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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 and 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 $Zn^{2+}-Cu^{2+}$ 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 in the binary systems. Results showed that, in the equilibrium modeling of the binary systems and in the prediction of the ternary system, the two 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 or destroyed (Anirudhan and Suchithra 2010). Moreover, heavy metals tend to accumulate in living organisms, causing various diseases and disorders (Barros et al. 2008).

Excessive zinc intake may lead to electrolyte imbalance, nausea, anemia and lethargy (Fairweather-Tait 1988; Prasad 1977, 1984; Vallee et al. 1957), and excessive intake of copper can lead to severe headaches, increased heart rate, nausea, hair loss, hypoglycemia, and damage to the kidneys and liver. It may also cause psychological problems, such as brain dysfunction, depression, and schizophrenia (Nolan 1983).

Industrial sectors which are likely to discharge metals in their wastewaters include mining operations, electroplating operations, metal processing, coal-fired power generation and the nuclear industry (Volesky 2001).

Among the heavy metal removal processes, the ion exchange process, shown in Eq. 1, is one of the most effective forms of wastewater treatment. Several studies have demonstrated the efficiency of ion exchange on heavy metal recovery from aqueous media (Lee et al. 2007; Chern and Chang 2000; Verbych et al. 2005; Juang et al. 2006; Hamdaoui 2009; Ostroski et al. 2011).

$$z_B A_S^{\pm z_A} + z_A B_R^{\pm z_B} \rightleftharpoons z_B A_R^{\pm z_A} + z_A B_S^{\pm z_B} \quad (1)$$

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.

On an industrial scale, the ion exchange process in fixed-bed columns is preferred. Several authors have reported the efficiency of this process (Ostroski et al. 2011; Borba et al. 2011; Shahbazi et al. 2011; Shaidan et al. 2012).

Mathematical modeling and process simulation are important tools in the design of fixed-bed columns, as

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mathematical models can be validated with experimental data obtained at laboratory scale, and subsequent simulation of experimental data can assist in its interpretation and analysis, as well as in the identification of mass transfer mechanisms, prediction of responses owed to changes in operational conditions, and process optimization.

Generally, the mathematical models used to simulate the ion exchange processes in fixed-bed column are composed by the following equations: mass balance in the fluid, mass balance in the solid phase and equilibrium relationship.

In a rigorous mathematical model of fixed-bed ion exchange, the law of mass action (LMA) can be used as equilibrium relationship. Therefore, the mathematical models used to describe the ion exchange dynamics in a fixed-bed column are complex and their solution require a lot of processing power, because it is necessary to solve a set of differential (mass balances) and nonlinear (LMA) equations.

D'Arisbo et al. (2013) compared the performance of a phenomenological and a hybrid model in the description of ion exchange process in a fixed-bed column. The systems investigated were Zn–Na, Fe–Na and Cu–Na. The LMA and an ANN were used to describe the phenomenological and hybrid model equilibrium, respectively. Performance was compared using experimental breakthrough curves. Both models successfully described the ion exchange process, but the hybrid model was, on average, 82 % less time-consuming.

1.1 Law of mass action

The LMA is a model foregrounded on the fact that ion exchange is a reversible process ruled by a chemical equilibrium, which 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 Eq. 2 (Borba et al. 2010):

$$K_{AB} = \left(\frac{y_A \gamma_{R_A}}{C_A \gamma_{S_A}}\right)^{z_B} \left(\frac{C_B \gamma_{S_B}}{y_B \gamma_{R_B}}\right)^{z_A} \tag{2}$$

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 and solid phases can be calculated using the Bromley (1973) and Wilson (1964) models, respectively.

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

$$\ln \gamma_{S_j} = \frac{-A_\phi z_j \sqrt{I}}{1 + \sqrt{I}} + F_j \tag{3}$$

The ionic strength I is given in Eq. 4:

$$I = \frac{1}{2} \sum_{j=1}^{n} z_j{}^2 m_j \tag{4}$$

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 Eq. 5.

$$F_j = \sum_{i=1}^{n} \dot{B}_{ij} Z_{ij}{}^2 m_i \tag{5}$$

where

$$Z_{ij} = \frac{z_i + z_j}{2} \tag{6}$$

$$\dot{B}_{ij} = \frac{\left(0.06 + 0.6 B_{ji}\right)|z_i z_j|}{\left(1 + \frac{1.5}{|z_i z_j|} I\right)^2} + B_{ji} \tag{7}$$

The subscripts i and j refer to the anions and cations in solution, respectively. Parameters A and B_{ij}, given by Zemaitis et al. (1986), depend on temperature.

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

$$\ln \gamma_{Rj} = 1 - \ln\left(\sum_{j=1}^{n} y_j \Lambda_{ij}\right) - \sum_{k=1}^{n} \left(\frac{y_k \Lambda_{ki}}{\sum_{i=1}^{L} y_j \Lambda_{kj}}\right) \tag{8}$$

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 Eq. 5.

1.2 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 which perform multifactorial analyses. Inspired by networks of biological neurons, artificial network models contain layers of simple computing nodes which 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 which can perform

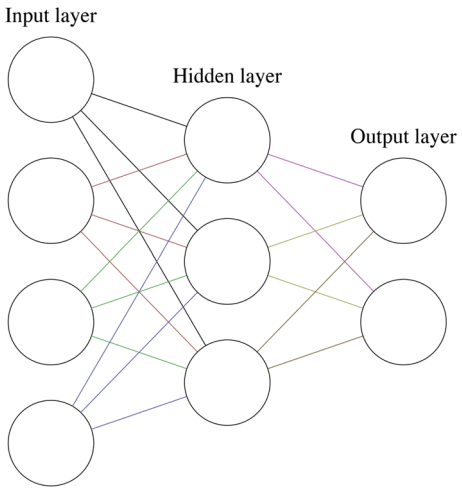

Fig. 1 Artificial Neural Network with one hidden layer

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). Figure 1 shows an Artificial Neural Network with a generic structure.

Thanks to their reliability and capacity in terms of capturing nonlinear relationships between variables in complex systems (Yetilmezsoy and Demirel 2008), ANNs can be a powerful and relevant alternative for modeling industrial processes.

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

2 Methods

The evaluation of the ANN methodology was undertaken by using equilibrium data of the binary systems $Cu^{2+}-Na^{+}$, $Zn^{2+}-Na^{+}$, $Zn^{2+}-Cu^{2+}$ and of the ternary system $Cu^{2+}-Na^{+}-Zn^{2+}$, both at concentrations of 1, 3 and 5 meq L^{-1} and a temperature of 298 K, as obtained by Borba et al. (2012). 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 was, respectively, four and three in all cases. The synaptic weights were initialized with random numbers between zero and one, and then determined by the minimization of the root-mean-square deviation (Eq. 9) by a nonlinear conjugate gradient algorithm (Wright and Nocedal 1999).

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

Data used to train and validate the ANNs consisted of 100 scores from each binary system, totaling 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. Finally, the ANNs were submitted to a prediction stage, using only experimental 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. All data were fed as a ternary system, meaning the composition of the absent species in binary systems was presumed to be zero.

During the training stage, when a minimum point was reached within the algorithm, the parameters were stored. The set of parameters was then used to validate the ANNs with the remaining 60 random scores and predict the output of the ternary data. The tolerance was then set to be less than the value previously achieved on the training stage objective function and the algorithm was restarted with a new random set of parameters. This was carried until no lower prediction error could be found.

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 15 neurons, in order to achieve good performance on the prediction of the ternary systems.

2.2 Data generation procedures

Experimental data obtained by Borba et al. (2012) 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. To obtain a consistent model, these data were produced by the LMA.

Activity coefficients in solid phase were calculated using Wilson's (1964) model. Equilibrium constants and Wilson's parameters as estimated by Borba et al. (2012) are presented in Table 1. Activity coefficients in the solution phase were calculated using Bromley's (1973) model whose parameters are presented in Table 2.

Table 1 Wilson's model parameters at 298 K (Borba et al. 2012)

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

Table 2 Bromley's model parameters at 298 K

A_ϕ	B_{CuCl_2}	B_{NaCl}	B_{ZnCl_2}
0.5162	0.0654	0.0364	0.0574

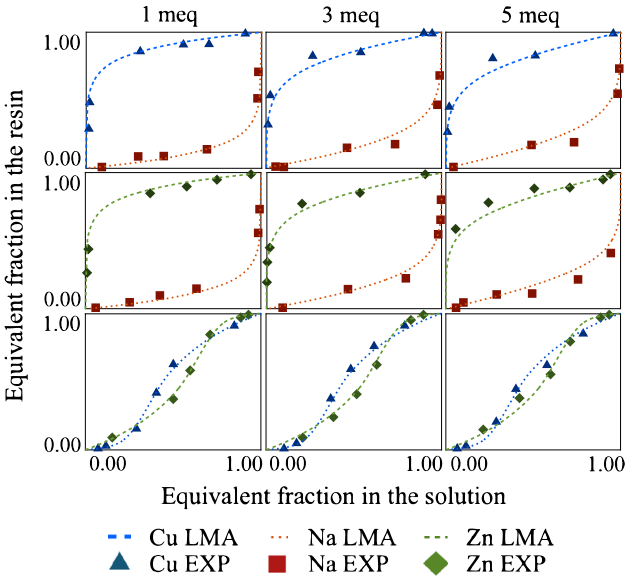

Fig. 2 Equilibrium curves for the Binary systems Cu^{2+}–Na^{+}, Zn^{2+}–Na^{+} and Zn^{2+}–Cu^{2+} by LMA

Table 3 Results form the application of ANNs to binary data

Structure	AAD (Training)	AAD (Validation)	AAD (Prediction)
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

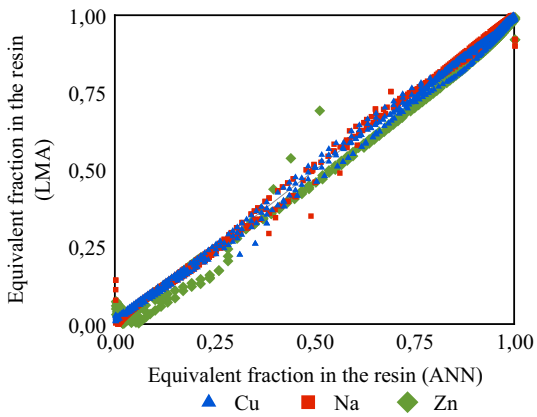

Fig. 3 Comparison of equivalent fraction in the resin obtained by ANN and LMA on the training stage

3 Results and discussion

3.1 Data generation analysis

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

The absolute average deviations (AAD) for the binary systems Cu–Na, Zn–Na and Zn–Cu, using the LMA were, respectively, 5.3564, 5.1324 and 2.0293. According to these results, the LMA described the experimental data of binary equilibrium in a precise way, therefore justifying the use of the equilibrium curves as datasets to train the neural network.

3.2 Modeling equilibrium data

Table 3 shows the tested structures and the absolute average deviation (AAD) for the training, validation and prediction stages. It also shows 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 to 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.

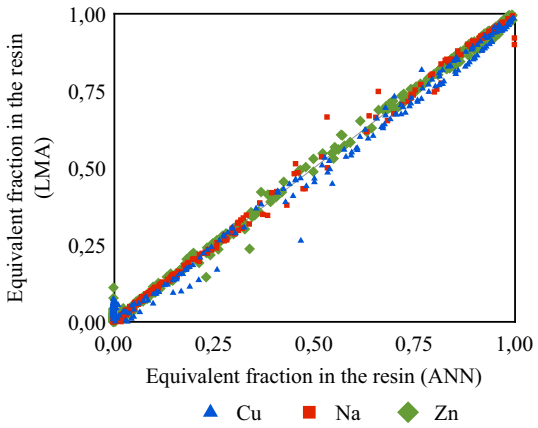

Fig. 4 Comparison of equivalent fraction in the resin obtained by ANN and LMA on the validation stage

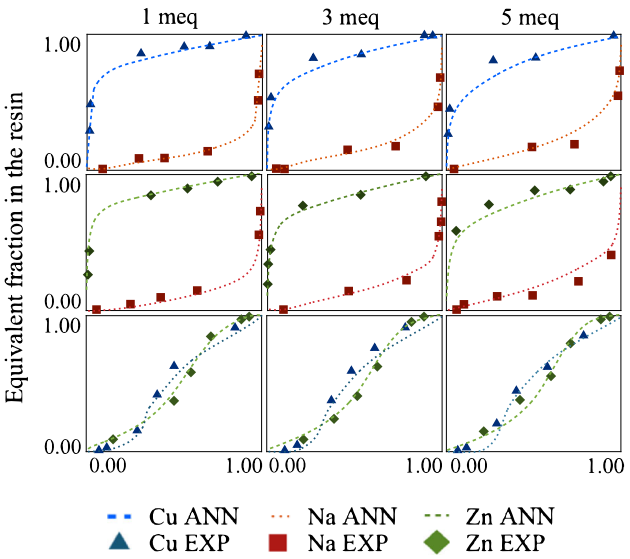

Fig. 5 Equilibrium curves for the Binary systems $Cu^{2+}-Na^{+}$, $Zn^{2+}-Na^{+}$ and $Zn^{2+}-Cu^{2+}$ by ANN (4-14-3)

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 with the experimental data and are presented in Fig. 6.

A nonlinear equation system was used to obtain ternary data through the use of the LMA. The results were also compared with experimental data and are presented in Fig. 7.

The absolute average deviations of the prediction of equilibrium ternary data by the LMA and ANNs, were, respectively 3.9984 and 6.5697. Aniceto et al. (2013) evaluated the use of ANN in modeling the ion exchange

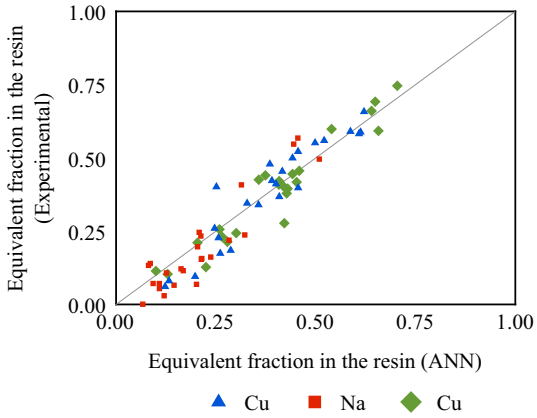

Fig. 6 Comparison between equivalent fractions in the resin obtained experimentally and by ANN

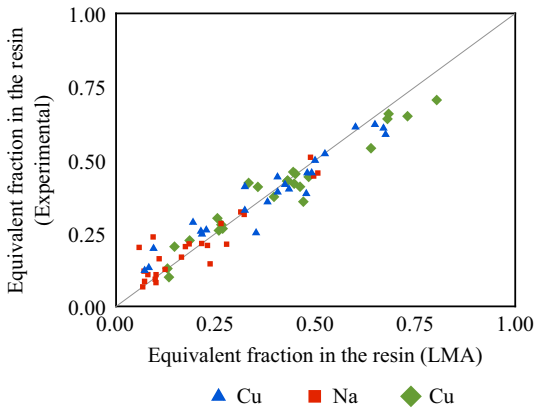

Fig. 7 Comparison between equivalent fractions in the resin obtained experimentally and by LMA

equilibrium of several binary and ternary systems using only experimental data. The global deviation found was 2.09 and 4.32 % for binary and ternary systems, respectively. This deviation is slightly lower than the deviation found in this work for the ternary system; however, as the ANN input data were generated using the LMA, their deviation was limited to the LMA's (ADD = 3.9984) and could hardly be lower than that. Canevesi et al. (2012) tested both the LMA and ANN methods to describe the ion exchange equilibrium in the binary systems $SO_4^{2-}-NO_3^{-}$, $SO_4^{2-}-Cl^{-}$, $NO_3^{-}-Cl^{-}$ and in the ternary system $SO_4^{2-}-Cl^{-}-NO_3^{-}$. The datasets used were also generated by the application of the LMA in the binary systems to predict ternary system. However, the LMA was not able to represent the experimental data accurately, causing the ANN to achieve a higher deviation (ADD = 13.5).

Figures 8 and 9 present the residue diagram related to the estimation of the composition in the resin for the ternary system. Residues were random for the LMA and ANN models, confirming the validity of both models.

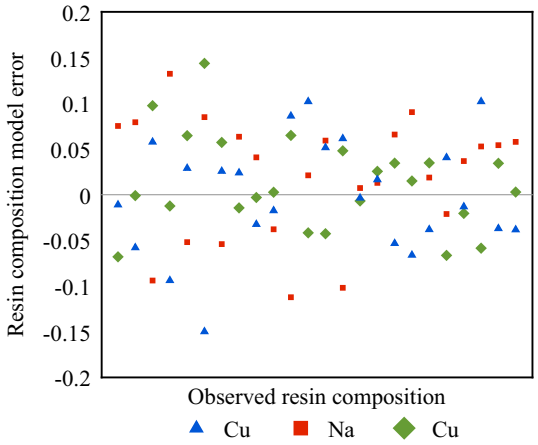

Fig. 8 Concentration in the solid phase residue diagram related to the ternary system (LMA)

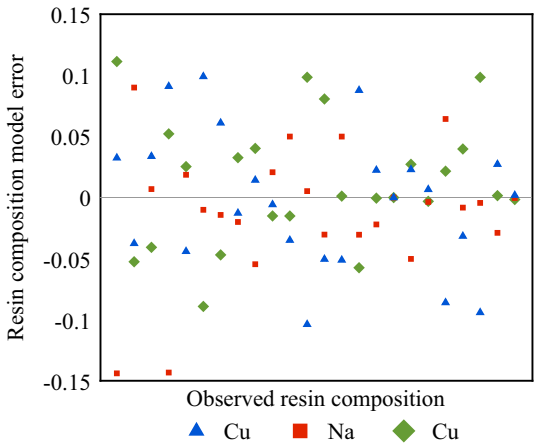

Fig. 9 Concentration in the solid phase residue diagram related to the ternary system (ANN)

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.

4 Conclusions

In the present investigation, the efficiency of Artificial Neural Networks was compared with the Law of Mass Action with regard to the representation of data of the binary (Cu–Na, Zn–Na and Zn–Cu) and ternary (Cu–Na–Zn) equilibrium. The prediction of the behavior of a ternary system using only data from binary systems was the main goal of the study, and has been successfully achieved.

The use of ANNs revealed a good capacity for the prediction of the ternary system. Although the Law of Mass Action (AAD = 4.00) presented a lower deviation than the Neural Networks (AAD = 6.57), this occurred mainly because the ANNs input data were generated using the LMA, meaning the ANNs error could never be lower than the LMA error.

ANNs calculate the fraction in phases in equilibrium explicitly, whereas LMA requires the solution of a non-linear equation system. Considering the expressive reduction in processing power and calculation times caused by ANNs, their application can be considered a valid alternative to conventional modeling of ion exchange fixed-bed columns.

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