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## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

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**To cite this Article** Loukidou, M. X. , Karapantsios, T. D. , Zouboulis, A. I. and Matis, K. A. (2005) 'Cadmium(II) Biosorption by *Aeromonas caviae*: Kinetic Modeling', Separation Science and Technology, 40: 6, 1293 — 1311

**To link to this Article:** DOI: 10.1081/SS-200052207

**URL:** <http://dx.doi.org/10.1081/SS-200052207>

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## Cadmium(II) Biosorption by *Aeromonas caviae*: Kinetic Modeling

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**Abstract:** Biosorption of cadmium 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 was conducted to test 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, cadmium(II), equilibrium study, kinetic study, metals

### INTRODUCTION

The pollution of the environment with toxic heavy metals is spreading throughout the world along with industrial progress. The commonly used treatment methods to remove heavy metals from wastewaters include chemical precipitation, ion exchange, reverse osmosis, and membrane processes. However, these methods are not effective when the heavy metal concentrations in the wastewater are low (e.g., less than  $100 \text{ mg L}^{-1}$ ) (1). The technologies are also expensive when a very low concentration of

Received 5 August 2004, Accepted 6 December 2004

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heavy metals in the treated water is required (2). Alternative means of treating wastewater have been studied. Biosorption, the uptake of heavy metals by nonliving biomass, has gained increased credibility during recent years, as it offers a technically feasible and economical approach (1, 2). Several of the biological materials investigated for heavy metals removal include bacteria, yeasts, algae, and fungi (3–7).

Cadmium (CdII) is widely used in rechargeable nickel-cadmium batteries, pigments, stabilizers, coatings, and alloys. Due to the severe toxicity of Cd(II), the EU Directive, World Health Organization (WHO), and U.S. Environmental Protection Agency (EPA) have set the maximum contaminant concentration level for Cd(II) in domestic water supplies as  $5 \mu\text{g L}^{-1}$  (8). The selection of Cd(II) 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 high priority for the application of novel treatment methods. However, the technological uses of Cd(II) may be considered to be increasing (3).

The present study aims to examine biosorption by using biomass of *Aeromonas caviae* as dead biomass. Despite the fact that this microorganism is often present in groundwater 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 (9).

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 cadmium 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.

## MATERIALS AND METHODS

### Biomass and Growth Conditions

*Aeromonas caviae*, a gram-negative bacteria isolated from the water wells near Thessaloniki (North Greece), was grown at  $29^{\circ}\text{C}$  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  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  ( $0.2 \text{ g L}^{-1}$ ). 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.

## Biosorption Experiments

### Equilibrium Study

Batch biosorption experiments were performed in conical flasks stirred in a reciprocal shaker (at 180 rpm) for 2 h at different temperatures (20, 40, and  $60^\circ\text{C}$ ) and for different biomass concentrations. An aqueous solution of Cd(II) of known concentrations [varying from 5 to  $350 \text{ mg L}^{-1}$ , prepared from  $\text{Cd}(\text{NO}_3)_2$  salt] was added to the biomass suspension, which was dispersed by using a hand homogenizer (Jencons, with  $45 \mu\text{m}$  clearance) in the appropriate aqueous volume, to produce the required concentration. The natural pH values of cell suspensions were measured to be 6.8. The pH of the metal solutions, which depends on the metal concentrations, ranged between 5.0 and 5.5. The pH was measured after mixing of the biomass suspension with the metal solution; it was found to be 5.0. The solution pH was adjusted by the addition of NaOH to 7.0, which was found to be the optimum pH value for Cd(II) biosorption during preliminary studies and was far from the precipitation value of metal hydroxide, according to the cadmium aqueous speciation (10). In all sets used in these experiments the system was well buffered and no change of pH value was observed. The mean values of three replicates of the batch experiments were presented.

The residual concentration of Cd(II) in solution was analyzed after the separation of used biosorbent by centrifugation at 3000 rpm for 15 min and by atomic absorption spectrophotometry (AAS, Perkin-Elmer, model 2360) (11).

### Kinetic Study

Batch biosorption experiments were carried out using different biomass concentrations (0.5, 1, and  $2 \text{ g L}^{-1}$ ), initial cadmium concentrations ( $5$  and  $50 \text{ mg L}^{-1}$ ), and coexisting concentrations of a common salt (0.01 and 0.5 M of  $\text{NaNO}_3$ ) at  $20^\circ\text{C}$ . All biosorption experiments were carried out at the optimum pH for Cd(II) adsorption (pH 7.0), as it was also determined during preliminary experiments. The mixing of biomass suspension with metal solution was done as described earlier. 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 lowest speed that gives reproducible sorption curves. The 2 mL samples

were withdrawn at selected time intervals (2 min) using a 10 mL syringe with filter ( $\varnothing$ 47 mm, ME 25 ST, 0.45  $\mu$ m, Schleicher & Schuell). The removed quantities were not affecting 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 the calculations.

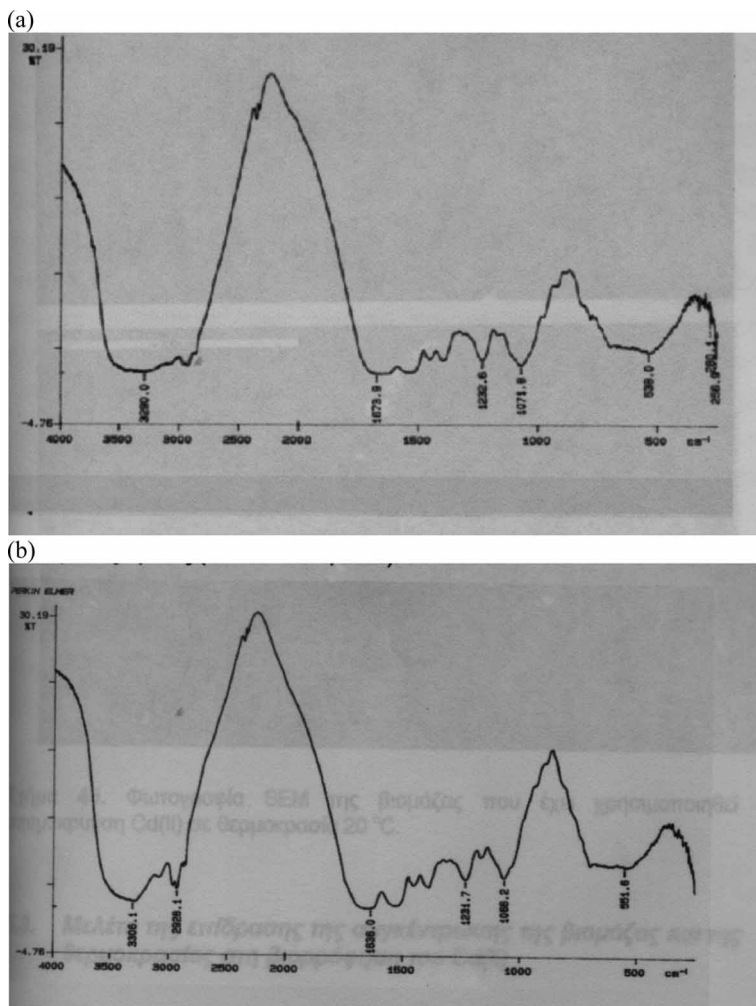
Finally, the residual concentration of Cd(II) in solution was analyzed by atomic absorption spectrophotometry (AAS, Perkin-Elmer, model 2360) (11).

## RESULTS AND DISCUSSION

### 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. Possible preliminary tests, which may be used to perform this selection, are the surface titration and the electrokinetic measurements of biomass (expressed as zeta potential). The results of titration experiments suggested the presence of carboxylic ( $pK_a$  of 4) and phosphate ( $pK_a$  of 6) groups on the bacterial cell wall. (see Reference 12). These types of acidic sites can remove 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 (13). For pH values greater than  $pK_a$  the sites are mainly in dissociated form and can exchange  $H^+$  with metal in solution. The zeta potential measurements may provide useful information regarding the net effective charge on the cell surface. The isoelectric point of biomass was found at pH 2.4. (see Reference 12). At low pH, cell wall ligands were closely associated with the hydronium ions  $H_3O^+$  and restricted the approach of metal cations as a result of the repulsive force. As the pH value was increased, carboxyl and phosphate groups gave an overall negative charge to the biomass, which was able to adsorb positively charged heavy metal ions and biosorp them onto the cell surface (12). Thus, the amino and carboxyl groups and the nitrogen and oxygen of the peptide bond could be available for characteristic coordination bonding with metallic ions (13).

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



**Figure 1.** Infrared spectra of the biomass: (a) before and (b) after Cd(II) sorption.

$1050\text{--}970\text{ cm}^{-1}$ . The appearance of peaks at  $3000$  and  $900\text{ cm}^{-1}$  indicate the role of carboxyl and phosphates groups during the uptake of Cd(II), respectively. Several peaks are visible at  $3500\text{--}3000\text{ cm}^{-1}$  (N-H stretching) and at  $1250\text{--}1000\text{ cm}^{-1}$  (C-N stretching), presenting amino groups (14). The Fourier transform Infrared (FTIR) spectral analyses of biomass loaded with Cd(II) indicated elongation of these bands after cadmium biosorption and suggested the role of these groups during biosorption of cadmium. Using the 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.

### 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 ( $q_{eq}$ ) and metal ions remaining in solution ( $C_{eq}$ ) at a constant temperature. The Langmuir equation refers to a monolayer sorption onto surfaces containing a finite number of accessible sites:

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

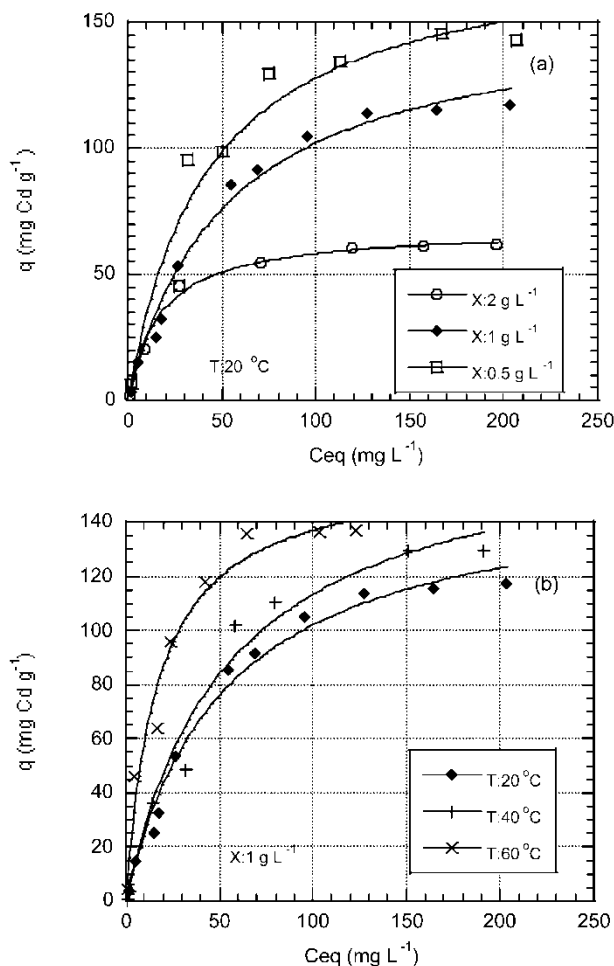
where  $q_{\max}$  is the maximum quantity of metal ions per unit weight of biomass to form a complete monolayer on the surface ( $\text{mg g}^{-1}$ ), whereas  $b$  is a constant related to the affinity of binding sites with the metal ions (sorbate,  $\text{L mg}^{-1}$ ). It should be noted that  $q_{\max}$  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 (15).

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

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

where  $K_F$  is an indicator of adsorption capacity ( $\text{L g}^{-1}$ ) and  $n$  indicates the effect of concentration on the adsorption capacity and represents the adsorption intensity (dimensionless) (15).

Experimental adsorption isotherms of cadmium cations, obtained with different initial biomass concentrations and temperatures, are presented in Fig. 2a and 2b, respectively, at the optimum pH value of 7, as determined during preliminary experiments (7). 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 shows 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 cadmium(II). The magnitude of the  $q_{\max}$  was found to span a range of values ( $68.17$  to  $175.11 \text{ mg g}^{-1}$ ) comparable to



**Figure 2.** Application of Langmuir model to biosorption of cadmium cations at pH 7 for: (a) different biomass concentrations; (b) different temperatures.

other types of 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 value of constant  $b$  corresponds to the concentration at which a cadmium(II) ion amount of  $q_{\max}/2$  is bound and indicates the affinity for the binding of cadmium(II) ions, implying strong bonding of Cd(II) to *A. caviae* bacterial biomass at these experimental conditions. The possibility of desorbing cadmium from biomass with a typical elution agent



**Table 1.** Freundlich and Langmuir models regression constants for different experimental conditions (standard deviation of calculated values are indicated in parenthesis)

Conditions		Freundlich constants $q_e = K_F C_e^{1/n}$			Langmuir constants $q_e = q_{\max} b C_e / (1 + b C_e)$		
T (°C)	Biomass load (g L <sup>-1</sup> )	K <sub>f</sub> (g L <sup>-1</sup> )	n (–)	r <sup>2</sup>	q <sub>max</sub> (mg g <sup>-1</sup> )	b (L mg <sup>-1</sup> )	r <sup>2</sup>
20	0.5	20.37(5.03)	2.59(0.15)	0.87	181.91(5.89)	0.03(0.01)	0.93
20	1.0	10.85(2.48)	2.12(0.50)	0.94	155.32(6.32)	0.019(0.003)	0.99
20	2.0	12.10(0.37)	3.06(0.78)	0.91	68.17(2.45)	0.06(0.002)	0.99
40	1.0	11.68(1.20)	2.09(0.28)	0.94	175.11(7.11)	0.018(0.003)	0.98
60	1.0	27.66(1.38)	2.84(0.12)	0.92	160.31(5.93)	0.06(0.004)	0.97

**Table 2.** Selected literature results; comparison of different biosorbents, regarding Cd(II) removal capacity (Langmuir model)

Biosorbent	$q_{\max}$ (mg L <sup>-1</sup> )	pH	T (°C)	$X_{\text{biomass}}$ (g L <sup>-1</sup> )	$C_o$ (mg L <sup>-1</sup> )	Reference
<i>Aeromonas caviae</i>	155.32	7	20	1.0	5–350	this paper
<i>B. licheniformis</i>	142.7	7	20	1.0	25–250	(20)
<i>Sphaerotilus natans</i>	115	6	25	0–1.0	25–400	(13)
<i>Sargassum fluitans</i>	101.4	7	25	—	25–300	(21)
<i>Rhizopus arrhizus</i>	24.6	3.5	26	—	25–400	(20)
<i>Rhizopus arrhizus</i>	26.8	7	26	3.0	—	(20)
<i>Saccharomyces cerevisiae</i>	0.56	5	25	2.0	100–500	(22)
<i>Pseudomonas aeruginosa</i>	42.6	6	25	1.0–2.0	—	(13)
<i>Streptomyces noursei</i>	3.4	6	30	3.5	—	(13)
<i>Alcaligenes sp.</i>	10.3	4–8	25	0.38	50–250	(13)

was examined with biomass previously used for sorption of Cd(II) and then desorbing the heavy metal with 0.1 M HCl or 0.1 M EDTA. It was observed that approximately 50% of cadmium was recovered after a desorption experiment lasting 2 h (data not shown). The fact that 100% recovery was not achieved may be due to the strong bonding of Cd(II) to *A. caviae* biomass.

The results presented at Table 1 demonstrate also that the biomass concentration strongly affected the amount of metal removed from aqueous solution. Increasing the amount of biomass added from  $0.5 \text{ g L}^{-1}$  to  $2.0 \text{ g L}^{-1}$  increased the amount of metal ion removed, but decreased the biosorptive uptake (from  $181.91$  to  $68.17 \text{ mg g}^{-1}$ ) that came directly from the calculation of biosorptive capacity ( $q = \text{mg metal ion removed g}^{-1} \text{ biomass}$ ). Moreover, at higher biomass concentrations, the aggregates formed during biosorption and they also reduced the effective adsorption area. In the presence of a high biomass concentration there is a very fast superficial adsorption onto cells that produces a lower metal concentration in solution than it does when the biomass concentration is lower (13).

The maximum biosorptive capacity was observed at  $40^\circ\text{C}$  (for  $1 \text{ g L}^{-1}$  biomass). An increase of temperature from  $20$  to  $40^\circ\text{C}$  resulted in enhancing the adsorption of Cd(II). Higher removal efficiencies at increased temperature conditions indicated that the adsorption of Cd(II) ions to *A. caviae* is of an endothermic nature. However, at higher temperatures the system energy seems to facilitate Cd(II) attachment onto cell surfaces, but when the temperature is even higher ( $60^\circ\text{C}$ ), a decrease of metal sorption may be expected, due to damage of certain surface sites of cell available for metal biosorption. This is opposite to what is physically expected and can be ascribed to the morphological changes of the biomass surface at different temperatures and the dependence of sorption capacity on temperature. Morphological studies of biomass surface were carried out by obtaining the electron micrographs of biomass at different temperature. The morphology of biomass at  $20^\circ\text{C}$  showed a patchy surface where smooth flake-like sections were separated by deep irregular grooves (data not shown), the morphologies of biomass at  $40$  and  $60^\circ\text{C}$  were distinctly different as well.

The values of the Freundlich constants showed a relatively easy uptake of Cd(II) cations 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 Cd(II) ions are favorably adsorbed under all the examined experimental conditions.

The adsorption isotherms obtained for Cd(II) 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 ( $5\text{--}350 \text{ mg L}^{-1}$ ). Yet, the correlation coefficients of the Langmuir curves were distinctly higher. This observation implies that monolayer biosorption, as well as heterogenous surface conditions may coexist under the applied

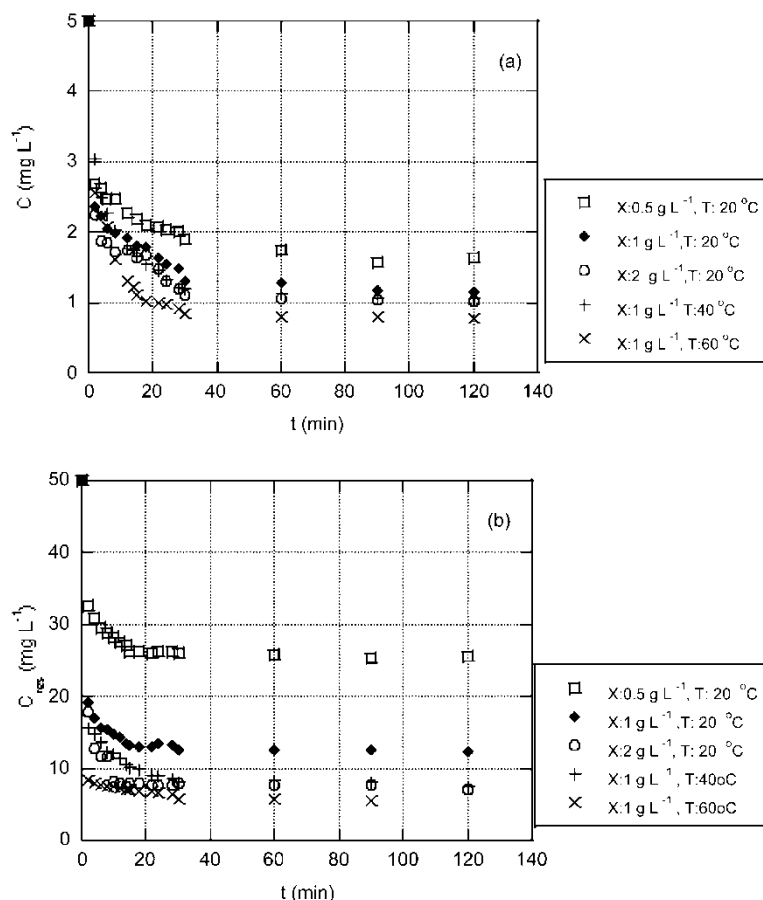
experimental conditions. Hence, the overall sorption of Cd(II) on the biomass is complex, involving more than one mechanism, such as ion exchange, surface complexation, or electrostatical attraction. In general, the Freundlich equation satisfactory describes experimental data over a wide range of values of  $\theta$  (fraction of surface coverage with the adsorbed solute) and for systems that follow the Langmuir isotherm. Even for a system which follows the Langmuir isotherm over a range of surface coverage between the extremes of  $\theta = 0$  and  $\theta = 1$ , the Langmuir isotherm is nearly equivalent with the case when  $\theta$  is proportional to a fractional power of  $C_{eq}$  (15). Therefore, both the Freundlich and Langmuir isotherms can be used to modelize biosorption data from dilute aqueous solutions.

### Kinetic Experiments

In order to investigate the mechanism of biosorption and potential rate controlling steps 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. Figures 3a and 3b present the remaining concentration of cadmium ions in the bulk solution as a function of time at different experimental conditions. Unless differently stated, runs were performed at 20°C and with  $1 \text{ g L}^{-1}$  biomass concentration. The very steep descent at the beginning of biosorption process was succeeded by a less rapid decay during the following 20–30 minutes. From that point on, the Cd(II) 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 minutes of the process. The rapid kinetics have significant practical importance, as they will facilitate smaller reactor volumes ensuring high efficiency and economy.

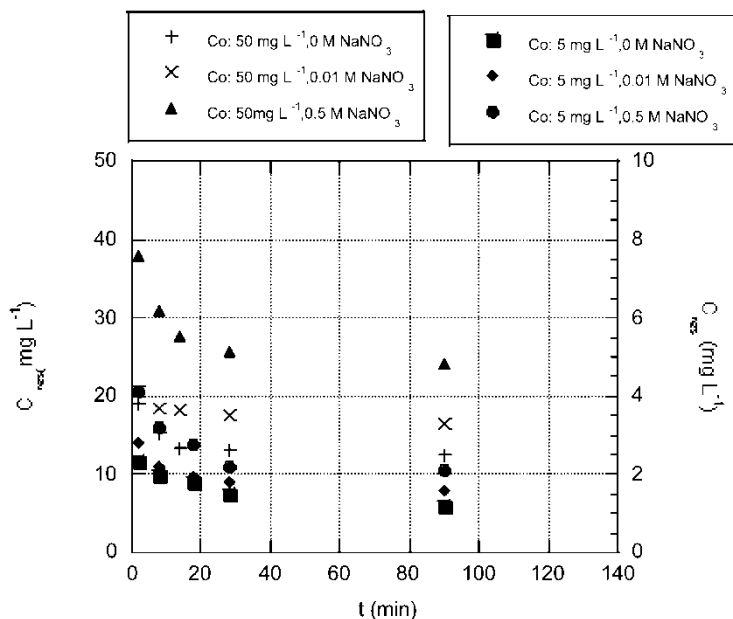
The application of different biomass (sorbent) concentrations has a direct effect on both total sorption capacity ( $C_o - C_{eq}$ ) and average sorption rate ( $\Delta C / \Delta t$ ); this is more obvious for the higher initial concentration. The adsorption capacity is markedly enhanced, over and above any other parameter, when increasing the initial concentration of Cd(II). Apparently, the initial concentration of metal provides an important driving force to overcome mass transfer resistance of Cd(II) between the aqueous and solid phase. The same qualitative trend is also observed when increasing the temperature (at constant biomass load  $1 \text{ g L}^{-1}$ ). However, in this case the enhancement of adsorption capacity is only moderate.

In order to identify whether the sorption of cadmium obeys a mechanism of electrostatic or chemical nature, some biosorption experiments were performed by adding various concentrations of sodium salt (initial metal



**Figure 3.** Biosorption kinetics of Cd(II) by *Aeromonas caviae* obtained for different initial cadmium concentrations of: (a) 5 mg L<sup>-1</sup>; (b) 50 mg L<sup>-1</sup> (pH: 7, agitation speed: 180 rpm).

concentrations 5 and 50 mg L<sup>-1</sup>, biomass concentration 1 g L<sup>-1</sup>). The impact of the presence of dissolved sodium ions on the kinetics of Cd(II) biosorption is shown in Fig. 4. It appears that as the dosage of salt increases both the sorption capacity and sorption rate of Cd(II) ions decrease. This effect is more intensive with the higher initial metal concentration (50 mg L<sup>-1</sup>). 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 sodium and cadmium cations during electrostatical binding to the biomass.



**Figure 4.** Biosorption kinetics of Cd(II) by *Aeromonas caviae* obtained for different concentrations of NaNO<sub>3</sub> and for 5 mg L<sup>-1</sup>; 50 mg L<sup>-1</sup> Cd(II) concentrations at pH 7.

### 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 complexity 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., 2000 (17) several reaction-based and diffusion-based models were tested for the simulation of the obtained experimental data. The kinetic models finally selected will be those, that not only closely fit 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 (17).

The best fit for the experimental series of this study was achieved by the application of a second order-type kinetic equation. The solution of the common second order reaction equation, based on the stoichiometry of one

metal ion per binding site, is (18):

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

where  $k_2$  is the reaction rate constant [(L/mg of metal)/min]. This kinetic model has been very effective, in describing the kinetics of adsorption of gases on solids (17). 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 (19):

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

where  $k_2$  is the reaction rate constant ( $\text{min}^{-1}$ ). When in the previous treatment,  $q_e$  that dictates the sorbate uptake is not important then a pseudo second order rate expression is more appropriate (16):

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

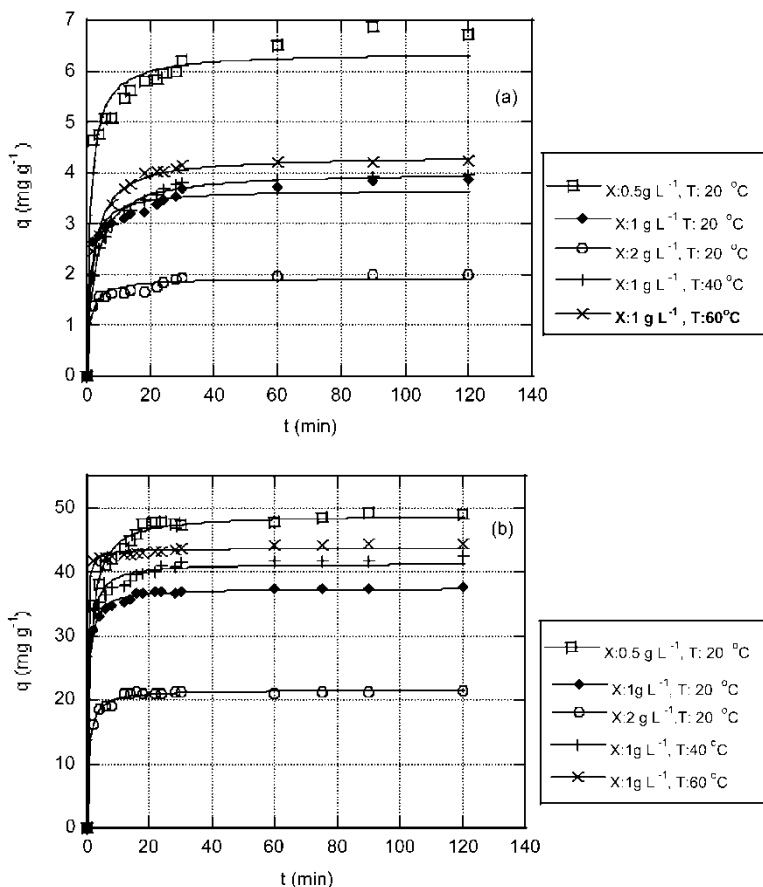
where  $k_m$  is the reaction rate constant [g biomass/mg (metal)/min], whereas  $q_m$  is a numerically determined parameter, which in the case of an ideal second order rate control corresponds to  $q_e$ .

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 cadmium on *A. caviae* is a chemical-reaction controlled, rather than a diffusion-controlled process (17). Moreover, the influence of ionic background (sodium) further supports the notion that sorption of cadmium follows (at least partly) a mechanism of chemical nature (Fig. 4).

Equation (3) clearly fails to capture the steep concentration decline during the early removal stage (data not shown). This is a direct indication that adsorption on solids from the liquid phase is a different process than is adsorption from a gas phase where traditionally the remaining bulk concentration dictates the overall kinetics (17).

On the other hand, Eqs. (4) and (5) provide a quite suitable description of data for advancing time (Figs. 5 and 6). 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 Fig. 5 and 6 implies that metal uptake by the sorbent is a satisfactory rate-controlling parameter under a second order reaction mechanism.

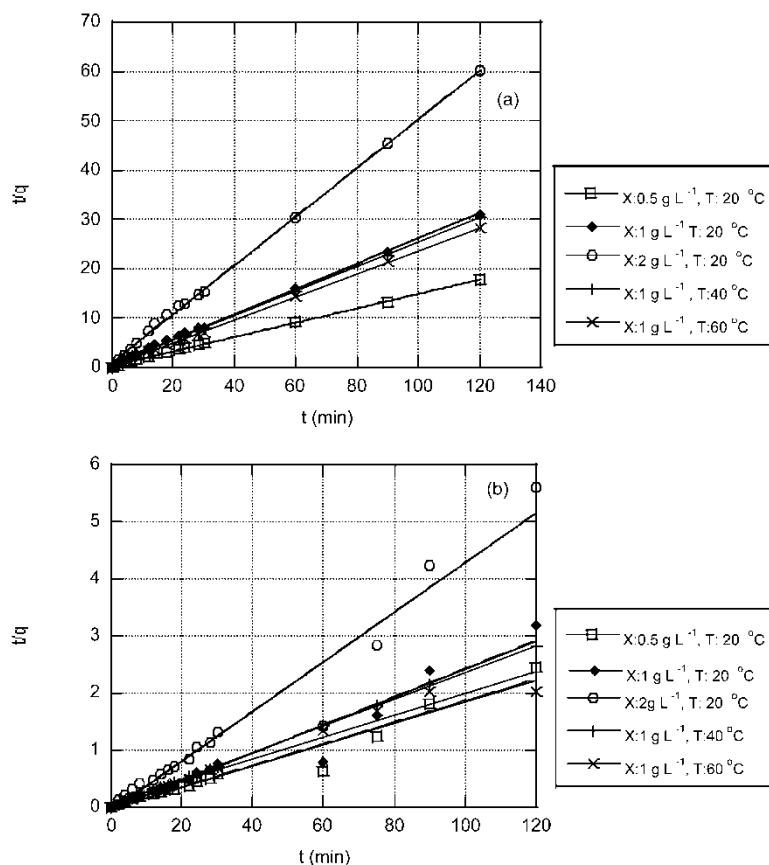
Table 3 displays the best-fit values of the kinetic rate parameters in Eqs. 4 and 5. The predicted equilibrium sorption capacities are quite close to the experimental values for both models. Nevertheless, the rate constant of the



**Figure 5.** Comparison of experimental uptake data with theoretical predictions (curves) based on the Ritchie second order kinetic equation (Eq. (4) for initial cadmium concentrations of: (a) 5 and (b) 50 mg L<sup>-1</sup> (pH: 7).

pseudo second order model,  $k_m$ , is monotonously correlated with changes in the biomass load and in the bulk concentration, features that have been encountered in the past regarding biosorption. On the contrary, the rate constant of the Ritchie second order equation,  $k_2$ , fluctuates beyond any physical reasoning. In addition, the pseudo-second order reaction (Eq. (5)) fitted the experimental data with a higher correlation coefficient ( $r^2 > 0.99$ ). Despite the goodness of fit for sorption at 40 and 60°C, the reaction rate constant of both models varies randomly with temperature. Preliminary calculations using the Arrhenius model between two temperatures gave activation energies every time that are always below 10 kJ/mol, which is far less than what is expected for reaction controlled sorption processes (17).





**Figure 6.** Comparison of experimental uptake data against theoretical prediction (curves) based on the pseudo second order equation (Eq. 5) for initial cadmium concentrations: (a) 5 and (b)  $50 \text{ mg L}^{-1}$  (pH: 7).

The morphological changes of the biomass surface at different temperatures and the dependence of sorption capacity on temperature may be blamed for this irregularity.

## 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

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

C <sub>o</sub> (mgL <sup>-1</sup> )	Conditions		Equili-brium	Pseudo second order equation			Ritchie second order equation		
	T (°C)	Biomass (mgL <sup>-1</sup> )	q <sub>eq</sub> (mg g <sup>-1</sup> )	q <sub>eq</sub> (mg g <sup>-1</sup> )	k <sub>m</sub> (gmg <sup>-1</sup> min <sup>-1</sup> )	r <sup>2</sup>	q <sub>eq</sub> (mg g <sup>-1</sup> )	k <sub>2</sub> (min <sup>-1</sup> )	r <sup>2</sup>
5	20	0.5	6.65	6.22	0.133	0.995	6.02	1.2	0.981
	20	1.0	3.53	3.66	0.192	0.991	3.50	1.15	0.975
	20	2.0	1.9	1.94	0.373	0.989	1.85	1.25	0.974
	40	1.0	3.44	3.98	0.118	0.993	3.98	0.41	0.992
	60	1.0	4.33	4.33	0.132	0.995	4.36	0.48	0.985
50	20	0.5	45.11	56.18	0.015	0.986	48.73	1.03	0.993
	20	1.0	32.32	43.48	0.034	0.990	37.25	2.20	0.998
	20	2.0	21.74	25	0.051	0.987	21.79	1.37	0.997
	40	1.0	36.20	41.67	0.034	0.999	40.73	2.06	0.992
	60	1.0	45.87	43.47	0.132	0.999	43.21	11.31	0.999

cultivation of the microorganism is a relatively simple procedure, while the cultivation medium can be obtained without excessive cost. Thus, nonliving biomass of *A. caviae* presents sufficient biosorption capacity for Cd(II) cations, 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 Cd(II) ions to *A. caviae* for varying temperatures and biomass concentrations. The calculated isotherm constants were used to compare the biosorptive capacity at different experimental conditions for the removal of Cd(II). The present results demonstrate that both models are suitable for describing the biosorption equilibrium of Cd(II) by the biomass in the examined concentration range. The applicability of the isotherm models to the Cd(II)-biomass system implies that both monolayer biosorption and heterogenous surface conditions exist under the experimental conditions used. Thus, the sorption of cadmium(II) ions on the biomass is complex, involving more than one mechanism.

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

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