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F. Pagnanelli[a]; A. Esposito[b]; L. Toro[a]; F. Vegliò[b]
[a] Dipartimento di Chimica, Facoltà di S.M.F.N., Università degli Studi "La Sapienza", Roma, Italy [b] Dipartimento di Ingegneria Chimica e di Processo "G.B. Bonino", Università degli Studi di Genova, Genova (Albaro), Italy

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COPPER AND CADMIUM BIOSORPTION ONTO *SPHAEROTILUS NATANS*: APPLICATION AND DISCRIMINATION OF COMMONLY USED ADSORPTION MODELS

F. Pagnanelli,[1],* A. Esposito,[2] L. Toro,[1] and F. Vegliò[2]

[1]Dipartimento di Chimica, Facoltà di S.M.F.N.,
Università degli Studi "La Sapienza", P. le A. Moro 5,
00185 Roma, Italy
[2]Dipartimento di Ingegneria Chimica e di Processo "G.B.
Bonino", Università degli Studi di Genova, via Opera Pia 15,
16145 Genova (Albaro), Italy

ABSTRACT

In this paper, the experimental data of copper and cadmium biosorption onto *Sphaerotilus natans* obtained under different operating conditions of pH (3 ÷ 6 units) and biomass concentration (0.5 ÷ 2 g/L) were reported. These experimental data, showing the good separative performances of *S. natans* and the strong effect of the selected operative factors, were represented by three different empirical models: Langmuir, Freundlich, and Redlich–Peterson isotherms. A statistical representation of the characteristic model parameters (parameter standard deviation and regression coefficient) along with a model discrimination analysis (model residual variance, *F*-test and residual analysis) were proposed in order to suggest a standardized procedure for treating the biosorption data.

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*Corresponding author. E-mail: francesca.pagnanelli@uniroma1.it

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Key Words: Heavy metal biosorption; Langmuir and Freundlich isotherms; Model discrimination

INTRODUCTION

The increase in heavy metal pollution, the more stringent environmental regulation along with the technical and economical inadequacy of the traditional technologies used to remove these pollutants, have focused the attention towards the research of new, economical, and easily available biosorbents. Biosorption of heavy metals is an innovative separation technology using inactive and dead biomasses (bacteria, yeast, fungi, and algae) to remove heavy metals even from very dilute aqueous solutions (1–12).

The complexity of the microorganism structure implies that different biosorption mechanisms can occur such as ion exchange, complexation, physical adsorption, and precipitation (1). Consequently, this biological phenomenon can be affected by many environmental factors such as pH, ionic strength, biomass concentration, temperature, and presence of different heavy metals in solution. All these factors have to be investigated in order to better understand how this phenomenon takes place and to optimize the operating conditions.

In the literature, there are numerous publications on biosorption in which the abilities of many biosorbents are reported in different operating conditions. In spite of this huge biosorption databank, it is quite impossible to compare data reported in the literature concerning the performances of the same sorbent material under different conditions and also those of different sorbents under the same operating conditions.

In many cases the estimated parameters were reported without the relative errors (3,7) and were found by linearizing the employed models (i.e., Langmuir and Freundlich equations) (5,8), while the use of simple mathematical programs (fitting nonlinear equations to data) would permit the evaluation of the characteristic parameters directly along with other important statistic parameters such as parameter standard deviation, residual variance, regression coefficient, skewness, and so on.

Moreover in very few cases (9) a statistical analysis of the possible equilibrium models used for representing the experimental data is reported. Very often one model is chosen among all the possible ones without giving any explanation for the selected choice.

The biosorption performances of a biomass are usually represented in isothermal graphs in which the equilibrium metal specific concentration in the solid phase (milligram of metallic ion per gram of biomass) is reported as a function of the metal equilibrium concentration in solution (milligram of metallic ion per liter of solution). These experimental data are usually represented by various simple empirical models (i.e., Freundlich and Redlich–Peterson isotherms) or by models derived from isotherms originally developed for different systems (i.e., Langmuir isotherm created for gaseous adsorption on planar surfaces) (13).

These models have been widely applied since they are simple, give a good description of the experimental behavior in a large range of operating conditions, and are characterized by a limited number of adjustable parameters.

In this article, the experimental results obtained for copper and cadmium biosorption on *Sphaerotilus natans* in different conditions of pH and biomass concentration (14) were used to propose a simple statistical discrimination analysis of different possible models. This analysis aims to select the most appropriate model among many feasible ones. The best model should satisfy some criteria such as the lowest number of coefficients and the simplest form consistent with reasonable error, rational physical consistency, and the minimum sum of squares of deviations between predicted and empirical values (15). Some simple statistical tools (regression coefficient, model variance, *F*-test, and residual analysis) were used in this paper to discriminate among different commonly used models (9).

MATERIALS AND METHODS

Biomass

S. natans is a gram-negative bacterium isolated from the waste streams of a water purification plant (16). The cultivation medium composition and operative conditions are reported in a previous work (16). The biomass produced was separated by centrifugation, washed by distilled water, lyophilized (17), and stored.

Biosorption Tests

Experimental tests were performed under different operating conditions: pH (levels: 3, 4, 5, and 6 units) and biomass concentration (levels: 0.5, 1.0, and 2.0 g/L) were investigated as factors (14). Two different heavy metals, copper and cadmium ($CuCl_2$ and $CdCl_2$, respectively), were tested for biosorption on *S. natans*. Each isothermal test at a specific condition of pH and biomass concentration was carried out by using an experimental procedure named as subsequent addition method (SAM) (6). This experimental procedure consists of successive spikes of a heavy metal concentrated solution to a cellular suspension kept under magnetic stirring. For each metal addition, residual metal concentration was determined on samples collected after the system has reached an equilibrium condition (30 min). Metal specific uptake q (mmol/g) was calculated by the mass balance of the metallic ion in the system (6,14).

Analytical Procedures

The residual metal concentrations in solution were analyzed by an atomic adsorption spectrophotometer. These analyses were carried out at 327 nm with a flow rate of 7 mL/min; the calibration was performed by using a standard solution, which is diluted by an automatic sampler obtaining 5 points for each calibration curve. The analysis of the metal concentration in solution is based on the mean values of three replicates and after each measure the instrument executes washing for 60 sec by an aqueous solution of hydrochloric acid.

RESULTS

The experimental data used in this paper for statistical data analysis and model discrimination are reported in Table 1 (14): the effect of pH and biomass concentration on copper and cadmium biosorption were already considered without taking into account different possible equilibrium models in data analysis. Therefore a model discrimination analysis was carried out in this paper to evaluate which model represents the experimental data better.

Experimental data of heavy metal biosorption can be represented by different ways, principally classified as empirical and mechanistic models. The empirical models are simple mathematical relationships, characterized by a limited number of adjustable parameters, giving a good description of the experimental behavior in a large range of operating conditions.

The most commonly used empirical adsorption models are the Langmuir, Freundlich, and Redlich–Peterson isotherms (16,18). These models cannot represent the effect of the environmental conditions (such as pH, ionic strength, temperature, and presence of multi-metal system) on biosorption performances, being able to fit only the set of data obtained at constant operating conditions.

A deeper understanding of biosorption phenomenon can be achieved using mechanistic models that are usually based on a preliminary biomass characterization and in the following formulation of a set of hypothesized reactions (ion exchange, complexation, surface micro-precipitation) among the adsorbent sites and heavy metals (6,19), also considering the particular solution chemistry of the metallic species (11,20). Electrostatic property (21) and heterogeneity of the sorbent surface (22) can be also considered in the general formulation of the mechanistic models generating very complicated models with many adjustable parameters.

Anyway the model growing complexity should be based on a wide and deep experimental investigation made up of independent sets of data, avoiding that a better fitting was reached only for the introduction of additional adjustable parameters without understanding and isolating the chemico-physical mechanisms operating.

The complexity of the mechanistic models and the experimental work necessary for their appropriate formulation make the use of the traditional empirical model still very diffuse especially at the first stage of a biosorption study. In this study three different models, largely reported in literature to represent biosorption isotherms, were considered as a case study: Langmuir, Freundlich, and Redlich–Peterson models.

The Langmuir isotherm (23) is the model mainly used (5,6,8,16,18,24) for the representation of biosorption data obtained in constant conditions of pH, ionic strength, and temperature.

The Langmuir model has a theoretical fundament: it hypothesizes chemical and/or physical interactions between solutes and active sites on the adsorbent surface and adsorption heat independent of the fraction of surface covered by the adsorbed solute.

The Langmuir isotherm is given by the following expression (Eq. 1):

$$q_{\mathrm{eq}} = \frac{q_{\max} \cdot b \cdot C_{\mathrm{eq}}}{1 + b \cdot C_{\mathrm{eq}}} \tag{1}$$

where q_{eq} is the adsorption capacity at the equilibrium solute concentration C_{eq} (milligram of solute adsorbed per gram of adsorbent); C_{eq} is the concentration of adsorbate in solution (mg/L); $q_{\max}$ is the maximum adsorption capacity corresponding to complete monolayer coverage (milligram of solute adsorbed per gram of adsorbent); b is a Langmuir constant related to the energy of adsorption (L/mg).

The Freundlich expression (13) is an empirical equation relative to sorption on heterogeneous surface. The Freundlich model can be derived by assuming a logarithmic decrease of the adsorption heat with the covered fraction of surface. The Freundlich equation (Eq. (2)) is commonly presented as (5,8,18):

$$q = K_{\mathrm{F}} \cdot C_{\mathrm{eq}}^{n} \tag{2}$$

where K_{F} and n are the mono-component Freundlich constants, characteristic of the system indicating, respectively, the adsorption capacity and intensity.

A further empirical isotherm (Eq. (3)) has been developed by Redlich and Peterson (5,11), incorporating three parameters to improve the fit by the

Table 1. Experimental Results Obtained for Copper and Cadmium Biosorption Experiments with pH (Levels: 3, 4, 5, and 6) and Biomass Concentration (Levels: 0.5, 1.0, and 2 g/L) as Factors (14)

	Biomass Concentration											
	Copper						Cadmium					
	0.5 g/L		1 g/L		2 g/L		0.5 g/L		1 g/L		2 g/L	
pH	C_{eq} meq/L	Q_{eq} meq/g	C_{eq} meq/L	q_{eq} meq/g	C_{eq} meq/L	Q_{eq} meq/g	C_{eq} meq/L	q_{eq} meq/g	C_{eq} meq/L	Q_{eq} meq/g	C_{eq} meq/L	q_{eq} meq/g
3	0.01	0.02	0.01	0.03	0.06	0.05	0.06	0.02	0.01	0.03	0.05	0.01
	0.01	0.03	0.02	0.05	0.12	0.10	0.09	0.03	0.03	0.04	0.10	0.02
	0.03	0.04	0.04	0.07	0.25	0.11	0.12	0.03	0.05	0.05	0.16	0.02
	0.04	0.05	0.08	0.07	0.42	0.11	0.16	0.04	0.09	0.05	0.23	0.03
	0.05	0.04	0.11	0.07	0.56	0.11	0.19	0.04	0.13	0.04	0.30	0.02
	0.31	0.06	0.43	0.08	0.71	0.11	0.51	0.05	0.16	0.04	0.38	0.02
4	0.01	0.02	0.15	0.17	0.04	0.06	0.06	0.03	0.004	0.028	0.14	0.02
	0.01	0.05	0.32	0.30	0.06	0.13	0.11	0.05	0.004	0.275	0.17	0.09
	0.01	0.08	0.59	0.33	0.17	0.15	0.17	0.07	0.002	0.349	0.19	0.17
	0.02	0.09	1.61	0.42	0.31	0.16	0.24	0.07	0.019	0.393	0.34	0.18
	0.02	0.13			0.44	0.17	0.30	0.08	0.049	0.422	0.49	0.20
	0.03	0.13			0.60	0.17	0.37	0.08	0.080	0.424	0.66	0.20

5	0.01	0.30	0.13	0.53	0.03	0.30	0.02	0.09	0.02	0.15	0.02	0.16
	0.02	0.61	0.32	0.99	0.21	0.53	0.03	0.19	0.08	0.28	0.07	0.30
	0.05	0.88	0.86	1.07	0.44	0.74	0.07	0.26	0.18	0.35	0.22	0.40
	0.05	1.22	1.28	1.31	0.82	0.87	0.10	0.31	0.31	0.39	0.38	0.50
	0.13	1.38	1.92	1.28	1.16	1.02	0.17	0.31	0.46	0.42	0.71	0.51
	0.16	1.66	2.49	1.33	1.67	1.08	0.24	0.31	0.63	0.42	0.98	0.55
					2.16	1.16						
	0.02	0.94	0.05	0.52	0.05	0.57	0.01	0.29	0.05	0.30	0.01	0.37
	0.04	1.24	0.08	0.77	0.08	0.86	0.03	0.39	0.13	0.39	0.03	0.56
	0.05	1.57	0.11	1.04	0.19	1.11	0.07	0.45	0.14	0.57	0.15	0.69
	0.09	1.83	0.20	1.24	0.38	1.33	0.13	0.48	0.38	0.50	0.34	0.78
	0.41	2.76	0.29	1.45	0.91	1.41	0.20	0.48	0.60	0.45		
			0.80	1.89								

Langmuir and Freundlich equations because of the major model flexibility:

$$q = \frac{K_R \cdot C_{eq}}{1 + a_R \cdot C_{eq}^{\beta}} \tag{3}$$

where K_R, a_R and β are the characteristic parameters.

These models have been chosen not only because they are the most used but also in order to compare two- and three-parameter models.

The Langmuir, Freundlich, and Redlich–Peterson models are not linear equations with respect to parameters. Anyway, for the Langmuir and Freundlich isotherms a linear regression can be performed after linearizing the equations. In the case of Langmuir, there are different available forms of linearization (Eqs. (4)–(7)):

$$\frac{C}{q} = \frac{1}{q_{max} \cdot b} + \frac{C}{q_{max}} \quad \text{Langmuir} \tag{4}$$

$$\frac{1}{q} = \frac{1}{q_{max}} + \frac{1}{q_{max} \cdot b} \cdot \frac{1}{C} \quad \text{Lineweaver–Burk} \tag{5}$$

$$q = q_{max} - \frac{1}{b} \cdot \frac{q}{C} \quad \text{Eadie–Hoffstie} \tag{6}$$

$$\frac{q}{C} = b \cdot q_{max} - b \cdot q \quad \text{Scatchard} \tag{7}$$

The calculated values of the two adjustable parameters can change for the same set of experimental data according to the chosen linearized form because of the inappropriate weighing of the experimental error related to each value of the dependent variable during the linear regression. In fact in each linearization the dependent variable and the associated error change requiring appropriate transformation of weighing (25).

In this study a nonlinear least square regression was performed using the SCIENTIST package in which the least squares fitting is performed using a modified Powell algorithm to find a local minimum, possibly the global minimum, of the sum of squared deviations between observed data and model calculations.

Nonlinear regression uses variables without any change with respect to the original nonlinear equation and makes the comparison between experimental and calculated profile easier and more direct (25).

In Fig. 1 an example of the application of the three models to the same set of data is reported.

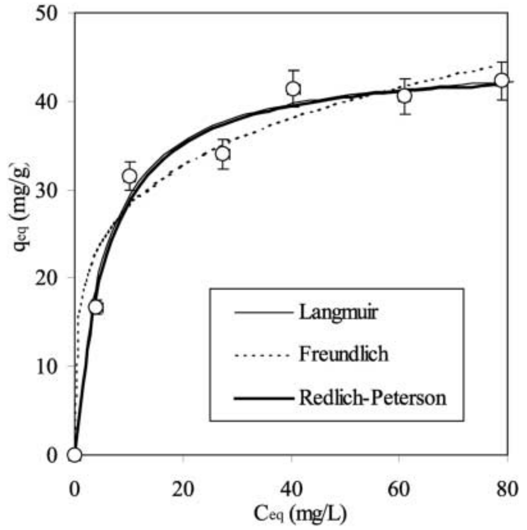

Figure 1. Langmuir, Freundlich, and Redlich–Peterson fittings of cadmium biosorption data at $pH = 5$ with $X = 1\,\mathrm{g/L}$.

The first step of this comparative analysis was the calculation of the characteristic parameters of each analyzed model for copper and cadmium biosorption in different experimental conditions. The SCIENTIST program (26) was used to calculate the parameters, the relative standard deviations, and the regression coefficient R^2 (Eq. 8):

$$R^2 = \frac{\mathrm{SS_R}}{\mathrm{SS_T}} \tag{8}$$

where $\mathrm{SS_R}$ and $\mathrm{SS_T}$ are given by the following expressions (Eqs. 9 and 10):

$$SS_\mathrm{R} = \sum_{i=1}^{n} (q_{i\mathrm{cal}} - q_m)^2 \tag{9}$$

$$SS_\mathrm{T} = \sum_{i=1}^{n} (q_{i\mathrm{exp}} - q_m)^2 \tag{10}$$

where $q_{i\mathrm{cal}}$ and $q_{i\mathrm{exp}}$ are, respectively, the metal specific uptake calculated by the model and experimentally measured, and q_m is the average of the experimental data.

Tables 2–4 show the results of the regression analysis for copper and cadmium biosorption respectively using the Langmuir, Freundlich, and Redlich–Peterson models.

The analysis of these data outputs that both the Langmuir and Freundlich models present low parameter standard deviations never larger than the same parameters, while the Redlich–Peterson model often gives errors exceeding the parameter values.

Table 2. Parameters, Relative Standard Deviations and Regression Coefficients (R^2) for Langmuir Modeling of Copper and Cadmium Biosorption onto *S. natans* at pH 3, 4, 5, and 6 with 0.5, 1.0, and 2.0 g/L of Biomass Concentration (X)

			Langmuir		
Metal	X (g/L)	pH	$q_{max} \pm \sigma_q$ (mg/g)	$b \pm \sigma_b$ (mg/L)	R^2
Copper	0.5	3.0	1.8 ± 0.1	2.6 ± 0.7	0.996
		4.0	12 ± 7	0.6 ± 0.5	0.975
		5.0	64 ± 8	0.7 ± 0.2	0.987
		6.0	(11 ± 3)×10	0.4 ± 0.2	0.983
	1.0	3.0	2.8 ± 0.2	1.9 ± 0.5	0.994
		4.0	11.6 ± 0.8	0.26 ± 0.09	0.993
		5.0	45 ± 2	0.17 ± 0.03	0.997
		6.0	73 ± 9	0.19 ± 0.05	0.994
	2.0	3.0	4.0 ± 0.3	0.5 ± 0.2	0.989
		4.0	5.9 ± 0.4	0.7 ± 0.2	0.992
		5.0	39 ± 3	0.12 ± 0.03	0.992
		6.0	53 ± 2	0.35 ± 0.05	0.996
Cadmium	0.5	3.0	3.3 ± 0.5	0.18 ± 0.06	0.993
		4.0	6.7 ± 0.6	0.11 ± 0.02	0.997
		5.0	21 ± 1	0.5 ± 0.1	0.995
		6.0	27.4 ± 0.6	3.6 ± 0.4	0.998
	1.0	3.0	2.7 ± 0.1	5 ± 2	0.996
		4.0	7 ± 1	6 ± 4	0.931
		5.0	25.6 ± 0.4	0.37 ± 0.03	0.999
		6.0	31 ± 4	0.5 ± 0.2	0.973
	2.0	3.0	1.6 ± 0.2	0.4 ± 0.2	0.987
		4.0	(2 ± 1)×10	0.04 ± 0.04	0.931
		5.0	31 ± 1	0.29 ± 0.05	0.997
		6.0	45 ± 2	1.0 ± 0.2	0.994

Table 3. Parameters, Relative Standard Deviations and Regression Coefficients (R^2) for Freundlich Modeling of Copper and Cadmium Biosorption onto *S. natans* at pH 3, 4, 5, and 6 with 0.5, 1.0, and 2.0 g/L of Biomass Concentration (X)

			Freundlich		
Metal	X (g/L)	pH	$K_F \pm \sigma_{KF}$ (L/g)	$n \pm \sigma_n$	R^2
Copper	0.5	3.0	1.24 ± 0.04	0.39 ± 0.06	0.995
		4.0	4.5 ± 0.3	0.8 ± 0.2	0.975
		5.0	25 ± 3	0.45 ± 0.08	0.983
		6.0	33 ± 3	0.6 ± 0.1	0.974
	1.0	3.0	1.7 ± 0.1	0.31 ± 0.08	0.985
		4.0	6 ± 1	0.16 ± 0.07	0.982
		5.0	15 ± 3	0.24 ± 0.05	0.992
		6.0	13 ± 2	0.58 ± 0.08	0.987
	2.0	3.0	2.0 ± 0.4	0.21 ± 0.08	0.980
		4.0	2.8 ± 0.4	0.24 ± 0.06	0.984
		5.0	9.9 ± 0.5	0.32 ± 0.01	0.999
		6.0	16 ± 1	0.42 ± 0.05	0.985
Cadmium	0.5	3.0	0.6 ± 0.1	0.5 ± 0.1	0.988
		4.0	1.1 ± 0.2	0.48 ± 0.08	0.992
		5.0	8 ± 1	0.32 ± 0.08	0.983
		6.0	18 ± 1	0.20 ± 0.03	0.990
	1.0	3.0	2.2 ± 1	0.09 ± 0.04	0.992
		4.0	5.2 ± 0.6	0.20 ± 0.09	0.942
		5.0	10 ± 1	0.26 ± 0.03	0.996
		6.0	14 ± 4	0.2 ± 0.1	0.949
	2.0	3.0	0.7 ± 0.2	0.2 ± 0.1	0.978
		4.0	2 ± 1	0.6 ± 0.2	0.924
		5.0	11 ± 1	0.26 ± 0.03	0.994
		6.0	22 ± 3	0.25 ± 0.05	0.982

On the other side the R^2 values are very good for all three models underlining that this parameter cannot be considered alone as a useful tool to evaluate if a model represents well the experimental data.

Besides the error parameters, another direct comparison among different models can be obtained by graphing the experimental data vs. the predicted values (scatter diagrams). These diagrams output the spreading of the experimental data with respect to the selected model: the more the model is suitable, the more are the data tightly and symmetrically distributed on the diagonal. In Figs. 2–4 are

Table 4. Parameters, Relative Standard Deviations and Regression Coefficients (R^2) for Redlich–Peterson Modeling of Copper and Cadmium Biosorption onto *S. natans* at pH 3, 4, 5, and 6 with 0.5, 1.0, and 2.0 g/L of Biomass Concentration (X)

			Redlich–Peterson			
Metal	X (g/L)	pH	$K_R \pm \sigma_{KR}$ (L/g)	$a_R \pm \sigma_{aR}$ (L/mg)^f	$\beta \pm \sigma_\beta$	R^2
Copper	0.5	3.0	6 ± 4	3.5 ± 3.5	0.8 ± 0.3	0.996
		4.0	$(1 \pm 5) \times 10$	1 ± 12	0.5 ± 2	0.975
		5.0	$(5 \pm 3) \times 10$	0.8 ± 1	1.0 ± 0.5	0.987
		6.0	35 ± 4	0.003 ± 0.03	5 ± 10	0.992
	1.0	3.0	3.5 ± 0.7	0.8 ± 0.4	1.4 ± 0.2	0.997
		4.0	1.7 ± 0.3	0.05 ± 0.03	1.2 ± 0.1	0.998
		5.0	7 ± 3	0.2 ± 0.1	1.0 ± 0.1	0.997
		6.0	11 ± 2	0.03 ± 0.05	1.6 ± 0.6	0.996
	2.0	3.0	1.2 ± 0.3	0.09 ± 0.08	1.4 ± 0.2	0.995
		4.0	3 ± 1	0.4 ± 0.4	1.1 ± 0.2	0.993
		5.0	$(7 \pm 9) \times 10$	7 ± 10	0.70 ± 0.03	0.999
		6.0	15 ± 2	0.18 ± 0.09	1.2 ± 0.2	0.997
Cadmium	0.5	3.0	0.37 ± 0.04	0.003 ± 0.005	2.5 ± 0.7	0.998
		4.0	0.5 ± 0.6	0.005 ± 0.003	1.8 ± 0.2	0.999
		5.0	7.0 ± 0.7	0.12 ± 0.05	1.4 ± 0.1	0.999
		6.0	$(12 \pm 2) \times 10$	5 ± 1	0.96 ± 0.03	0.999
	1.0	3.0	7 ± 2	1.9 ± 0.9	1.12 ± 0.08	0.987
		4.0	$2 \times 10^5 \pm 3 \times 10^7$	$5 \times 10^3 \pm 6 \times 10^6$	0.8 ± 0.3	0.942
		5.0	11 ± 1	0.5 ± 0.1	0.94 ± 0.03	0.999
		6.0	7 ± 2	0.06 ± 0.07	1.4 ± 0.3	0.986
	2.0	3.0	0.26 ± 0.03	0.012 ± 0.009	1.9 ± 0.2	0.998
		4.0	0.6 ± 0.2	$3 \times 10^{-5} \pm 4 \times 10^{-4}$	3 ± 3	0.942
		5.0	14 ± 4	0.6 ± 0.3	0.99 ± 0.05	0.999
		6.0	$(5 \pm 2) \times 10$	1.0 ± 0.7	1.0 ± 0.1	0.994

reported the scatter diagrams for copper and cadmium biosorption modeled by the Langmuir, Freundlich, and Redlich–Peterson equations.

These graphs output that no significant difference can be detected between these models and copper data seem to be always more dispersed than those for cadmium.

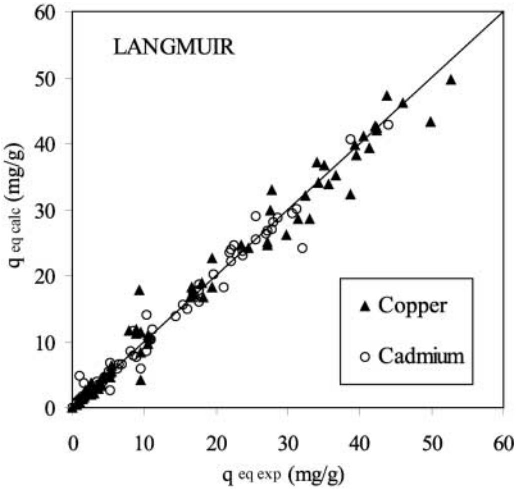

Figure 2. Scatter diagram for Langmuir fitting of copper and cadmium biosorption data onto *S. natans* at pH 3, 4, 5, and 6 with 0.5, 1.0, and 2.0 g/L of biomass concentration.

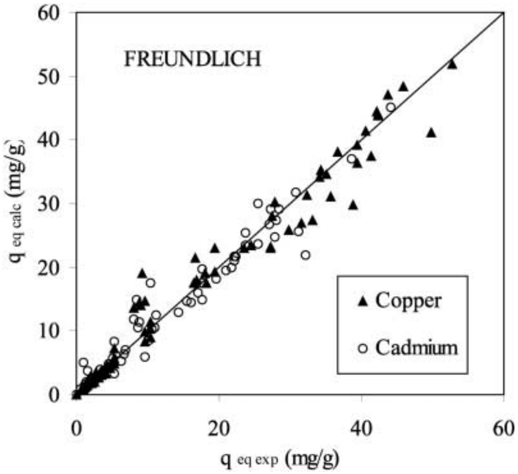

Figure 3. Scatter diagram for Freundlich fitting of copper and cadmium biosorption data onto *S. natans* at pH 3, 4, 5, and 6 with 0.5, 1.0, and 2.0 g/L of biomass concentration.

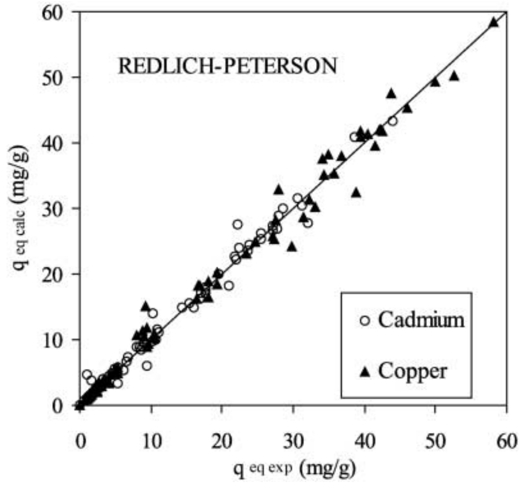

Figure 4. Scatter diagram for Redlich–Peterson fitting of copper and cadmium biosorption data onto *S. natans* at pH 3, 4, 5, and 6 with 0.5, 1.0, and 2.0 g/L of biomass concentration.

The residual variance S_R^2 (Eq. 11) is a quantitative measure of the deviation between experimental and predicted values:

$$S_{\mathrm{R}}^2 = \frac{\sum_{i=1}^{n} (q_{i\mathrm{exp}} - q_{i\mathrm{cal}})^2}{n - p} \tag{11}$$

where $q_{i\mathrm{cal}}$ and $q_{i\mathrm{exp}}$ are, respectively, the metal specific uptake calculated by the model and measured experimentally, n is the total number of experimental point and p is the number of estimated parameters.

The model residual variances for Langmuir, Freundlich, and Redlich–Peterson are reported in Table 5: as a general observation no apparent significant difference can be evidenced between the models even though the mean values of the residual variances (S_{RM}^2) change for each model in the following growing order: Redlich–Peterson ($S_{\mathrm{RM}}^2 = 2.999$) < Langmuir ($S_{\mathrm{RM}}^2 = 4.611$) < Freundlich ($S_{\mathrm{RM}}^2 = 8.203$).

In order to determine the statistical significance of the model variance, an F-test can be carried out evaluating and comparing the calculated F values (Eq. 12) with the tabulated ones:

$$F_{\mathrm{cal}} = \frac{S_{\mathrm{R}}^2}{S_{\mathrm{E}}^2} \tag{12}$$

S_R^2 is the model variance (Eq. 11) and S_E^2 is the error variance (Eq. 13):

$$S_E^2 = \frac{\sum_{j=1}^{m} (q_j - q_m)}{m - 1} \tag{13}$$

where m is the number of replicates, q_m is the average value of q_j at a certain value of metal concentration C_i.

The error variance was calculated by replicated tests (with 5 degrees of freedom), and the related σ_e (standard error) was considered constant and estimated to be 10 % of the experimental values.

If $F_{cal} = S_R^2/S_E^2$ is greater than $F_{1-\alpha}$, the variance due to the model is significantly different with respect to the error variance for the selected level of significance. The F-test on the variance ratio can demonstrate if the S_R^2 value is only due to the statistical random error ($F_{cal} < F_{1-\alpha}$) or if there is also a systematic contribution due to an incorrect model used for biosorption data ($F_{cal} > F_{1-\alpha}$).

In Table 5 the calculated F values (Eq. 12) for the Langmuir and Freundlich models are reported along with the tabulated F values for a certain level of significance ($1 - \alpha = 0.90$) and the relative degrees of freedom (number of data less than the number of estimated parameters).

By analysing Table 5 it is possible to see that using the Langmuir, Freundlich, and Redlich–Peterson equations, the model variances are not significant in all the tested conditions, so these models can be considered suitable to represent the experimental data.

Nevertheless it is possible to see that F calculated values in (Table 5), are generally minor than one: this means that the model residual variances are less significant than the variance due to the experimental errors. This observation indicates that a model is able to fit not only the data profile but also the experimental error fluctuations. In these conditions the use of a more flexible model as the three-parameter Redlich–Peterson one seems to be useless because the two-parameters models already present F values less than one.

A model could pass the F-test ($F_{cal} < F_{1-\alpha}$) even if important discrepancies can still exist. The analysis of the residuals (Eq. 14) examining the deviations between experimental and predicted values can detect the presence of such discrepancies.

$$z_i = \frac{q_{i\text{cal}} - q_{i\text{exp}}}{\sqrt{S_R^2}} \tag{14}$$

If a model fits well the experimental data, the residuals should be randomly distributed, while systematic deviations indicate that the model may be not a

Table 5. Model Residual Variances (S_R^2), Degree of Freedom (df), Calculated and Tabulated Values (F_{cal} and $F_{1-\alpha}$) for the Langmuir, Freundlich, and Redlich–Peterson Modeling of Copper and Cadmium Biosorption onto *S. natans* at pH 3, 4, 5, and 6 with 0.5, 1.0, and 2.0 g/L of Biomass Concentration (X)

				Langmuir		Freundlich		Redlich–Peterson		
Metal	X (g/L)	pH	df	S_R^2 (mg/L)	F_{cal} S_R^2/S_E^2	S_R^2 (mg/L)	F_{cal} S_R^2/S_E^2	S_R^2 (mg/L)	F_{cal} S_R^2/S_E^2	$F_{1-\alpha=0.90}$
Copper	0.5	3.0	4	0.007	0.208	0.009	0.262	0.006	0.193	3.520
		4.0	6	0.331	0.230	0.329	0.228	0.327	1.634	3.405
		5.0	5	18.662	0.456	25.456	0.621	18.624	14.550	3.453
		6.0	5	30.396	0.251	45.832	0.379	13.610	6.187	3.520
	1.0	3.0	4	0.026	0.328	0.068	0.871	0.012	0.168	3.520
		4.0	4	0.790	0.587	2.010	1.494	0.224	0.771	3.453
		5.0	5	5.162	0.255	12.682	0.626	5.137	5.707	3.453
		6.0	5	6.778	0.127	14.458	0.271	4.459	3.054	3.453
	2.0	3.0	5	0.130	0.810	0.240	1.500	0.061	0.763	3.453
		4.0	5	0.200	0.573	0.387	1.111	0.178	1.510	3.453
		5.0	6	6.523	0.429	0.754	0.050	0.668	1.028	3.405
		6.0	9	3.913	0.139	13.469	0.479	3.086	5.240	3.316

Cadmium	0.5	3.0	5	0.023	0.213	0.041	0.375	0.007	0.112	3.453
		4.0	5	0.043	0.095	0.120	0.267	0.005	0.039	3.453
		5.0	5	1.260	0.286	4.428	1.004	0.262	0.624	3.453
		6.0	5	0.908	0.121	5.620	0.749	0.641	1.170	3.453
	1.0	3.0	5	0.031	0.425	0.057	0.787	0.019	0.359	3.453
		4.0	5	2.362	4.821	1.983	4.046	1.983	14.164	3.453
		5.0	5	0.194	0.030	2.014	0.307	0.081	0.158	3.453
		6.0	5	17.910	1.864	33.658	3.502	9.499	15.320	3.453
	2.0	3.0	5	0.023	0.883	0.038	1.492	0.000	0.013	3.453
		4.0	5	6.386	1.597	7.136	1.784	5.369	13.423	3.453
		5.0	5	1.691	0.176	3.728	0.388	0.809	1.304	3.453
		6.0	4	6.910	0.341	22.368	1.105	6.909	6.142	3.520

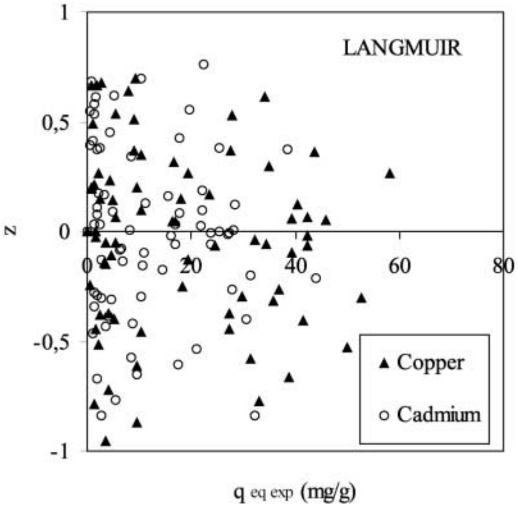

Figure 5. Residual distribution for Langmuir fitting of copper and cadmium biosorption data onto *S. natans* at pH 3, 4, 5, and 6 with 0.5, 1.0, and 2.0 g/L of biomass concentration.

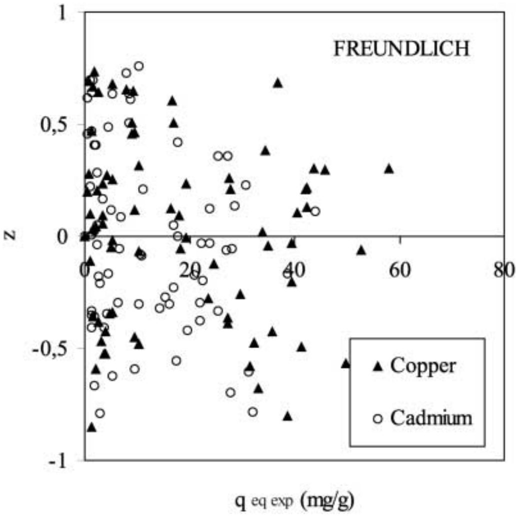

Figure 6. Residual distribution for Freundlich fitting of copper and cadmium biosorption data onto *S. natans* at pH 3, 4, 5, and 6 with 0.5, 1.0, and 2.0 g/L of biomass concentration.

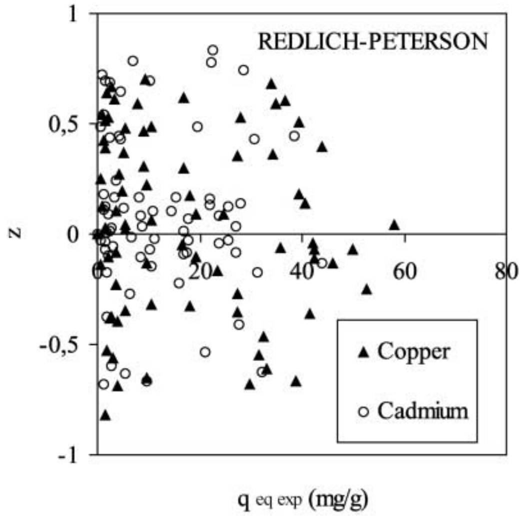

Figure 7. Residual distribution for Redlich–Peterson fitting of copper and cadmium biosorption data onto *S. natans* at pH 3, 4, 5, and 6 with 0.5, 1.0, and 2.0 g/L of biomass concentration.

good representation for the set of data. The residual patterns could also be used to improve and optimize a model.

In Figs. 5–7 the residuals calculated for the tested models were reported as a function of the calculated value of the metal specific uptake. It is possible to see that all the models present z residuals ranging from -2 to +2, but considering the ideal random distribution the Langmuir model seems to be the best one. In fact the Freundlich model presents a z distribution shifted to positive values for copper (as for Redlich–Peterson) and to negative ones for cadmium.

A quantitative measure of the asymmetry of the z residual distribution is the skewness α_3 defined as follow (Eq. 15):

$$\alpha_3 = \frac{\mu_3}{\sigma^3} \tag{15}$$

where μ_3 is the third order moment and σ^3 is the standard deviation (15).

The skewness values are reported in Table 6 for the Langmuir, Freundlich, and Redlich–Peterson models in all the tested conditions. The analysis of these data outputs that considering the single data set for each tested condition of pH and biomass concentration the skewness values between -1 and +1 can be considered not significant; while outranging values indicate the likelihood of a few large positive ($z_i > 1$) or negative ($z_i < -1$) residuals having an undue effect

Table 6. Skewness Values for Langmuir, Freundlich, and Redlich–Peterson Modeling of Copper and Cadmium Biosorption onto *S. natans* at pH 3, 4, 5, and 6 with 0.5, 1.0, and 2.0 g/L of Biomass Concentration (X)

Metal	pH	$X = 0.5$ g/L	$X = 1.0$ g/L	$X = 2.0$ g/L
Langmuir				
Copper	3.0	−1.37	0.46	−0.22
	4.0	1.15	−0.04	−0.10
	5.0	−0.42	0.16	−3.73
	6.0	1.02	−0.21	1.15
Cadmium	3.0	−1.07	−2.56	0.93
	4.0	1.97	−1.11	0.71
	5.0	0.43	−0.54	1.59
	6.0	1.25	−2.52	0.96
Freundlich				
Copper	3.0	−1.52	0.31	0.29
	4.0	0.71	0.67	1.15
	5.0	−1.98	−0.11	−1.41
	6.0	0.52	−0.15	0.55
Cadmium	3.0	0.85	−1.94	1.04
	4.0	1.53	0.37	0.63
	5.0	0.64	1.45	−0.08
	6.0	1.62	−1.55	0.92
Redlich–Peterson				
Copper	3.0	−1.87	0.66	0.56
	4.0	0.89	−0.28	−0.55
	5.0	−0.59	0.49	−0.88
	6.0	0.21	0.33	1.86
Cadmium	3.0	−1.06	−0.14	−0.52
	4.0	−0.62	0.37	0.45
	5.0	−0.20	−1.03	−1.04
	6.0	−0.36	0.23	0.94

on the fit. The skewness values reported in Table 6 permit one to evaluate the model goodness for each one of the tested conditions. The general patterns of the residuals for copper and cadmium (Fig. 5–7) are not confirmed for the single set of data showing the importance of comparing quantitatively the residual distribution characteristics in each experimental condition. Also in this case it is not possible to discriminate between the Langmuir and Freundlich models: it can be concluded that in the tested conditions both models are suitable to represent the experimental data.

CONCLUSIONS

In this paper three commonly used adsorption models (Langmuir, Freundlich, and Redlich–Peterson) were applied to represent biosorption of copper and cadmium onto a biomass in different operating conditions.

A simple statistical procedure is applied in order to evaluate which one of the tested model represents the experimental data better. The first analysis of the parameter standard deviations outputs that the three-parameters model (Redlich–Peterson) is not useful to represent the data according to the principle that a model should have the minimum number of adjustable parameters consistent to acceptable errors. In this case two-parameter models (Langmuir and Freundlich) fit the experimental data even better than the Redlich–Peterson model, which presents parameter deviations greater than the same parameter values. The comparison between the three models also underlines the uselessness of the regression coefficients in comparing these models. The comparison among the models was also carried out by considering the deviations between experimental and predicted values in a qualitative (the scatter diagrams) and also quantitative (residual variances and *F*-test) way. Both scatter diagrams and *F*-test were not able to discriminate between Langmuir and Freundlich models; anyway using a three-parameter model, such as Redlich–Peterson one, seems to be useless because model residual variances are even smaller than the error variances

The analysis of the residual distribution using residual graphs outputs a less random distribution in the case of the Freundlich model considering all the data of copper and cadmium. Anyway, the skewness values relative to each set of data obtained in different operating conditions of pH and biomass concentration do not permit one to discriminate between the models. Considering these results, both the Langmuir and Freundlich models are suitable to describe the reported experimental data. Moreover the results here reported show the suitability of *S. natans* as a potentially useful biosorbent material for heavy metal separation processes from contaminated industrial waters, although further work is in progress in order to evaluate this possibility.

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