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Equilibrium and kinetic modeling of chromium(VI) biosorption by *Aeromonas caviae*

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Abstract

Biosorption of hexavalent chromium, from aqueous solutions, on *Aeromonas caviae* particles was investigated in a well-stirred batch reactor. Equilibrium and kinetic experiments were performed at various initial bulk concentrations, biomass loads, temperatures and ionic background. Equilibrium data were well described by typical Langmuir and Freundlich adsorption isotherms. Furthermore, a detailed analysis has been conducted testing several chemical reaction kinetic models in order to identify a suitable kinetic equation, assuming that biosorption is chemical sorption controlled. Predictions based on the so-called pseudo second order rate expression were found in satisfactory accordance with experimental data.

Keywords: Biosorption; Chromium(VI); Equilibrium study; Kinetic study; Metals

1. Introduction

The effective removal of heavy metals from aqueous wastes is among the most important issues for many industrialized countries. The treatment methods used to remove heavy metals from wastewaters include, mainly, chemical precipitation but also ion exchange, adsorption or membrane processes [1]. However, biosorption, i.e. the uptake of heavy metals by non-living biomass, has gained increased credibility during recent years, as it offers a technically feasible and economical approach [2]. It could be considered as an eco-friendly device to the existing high cost technologies. Generally, biosorptive processes can reduce capital costs by 20%, operational costs by 36% and total treatment costs by 28%, compared with the conventional systems [3]. Several biological materials were investigated for the removal of heavy metals including bacteria, yeasts, algae and fungi [3–6].

Several wastewaters, such as those produced during dyes and pigments production, film and photography, galvanometry, metal cleaning, plating and electroplating, leather and mining, may contain undesirable amounts of chromium(VI) anions, according to the respective water standards [1]. Due to the severe toxicity of Cr(VI), the EU Directive, WHO and US EPA have set the maximum contaminant concentration level for Cr(VI) in domestic water supplies as $50\,\mu g\,L^{-1}$ [7]. The selection of Cr(VI) in order to examine its removal by the application of biosorption is due to the fact that it is a toxic metal of high environmental risk, hence of immediate priority for the application of novel treatment methods. Furthermore, it is noted that Cr(VI) behaves as an oxyanion (CrO_4^{2-} or $Cr_2O_7^{2-}$) in aqueous solution, according to the aquatic chemistry of chromium [8]. Therefore, it cannot be precipitated and also it may not bind to negatively charged common functional group of biomass surfaces such as carboxylates, because of the respective charges repulsion.

Although most current research of biosorption is oriented towards the removal of heavy metal cations, the uptake of toxic metal anionic forms by biomass has become a growing concern in this field. The removal of Cr(VI) using peat-moss, corn-cob and seaweed biomass has been previously studied with promising results [9]. The biosorption of Cr(VI) on algae *Spirogyra* was evaluated by Langmuir isotherms obtained at a number of different equilibrium pH values at an optimum algae concentration of $5\,g\,L^{-1}$. The maximum Cr(VI) adsorption at optimum pH of 2 was found to be $14.7\,mg\,g^{-1}$ [8]. Protonated or Ca-form from *Sargassum* seaweed biomass bound up to $40\,mg\,g^{-1}$ of Cr(VI) by simultaneous anion exchange and Cr(VI) to Cr(III) reduc-

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tion [10]. Several biomasses such as *Streptomyces noursei*, *Rhizopus arrhizus* and *Chlorella vulgaris* had shown sufficient uptake rates of Cr(VI) in the order of 10.6, 8.8 and 24 mg g^{-1}, respectively [2]. The dead biomass of *Rhizopus nigricans*, a by-product of fermentation industry as well as *Chlorella vulgaris* were found to be potential biosorbent materials for the removal of Cr(VI) [11]. Biosorption of Cr(VI) onto cone biomass of *Pinus sylvestris* was studied at varying experimental conditions and the maximum adsorption capacity was found to be 201.81 mg g^{-1} at pH 1 [12]. Nevertheless, studying of toxic anions biosorption remains an open and interesting challenge.

The aim of the present work is the study of biosorption by using *Aeromonas caviae*, as dead biomass. Despite the fact that this microorganism is often present in groundwaters and, generally, in aquatic environments, no pertinent publications could be found regarding its use for the removal of heavy metals from wastewaters. The purpose of selecting this bacterium for biosorption is, apart from its originality, chiefly to assess the possibility of utilizing a specific bacterial biomass, which exhibits a particular tolerance towards heavy metals [13].

Equilibrium and kinetic analyses may lead to suitable rate expressions, characteristic of possible reaction mechanisms. Many studies engaged so far to examine sorption phenomena involved analysis of batch experiments, where data were sampled at even time intervals over the entire course of the process. As a result, fast changing kinetic data characteristic of the phenomena just after the onset of sorption could not be accurately depicted in an adequately short time scale. Thus, a main objective of the present study was to investigate the kinetic mechanism of chromium sorption on biomass particles, putting more emphasis on samples collected at short periods of time after the beginning of the process, where the major part of the adsorption process occurs.

2. Materials and methods

2.1. Biomass and growth conditions

Aeromonas caviae, a gram-negative bacteria isolated from the water wells near Thessaloniki (North Greece), was grown at 29 °C in a rotating shaker for 24 h in a liquid medium containing: yeast extract (0.5%, w/v), tryptone (1%, w/v), NaCl (0.5%, w/v) and $FeSO_4 \cdot 7H_2O$ (0.2 g L^{-1}). The produced biomass was separated by centrifugation at 3000 rpm, washed several times by a solution of NaCl (0.9%, w/v), sterilized and stored as a slurry.

2.2. Biosorption experiments

2.2.1. Equilibrium study

Batch biosorption experiments were performed in conical flasks stirred in a reciprocal shaker (at 180 rpm) for 2 h at different temperature (20, 40 and 60 °C) and for different biomass concentration. An aqueous solution of Cr(VI) of known concentration (varying from 5 to 350 mg L^{-1}, prepared from $K_2Cr_2O_7$ salt) was added to the biomass suspension, which was dispersed by using a hand homogeniser (Jencons, with 45 μm clearance) in the appropriate aqueous volume, to produce the required concentration. The solution pH was adjusted by the addition of HNO_3 to 2.5, which was found to be the optimum pH value for Cr(VI) biosorption during preliminary studies [14]. The natural pH values of cell suspensions were measured to be 6.8. The pH of the metal solutions, which depend on the metal concentrations, ranged between 5 and 5.5. The pH was measured after mixing of biomass suspension with metal solution; it was found to be 5. In all sets of experiments the system was well buffered and no change of pH value was observed. Otherwise, the pH measurements before and after Cr removal indicating only a negligible increase in solution pH (pH 2.5–2.6), thereby indicated the absence of any ion-exchange mechanism. The mean values of three replicates of the batch experiments were presented.

The residual concentration of Cr(VI) in solution was analyzed after the separation of used biosorbent by centrifugation at 3000 rpm for 15 min, using UV–vis. spectrophotometry (HITACHI UV-200), applying a colorimetric spectrophotometry method at 540 nm and using diphenylcarbazide [15]. No other ions interfere the analysis, as the reaction with diphenylcarbazide is specific for chromium(VI).

2.2.2. Kinetic study

Batch biosorption experiments were carried out using different biomass concentrations (0.5, 1 and 2 g L^{-1}), initial chromium concentrations (5 and 50 mg L^{-1}), and co-existing concentrations of a common salt (0.01 and 0.5 M of $NaNO_3$) at 20 °C. Nitrate salt was selected as a possibly inhibiting anion because of its low tendency for complex formation with most metals. All biosorption experiments were carried out at the optimum pH for Cr(VI) adsorption (pH 2.5), as it was also determined during preliminary experiments. The mixing of biomass suspension with metal solution was done as described above. The experiments were performed in an Erlenmeyer flask at 180 rpm agitation speed (Heidolph type, RZR 2102). This speed was selected (after preliminary tests) as the lower speed that gives reproducible sorption curves. 2 mL samples were withdrawn at selected time intervals (2 min) using a 10 mL syringe with filter (Ø 47 mm, ME 25 ST, 0.45 μm, Schleicher and Schuell). The removed quantities did not affect the working volume of the reactor, which was 400 mL. All kinetic experiments were carried out in triplicate and the mean values were used in calculations.

Finally, the residual concentration of Cr(VI) in solution was analyzed applying a colorimetric spectrophotometry method at 540 nm and using diphenylcarbazide [15].

3. Results and discussion

3.1. Biomass characterization

Among the most important aspects that have to be evaluated in a biosorption study, is the selection of a suitable microorganism, capable of sequestering large amounts of heavy metals from wastewaters. A possible preliminary test, which may be used to perform this selection, is the surface titration of biomass [18]. With this experimental procedure a rough characterisation of the selected biomass can be obtained, mainly when ionic exchange is the prevalent mechanism in the removal of heavy metals from wastewater [16]. In order to gain closer insight of biomass surface properties, a suspension of biomass was potentiometrically titrated applying 0.1N NaOH. The respective curve is displayed in Fig. 1. The results of titration experiments permit the qualitative and semi-quantitative determination of the nature and number of acidic sites present on the bacterial cell wall. The curve shows at least two flexion points at approximately pH 4 and 6, corresponding to the pK_a values of acidic groups. It may be suggested that these two groups are carboxylic and phosphate [17]. These types of acidic sites are capable of removing metallic ions, usually cations, from aqueous solutions through the application of different mechanisms, such as cell surface sorption (complexation, surface precipitation etc.), as well as by extracellular and intracellular accumulation [16]. At low (acidic) pH values the protonated carboxyl or phosphate groups are positively charged and therefore, they will electrostatically attract anions.

Furthermore, analyzing the highly complex IR spectrum certain characteristic peaks can be identified (Fig. 2), as well as it was illustrated that the cell wall contains two or more main functional groups responsible for the uptake of heavy metals. The 1071 and 1673 cm^{-1} bands in the non-loaded biomass are due to C–O and C=O stretchings representing carbonyl and carboxyl groups, whereas the group of phosphate presents certain other characteristic absorption peaks, such as P=O stretching at 1150 cm^{-1}, P–OH stretching at 1040–910 cm^{-1} and P–O–C stretching at 1050–970 cm^{-1}.

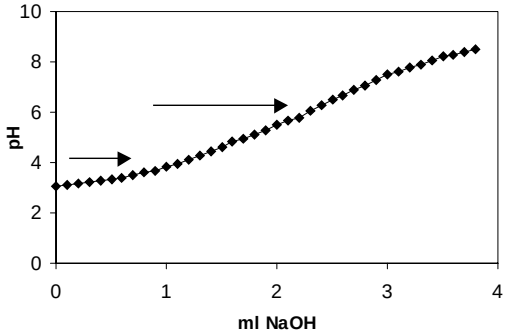

Fig. 1. Biomass potentiometric titration: 1 g of biomass is potentiometrically titrated with 0.1N NaOH.

The appearance of peaks at 3000 and 900 cm^{-1} indicate the role of carboxyl and phosphates groups during the uptake of Cr(VI), respectively. Several peaks are visible at 3500–3000 cm^{-1} (N–H stretching) and at 1250–1000 cm^{-1} (C–N stretching), presenting amino groups [20]. The FTIR spectral analyses of biomass loaded with Cr(VI) indicated elongation of these bands after chromium biosorption and suggesting the role of these groups during biosorption of chromates. Some binding of metal probably takes place also on nitrogen-containing groups. With IR spectrum, analysis on the nature of the cell membrane, can be approached qualitatively, although additional measurements under diverse experimental conditions are necessary to produce further experimental evidence.

The magnitude of electrostatic interaction between the bacteria cell surfaces and a metal ion is a function of electrokinetic potential (expressed here as zeta potential). Zeta potential measurements may provide useful information, regarding the net effective charge on the cell surface. Electrokinetic measurements of *A. caviae* biomass against the pH values are shown in Fig. 3. The pH affects the availability of metal ions in solution (speciation). At the optimum sorption pH value (2.5), the dominant species of Cr ions in solution are CrO_4^{2-} and $Cr_2O_7^{2-}$ [8]. These anions would be expected to interact more strongly with the ligands carrying positive charges. As the pH value was lowered, the overall surface charge of cell surface will become positive, whereas at higher pH values the overall surface charge will become negative. However, heavy metals have a strong affinity with proteins of the cell wall. As the pH is lowered the overall surface charge on the cells will become positive or less negative, which will promote the approach of negatively charged metal ions. The amino and carboxyl groups and the nitrogen and oxygen of the peptide bond could be available for characteristic coordination bonding with metallic ions. It was found that at low pH values the protonation of functional groups (e.g. carboxyl and amino groups) gives an overall positive charge to biomass, which was able to adsorb negatively charged heavy metal ions [5].

3.2. Equilibrium modeling

Analysis of equilibrium data is important for developing an equation that can be used for design purposes. Classical adsorption models, such as the Langmuir and Freundlich models, have been extensively used to describe the equilibrium established between adsorbed metal ions on the biomass (q_e) and metal ions remaining in solution (C_e) at a constant temperature. The Langmuir equation refers to a monolayer sorption onto surfaces containing a finite number of accessible sites:

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (1)$$

where q_{max} is the maximum quantity of metal ions per unit weight of biomass to form a complete monolayer on the

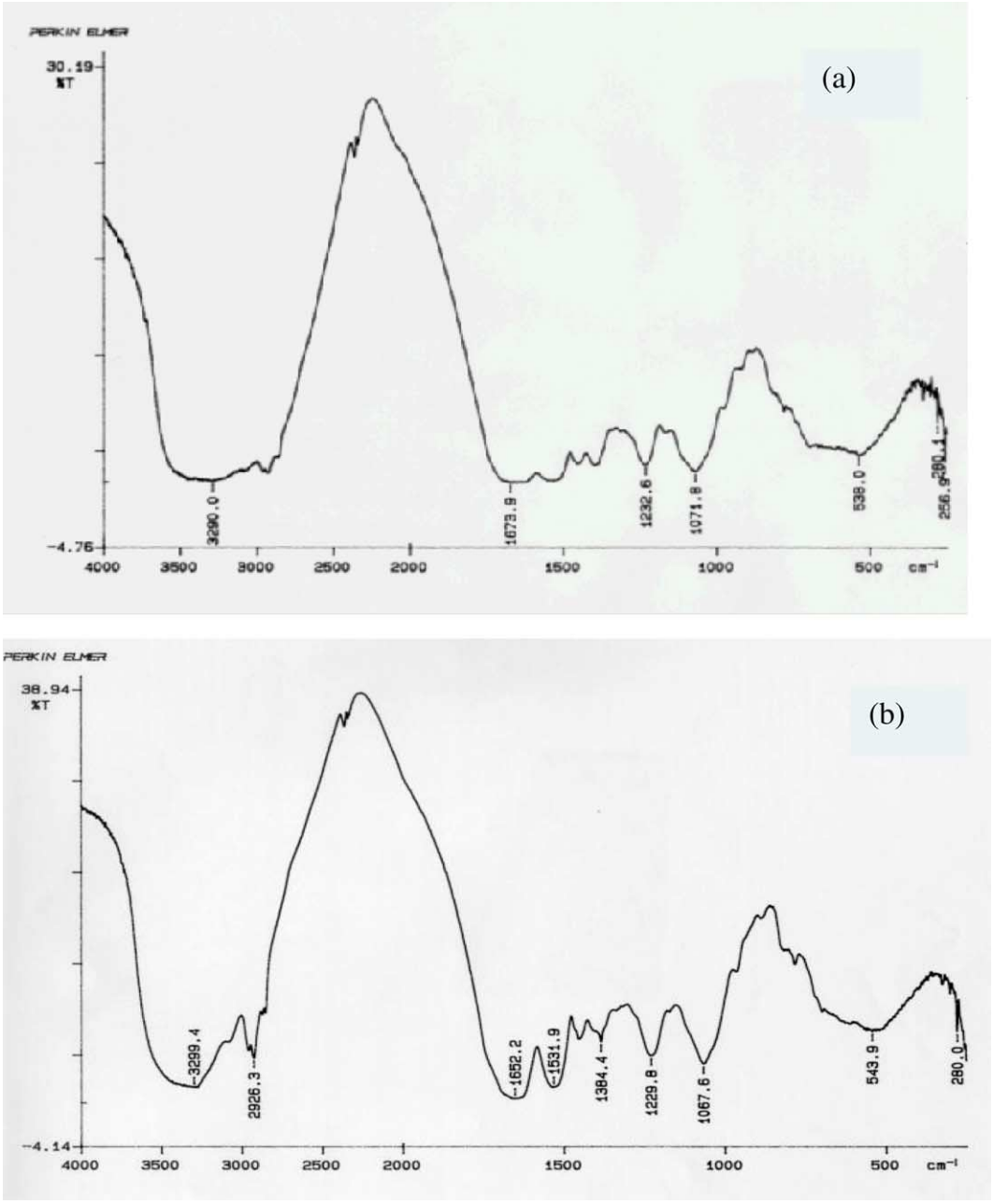

Fig. 2. Infrared spectra of the biomass: (a) before and (b) after Cr(VI) sorption.

surface (mg g^{-1}), whereas b is a constant related to the affinity of binding sites with the metal ions (sorbate, L mg^{-1}). It should be noted, that q_{max} represents a practical limiting adsorption capacity corresponding to the surface of sorbent fully covered by metal ions. This quantity is particularly useful in the assessment of the adsorption performance, especially in cases where the sorbent does not reach its full saturation as it enables the indirect comparison between different sorbents [19].

The empirical Freundlich equation accounts macroscopically for sorption on heterogenous surfaces:

$$q_e = K_F C_e^{1/n} \quad (2)$$

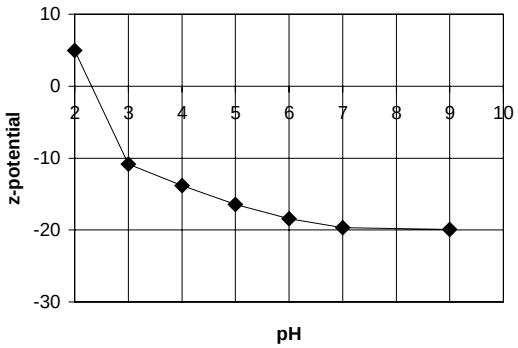

Fig. 3. Zeta potential measurements of *Aeromonas caviae*.

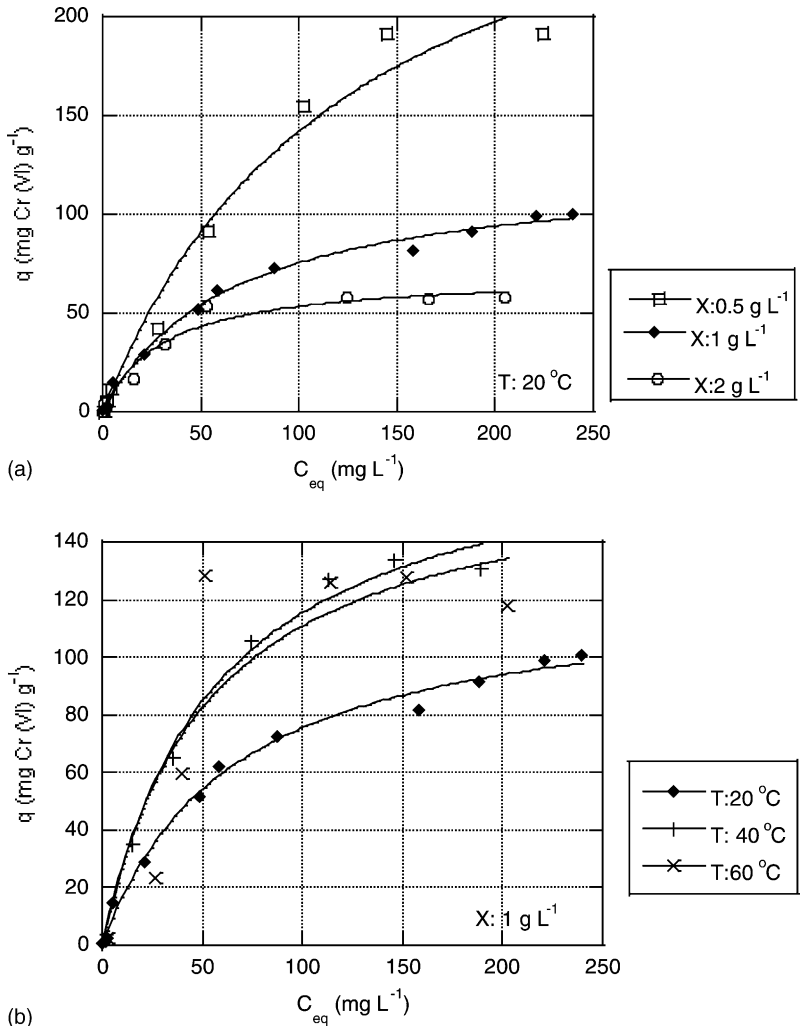

Fig. 4. Application of Langmuir model to biosorption of chromates at pH 2.5 for: (a) different biomass concentrations; (b) different temperatures.

where K_F is an indicator of adsorption capacity (L g^{-1}) and n indicates the effect of concentration on the adsorption capacity and represents the adsorption intensity (dimensionless) [19].

Experimental adsorption isotherms of chromate anions, obtained with different initial biomass concentrations and temperatures, are presented in Figs. 4(a) and (b), respectively, at the optimum pH value of 2.5, as it was determined during preliminary experiments [14]. For each isotherm the initial metal concentration was varied, while the biomass load and temperature were kept constant. The Langmuir and Freundlich adsorption constants evaluated from the isotherms with the correlation coefficients are presented in Table 1. The q_{max} value is the maximum value of q_{eq}, which is important to identify which biosorbent show the highest uptake capacity and as such, is useful in scale-up considerations. The maximum capacity q_{max} defines the total capacity of biosorbent for chromium(VI). The magnitude of the q_{max} was found to span to a range of values (69.95–284.44 mg g^{-1}) comparable to other types of

Table 1
Freundlich and Lagmuir models regression constants for different experimental conditions

Conditions		Langmuir constants			Freundlich constants		
T (°C)	Biomass load (g L^{-1})	q_{max} (mg g^{-1})	b (L mg^{-1})	r^2	K_f (L g^{-1})	n (–)	r^2
20	0.5	284.44	0.010	0.962	11.97	1.88	0.936
20	1	124.46	0.015	0.993	7.60	2.10	0.979
20	2	69.95	0.030	0.969	8.20	2.57	0.914
40	1	181.48	0.017	0.993	11.76	2.07	0.965
60	1	169.10	0.020	0.791	13.64	2.27	0.717

Table 2
Selected literature results; comparison of different biosorbents, regarding Cr(VI) removal capacity (Langmuir model)

Biosorbent	q_{max} (mg L^{-1})	pH	T (°C)	$X_{biomass}$ (g L^{-1})	C_o (mg L^{-1})	Reference
Aeromonas caviae	124.46	2.5	20	1	5–350	This paper
Chlorella vulgaris	24	2	25	1	25–250	[2]
Zooglera ramigera	3	2	25	–	25–400	[2]
Halimeda opuntia	40	4.1	26	–	25–400	[2]
Rhizopus arrhizus	62	2	25	1	25–400	[24]
Rhizopus arrhizus	8.8	2	25	–	–	[2]
Rhizopus nigrificans	123.45	2	25	1	50–500	[11]
Sargassum	40	2	–	1	–	[10]
Spirogyra	14.7	2	18	5	1–25	[9]
Pinus sylvestris	201.81	1	25	1	50–300	[12]

biomass earlier reported (Table 2). Although a direct comparison of biomass with other reported biosorbents is difficult due to the varying experimental conditions employed in those studies, *A. caviae* possesses reasonable sorption efficiency in comparison with other biosorbents.

In addition, the values of constant b, corresponds to the concentration at which a chromium(VI) ion amount of $q_{max}/2$ is bound and indicates the affinity for the binding of chromium(VI) ions, imply strong bonding of Cr(VI) to *A. caviae* bacterial biomass, at these experimental conditions. The possibility of desorbing chromium from biomass with a typical elution agent was examined with biomass previously used for sorption Cr(VI) and then desorbing the heavy metal with 0.05 M Na_2SO_4. It was observed that

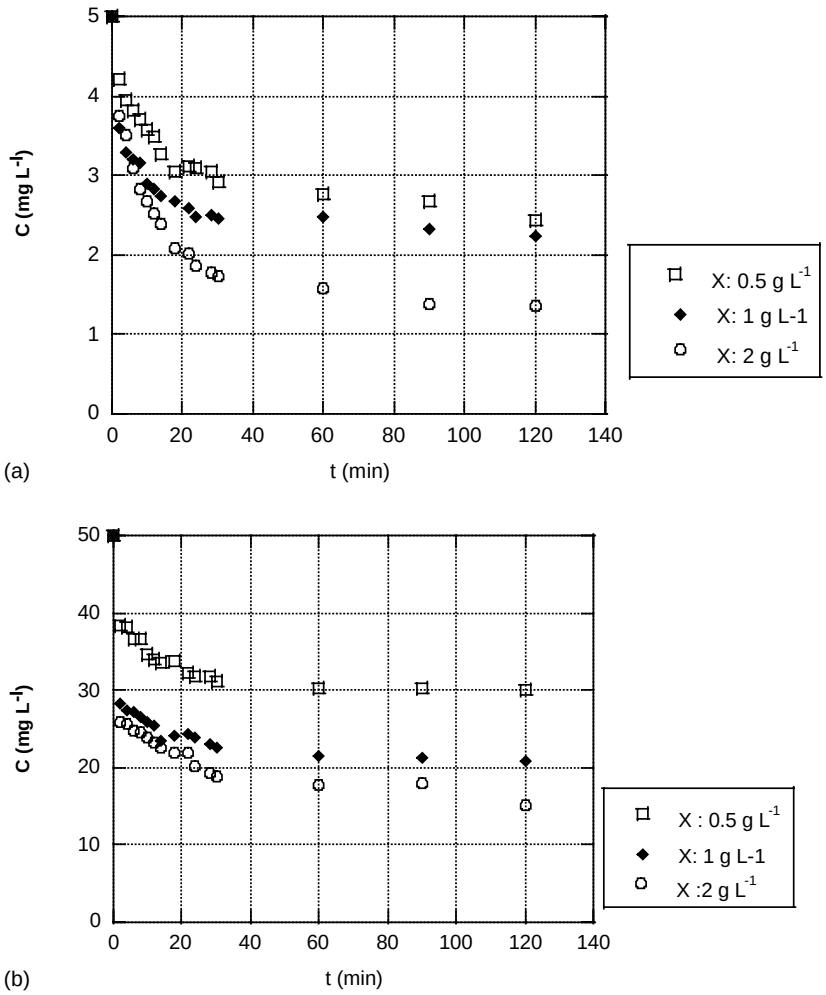

Fig. 5. Biosorption kinetics of Cr(VI) by *Aeromonas caviae* obtained for different initial chromium concentrations of: (a) 5 mg L^{-1}; (b) 50 mg L^{-1} (pH: 2.5, agitation speed: 180 rpm).

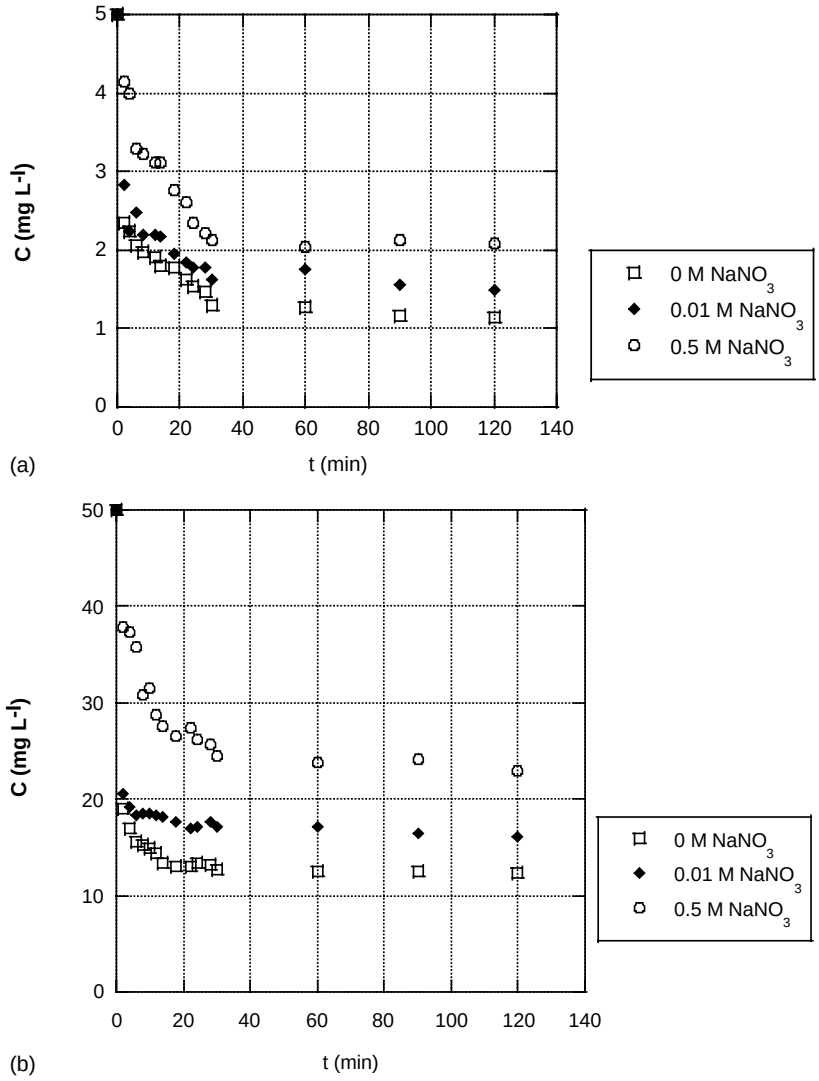

Fig. 6. Biosorption kinetics of Cr(VI) by *Aeromonas caviae* obtained for different concentrations of $NaNO_3$ and for: (a) 5 mg L^{-1}; (b) 50 mg L^{-1} Cr(VI) concentrations at pH: 2.5.

50% approximately of chromium was recovered after desorption experiment lasting 2 h (data not shown). The fact that 100% recovery was not achieved may be due to the strong bonding of Cr(VI) to *A. caviae* biomass.

The results presented at Table 1 demonstrate that the biomass concentration strongly affected the amount of metal removed from aqueous solution. Moreover, as the biomass concentration rises, the maximum biosorption capacity drops, indicating a poorer biomass utilization (lower efficiency).

The maximum biosorptive capacity was observed at 40 °C (for 1 g L^{-1} biomass). An increase of temperature from 20 to

Table 3
Determination of kinetic parameters and comparison with sorption capacities at equilibrium for *T*: 20 °C

Conditions		Equilibrium	Pseudo second order equation			Ritchie second order equation		
C_o (mg L^{-1})	Biomass concen-tration (mg L^{-1})	q_{eq} (mg g^{-1}) (Exp.)	q_{eq} (mg g^{-1})	k_m (g mg^{-1} min^{-1})	r^2	q_{eq} (mg g^{-1})	k_2 (min^{-1})	r^2
5	0.5	5.05	5.19	0.38	0.993	5.05	0.148	0.979
	1	2.48	2.79	0.58	0.998	2.7	0.394	0.979
	2	1.76	1.89	0.195	0.998	1.91	0.172	0.991
50	0.5	42.58	40	0.595	0.999	39.36	0.407	0.959
	1	29.14	29.41	0.735	0.999	27.57	1.197	0.970
	2	17.06	17.24	0.586	0.997	15.56	0.958	0.937

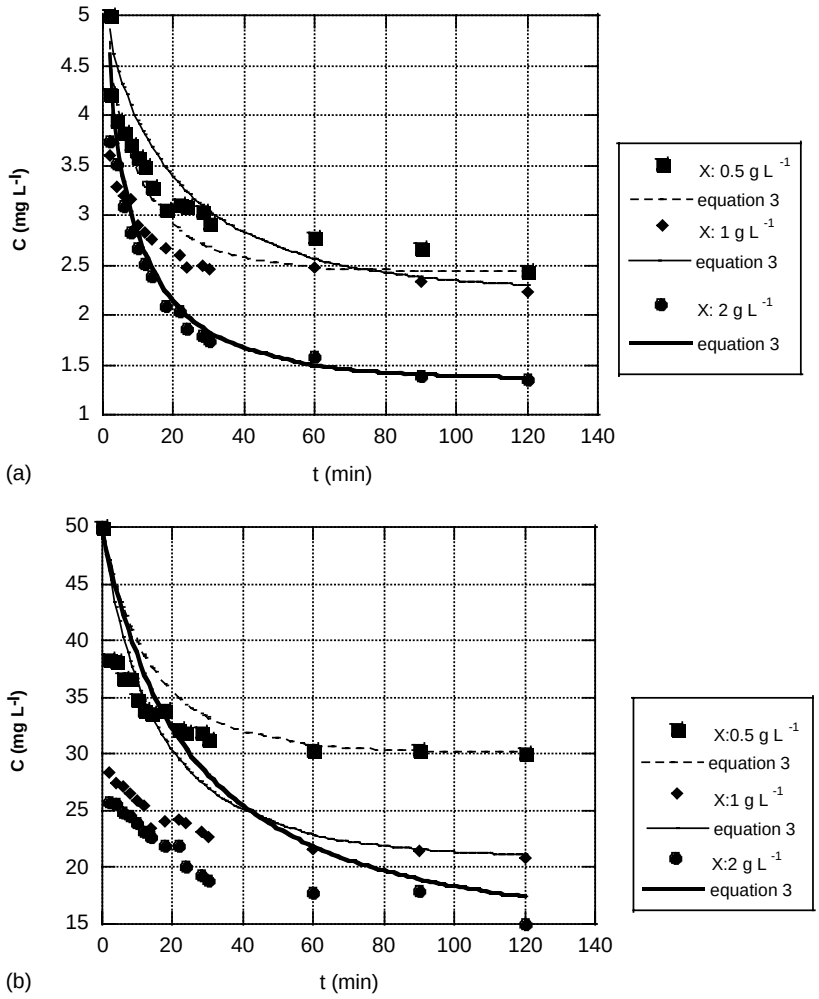

Fig. 7. Chromium biosorption kinetics for different initial chromium concentrations: (a) 5 and (b) 50 mg L^{-1}. The solid lines represent the chromium concentration profiles predicted by the application of 2nd order-type chemical reaction (Eq. (3), pH: 2.5).

40 °C resulted in enhancing the adsorption of Cr(VI). When the temperature is raised from 20 to 60 °C the biosorptive capacity increased from 124.46 to 169.10 mg g^{-1}. Higher removal efficiencies at increased temperature conditions indicated that the adsorption of Cr ions to *A. caviae* is of endothermic nature. At higher temperatures the energy of system seems to facilitates Cr(VI) attachment onto cell surface, but when the temperature is even higher, a decrease of metal sorption may be expected, due to damage of certain surface sites of cell available for metal biosorption. Morphological studies of biomass surface were carried out by obtained the electron micrographs of biomass at different temperature. The morphology of biomass at 20 °C showed a patchy surface where smooth flake-like sections were separated by deep irregular grooves (data not shown), as well as the morphology of biomass at 40 and 60 °C were distinctly different. No flakes or grooves were noticeable but instead the surface appears quite uneven and fragment with prominent ridges emerging, here and there.

The values of the Freundlich constants showed a relatively easy uptake of Cr(VI) anions with high biosorptive capacity of *A. caviae*. In particular, the value of *n*, which is related to the distribution of bonded ions on the sorbent surface, is greater than unity, indicating that Cr(VI) ions are, favorably, adsorbed under all the examined experimental conditions.

The adsorption isotherms obtained for Cr(VI) ions uptake by *Aeromonas caviae* were found to follow at a satisfactory extent both the Freundlich and Langmuir predictions within the studied metal concentration range (5–350 mg L^{-1}). Yet, the correlation coefficients of the Langmuir curves were distinctly higher. This observation implies that monolayer biosorption, as well as heterogenous surface conditions may co-exist under the applied experimental conditions. Hence, the overall sorption of Cr(VI) on the biomass is complex, involving more than one mechanisms, such as ion exchange, surface complexation and electrostatical attraction. In general, the Freundlich equation satisfactory describes experimental data over a wide range of values of θ (fraction of surface coverage with the adsorbed solute) and for systems that does follow the Langmuir isotherm. Even for a system, which does follow the Langmuir isotherm, over a range of surface coverage between the extremes of $\theta = 0$ and $\theta = 1$,

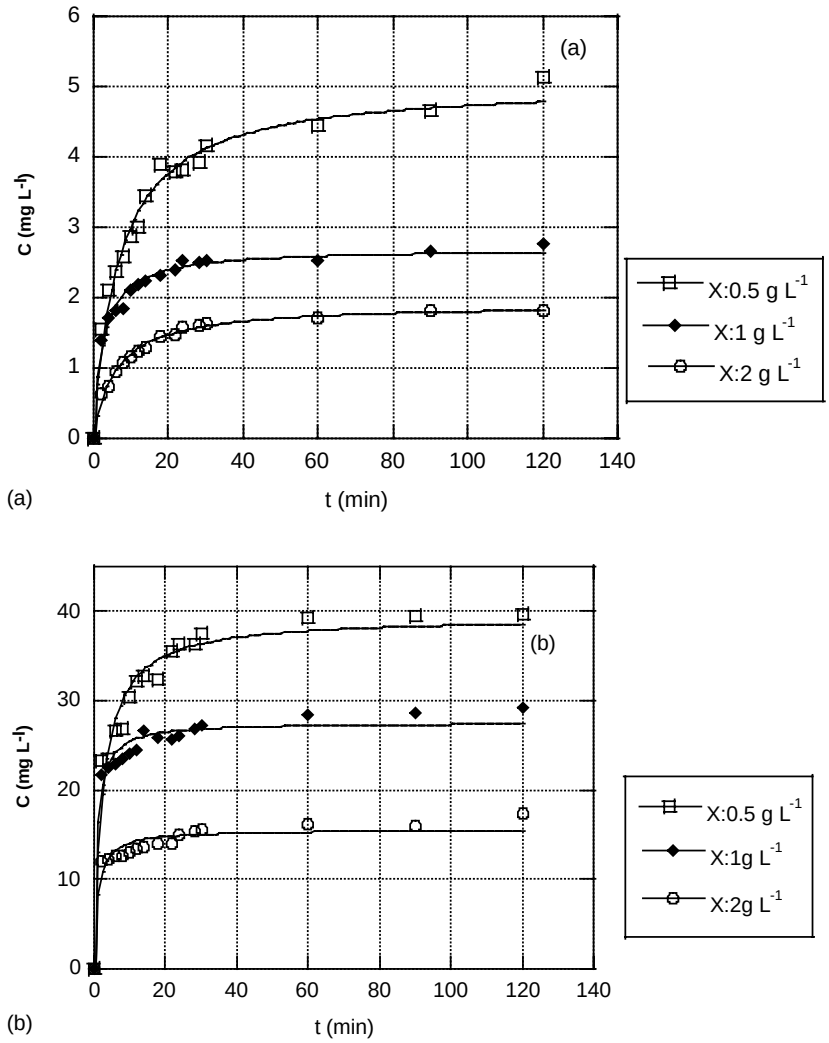

Fig. 8. Comparison of experimental uptake data with theoretical predictions (curves) based on the Ritchie second order kinetic equation (Eq. (4)) for initial chromium concentrations of: (a) 5 and (b) 50 mg L^{-1} (pH: 2.5).

the Langmuir isotherm is nearly equivalent with the case when θ is proportional to a fractional power of C_e [19]. Therefore, both the Freundlich and Langmuir isotherms can be used to modelize biosorption data from dilute aqueous solutions.

3.3. Kinetic experiments

In order to investigate the mechanism of biosorption and potential rate controlling step, such as mass transport and chemical reaction processes, kinetic models have been used to test experimental data. Moreover, information on the kinetics of metal uptake is required for selecting optimum operational conditions for full-scale batch metal removal processes. Figs. 5(a) and (b) present the remaining concentration of chromates in the bulk solution as a function of time at different experimental conditions. Unless differently stated, runs were performed at 20 °C and with 1 g L^{-1} biomass concentration. The very steep descent at the beginning of biosorption process was succeeded by a less rapid decay during the following 20–30 min. From that point on, the Cr(VI) concentration declines at a much lower rate and gradually levels-off towards the end of the experiment (120 min). Thus, the major part of adsorption takes place within the first 30 min of the process. The rapid kinetics has significant practical importance, as it will facilitate smaller reactor volumes ensuring high efficiency and economy.

The application of different biomass (sorbent) concentrations has a direct effect on both total sorption capacity ($C_o - C_e$) and average sorption rate ($\Delta C/\Delta t$); this is more obvious for the higher initial concentration. The adsorption capacity is markedly enhanced, over and above any other parameter, when increasing the initial concentration of Cr(VI). Apparently, the initial concentration of metal provides an important driving force to overcome mass transfer resistance of Cr(VI) between the aqueous and solid phase. Kinetic curves obtained at different temperatures are not presented

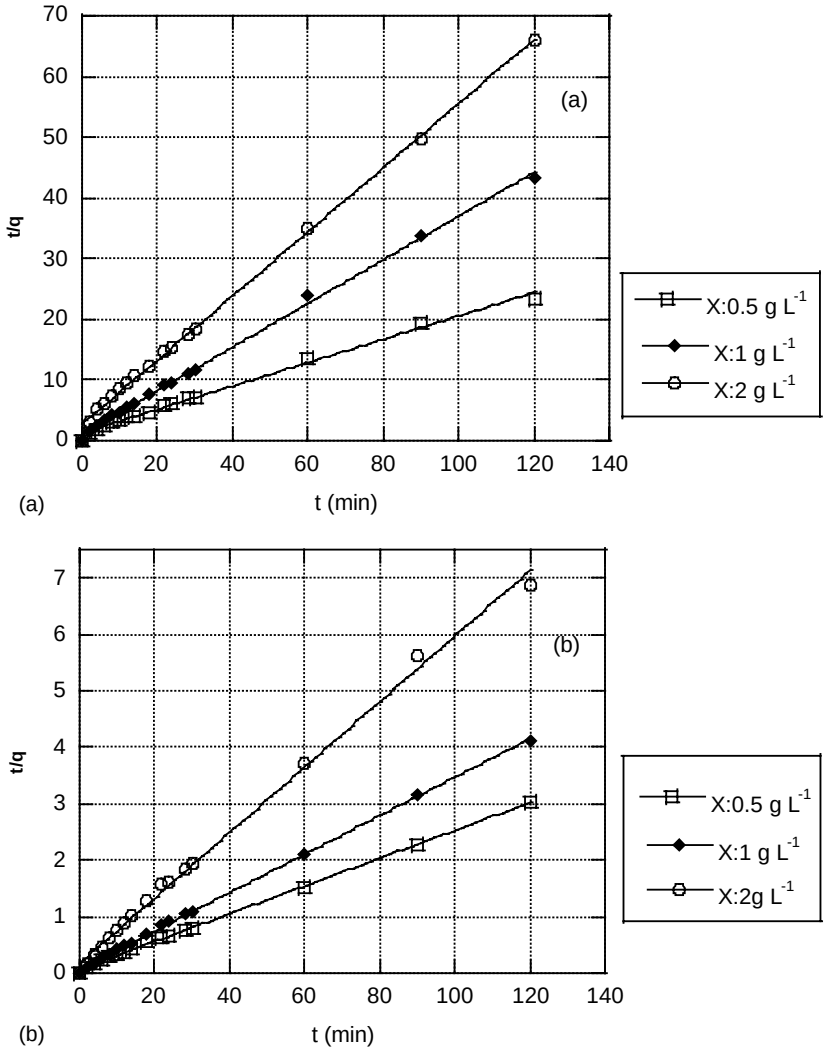

Fig. 9. Comparison of experimental uptake data against theoretical prediction (curves) based on the pseudo second order equation (Eq. (5)) for initial chromium concentrations: (a) 5 and (b) 50 mg L^{-1} (pH: 2.5).

because the surface of biomass exhibits an appreciably different morphology at each different temperature and this invalidates any meaningful quantitative comparison among curves.

In order to identify whether the sorption of chromium obeys a mechanism of electrostatic or chemical nature, some biosorption experiments were performed by adding various concentrations of nitrate salt (initial metal concentrations 5 and 50 mg L^{-1}, biomass concentration 1 g L^{-1}). The impact of the presence of dissolved nitrate ions on the kinetics of Cr(VI) biosorption is shown in Fig. 6. It appears that as the dosage of salt increases both the sorption capacity and sorption rate of Cr(VI) ions decrease. This effect is more intensive with the higher initial metal concentration (50 mg L^{-1}). The added ionic background alters both the equilibrium and the kinetic behavior of the sorbate/sorbent system. The effect of ionic strength may be explained as the outcome of the competition between nitrate and chromium anions during electrostatical binding to the biomass.

3.4. Kinetic modeling

Mathematical models that can describe the behavior of a batch biosorption process operated under different experimental conditions are very useful for scale up studies or process optimization. A number of models with varying degrees of complexicity have been developed to describe the kinetics of metal biosorption in batch systems. According to the kinetic model selection criteria, proposed by Ho et al. [21] several reaction-based and diffusion-based models were tested for the simulation of the obtained experimental data. The finally selected kinetic models will be those, which not only fit closely the data, but also represent reasonable sorption mechanisms. In this study the biomass was employed as a free cell suspension in a well-agitated batch system, where all the cell wall binding sites were readily available for metal uptake, hence the effect of external film diffusion on biosorption rate can be safely assumed as less significant and can be ignored in the subsequent analysis [21].

The best fit for the experimental series of this study was achieved by the application of second order-type kinetic equation. The solution of the common second order reaction equation, based on the stoichiometry of one metal ion/binding site, is [22]:

$$C_t = \frac{C_o}{1 - (C_o/C_e)\exp(-k_2 C_e t)} \quad (3)$$

where k_2 is the reaction rate constant (L/(mg metal min)). This kinetic model has been very effective, in describing the kinetics of adsorption of gases on solids [21]. When the rate of sorption depends not on bulk concentration, but on the uptake of metal by the sorbent, this can be described by the so-called Ritchie second order equation, according to which one metal ion is connected with two binding sites [23]:

$$q_t = q_e \left\{1 - \left[\frac{1}{1 + k_2 t}\right]\right\} \quad (4)$$

where k_2 is the reaction rate constant (min^{-1}). When in the above treatment, q_e that dictates the sorbate uptake is not important then a pseudo second order rate expression is more appropriate [21]:

$$\frac{t}{q_t} = \frac{1}{k_m q_m^2} + \frac{1}{q_m} t \quad (5)$$

where k_m is the reaction rate constant (g biomass/(mg metal min)), whereas q_m is a numerically determined parameter, which in the case of an ideal second order rate control corresponds to q_e.

The relatively short contact time, necessary for achieving equilibrium conditions, apart from the evident processing advantages, is considered as an initial indication that adsorption of chromates on *A. caviae* is a chemical-reaction controlled, rather than a diffusion controlled process [21]. Moreover, the influence of ionic background (nitrates) supports further the notion that sorption of chromium follows (at least partly) a mechanism of chemical nature.

Eq. (3) clearly fails to capture the steep concentration decline during the early removal stage (Fig. 7). This is a direct indication that adsorption on solids from the liquid phase is a different process, than adsorption from a gas phase where, traditionally, the remaining bulk concentration dictates the overall kinetics [21].

On the other hand, Eqs. (4) and (5) provide a quite suitable description of data for advancing time (Figs. 8 and 9). It is noteworthy that both models adequately describe the rapid rate of adsorption during the first minutes of the experiments. The overall goodness of the fit in Figs. 8 and 9 implies that metal uptake by the sorbent is a satisfactory rate-controlling parameter under a second order reaction mechanism.

Table 3 displays the best-fit values of the kinetic rate parameters in Eqs. (4) and (5). The predicted equilibrium sorption capacities are quite close to the experimental values for both models. Yet, the pseudo-second order reaction (Eq. (5)) fitted the experimental data with a higher correlation coefficient ($r^2 > 0.99$).

4. Conclusions

Biosorption of heavy metals is one of the promising technologies involved in the removal of heavy metals from wastewaters. *Aeromonas caviae* was selected for studying biosorption due to its originality as well as to assess the possibility of utilizing a waste biomass for heavy metal removal. The cultivation of the microorganism is a relatively simple procedure, while the cultivation medium can be obtained without excessive cost. Thus, non-living biomass of *A. caviae* presents sufficient biosorption capacity for Cr(VI) anions, in comparison with other types(sources) of biosorbent materials. The obtained results show that temperature, initial metal and biomass concentrations highly affect the overall metal uptake capacity of biosorbent.

The Freundlich and Langmuir adsorption models were employed for the mathematical description of biosorption equilibrium data, regarding the biosorption of Cr(VI) ions to *A. caviae* for varying temperatures and biomass concentrations. The calculated isotherm constants were used to compare the biosorptive capacity at different experimental for the removal of Cr(VI). The present results demonstrate that the Langmuir model fits a little better than the Freundlich model the adsorption equilibrium data in the examined concentration range.

The obtained kinetic information has a significant practical value for technological applications, since kinetic modeling successfully replaces time and material consuming experiments, necessary for process equipment design. The suitability of a pseudo second order chemical reaction for the sorption of Cr(VI) ions onto this biomass is apparent, as this kinetic model describes adequately the largest part of the process.

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