrium metal uptake and adsorption yield. The increase of chromium concentration in solution from 10 to 200 mg/L led to increase of the amount of chromium adsorbed by biomass from 1.2 to 11.2 mg/g for Cr(III) and from 0.6 to 9.5 mg/g for Cr(VI).

The adsorption plots of Langmuir and Freundlich isotherm model for biosorption of Cr(III) and Cr(VI) ions by *S. platensis* presented in Fig. 5. The adsorption constants evaluated from the isotherms with the correlation coefficients are given in Table 2.

The obtained values of correlation coefficients show that Langmuir model described better the Cr(III) biosorption process by *S. platensis* and Cr(VI) biosorption fits better into Freundlich isotherm. The Langmuir model is used to estimate the maximum uptake values, which could not be reached in the experiments. The determined q_{max} value of Cr(III) by was found to be 25 mg/g and of Cr(VI) 16.8 mg/g.

Applicability of Langmuir and Freundlich models to the Cr(VI)–Cr(III) biosorption indicates that both monolayer biosorption and heterogeneous energetic distribution of active sites on the surface of biosorbent are possible. The values of R_L for both chromium forms were lower that 1 (0.5 for Cr(III) and 0.56 for Cr(VI)), confirming the favourable biosorption of chromium ions by spirulina biomass.

Both Freundlich and Langmuir adsorption models were applicable for Cr(VI) removal by three algal species in Domnez *et al.*[9] study. Lodi and co-authors[10] showed that Langmuir model described better the Cr(III) biosorption process by S. *platensis* and Cr(VI) biosorption by *C. vulgaris* fits better into Freundlich isotherm[13]. Table 3 shows the maximum biosorption capacity obtained for other biosorbents.

The values of maximum biosorption capacity found in this work were comparable with values presented in the literature.

Thermodynamic study

The effect of temperature, ranging from 293 to 323 K, on the removal of Cr(III) and Cr(VI) ions was evaluated at contact time of 60 min. Increase of temperature from 293 to 323 K lead to decrease of biomass biosorption capacity from 1.025 to 0.675 mg/g for Cr(III) and from 0.66 to 0.49 mg/g for Cr(VI).

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. 6) and the obtained data are presented in Table 4.

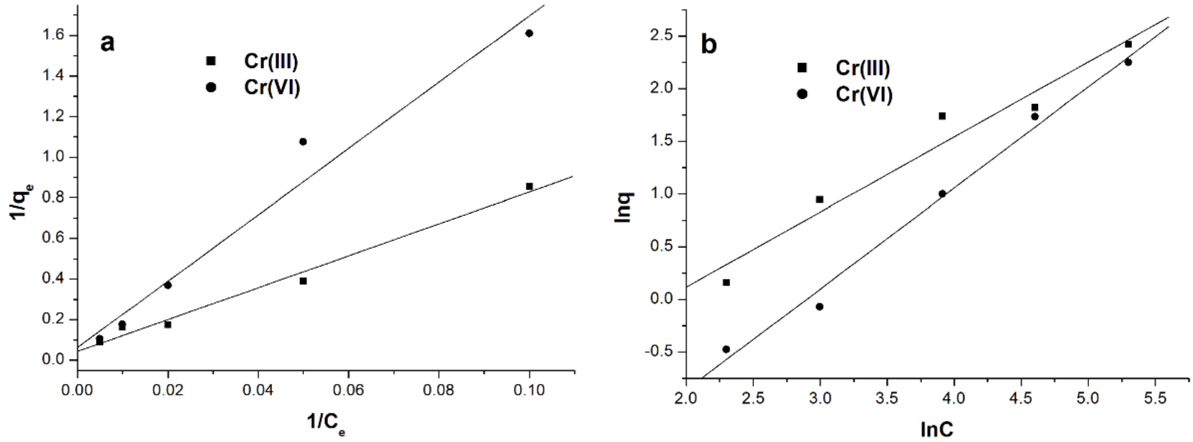

Fig. 5 – Langmuir (a) and Freundlich (b) isotherm models.

Table 2

Isotherm parameters for the biosorption of chromium ions on *S. platensis* biomass

Langmuir model		Freundlich model	
Cr(III)			
R^2	0.99	R^2	0.98
Q max	25.0 mg/g	$\ln K_f$	-1.31
b	0.005	n	1.4
Cr(VI)			
R^2	0.985	R^2	0.995
Q max	16.8 mg/g	$\ln K_f$	-2.77
b	0.004	n	1.04

Table 3

Cr(VI)/Cr(III) biosorption by different type of sorbents

Metal	**Biosorbent**	**q_{max}, mg/g**	**Reference**
Cr(VI)	*Chlorella vulgaris*	23	Donmez *et al.*[9]
Cr(VI)	*Scenedesmus obliquus*	15.6	Donmez *et al.*[9]
Cr(VI)	*Synechocystis* sp.	19.2	Donmez *et al.*[9]
Cr(VI)	*Poly(methyl methacrylate)–grafted Hyparrhenia hirta (PMMA-g-Hh) biopolymer*	4.02-19.95	Guyo *et al.*[15]
Cr(III)	*Spirulina* sp.	38.5-185	Chojnacka *et al.*[8]
Cr(III)	*Spirulina platensis*	30.1-36.8	Lodi *et al.*[10]

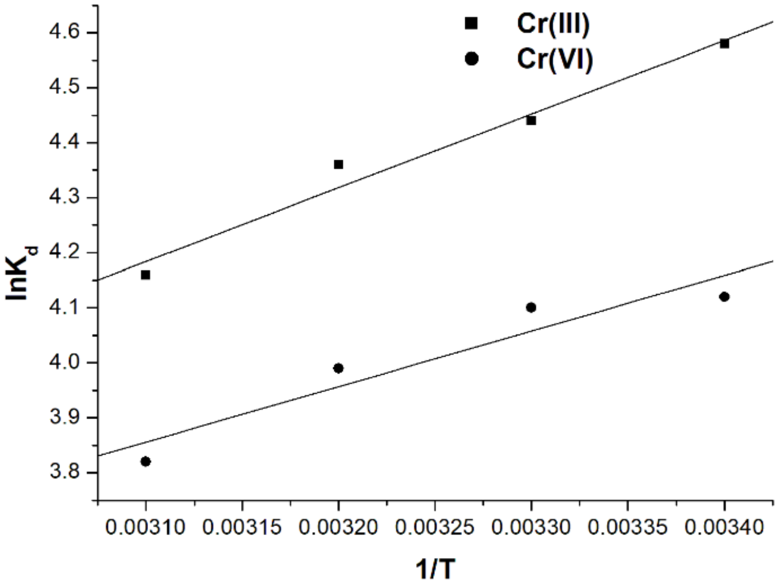

Fig. 6 – Dependence of $\ln K_d$ vs. 1/T.

Table 4

Thermodynamic parameters for Cr(III)/Cr(VI) biosorption on *S. platensis*

Temperature, K	ΔG°, kJ/mol		ΔH°, kJ/mol		ΔS°, J/mol·K	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
293	-11.24	-9.01	-11.1	-8.4	0.35	2.1
303	-11.25	-9.03				
313	-11.25	-9.05				
323	-11.25	-9.08				

A negative value of ΔG° indicates the feasibility of the process and spontaneous nature of the biosorption. The negative values of ΔH° suggests the exothermic nature of biosorption and the positive value of ΔS° confirms the increased randomness at the solid–solution interface during biosorption.

Cr(VI) removal from industrial effluent

Upon completion of batch adsorption experiments, the efficiency of *S. platensis* biomass in the removal of Cr(VI) from industrial effluent as a function of time and sorbent dosage was evaluated. To study the effect of contact time on Cr(VI) absorption experiment was performed at sorbent dosage 0.7 g, determined as more efficient dosage in batch experiments. The data presented in Fig. 7 show that equilibrium was reached after 45 min of interaction. However, the efficiency of Cr(VI) removal was lower than in batch experiments, that can be explained by higher chromium concentration in effluent.

Thus, to increase the efficiency of Cr(VI) ions removal the sorbent dosage was increased from 0.7 to 2.0 g (Fig. 8).

With the increase of sorbent dosage Cr(VI) removal increased from 50 to 72%. In our previous study it was shown that at Cr(VI) was completely removed from wastewater at initial chromium concentration 9.1 mg/L, sorbent dosage 1.0 g during one hour.[16]

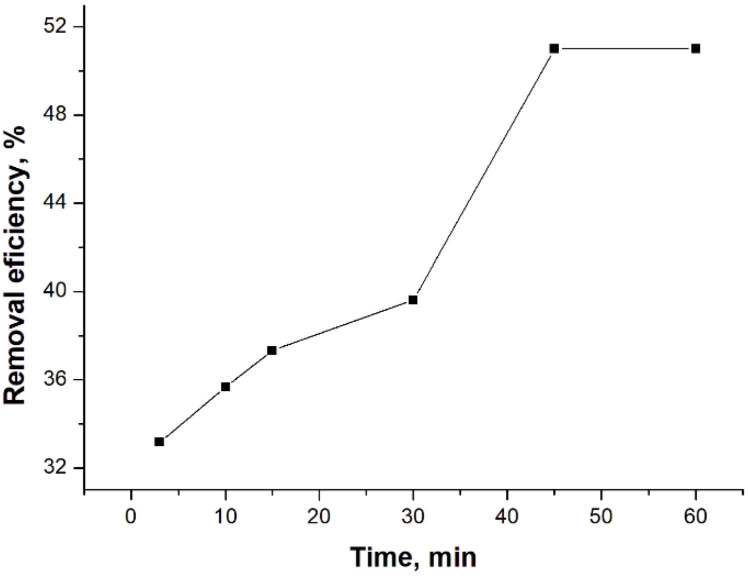

Fig. 7 – Effect of contact time on the sorption of Cr(VI) ions by *S. plat*ensis biomass (T 293 K; C_0 27 mg/L; sorbent dosage 0.7 g, pH 4).

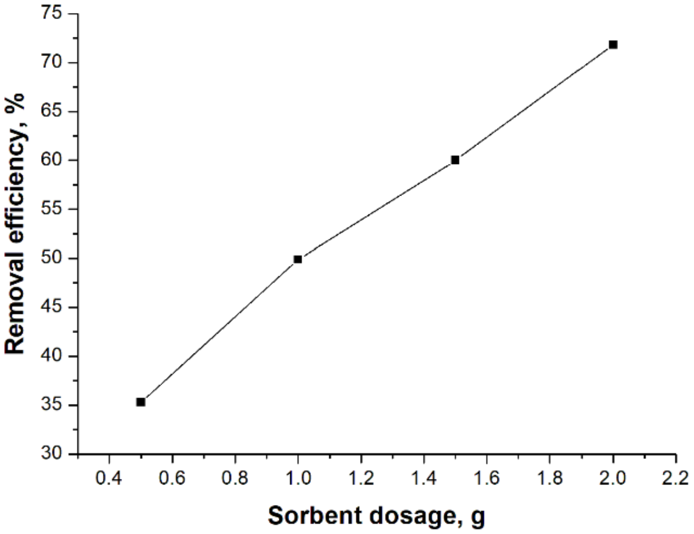

Fig. 8 – Effect of biosorbent dose on removal efficiency of Cr(VI) ions by *S. platensis* biomass (T 293 K; C_0 10 mg/L; adsorption time 45 min, pH 4).

CONCLUSION

Spirulina platensis can be efficiently applied for Cr(III)/Cr(VI) biosorption from batch solutions and industrial effluents. The maximum biosorption capacity of Cr(III) 25.0 mg/g was achieved at pH 3.0, sorbent dosage 0.3 g in 50 mL (or 10 mg/mL) during 30 min interaction and for Cr(VI) 16.8 mg/g at pH 2.0, sorbent dosage 0.7 g in 50 ml (or 14 mg/ml) during 45 min interaction. Biosorption equilibrium data for Cr(III) fit well the Langmuir model and for Cr(VI) and the Freundlich one. Kinetic studies reveal that Cr(III)/Cr(VI) biosorption by spirulina biomass could be described more favorably by the pseudo-second-order kinetic model. The process of Cr(III)/Cr(VI) biosorption was spontaneous and exothermic in nature. Cr(VI) biosorption from industrial effluent constituted 72% at Cr(VI) concentration in effluent 27 mg/L, pH 4, sorbent dosage 2.0 g and interaction time 45 min.

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