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Predictive Modeling of Competitive Biosorption Equilibrium Data

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Abstract This paper compares regression and neural network modeling approaches to predict competitive biosorption equilibrium data. The regression approach is based on the fitting of modified Langmuir-type isotherm models to experimental data. Neural networks, on the other hand, are non-parametric statistical estimators capable of identifying patterns in data and correlations between input and output. Our results show that the neural network approach outperforms traditional regression-based modeling in correlating and predicting the simultaneous uptake of copper and cadmium by a microbial biosorbent. The neural network is capable of accurately predicting unseen data when provided with limited amounts of data for training. Because neural networks are purely data-driven models, they are more suitable for obtaining accurate predictions than for probing the physical nature of the biosorption process.

Keywords: adsorption, biosorption, modeling, multicomponent isotherm, neural network

INTRODUCTION

Biosorption is a novel environmental technology that employs microbial or plant biomass for the cleanup of metal-bearing industrial wastewaters [1]. The basis of metal biosorption has been attributed to the existence of a myriad of surface ligands like carboxyl, sulfate, amino, and hydroxyl moieties. These ligands differ in their affinity and specificity for metal binding. As a result, biosorption is a non-specific process. A given biomass will bind more than one metal ion when exposed to industrial waste streams that typically contain several metal ions. Hence, equilibrium and kinetic data obtained from single metal systems is of limited practical use. Reliable data on multimetal systems is essential for process design and optimization.

Despite the practical importance of multimetal biosorption, very few studies have addressed the measurement of multimetal equilibrium data. This is because the conventional batch techniques for generating such data are very laborious, time consuming, and require large amounts of toxic chemicals due to the numerous possible combinations of metal ions and biomass species. One way to reduce extensive manual manipulation is to use modeling tools to predict biosorption equilibrium data. Because metal biosorption is a non-specific process with each metal binding site being able to take up any number of metal species, competition for binding sites among metal species within a mixed metal solution is likely. Indeed, most of the reported results show that the uptake of a particular metal ion from a multimetal system was reduced when compared to uptake obtained from single metal solutions, reflecting the presence of competitive binding [2-7].

Various equilibrium isotherm models, usually of the regression form, are available for describing competitive biosorption. In most cases the measured data can be successfully described using simple extensions of classical isotherm models such as the Langmuir or Freundlich model. An adequate body of work on the use of such empirical isotherm models to describe the effect of competition on metal biosorption exists in the literature [8-11]. However, most of these studies have treated the models as mathematical functions for *correlating* measured data where model calibration is based on all available experimental data. The ability of these models to *predict* unseen data (*i.e.*, data not used for curve fitting/model calibration) has not been adequately established.

Recently, there has been a growing interest in applying novel modeling techniques such as artificial neural networks to the area of biosorption [12-14]. The predictive power of neural networks stems from their ability to correlate data without prior knowledge of the physical characteristics and mechanisms of the system under investigation. This work compares the ability of two different approaches based on Langmuir-type and neural network models to predict published equilibrium data on the simultaneous biosorption of copper and cadmium by a microbial biosorbent [2].

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METHODS

Regression Modeling

Various isotherm models based on the adaptations of single-component Langmuir and Freundlich equations have been used by researchers to describe competitive biosorption equilibrium data. For example, the extended Langmuir-Freundlich isotherm model has been used successfully as an empirical equation for describing competitive equilibrium data. The model equations for a binary metal system are

$$q_1 = \frac{q_{m1} b_1 C_1^{1/n_1}}{1 + b_1 C_1^{1/n_1} + b_2 C_2^{1/n_2}} \qquad q_2 = \frac{q_{m2} b_2 C_2^{1/n_2}}{1 + b_1 C_1^{1/n_1} + b_2 C_2^{1/n_2}} \tag{1}$$

where q and C are the metal concentration in the biosorbent and solution at equilibrium, respectively, q_m is the maximum sorption capacity of the biosorbent, b is the apparent affinity constant, and n is the Langmuir-Freundlich exponent. A nonlinear least-squares regression program predicated on the Levenberg-Marquardt method was used to fit Eq. (1) to experimental equilibrium data reported by Pagnanelli *et al.* [2].

Neural Network Modeling

A neural network is a mathematical representation of the brain's neurological functioning. It simulates the brain's learning process by mathematically modeling the network structure of interconnected nerve cells. Because neural networks operate directly on input-output data, the essential requirement for neural network modeling is sufficient amounts of data. A neural network is thus a purely data-driven model made up of interconnected processing elements called neurons that are organized in layers [15].

A typical neural network has an input layer, one or more hidden layer, and an output layer. The neurons in the hidden layer, which are linked to the neurons in the input and output layers by adjustable weights, enable the network to compute complex associations between the input and output variables. The inputs of the neurons in the hidden and output layers are summed and the resulting summation is processed by an activation function. A nonlinear sigmoid function is commonly used as an activation function in neural network modeling. The process of determining the adjustable weights is known as training and it is analogous to the process of determining the adjustable parameters of an isotherm model by regression. The weights are initially selected random and an iterative algorithm is then used to find weights that minimize differences between the network-calculated and actual outputs. The most commonly used algorithm is the backpropagation algorithm. In this training algorithm, the error between the results of the output neurons and the actual output is calculated and propagated backward through the network. The algorithm adjusts the weights in each successive layer to reduce the error. This procedure is repeated until the error between the actual and network-calculated output satisfies a prespecified error criterion. Neural network modeling is thus a curve fit in multidimensional space.

Table 1. Configuration of the feedforward neural network

Number of hidden layers	1
Number of hidden neurons	10
Activation function	Sigmoid
Training algorithm	Backpropagation
Training parameters	
Learning rate	0.2
Momentum	0.5

In general, feedforward neural networks with one hidden layer containing a sufficiently large number of hidden neurons have been shown to be capable of providing accurate approximations for any continuous nonlinear function [16]. Because no specific guidelines exist for choosing the optimal number of hidden neurons for a given problem, this network parameter is often optimized according to some empirical rules combined with trial and error. In this work, a neural network model with a single hidden layer was developed using Matlab v6.5 under the Windows NT environment. The optimal number of neurons in the hidden layer was determined using an empirical approach based on the concept of incremental pruning. A series of neural networks with increasing number of hidden neurons were constructed and trained. It was found that the error between the actual and network-calculated outputs reached a minimum value for neural networks with 10 or more hidden neurons. To avoid the pitfall of overfitting of data, the number of hidden neurons was limited to 10. Table 1 reports the configuration of the neural network used in this work.

RESULTS AND DISCUSSION

Published data on the simultaneous biosorption of copper and cadmium by *Arthrobacter* sp. biomass [2] was selected for modeling in this work. The numerical data at two pH levels is reproduced here in Table 2. The results suggest that the main effect observed for the simultaneous biosorption data was a reduction in the uptake of one metal in the presence of the other when compared to the single-metal biosorption of either metal. Simulation results obtained from modified Langmuir-type models suggest that the uptake of cadmium was markedly inhibited in the presence of copper whereas the biosorption of copper was not greatly reduced by the presence of cadmium [2]. Mutual suppression of uptake is commonly observed in two-metal systems due to competition between the metal ions for the same surface binding sites.

To assess the relative performance of the two modeling approaches the data patterns in Table 2 were split into two categories. The data patterns used to optimize the adjustable parameters of the Langmuir-Freundlich equation and the weights of the neural network were termed

Table 2. Experimental data from Pagnanelli *et al.* [2] for the biosorption of copper and cadmium on *Arthrobacter* sp. at two pH levels

Data pattern	C_{Cu} (mmol/L)	C_{Cd} (mmol/L)	q_{Cu} (mmol/g)	q_{Cd} (mmol/g)
pH 4				
1	0.282	0.358	0.026	0.016
2	0.833	0.926	0.053	0.026
3	1.146	1.220	0.051	0.027
4	1.717	1.814	0.058	0.026
5	0.396	0.567	0.042	0.025
6	0.396	0.567	0.040	0.023
7	1.287	0.566	0.063	0.025
8	0.374	2.211	0.042	0.028
9	0.822	2.243	0.056	0.029
10	0.125	0.254	0.024	0.017
11	0.366	0.895	0.037	0.024
12	1.237	0.125	0.061	0.017
13	0.894	1.570	0.054	0.025
14	1.562	0.237	0.063	0.021
15	2.012	1.236	0.071	0.027
16	1.434	1.508	0.056	0.028
17	0.562	0.631	0.040	0.021
18	0.828	1.109	0.051	0.026
pH 5				
19	0.193	0.331	0.060	0.016
20	0.475	0.630	0.075	0.024
21	1.041	1.235	0.101	0.029
22	1.303	1.530	0.119	0.028
23	1.590	1.837	0.123	0.033
24	0.559	0.482	0.080	0.020
25	1.012	0.546	0.109	0.019
26	1.442	0.568	0.120	0.018
27	0.321	1.006	0.049	0.040
28	1.062	1.148	0.110	0.029
29	0.523	0.326	0.075	0.015
30	0.155	0.266	0.040	0.018
31	0.325	1.256	0.053	0.032
32	1.569	2.145	0.145	0.036
33	2.015	0.124	0.165	0.006
34	0.856	1.256	0.094	0.032
35	0.748	0.938	0.085	0.025
36	0.323	1.558	0.054	0.038
37	1.236	0.326	0.123	0.015

the "calibration" or "training" set (data patterns 1-15 and 19-34) while the data patterns used to evaluate the predictive capability of the two models were called the "validation" or "test" set (data patterns 16-18 and 35-37). Interpolative predictions of the two modeling approaches over the validation/test data sets are reported in the next section.

Regression Modeling

Because of limited data patterns in the calibration sets and the fact that Eq. (1) contains five adjustable parameters, satisfactory convergence in the curve fitting exercise was not always achieved. To ensure convergence, the

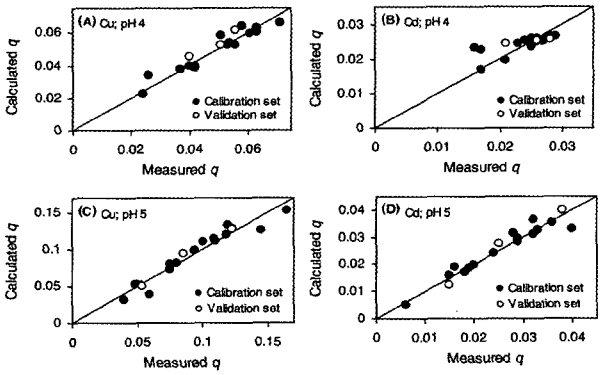

Fig. 1. Copper and cadmium uptake values calculated by Eqs. (2) and (3) versus actual uptake values at pH 4 (A and B) and pH 5 (C and D).

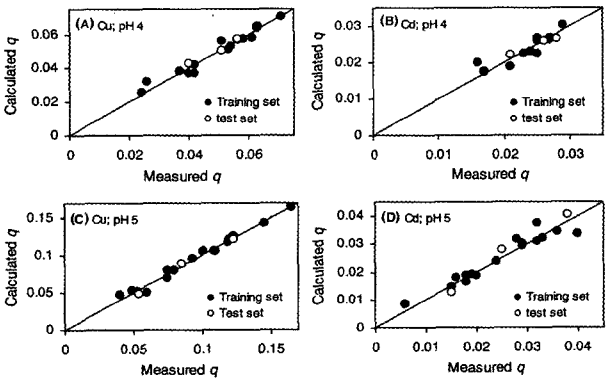

Fig. 2. Neural network-calculated copper and cadmium uptake values versus actual uptake values at pH 4 (A and B) and pH 5 (C and D).

functional form of the extended Langmuir-Freundlich model was modified. The resulting best-fit equations are simple variants of Eq. (1):

$$\text{pH 4:}\quad q_{Cu}=\frac{0.132C_{Cu}^{0.51}}{1+0.4C_{Cu}+C_{Cd}^{0.001}} \qquad q_{Cd}=\frac{C_{Cd}^{1.12}}{1+38.08C_{Cd}+C_{Cu}} \tag{2}$$

$$\text{pH 5:}\quad q_{Cu}=\frac{0.251C_{Cu}}{1+1.128C_{Cu}+0.167C_{Cd}} \qquad q_{Cd}=\frac{0.08C_{Cd}^{0.82}}{1+C_{Cd}^{0.82}+C_{Cu}^{0.73}} \tag{3}$$

Fig. 1 displays the experimental values of q_{Cu} and q_{Cd} belonging to the calibration data sets (solid circles) and the validation data sets (open circles) versus the corresponding values calculated by Eqs. (2) and (3). The criterion for measuring the accuracy of Eqs. (2) and (3) is the mean absolute relative error (MARE):

$$\text{MARE}\,(\%)=\frac{100}{m}\sum_{k=1}^{m}\frac{|q_{exp,k}-q_{cal,k}|}{q_{exp,k}} \tag{4}$$

Table 3. MARE from Eqs. (2) and (3) and the 3-10-2 neural network for correlating and predicting the data patterns listed in Table 2

Model	MARE (%)			
	pH 4		pH 5	
	Cu	Cd	Cu	Cd
Part A: Eqs. (2) and (3)				
Calibration/training set	6.7	9.5	8.4	6.7
Validation/test set	9.3	9.1	7.0	10.8
Part B: neural network				
Calibration/training set	5.3	5.6	4.9	8.4
Validation/test set	3.4	3.5	5.3	10.9

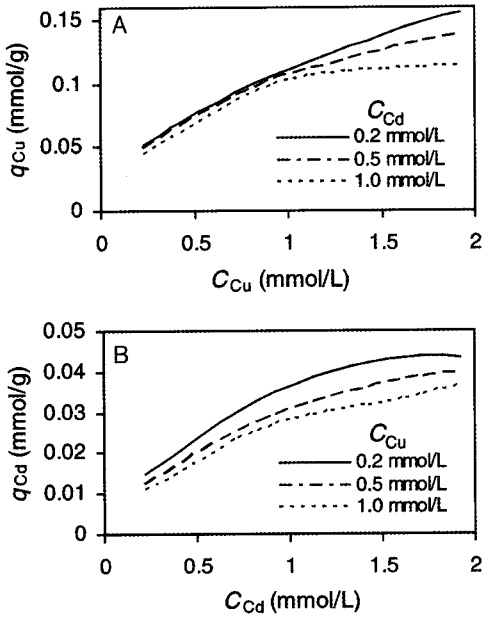

Fig. 3. Neural network-calculated competitive isotherms for the binary metal system at pH 5. (A) The effect of cadmium on the equilibrium isotherms for copper; (B) The effect of copper on the equilibrium isotherms for cadmium.

where q_{exp} represents experimental data, q_{cal} refers to model calculation, and m is the number of data patterns. The MARE in the two equations' estimates of q_{Cu} and q_{Cd} are tabulated in part A of Table 3. A line of unit slope, *i.e.*, the line of perfect fit with points corresponding to zero MARE is also shown in Fig. 1. The data point scatter of the regression modeling approach can be clearly seen in Fig. 1.

Neural Network Modeling

The feedforward neural network developed in this work consisted of a single hidden layer with 10 neurons, three input neurons representing the two solution phase equilibrium concentrations (the independent variables in the extended Langmuir-Freundlich equation: C_{Cu} and C_{Cd}) and pH, and two output neurons representing the two biosorbent phase equilibrium concentrations (the dependent variables in the extended Langmuir-Freundlich equation: q_{Cu} and q_{Cd}). The topology of the neural network is designated 3-10-2 (3 input neurons-10 hidden neurons-2 output neurons). The network was trained using the training data sets (data patterns 1-15 and 19-34). Its predictive capability was assessed using the test data sets (data patterns 16-18 and 35-37). Fig. 2 shows the network-calculated output for the training and test data sets plotted against the corresponding experimental data. The solid circles represent the network-*trained* output while the open circles denote the network-*predicted* output for input variables belonging to the test sets. The neural network model not only fit the training data very well but also provided predictions for test data that were very close to those measured experimentally. The MARE values for the training and test sets are listed in part B of Table 3.

Table 3 indicates that the neural network outperforms Eqs. (2) and (3) in terms of MARE in all but one case. The reductions in MARE achieved by the neural network predictions over the regression predictions are in the range of 1.7~5.9%. These numbers translate into improvements of 24~63% in prediction accuracy. Comparison of Figs. 1 and 2 confirms the tendency of the neural network's predictions to be closer to the line of perfect prediction than those of regression. These results establish the effectiveness of the neural network approach as a predictive modeling strategy for competitive biosorption equilibrium data.

From a practical standpoint, the ability of neural networks to predict multimetal equilibrium data could significantly reduce the amount of experimentation required for biosorption studies. A suitably trained neural network with good predictive capability for interpolation can be used to generate highly accurate q versus C isotherm plots. For example, the 3-10-2 neural network can be used to generate the competitive equilibrium isotherms shown in Fig. 3. The extent of competitive biosorption in the binary metal system can be easily deduced from Fig. 3 but it is not immediately apparent from the numerical data tabulated in Table 2. Generating competitive isotherms experimentally using conventional batch techniques is not an easy task, because it is not possible to control the equilibrium concentrations of metal ions. As a result, such studies often yield a collection of paired equilibrium data points with each point lying on a different

isotherm. This is the reason why multimetal biosorption data is often reported in tabular form.

CONCLUSION

We have demonstrated the application of regression and neural network models to a two-metal biosorption system and found the neural network modeling approach to be superior to the regression modeling approach based on modified Langmuir-type models. The neural network trained with limited amounts of data is able to capture the nonlinear and interacting relationships between equilibrium concentrations in the solution and biosorbent phases. For this reason, neural network modeling serves as a viable alternative to the traditional regression modeling approach and holds considerable promise for the study of multimetal biosorption systems. However, it should be noted that neural networks are better at interpolation than extrapolation due to their empiricism.

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