

# Diffusion kinetic study of cadmium(II) biosorption by *Aeromonas caviae*

Maria X Loukidou, Thodoris D Karapantsios, Anastasios I Zouboulis and Kostas A Matis\*

Chemical Technology Division, School of Chemistry, Aristotle University, GR-54124 Thessaloniki, Greece

**Abstract:** The removal of cadmium from aqueous solution by sorption 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 and temperatures. Biosorption equilibrium was established in about 1 h and biosorption was well described by the Langmuir and Freundlich biosorption isotherms. The maximum biosorption capacity was found as 155.32 mg Cd(II) g<sup>-1</sup> at 20 °C. The obtained sorption capacity is appreciably high for most experimental conditions; so *A. caviae* may be considered as a suitable biosorbent for the removal of cadmium. Moreover, the sorption rate of cadmium onto *A. caviae* particles was particularly sensitive to initial bulk concentration and solid load. A detailed analysis was conducted, examining several diffusion (external and intraparticle) kinetic models in order to identify a suitable rate expression. The results are discussed and indicate that biosorption of cadmium is a complex process that is described more correctly by more than one model.

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**Keywords:** biomass; modelling; diffusion; equilibrium; metal removal; wastewater

## NOTATION

$b$	Langmuir constant (dm <sup>-3</sup> mg <sup>-1</sup> )
$C$	Metal bulk concentration (mg dm <sup>-3</sup> )
$D_c$	Intraparticle diffusion coefficient (m <sup>2</sup> s <sup>-1</sup> )
$K_F$	Freundlich constant (mg(g(mg dm <sup>-3</sup> ) <sup>-1/n</sup> ) <sup>-1</sup> )
$K_m$	External mass transfer coefficient (m s <sup>-1</sup> )
$n$	Freundlich constant (dimensionless)
$q$	Specific metal uptake (mg g <sup>-1</sup> )
$q_{\max}$	Langmuir constant (mg g <sup>-1</sup> )
$R_c$	Mean particle radius (m)
$S$	Specific surface area of biosorbent per unit volume of reactor (m <sup>2</sup> m <sup>-3</sup> )
$t$	Time (min)
$T$	Temperature (°C)
$X$	Biomass loading per unit volume of solution (g dm <sup>-3</sup> )
$\alpha$	Degree of conversion
$\xi$	Numerically determined parameter
$\Lambda$	Fraction of metal ultimately sorbed by the sorbent

## 1 INTRODUCTION

The removal of heavy and toxic metals from the aquatic environment is one of the important issues in many industrialized countries. The commonly-used treatment methods to remove Cd(II) ions from wastewaters include chemical precipitation, ion

exchange, adsorption and membrane processes (ie reverse osmosis). Biosorption, the uptake of heavy metals by dead biomass, has however gained credibility during recent years, as it offers a technically feasible and economical approach.<sup>1,2</sup> Several biological materials have been investigated for heavy metals removal, including bacteria, yeasts, algae and fungi.<sup>3–8</sup>

The present study had the scope of examining biosorption by using biomass of *Aeromonas caviae*. Despite the fact that this microorganism is often present in groundwater and generally in aquatic environments, little attention seems to have been given to its resistance to heavy metals.<sup>9</sup> The purpose of selecting this bacterium for studying biosorption was, apart from its originality, to assess the possibility of utilizing a waste biomass for heavy metal removal. Equilibrium and kinetic analyses not only allow the estimation of sorption rates, but also lead to suitable rate expressions characteristic of possible reaction mechanisms.<sup>10,11</sup> To describe the equilibrium metal uptake, the known Langmuir adsorption equation was used and a meticulous kinetic study was performed in order to gain insight on the particular biosorption process.

Sorption kinetics may be controlled by several independent processes, which may act in series or in parallel, as reviewed by Ho *et al.*<sup>12</sup> These steps fall in one of the following general categories: (i) bulk diffusion, (ii) external mass transfer (film

\* Correspondence to: Kostas A Matis, Chemical Technology Division, School of Chemistry, Aristotle University, GR-54124, Thessaloniki, Greece

E-mail: kamatis@chem.auth.gr

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diffusion), (iii) chemical reaction (or chemisorption), and (iv) intraparticle diffusion. For sufficiently high agitation speed in the reaction vessel, the bulk diffusion step can be safely ignored since then sorption onto the adsorbent is decoupled from mass transfer in the bulk mixture.

It is common that more than one step can contribute to the system's performance at the same time. In this case, the extensive interrelationships between the various equations make the overall kinetic model exceedingly complicated to evaluate. A simplifying approach to circumvent this problem is to assume that each one of the co-current processes dominates over the others (ie the rate controlling step) at specific time regimes of the process and then study them independently;<sup>13</sup> this approach was also adopted in this study.

In this respect, the diffusion steps, (ii) and (iv), have been investigated in this paper. External mass transfer has been customarily analysed in the literature by adopting a pseudo first-order reaction model.<sup>12</sup> This approach tacitly assumes that the sorbate concentration at the sorbent surface is zero at all times. Nevertheless, this is not true, particularly in cases where a significant quantity of sorbate is adsorbed rapidly at the beginning of the process. A more realistic model should consider instead a rapid equilibrium being established between the sorbate at the interface and that present on the sorbent surface, according to Puranic *et al*,<sup>14</sup> and the latter concept was adopted in the present work. For intraparticle diffusion, Crank proposed an intraparticle diffusion model, which takes into account the continuously decreasing bulk concentration due to sorbate removal.<sup>15</sup> This gives rise to a time-dependent boundary condition for the concentration at the surface of the adsorbent, which is an important feature of the process and has been taken into account in this work.

Many studies engaged so far to examine sorption phenomena involved analysis of batch experiments, where data were sampled at equal 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 primary objective of the present study was to investigate in-depth the kinetic mechanism of cadmium sorption on biomass 'particles', putting more emphasis on samples collected shortly after the initiation of the process, where the major part of sorption occurs. The calculated kinetic parameters are of a great practical value for technological applications, since kinetic modelling successfully replaces the time- and material-consuming experiments necessary for process equipment design.

## 2 MATERIALS AND METHODS

### 2.1 Biomass

*Aeromonas caviae* is a Gram-negative bacterium isolated from raw water wells. The cultivation medium

consisted of yeast extract (0.5% w/v), tryptone (1% w/v), NaCl (0.5% w/v) and iron solution [as a dilute solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  ( $0.2 \text{ g dm}^{-3}$ )]. The biomass was grown at 29 °C in a rotating shaker for 24 h. The produced biomass was separated by centrifugation, washed several times by a solution of NaCl (0.9%), sterilized and then stored.

### 2.2 Biosorption experiments

Laboratory biosorption experiments were carried out at different biomass feeds (0.5, 1 and  $2 \text{ g dm}^{-3}$ ), initial cadmium concentrations (5 and  $50 \text{ mg dm}^{-3}$ ), and temperatures (20, 40 and 60 °C). The batch experiments were performed in Erlenmeyer flasks ( $500 \text{ cm}^3$ ) at an agitation speed of 180 rpm (Heidolph type, RZR 2102), which was high enough to eliminate concentration profiles inside the flasks. The reproducible sorption curves indirectly confirmed this. By adding small amounts of  $\text{HNO}_3$  or NaOH solutions, the initial pH of the solution was adjusted to 7, ie  $\sim 2$  pH units far from the precipitation value as metal hydroxide, according to the cadmium aqueous speciation.

For the equilibrium experiments, ample time ( $\sim 2$  h) was allowed after the inception of sorption to ensure that the experiments were concluded. For the kinetics study of cadmium sorption,  $2 \text{ cm}^3$  samples were acquired at selected time intervals using a  $10 \text{ cm}^3$  syringe. The residual concentration of the metal in all samples was analysed by atomic absorption spectrophotometry (AAS, Perkin-Elmer, model 2360).

To compare measurements from various experiments for the kinetics investigation it was necessary to introduce a dimensionless degree of conversion,  $\alpha$ . Thus, by normalizing the remaining ion concentration,  $C_t$ , with respect to some reference value, an index of sorption can be defined. Taking advantage of the values of  $C_t$  before the onset of sorption,  $C_o$ , and for completed sorption,  $C_\infty = C_e$ , the following degree of conversion is proposed:

$$\alpha = \frac{C_o - C_t}{C_o - C_e} \quad (1)$$

## 3 RESULTS AND DISCUSSION

### 3.1 Biosorption

#### 3.1.1 Macroscopic observations

Optical microscopy and stereomicroscopy revealed that the biomass particles withdrawn from the agitated suspension were sharp-edged 3D structures with arbitrary shapes and size in the range 10–100  $\mu\text{m}$ . Only a few particles appeared as roughly spherical, while many of them had faceted sides. If one considers the size of a single *A. caviae* microorganism ( $\sim 0.5 \mu\text{m}$  diameter and  $\sim 2 \mu\text{m}$  length), it is apparent that the dead biomass particles were actually clusters or aggregates of microorganisms brought together either by the biomass production procedure or, maybe, by

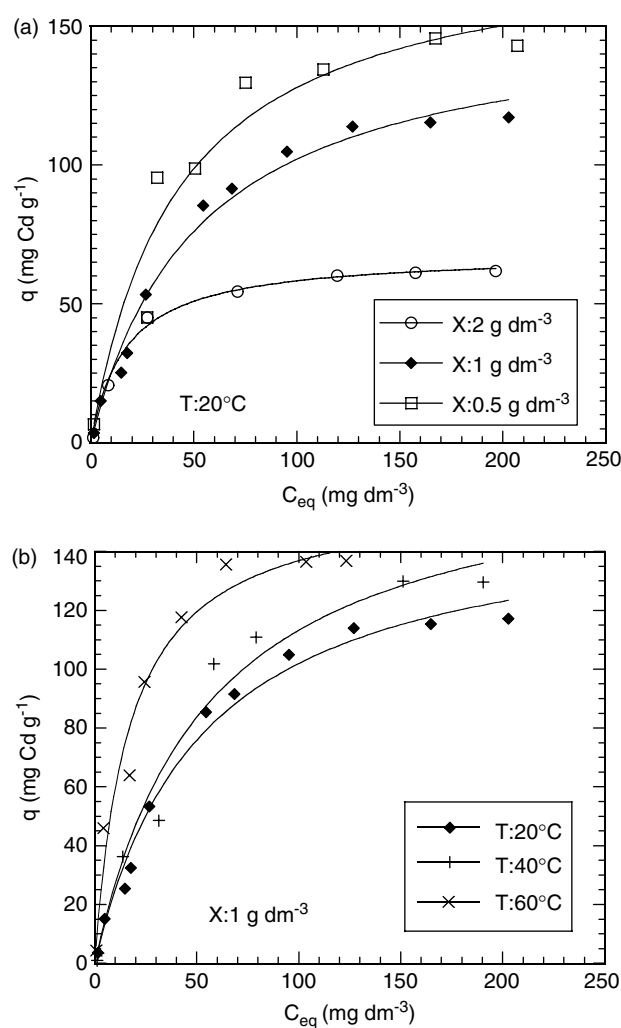
the shearing action during agitation. In either case, this description leaves room for the hypothesis of micropores and macropores existing in the body of such clusters; an important argument regarding the possibility of intraparticle diffusion.

Morphological studies of the biomass surface were carried out by obtaining the electron micrographs of biomass at different temperatures. 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 particles after Cd(II) ions were sorbed (again at 20 °C) bore practically no difference from that prior to biosorption. This was so even though the microanalyser of the SEM showed that the amount of sorbed Cd(II) steadily increased in samples acquired at progressively longer sorption times (the respective data not presented here). In contrast, the gross features of the biomass at 40 and 60 °C were distinctly different from that at 20 °C. No flakes or grooves were noticeable but instead the surface appears quite uneven and fragmented with prominent ridges emerging, here and there.

### 3.1.2 Equilibrium experiments

Experimental adsorption isotherms of cadmium ions obtained at several biomass concentrations and temperatures are presented in Fig 1 (a and b, respectively). For each isotherm the initial metal concentration was varied while the biomass concentration and temperature were kept constant. The pH value was kept constant at 7 for all experimental runs. The solid lines in the figures represent the best fit of the Langmuir equation to the measured data.

Table 1 displays the results of fitting the Langmuir and Freundlich equations to the obtained data. Apparently, the Langmuir equation describes quite satisfactorily the sorption curves, as demonstrated by the higher values of the correlation coefficient (denoted as  $r^2$ ). The  $q_{max}$  value is the maximum value of  $q_e$ , which is important for identifying 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 biosorption capacity,  $q_{max}$ , spans a range of values (68.17–175.11 mg g<sup>-1</sup>), comparable to other types of



**Figure 1.** Application of equilibrium Langmuir model to cadmium biosorption: (a) at different biomass concentrations; (b) at different temperatures.

biomass earlier reported.<sup>5</sup> In addition, the values of constant  $b$  clearly imply strong bonding of Cd(II) to *A. caviae* bacterial biomass, at these experimental conditions. The values of the Freundlich constants depict a relatively easy uptake of Cd(II) with high biosorptive capacity of *A. caviae*.

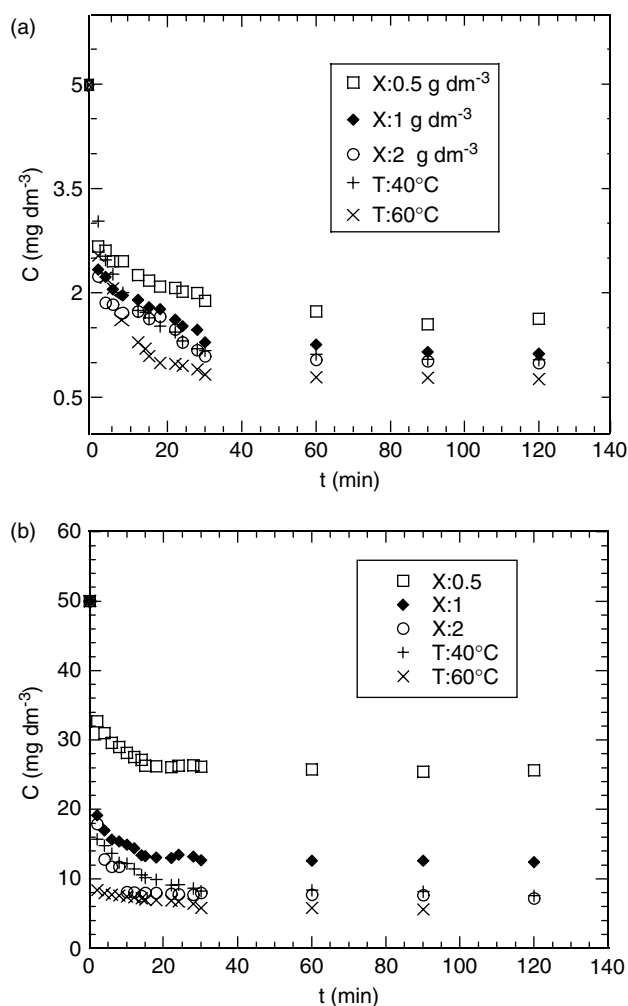
### 3.1.3 Kinetic experiments

Figure 2 presents the remaining concentration of cadmium in the bulk solution as a function of

**Table 1.** Langmuir and Freundlich model regression constants<sup>a</sup>

Condition		Langmuir isotherm constants			Freundlich isotherm constants		
T (°C)	Biomass load (g dm <sup>-3</sup> )	$q_{max}$	$b$	$r^2$	$K_f$	$n$	$r^2$
20	0.5	181.91	0.03	0.9308	20.37	2.59	0.8713
20	1	155.32	0.019	0.9864	10.85	2.12	0.9360
20	2	68.17	0.06	0.9936	12.1	3.06	0.9089
40	1	175.11	0.018	0.9771	11.68	2.09	0.9372
60	1	160.31	0.06	0.9657	27.66	2.84	0.9245

<sup>a</sup> The known equations were employed to describe the equilibrium metal uptake:  $q_e = \frac{q_{max}bC_e}{1 + bC_e}$  and  $q_e = K_f C_e^{1/n}$  (where  $q_{max}$ ,  $b$ ,  $K_f$  and  $n$  are constants).



**Figure 2.** Cadmium biosorption kinetics by *Aeromonas caviae* obtained at initial cadmium concentrations of: (a)  $5 \text{ mg dm}^{-3}$ ; (b)  $50 \text{ mg dm}^{-3}$  (pH: 7, agitation speed: 180 rpm).

time at different experimental conditions. Unless stated differently, runs were performed at  $20^\circ\text{C}$  and with  $1 \text{ g dm}^{-3}$  biomass load. The qualitative resemblance among curves is considerable, despite the different experimental conditions. Overall, there is a monotonous decreasing trend with time. The very steep descent at the beginning of sorption has been succeeded by a less rapid decay down to about 20–30 min. From then on, the Cd(II) concentration

gradually levels off and remains almost constant till the end of the experiment (120 min). Thus, the major part of sorption took place within the first 30 min of the process. The rapid kinetics has significant practical importance, as it facilitates smaller reactor volumes ensuring high efficiency and economy.

Moreover, the time required to reach the final equilibrium was practically the same for all experimental conditions. Changing the solids load had a prominent effect on both sorption capacity and sorption rate. The same also held when the temperature of the bulk was varied. Interestingly, the curves obtained at  $20^\circ\text{C}$  with a  $2 \text{ g dm}^{-3}$  biomass load approximately overlap with those obtained at  $40^\circ\text{C}$  with  $1 \text{ g dm}^{-3}$  biomass load. Thus, adjusting the temperature or the biomass load in the examined range of values can lead to a comparable metal removal.

As the biomass concentration rises, both the biosorption capacity,  $q_{\text{max}}$ , and the equilibrium metal uptake,  $q_e$  (the total amount of Cd(II) ions sorbed at equilibrium per unit mass of biosorbent), drop, manifesting a poorer biomass utilization (low efficiency). The latter is presented in Table 2 where other useful equilibrium quantities are also displayed. The application of different biomass (sorbent) concentrations has a direct effect on the absolute metal uptake,  $\Delta C (= C_0 - C_{\text{eq}})$ , and the relative metal uptake,  $\Lambda (= \Delta C/C_0)$ ; this is more obvious for the higher initial concentration. In particular, varying the biosorbent mass from 0.5 to  $2 \text{ mg dm}^{-3}$  increases the absolute metal uptake by 19% for the lower metal concentration ( $C_0 = 5 \text{ mg dm}^{-3}$ ) and by 75% for the higher metal concentration ( $50 \text{ mg dm}^{-3}$ ). It must be stressed that the equilibrium properties do not change proportionally with biomass load. This may be attributed to a possible aggregation of solids occurring at higher biomass loads capable of reducing the effective adsorption area.<sup>16</sup>

The same qualitative trend is also observed when increasing the temperature (at constant biomass load,  $1 \text{ mg dm}^{-3}$ ). However, in this case the enhancement is only moderate;  $\sim 10\%$  for  $C_0 = 5 \text{ mg dm}^{-3}$  and  $\sim 20\%$  for  $C_0 = 50 \text{ mg dm}^{-3}$ . The key role of the initial metal concentration is clearly inferred from Table 2. So, at a higher initial concentration of Cd(II)

**Table 2.** Equilibrium quantities obtained at different initial metal concentrations, biomass (solid) loads and temperatures

$C_0$ ( $\text{mg dm}^{-3}$ )	T ( $^\circ\text{C}$ )	Biomass		$C_{\text{eq}}$ ( $\text{mg dm}^{-3}$ )	$\Delta C = C_0 - C_{\text{eq}}$ ( $\text{mg dm}^{-3}$ )	$\Lambda = \Delta C/C_0$	$q_{\text{eq}}$ ( $\text{mg g}^{-1}$ )
		load ( $\text{g dm}^{-3}$ )					
5	20	0.5		1.639	3.361	0.679	6.722
		1		1.137	3.863	0.773	3.863
	40	2		1.005	3.995	0.799	1.998
		1		1.051	3.949	0.79	3.948
	60	1		0.773	4.227	0.845	4.227
50	20	0.5		25.56	24.431	0.488	48.863
		1		12.35	37.641	0.753	37.641
	40	2		7.135	42.865	0.857	21.432
		1		7.564	42.436	0.849	42.436
	60	1		5.58	44.420	0.888	44.42

the sorption capacity is markedly enhanced over and above any other parameter. Apparently, the initial metal concentration provides an important driving force to overcome mass transfer resistance of Cd(II) between the aqueous and solid phase.

## 3.2 Diffusion kinetics and modelling

### 3.2.1 Theoretical development

**3.2.1.1 Intraparticle diffusion.** The solution of the diffusion equation for a time dependent boundary condition for the concentration at the surface of the adsorbent particle and a concentration independent diffusivity is:<sup>16</sup>

$$\alpha = 1 - 6 \sum_{n=1}^{\infty} \frac{\exp(-\xi p_n^2 t)}{9\Lambda/(1-\Lambda) + (1-\Lambda)p_n^2} \quad (2)$$

where  $p_n$  is given by the non-zero roots of

$$\tan(p_n) = \frac{3p_n}{3 + p_n^2/(1-\Lambda)} \quad (3)$$

and  $\Lambda \equiv (C_o - C_\infty)/C_o$  is the relative metal uptake already defined in Table 2.

Equation (2) can be solved numerically to determine  $\xi$ , the effective diffusional time constant, which for the case of particle diffusion control is equal to  $D_c/R_c^2$ ,  $D_c$  and  $R_c$  being the intraparticle diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ ) and mean particle radius (m), respectively. For  $\Lambda$  greater than about 0.1, the effect of a diminishing bulk concentration becomes significant and under these conditions, the assumption of a constant metal concentration at the surface of the biosorbent would lead to an erroneously high apparent diffusivity.

Since our interest is chiefly focused in the short time region ( $\sqrt{D_c t}/R_c^2 < 0.2$ ), where eqn (2) converges slowly, at least 200 terms have been used in the summation to achieve satisfactory accuracy.

**3.2.1.2 External mass transfer.** An overall mass balance of the sorbate across the biosorbent surface is written as:

$$Xq_t + C_t^s = C_o \Leftrightarrow q_t = \frac{(C_o - C_t^s)}{X} \quad (4)$$

where  $q$  is the specific metal uptake (mg of metal per g of biomass),  $C$  is the metal bulk concentration ( $\text{mg dm}^{-3}$ ) and  $X$  is the biomass feeding per unit volume of solution ( $\text{g dm}^{-3}$ ). Subscripts 'o' and 't' denote conditions at the beginning and any other instant of the process, respectively. The superscript 's' denotes conditions at the biosorbent interface.

The following relationships for external mass transfer were derived after some algebra combining eqn (4), the Langmuir adsorption isotherm and the rate equation of change in the bulk concentration:

$$\frac{dC_t}{dt} = -K_m S (C_t - C_t^s) \quad (5)$$

$$\frac{dC_t^s}{dt} = \left( \frac{K_m S}{Xq_{\max} b} \right) [(C_t - C_t^s)(1 + bC_t^s)^2] \quad (6)$$

where  $K_m$  is the external mass transfer coefficient ( $\text{m s}^{-1}$ ) and  $S$  is the specific surface area of the biosorbent particles per unit volume of the reactor ( $\text{m}^2 \text{m}^{-3}$ ).

Using the following dimensionless variables:

$$C^* = C_t/C_o, C_s^* = C_t^s/C_o^s \quad \text{and} \quad t^* = t/\tau,$$

where  $C_o^s$  has been determined from eqn (4), and  $\tau$  is the total adsorption time, eqns (5) and (6) convert to:

$$\frac{dC^*}{dt^*} = -K_m S \tau (C^* - C_s^*) \quad (7)$$

$$\frac{dC_s^*}{dt^*} = \left( \frac{K_m S \tau}{Xq_{\max} b} \right) [(C^* - C_s^*)(1 + bC_o C_s^*)^2] \quad (8)$$

which is a system of two first-order ordinary differential equations that must be solved simultaneously. The initial conditions are:

$$C^* = 1 \quad \text{and} \quad C_s^* = 0 \quad \text{at} \quad t^* = 0.$$

It must be noted that normalizing  $C_t^s$  with respect to  $C_o^s$ —and not with  $C_o$  as done by other authors—<sup>14</sup> and also  $t$  with respect to  $\tau$ , improved markedly the stability and convergence characteristics of the solution due to the comparable spreading of all variables over the computational domain.

Equations (2) and (3), and (7) and (8) have been solved numerically to determine  $\xi$  and  $K_m S$ , respectively.

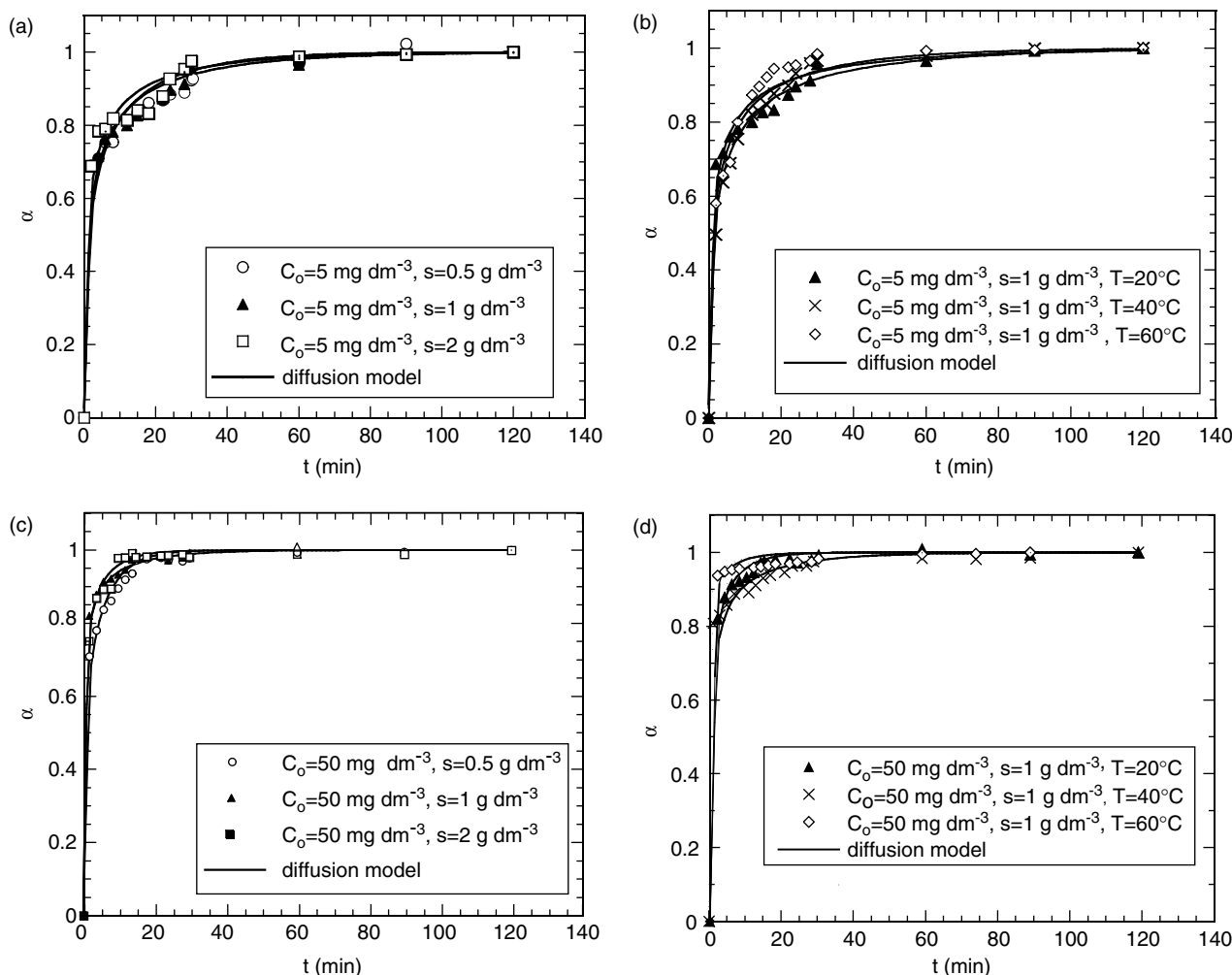
The non-linear numerical regression to fit experimental data to those equations is performed by the Levenberg–Marquardt method, which gradually shifts the search for the minimum of the Sum of the Errors Squared (SSE):<sup>17</sup>

$$\text{SSE} = \sum_i \left[ \frac{(q_{\text{exp},i} - q_{\text{cal},i})^2}{q_{\text{exp},i}^2} \right] \quad (9)$$

from steepest descent to quadratic minimization (Gauss–Newton).

### 3.2.2 Kinetic modelling

Figure 3 presents the results of fitting eqn (2) to biosorption data obtained with different initial concentrations, solids loads and temperatures. It is apparent that despite some scatter in measurements the finite volume diffusion model can describe fairly well the entire range of data, including also the steep concentration gradient at short times. Table 3 displays the values of  $\Lambda$ ,  $\xi$  and the computed values of  $D_c$  (for  $R_c = 5 \mu\text{m}$ ). It must be stressed that it is beyond the scope of this work to provide accurate diffusivity values, as our primary concern has been to obtain a reliable rate expression equation and gain some insight on the possible mechanism of the process. That is why the calculated diffusivity values refer to the simplest case of a single microporous sorbent particle of just a representative size. The  $D_c$  values vary within the



**Figure 3.** Experimental degree of conversion  $\alpha$  against predictions based on the solution of the diffusion equation (eqn (2)) at initial cadmium concentrations of:  $5 \text{ mg dm}^{-3}$  for (a) various biomass loads, (b) various temperatures and  $50 \text{ mg dm}^{-3}$  for (c) various biomass loads and (d) various temperatures.

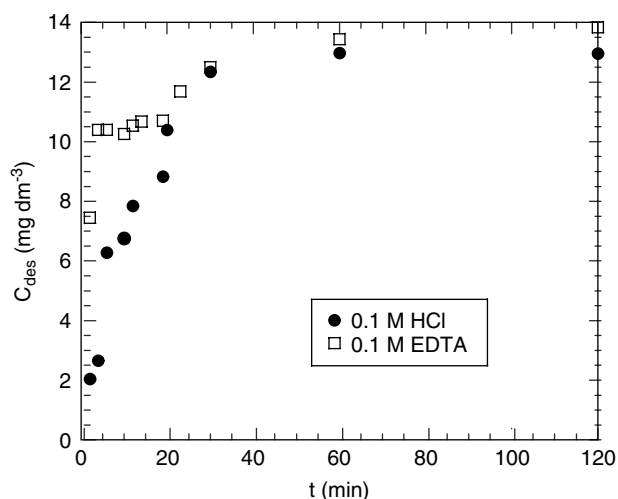
**Table 3.** Rate parameters computed for intraparticle diffusion and external mass transfer combined with favourable adsorption models

$C_o$ ( $\text{mg dm}^{-3}$ )	$T$ ( $^{\circ}\text{C}$ )	Biomass load		$\Lambda = \Delta C/C_o$	$\xi * 10^5$ ( $\text{s}^{-1}$ )	$D_c \times 10^{16}$ ( $\text{m}^2 \text{s}^{-1}$ )	$K_m S^* 10^4$ ( $\text{s}^{-1}$ )
		$T$ ( $^{\circ}\text{C}$ )	( $\text{g dm}^{-3}$ )				
5	20	0.5	0.679	5.7	14.2	2.5	
		1	0.773	3.7	9.2	3.7	
		2	0.799	3.8	9.6	4.5	
	60	1	0.79	2.7	6.7	9	
		1	0.845	2.3	5.8	10	
50	20	0.5	0.488	19.3	48.3	3	
		1	0.753	15.3	38.3	5.5	
		2	0.857	7	17.5	3.5	
	60	1	0.849	5.3	13.3	4.8	
		1	0.888	13.6	34.2	2.9	

same order of magnitude with clearly higher values at higher initial concentrations. Such dependence of the diffusion coefficient on bulk concentration is customarily attributed to the decreasing slope of a non-linear equilibrium curve, eg Langmuir isotherm.<sup>18</sup>

The diffusivity values shown in Table 3 lie in a realistic range of values for such systems.<sup>13,18</sup> It should be mentioned that the former authors employed

successfully the same model in studying intraparticle diffusion during the sorption of cadmium on chitosan sorbents. The diffusivity values obtained at 40 and 60 °C are below the values obtained at 20 °C, which 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.



**Figure 4.** Cadmium desorption: effect of different desorption agent,  $C_{des}$  is the desorbed concentration of cadmium (condition:  $C_{eq} = 37.641 \text{ mg dm}^{-3}$ , biomass load:  $1 \text{ g dm}^{-3}$ , pH: natural).

A way to check further on the possibility of a pore diffusion-controlled mechanism is to perform desorption kinetic tests with biomass previously used for sorption. Figure 4 shows such tests with two typical elution agents, namely HCl and EDTA. The biomass used for desorption was originally subjected to adsorption at  $20^\circ\text{C}$  with  $50 \text{ mg dm}^{-3}$  initial metal concentration and  $1 \text{ g dm}^{-3}$  biomass load. For these particular conditions, the total amount of biosorbed cadmium was  $37.641 \text{ mg dm}^{-3}$ . As can be seen, desorption was not instantaneous, despite the particularly favourable conditions and this may be attributed, at least in part, to a back-diffusion process of a portion of the metal that was originally sorbed on internal sites of the porous biomass.

For the case of a non-porous biomass particle, transport of solute inside the particle may be neglected and it can be assumed that biosorption occurs mainly at the particle surface (cell wall). This idea can be effectively extended to cases of relatively large macropores where the cadmium ions may have a ready access to react with internal surface sites.

The preliminary effort to fit eqns (7) and (8) to the entire time records of the acquired sorption data led to poor results; the prompt removal of cadmium just at the onset of sorption was chiefly blamed for this. The steep concentration gradient of the initial removal stage may be tentatively explained if one considers an ion exchange surface. This involves cadmium molecules being sorbed on the biomass surface where initially there are no other such molecules and consequently adsorbate–adsorbate interactions are negligible, leading to the formation of a monolayer. The Langmuir isotherms obtained during the equilibrium study lends further support to the notion of a monolayer. As soon as the monolayer reaches saturation, spatial rearrangement of the molecules may start, yielding a further increase in cadmium molecules but at a reduced rate. This

second step may well be an external film diffusion-controlled phenomenon. This is so because when (suspended) particles move at a comparable speed with the agitated (carrier) liquid, the boundary layer around the particles usually is not completely suppressed.

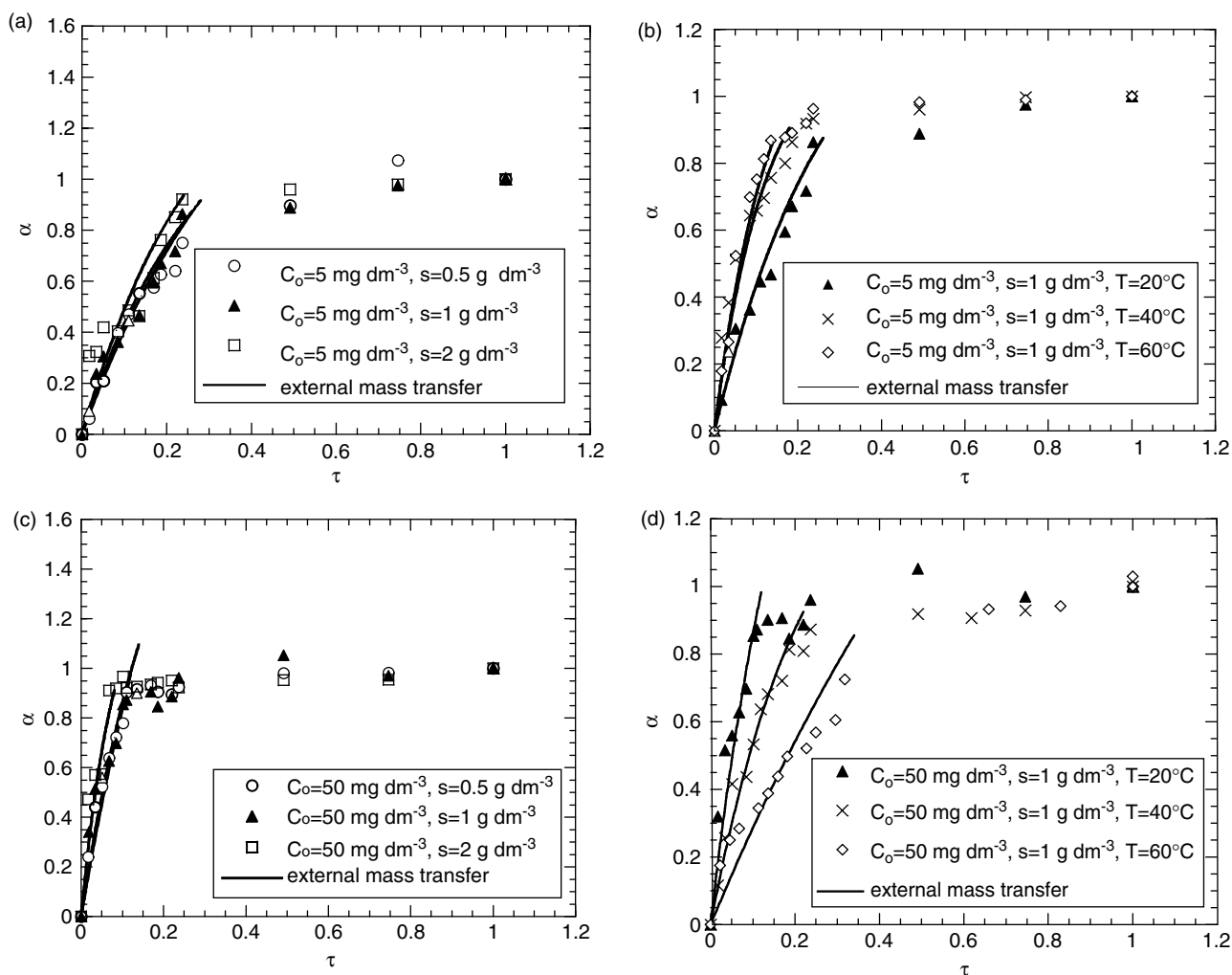
Consequently, one may argue that at the beginning of sorption cadmium is sorbed according to a very fast and highly favourable chemical mechanism like the one described above but soon external film diffusion comes into play. On this account, if one ignores the very first minute of sorption, the remaining curves were fitted quite well by the model, eqns (7) and (8). Figure 5 displays these results. Near the end of sorption (for  $\alpha$  higher than 0.9) a much slower process, eg intraparticle diffusion, becomes gradually the rate-controlling step. Yet, this is a regime of no practical significance.

Table 3 presents the computed mass transfer rate constant,  $K_m S$ . Again, the values obtained at  $40$  and  $60^\circ\text{C}$  have been excluded from comparisons. As regards the effect of changing the solids load it appears that  $K_m S$  is hardly changed. To assess the statistical significance of the determination, a derivative time series analysis has been performed where  $d\alpha/dt$  is plotted against  $t$  and then, a Hanning low pass filter has been applied to flatten out the signal undulations until  $d\alpha/dt$  versus  $\alpha$  becomes a reasonably smooth curve (local maxima below 1% of average  $\alpha$ ).<sup>19</sup> Next, the integrated smoothed signal  $\alpha(t)$  has been processed as before and resulted in  $K_m S$  values between  $2.9 \times 10^{-4}$  and  $4.5 \times 10^{-4} \text{ s}^{-1}$  with no preferential trend with respect to biomass load. This is an additional positive sign that external mass transfer may be the predominant mechanism of the sorption process after the initial fast cadmium removal.

#### 4 CONCLUDING REMARKS

The biosorption of Cd(II) was studied using *Aeromonas caviae* particles in a batch reactor. The Langmuir and Freundlich adsorption models were shown to be employed successfully to describe mathematical biosorption equilibrium data of Cd(II) ions at various temperatures and biomass loads. Then, the calculated isotherm constants were used to assess the biosorptive capacity of the biomass. The maximum removal capacity of Cd(II) using non-living cells of *A. caviae* was found to be  $155.32 \text{ mg g}^{-1}$ , while the removal of Cd(II) was slightly affected by the temperature changes. However, the abnormal temperature dependence of sorption rate was attributed to alterations of the surface morphology of biomass particles. The obtained favourable biosorption results, in terms of capacity, of the examined metal ion onto *A. caviae* biomass possibly demonstrates a potential for the technological treatment of aqueous waste streams by a cheap waste material.

A kinetic investigation was conducted (in the second part of this study), analysing various kinetic rate expressions mechanisms. Evidence has been



**Figure 5.** Experimental degree of conversion  $\alpha$  against predictions based on the solution of the mass transfer equation (eqns (7) and (8)) at initial cadmium concentrations of:  $5 \text{ mg dm}^{-3}$  for (a) various biomass loads, (b) various temperatures and  $50 \text{ mg dm}^{-3}$  for (c) various biomass loads and (d) various temperatures.

provided that the sorption of cadmium on *A. caviae* is a complex process. A finite volume diffusion model with a time-dependent concentration at the surface of the biosorbent was found to closely fit the experimental data for the largest part of the process. Alternatively, the scenario of an external surface chemical enhancement (dominating the very beginning of the process) being followed by external film diffusion, was also found to meet the fitting requirements and deserves attention on physical grounds.

In view of the above, we are tempted to argue that biosorption of cadmium is more correctly described by more than one model, as is often the case with the sorption of metal ions.<sup>18</sup> This perhaps is contrary to the customary approach as reported to the literature, where just one kinetic model is selected and if it shows a ‘satisfactory fit’ with experimental data (based on a correlation coefficient analysis), then this model is readily accepted.<sup>12</sup> In this sense, it is hoped that the present work constitutes another important contribution to the field, underlying the need for testing several theoretical

models before definitive statements can be made about the process mechanism(s).

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