X Encontro Brasileiro sobre Adsorção
27 a 30 de Abril de 2014
Guarujá - SP

PREDICTION OF ION EXCHANGE EQUILIBRIUM OF Cu^{2+}-Na^{+}-Zn^{2+} TERNARY SYSTEM USING ARTIFICIAL NEURAL NETWORKS

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ABSTRACT: The Law of Mass Action (LMA) is generally used to describe the equilibrium of ion exchange processes. This is a rigorous methodology in terms of thermodynamics that considers the non-idealities in the solid and solution phases. However, Artificial Neural Networks (ANNs) can also be effectively used in phase equilibrium modeling. In the current study, ANNs were used to describe the ion exchange equilibrium in the binary systems Cu^{2+}-Na^{+}, Zn^{2+}-Na^{+} and Cu^{2+}-Zn^{2+} and in the ternary system Cu^{2+}-Na^{+}-Zn^{2+}, using the resin Amberlite IR 120 as ion exchanger. The datasets used in the training stage of the ANNs in this study were generated by the application of the LMA on the binary systems. Results showed that, in the equilibrium modeling of the binary systems and in the prediction of the ternary system, both methodologies had similar performance and can be used to describe binary and ternary equilibrium.

KEYWORDS: artificial neural networks (ANNs); law of mass action (LMA); ion exchange; heavy metals.

1. INTRODUCTION

The release of heavy metals, such as zinc and copper, into the natural environment is one of the main causes of industrial pollution and has resulted in a number of environmental problems. Heavy metals have a cumulative effect and cannot be degraded nor destroyed. (Anirudhan and Suchithra, 2010). Moreover, heavy metals tend to accumulate in living organisms, causing various diseases and disorders (Barros *et al.*, 2003).

Excessive zinc intake may lead to electrolyte imbalance, nausea, anemia and lethargy (Fairweather-Tait, 1988; Prasad, 1976; Prasad, 1984; Valee *et al.*, 1957), while excessive intake of copper can lead to severe headaches, increased heart rate, nausea, hair loss, hypoglycemia, damage of kidney and liver. It may also cause psychological problems, such as brain dysfunction, depression, and schizophrenia (Nolan, 1983).

Table 1 lists the industrial sectors that are likely to bear heavy metal in its wastewaters (Volesky, 2001).

Table 1. Major metal-bearing industry sectors.

Industry	Metals
Mining operations	Cu, Zn, Pb, Mn, U
Electroplating operations	Cr, Ni, Cd, Zn
Metal processing	Cu, Zn, Mn
Coal-fired power generation	Cu, Cd, Mn, Zn
Nuclear industry	U, Th, Ra, Sr, Eu, Am

Among the heavy metal removal processes, the ion exchange process, shown in Equation 1, is very effective to remove various heavy metals and can be easily recovered and reused by regeneration operation (Lee *et al.*, 2007).

$$z_B A_S^{\pm z_A} + z_A B_R^{\pm z_B} \leftrightarrow z_B A_R^{\pm z_A} + z_A B_S^{\pm z_B} \quad (01)$$

Where A and B represent the ion pairs, z represents the charge of the ionic species, S represents the solution phase and R the solid one.

The most common mathematical models which represent the ion exchange equilibrium are Langmuir Isotherms and the Law of Mass Action (LMA), however, the former doesn't take into account the effects of the counter-ion and the ionic strength of the solution, and the latter requires multiple parameters which are commonly not found in the literature and depends on the resolution of non-linear equation systems.

1.1. Law of Mass Action

The LMA is a model foregrounded on the fact that ion exchange is a reversible process, which is ruled by a chemical equilibrium that defines the selectivity of the ion exchanger (Canevesi et. al, 2012). The thermodynamic equilibrium constant (K_{AB}) for the ion exchange reaction between species A and B is defined by Equation 2 (Borba 2010):

$$K_{AB} = \left(\frac{y_A \gamma_{R_A}}{C_A \gamma_{S_A}}\right)^{z_B} \left(\frac{y_B \gamma_{S_B}}{y_B \gamma_{R_B}}\right)^{z_A} \quad (02)$$

Where z_j is the valence of species *j*; y_j is the equivalence fraction of species *j* in the resin phase; C_j is the equivalent concentration of species *j* in the liquid phase; γ_{R_j} is the activity coefficient of species j in the solid phase; and γ_{S_j} is the activity coefficient of species j in the solution phase.

If non-ideal behavior of the fluid and the solid phases is taken into consideration, then the activity coefficients should be calculated. Activity coefficients in solution phase can be calculated using Bromley's (1973) model while activity coefficients in solid phase can be calculated using Wilson's (1964) model.

The expression (Equation 3) proposed by Bromley considers the effect of all species (cations and anions) present.

$$\ln \gamma_{S_j} = \frac{-A_\phi z_j \sqrt{I}}{1+\sqrt{I}} + F_j \quad (03)$$

The ionic strenght I is given in Equation 4.

$$I = \frac{1}{2} \sum_{j=1}^{n} z_j{}^2 m_j \quad (04)$$

Where *n* is the number of species in solution and m_j is the molality of species *j* in solution.

The term F_j is the sum of the interaction parameters. For each cationic species *j* in a multi-component solution, this term is given by Equation 5.

$$F_j = \sum_i \dot{B}_{ji} Z_{ji}{}^2 m_i \quad (05)$$

Where

$$Z_{ji} = \frac{z_i + z_j}{2} \quad (06)$$

$$\dot{B}_{ji} = \frac{(0.06 + 0.6 B_{ji}) |z_i z_j|}{\left(1 + \frac{1.5}{|z_i z_j|} I\right)^2} + B_{ji} \quad (07)$$

The subscripts *i* and *j* refer to the anions and cations in solution, respectively. Parameters A_ϕ and B_{ij}, given by Zemaitis et. al. (1950), depend on temperature.

Equation 8 gives Wilson's model equation for the calculation of the activity coefficients of species A and B on solid phase.

$$\ln \gamma_{R_j} = 1 - ln\left(\sum_{j=1}^{n} y_j \Lambda_{ij}\right) - \sum_{k=1}^{n} \left(\frac{y_k \Lambda_{ki}}{\sum_{j=1}^{L} y_j \Lambda_{kj}}\right) \quad (08)$$

Where *n* is the species number in the resin phase and Λ is the Wilson's model interaction parameter.

The term F_j is the sum of the interaction parameters. For each cationic species j in a multi-component solution, this term is given by Equation 5.

1.1. Artificial Neural Networks

An important alternative for the modeling of ion exchange equilibrium is the use of Artificial Neural Networks (ANNs).

ANNs are computational methodologies that perform multifactorial analyses. Inspired by networks of biological neurons, artificial network models contain layers of simple computing nodes that operate as nonlinear summing devices. These nodes are richly interconnected by weighted connection lines, and the weights are adjusted when data are presented to the network during a "training" process. Successful training can result in ANNs that can perform tasks such as predicting an output value, classifying an object, approximating a function, recognizing a pattern in multifactorial data, and completing a known pattern. (Dayhoff and DeLeo, 2001).

Due to the reliability and capacity of capturing non-linear relationships existing between variables in complex systems (Yetilmezsoy and Demirel, 2007), ANNs can be a powerful and relevant alternative for modeling industrial processes.

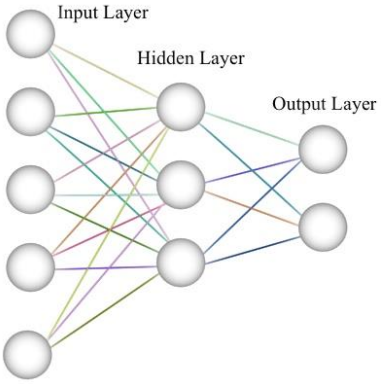

Figure 1. Artificial Neural Network with one hidden layer.

Although the number of parameters to be determined is higher, ANN is a method that calculates variables in an explicit way, meaning that, unlike the LMA, it does not require the solution of a system of non-linear equations (Canevesi *et al.*, 2012).

2. METHODS

The evaluation of the ANN methodology was undertaken by using equilibrium data of the binary systems Cu^{2+}-Na^{+}, Zn^{2+}-Na^{+}, Cu^{2+}-Zn^{2+} and of the ternary system Cu^{2+}-Na^{+}-Zn^{2+}, both at concentrations 1, 3 and 5 meq.L^{-1} and temperature 298 K, obtained by Borba (2010). The author investigated the ion exchange of these ions in solution using the synthetic resin Amberlite IR 120, whose capacity for cation exchange is 5.135 meq.g^{-1}.

2.1. Modeling by ANNs

The ANNs used a logistic function as activation function and only one hidden layer.

The number of neurons in the input and output layers were, respectively, 4 and 3 in all cases. The synaptic weights were initialized with random numbers between 0 and 1, and then determined by the minimization of the root-mean-square deviation (Equation 9) by a nonlinear conjugate gradient algorithm (Wright & Nocedal, 1999).

$$F_{OBJ} = \sqrt{\frac{1}{n\,data}\sum_{n=1}^{n\,comp}\sum_{p=1}^{p\,exp}[(X_R^n)_P^{EXP} - (X_R^n)_P^{MOD}]^2} \quad (9)$$

Data used to train and validate the ANNs consisted of 100 scores from each binary system, totalizing 300 scores, where 80% of the dataset (240 randomly chosen scores) was used in the training stage and 20% of the dataset (60 randomly chosen scores) was used in the validation stage. However, data were fed as a ternary system. In other words, the composition of the absent species in the binary system was presumed to be zero.

Input variables were the total concentration of the solution phase (meq.L^{-1}) and the compositions of each species in solution phase, while output variables were the compositions of each species in solid phase.

Total concentration of the metal in solution phase and compositions in the solution phase were used as input variables and compositions in solid phase were used as output variables.

Several network structures were tested, by varying the number of neurons in the hidden layer between 4 and 20 neurons, in order to achieve good performance on the prediction of the ternary systems.

2.1. Data generation

Experimental data obtained by Borba (2010) consisted of 56 scores divided amongst the three binary systems. In order to train the ANNs, more data were required to efficiently represent a larger variety of compositions of all the species in solution and solid phase in the ion exchange process. As a means to obtain a consistent model, these data were produced by LMA.

Activity coefficients in solid phase were calculated using Wilson's (1964) model. Equilibrium constants and Wilson's parameters, estimated by Borba (2010) are presented in Table 2. Activity coefficients in the solution phase were calculated using Bromley's (1973) model whose parameters are presented in Table 3.

Table 2. Wilson's model parameters at 298 K.

System	K_{eq}	Parameters of Wilson's equation	
		Λ_{12}	Λ_{21}
Cu-Na	0.3258	2.7286	0.3666
Zn-Na	0.3782	2.0750	1.0485
Zn-Cu	0.9817	1.1769	0.0896

The number of neurons in the input and output layers were, respectively, 4 and 3 in all cases. The synaptic weights were determined by the minimization of the root-mean-square deviation (Equation 9) by a nonlinear conjugate gradient algorithm (Wright & Nocedal, 1999).

Table 3. Bromleys's model parameters at 298 K.

A_{Φ}	B_{CuCl2}	B_{NaCl}	B_{ZnCl2}
0.5162	0.0654	0.0364	0.0574

3. RESULTS AND DISCUSSION

3.1. Data generation

Initially the equilibrium curves were built using the LMA, using Equation 1 and the parameters presented in Table 1. The obtained results are presented in Figure 2 for the binary systems Cu^{2+}-Na^{+}, Zn^{2+}-Na^{+} and Zn^{2+}-Cu^{2+}, respectively.

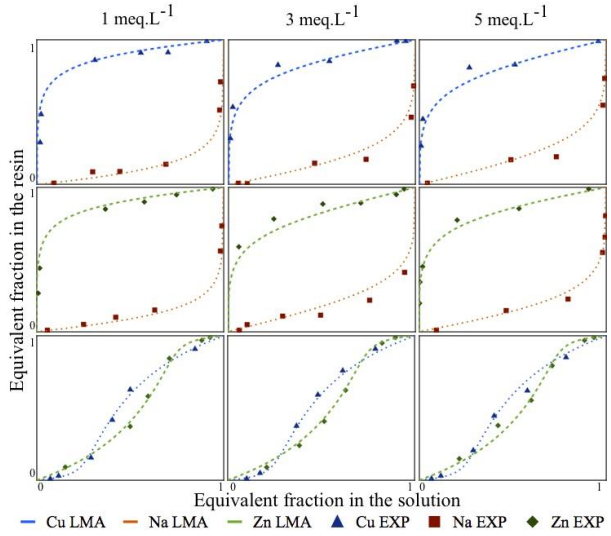

Figure 2. Equilibrium curves for the Binary systems Cu^{2+}-Na^{+}, Zn^{2+}-Na^{+} and Zn^{2+}-Cu^{2+} by LMA.

Table 4 presents the absolute average deviations (AAD) from the LMA for each system.

According to the absolute average deviations, the Law of Mass Action described in a precise way the experimental data of binary equilibrium, therefore justifying the use of the equilibrium curves as datasets to train the neural network.

Table 4. Results form the application of LMA to binary data.

System	AAD
Cu-Na	5.3563
Zn-Na	5.1324
Zn-Cu	2.0293

3.1. Modeling equilibrium data

Several structures were tested to model the binary data in the training stage of the Artificial Neural Networks using 80% of the generated data chosen randomly. Posterior to the training stage, the ANNs were submitted to a validation stage using the remaining not used 20% generated data. Finally, the ANNs were submitted to a prediction stage, using only ternary equilibrium data. Thereby obtaining the structure that best represented the equilibrium data analyzed in addition to successfully predicting the behavior of ternary data equilibrium.

Table 5 shows the tested structures and the absolute average deviation (AAD) for the training, the validation and the prediction stages. Also showing that the ANN with 14 neurons in the hidden layer had the best performance, as it successfully described the experimental binary data with similar precision of the LMA model while achieving the lowest AAD of the prediction stage. Figures 3 and 4 directly compare the values of equivalent fraction in the resin obtained by the ANN (structure 4-14-3) and the LMA.

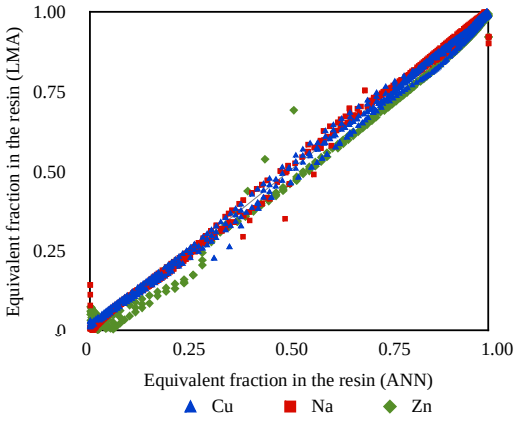

Figure 3. Comparison of equivalent fraction in the resin obtained by ANN and LMA on the training stage.

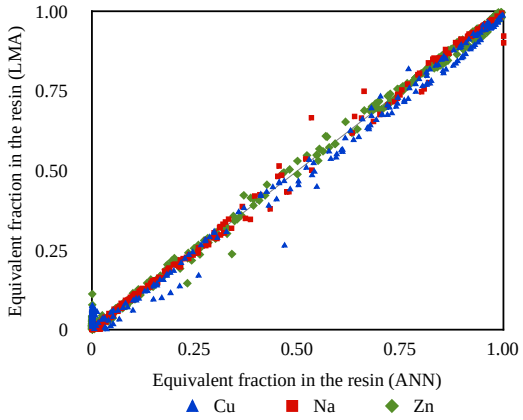

Figure 4. Comparison of equivalent fraction in the resin obtained by ANN and LMA on the validation stage.

Table 5. Results from the application of ANNs to binary data.

Structure	AAD (Training)	AAD (Validation)	AAD (Prediction)
4-4-3	2.9679	2.6868	9.7694
4-5-3	2.2358	2.0174	9.5619
4-6-3	1.6899	1.4487	8.7044
4-7-3	1.5100	1.3697	9.2653
4-8-3	2.6861	2.4882	7.2843
4-9-3	2.2416	2.1481	7.9458
4-10-3	1.5456	1.2623	9.0990
4-11-3	2.1445	1.9920	7.5164
4-12-3	1.3902	1.2156	9.4888
4-13-3	2.5914	2.3263	7.4862
4-14-3	2.2829	2.0906	6.5697
4-15-3	1.4362	1.1736	8.5470
4-16-3	2.4160	2.2182	8.6353
4-17-3	1.6718	1.4439	8.9175
4-18-3	1.7866	1.5872	8.5264
4-19-3	1.4694	1.2391	8.8479
4-20-3	1.6853	1.3443	8.4258

Figure 5 presents the equilibrium curves obtained by the ANN (structure 4-14-3).

To evaluate the prediction capacity of the ANNs, which were trained using only binary equilibrium data, the ternary results were compared to the experimental data and are presented on Figure 6.

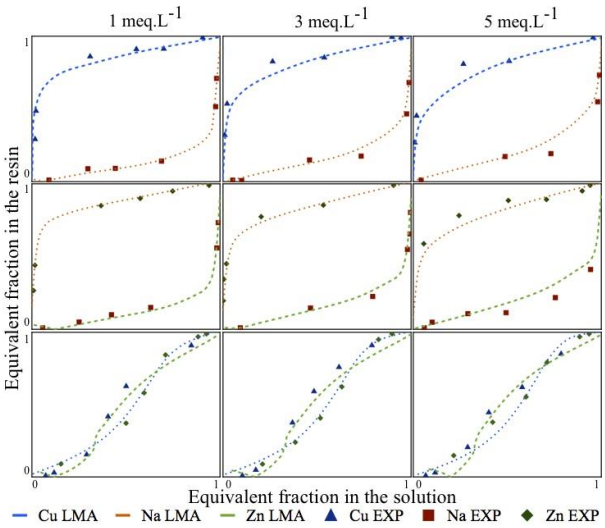

Figure 5. Equilibrium curves for the Binary systems Cu^{2+}-Na^{+}, Zn^{2+}-Na^{+} and Zn^{2+}-Cu^{2+} by ANN (4-14-3).

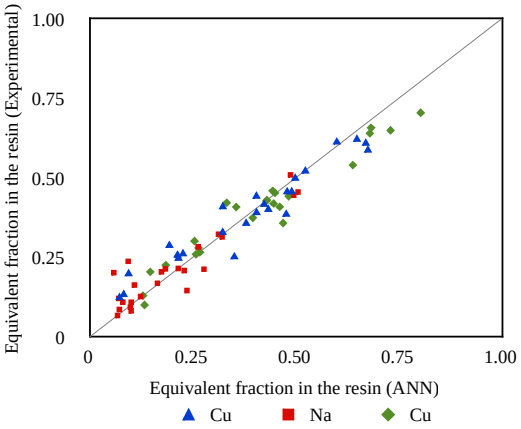

Figure 6. Equivalent fractions in the resin (ANN).

A non-linear equation system was used to obtain ternary data through the use of LMA. The results were also compared to experimental data and are presented on Figure 7. Methodology used to obtain the results in Figure 7 is presented by Borba *et al* (2010).

The absolute average deviations of the prediction of equilibrium ternary data by the LMA and ANNs, were, respectively 3.9984 and 6.5697.

Figures 8 and 9 present the error diagram related to the estimation of the composition in the resin for the ternary system.

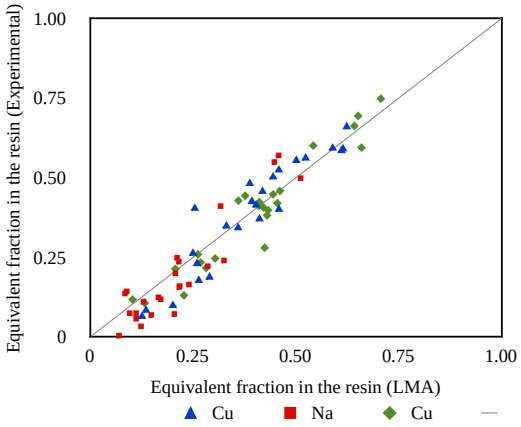

Figure 7. Equivalent fractions in the resin (LMA).

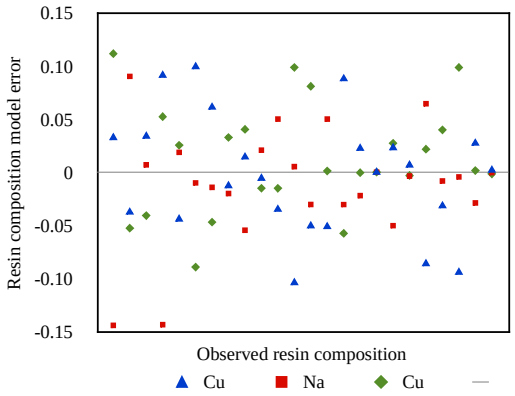

Figure 8. Concentration in the solid phase error diagram related to the ternary system (LMA).

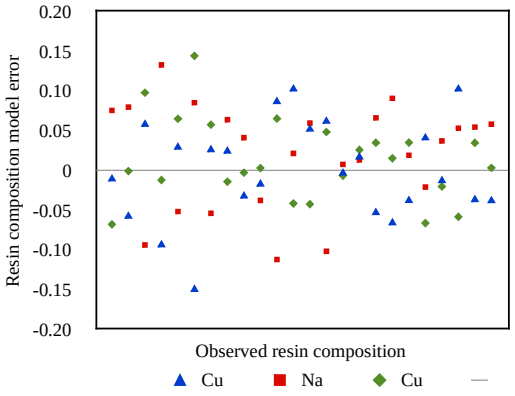

Figure 9. Concentration in the solid phase error diagram related to the ternary system (ANN).

The diagrams indicate the residue is in the range of -0.14 to 0.11, for the LMA, and -0.15 to 0.14, for the ANNs.

5. CONCLUSIONS

In present investigation, the efficiency of the Artificial Neural Networks was compared with the Law of Mass Action with regard to the representation of data of the binary (Cu^{2+}-Na^{+}, Zn^{2+}-Na^{+} and Cu^{2+}-Zn^{2+}) and ternary (Cu^{2+}-Na^{+}-Zn^{2+}) equilibrium.

ANNs described with efficiency the binary equilibrium data, which may be represented from AAD rates and compared to the LMA in Tables 3 and 4, with similar results obtained by ANNs and LMA.

ANNs also revealed a good capacity for the prediction of the ternary system. Although Artificial Law of Mass Action (AAD = 4.00) presented a lower deviation than the Neural Networks (AAD = 6.57), both methodologies managed to predict satisfactorily the behavior of the ternary system equilibrium.

Therefore, the application of ANNs can be considered a valid alternative to conventional modeling since it calculates explicitly the fraction in phases in equilibrium while LMA requires the solution of non-linear equation system.

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