Nonlinear Autoregressive with Exogenous Input (NARX) approach for modeling of the single-multi metals adsorption from aqueous solution by resin

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Abstract In this study, Nonlinear Autoregressive with Exogenous Input (NARX) neural network model was developed to predict the adsorption efficiency of Cd^{2+}, Ni^{2+} and Zn^{2+} ions from aqueous solution using a tannin (valonia type) resin as adsorbent. These ions are frequently encountered in a mixture in various industrial waste waters. The experiments have been performed for the chosen pH 5.0, 20 °C temperature, 350 rpm agitation rate and in the concentration range from 10 to 150 mg.L^{-1} for single ions and their binary and ternary mixtures in aqueous solutions. Experiments with three metals were composed of seven tests; three separate single metal (Cd^{2+}, Ni^{2+} and Zn^{2+}), three binary mixtures (Cd^{2+}+Ni^{2+}, Ni^{2+}+Zn^{2+}, Cd^{2+}+Zn^{2+}), and one ternary mixture (Cd^{2+}+Ni^{2+}+Zn^{2+}). The NARX technique was used to fit the adsorption efficiency.

Keywords: NARX, artificial intelligence, modeling, adsorption, heavy metals

1. Introduction

Adsorption is one of the most effective wastewater treatment technique for removal of heavy metal ions. Many studies note that metals could be removed from waste waters through adsorption, even if they were present as mixtures of metals, rather than as a single element (Padilla-Ortega *et al.*, 2013; Markiewicz-Patkowska *et al.*, 2005; Li *et al.*, 2015; Bediako *et al.*, 2015).

There are even studies specifically focusing on competitive sorption, or synergistic/antagonistic effects caused by individual constituents of mixtures, within the wider framework of sorption studies (Tovar-Gómez *et al.*, 2015; Unuabonah *et al.*, 2016; Atouei *et al.*, 2016).

Recent years saw an increased use of NARX model for environment-related cases such as forecasting peak air pollution levels, solar forecasting or water treatment. For instance, the scientists have developed successful forecast models using NARX, for estimation of ozone concentration levels (Pisoni *et al.*, 2009), solar energy forecasting (Tao *et al.*, 2010), prediction of biogas production rate (Dhussa *et al.*, 2014), management of wastewater treatment plant (Hong and Bhamidimarri, 2003), flood water level (Ruslan *et al.*, 2014), prediction of electricity prices (Andalib and Atry, 2009) etc.

The experimental data obtained in a study investigating the efficiency of Zn adsorption from wastewater, using activated almond shell, and the NARX model formulated on the basis of these data were used to compare the results. In conclusion, the use of NARX model was reported to be an easy-to-implement and handy model for the estimation of adsorption efficiency (Çoruh *et al.*, 2014).

When the studies done using NARX and ANN are examined Neural Network applications such as the NARX model can be used to make estimations without experiments, where the latter would be impossible or costly, or would require unaffordable amounts of time or labor (Haddad *et al.*, 2015).

The principal aim of the present work was to study single-multi metals (Cd^{2+}, Ni^{2+} and Zn^{2+}) removal from aqueous solutions by adsorption. In addition, a neural network modeling was performed by Nonlinear Autoregressive with Exogenous Input Network Model (NARX) using adsorption experiment results.

2. Material and Method

2.1. Batch Experiments

In this study, experiments were carried out to estimate sorptivity of valonia resin and their selectivity towards Cd^{2+}, Ni^{2+} and Zn^{2+} ions separately and in combinations. Metal adsorption studies were performing using Valonia tannin resin (38-53 µm particle size) (Yurtsever and Şengil, 2012) in different initial concentrations (10, 25, 50, 75, 100 and 150 mg/L), 350rpm agitation rate, during 180 minutes at room temperature and pH: 5. Adsorption kinetics are fitted pseudo-second-order kinetic model for three metals.

Isoterm data for single metal adsorption revealed that the highest level of adsorption was that of Ni^{2+}, followed by Cd^{2+}, while that of Zn^{2+} was the lowest. Adsorption experiments led to the production of the graphs showing that, absorption rates in dual metal solutions followed the pattern Zn^{2+}>Ni^{2+} and Zn^{2+}>Cd^{2+}, and that the adsorption rates of these ions exhibit a marked difference. Furthermore, the adsorption rates for Ni^{2+} and Cd^{2+} were very close, and followed the pattern Ni^{2+}>Cd^{2+}. The triple ion mixture, on the other hand, exhibited adsorption rates to match the pattern Zn^{2+}>Ni^{2+}>Cd^{2+}.

2.2. Nonlinear Autoregressive with Exogenous Input

Artificial Neural Networks (ANN) refer to structures developed with inspiration from human mind, imitating the central nervous system in the brain with a view to creating large-scale artificial parallel networks, and training of such networks to solve specific problems (Anderson *et al.* 1992). ANN is well known technique is solving nonlinear systems and NARX network model is one class of ANN model. The NARX is a feedforward dynamic network commonly used for input-output modeling of nonlinear dynamical systems (Chen *et al*., 1990; Nunoo, 2013). The NARX model is based on the linear time-series ARX model.

A NARX network can be mathematically expressed by Eq. (1).

$$y(n+1) = f[y(n), \dots, y(n-dy+1); u(n-k), u(n-k-1), \dots, u(n-k-du+1)] \quad (1)$$

where u(n)∈R and y(n)∈R denote, respectively, the input and output of the model at discrete time step n, while du ≥ 1, dy ≥ 1 and du ≤ dy, are the input-memory and output-memory orders, respectively. The parameter k (k ≥ 0) is a delay term, known as the process dead-time (Xie *et al*., 2009).

3. Modeling

3.1. Data Collection

The present study is based on a total of 552 experiments; 120 Cd^{2+} based, 120 Ni^{2+} based, 120 Zn^{2+} based, 48 Cd^{2+}+Ni^{2+} based, 48 Cd^{2+}+Zn^{2+} based, 48 Ni^{2+}+Zn^{2+} based, and 48 Cd^{2+}+Ni^{2+}+Zn^{2+} based. Each metal group in these experiments had been in the initial concentration ranges of 10, 25, 50, 75, 100, or 150, while adsorption time range was set at 1-180. The adsorption rates observed in these experiments and the input parameters were reviewed on a statistical basis, with the results shown in Table 1. Also, the single and multi-metal groups in use are numbered from 1 to 7. The numbering scheme is as follows: 1-Cd^{2+}, 2-Ni^{2+}, 3-Zn^{2+}, 4-Cd^{2+}+Ni^{2+}, 5- Cd^{2+}+Zn^{2+}, 6-Ni^{2+}+Zn^{2+}, 7-Cd^{2+}+Ni^{2+}+Zn^{2+}.

Table 1. Descriptive statistics of experimental data

Analysis Parameter	Initial Concentration ($mg.L^{-1}$)	Adsorption Time (min.)	Cd^{2+}	Ni^{2+}	Zn^{2+}
Mean	68.3	58.58	14.71	18.6	20.18
Standard Error	2.01	2.44	0.93	1.09	1.21
Median	62.5	35	0	0	0
Standard Deviation	47.18	57.41	21.75	25.48	28.45
Sample Variance	2226.26	3296.22	472.96	649.3	809.14
Minimum	10	1	0	0	0
Maximum	150	180	79.5	86.81	99.99
Count	552	552	552	552	552
Mean	68.3	58.58	14.71	18.6	20.18
Standard Error	2.01	2.44	0.93	1.09	1.21

3.2. Modeling with NARX

In this study, 3 x 10 x 3 Nonlinear Autoregressive with Exogenous Input Network Model (NARX) with tangent sigmoid transfer function (tansig) at hidden layer were used. The input layer made use of initial concentration, adsorption time and metal type parameters, while the exit layer used Cd^{2+}, Ni^{2+} and Zn^{2+} adsorption results. Adsorption values were used as test data, training data and validation for NARX modeling. 70% of the data were used for training, whereas a further 15% used for validation and 15% for testing. The data was divided randomly.

Experimental data-sets were scaled between 0.1 and 0.9 using the normalization equation below in order to reduce dimensional effects of the input parameters in different ranges of values with keeping the relationship between dependent and independent variables.

$$X_n = 0.1 + 0.8\frac{X - X_{min}}{X_{max} - X_{min}} \quad (2)$$

where X_n is the normalized value of the corresponding X, X_{min} is the minimum values of X, and X_{max} is the maximum values of X.

The study was completed by creating a model using NARX neural network applications to estimate the results obtained through adsorption experiments. All of the procedures for training and testing the proposed NARX model were performed using MATLAB 2016b, a multi-paradigm numerical computation software.

The architecture of NARX neural network model for single-multi metals adsorption rate are shown in Fig. 1.

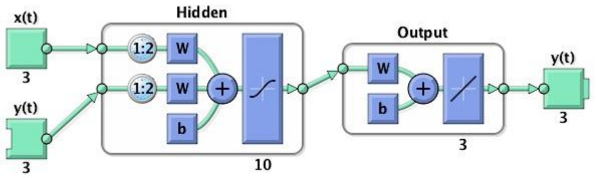

Figure 1. The NARX neural network model for single-multi metals adsorption rate

Fig. 2 shows that the Mean Square Error (MSE) value for the train results is 1E-3 and the test results is 9.96E-4. These results indicate that the model we employed is acceptable for estimations.

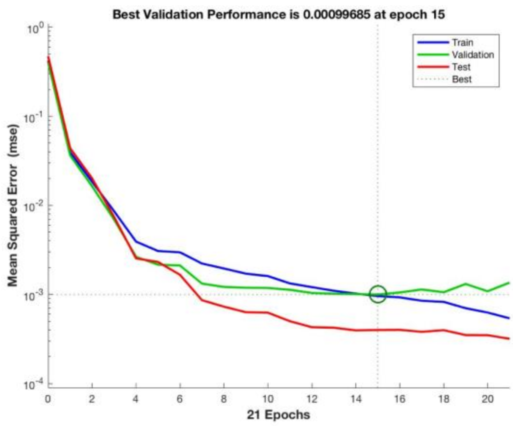

Figure 2. The performance of NARX neural network model

Fig. 3 shows that a comparison between the NARX model results and experimental data showed that the NARX model is able to predict the removal of zinc, cadmium and nickel ions from aqueous solution.

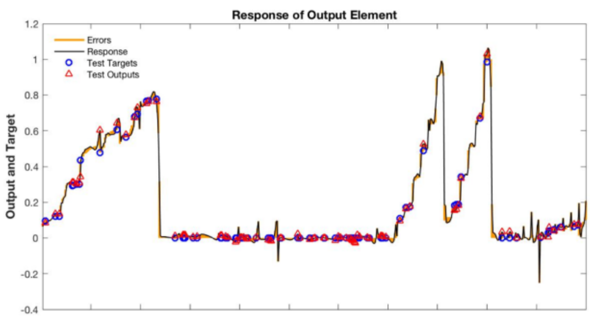

Figure 3. Response of output element in the NARX neural network model

Fig. 4 can help in assessing the value of the regression line to account for the variation between the experiment results and predicted results. Moreover, the R^2 values in Fig. 4 support the conclusions presented in Fig. 3. It is evident in Fig. 4 that, during the training stage R^2 was 0.994, while in the test stage it was 0.997.

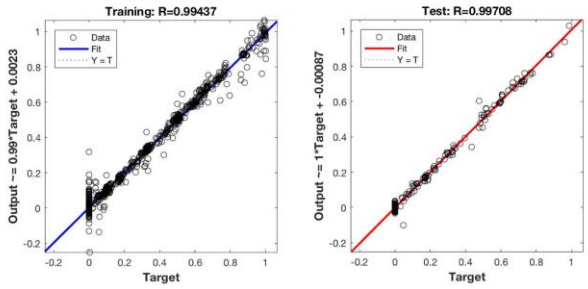

Figure 4. Training and test regression in the NARX neural network model

4. Conclusions

In this study, nonlinear autoregressive model processes with exogenous input (NARX) neural networks are used for the prediction of heavy metal adsorption rate. This NARX model demonstrated effective prediction with a R^2 and MSE of about 0.9970 and 9.96E-4, respectively for the single-multi metals adsorption rate. The NARX modeling results showed that results with high accuracy can be obtained according to the desired input parameters without performing costly experiments. For this reason, the developed NARX model in this study has an acceptable generalization ability and validity.

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