Trends in
Chemical
Engineering
Vol. 13, 2010

Review

Biosorption of metal ions

M. X. Loukidou, E. N. Peleka*, Th. D. Karapantsios, and K. A. Matis
Section of Chemical Technology & Industrial Chemistry, School of Chemistry,
Aristotle University (Box 116), GR-54124 Thessaloniki, Greece

ABSTRACT

Dilute aqueous solutions, generated or used by industry, can contain a variety of different metal ions. Various processes are suitable for reclamation of heavy metals and among them, biosorption constitutes an alternative. The ability of microorganisms to remove metal ions from solution is a well known phenomenon. Applications of biosorption make use of dead biomass, which does not require nutrients and can be exposed to environments of high toxicity. Focus of this paper constitutes, among other, the kinetics of the biosorption process that is still quite ambiguous; as example, the use of *Aeromonas caviae* is given for the removal of cadmium or chromate ions in a stirred batch reactor. The Elovich rate equation has been applied to the experimental data in the present and critically commented in comparison with the literature.

KEYWORDS: equilibrium, modeling, chemisorption, mass transfer, adsorbents

INTRODUCTION

It has been well established nowadays that dissolved heavy metals escaping into the environment pose a serious health hazard; their threatening presence was even linked to the demise of the Roman empire [1]. The control of heavy metal emissions is best done right at their source, before the toxic metals entering the complex ecosystem as the metallic species accumulate in living tissues throughout the food chain, which certainly has humans at its top. For instance, the so-called environmental crime of Assopos river (north of Athens), a case that has recently reached the courts, as can be read in the local newspapers; the river was used for some time to receive almost untreated effluent from nearby industries and as result, to contain high concentration of toxic metals, such as hexavalent chromium of the order of 100 mg L^{-1}.

So, the ability of microorganisms to remove metal ions is a known phenomenon; biosorption was termed the process that makes use of dead biomass, usually from fermentation wastes or by-products [2]. This application was proved to remove greater quantities of dissolved metals, be more selective and technologically promising, e.g. in elution and regeneration, reducing problems with toxicity etc. Nevertheless, efforts have been conducted to isolate bacteria strains from metal-polluted strains, i.e. mining and industrial areas, and investigate them as possible effective biosorbents [3].

A comparison of the various treatment processes for metal-laden wastewaters was published, among others, by Eccles [4] giving their characteristics and disadvantages when applied to dilute aqueous solution. The use of a biological process with a commercially available adsorbent material (AMT-Bioclaim) was shown under specific experimental conditions to decrease the operation running costs by 36% and total cost by 28% compared to conventional techniques like ion exchange and chemical precipitation. A two-stage countercurrent (of the polluted aqueous

---

*Corresponding author
peleka@chem.auth.gr

system and the pretreated biomass) flowsheet was also proposed, following extensive pilot plant tests; with each stage containing biosorption of metals and appropriate separation of loaded biomass, and these stages were followed by only one elution stage [5]. May be the difficulty in biomass separation (harvesting) was advocated as one of the main disadvantages of biosorption and for this reason, flotation has been thoroughly examined.

Engineering considerations are central in decisions concerning the commercial future of biosorption, hence the study of relative kinetics and modeling is of outmost importance [6]. Among the various applied kinetic equations belongs the Elovich equation, known as many others from the kinetics of chemisorption of gases on solids, but used by Cheung *et al.* [7] for cadmium-contaminated water and bone char as the adsorbent. Adsorption on solids from a liquid phase is perhaps a different process than adsorption from a gas phase where traditionally the remaining bulk concentration dictates the kinetics.

Perhaps, a strong argument in favour of searching for the actual mechanism is that if we find one which we think represents what truly occurs, extrapolation to new operating conditions is more safely done. Very precise and reproducible data should be also used, which in itself is quite a problem in biosorption. To recall a good students handbook by Levenspiel [8], there is no reason why we should not use the simplest and easiest-to-handle equation of satisfactory fit. Unfortunately, if a number of alternative mechanisms fit the data equally well, we must recognize that the model selected can only be considered to be one of good fit, not one that represents reality.

The kinetic mechanism of metal sorption on biosorbent particles was investigated [9] putting more emphasis on samples collected at short times after the initiation of the process (where the major part of the adsorption occurs) and following the known concept of the rate controlling step, a simplifying approach. For the case of a non-porous biomass, 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 metal ions may have a ready access to react with internal surface sites. For sufficiently high agitation speed in the reaction vessel the bulk diffusion step can be safely ignored since then sorption onto sorbent particles is decoupled from mass transfer in the bulk mixture.

The finally chosen kinetic models were those, which not only fit closely the data, but also represent reasonable sorption mechanisms. To compare measurements from various experiments it was first necessary to introduce a dimensionless degree of conversion. 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. The adsorption rate of metal ions onto *Aeromonas caviae* was found to be particularly sensitive to initial bulk concentration, biomass load and ionic strength of the solution.

EXPERIMENTAL PART

Aeromonas caviae is a Gram-negative bacterium isolated from raw water wells near Thessaloniki. It was cultivated in the laboratory, the produced biomass separated by centrifugation, washed and sterilized. Its characterisation (potentiometric titration, infrared spectra, zeta-potential measurements, desorption tests) and in-depth investigation was elsewhere recorded by Loukidou *et al.* [9].

The biosorption experiments were carried out at different: biomass feed (0.5, 1 and 2 g L^{-1}), initial cadmium or chromium(VI) concentration (5 and 50 mg L^{-1}), temperature (20, 40 and 60 °C). The batch experiments were performed in Erlenmeyer flasks (500 mL) at a 180 rpm agitation speed, which was high enough to eliminate concentration profiles inside the flasks. The coexisting presence of a common salt ($NaNO_3$) was also examined. By adding small amounts of HNO_3 or NaOH solutions, the initial pH of the solution was adjusted (far from the precipitation value as hydroxide for the case of cadmium); the optimum pH value was found in the case of chromates. The residual concentration of cadmium in all samples was chemically analyzed by atomic absorption spectrophotometry (AAS), and of chromium in a UV-vis. spectrophotometer at 540 nm using diphenyl carbazide, in the normal manner.

All kinetic tests were carried out in triplicate and the mean value was used in calculations.

RESULTS AND DISCUSSION

Biosorption kinetics

Aeromonas caviae is often present in groundwaters and exhibits particular tolerance to heavy metals [10]. The purpose of selecting this bacterium for such a study, apart from its originality and as proved, its effectiveness as a biosorbent (the maximum capacity for cadmium ions spanning in the range -68-182 mg g^{-1}), was mainly its rather rare property to be able to remove both cations and anions. In this way, no specific modification/pretreatment was required, such as experimented in other cases [11].

A usually necessary and rather simple attempt is to try and differentiate between chemical kinetics and mass transfer. The diagram of the biosorbent capacity (q) with the square root of contact time (t^{05}) is shown as Fig. 1, with kd the diffusion coefficient [mg g^{-1} $min^{-0,5}$]; it is well observed the known criterion is not obeyed by the data. As referred by Ho *et al.* [6], in their overview, this relationship is used as criterion if the rate limiting step is intraparticle diffusion, in case of obtaining a straight line passing through the origin. Numerous researchers found that this equation described the kinetics of sorption of dyes in biosorbents.

Concerning the Elovich equation, according to ref. [7], this has been successfully used also in the sorption of zinc ions on soils, and in the sorption of iron, cobalt, nickel, copper and zinc ions on

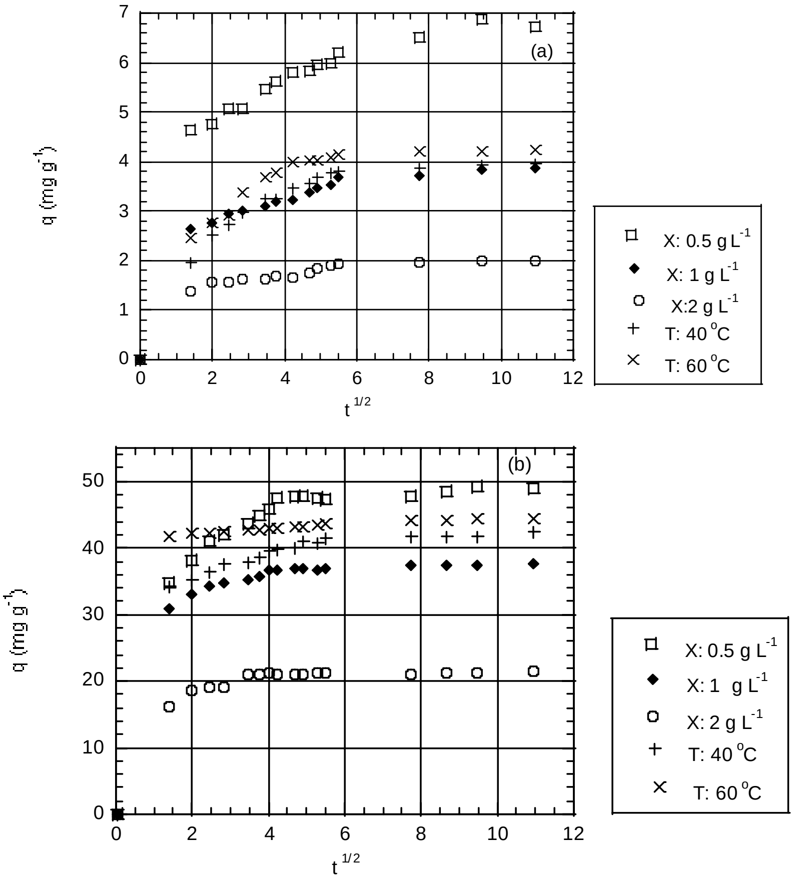


Fig. 1. Graph of biosorptive capacity (q_t, mg g^{-1}) of *Aeromonas caviae* with the square root of contact time according to the following equation, at various experimental conditions; for initial concentration of cadmium ions (a) 5 and (b) 50 mg L^{-1} (where X is the biomass concentration): $q = k_d t^{0.5}$, where k_d the diffusion coefficient.

solvent-impregnated resins. The general explanation for this form of kinetic law involves a variation of the energetics of chemisorption with the extent of surface coverage. Another plausible explanation could be that the active sites are heterogeneous in nature and hence, exhibit different activation energies for sorption. If the biosorption of the examined metal ions (zinc and chromates) onto *A. caviae* is predominantly chemisorption, the Elovich model may be applied to describe the system. The mechanism of biosorption is of course critical to the application of a solution method.

Our effort to correlate the experimental data with this model equation is presented as Figs. 2 and 3. When the initial concentration of the aqueous solution (effluent) increased, the constant *a* of the Elovich equation was observed to increase and constant *b* decreased. When the mass of biosorbent increased, both constants *a* and *b* increased at the same time. Teng and Hsieh [12] proposed that the constant *a* is related to the rate of chemisorption and the constant *b* is related to the surface coverage.

Therefore, increasing the concentration of solution and the mass of biosorbent will increase the rate of chemisorption. If the constant *b* is related to the extent of surface coverage, then the increasing of solution concentration will decrease the available sorption surface for the sorbates. An increase in the mass of biomass will increase the available surface for the sorbates.

Table 1 presents the respective calculations for the two constants of the equation, showing also quite

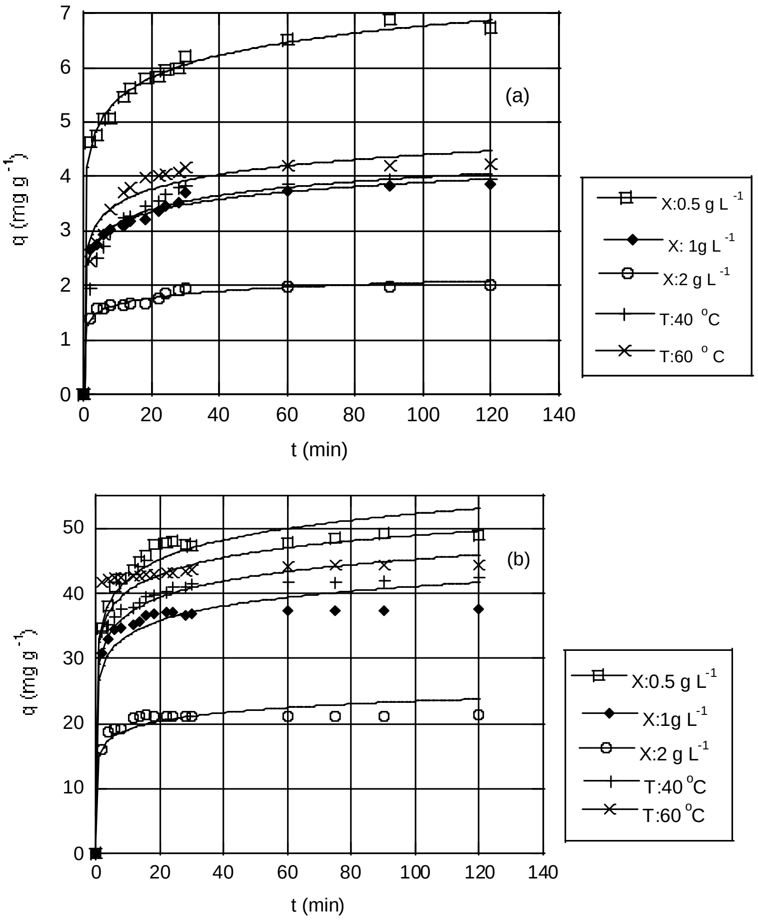


Fig. 2. Comparison of biosorption experimental data with theoretical predictions according to the Elovich model; for initial concentration of Cd(II) (a) 5 and (b) 50 mg L^{-1} (at pH 7): dq_t / dt = $a \exp(-\beta q_t)$, with α and β the constants of the equation; initial conditions for its integration q = q_t at time t = t and q = 0 at t = 0.

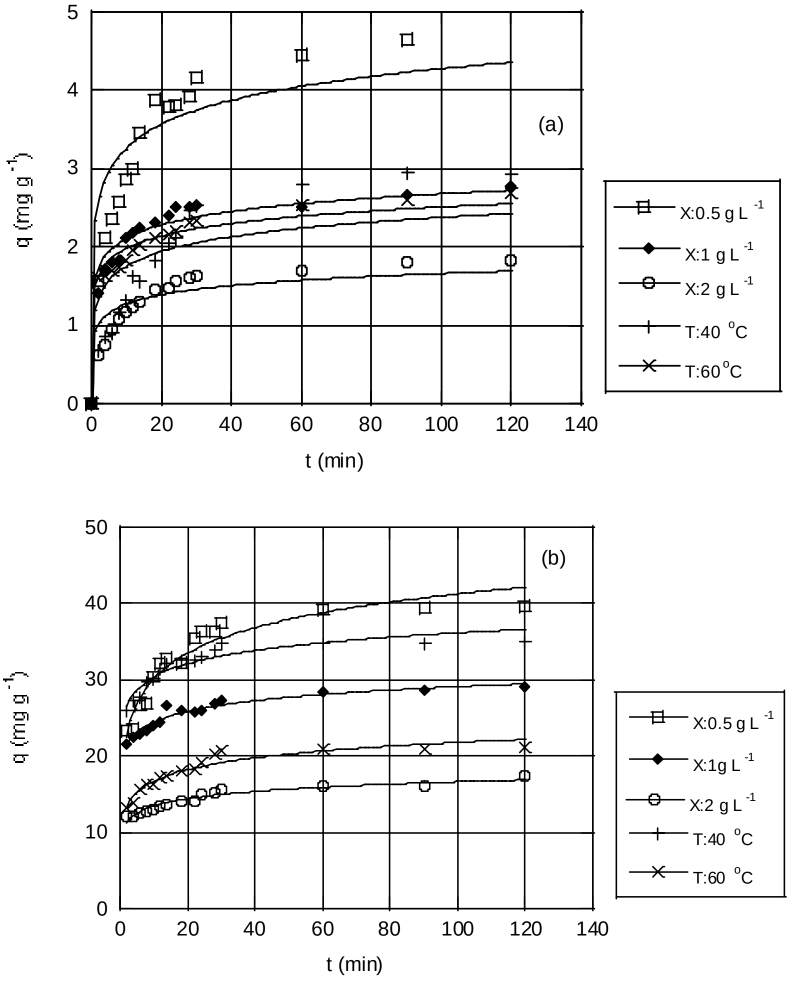


Fig. 3. Comparison of biosorption experimental data with theoretical predictions according to the Elovich model; for initial concentration of Cr(VI): (a) 5 and (b) 50 mg L^{-1}(at pH 2.5).

Table 1. Kinetic parameters as calculated for the Elovich model (case of cadmium).

C_o (mg L^{-1})	**Conditions**		**Elovich**		
	T (° C)	Biomass (g L^{-1})	α (mmol h^{-1} g^{-1})	B (mmol g^{-1})	r^2
5	20	0.5	0.74	1.70	0.995
	20	1	0.55	2.97	0.993
	20	2	0.50	5.69	0.985
	40	1	0.51	2.73	0.948
	60	1	0.55	2.53	0.953
50	20	0.5	1.52	0.23	0.972
	20	1	1.32	0.3	0.936
	20	2	1.52	0.87	0.936
	40	1	1.40	0.27	0.960
	60	1	1.62	0.27	0.880

an acceptable fit based on the observed correlation coefficient (r^2); quite similar were the results for the case of chromates. Other equations tried less effectively on the present system, i.e. "worse"-fit models, were the following: zero, first order, parabolic diffusion [6], Ritchie equation [7], and also the shrinking core model [13].

If one stopped searching up to this point, then the conclusion is apparent. Nevertheless, the suitability of a pseudo 2nd order chemical reaction for the biosorption of these ions was suggested, following further investigation [14]. In the latter equation, in essence a numerically determined parameter was used in place of the equilibrium capacity and in this treatment, one bivalent ion is considered to occupy two binding sites.

To prove that a certain mechanism is followed we must show that the family of curves representing the rate equation type of the favoured mechanism fits the data so much better than the other families that the others can be rejected. We should bear in mind that it is not good enough to select the mechanism that well fits, or even best fits the data. Differences in fit may be so slight as to be explainable entirely in terms of experimental error; in statistical terms, these differences may not be significant.

Biosorption vs adsorption

Metal recovery or removal from solution may involve the following pathways:

1. The binding of metal cations to cell surfaces, or within the cell wall, where microprecipitation may enhance uptake.
2. Translocation of the metal into the cell, possibly by active (metabolic energydependent) transport; the active uptake or concentration of metal by living microbial cells is often termed bioaccumulation.
3. The formation of metal-containing precipitates, by reaction with extracellular polymers or microbially produced anions such as sulphide or phosphate.
4. The volatilization of the metal by biotransformation - see also Fig. 4.

Comparisons of sorbents are generally difficult because of inconsistencies in data presentation. Such an effort from our lab work is shown in the present paper with Figs. 5 and 6, for quite similar

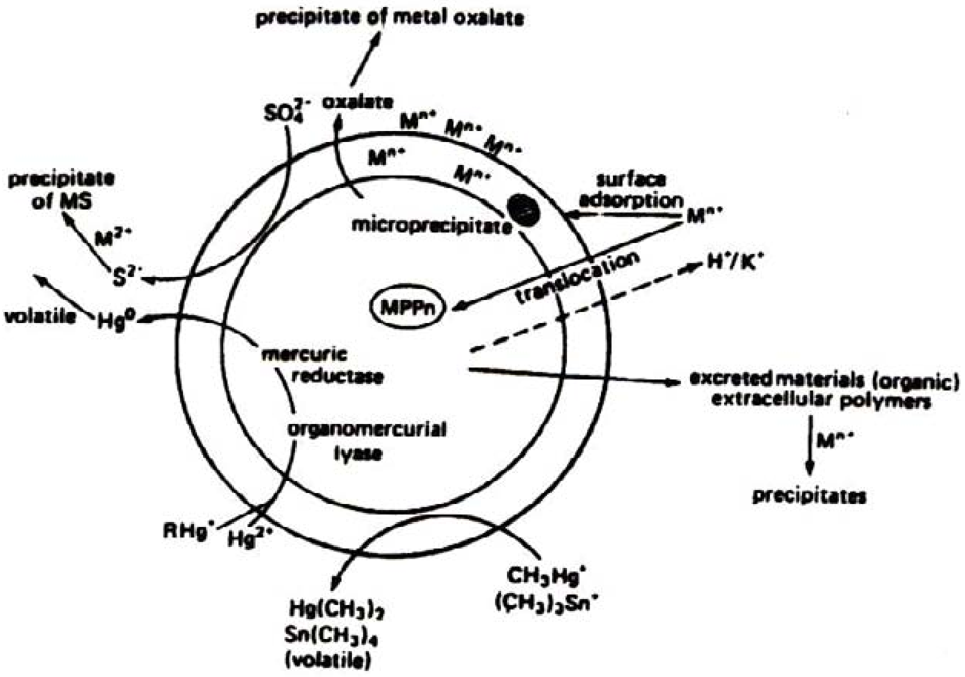
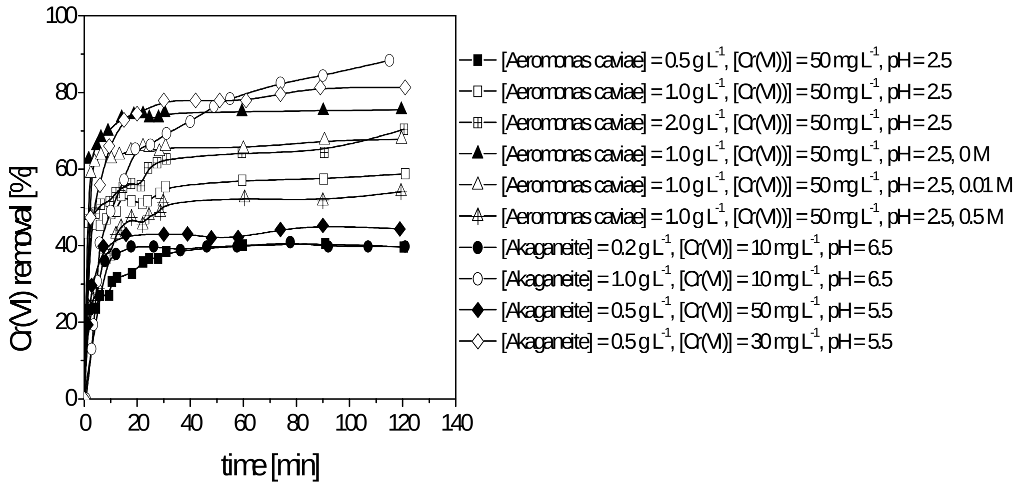


Fig. 4. Possible pathways for metal ions removal by microorganisms. Reprinted with kind permission from Springer Science + Business Media B.V.: Hughes, M. N. and Poole, R. K. 1989, Metals and Microorganisms, Chapman and Hall: London, 328.

a



b

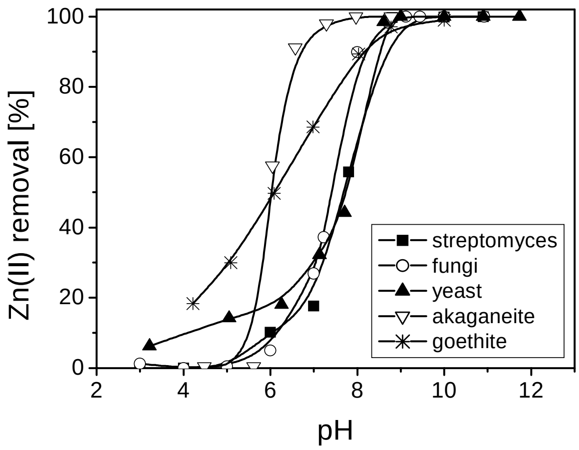


Fig. 5. (a) Kinetics of Cr(VI) sorption on various sorbents for various experimental conditions; a comparison [16]; (b) influence of pH on zinc removal for different sorbent types [17].

experimental conditions, for biosorbents and respectively typical inorganic sorbents removing both chromate oxyanions and heavy metal cations (i.e. cadmium and zinc). The influence of significant parameters like pH, contact time, and sorbent concentration on metal ion removal (expressed %) was studied. It could be argued that the results are rather comparable.

A vast array of biological materials, especially bacteria, algae, yeasts and fungi have received increasing attention for heavy metal removal and recovery due to their good performance, low cost and large available quantities [20]. The use of low-cost sorbents has been investigated as a replacement for current costly methods of removing heavy metals from solution. Natural materials or waste products from certain industries with a high capacity for heavy metals can be obtained, employed, and disposed of with little cost; comparison tables from the literature were given [21]. It was concluded that due to the scarcity of consistent cost information, cost comparisons were difficult to make.

In order, finally, to shed perhaps some more light on the whole questioning as far as kinetics is concerned, mention will be given to the respective calculations of thermodynamic parameters of this biosorption system. The values of the apparent standard thermodynamic equilibrium constant (Kc°) of biosorption at different concentration were found in order to find the value of ΔG°, standard Gibbs free energy; this for cadmium at 20 °C was found to be -1.7 kJ mol^{-1}, where the negative figure

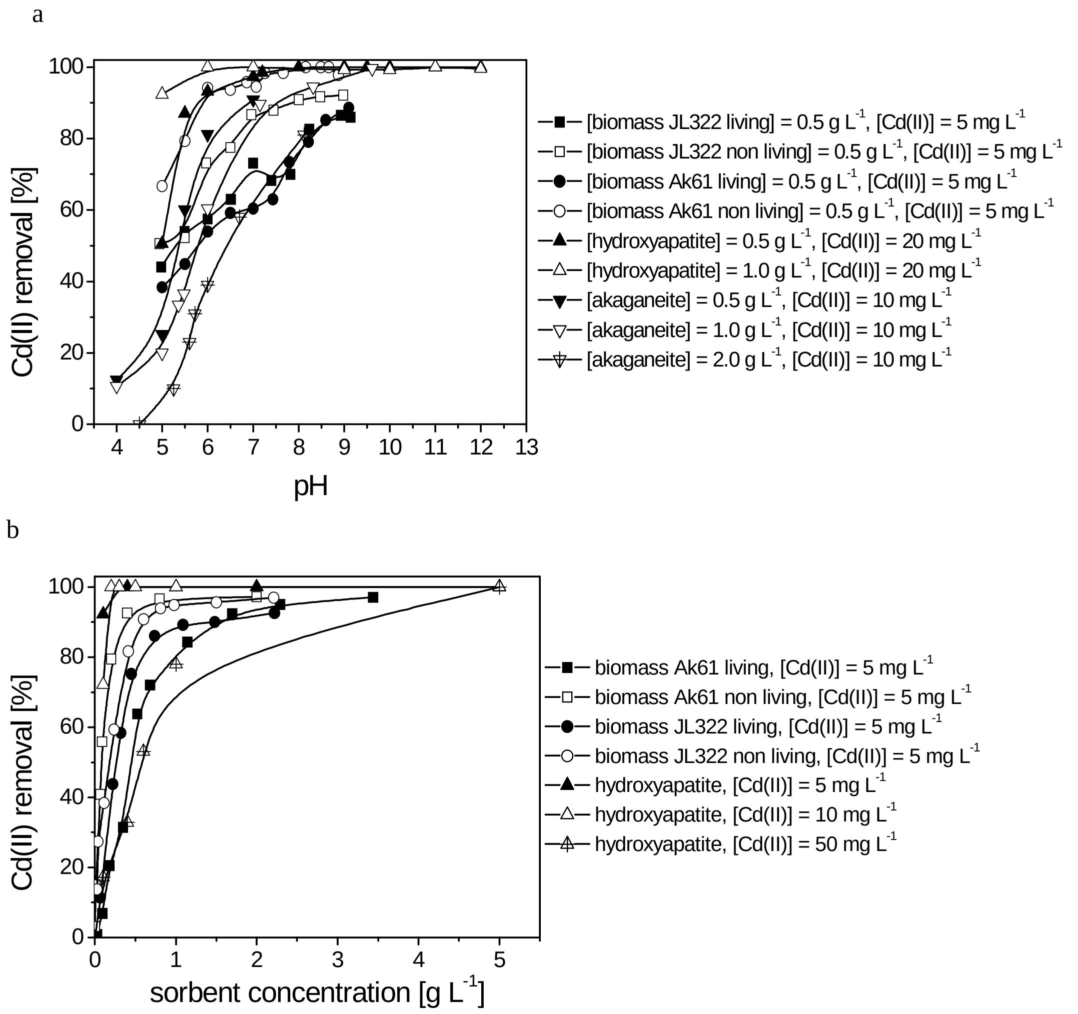


Fig. 6. Cadmium removal for different sorbent types: (a) influence of solution pH [18]; (b) effect of sorbent concentration [19].

is due to the fact that the process is spontaneous with high affinity of the metal to the biomass.

The standard enthalpy and entropy changes determined from the In Kc° vs. 1/T diagram were 14.5 kJ mol^{-1} and 0.06 kJ mol^{-1} K^{-1}, respectively. The positive value of ΔH^0 suggests the endothermic nature of biosorption. The positive value of ΔS^0 confirms the increased randomness at the solid-solution interface during biosorption. Reasonably similar were the findings and also procedure of Aksu [22]. On the other hand, for the adsorption of cadmium on akaganéite, Deliyanni and Matis [18] found an enthalpy change of 104.75 kJ mol^{-1} (also an endothermic phenomenon) and considered it as chemisorption.

For the case of chromates and *A. caviae*, respectively were found: at 20 °C $\Delta G° = -0.65$ kJ mol^{-1}, $\Delta H^0 = 7.6$ kJ mol^{-1} and $\Delta S^0 = 0.03$ kJ mol^{-1} K^{-1}. From initial calculations, the obtained activation energies were lower than 10 kJ mol^{-1}, being usually the accepted limit for the differentiation between chemi- with physisorption. The value, in contradiction with the aforementioned, indicates rather a physical phenomenon than chemisorption. Sorption of heterogeneous liquid-solid systems has been usually accepted to follow Arrhenius kinetics; however, in order to apply the model in such systems, the morphology of the reactive surface as well as the final biosorption capacity must not vary with temperature, conditions often overlooked.

Analysis of equilibrium data is important for developing an equation that can be used for design purposes. Classical adsorption 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 at a constant temperature [6]. Apart from the well known Langmuir and Freundlich isotherms, other isotherms were also used either with two parameters (the Temkin, Dubinin-Radushkevich, Flory-Huggins, Halsey, and the Brunauer-Emmer-Teller model) or three parameters isotherms (Sips, Toth, Redlich-Paterson) etc. [23].

The adsorption isotherms obtained for Cd(II) and 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 [9, 14]. Yet, the correlation coefficients of the Langmuir curves were a little better. This observation implies that monolayer biosorption, as well as heterogeneous surface conditions may co-exist under the applied experimental conditions. Hence, the overall sorption of metal ions on the biomass may involve more than one mechanism, such as ion exchange, surface complexation and electrostatical attraction.

The values of the Freundlich constants showed a relatively easy uptake of metal ions with high biosorptive capacity of *A. caviae.* In particular, the value of n (parameter in the integer), which is related to the distribution of bonded ions on the sorbent surface, is greater than unity, indicating that the ions are favorably adsorbed under all the examined experimental conditions. In general, the Freundlich equation satisfactorily 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, in the Ritchie equation, between the extremes of $\theta=0$ and $\theta=1$, the Langmuir isotherm is nearly equivalent with the case when θ is proportional to a fractional power of C_{eq} [24]. Therefore, both isotherms can be used to model biosorption data from dilute aqueous solutions.

It is true that the ability of the different biosorbents to remove toxic metals varies depending on the type of microorganism and the applied conditions - see for instance Table 2, for the case of chromates sorption, compared with a maximum capacity spanning in the range -70-285 mg g^{-1} for *A. caviae.* Our results (presented previously as tables) demonstrated 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 poorer biomass utilization. Further, it was suggested that the sorption of metals is more correctly described by more than one model [31].

Table 2. Comparison of different biosorbents based on their maximum capacity for chromates.

Biomass	**q_{max}** (mg g^{-1})	**pH** **(-)**	**T** (° C)	**C_0** (mg L^{-1})	**X** (gL^{-1})	**Reference**
Zoogloera ramigera	3	2	25	25 - 400		25
Saccharomyces cerevisiae	3	1-2	25	25 - 400		25
S. equisimilis	11.8	2	30	50	2	26
Streptomyces noursei	10.6	5.5	26	~	~	27
Saccharomyces cerevisiae	4.4	2	30	50	2	26
Rhizopus arrhizus	4.5	1-2	25	25 - 400		25
A. niger	113	2	30	150	0.5	26
Firms sylvestris	201.81	1	25	50 - 300	1	28
C. vulgaris	3.5	1-2	25	25 - 400	~	29
Rhizopus nigricans	47	2	30	100	0.5	30

Kinetic analyses not only allow estimation of sorption rates but also lead to suitable rate expressions characteristic of possible reaction mechanisms.

Modification of the sorbents can also improve adsorption capacity [11]. The hydrophobicity of bacteria cells is mainly due to the properties of the cell wall (i.e. the biosorption sites), which strongly depend upon the presence of various polysaccharides, proteins and lipids that form a biopolymer layer; the properties of the latter can be also changed with the conditions of growth. An interesting proposal was recently made for biosorbent product development from new materials, like olive pomace wastes, guided by active site characterization [32].

The magnitude of electrostatic interaction between the sorbents surfaces and a metal ion is a function of electrokinetic potential, expressed usually as ζ-potential. Electrokinetic measurements may provide useful information regarding the net effective charge on the (bio)sorbent surface and for example, the suitable flocculant or surfactant (cationic or anionic) to be used to downstream separation. Such measurements have been often applied when studying the mechanism of the removal process, as presented in Figure 7; the characteristics and behaviour of biosorbents compared with the inorganic sorbents are not shown quite similar.

The Gram-positive bacterial cell wall, such as the examined *Actinomycetes* strains (in Fig. 7b) by Kefala *et al.* [18], consists mainly of a number of polymers containing various acidic groups, which may deprotonate with rising pH values of biomass suspensions. Between pH 3-10 protons were expected to be released, particularly from phosphoryl and carboxyl groups. Due to the deprotonation, an electronegative potential develops in the cell wall, as indicated by the electrokinetic data. Concerning *A. caviae* measurements (shown in Fig. 7a) it was found that the cell wall contained two or more main functional groups responsible for the uptake of heavy metals, i.e. carboxyl, phosphate and possibly, nitrogen-containing groups [14]. On the other hand, akaganéite showed a point of zero charge at ~7.3, initially (being decreased when an oxyanion was adsorbed); in the case of cation adsorption on akaganéite, it was observed that for a change of about 2.5 pH units (from 5.5-8, approximately) the removal rates were changed from almost 0 to 95% (Deliyanni and Matis in ref. [18]).

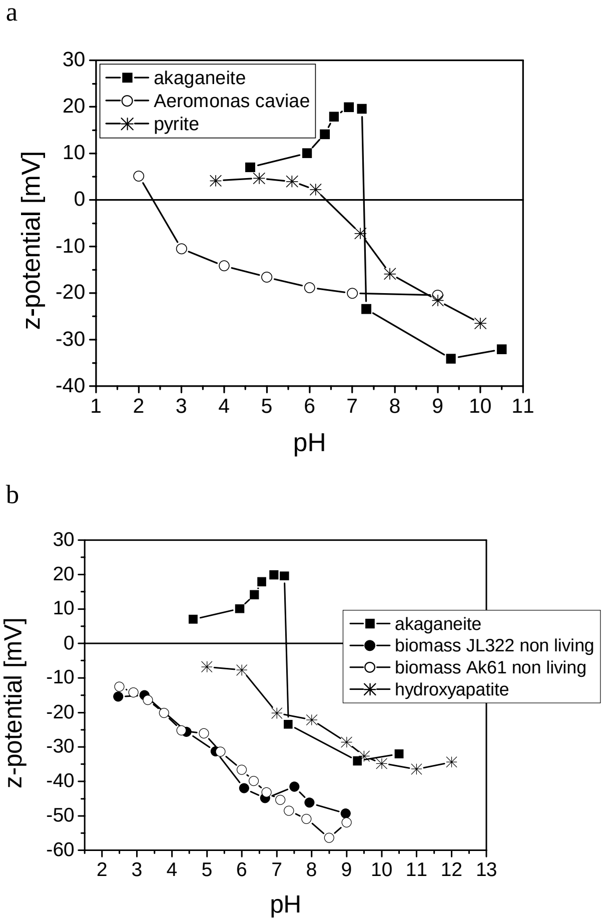


Fig. 7. Zeta-potential measurements against the solution pH in the aforementioned work, for comparison reasons, when chromate oxyanions or metal (zinc or cadmium) cations were removed [33, 34].

The specific surface area of *Penicillium chrysogenum* was elsewhere calculated from the nitrogen adsorption curve as 9.7 m^2 g^{-1}, much smaller than other typical inorganic adsorbents; the pore volume (calculated from the desorption curve) for this fungal biomass was found to be 0.016 cm^3 g^{-1} [35]. Taking into account that the specific surface area and the pore volume were small, the pore size distribution was not of any significant importance (which may affect the kinetics, too); noting as well the possible influence of the needed specific treatment of the said biosorbent, being of organic matter, for the above measurement. A table was presented [36] with values for the surface areas of selected porous solid materials but measured by different techniques; due to the varying range obtained, a question was also raised about the true surface areas of biomass.

So, abnormal temperature dependence of sorption rate was also found [9, 14], attributed to alterations of the surface morphology of biomass particles. The gross features of the biomass at 40 and 60 °C observed by SEM photographs 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. Evidence has been provided, in conclusion, that this is a complex process.

Concluding, various arguments were above raised concerning the kinetics of biosorption and mainly regarding the:

(i) influence of temperature,
(ii) rate-determining step(s),
(iii) specific surface area and nature of biomasses,
(iv) type of isotherm followed, and
(v) maximum loading capacity.

Rather contradictory indications on the subject were pointed out. The scenario of an external surface chemical enhancement, dominating the very beginning of the process, being followed by external film diffusion, looks to be quite possible. Therefore, a two stage kinetic mechanism is rather proposed, as it meets the fitting requirements and deserves attention on physical grounds. The obtained information has a practical value for technological applications, since modeling successfully replaces time and material consuming experiments, necessary for process equipment design.

Engineering considerations are also central in decisions concerning the commercial future of biosorption, and a practical solution is needed for certain problems, such as the efficient separation of metal-loaded biomass. Nevertheless, the use of biological materials for removing and recovering heavy metals from contaminated wastewaters has emerged as a potential alternative method to conventional treatment techniques and so, it is quite well studied.

REFERENCES

1. Volesky, B. 2001, Hydrometallurgy, 59, 203.
2. Zouboulis, A. I., Matis, K. A., and Hancock, I. C. 1997, Sep. Purif. Methods, 26, 255.
3. Zouboulis, A. I., Loukidou, M. X., and Matis, K. A. 2004, Process Biochem., 39, 909.
4. Eccles, H. 1999, Trends Biotech., 17, 462.
5. Zouboulis, A. I., Lazaridis, N. K., and Matis, K. A. 2002, J. Chem. Tech. Biotechnol., 77, 958.
6. Ho, Y. S., Ng, J. C. Y., and McKay, G. 2000, Sep. Purif. Methods, 29, 189.
7. Cheung, C. W., Porter, J. F., and McKay, G. 2001, Wat. Res., 35, 605.
8. Levenspiel, O. 1972, Chemical Reaction Engineering, 2nd ed. Wiley, New York, 466.
9. Loukidou, M. X., Karapantsios, Th. D., Zouboulis, A. I., and Matis, K. A. 2004, J. Chem. Tech. Biotech., 79, 711; Ind. Eng. Chem. Res., 43, 1748.
10. Miranda, C. D. and Castillo, G. 1998, Sci. Total Envir., 224, 167.
11. Loukidou, M. X., Matis, K. A., Zouboulis, A. I., and Liakopoulou-Kyriakidou, M. 2003, Wat. Res., 37, 4544.
12. Teng, H. and Hsieh, C. 1999, Ind. Eng. Chem. Res., 38, 292.
13. Rao, M. G. and Gupta, A. K. 1982, Chem. Eng. J., 24, 181.
14. Loukidou, M. X., Zouboulis, A. I., Karapantsios, Th. D., and Matis, K. A. 2004, Coll. Surf. A, 242, 93; Sep. Sci. Tech., 40, 1293.
15. Hughes, M. N. and Poole, R. K. 1989, Metals and Microorganisms, Chapman and Hall: London, 328.
16. Loukidou, M. X., Zouboulis, A. I., Karapantsios, Th. D., and Matis, K. A. 2004, Coll. Surf. A, 242, 93; Lazaridis, N. K., Bakoyannakis, D. N., and Deliyanni, E. 2005, Chemosphere, 58, 65.
17. Zouboulis, A. I., Rousou, E. G., Matis, K. A., and Hancock, I. C. 1999, J. Chem. Technol. Biotechnol., 74, 429; Deliyanni, E. A., Lazaridis, N. K., Peleka, E. N. and Matis K. A. 2004, Envir. Sci. and Tech. (ESPR), 11, 18; Deliyanni, E. A., Peleka, E. N., and Matis, K. A., 2007, J. Hazard. Mater., 141, 176.

18. Mandjiny, S., Zouboulis, A. I., and Matis, K. A. 1995, Sep. Sci. Tech. 30, 2963; Deliyanni, E. and Matis, K. A. 2005, Sep. Purific. Tech., 45, 96; Kefala, M. I., Zouboulis, A. I., and Matis, K. A. 1999, Envir. Pollution, 104, 283.
19. Mandjiny, S., Zouboulis, A. I., and Matis, K. A. 1995, Sep. Sci. Tech., 30, 2963; Kefala, M. I., Zouboulis, A. I., and Matis, K. A. 1999, Envir. Pollution, 104, 283.
20. Wang, J. and Chen, C. 2009, Biotech. Adv., 27, 195.
21. Bailey, S. E., Olin, T. J., Bricka, R. M., and Adrian, D. D. 1999, Wat. Res., 33, 2469.
22. Aksu, Z. 2002, Proc. Biochem., 38, 89.
23. Febrianto, J., Kosasih, A. N., Sunarso, J., Ju, Y.-H., Indraswati, N., and Ismadji, S. 2009, J. Hazardous Mater., 162, 616.
24. Yiacoumi, S. and Tien, C. 1995. Kinetics of Metal Ion Adsorption from Aqueous Solutions, Kluwer, Boston.
25. Nourbakhsh, M., Sag, Y., Ozer, D., Aksu, Z., Kutsal, T., and Caglar, A., 1994, Proc. Biochem., 29, 1.
26. Goyal, N., Jain, S. C., and Banerjee, U. C. 2003, Adv. Envir. Res., 7, 311.
27. Mattuscha, B. and Stranbe, G. 1993, J. Chem. Tech. Biotechnol., 58, 57.
28. Ucun, H., Bayhan, Y. K., Kaya, Y., Cakici, A., and Algur O. F. 2002, Bioresource Tech., 85, 155.
29. Aksu, Z., 2001, Sep. Purific. Tech., 21, 285.
30. Bai, R. S., and Abraham, T. E., 2001, Bioresource Tech., 79, 73.
31. Smith, E. H., 1996, Wat. Res., 30, 2424.
32. Pagnanelli, F., Mainelli, S., and Toro, L. 2008, Wat. Res., 42, 2953.
33. Loukidou, M. X., Zouboulis, A. I., Karapantsios, Th. D., and Matis, K. A. 2004, Coll. Surf. A, 242, 93; Deliyanni, E. A., Peleka, E. N., and Matis, K. A. 2007, J. Hazard. Mater., 141, 176; Zouboulis, A. I., Kydros, K. A., and Matis, K. A. 1995, Wat. Res., 29(7), 1755.
34. Mandjiny, S., Zouboulis, A. I., and Matis, K. A. 1995, Sep. Sci. Tech., 30, 2963; Deliyanni, E., and Matis, K. A. 2005, Sep. Purific. Tech., 45, 96; Kefala, M. I., Zouboulis, A. I., and Matis, K. A. 1999, Envir. Pollution, 104, 283; Deliyanni, E. A., Peleka, E. N., and Matis, K. A. 2007, J. Hazard. Mater., 141, 176.
35. Matis, K. A., Zouboulis, A. I., and Loukidou, M. X. 2002, in V. Intl. Conf. Metallurgy, Refractories and Environment, TU Kosice, High Tatras, Slovakia.
36. Schneider, I. A. H., Rubio, J., and Smith, R. W. 2001, Int. J. Min. Process., 62, 111.