
Metal ions biosorption from dilute aqueous solution

K.A. Matis*, A.I. Zouboulis, N.K. Lazaridis
and Th.D. Karapantsios

Laboratory of General and Inorganic Chemical Technology,
School of Chemistry, Aristotle University,
GR 54124 Thessaloniki, Hellas

E-mail: kamatis@chem.auth.gr E-mail: zoubouli@chem.auth.gr

E-mail: nlazarid@chem.auth.gr E-mail: karapant@chem.auth.gr

*Corresponding author

Abstract: Biosorption, using non-living biomass (mostly suspended), is briefly reviewed in this paper as applied to toxic metal ions removal, with particular focus on the kinetics and engineering considerations of the process. Several diverse kinetic models were successful in fitting the experimental data. Evidence was provided that the metal biosorption (on *Aeromonas caviae* biomass) is a complex process. The examination of satisfactory and innovative wastewater treatment techniques has become an important requirement nowadays, and one of the significant subjects under investigation is the effective recycling of water and for precious or strategic metals themselves.

Keywords: cations; oxyanions; separation; kinetics; modelling; biosorbent; biomass.

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Biographical notes: Kostas A. Matis had his first degree in Chemistry in the Department where he is currently also working; an MSc and a PhD, on December 1997, in the (then) Chemical Engineering Department, University of Newcastle upon Tyne, UK. His main field of specialisation is separation science and technology (mainly, flotation), other fields being wastewater treatment, environmental biotechnology, inorganic materials and mineral processing. He is the author of about 120 papers in refereed journals that received more than 700 citations, three patents, ~50 communications to scientific meetings and also editor of three books.

Anastasios Zouboulis is the author/co-author of more than 120 scientific papers, supervised five PhD and ten MSc Theses and participated in 40 national and international research and demonstration projects, regarding mainly the fields of wastewater treatment processes, environmental biotechnology, as well as the treatment of industrial solid toxic wastes. His international reputation was recently recognised by his election as (foreign) member in the Russian Academy of Sciences. He is acting often as reviewer/evaluator for several EU or national research projects and he is member of the Editorial Board of scientific journals (*Separation Science & Technology* and *Chemosphere*).

Nikolaos Lazaridis is an Assistant Professor in the Division of Chemical Technology, School of Chemistry, Aristotle University of Thessaloniki. His specialisation is in the field of environmental separation processes as: flotation, sorption, membrane filtration. He is author/co-author of more than 35 papers published in scientific journals and is acting often as a reviewer for several scientific journals. He has participated in 15 national and international research projects funded by E.U.

Thodoris Karapantsios obtained an honors Diploma in Chemical Engineering from the Aristotle University of Thessaloniki, Greece, in 1986. He also holds a MS degree from the University of Rochester, USA, 1989 and a PhD Degree from the Aristotle University of Thessaloniki, 1993. He is currently an Assistant Professor at the Department of Chemistry of the Aristotle University of Thessaloniki. His main research interests are in the field of multiphase and interfacial dynamics with/without heat and mass transfer. He is author or co-author of more than 40 publications in scientific journals and more than 50 publications in conference proceedings.

1 Introduction

Environmental problems are becoming more and more acute all over the world. It is known that many specific industrial wastewater streams with large flows contain heavy metals in concentrations up to 500 mg/L, which have to be removed prior to water recycling, indirect discharge into the sewage system or direct discharge into surface waters. Some examples of such industrial wastewater are the following: (a) rinsing water in metal-working enterprises, containing Cu, Ni, Zn, Sn, Cd, Pd, Ag, Al, Au, Cr, Mo, etc.; (b) rinsing water in the semiconductor industry, containing Cu, Sn, Pb, Sb; (c) wastewater from the copper industry, containing As, Se and (d) other types of water in which the presence of toxic metals causes problems; this project, commented further in the following, was a contribution to the key action of EU 'Waste water treatment and reuse', belonging to the 5th Framework programme. The ability of microorganisms to remove metal ions from solution has been a phenomenon well known, as is the problem of toxic metal contamination of water (European Union, 2004; Zouboulis et al., 1997).

When discharged directly into rivers, polluted wastewater poses a great risk to the aquatic ecosystem, whilst discharge into the sewage system negatively affects bio-sludge activity and leads to contamination of the excess sludge to be disposed of. As a result of the standards specified in the Water Resources Act, which was amended in 1986, industry takes precautions against these risks by treating dangerous components in a partial stream, i.e., before being mixed with other types of wastewater. So, research was focused on the development of highly selective bonding agents (often denoted as BA) with fast reaction kinetics for the removal of heavy metal ions. The latter may lead to a better use of the capacity of the bonding agents, resulting in smaller units and low residual concentration of toxic metals in the treated water streams, to comply with individual standards for water reuse or discharge.

Apart from biosorbents, other typical materials extensively used are the zeolites, apatites and the various iron sorbents (Peleka et al., 2005). These BA materials are broadly classified into three classes: the carbon sorbents (active carbons, activated carbon fibres, molecular carbon sieves, fullerenes, heterofullerenes, nanomaterials, etc), the

mineral sorbents (silica gel, activated alumina, oxides of metals, hydroxides of metals, zeolites, clay minerals, inorganic nanomaterials, etc) and the other ones (synthetic polymers, composite sorbents, mixed sorbents, etc.). Cost is also an important parameter for comparing the sorbent materials. Potentially low-cost sorbents such as natural materials and industrial wastes or by-products have recently been of increasing demand for heavy metals.

The knowledge of the governing chemical state of the metal ion to be removed is a prerequisite, in an effort that to base any new development upon a solid scientific foundation (Evanko and Dzombak, 1997). The impact of chemical speciation is important on any process investigated including adsorption, ion exchange or precipitation. These often act together and the dominance of one specific is often hard to be distinguished without careful chemical measurements and advanced analytical techniques. Identifying the bonding mechanism of metals on the agent/sorbent applied is significant because the mechanism could dictate the mobilities of the species in their existing environment.

A new treatment process aimed at water and metal reuse was developed for the selective separation of heavy metals from wastewater, to reduce costs and mitigate the environmental impact of wastewater pollutants (Mavrov et al., 2003). One of the variants, being divided into three stages, was the separation of the formed BA-metal complexes by crossflow microfiltration/ultrafiltration for wastewater with metal concentrations less than 50 mg/L, as shown in Figure 1. The advantages of both dispersed-air flotation and microfiltration processes were also utilised in an innovative compact hybrid cell (Blöcher et al., 2003). Air bubbling is one of the techniques used to limit membrane fouling. Under appropriate conditions, it could be used also as the transport means for flotation, the latter being used as the pretreatment stage. Following the laboratory experiments, a hybrid rig was tested by a multinational group of the project on-site, at the Assarel-Medet open pit copper mine effluent near Panagyurishte Bulgaria (see Figure 2).

Figure 1 Combined flotation-MF system (of the METASEP programme)

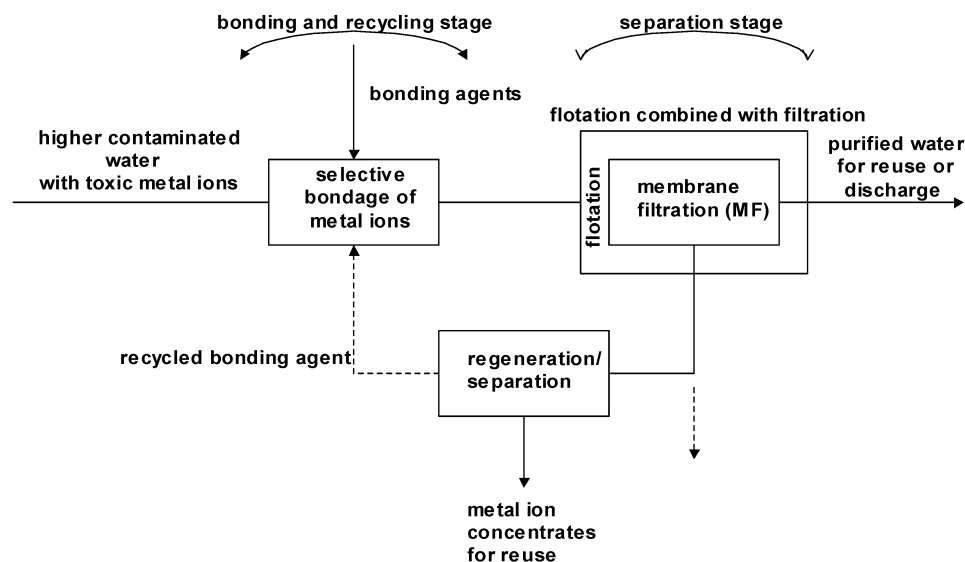
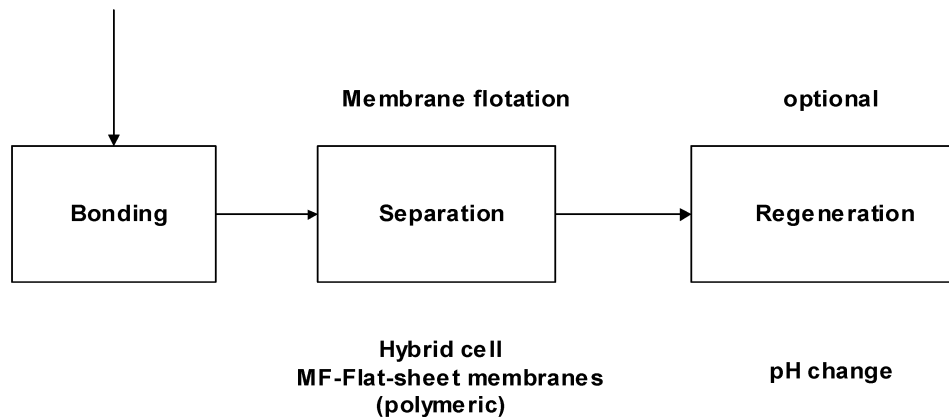


Figure 2 Flowsheet of the planned process for the on-site experiments (EU project, contract no. EVK1-CT-2000-00083). Composition of the water: sulphate<4200, Fe~8, Cu~240, Mn~40, Pb~0.2, Mg~260, Ca~270 mg/L, pH~3.5

**mod. Lewatit TP 208
SD 3166 (optional)
with NaOH (optional)**

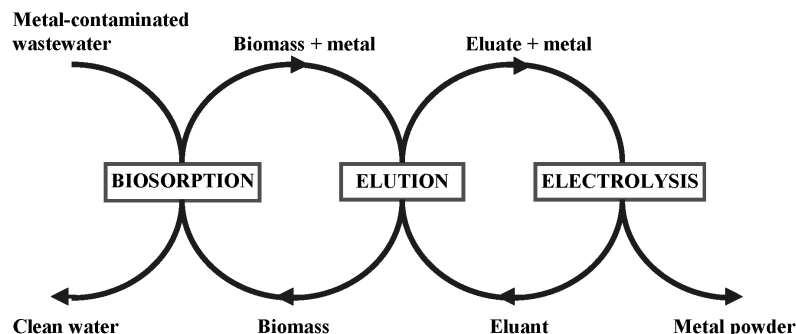


2 The process

Bacillus laterosporus or *B. licheniformis*, isolated from polluted industrial soils and suitably grown following an appropriate screening, were tested for zinc and chromates (Zouboulis et al., 2004); in this paper, are also commented the advantages and disadvantages (technological or economic constraints) of the conventional metal removal processes such as chemical precipitation, electrochemical treatment, reverse osmosis, ion exchange and adsorption. Phytoremediation has also emerged as another alternative for using biological systems (here, plants such as the African shoots population) for removing pollutants from the environment (Gardea-Torresdey et al., 1998).

In an older EU project, electrolysis by a rotating cathode cell was proposed as the final stage for the metal recovery from wastewaters, the initial being biosorption (Butter et al., 1998). The conceptual flow diagram of total process was illustrated showing recycle routes for biomass and eluant, while the resulting clean water could be also recycled for industrial use (see Figure 3). Flotation was studied in depth for the solid/liquid separation step, i.e., harvesting of metal-laden biomass, downstream following biosorption; the combined process was termed biosorptive flotation (Matis et al., 1994). Flotation constitutes a fast (compared with settling) separation technique, particularly effective for ultrafine and light suspended particles, as also the biological materials are. Except from dispersed biomass systems (which offer high surface area), immobilised ones are often used in practice, as in the case of fungal biomass in a polyacrylonitrile-binding matrix (Zouboulis et al., 2003). The operation of fixed-bed (column) adsorbers is usually expressed graphically by the concept of the breakthrough curve; so, various similar approaches are followed for their modelling, and among them is the bed depth-service time (BDST) correlation (Lehmann et al., 2001).

Figure 3 Schematic diagram of total process showing recycle routes for biomass and eluant (EU Environment programme, contract no. EVWA CT920003)



Various types of biological materials have been tried in the laboratory as effective biosorbents, including strains obtained from appropriate libraries (i.e., Microbiology Dept., Univ. Newcastle-upon-Tyne), like the *Actinomyces* (Kefala et al., 1999) and waste or by-product biomasses and non-living microorganisms, produced in thousand of tons each year by several industries, usually from fermentation. Such examples include the yeast, the most important commercial microorganisms – see, for instance, the application of *Saccharomyces carlsbergensis* and *S. cerevisiae*, from breweries, to mixture of metals, by Zouboulis et al. (1999, 2001), where *Streptomyces rimosus* and *Penicillium chrysogenum* both from pharmaceutical industries were also tested. The observed metal cations removal (quite selective for the case of copper) was compared in the lab with other conventional separation techniques, as filtration, centrifugation and flotation.

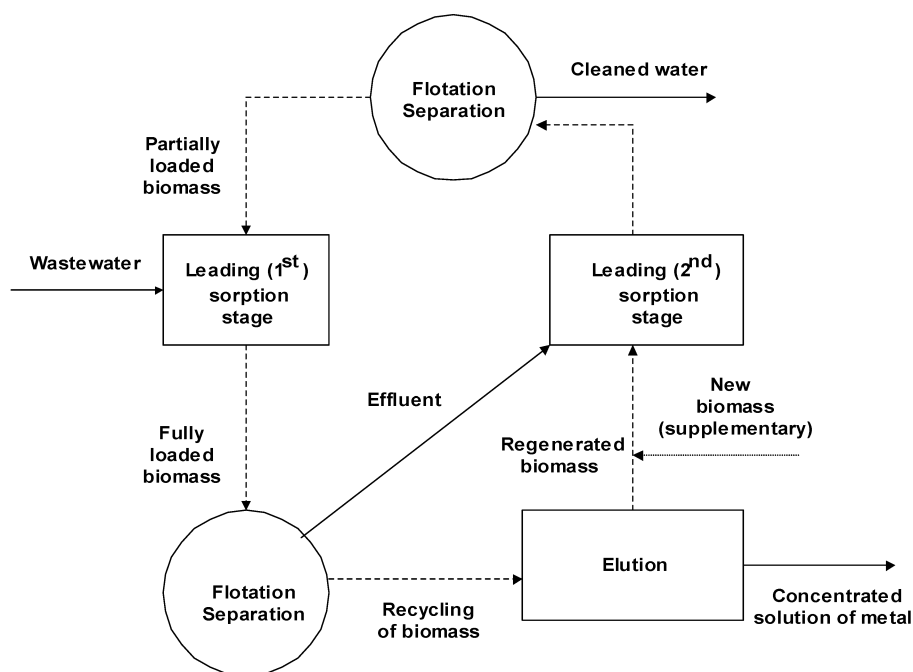
Several reviews of this scientific area also exist, as for instance the paper by Volesky (2001); in that, it was alleged that conservative estimates give new biosorbents the potential share amounting to US\$27 million/year of the currently existing environmental market in North America alone. Biosorption is an area of endeavour that occupies an interface between biology, chemistry and engineering. Future progress may depend on the successful interaction among these disciplines.

Mention is finally given to a review by Aksu (2005) of the process applied to hazardous organic compounds such as the phenolics, pesticides, etc. Recently, promising papers have appeared in the literature: for example, on the modelling of the acid–base properties of biosorbents by Pagnanelli et al. (2004), the use of biomaterials from marine algae compared with commercial resins by Feng and Aldrich (2004), the removal of radionuclides by Psareva et al. (2004), following the Chernobyl power station disaster in Ukraine and the application of agricultural by-products by Ho et al. (2004).

Multi-cycles testing for biosorption, elution and recycling the biosorbent has been thoroughly conducted. The overlapping and interconnection of the various stages of a process are stressed; so the conditions of the separation technique should be compatible with the other parts of the metal removal downstream, during continuous flow operation. A surfactant could be ideal for flotation, for instance, but in the meantime intervene in the next cycle of metal biosorption following desorption (Matis et al., 1996). In this publication, the influence of a filter aid, contained in the industrial biomass, as is often the case, on biosorption was also investigated and found not to interfere, although it did not contribute to metal removal either.

Accurate cost assessments generally are difficult to obtain for any treatment process owing to commercial confidentiality. This has also proved true for biosorption processes, which may be used for primary treatment or as secondary (polishing) treatment step. To some extent, the cost of wastewater treatment is site specific and therefore, it is unrealistic to compare two separate situations too rigorously. As far as the flowsheet configuration for the pilot-scale experiments is concerned, that of a two-stage countercurrent scheme was tested and then selected, having one leading and then one polishing biosorption reactor, with only one elution stage following in the end as a recycle loop (see Figure 4).

Figure 4 Flowsheet of the proposed (two-stage countercurrent) biosorptive flotation process (EU Environment and Climate program, contract no. ENV94-CT95-0068, with acronym Bioelecdetox)



The above was recorded in-detail by Matis et al. (2003) at pilot-scale work for fungal biomass with trade name Mycan applied to two different solutions (a lean and a strong one) of Cu, Ni and Zn in tap water and with grape stalks by Zouboulis et al. (2002); the latter is a winery by-product. Efforts to compare the two used biosorbents were also carried out. The elution of biomass, collected from the separation stage, was performed using a Nütsche vacuum filter. The eluted biomass was used for a second treatment cycle; when required to replace any biomass losses, new wet biomass was added. The desorption of metals from the floated biomass was carried out using a mixture of sodium sulphate (1 M) and sodium citrate (0.1 M).

Two known sorption parameters were calculated, from the pilot-plant results: (i) biosorbent capacity, q [$\mu\text{mol g}^{-1}$], and (ii) distribution coefficient, D [L g^{-1}]. The distribution coefficient is generally defined as the ratio of the amount of metal ion sorbed per gram of dry sorbent to its concentration in the outlet solution (Lehto and

Harjula, 1995). Biosorbent-loading capacity is defined here (i.e., there are similar parameters defined accordingly) as the number of equivalents of metal sorbed per gram of dry sorbent/ion exchanger material under actual conditions. IUPAC recommendations also defined a practical specific capacity as the total amount of ions taken up per gram.

For a biosorbent, the case becomes more complex owing to the various groups, on the material cell walls, available as possible sorption sites. Both parameters should be taken into account when an optimum exchanger is to be chosen for prospective application. When competitive ions are present, as in real waste streams, a selectivity separation factor (determined from the capacity) of the sorbents should be considered. For polishing of pretreated streams, targeted to as low an outlet concentration as practically achievable, sorbent materials with high D should be preferred over materials with large q .

Sorption is (by definition) a general term describing the attachment of charged species (like the toxic metal ions) from a solution to a coexisting solid surface. Sorption kinetics may be controlled by several independent processes that can act in series or in parallel; these fall in one of the following general categories:

- bulk diffusion
- external mass transfer (film diffusion)
- chemical reaction (chemisorption)
- intraparticle diffusion.

Kinetic analyses not only allow estimation of sorption rates but also lead to suitable rate expressions characteristic of possible reaction mechanisms (Tien, 1994; Yiacoumi and Tien, 1995; Xu and Schwartz, 1994).

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. Apart from that, it is quite common that more than one process can contribute in the system 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 rather simplifying approach to circumvent this problem is to assume that each one of the cocurrent processes dominates over the others (i.e., the rate controlling step) at specific time regimes of the process and then study them independently (Hill, 1977); this approach was also adopted in this paper.

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 primary objective of the present is to investigate the kinetic mechanism of metal sorption on sorbent particles, putting more emphasis on samples collected at short times after the initiation of the process, where the major part of the adsorption occurs.

In order to identify the most appropriate mechanism for a process, several models apparently must be checked for suitability and consistency in a broad range of the system parameters. The model selection criteria proposed by Ho et al. (2000) concerning sorption of pollutants in aqueous systems were used, as a general guideline. According to this, several reaction-based and diffusion-based models were tested in simulating our data. The finally chosen kinetic models are those that not only fit the data closely but also represent reasonable sorption mechanisms.

An overall mass balance of the sorbate across the sorbent surface can be written as:

$$Xq_t + C_t^s = C_o \text{ and } q_t = \frac{(C_o - C_t^s)}{X} \quad (1)$$

where q is the specific metal uptake (mg of metal per g of biosorbent), C is the metal bulk concentration (mg L⁻¹) and X is the sorbent feeding per unit volume of solution (g L⁻¹). 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. For adequately long adsorption times:

$$q_t \approx q_e \text{ and } C_t^s \approx C_e^s \approx C_e$$

where the subscript e denotes equilibrium conditions. Known adsorption models have been usually employed to describe the equilibrium metal uptake.

To compare measurements from various experiments for a kinetics investigation, it is often necessary to introduce a dimensionless degree of conversion. Thus, by normalising the remaining ion concentration, C_t , with respect to some reference value, an index of sorption is 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:

$$\alpha = \frac{C_o - C_t}{C_o - C_e} \quad (2)$$

Kinetic studies customarily utilise the basic conversion rate equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3)$$

where $f(\alpha)$ is a conversion-dependent function and $k(T)$ is the reaction rate constant. Sorption of heterogeneous liquid–solid systems has been usually accepted to follow Arrhenius kinetics, which means that the temperature dependence of the rate constant k may be described by the well-known expression:

$$k(T) = A \exp(-E / RT). \quad (4)$$

However, in order to apply the model in such systems, the morphology of the reactive surface as well as the final sorption capacity – conditions commonly overlooked by many workers – must not vary with temperature (Smith, 1981).

The used example for this investigation was the removal and depletion of divalent cadmium and chromates from aqueous solutions by biosorption on *Aeromonas caviae*. This microorganism is often present in groundwater and generally in aquatic environments. By adding small amounts of HNO₃ or NaOH solutions, the initial pH of the solution was adjusted to 7, i.e., far from the precipitation value as metal hydroxide, according to the cadmium aqueous speciation (Mineql+, 1994). It is noted that chromium oxyanions in solution, at their optimum sorption pH value (of 2.5), exist dominantly as CrO₄²⁻ and Cr₂O₇²⁻ species. As shown by electrokinetic measurements, most of the biosorbents exhibit negative surface charge (Matis and Zouboulis, 1994), hence they could easily adsorb metal cations unless their surface (cell wall) is modified by a suitable chemical pretreatment, i.e., using common surfactants. A possible

strategy for the removal of arsenates employing fungal biomass was reported by Loukidou et al. (2003).

3 Biosorption kinetics and modelling

First-order reaction kinetics were employed in many cases to describe biosorption, particularly of dyes (Mittal and Gupta, 1996; Waranusantigul et al., 2003; Gong et al., 2005). Volesky (1999) illustrated that adsorption is different from ion exchange. Surface precipitation was also investigated for the biosorption of metals against exchange adsorption elsewhere (Schneider et al., 2001). More than one sorption models were often reported to describe a case study correctly (Smith, 1996). Evidence is provided below that the examined system is a complex process. Attention should be paid to any possible experimental error.

Experimental adsorption isotherms of metal cations or oxyanions, obtained with different sorbent concentrations, temperatures, etc. are usually presented as figures and then, tables display the results of fitting the Langmuir and/or the Freundlich model to the obtained data; the values of the respective correlation coefficient (r^2), if high, are often used to demonstrate a satisfactory description. The assumptions involved in these models were well described, among others, by Volesky (1999). The Langmuir isotherms obtained during the equilibrium study lend further support to the notion of a monolayer. On the other hand, the Freundlich isotherm is heavily used in industry. This model is often accurate for higher concentration but inaccurate at lower concentrations, owing to its power law nature. The equilibrium properties do not change proportionally with the sorbent addition, possibly because of an aggregation of solids occurring at higher loads and hence the reducing of effective adsorption area (Esposito et al., 2001).

From the chemical reaction category (chemisorption), the best fit for the data sets of our study has been achieved by second order-type chemical reactions (Loukidou et al., 2004a). The solution of the standard second order reaction equation based on a constant stoichiometry of one metal ion per binding site, is (e.g., 3):

$$C_t = \frac{C_o}{1 - C_o/C_e \exp(-k_1 C_e t)} \quad (5)$$

where k_1 is the reaction rate constant [$L \times (\text{mg}^{-1} \text{ of metal}) \times \text{min}^{-1}$]. This adsorption model has been very effective in describing the kinetics of adsorption of gases on solids. Nevertheless, when the data were plotted as a figure, it was shown that equation (5) clearly failed to capture the steep concentration gradient of the early removal stage. This was a direct indication that adsorption on solids from a liquid phase is a process different from the adsorption from a gas phase where, traditionally, the remaining bulk concentration dictates the kinetics.

If the rate of sorption depends not on bulk concentration but on uptake by the sorbent, this can be described by the so-called Ritchie second order equation, according to which one metal ion occupies two binding sites (Ritchie, 1977). When in the aforementioned treatment it is not necessarily the equilibrium biosorbent capacity, q_e , that dictates the sorbate uptake, a pseudo second order rate expression, where a numerically determined parameter may be included, is more appropriate, (Ho, 1995); this under-ideal second order rate control corresponds to q_e . It is noted that in the literature, various other

kinetic equations – zero, first (forward or reversible) order, Langmuir-Hinshelwood, Elovich-type, etc. – have been attempted (Ho et al., 2000).

The latter equations provided quite a suitable description of data for advancing time (Loukidou et al., 2004a); the numerically best-fit values of the rate parameters of these equations were also displayed as a table. It is noteworthy that both models adequately capture the rapid rate of adsorption during the first minutes of the experiments. This already implies that the metal uptake by the biosorbent is a satisfactory rate-controlling parameter under a second order reaction mechanism. The predicted equilibrium sorption capacities were quite close to the experimental values for both models. Nevertheless, the rate constant of the pseudo second order model was monotonously correlated with changes in the biomass load and in the bulk concentration – features that have been encountered in the past, regarding biosorption (Cheung et al., 2001).

On the contrary, the rate constant of the Ritchie second order equation was found to fluctuate beyond any physical reasoning. In addition, this equation exhibited better fitting statistics. Despite the goodness of fit for sorption at 40°C and 60°C, the reaction rate constant of both models varied randomly with temperature. Preliminary calculations using the Arrhenius model, between two temperatures every time, gave activation energies always below 10 kJ/mol, which is far less than what is expected for reaction-controlled sorption processes. The morphological changes of the biomass surface at different temperatures and the dependence of sorption capacity on temperature may be blamed for this irregularity.

For intraparticle diffusion, Crank (1975) proposed a model, which takes into account the continuously decreasing bulk concentration owing to sorbate removal. This gives rise to a time-dependent boundary condition for the concentration at the surface of the sorbent particle. The solution of the diffusion equation for such a boundary condition and a concentration-independent diffusivity followed, and the equation was solved numerically to determine the effective diffusional time constant, ξ , which for the case of particle (also called micropore) diffusion control equals 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. The same expression is the solution of the diffusion equation for a (macro) pore diffusion control, but only in cases where the equilibrium isotherm is linear ($q_e \approx K \times C_e$) for the concentration range under investigation. Then, the constant, which equals to $(D_p/R_p^2)/[1+(1-\varepsilon_p)K/\varepsilon_p]$, where $\varepsilon_p D_p/[1+(1-\varepsilon_p)K]$, is the effective macropore diffusivity, K is the equilibrium constant, ε_p is the void volume fraction and R_p is the radius of the particle (Loukidou et al., 2004b).

Since the experimental procedure in this paper is based on measuring the remaining metal concentration in the bulk, the fraction of metal ultimately adsorbed by the biosorbent, Λ , is always above 0.5. For Λ 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 sorbent will lead to an erroneously high apparent diffusivity. Provided that the employed concentration step in a sorption experiment corresponds to a linear section of the equilibrium isotherm, the constant K can be replaced by the local slope of the isotherm, dq_e/dC_e . This is approximately valid for the concentrations employed in this work as can be seen from the experimental isotherms. Since our interest is chiefly focused in the short time region

($\sqrt{D_{c,p}t/R_{c,p}^2} < 0.2$) where the model for intraparticle diffusion converges slowly, at least 200 terms are used in the summation to achieve satisfactory accuracy.

External mass transfer has been customarily analysed in literature by adopting a pseudo first-order reaction model (Dzul Erosa et al., 2001). This approach tacitly assumes that the sorbate concentration at the biosorbent surface is zero at all times. However, 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 biosorbent surface, according to Puranik et al. (1999), and this concept has been also adopted by the authors.

If one combines the mass balance across the sorbent surface, equation (1), the Langmuir adsorption isotherm (if that is followed/accepted) and the rate equation of change in the bulk concentration, one ends up after some algebra with an appropriate expression for the external mass transfer, which by inserting dimensionless variables was converted to a system of two first-order ordinary differential equations that must be solved simultaneously, taking into consideration the initial conditions. It is noted that normalising C_t^s with respect to C_o^s – and not C_o as Puranik et al. (1999) did – and also t with respect to the total adsorption time improved markedly the stability and convergence characteristics of the solution owing to the comparable spreading of all variables over the computational domain. These were also solved numerically by Loukidou et al., (2004b) in order to determine respectively ζ and $K_m S$, the product of the external mass transfer coefficient (K_m , in m s^{-1}) by the specific surface of the biosorbent particles per unit volume of the reactor (S , in $\text{m}^2 \text{m}^{-3}$). The non-linear numerical regression to fit experimental data to those equations was performed by the Levenberg-Marquardt method, which gradually shifted the search for the minimum of the sum of the errors squared from steepest descent to quadratic minimisation, i.e., Gauss-Newton (Bates and Watts, 1988).

The fitting of equation of intraparticle diffusion was conducted to biosorption data obtained with different initial concentrations, solids loads and temperatures. It was apparent that despite some scatter in measurements, the finite volume diffusion model could describe fairly well the entire range of data, including also the steep concentration gradient at short times. The values of Λ , ζ and the computed values of D_c were also displayed as a table. Such behaviour has been customarily met as a consequence of the decreasing slope of a non-linear equilibrium curve, e.g., Langmuir isotherm, which causes the diffusivity to increase rapidly with increasing concentration (Smith, 1996).

A way to check further on the possibility of a pore diffusion-controlled mechanism was to perform desorption kinetic tests with adsorbent previously used for sorption. For the case of a non-porous biosorbent particle, transport of solute inside the particle may be neglected, and it can be assumed that biosorption occurs mainly at the particle surface. 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.

It was argued that at the beginning of the process, the metal ion was sorbed according to a quite fast and highly favourable chemical mechanism such as ion-exchange, but soon external film diffusion came into play (Loukidou et al., 2004b). On this account, if one ignores the very first minute of sorption, the remaining curves were fitted pretty well by the model. Near the end of biosorption (for α higher than 0.9), a much slower process, e.g., intraparticle diffusion, gradually became the rate-controlling step. Yet, this is a

regime of no practical significance. The mass transfer rate constant, $K_m S$, were computed.

As regards the effect of changing the solids load, it appears that $K_m S$ is virtually not affected. To assess the statistical significance of the determination, a derivative time series analysis where da/dt is plotted against t has been performed and then, a Hanning low pass filter has been applied to flatten out the signal undulations until da/dt vs. α becomes a reasonably smooth curve (Bendar and Piersol, 1986). Next, the integrated smoothed signal $\alpha(t)$ has been processed as before and has resulted in $K_m S$ values closely comparable to the values obtained from the unfiltered data, 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 biosorption process after the initial fast metal removal.

4 Concluding remarks

In the paper, asking in its title 'why select a biological process' and trying to explain the disappointing lack of application of this science to technology, Eccles (1999) stated that a small number of pilot-plant studies have been carried out to investigate the potential of microorganisms to remove metals from liquid wastes. It is believed from the aforementioned that our laboratory (with initials LGICT) has contributed in this aspect, among others. Another advantage of the proposed process is that its basic unit processes are rather conventional and widely applied in the field. The application of the various units may be novel, but the underlying methodology is familiar. For instance, adsorption and ion exchange are already established processes in water and wastewater treatment.

As a conclusion in the kinetics example thoroughly studied, we may say that the conducted analysis has been rather not capable of providing strong evidence in favour of any of the examined mechanisms, since several diverse kinetic models were successful in fitting the experimental data. These are a Ritchie 2nd order chemical reaction and a finite volume diffusion, which just by themselves, may effectively describe the largest part of the process. Alternatively, an external surface enhancement dominates the very beginning of the process and is followed by external film diffusion. One is tempted to argue that sorption may be more correctly described by more than one models, as is often the case with the sorption of metal ions. Perhaps, the questioning on surface kinetics of Levenspiel (1999) is also known, concluding that it is good enough to use the simplest available correlating rate expression.

The adsorption rate of cadmium cations and chromium(VI) oxyanions onto the biosorbent 'particles' was particularly sensitive to initial bulk concentration, biomass load and ionic strength of the aqueous solution (effluent). The abnormal temperature dependence of biosorption rate was attributed to the alterations of the surface morphology of biomass particles, as shown by SEM.

It is stressed that biosorptive treatments need not necessarily replace existing methodologies but may act as polishing systems to processes, which are not completely efficient, by complementing them. It is a reality that large producers and users of chemicals prefer to use processes and technologies that are robust and well understood over those that are newer, even when those newer technologies offer better economics and/or are more environmentally friendly. Therefore, the demonstration of commercial feasibility is essential to overcome a natural reluctance to use that new technology.

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References

- Bates, D.M. and Watts, D.G. (1988) *Nonlinear Regression Analysis and its Applications*, Wiley, New York.
- Bendar, J.S. and Piersol, A.G. (1986) *Random Data: Analysis and Measurement Procedures*, Wiley, New York.
- Blöcher, C., Dorda, J., Mavrov, V., Chmiel, H., Lazaridis, N.K. and Matis, K.A. (2003) 'Hybrid flotation-membrane filtration process for the removal of heavy metal ions from wastewater', *Wat. Res.*, Vol. 37, pp.4018–4026.
- Butter, T.J., Evison, L.M., Hancock, I.C., Holland, F.S., Matis, K.A., Philipson, A., Sheikh, A.I. and Zouboulis, A.I. (1998) 'The removal and recovery of cadmium from dilute aqueous solutions by biosorption and electrolysis at laboratory scale', *Wat. Res.*, Vol. 32, pp.400–406.
- Cheung, C.W., Porter, J.F. and McKay, G. (2001) 'Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char', *Wat. Res.*, Vol. 35, pp.605–612.
- Crank, J. (1975) *Mathematics of Diffusion*, Oxford University Press, London.
- Dzul Erosa, M.S., Saucedo, T.I., Navarro Mendoza, R., Avila Rodriguez, M. and Guibal, E. (2001) 'Cadmium sorption on chitosan sorbents: kinetic and equilibrium studies', *Hydrometallurgy*, Vol. 61, pp.157–167.
- Eccles, H. (1999) 'Treatment of metal contaminated wastes: why select a biological process?', *TIBTECH*, Vol. 17, pp.462–465.
- Esposito, A., Pagnanelli, F., Lodi, A., Solisio, C. and Vegliò, F. (2001) 'Biosorption of heavy metals by *Sphaerotilus natans*: an equilibrium study at different pH and biomass concentration', *Hydrometallurgy*, Vol. 60, pp.129–141.
- European Union (2004) *Energy, Environment and Sustainable Development Project (with acronym METASEP)*, Public Report, Contract No. EVK1-CT-2000-00083, Brussels, p.50.
- Evanko, C. and Dzombak, D. (1997) 'Remediation of metals-contaminated soils and groundwater', *Ground-Water Remediation Technologies Analysis Center*, TE-97-01, Pittsburgh.
- Feng, D. and Aldrich, C. (2004) 'Adsorption of heavy metals by biomaterials derived from the marine alga *Ecklonia maxima*', *Hydrometallurgy*, Vol. 73, pp.1–10.
- Gardea-Torresdey, J.L., Gonzalez, J.H., Tiemann, K.J., Rodriguez, O. and Gamez, G. (1998) 'Phytofiltration of hazardous cadmium, chromium, lead and zinc ions by biomass of *Medicago sativa* (alfalfa)', *J. Hazardous Mater.*, Vol. 57, pp.29–39.
- Gong, R., Ding, Y., Yang, C., Liu, H. and Sun, Y. (2005) 'Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution', *Dyes Pigments*, Vol. 64, pp.187–192.
- Hill, C.G. (1977) *An Introduction to Chemical Engineering Kinetics and Reactor Design*, Wiley, New York, pp.24–166.
- Ho, Y.S. (1995) *Adsorption of Heavy Metals From Waste Streams by Peat*, Chem. Eng. Dept., Univ. Birmingham, UK.
- Ho, Y.S., Chiu, W.T., Hsu, C.S. and Huang, C.T. (2004) 'Sorption of lead ions from aqueous solution using tree fern as a sorbent', *Hydrometallurgy*, Vol. 73, pp.55–61.
- Ho, Y.S., Ng, J.C.Y. and McKay, G. (2000) 'Kinetics of pollutant sorption by biosorbents: review', *Sep. Purific. Methods*, Vol. 29, pp.189–232.

- Kefala, M.I., Zouboulis, A.I. and Matis, K.A. (1999) 'Biosorption of cadmium ions by *Actinomyces* and separation by flotation', *Envir Pollution*, Vol. 104, pp.283–293.
- Lehmann, M., Zouboulis, A.I. and Matis, K.A. (2001) 'Modelling the sorption of metals from aqueous solutions on goethite fixed-beds', *Envir. Pollution*, Vol. 113, pp.121–128.
- Lehto, J. and Harjula, R. (1995) 'Experimentation in ion exchange studies – the problem of getting reliable and comparable results', *Reactive Functional Polymers*, Vol. 27, pp.121–146.
- Levenspiel, O. (1999) *Chemical Reaction Engineering*, 3rd ed., Wiley, New York, pp.380, 381.
- Loukidou, M.X., Karapantsios, Th.D., Zouboulis, A.I. and Matis, K.A. (2004b) (i) 'Equilibrium and kinetic modeling of chromium(VI) biosorption by *Aeromonas caviae*', *Coll. Surf. Vol. A* 242, pp.93–104; (ii) 'Cadmium(II) biosorption by *Aeromonas caviae*: kinetic modelling', *Sep. Sci. Tech.*, Vol. 40, pp.1293–1311.
- Loukidou, M.X., Karapantsios, Th.D., Zouboulis, A.I. and Matis, K.A. (2004a) (i) 'Diffusion kinetic study of chromium(VI) biosorption by *Aeromonas caviae*', *Ind. Eng. Chem. Res.*, Vol. 43, pp.1748–1755; (ii) 'Diffusion kinetic study of cadmium(II) biosorption by *Aeromonas caviae*', *J. Chem. Tech. Biotech.*, Vol. 79, pp.711–719.
- Loukidou, M.X., Matis, K.A., Zouboulis, A.I. and Liakopoulou-Kyriakidou, M. (2003) 'Removal of As(V) from wastewaters by chemically modified fungal biomass', *Wat. Res.*, Vol. 37, pp.4544–4552.
- Matis, K.A. and Zouboulis, A.I. (1994) 'Flotation of cadmium-loaded biomass', *Biotech. Bioengg.*, Vol. 44, pp.354–360.
- Matis, K.A., Zouboulis, A.I. and Hancock, I.C. (1994) 'Waste microbial biomass for cadmium ion removal: application of flotation for downstream separation', *Bioresource Tech.*, Vol. 49, pp.253–259.
- Matis, K.A., Zouboulis, A.I. and Lazaridis, N.K. (2003) 'Heavy metals removal by biosorption and flotation', *Water, Air, and Soil Pollution: Focus*, Vol. 3, pp.143–151.
- Matis, K.A., Zouboulis, A.I., Grigoriadou, A.A., Lazaridis, N.K. and Ekateriniadou, L.V. (1996) 'Metal biosorption – flotation. Application to cadmium removal', *Appl. Microbiol. Biotechnol.*, Vol. 45, pp.569–573.
- Mavrov, V., Erwe, T., Blöcher, C. and Chmiel, H. (2003) 'Study of integrated processes combining adsorption, membrane separation and flotation for heavy metal removal from wastewater', *Desalination*, Vol. 157, pp.97–104.
- Mineql+ (1994) *Software Package Version 3.04a*, Environmental Research Software, Hallowell, USA.
- Mittal, A.K. and Gupta, S.K. (1996) 'Biosorption of cationic dyes by dead macro fungus *fomitopsis carnea*: batch studies', *Wat. Sci. Tech.*, Vol. 34, No. 10, pp.81–87.
- Pagnanelli, F., Vegliò, F. and Toro, L. (2004) 'Modelling of the acid-base properties of natural and synthetic adsorbent materials used for heavy metal removal from aqueous solutions', *Chemosphere*, Vol. 54, pp.905–915.
- Peleka, E.N., Matis, K.A., Erwe, T., Mavrov, V. (2005) 'Bonding of toxic metal ions in industrial water supply, in domestic, municipal and industrial water supply and waste disposal', Lehr, J.H. (ed.): *The Encyclopedia of Water*, Wiley, USA, Vol. 1, pp.586–591.
- Psareva, T.S., Zakutevskyy, O.I., Chubar, N.I., Strelko, V.V., Shaposhnikova, T.O., Carvalho, J.R. and Neiva Correia, M.J. (2004) 'Uranium sorption on cork biomass', *Coll. Surf. Vol. A* 252, pp.231–236.
- Puranik, P.R., Modak, J.M. and Paknikar, K.M. (1999) 'A comparative study of the mass transfer kinetics of metal biosorption by microbial biomass', *Hydrometallurgy*, Vol. 52, pp.189–197.
- Ritchie, A.G. (1977) 'Alternative to the Elovich equation for the kinetics of adsorption of gases on solids', *J. Chem. Soc.-Farad. Trans.*, Vol. 73, pp.1650–1653.
- Schneider, I.A.H., Rubio, J. and Smith, R.W. (2001) 'Biosorption of metals onto plant biomass: exchange adsorption or surface precipitation?', *Int. J. Min. Process*, Vol. 62, pp.111–120.

- Smith, E.H. (1996) 'Uptake of heavy metals in batch systems by a recycled iron-bearing material', *Wat. Res.*, Vol. 30, pp.2424–2434.
- Smith, J.M. (1981) *Chemical Engineering Kinetics*, 3rd ed., McGraw-Hill, Singapore, pp.37–92, 636–645.
- Tien, C. (1994) *Adsorption Calculations and Modelling*, Butterworth-Heinemann, Boston.
- Volesky, B. (1999) *Biosorption of Heavy Metals*, Chapter 6, CRC Press, Boca Raton, Florida, see also the respective site: <http://www.biosorption.mcgill.ca/>.
- Volesky, B. (2001) 'Detoxification of metal-bearing effluents: biosorption for the next century', *Hydrometallurgy*, Vol. 59, pp.203–216.
- Waranusantigul, P., Pokethitiyook, P., Kruatrachue, M. and Upatham, E.S. (2003) 'Kinetics of basic dye (methylene blue) biosorption by giant duckweed (*Spyrodela polyrrhiza*)', *Envir. Pollution*, Vol. 125, pp.385–392.
- Xu, Y. and Schwartz, F.W. (1994) 'Sorption of Zn^{2+} and Cd^{2+} on hydroxyapatite surfaces', *Environ. Sci. Technol.*, Vol. 28, pp.1472–1480.
- Yiacoumi, S. and Tien, C. (1995) *Kinetics of Metal Ion Adsorption from Aqueous Solutions*, Kluwer Academic, Boston.
- Zouboulis, A.I., Lazaridis, N.K. and Matis, K.A. (2002) Removal of toxic metal ions from aqueous systems by biosorptive flotation, *J. Chem. Tech. Biotechnol.*, Vol. 77, pp.958–964.
- Zouboulis, A.I., Loukidou, M.X. and Matis, K.A. (2004) 'Biosorption of toxic metals from aqueous solutions by bacteria strains isolated from metal-polluted soils', *Process Biochem.*, Vol. 39, pp.909–916.
- Zouboulis, A.I., Matis, K.A. and Hancock, I.C. (1997) 'Biosorption of metals from dilute aqueous solutions', *Sep. Purif. Methods*, Vol. 26, pp.255–295.
- Zouboulis, A.I., Matis, K.A., Loukidou, M.X. and Šebesta, F. (2003) 'Metal biosorption by PAN-immobilised fungal biomass in simulated wastewaters', *Coll. Surf. A*, Vol. 212, pp.185–195.
- Zouboulis, A.I., Matis, K.A., Rousou, E.G. and Kyriakidis, D.A. (2001) 'Biosorptive flotation for metal ions recovery', *Wat. Sci. Tech.*, Vol. 43, No. 8, pp.123–129.
- Zouboulis, A.I., Rousou, E.G., Matis, K.A. and Hancock, I.C. (1999) 'Removal of toxic metals from aqueous mixtures: Part 1. Biosorption', *J. Chem. Tech. Biotechnol.*, Vol. 74, pp.429–436.