

Web Working Papers
by

The Italian Group of Environmental Statistics



Gruppo di Ricerca per le Applicazione della Statistica
ai Problemi Ambientali

www.graspa.org

Statistical Sensitivity Analysis of heavy metal biofilter
models

A. Fassò, A. Esposito, E. Porcu, A.P. Reverberi, F. Vegliò

GRASPA Working paper n.14, December 2002, reprint June 2005

Statistical Sensitivity Analysis of heavy metal biofilter models

A. Fassò^{*†}, A. Esposito[‡], E. Porcu[§], A.P. Reverberi³, F. Vegliò³

June 8, 2005

Abstract

In this paper we consider the statistical sensitivity analysis of the heavy metals biosorption from contaminated wastewater packed column reactors.

In particular the model considered to describe the biosorption phenomenon is the Advection Dispersion Reaction equation under concepts of rapid local equilibrium. This allows computer simulation with random input parameters chosen from appropriate probability distribution.

In order to have a statistical framework for analysing the simulated data and assessing input importance, we introduce heteroskedastic and multivariate sensitivity analysis, which extends standard sensitivity analysis. We then apply the method to simulated data and draw conclusions on the fixed packed reactor efficiency.

Keywords: Multivariate SA, Heteroskedastic SA, Heavy Metals Biosorption

1 Introduction

Heavy metals are toxic pollutants released into the environment by industrial, mining and agricultural activities. Due to non-biodegradability of these

^{*}Dept. of Engineering, University of Bergamo, Italy. (email: fasso@unibg.it).

[†]Work partially supported by italian MURST-2000 grant.

[‡]Dept. of Chemical and Process Engineering "G.B. Bonino", University of Genova, Italy, via Opera Pia, 15, 16145 Genova, (email: veglio@unige.it) and veglio@ing.univar.it

[§]Dept. of Quantitative Methods, University Milano Bicocca, Italy. (email: emilio.porcu@unimib.it).

pollutants, environmental risk increases as accumulation and concentration take place.

The main treatments used to remove heavy metals from waste waters are precipitation, ion exchange and reverse osmosis. The application of such processes is often limited because of technical and/or economic constraints. For example, precipitation, which is used as preliminary process, can not guarantee the metal concentration limits required by regulatory standards. Moreover, it produces wastes which are difficult to be disposed. On the other hand ion exchange and adsorption processes are very effective but need expensive adsorbent materials and difficult plant management (Volesky, 2001).

There are two main reasons inducing to consider biosorption for wastewater treatment. The former is represented by the good performance in metal removal, often comparable with reverse osmosis. The latter is given by low costs and availability in nature of adsorbent bio-material (Volesky, 2001).

Because of this, in the last ten years, many researchers have studied the biosorption phenomenon analyzing different aspects: equilibrium studies with free microorganisms (Vegliò et al., 1997b; Pagnanelli et al., 2000; Esposito et al., 2001; Sag et al., 2000a, 2001a), microorganisms in packed columns (Kratochvil et al., 1997, 2000; Sag et al., 2001b), single and multicomponent systems (Sag et al., 2001a; Kratochvil et al., 2000; Pagnanelli et al., in press), kinetic studies (Vegliò et al., 1998; Vegliò et al., 1997c; Sag et al., 2000b) and biosorption of heavy metals in membrane reactor systems (Beolchini et al., 2001). A recent review of very wide biosorption literature can be found in Vegliò et al., 1997a, Volesky, 2001, Kratochvil et al., 1998b.

One aspect to be considered with natural or artificial immobilized biomass is the behavior in fixed bed reactor systems: mathematical modelling for a fixed bed has been generated mainly from research on activated carbon sorption, ion exchange or chromatography applications (Hatzikioseyan et al., 1999, 2001).

Despite to an exhaustive literature regarding mathematical modelling of fixed bed reactors (see e.g. Kratochvil et al., 2001, and references therein), only few authors used SA, which could be more effective to evaluate the impact of the main process parameters to this kind of reactors. Originally, SA has been carried out changing "one factor at time" (OAT). The papers of Hatzikioseyan et al. (1999, 2001) show that SA results are important and consistent with the physical meaning of the biosorption process. Nevertheless as it will be clear from section 3, important lack of information is possible if nonlinearities or significant interaction effects are present among the investigated input parameters.

In this work, we use variance-based Monte Carlo SA which allows to account for interaction and nonlinearities, see e.g. Fassò and Perri (2001)

or Saltelli et al. (2000). In particular, in section 3, after recalling the main rationale of Monte Carlo standard *SA*, we propose a new extension of *SA* to cope with multivariate and heteroskedastic models. Then, in section 4, *SA* is applied to assess the influence of main fixed bed reactor parameters on the heavy metal biosorption performance from two different perspectives.

In the first case, using a so-called "Global *SA*", a wide process parameters variation range is considered. In this manner it is possible to establish guideline criteria for preliminary design of fixed bed reactor or packed columns. For example, this approach may give useful information about the nature of the biosorbent (adsorption capacity, biosorbent density), the column packaging arrangement (void degree) or operating conditions (volumetric flow rate).

In the second case, small variations around a known central value of these parameters are considered. This allows to define which parameters require high measurement accuracy through experimental work. This second approach is called here "Local *SA*".

2 Biosorption in Packed Column Reactor

2.1 Hypothesis and model formulation

In the present work the model considered to describe the biosorption phenomenon in the fixed bed reactor is the Advection Dispersion Reaction (ADR) equation under concepts of rapid local equilibrium. This approach is very common in chromatography and ion exchange applications (Hatzikioseyan et al., 1999, 2001). It also permits to describe the heavy metal removal considering the main operative aspects of the system such as biosorbent characteristics, column package arrangement and geometrical dimension of the column.

The theoretical details on simulating fixed bed reactors in biosorption studies have been analyzed by Hatzikioseyan et al., (1999, 2001) and Kratochvil et al. (2001). This approach is based on the mathematical solution of the material balance equations in the liquid phase coupled with the equilibrium information for the solute biosorbed by the solid phase. This equation, simplified in one dimensional form for a single solute, is reported in following partial differential equation (*PDE*):

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} - \rho_s \frac{1 - \varepsilon}{\varepsilon} \frac{\partial q}{\partial t} \quad (1)$$

where z is the axial coordinate in the column (m), t is time, C is the heavy

metal concentration (mg/L), D_a is the axial dispersion coefficient (m^2/s), u is the flow velocity (m/s), ρ_s is the sorbent density (kg/m^3), ϵ is the void degree, and q is the heavy metal concentration in the sorbent (mg/g).

The right hand side of this equation incorporates the diffusive, bulk solute movement and the sorption process respectively. The solution of equation (1) describes the performance and the process dynamics of a sorption packed column.

The most important term of the solute material balance is the rate of the solute uptake in the solid phase as described by the term $\frac{\partial q}{\partial t}$. A simple approach for the model sorption phenomenon is to assume that mass transfer resistance in the liquid and solid phase are negligible and the biosorption reaction is instantaneous. This gives a local equilibrium between the liquid and solid phase in each section of the column.

The most common relationship used to describe the biosorption equilibrium term is the following Langmuir equation:

$$q = \frac{q_{\max}C}{\frac{1}{b} + C} \quad (2)$$

where q and C are the equilibrium solute concentrations in the solid (mg/g) and liquid (mg/L) phase respectively, q_{\max} (mg/g) and b (L/mg) are parameters to be estimated by equilibrium experimental tests (Esposito et al., 2001).

Using dimensionless variables, the following equation (3) is reported together with appropriate boundary and initial conditions:

$$\left\{ \begin{array}{l} \frac{\partial C'}{\partial t'} = \frac{1}{Pe \left(1 + K \frac{K_{ads}}{(K_{ads} + C')^2}\right)} \frac{\partial^2 C'}{\partial z'^2} - \frac{1}{\epsilon \left(1 + K \frac{K_{ads}}{(K_{ads} + C')^2}\right)} \frac{\partial C'}{\partial z'} \\ t' = 0 \xrightarrow{0 < z' < 1} C' = 0 \\ z' = 0 \xrightarrow{\forall t'} C' = 1 \\ z' = 1 \xrightarrow{\forall t'} \frac{\partial C'}{\partial z'} = 1 \end{array} \right. \quad (3)$$

where $K = \frac{\rho_s(1-\epsilon)q_{\max}}{C_0\epsilon}$, $K_{ads} = \frac{1}{bC_0}$, $Pe = \frac{u_0L}{D_h}$, $C' = \frac{C}{C_0}$, $Z' = \frac{Z}{L}$, $t' = \frac{tu_0}{L}$, L is the column length, $u = \frac{u_0}{\epsilon}$ and u_0 is the specific bed velocity.

In the operative range conditions analyzed here, the axial dispersion coefficient (D_a) can be expressed as (Hatzikioseyan et al., 1999):

$$D_a = \frac{\mu_L}{\rho_L} \frac{N^0}{0.20 + 0.011 (N^0)^{0.48}} \quad (4)$$

where $N^0 = d_p u_0 \frac{\rho_L}{\mu_L}$, μ_L is the fluid viscosity ($kg/m \times s$), ρ_L is the liquid density (kg/m^3) and d_p is the adsorption particle diameter (mm).

2.2 Efficiency assessment

The outputs considered to assess the performance of the fixed bed column were the breakthrough time (t_b^*) and the length of unused bed (LUB^*) (Hatzikioseyan et al., 1999). The quantity t_b^* is the column working time over which it is necessary to regenerate the fixed bed. In our setup t_b^* is defined as the time over which the outlet metal concentration exceeds 5% of the inlet concentration C_0 .

The length LUB , representing the column efficiency with respect to the ideal conditions (Plug Flow Reactor), is evaluated as reported in the following equation

$$LUB^* = \left(1 - \frac{t_1}{t_2}\right) L$$

where

$$t_1 = \int_0^{t_b^*} \left(1 - \frac{C_{outlet}}{C_0}\right) dt$$

and

$$t_2 = \int_0^{\infty} \left(1 - \frac{C_{outlet}}{C_0}\right) dt.$$

In the following sections we will use the dimensionless quantities given by $LUB = \frac{LUB^*}{L}$ and $t_b = \frac{t_b^* u_0}{L}$. Further details of these outputs may be found in Hatzikioseyan et al. (1999).

2.3 Numerical solution of the partial differential equation

The numerical solution of *PDE* given by equation (3) has been obtained by using a Fortran routine denominated PDECOL (Transaction of mathematical software, 1992). PDECOL is the driver routine for a sophisticated package designed to solve the general system of nonlinear *PDE* of at most second order on the established time and length intervals.

3 Statistical Models and Sensitivity Analysis

Generally speaking, sensitivity analysis (SA) is concerned with the mathematical model representation of a physical system and attempts to assess the sensitivity of the model output to variations of model inputs given by variables or parameters and variations of model assumptions. We then have a function

$$y = f(x_1, \dots, x_k) = f(\mathbf{x})$$

relating the k -dimensional parameter vector $\mathbf{x} = (x_1, \dots, x_k)'$ to the model output y . The function f is not known in closed form but, as long as model assumptions are valid, it is computable, through computer runs, for every \mathbf{x} in an appropriate range, say \mathbf{D} . For example, the packed column setup we are going to consider in section 4 below, is $\mathbf{x} = (\mu_L, \rho_L, u_0, \varepsilon, d_p, \rho_S, q_{\max}, b)'$ and $y = t_b$ or LUB .

3.1 One-factor-at-time SA

Sometimes we are interested in small variations around a known central value \mathbf{x}_0 . The simplest and often simplistic approach to this problem is the so-called one-factor-at-time SA or OAT, where we use a first order expansion around the base case \mathbf{x}_0 :

$$f(\mathbf{x}_0 + \Delta) \cong f(\mathbf{x}_0) + \sum_{i=1}^k \frac{\partial f(\mathbf{x}_0)}{\partial x_i} \Delta_i. \quad (5)$$

For example, in chemical kinetics SA literature (Turanyi and Rabitz, 2000), $\frac{\partial f}{\partial x_i}$ is called first order local sensitivity and the OAT approach, using only $k + 1$ runs, may be used to get the finite difference approximation to first order local sensitivity, i.e.

$$\frac{\partial f}{\partial x_i} \cong \frac{y(x_{0,i} + \Delta_i) - y(x_{0,i})}{\Delta_i},$$

for small perturbations Δ_i . This approach is cheap in computing time but it heavily relies on the linearity assumption and the $k + 1$ data collected cannot give much information on the validity of this assumption.

The next step is based on repeated OAT which considers n replicates of x_i with the other coordinates, x_j with $j \neq i$, fixed at the base case value $x_{0,j}$. We then compute importance measures based on output uncertainty due to x_i uncertainty, *ceteris paribus*. For example, we can use this data to compute variance ratios

$$\frac{S(y(x_i))^2}{S(x_i)^2}$$

where $S(x_i)^2 = \frac{1}{n-1} \sum_{j=1}^n (x_{ji} - \bar{x}_i)^2$ is the variance of the n replicates of x_i and, similarly, $S(y(x_i))^2$ is the sample variance of simulated y 's due to x_i variation.

Then using nk runs, OAT statistics allow parameter ranking according to their importance but cannot be used to assess interactions among inputs. Moreover all these results are local in the sense that they use the base case as reference, and changing it may cause a change to conclusions.

3.2 Monte Carlo SA

The discussion of this and the following sections suppose that extensive data $\mathbf{z}_i = (y_i, \mathbf{x}_i)$ are available from f by simulating the packed column reactor, for example via fast numerical integration of the biofilter PDE of section 2. Using these data and some statistical approach, for example the least squares (LS) method, it is possible to get a simplified version \hat{f} of f such that

$$y = \hat{f}(\mathbf{x}) + e.$$

As long as the computer model f is a good representation of the physical system and the error e is small in some sense, the statistical model \hat{f} can be used for insight into the system dynamics and in particular for quantitative SA, i.e. the numeric assessment of the influence or importance of the various parameters to the system output. A standard assumption on e is that it behaves like an error having the Gaussian distribution and being independent on \mathbf{x} .

Recent accounts of SA are given in Fassò and Perri (2001) and Saltelli et al. (2000). According to these, modern SA is essentially based on some kind of variance decomposition. These variance methods are useful when one is interested in SA of f on a range of values and not only around one fixed value \mathbf{x}_0 . In the former case it is often useful to suppose that the input \mathbf{x} varies according to some known distribution $p(\mathbf{x})$. Two common examples are independent rectangular and Gaussian correlated random variables.

Some variance SA methods are model-free and/or nonparametric in that they do not try to fully model f and are mainly aimed to estimate importance or sensitivity measures. Here we prefer parametric SA giving a model $\hat{f}(\mathbf{x}; \boldsymbol{\beta})$, which depends on the unknown parameter vector $\boldsymbol{\beta}$ and can be used for interpreting the real system and computing importance measures.

The Monte Carlo method used in the sequel is based on random selection or sampling from the distribution $p(\mathbf{x})$. In practice this is easily done using random number generators available in many software packages. Some remarks may be useful for generating multivariate normal variates \mathbf{x} with specified covariance matrix $\boldsymbol{\Sigma}$ and expectation vector $\boldsymbol{\eta}$. In this case, using modern matrix oriented mathematical and statistical packages, it is often easier to start generating a vector $\boldsymbol{\xi}$ of independent standard normal variates with zero mean and unit variance. Then the simulation of the correlated \mathbf{x} is given by

$$\mathbf{x} = \boldsymbol{\eta} + \boldsymbol{\Sigma}^{1/2} \boldsymbol{\xi}$$

where $\boldsymbol{\Sigma}^{1/2}$ is an appropriate matrix, e.g. the Cholesky decomposition of $\boldsymbol{\Sigma}$, such that $\boldsymbol{\Sigma} = \boldsymbol{\Sigma}^{1/2} (\boldsymbol{\Sigma}^{1/2})'$ and the prime denotes matrix transposition.

Sometimes it may be useful to have inputs which are incorrelated not only at the level of the parent distribution $p(\mathbf{x})$ but incorrelation or orthogonality is required for the particular Monte Carlo sample at hand. To do this we use the linear transform

$$\mathbf{x}_i = \hat{\Sigma}^{-1/2} \boldsymbol{\xi}_i \quad (6)$$

where $\hat{\Sigma}$ is the sample covariance matrix of the simulated $\boldsymbol{\xi}_1, \dots, \boldsymbol{\xi}_n$, which gives incorrelated inputs to the simulation model. We may then run the computer model on orthogonal inputs to get $y_1 = f(\mathbf{x}_1), \dots, y_n = f(\mathbf{x}_n)$.

In order to use a linear regression, we use a post-simulation input transform $\mathbf{u} = u(\mathbf{x})$ which may encompass orthogonal polynomial nonlinearities and interactions and then we fit the standard linear model \hat{f} given by

$$\tilde{y} = \boldsymbol{\beta}' \tilde{\mathbf{u}} + e = \sum_j \beta_j \tilde{u}_j + e \quad (7)$$

to the simulated zero mean deviates $\tilde{y} = y - \bar{y}$, and $\tilde{u} = u - \bar{u}$. In the sequel the tilde will be omitted for notational simplicity.

When the components u_j are incorrelated, the output variance σ_y^2 can be decomposed as

$$\sigma_y^2 = \sum_j \beta_j^2 \sigma_{u_j}^2 + \sigma_e^2. \quad (8)$$

and using the LS estimate $\hat{\beta}_j$ a similar decomposition holds for sample variances $S_y^2, S_{u_j}^2$ and S_e^2 computed with the same denominator e.g. $\frac{1}{n-1}$. This decomposition holds exactly if we use orthogonal inputs given by (6), otherwise it holds for large samples under parent distribution incorrelation. It follows that the *importance measure* or *sensitivity index* given by

$$SI_j = \hat{\beta}_j^2 \frac{S_{u_j}^2}{S_y^2}$$

can be used to assess the influence of the j^{th} input to the model output.

In fact these indexes sum to the total variance percentage explained by the model, i.e.

$$\sum_j SI_j = \mathbf{R}^2 = 1 - \frac{S_e^2}{S_y^2}$$

where \mathbf{R}^2 is the well known multiple determination coefficient and the parameters can be ranked accordingly.

Some remarks are useful for contrasting regression analysis in simulation models and in the standard statistical model. Whenever the setup is rather similar, in the latter y is a random variable even when the particular \mathbf{x} used

is known. In the former, after fixing the parameters nothing is random and replications give the same output value. Hence, if the model \hat{f} were of the same form of f , then, after having enough data, one could get the true f by interpolation. This means that if f is approximately linear, then partial correlation coefficients are very near to one in absolute value. Moreover standard t and F tests loose standard sampling theory interpretation and p-values have to be interpreted with caution.

We than conclude that the error e , conditionally on \mathbf{x} , is not random and $e = e(\mathbf{x})$. Nevertheless, in some cases it may happen that statistics based on $e(\mathbf{x}_i)$ and \mathbf{x}_i in large samples behaves like those coming from independent random variables. This means that for general transforms $s(e)$ and $t(\mathbf{x})$ we have

$$\frac{1}{n} \sum s(e(\mathbf{x}_i)) t(\mathbf{x}_i) \cong E[s(e(\mathbf{x}))] E[t(\mathbf{x})]$$

where E is the expected value and the approximation holds in the sense of a standard stochastic convergence. As a particular case, in the linear LS model it is well known that $\frac{1}{n} \sum e(\mathbf{x}_i) \mathbf{x}_i = 0$ and in the nonlinear LS model this holds only for large samples. Graphical analysis may help in practice for evaluating these assumptions. For example, Figure 1 below shows that $e(\mathbf{x})^2$ is almost incorrelated with ε but strongly correlated with ρ_S and q_{\max} .

3.3 Multivariate SA

In this section we extend the previously introduced *SA* concepts to the multivariate regression model. For the sake of simplicity we consider only the bivariate case, which is the case study of next section. Of course this approach readily extend to a generic multivariate model.

Now the model output $y = (LUB, t_b)'$ is bidimensional and f is a vector-valued function. In this case we have the following matrix notation for the multivariate regression model

$$\begin{pmatrix} y_1 \\ y_2 \end{pmatrix} = \begin{pmatrix} \beta'_1 \\ \beta'_2 \end{pmatrix} \mathbf{u} + \begin{pmatrix} e_1 \\ e_2 \end{pmatrix} = \mathbf{B}\mathbf{u} + \mathbf{e} \quad (9)$$

and the multivariate LS method (see e.g. Rencher, 1995) simply gives

$$\hat{\mathbf{B}} = \begin{pmatrix} \hat{\beta}(y_1) \\ \hat{\beta}(y_2) \end{pmatrix}$$

where $\hat{\beta}(y_1)$ is the ordinary LS estimate for the first equation of (9) considered alone as in the previous section.

SA can now be applied to the variance-covariance matrix extending the variance decomposition (8). Using covariance matrices and matrix notation we get

$$\mathbf{S}_y = \mathbf{B}\mathbf{S}_u\mathbf{B}' + \mathbf{S}_e.$$

In order to get scalar valued indexes some metric for matrices is required. Various options are available, for example trace or determinant or the approach based on likelihood decomposition which combines both.

Here, for the sake of simplicity, we use the trace metric which retains additivity. We then have

$$\begin{aligned} \text{tr}(S_y) &= S_{y_1}^2 + S_{y_2}^2 \\ &= \sum_j SI_j(y_1) S_{y_1}^2 + \sum_j SI_j(y_2) S_{y_2}^2 + S_{e_1}^2 + S_{e_2}^2 \end{aligned}$$

and the natural multivariate sensitivity index for j^{th} input is the simple or the weighted average, i.e.

$$SI_j(y) = \frac{SI_j(y_1) + SI_j(y_2)}{2} \quad (10)$$

$$SI_j(y) = \frac{SI_j(y_1) S_{y_1}^2 + SI_j(y_2) S_{y_2}^2}{S_{y_1}^2 + S_{y_2}^2} \quad (11)$$

respectively. The first formula is appropriate for scale invariant SA and is the same as the second one if we use standardized outputs with unit variance.

3.4 Heteroskedastic SA

In technological scalar regression models it may happen that the error variance is not constant but changes with some factors v_j . In this case the model is called heteroskedastic and equation (7) is completed with

$$\begin{aligned} e &= \zeta h \\ h^2 &= \alpha_0 + \sum_j \alpha_j v_j \end{aligned} \quad (12)$$

where ζ is an independent standard Gaussian sequence of errors with zero mean and unit variance. Coefficients β and α , of equations (7) and (12) respectively, can be jointly estimated via Gaussian maximum likelihood or by iterated weighted LS.

In this case the ANOVA decomposition (8), similarly to mixed models, is extended to cope with random effect components, namely

$$\sigma_y^2 = \sum_j \beta_j^2 \sigma_{u_j}^2 + \sum_j \alpha_j E(v_j) + \alpha_0 \quad (13)$$

Correspondingly the heteroskedastic sensitivity index, say HSI , can be decomposed in a linear SI and a skedastic SI , i.e.

$$HSI_j = SI_j + SI_j^*.$$

where u_j and v_j refer to the same input.

For example, consider the case where the inputs are not transformed, $\mathbf{u} = \mathbf{x}$, and $v_1 = x_1$ in equation (12). We then have a skedastic component given by

$$h^2 = \alpha_0 + \alpha_1 x_1 + \alpha_2 x_1^2 \quad (14)$$

and the following sensitivity index structure:

$$HSI_1 = SI_1 + SI_1^* = \frac{\beta_j^2 \sigma_{u_j}^2}{\sigma_y^2} + \frac{\alpha_1 E(x_1) + \alpha_2 E(x_1^2)}{\sigma_y^2} \quad (15)$$

and the other sensitivities are unchanged, $HSI_j = SI_j$, for $j = 2, \dots, k$.

4 Computer Simulation Results

In this section we discuss the computer experiment designs and statistical results. Since computing time was not a problem we choose to run large experiments allowing us to check different models and to focus mainly on approximation rather than be concerned with relevant estimation uncertainty and overfitting hazard. Hence the final polynomial heteroskedastic solution is not due to reduced dimensionality of simulated data.

In this section we start with Global SA to get a global picture of our system. Then we consider Local SA . Here "local" means that the parameter range \mathbf{D} is small but we still use the Monte Carlo approach in order to get the most of flexibility in modelling and post-modelling diagnostic and uncertainty assessment.

4.1 Global SA

Global sensitivity has been carried out to identify those process parameters having larger influence on fixed bed reactor efficiency. To do this, fluid

dynamic process factors and chemical-physical characteristics of biosorbent have been considered as input data and randomly changed in the simulations.

In particular the fluid dynamic factors considered are: liquid viscosity (μ_L), liquid density (ρ_L), specific bed velocity (u_0) and column void degree (ε). Whereas the chemical-physical characteristics taken into account are, adsorption particle diameter (d_p) with assumed spherical shape, density of the biosorbent (ρ_S) and adsorption characteristics (q_{max} and b or Langmuir constants).

All these factors were simultaneously varied in a range suitable for process design purposes, also considering other similar works (e.g. Hatzikioseyan et al., 1999). Table 1 lists these data inputs and their range \mathbf{D} . Independent rectangular distributions have been used in this first simulation study. Using this setup, $n = 10,000$ simulations z_1, \dots, z_n have been generated giving n random vectors of the input factors \mathbf{x}_i , orthogonalized using equation (6) and n output $y_i = (t_{b,i}, LUB_i)$ computed as in section 2.2.

	Min	Max	Mean	Std
μ_L	0.298	0.903	0.603	0.173
ρ_L	0.801	1.200	1.001	0.115
u_0	196.801	603.791	402.047	115.470
ε	0.199	0.402	0.300	0.058
d_p	0.045	1.004	0.521	0.274
ρ_S	0.694	1.602	1.153	0.260
q_{max}	19.812	60.079	39.808	11.547
b	0.972	4.028	2.505	0.866
t_b	0.228	0.743	0.450	0.102
LUB	0.059	0.422	0.186	0.060

Table 1: Parameter and output statistics for global SA

4.1.1 Data Analysis and Modelling

The modelling philosophy has been incremental, starting from a simple linear model as in equation (7) with $\mathbf{u} = \mathbf{x}$, deleting unimportant variables and then adding quadratic and interactions when needed. As mentioned above, p-values and standard test F or t test were used with some caution because of the very large sample and the non stochastic error structure. An important tool was the graphical analysis of residuals. Along these lines we searched for a model having residuals almost independent from the x and normally distributed or, at least symmetric around zero and of course with small Mean Squared Error (MSE) and little complexity as measured by the Akaike Information Criterion (AIC).

As will be clear from the results, the modelling process was successfully performed by filtering out every signal appearing between the transformed inputs \mathbf{u} and the residuals.

All variables, both input and output, in the sequel are zero mean deviates. Moreover the linear inputs \mathbf{x} are orthogonal as explained in section 3.2 and the quadratic and interaction components have been orthogonalized after running the model so that they have to be interpreted as quadratic effects after discounting for the linear ones.

4.1.2 Modelling t_b

Omitting the unimportant variables we get the following simple model for t_b , with \pm standard deviation reported in brackets for all coefficients and error:

$$t_b = 0.187 (\pm 0.003) \varepsilon + 0.237 (\pm 7 \times 10^{-4}) \rho_S + 0.00686 (\pm 2 \times 10^{-5}) q_{\max} + e (\pm 0.018). \quad (16)$$

Despite the preliminary very good fitting $R^2 = 96.90\%$, from Figures 1 - 3 we see that some nonlinear relationship is present after filtering the linear components. The symmetric behavior of the residuals from Figures 1 hints both for heteroskedasticity or interactions. The same conclusions may be achieved from the normal probability plot and the histogram with superimposed Gaussian of Figure 3 which show high tails and kurtosis $k(e) = 3.5$. Moreover the fitted against observed plot of Figure 2 hints for nonlinearity.

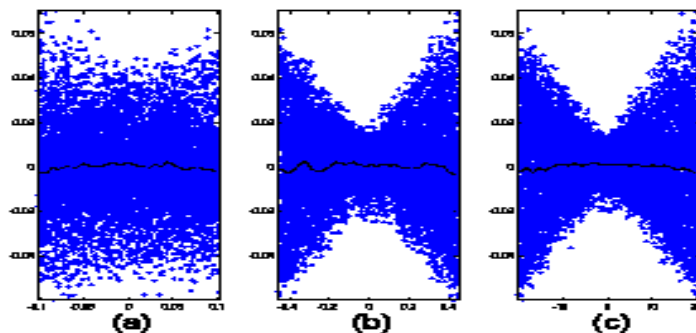


Figure 1: Residuals of t_b model (16) vs. parameters. (a) ε , (b) ρ_S , (c) q_{\max} .

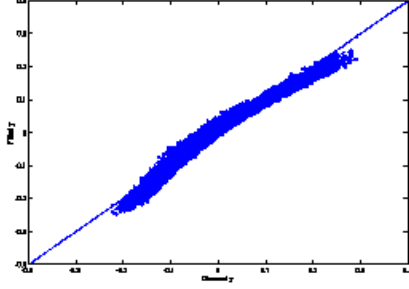


Figure 2: t_b values fitted by model (16) vs. observed.

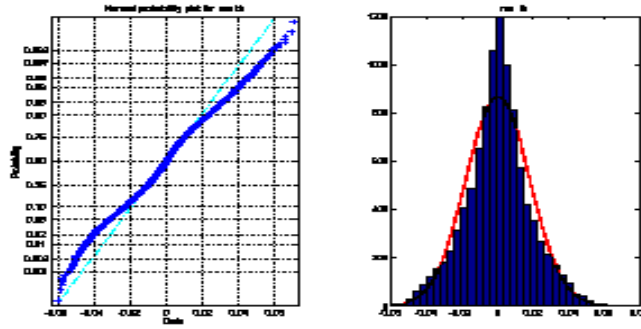


Figure 3: Residuals of t_b model (16). Normal probability plot and histogram

We then get the following second order model

$$\begin{aligned}
 t_b = & 0.187 (\pm 9 \times 10^{-4}) \varepsilon + 0.237 (\pm 2 \times 10^{-4}) \rho_S \\
 & + 0.00686 (\pm 10^{-5}) q_{\max} - 0.230 (\pm 0.0033) \varepsilon \rho_S \\
 & - 0.0071 (\pm 2 \times 10^{-5}) \varepsilon q_{\max} + 0.0054 (\pm 2 \cdot 10^{-5}) \rho_S q_{\max} \\
 & - 0.329 (\pm 0.016) \varepsilon^2 - 0.00001 (\pm 8 \cdot 10^{-6}) q_{\max}^2 + e (\pm 0.0049).
 \end{aligned} \tag{17}$$

Note that, thanks to orthogonality, the coefficients of the linear component are unchanged but all standard errors decreased and fitting is now very high with $R^2 = 99.77\%$ and root MSE given by $RMSE = 0.015$. Moreover from Figures 4 - 6 we get an almost perfect Gaussian error distribution with no dynamical signal to reasonably extent low skewness, $s_k = -0.03$ and Gaussian kurtosis $k(e) = 3.03$. The pure quadratic components ε^2 and q_{\max}^2 add very little in terms of variance, see the sensitivity table 2 below, but they have been retained in the model because improve both Gaussian fitting and dynamics filtering as shown by Figures 6 and 4 respectively.

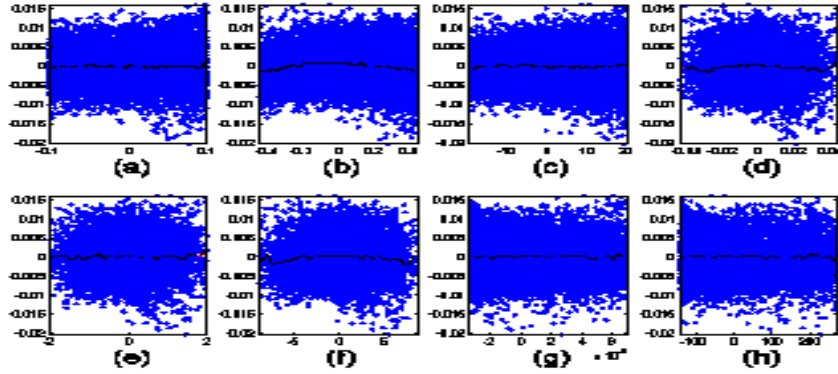


Figure 4: Residuals of t_b model (17) vs. parameters, quadratic and interaction terms. (a) ε , (b) ρ_S , (c) q_{\max} , (d) $\varepsilon\rho_S$, (e) εq_{\max} , (f) $\rho_S q_{\max}$, (g) ε^2 , (h) q_{\max}^2 .

Remembering the non-stochastic nature of our simulation model one could search for a more detailed description. For example, if one would use all 8 parameters and their 36 quadratic and interaction terms, would get $R^2 = 99.985\%$ and $RMSE = 0.0013$. In this case residual uncertainty would be about a quarter of model (17) but we omit these components because inessential for the present work.

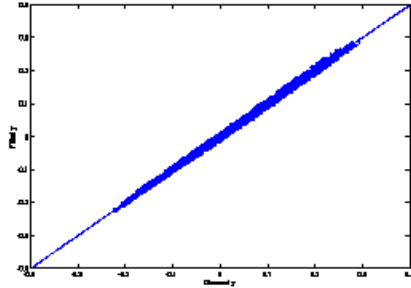


Figure 5: t_b values fitted by model (17) vs. observed.

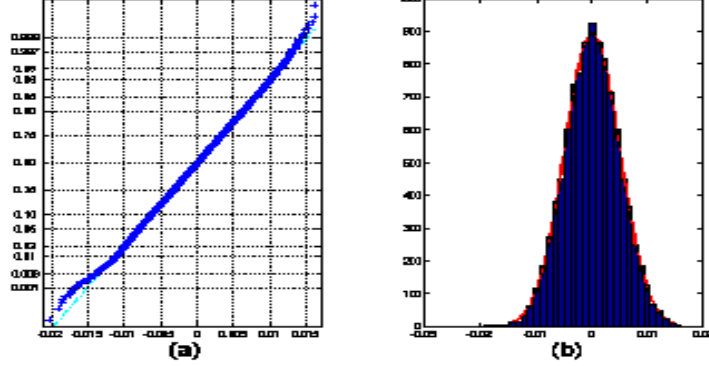


Figure 6: Residuals of t_b model (17) : (a) normal probability plot; (b) histogram

4.1.3 Modelling LUB

Following the approach of previous section we get the following second order model for $L = 100 \times LUB$

$$\begin{aligned}
L = & 5.89 (\pm 0.02) d_p + 62.6 (\pm 0.098) \varepsilon - 10.0 (\pm 0.02) \rho_S \\
& - 0.297 (\pm 0.0005) q_{\max} + 0.722 (\pm 0.006) b + 21.0 (\pm 0.4) d_p \varepsilon \quad (18) \\
& - 0.0298 (\pm 0.002) d_p q_{\max} - 18.0 (\pm 0.4) \varepsilon \rho_S - 0.514 (\pm 0.008) \varepsilon q_{\max} \\
& + 0.0776 (\pm 0.002) \rho_S q_{\max} - 6.12 (\pm 0.09) \rho_S^2 - 0.00527 (\pm 5 \times 10^{-5}) q_{\max}^2 \\
& + e (\pm 0.56).
\end{aligned}$$

This model has a very good fitting with $R^2 = 99.12\%$.

Nevertheless, from the first plot of Figure ?? we see that the conditional variance of $e(\mathbf{x})$ increases with d_p . Moreover, from the graphical analysis of residual distribution, which similar to Figure 3 but is omitted for shortness, we see that the residuals have high tails and high kurtosis, being $k(e) = 5.07$. We then fit the skedastic component given by equation (14) and get the following quadratic equation

$$h(\mathbf{u})^2 = 0.0973 (\pm 0.021) - 0.389 (\pm 0.093) d_p + 1.221 (\pm 0.087) d_p^2. \quad (19)$$

Note that, contrary to regression equation (18), here d_p is the nonzero mean original parameter. The heteroskedastic model greatly improves error normality since now we have $k\left(\frac{e}{h}\right) = 3.02$.

Moreover Figure 8 shows that after fixing ε, ρ_S and q_{\max} , output uncertainty strongly depend on d_p being generally increasing with d_p . Hence the

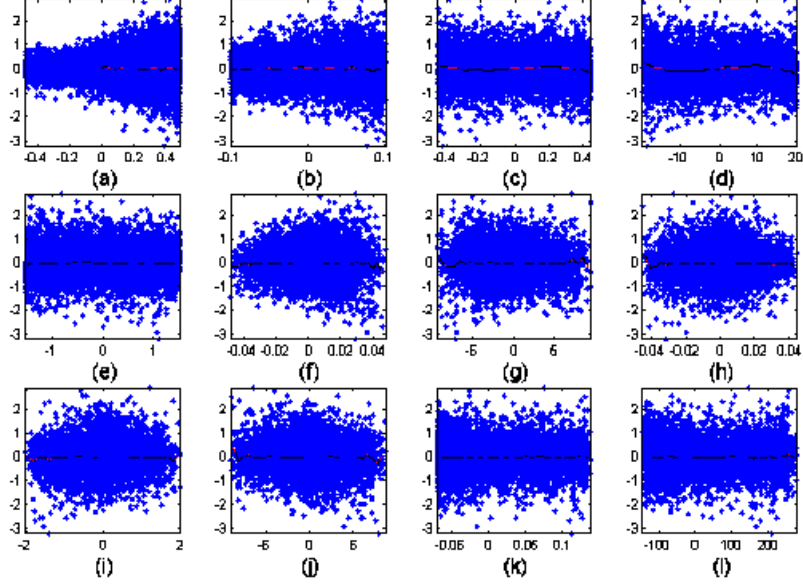


Figure 7: Residuals of LUB model (18) vs. parameters, quadratic and interaction terms. (a) d_p , (b) ε , (c) ρ_S , (d) q_{\max} , (e) b , (f) $d_p \varepsilon$, (g) $d_p q_{\max}$, (h) $\varepsilon \rho_S$ (i) εq_{\max} , (j) $\rho_S q_{\max}$, (k) ρ^2 , (l) q_{\max}^2 .

heteroskedastic model gives a further reduction of the output uncertainty especially for packed column reactors with small particles diameters d_p . This point is not much evident from inspection of sensitivity indexes only. For example in table 2 we have $HSI(d_p) = 0.0726 + 0.0061 = 0.0787 \cong SI(d_p)$ because there the error e is already small with respect to LUB variance σ_y^2 and detailed input-output modelling gives further insight into system dynamics and output uncertainty.

Since the correlation coefficient between the errors of the LUB model (18) and the t_b model (17) is quite small, being -0.109 , we can conclude that the residual uncertainty of the two subsystems is almost independent.

4.1.4 Results and Discussion

In the table 2 below SA is summarized including SI from both univariate models, the heteroskedastic indexes and the multivariate ones. The multivariate SI 's are based on the simple average formula (10) and the weighted averages (11) are not reported here since, in this case, the results are essentially the same.

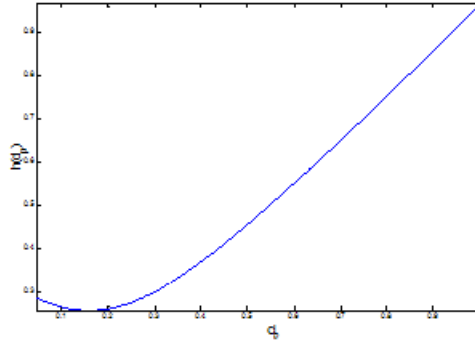


Figure 8: Skedastic function $h(d_p)$ for LUB model from equation (19)

It can be observed that the investigated process parameters do not influence the fixed bed reactor efficiency at the same extent. In particular, as the last column of table 2 shows, the maximum heavy metal up-take (q_{max}) is the most important process parameter of this system being 46.9% its overall importance and being 34% and 59.8% the importances of this parameter on LUB and t_b respectively. This conclusion is in agreement with those ones reported in similar works and physically acceptable.

For analogous reasons, the biosorbent density (ρ_S) is the second significant parameter, being its overall importance given by 27.7% and 36% and 19.3% the importances for t_b and LUB respectively. As also reported by Hatzikioseyan et al. (2001), the increase in density ρ_S produces an increase in adsorbing material in the fixed bed, improving both t_b and LUB outputs.

Regarding the other input parameters, the most relevant factor is the fixed bed void degree (ε) with an influence on LUB of 36%: as above reported q_{max} and ρ_S were the most important for t_b .

The characteristics of the biosorbent materials seem to be more important than fluid dynamic factors in the range of the investigated conditions for the selected equilibrium local model.

Whenever in the table, linear and quadratic effects are summed up for shortness, it is seen from section 3 that, in principle, they could be separated and assessed separately. As a matter of fact we can conclude that, quadratic, interaction and skedastic components are less important than linear ones for the output variance in our case.

	t_b	LUB			Multivariate SI
		skedastic			
		linear SI	SI*	H-SI	
q_{\max}	59.75%	34.01%		34.01%	46.88%
ρ_S	36.05%	19.27%		19.27%	27.66%
ε	1.12%	36.47%		36.47%	18.79%
d_p		7.26%	0.61%	7.88%	3.94%
b		1.09%		1.09%	0.54%
$\rho_S - q_{\max}$	2.52%	0.15%		0.15%	1.34%
$\varepsilon - q_{\max}$	0.21%	0.33%		0.33%	0.27%
$\varepsilon - \rho_S$	0.11%	0.20%		0.20%	0.16%
$d_p - \varepsilon$		0.31%		0.31%	0.15%
$d_p - q_{\max}$		0.03%			
Totals	99.77%	99.11%		99.70%	99.74%
R^2	99.77%	99.11%			
Output Std	0.1025	0.060			
Model RMSE	0.015292	0.00023			

Table 2: Global SA for t_b and LUB

4.2 Local SA

Local Sensitivity Analysis was carried out using the same input parameters utilized in the Global SA but selecting an appropriate configuration of this system (see Table 3) and selecting for these average values appropriate probability distributions of the experimental error. In particular, $n = 1,000$ simulations were computed by sampling (q_{\max}, b) from the bivariate normal distribution with correlation coefficient 0.30 (Esposito et al, 2001) and all the other input parameters from the rectangular distribution. The particular normal distribution was chosen to account for the uncertainty coming from empirical estimation of equation (2).

In this manner the main goal of Local SA was to evaluate which parameters must be estimated with major precision during the experimental work to avoid large errors on the evaluation of the output process parameters such as t_b and LUB .

	Min	Max	Mean	Std
μ_L	0.55	0.65	0.60	0.03
ρ_L	0.95	1.05	1.00	0.03
u_0	399.97	400.03	400.00	0.01
ε	0.25	0.35	0.30	0.03
d_p	0.07	0.13	0.10	0.01
ρ_S	1.05	1.15	1.10	0.03
q_{\max}	29.36	52.87	40.07	3.97
b	0.46	4.44	2.50	0.63
t_b	0.37	0.53	0.45	0.03
LUB	0.10	0.22	0.16	0.02

Table 3: Parameter and output statistics for local SA

4.2.1 Comparing Local and Global SA

Following the approach of previous sections we get the following model for t_b

$$\begin{aligned}
t_b = & 0.217 (5 \cdot 10^{-4}) \varepsilon + 0.242 (5 \cdot 10^{-4}) \rho_S + 0.00664 (\pm 10^{-6}) q_{\max} \\
& - 0.00387 (\pm 2 \cdot 10^{-5}) b - 0.298 (\pm 0.016) \varepsilon \rho_S \\
& - 0.006 (10^{-4}) \varepsilon q_{\max} + 0.0052 (\pm 0.00012) \rho_S q \\
& - 0.328 (\pm 0.018) \varepsilon^2 - 10^{-5} (\pm 6 \cdot 10^{-7}) q_{\max}^2 \\
& - 0.00026 (\pm 2 \cdot 10^{-5}) b^2 + e (\pm 0.00042).
\end{aligned} \tag{20}$$

As expected, fitting is higher here than the global model (17), being $R^2 = 99.98\%$ and kurtosis $k(e) = 2.81$. Now we have the new terms b and b^2 and differences are statistically significant at standard levels using for example the symmetry test. Nevertheless the two models are quite similar having most coefficients very close.

For the *LUB* output we have

$$\begin{aligned}
100 \times LUB = & 5.94 (\pm 0.27) d_p + 55.1 (\pm 0.13) \varepsilon - 10.3 (\pm 0.14) \rho_S \\
& - 0.277 (\pm 0.001) q_{\max} + 0.774 (\pm 0.006) b \\
& - 0.00495 (\pm 2 \times 10^{-4}) q_{\max}^2 + e (\pm 0.12).
\end{aligned} \tag{21}$$

with $R^2 = 99.63\%$ and $k(e) = 2.92$. Comments and conclusions similar to t_b model hold. In addition the residual heteroskedasticity of model (18) is not important now because the range of d_p is quite reduced and this is consistent with the global model plot (a) of Figure ??.

Despite these similarities, the SI's reported in table 4 are quite different with respect to global SI's of table 2. Of course Global and Local SA had been equivalent if all the parameter *std's* had been changed by the same rate but this is not our case, as shown by the last columns of tables 1 and 3.

	t_b	LUB	MSI
q_{\max}	88.022%	29.809%	58.916%
ε	4.958%	61.656%	33.307%
ρ_S	6.139%	2.141%	4.140%
b	0.753%	5.844%	3.299%
d_b		0.179%	0.090%
$\varepsilon - q_{\max}$	0.056%		0.028%
$\rho_S - q_{\max}$	0.043%		0.022%
$\varepsilon - \rho_S$	0.008%		0.004%
Totals	99.98%	99.63%	99.80%
R^2	99.98%	99.63%	
Output Std	0.0281	0.0202	
Model RMSE	0.00042	0.0012	

Table 4: Local SA for t_b and LUB

4.2.2 Results and Discussion

From the analysis of the results reported in Table 4, it is possible to highlight as the experimental error of the input data, produces large variations of the outputs LUB and t_b , with relevant standard deviation values of their respective experimental error.

In particular, the parameters more affecting the outputs are q_{\max} , giving 88% importance on t_b and 29.8% on LUB, and the void degree ε , giving 61.7% on LUB and 5% on t_b .

Since input parameters b and ρ_S have little influence on t_b and LUB, q_{\max} and ε should be estimated with more precision to avoid large experimental error both on t_b and LUB.

5 Conclusions

A standard procedure to evaluate the influence of process parameters on the performance of fixed bed reactors used to remove heavy metals from wastewaters by biosorption has been proposed.

The statistical approach is based on Extended Global and Local Sensitivity Analysis which generalizes standard SA to cope with heteroskedastic and multi-output systems. With this approach, interaction effects can also be estimated. On the other hand, SA based on changing one-factor-at-time may result in losing this information which may be important for the selected process.

The influence of the main process parameters on the heavy metal biosorption has been estimated for design purposes and as a useful tool to plan

experimental runs in terms of experimental error variance.

Moreover, simple polynomial relationships can be generated from simulation results and used as simple mathematical formulas to find changes in the output model parameters with respect to any change in the input data considered in the formulated model.

References

- [1] Beolchini F, Pagnanelli F, Vegliò F. 2001. Modeling of copper biosorption by *Arthrobacter* sp. in a UF/MF membrane reactor. *Environmental Science and Technol.*, 35, 3048-3054.
- [2] Esposito A, Pagnanelli F, Lodi A, Solisio C, Vegliò F. 2001. Biosorption of heavy metals by *Sphaerotilus natans*: an equilibrium study at different pH and biomass concentrations. *Hydrometallurgy*, 60, n.2, 129-141.
- [3] Fassò A., Perri P.F. 2001. Sensitivity Analysis. In A. El-Shaarawi, W. Piegorsch (eds). *Encyclopedia of Environmetrics*. Volume 4, pp 1968-1982, Wiley, New York.
- [4] Hatzikioseyan A, Tsezos M, Mavituna F. 2001. Application of simplified rapid equilibrium models in simulating experimental breakthrough curves from fixed bed biosorption reactor. *Hydrometallurgy*, 59 , p.395-406.
- [5] Hatzikioseyan A, Mavituna F, Tsezos M. 1999. Modelling of fixed bed biosorption in continuous metal ion removal processes. The case of single solute local equilibrium. In: *Biohydrometallurgy and the Environment Toward the Mining of the 21st Century*, part B (R. Amils and A. Ballester Eds), Elsevier, p.429-448.
- [6] Kratochvil D, Volesky B. 2000. Multicomponent biosorption in fixed bed. *Water Research*, Vol.34, Issue 12, p.3186-3196.
- [7] Kratochvil D, Volesky B, Demopoulos G. 1997. Optimizing Cu removal/recovery in a biosorption column. *Water Research*, Vol.31, Issue 9, p.2327-2339.
- [8] Kratochvil D, Volesky B. 1998. Advances in the biosorption of heavy metals. *Trends in Biotechnology*, Vol.16, Issue 7, 291-300.

- [9] Pagnanelli F, Pietrangeli Papini M, Toro L, Trifoni M, Vegliò F. 2000. Biosorption of metal ions on *Arthrobacter* sp.: biomass characterisation and biosorption modelling. *Environmental Science and Technol.*, 34, 2773-2778.
- [10] Pagnanelli F, Esposito A, Vegliò F. 2002. Multimetallic modeling for biosorption of binary systems. *Water Research*, in press.
- [11] Rencher A. C. 1995. *Methods of Multivariate Analysis*. Wiley, New York.
- [12] Sag Y, Atacolu I, Kutsal T. 2000a. Equilibrium parameters for the single - and multicomponent biosorption of Cr(VI) and Fe(III) ions on *R. Arrhizus* in a packed column. *Hydrometallurgy*, Vol.55, Issue 2, 165-179.
- [13] Sag Y, Aktay Y. 2000b. Mass transfer and equilibrium studies for the sorption of chromium ions onto chitin. *Process Biochemistry*, Vol.36, p.157-173.
- [14] Sag Y, Akcael B, Kutsal T. 2001a. Evaluation, interpretation and representation of three-metal biosorption equilibria using a fungal biosorbent. *Process Biochemistry*, Vol.37, Issue 1, 35-50.
- [15] Sag Y, Aktay Y. 2001b. Application of equilibrium and mass transfer models to dynamic removal of Cr(VI) ions by Chitin in packed column reactor. *Process Biochemistry*, Vol.36, p.1187-1197.
- [16] Saltelli A, Chan K, Scott M. 2000. *Sensitivity Analysis*. Wiley, New York.
- [17] *Transaction of mathematical software*, 1992, Vol.18 N0. 3 September 1992 pp 343-344)
- [18] Turanyi T, Rabitz H. 2000. Local Methods, in *Sensitivity Analysis*, Saltelli A, Chan K, Scott M. eds. Wiley, New York.
- [19] Vegliò F, Beolchini F. 1997a. Removal of metals by biosorption: a review. *Hydrometallurgy*, Vol. 44 - p. 301-316 .
- [20] Vegliò F, Beolchini F, Gasbarro A. 1997b. Biosorption of toxic metals: an equilibrium study using free cells. *Process Biochemistry*, Vol.32, n.2, 99-105.
- [21] Vegliò F, Beolchini F, Gasbarro A, Lora S, Corain B, Toro L. 1997c. Polyhydroxoethylmethacrylate (polyHEMA)-trimethylolpropanetrimethacrylate (TMPTM) as a support for

- metal biosorption with *Arthrobacter* sp. *Hydrometallurgy*, Vol.44, 317-320.
- [22] Vegliò F, Beolchini F, Toro L. 1998. Kinetic modelling of copper biosorption by immobilised biomass. *Industrial & Engineering Chemistry Research*, 37 (3), 1107-1111.
- [23] Vegliò F, Esposito A, Pagnanelli F. 2002. pH related equilibria models for biosorption in single metal systems. *Chem. Eng. Science* , in press.
- [24] Volesky B. 2001. Detoxification of metal-bearing effluents: biosorption for the next century. *Hydrometallurgy*, Volume 59, Issues 2-3, p.203-216.