

Technical Note  
**Modelling of equilibrium heavy metal biosorption data  
at different pH: a possible methodological approach**

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ABSTRACT

In this paper a methodological approach to study and model equilibrium of heavy metals during biosorption has been proposed and discussed. Two cases of copper biosorption are reported as examples: biosorption of copper onto *Sphaerotilus natans* and copper adsorption onto calcium alginate. Different empirical and semi-empirical models have been proposed and summarised, to consider the pH effect on heavy metal up-take. The proposed models, originated from Langmuir isotherm, may be useful to fit experimental data by just monitoring the pH avoiding thus its control. The adsorption isotherms were built considering experimental procedures at constant pH and pH edge conditions. Both empirical and semi-empirical models were able to fit these experimental results. The empirical approach can be applied in single cases considering the selected experimental results, whereas the proposed semi-empirical models seem to be more generally applicable. Although the validity of these last models should be checked also in other cases, this approach may be useful to describe and fit biosorption data in a single metal system during the building of an adsorption isotherm: the simple equilibrium pH monitoring during the tests (also carried out in pH-edge conditions) and the introduction of this factor as independent variable in the equilibrium modelling is suggested as methodological approach to study biosorption in a single metal system. The use of these models may be useful also in successive studies in which the experimental results are described by mechanistic models (like Surface Complex Model – SCM) permitting a right interpolation of the data. The results are not conclusive because the effect of some important factors as biomass concentration and presence of other ions in solution are not considered in these models. © 2003 SDU. All rights reserved.

Keywords: Biosorption; Heavy metals; Equilibrium; Modelling; pH-effect

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## 1. INTRODUCTION

Biosorption may be a suitable wastewater technology to remove heavy metals as demonstrated by several researchers, because it enables the use of cheap adsorption materials that can be competitive with respect to conventional technologies (Volesky, 2001; Kratochvil and Volesky, 1998). In the last ten years many efforts have been addressed to develop new technologies mainly using heavy metal biosorption.

Some papers that try to summarise the results reported on biosorption of heavy metals are available on the wide available literature (Volesky, 2001; Kratochvil and Volesky, 1998; Vegliò and Beolchini, 1997) considering single (Esposito *et al.*, 2001; Sag *et al.*, 2000) and multi-metal systems (Pagnanelli *et al.*, 2001, 2002a; Sag *et al.*, 2000, 2001).

Biosorption of heavy metals can be explained by considering different kinds of chemical and physical interactions among the functional groups present on the cell wall and the heavy metals in solution (Vegliò and Beolchini, 1997). The active sites present on cell wall are very different according to the nature of the biosorbent: carboxylic, phosphate, sulphate, amino, amidic and

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hydroxylic groups are the most commonly found (Cox *et al.*, 1999; Plette *et al.*, 1995). Acidic nature ( $pK_a$ ) and concentration of the active sites may be usually determined by potentiometric titration of the biomass (Pagnanelli *et al.*, 2000; Davis *et al.*, 2000). The analysis of these experimental curves outputs the influence of pH on the deprotonation of the functional groups on cell wall (Esposito *et al.*, 2001). For pH values greater than  $pK_a$  the sites are mainly in dissociated form and can exchange  $H^+$  with metals in solution. At pH lower than  $pK_a$  values, complexation phenomena can also occur, especially for the carboxylic group (Fourest and Volesky, 1996). pH is one of the most influencing factors on heavy metal biosorption: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, and precipitation are strongly influenced by pH and, on the other side, it strongly influences the speciation and the biosorption availability of the heavy metals (Warren and Ferris, 1998; Corapcioglu and Huang, 1987; Yang and Volesky, 1999).

The effect of pH on heavy metal biosorption can not be considered by simple empirical and physical equations such as derived by Freundlich and Langmuir models (Esposito *et al.*, 2001, 2002). These adsorption isotherms can be used to fit only experimental data obtained at constant equilibrium pH (Esposito *et al.*, 2001).

Mechanistic models are in general more powerful to describe the pH effect on the biosorption performance because they are usually based on a preliminary biomass characterisation and on the subsequent formulation of a set of reactions among the adsorbent sites and heavy metals, whose particular solution chemistry is taken into account (Warren and Ferris, 1998; Yang and Volesky, 1999).

In this work, some empirical and semi-empirical models are summarised to be used in heavy metal data fitting of equilibrium adsorption results obtained under different pH conditions: this approach permits to analyse equilibrium data, thus avoiding pH control during a selected trial. The control of pH at a constant value is in general necessary to build an adsorption isotherm: the approach reported here requires only the evaluation of the equilibrium pH in correspondence with the equilibrium heavy metal concentration also using pH-edge tests. This analysis may be useful to carry out data fitting and to permit useful interpolation finalised to the formulation of mechanistic models. *Sphaerotilus natans* and calcium alginate have been considered in this work as examples. More details about the experimental procedures are not here reported and can be found elsewhere (Esposito *et al.*, 2001, 2002; Vegliò *et al.*, 2002).

## 2. MATHEMATICAL MODELS

The proposed empirical and semi-empirical models used to fit equilibrium data are summarised in the following equations (Vegliò *et al.*, 2002):

$$\text{Model 1: } q = \frac{\alpha_1 \cdot pH + \alpha_2}{\alpha_3 + pH} \cdot \frac{C_{eq}}{(\alpha_4 \cdot pH + \alpha_5) + C_{eq}} \quad (1)$$

$$\text{Model 2a: } q = \frac{\alpha_1 \cdot e^{\alpha_2 \cdot pH}}{1 - \frac{\alpha_1}{\alpha_3} \cdot (1 - e^{\alpha_2 \cdot pH})} \cdot \frac{C_{eq}}{\alpha_4 + C_{eq}} \quad (2a)$$

$$\text{Model 2b: } q = \frac{\alpha_1 \cdot e^{\alpha_2 \cdot pH}}{1 - \frac{\alpha_1}{\alpha_3} \cdot (1 - e^{\alpha_2 \cdot pH})} \cdot \frac{C_{eq}}{(\alpha_4 \cdot pH + \alpha_5) + C_{eq}} \quad (2b)$$

$$\text{Model 3a: } q = \frac{\alpha_1}{1 + \frac{10^{-pH}}{\alpha_2}} \cdot \frac{C_{eq}}{\alpha_3 + C_{eq}} \quad (3a)$$

Model 3b: 
$$q = \frac{\alpha_1}{1 + \frac{10^{-pH}}{\alpha_2}} \cdot \frac{C_{eq}}{\alpha_3 \cdot \left(1 + \frac{10^{-pH}}{\alpha_2}\right) + C_{eq}} \quad (3b)$$

Model 3c: 
$$q = \frac{\alpha_1}{1 + \frac{10^{-pH}}{\alpha_2}} \cdot \frac{C_{eq}}{\alpha_3 \cdot \left(1 + \frac{10^{-pH}}{\alpha_4}\right) + C_{eq}} \quad (3c)$$

These equations have been applied to describe the equilibrium of copper (II) biosorption on *Sphaerotilus natans* (Esposito *et al.*, 2001) and calcium alginate (Vegliò *et al.*, 2002) at different pH.

All these equations have been built considering Langmuir as a reference model, introducing the pH effect in the two parameters  $q_{max}$  and  $b$  (Esposito *et al.*, 2001): in fact at constant pH all equations degenerate in the classical Langmuir model.

The empirical model reported in equation (1) was named Model 1; in equations (2a) and (2b) two different versions of the logistic equation coupled with Langmuir model have been shown (Vegliò *et al.*, 2002): both models were named Model 2a and 2b; the equations (3a), (3b) and (3c) have been originated from non-competitive biosorption models (Esposito *et al.*, 2001; Vegliò *et al.*, 2002) with some empirical changes introduced considering the obtained experimental data (these were named Model 3a, 3b and 3c respectively).

In particular Model 1 is an example of empirical model originated from the analysis of equilibrium biosorption data: the form of the model has been deduced after the analysis of the equilibrium data using a classical Langmuir model analysing the heavy metal up-take at different pH (in particular each adsorption isotherm has been evaluated considering experimental data carried out at constant pH). Figure 1 shows an example of this model building using calcium alginate as adsorbent material (Vegliò *et al.*, 2002). In particular several adsorption isotherms were obtained from biosorption equilibrium data at different pH: Langmuir model has been used to fit this experimental data and the two parameters  $q_{max}$  and  $K_s$  were related to the different pH conditions as reported in Figure 1. Obviously the form of the Model 1 is not general: in fact the same equation can not be applied for the analysis of copper biosorption data obtained for *Sphaerotilus natans* as shown in Figure 2. In other words, as well known, the empirical models are in general built on specific experimental results.

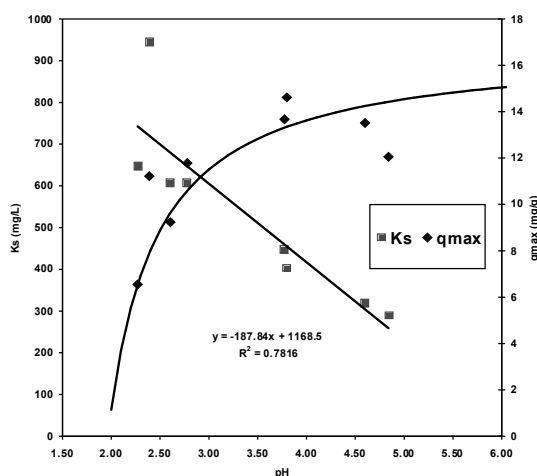


Figure 1. Effect of pH on  $q_{max}$  and  $K_s$  estimated by Langmuir model for copper adsorption on calcium alginate (Vegliò *et al.*, 2002)

Model 2a has been successfully used to fit copper biosorption data using *Sphaerotilus natans* and calcium alginate (Esposito *et al.*, 2001; Vegliò *et al.*, 2002): the application of this equation

has been suggested by the Logistic model used to describe microbial growth in batch conditions (Aiba, 1973), considering the  $q_{\max}$  behaviour with respect to pH. Model 2b is an extension of Model 2a in which  $1/b$  (or  $K_s$ ) values have been changed introducing in the model a functional dependence with pH as suggested by its behaviour shown in Figure 1.

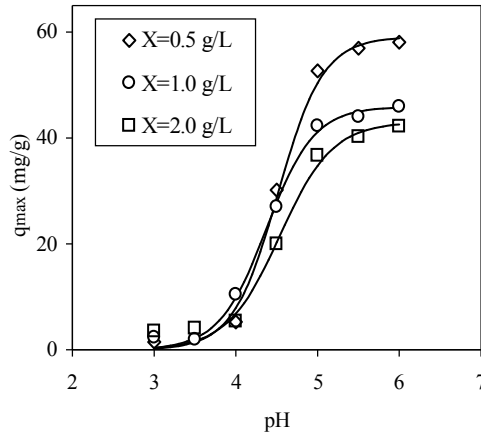
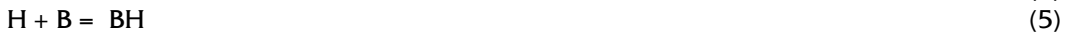


Figure 2. Effect of pH on maximum copper specific up-take ( $q_{\max}$ ) at different biomass concentrations ( $X$ ) of *Sphaerotilus natans* (Esposito *et al.*, 2001)

Obviously an empirical model is able to simulate heavy metal uptake as a pH-dependent function, but it does not give any information about the mechanisms operating in the system. Nevertheless these models may be applied during data interpolation to evaluate heavy metal uptakes for different concentrations and pH values.

In analogy with the description of kinetic behaviour of enzyme and microbial growth (Aiba, 1973) a suitable mathematical model was evaluated assuming a non-competitive mechanism of interaction between heavy metal and hydrogen ions in solution (Esposito *et al.*, 2001). This kind of model allows to obtain a relation among the specific metal uptake ( $q$ ) and the metal concentration in solution ( $C_{eq}$ ) at different equilibrium pH (Vegliò *et al.*, 2002). Assuming that the cell wall was characterized principally by one kind of active sites, the following reactions can be postulated (the charge of the ionic species has been neglected):



where Me, B, MeB, H, BH and BHMe represent metal in solution, biomass, complex biomass-metal, proton, biomass-proton complex and biomass-proton-metal complex respectively.

Equilibrium relationships can be written by applying the equilibrium mass law for the postulated chemical reactions:

$$K_s = \frac{[Me] \cdot [B]}{[MeB]} \quad (7)$$

$$K_i = \frac{[B] \cdot [H]}{[BH]} \quad (8)$$

$$K_{mi} = \frac{[BH] \cdot [Me]}{[BHMe]} \quad (9)$$

Considering the material balance of the total adsorbing sites (noted as  $B_{\text{tot}}$ ):

$$[B_{\text{tot}}] = [B] + [MeB] + [BH] + [BHMe] \quad (10)$$

and according to the non-competitive hypothesis ( $K_{mi}=K_s$ ) (Aiba *et al.*, 1973), the following model can be obtained using equations 7-10:

$$[MeB] = \frac{[B_{tot}]}{\left(1 + \frac{[H]}{K_f}\right)} \cdot \frac{[Me]}{(K_s + [Me])} \quad (11)$$

Changing the symbols in equation (11) Model 3a can be obtained (in particular  $q = [MeB]$  and  $C_{eq} = [Me]$ ). A further implementation can be carried out if a relation between  $K_s$  and pH is introduced in Model 3a. The influence of pH on  $K_s$  parameter could be introduced by empirical observation (as reported in Figure 1) or considering a mixed competitive and non-competitive mechanism on the adsorption sites of protons and metal ions: Models 3b and 3c are generated with this last dependence. In the first case (Model 3a) the effect of pH is considered with one constant alone ( $\alpha_2$ ), whereas in the second model (3b) the effect of pH is taken into consideration with two different constants ( $\alpha_2$  and  $\alpha_4$ ).

The experimental data ( $q$  and  $C_{eq}$ ) obtained at different equilibrium pH can be fitted by a non linear regression method to evaluate the adjustable parameters of each model ( $\alpha_i$ ;  $i = 1, \dots, p$ ) minimizing the sum of the squared deviations from experimental and predicted values of  $q$ : as an example, Table 1 reports the estimated values of the model constants for copper adsorption data onto calcium alginate and *Sphaerotilus natans*, along with other statistical parameters (Himmelblaud, 1978; Montgomery, 1991) which also allow the evaluation of the model validity (Ho and McKay, 2000; Pagnanelli *et al.*, 2002b). In particular:

- a) the parameter standard deviation as parameter error,
- b) the model residual variances ( $S^2_{res}$ ),

$$S^2_{res} = \frac{\sum_{i=1}^n (q_{iexp} - q_{ical})^2}{n - p} \quad (12)$$

where  $q_{ical}$  and  $q_{iexp}$  are respectively the specific metal uptake calculated by the model and measured experimentally,  $n$  is the total number of experimental points,  $p$  is the number of estimated parameters and  $S^2_{res}$  is the residual model variance ( $mg^2/g^2$ ).

Table 1

Parameter estimation of the selected models obtained from the data fitting of equilibrium biosorption of copper(II) onto calcium alginate and *Sphaerotilus natans*

Model	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_4$	$\alpha_5$	p	$S^2_{res}$	note
N°1	$17 \pm 2$	$-32 \pm 2$	$-1.3 \pm 0.4$	$-69 \pm 4$	$740 \pm 190$	5	0.98	a
N°2 a	$0.2 \pm 0.2$	$1.8 \pm 0.4$	$14.9 \pm 0.6$	$480 \pm 50$		4	0.96	a
N°2 b	$0.2 \pm 0.1$	$1.8 \pm 0.5$	$14.9 \pm 0.7$	$-25 \pm 40$	$570 \pm 180$	5	0.96	a
N°3 a	$14.4 \pm 0.5$	$0.0040 \pm 0.0004$	$480 \pm 50$			3	0.97	a
N°3 b	$13.6 \pm 0.4$	$0.0060 \pm 0.0005$	$390 \pm 40$			3	0.91	a
N°3 c	$13.1 \pm 0.4$	$0.008 \pm 0.002$	$345 \pm 40$	$0.003 \pm 0.002$		4	0.91	a
N°2 a	$3.7 \pm 0.9 \cdot 10^{-4}$	$2.6 \pm 0.5$	$100 \pm 10$	$1.8 \pm 0.3$		4	11.20	b
N°2 a	$2.2 \pm 0.2 \cdot 10^{-2}$	$1.6 \pm 0.2$	$90 \pm 10$	$5.5 \pm 0.7$		4	2.33	c
N°2 a	$4.5 \pm 0.5 \cdot 10^{-3}$	$1.9 \pm 0.2$	$68 \pm 8$	$3.9 \pm 0.7$		4	5.85	d
N°3 a	$110 \pm 10$	$1.9 \pm 0.3 \cdot 10^{-5}$	$1.9 \pm 0.3$			3	11.01	b
N°3 a	$75 \pm 6$	$1.4 \pm 0.2 \cdot 10^{-5}$	$4.9 \pm 0.6$			3	3.20	c
N°3 a	$62 \pm 5$	$1.2 \pm 0.2 \cdot 10^{-5}$	$3.6 \pm 0.6$			3	5.94	d

a Data fitting results obtained by calcium alginate (Vegliò *et al.*, 2002).

b Data fitting results obtained by *Sphaerotilus natans* (biomass concentration 0.5g/l) (Esposito *et al.*, 2001).

c Data fitting results obtained by *Sphaerotilus natans* (biomass concentration 1.0g/l) (Esposito *et al.*, 2001).

d Data fitting results obtained by *Sphaerotilus natans* (biomass concentration 2.0g/l) (Esposito *et al.*, 2001).

The performances of the selected models were also compared by using an F-Test (not reported here) (Vegliò *et al.*, 2002). This statistical tool allows to evaluate if there is a difference in the accuracy of the investigated models. In general the residual variance of the model

expected to produce a better fitting is placed on the denominator. In the case of calcium alginate tests, F values are calculated as empirical model variance divided by the non-competitive model variance (Model 3b). If  $F > F_{n1, n2, 1-\alpha}$  (Himmelblau, 1978) there is a significant difference between the two models (in terms of residual variance). The model with the lowest residual variance can be therefore considered as the best model according to the chosen level of significance ( $1-\alpha$ ). For example, the calculated and tabulated F values for the relative degree of freedom and significance level ( $1-\alpha=0.99$ ) were evaluated for calcium alginate tests: in all tested conditions no significant difference can be observed among the selected models; in other words, all the models are able to fit the investigated experimental data with the same accuracy.

Similar results were obtained considering the data fitting of the experimental results obtained by *Sphaerotilus natans*: the same F-test procedure utilised for calcium alginate were applied to these experimental data with similar conclusions.

Considering the results of the F-tests above reported and the scatter diagrams (Figure 3 as an example), we can conclude that the best models are N°3a and 3b as they have the lowest  $S^2_{res}$  values, they are physically sound and are able to describe the experimental results with the lowest number of adjustable parameters ( $p=3$ ): Figures 4a and b present the simulation obtained by Model N°3b with respect to biosorption equilibrium for calcium alginate and *Sphaerotilus natans* respectively as an example.

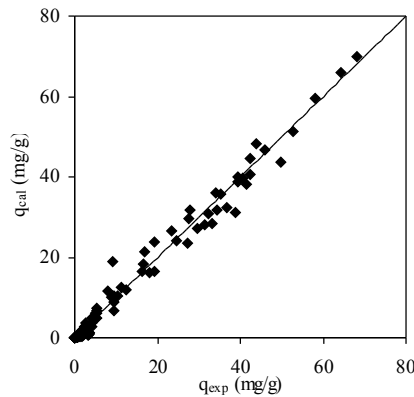


Figure 3. q calculated vs. q experimental values obtained by Model 3a in the data fitting of biosorption results of copper (II) onto *Sphaerotilus natans*

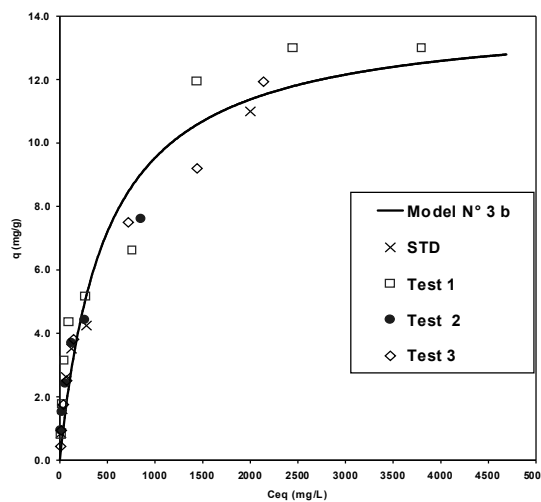


Figure 4a. Simulation results obtained by Model N°3b at pH=4 with respect the adsorption equilibrium results carried out at pH 4.0 with calcium alginate: STD (standard tests - 5ml of beads; pH=4.0; Temperature 22°C); Test 1 (pH-edge test - 5ml of beads; pH=3.9; Temperature 22°C); Test 2 (pH-edge test - 5ml of beads; pH=3.8; Temperature 22°C); Test 3 (pH-edge test - 10ml of beads; pH=3.8; Temperature 22°C) (Vegliò *et al.*, 2002)

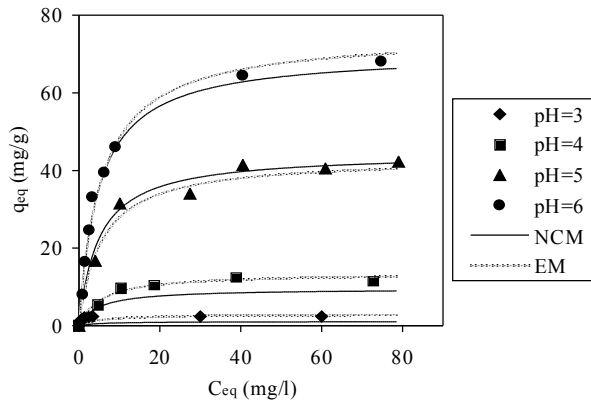


Figure 4b. Empirical (EM) and non-competitive (NCM) pH-related models (Model 2a and 3a respectively) for copper (II) biosorption with 1g/l of *Sphaerotilus natans* concentration (Esposito *et al.*, 2001)

Finally, Figure 5 shows simulation for calcium alginate tests to highlight the effect of pH on copper biosorption, using Model N° 3 b:  $K_s^{app}$  indicated, represent the  $K_s$  Langmuir constant, and its dependence with respect to pH: this dependence is well described by the investigated model N°3 b.

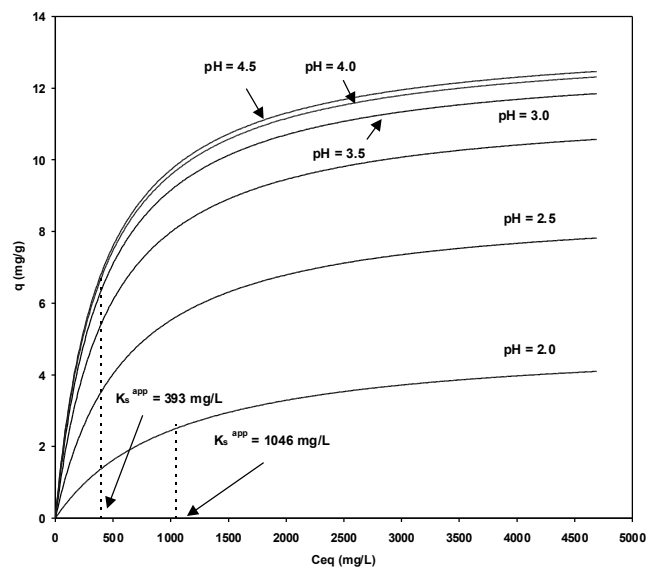


Figure 5. Effect of pH on the copper adsorption on calcium alginate obtained with Model N°3 b (Vegliò *et al.*, 2002)

### 3. CONCLUSIONS

In this paper the experimental results of copper biosorption onto *Sphaerotilus natans* and calcium alginate are summarised to highlight a methodological approach during fitting of copper (II) equilibrium biosorption data, including pH as independent variable of the proposed models. In this manner it is possible to carry out biosorption tests avoiding pH control during the building of an adsorption isotherm by just monitoring the equilibrium pH during the biosorption runs, as obtained in pH edge tests (Vegliò *et al.*, 2002). Moreover it is possible to use more useful equilibrium models that include the pH influence on the biosorption properties of the selected heavy metals. Obviously the empirical models can be built on specific experimental

results so their validity is not general: an example of this approach has been discussed with models 1 and 2a, b. The simple physical model described in equation 3a seems to be more general: in this case the effect of the copper up-take with respect to pH and equilibrium concentration in solution is taken into account in a more satisfactory way for the two different sorbent materials. It is clear that further experimental tests with other biosorbing materials should be investigated to assess and validate the use of the proposed models. In any case, both empirical and semi-empirical models can represent adequately the experimental data and may be useful in the development of mechanistic models (like Surface Complex Model – SCM), permitting a right interpolation of the data results obtained for different equilibrium pH.

## LIST OF SYMBOLS

b	Langmuir constant	(l/mg)
C <sub>eq</sub>	heavy metal equilibrium concentration	(mg/l)
K <sub>s</sub>	Langmuir constant (1/b)	(mg/l)
n	number of experimental points	
p	number of model parameters	
q <sub>max</sub>	maximum heavy metal up-take	(mg/g)
q	equilibrium heavy metal up-take	(mg/g)
S <sup>2</sup> <sub>res</sub>	residual variance	(mg <sup>2</sup> /g <sup>2</sup> )
α <sub>1</sub>	model parameter (Model 1)	(pH <sup>-1</sup> )
α <sub>1</sub>	model parameter (Model 2a, b and 3a, b, c)	(mg/g)
α <sub>2</sub>	model parameter (Model 1)	(pH)
α <sub>2</sub>	model parameter (Model 2a,b)	(pH <sup>-1</sup> )
α <sub>2</sub>	model parameter (Model 3a,b,c)	(eq/l of H <sup>+</sup> )
α <sub>3</sub>	model parameter (Model 1)	(pH)
α <sub>3</sub>	model parameter (Model 2a, b)	(mg/g)
α <sub>3</sub>	model parameter (Model 3a, b, c)	(mg/l)
α <sub>4</sub>	model parameter (Model 1 and 2b)	(pH <sup>-1</sup> )
α <sub>4</sub>	model parameter (Model 2a)	(mg/l)
α <sub>4</sub>	model parameter (Model 3c)	(eq/l of H <sup>+</sup> )
α <sub>5</sub>	model parameter (Model 1 and 2b)	(mg/l)

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