Iranian Journal of Analytical Chemistry
Volume 7, Issue 1, March 2020 (78-87)

مجله ایرانی شیمی تجزیه
دوره۷، شماره ۱، فروردین ماه ۱۳۹۹ (۸۷-۷۸)

Application of Artificial Neural Network Modeling in Prediction of The Extraction Yield of Copper-Morin Complex from Aqueous Media Utilizing a Molecularly Imprinted Polymer Coated Stir Bar

Sayyed Hossein Hashemi[1,*], Massoud Kaykhaii[2], Mohammad Shakeri[3]
1. Department of Marine Chemistry, Faculty of Marine Science, Chabahar Maritime University, P.O. Box 98617-85553, Chabahar, Iran.
2. Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, Zahedan, Iran
3. Department of Chemistry, University of Zabol, Zabol, Iran

Received: 21 February 2020 **Accepted:** 17 March 2020
DOI: 10.30473/ijac.2020.51710.1167

Abstract
In this research, a new modeling method based on three-layer artificial neural network (ANN) technique was applied to predict the extraction yield of copper-morin complex from aqueous samples by means of molecularly imprinted stir bar sorptive extraction. Input variables of the model were pH of the solution, absorption and desorption times, stirring rate, temperature, and amount of morin ligand; while the output was extraction yield of copper ions. It was found that a network with 12 hidden neurons is highly accurate in predicting extraction recovery of copper-morin complex. The mean squared error and correlation coefficient between the experimental data and the ANN predictions were achieved as 0.0009 and 0.9999 for training, 0.0032 and 0.976 for validation and 0.0030 and 0.96666 for testing data sets. Under the optimum conditions, the linear range found to be in the range of 5-1000 μg L^{-1} with the detection limit of 0.38 μg L^{-1}. The relative standard deviation was obtained to be below 5.3%. The method was successfully applied for preconcentration and determination of Cu in a few real samples.

Keywords
Artificial Neural Network; Copper Extraction; Molecularly Imprinted Stir Bar Sorptive Extraction; Water Analysis.

1. INTRODUCTION

Copper is an essential trace element for humans that plays an important role in biochemical processes and living organisms (e.g. in tissue oxygen transfer and in iron metabolism). This metal is applied in numerous industrial processes including electroplating, metal processing, printed circuit board manufacturing and metal finishing [1, 2]. Copper concentrations (at the level of 0.0001–0.010 wt%) should be monitored in a large group of materials, including food products and biological, environmental and metallurgical samples. An excess of copper has an adverse effect on human beings causing the development of anemia, hepatic damage and neural disorders [3,4]. Cu (II) is the most generally occurring species of copper in the environment and the most toxic form to living organisms [5]. It has been listed as one of the most commonly discharged priority pollutants by the US Environmental Protection Agency [6]. Therefore, determination of this analyte is a requirement in many environmental, food and water sample with a sensitive method.

Stir bar sorptive extraction (SBSE) coated by polydimethylsiloxane (PDMS) was first reported in 1999 derived from solid phase microextraction [7, 8]. Since SBSE method became very common for the analysis of environmental and biomedical samples after then; it was commercialized by GERSTEL GmbH & Co., Germany, under the name Twister®. This commercial stir bar, coated with non-polar PDMS, showed excellent affinity to non-polar and weakly polar analytes [9, 10]. Researchers developed various other coatings for extraction of semi- to polar compounds; however, these coatings are still non-specific sorbents.

Molecularly imprinted polymer (MIP) is a fast growing area of modern chemistry with large possibilities for both fundamental research and applied analytical tasks. MIPs have very high selectivity as phase coating on SBSE which has the ability to be used for many types of analytes. Generally, MIP is a kind of solid-phase extraction to generate the binding sites with a high affinity and selective recognition for the target molecule [7,8]. Artificial neural network (ANN) is a highly simplified model of the structure of biology

*Corresponding Author: h_hasshemi_85@yahoo.com

network [11]. It is a modeling tool capable of solving non-linear and linear multivariate regression problems [12,13]. An artificial neuron is the fundamental processing element of ANN. A biological neuron receives inputs from other sources, combines them, on the result performs usually a nonlinear operation, and presents the final results as output [14]. Since an ANN learns from examples and recognizes patterns in a series of input and output data without any prior assumptions about their nature and interrelations, the advantage of ANN is that it does not need any mathematical model [11]. ANN eliminates the limitations of the classical method by extracting the desired information by using the input data. Sufficient input needs for applying ANN and output data instead of mathematical equation [15]. In this paper, a molecularly imprinted polymer-coated stir bar (MIPSB) was fabricated based on the method presented in one of our previous works [7], and applied for the effective extraction and enrichment of copper as Cu-morin complex. Extraction efficiency of the complex was compared with the ANN predictions.

2. EXPERIMENTAL

2.1. Materials and methods

4-Vinylpyridine (VP) and 2, 2-azobisisobutyronitrile (AIBN) were purchased from Sigma-Aldrich (St. Louis, MO, USA). $CuSO_4.5H_2O$ (Merck KGaA, Darmstadt, Germany) was of the highest purity available. Reagent grade 3, 5, 7, 2, 4-pentahydroxyfavone (morin, 97.0% purity) was also obtained from the same company. All acid used were of the highest purity available and applied without further purification. A stock solution of the analyte (1000 mg L^{-1}) was prepared by dissolving a proper amount of $CuSO_4.5H_2O$ in ultrapure water in a 100 mL flask. Working solutions were obtained by suitable dilution of this solution with doubly distilled water.

2.2. Apparatus

Copper measurements were carried out by a Konik Won M300 (Barcelona, Spain) flame atomic absorption spectrometer (FAAS). A hollow cathode lamp was utilized that was placed on the most sensitive wavelength for copper at 324.8 nm. Bandwidth of 1.2 nm was applied. A model 630 Metrohm (Switzerland) pH meter was used for pH measurements.

2.3. Pretreatment of the stir bar

A thin hollow glass bar (15×4 mm) was filled with a magnet bar and sealed from both sides by flame. It was cleaned by distilled water, and subsequently was treated by 1.0 mol L^{-1} sodium hydroxide for 8 h, put in distilled water for 1 h and finally treated by 1 mol L^{-1} hydrochloric acid for 1 h. After then, it was washed by doubly distilled water for many times and dried in an oven at 150 ^{0}C for 1 h. Silanization of this stir bar was performed by putting it for 3 h in 25% V/V 3-(methacryloxy) propyltrimethoxy silane solution in acetone. Finally, the stir bar was washed by methanol and dried.

2.4. Preparation of MIPSB

$CuSO_4.5\ H_2O$ (0.24 g), morin (0.20 g), VP (0.40 g), EDMA (3.8 mL) and AIBN (50 mg) were dissolved in 15 mL of methanol and deoxygenized for 5 min by a stream of nitrogen. Then, the silylated SBSE was put in this solution and kept at 60 ^{0}C in a water bath. After 10 h and completion of polymerization, it was taken out and washed by 10% V/V CH_3COOH solution to remove the copper-morin complex from it.

2.5. Extraction procedure

Copper extraction was performed by dipping SBSE into 25 mL solution containing copper ions. The pH of this solution was adjusted to desired value (5.5) by drop-wise addition of either 0.1 M of NaOH or 0.1 M of HCl. Then, suitable amounts of morin (100 mg L^{-1}), as a complexing ligand, were added. To investigate the MIPSB extraction operating conditions for Cu determination, various factors which could influence on the performance of MIPSB such as the extraction and desorption times, mole ratio of morin to the copper, pH, temperature and stirring rate were studied for a standard solution including 12.5 µg of copper. After extraction, the stir bar was taken out and gently dried under N^2 stream. Desorption was performed in 10% (v/v) acetic acid solution at a pre-set stirring rate and time. The eluents were evaporated to almost dryness, then 2 mL of 1 mol $L^{-1}HNO_3$ was added and this solution was analyzed by FAAS for its Cu content. All runs were carried out for at least 3 times. The extraction yield of copper was calculated from Eq. 1:

$$Y = (C_B/C_A) \qquad \text{(Eq. 1)}$$

Where C_A and C_B are the concentrations of Cu ions in the solution before and after extraction, respectively. The experimental data and the ANN predictions are shown in Table 1 and compared.

In the present study, Neural Network Toolbox 7.11a of MATLAB mathematical software (Natick, MA, USA) was applied to predict the recovery of copper from water samples. ANN has

nonlinear characteristic and is applied to solve nonlinear equations/ or complicated calculations [16]. ANN utilized for solving non-linear regression problems is the multi-layer feed-forward neural network (FFNN). The network has an input layer, hidden layers and an output layer. The inputs for the network was extraction and desorption times, mole ratio of ligand to the analyte, pH, temperature and stirring rate and the output was the extraction yield of copper.

Fig. 1 shows the structure of proposed ANN. Here, the scaled date are passed into the input layer and then propagated from the input layer to the hidden layer, before they finally reach the output layer of the network [17]. Every node in the hidden or output layer will firstly act as a summing junction which is a single neuron summarizes the w and b into a net input Y_i known as argument to be processed and combines the inputs using Eq. 2 [18].

$$Y_i = \sum_{j=1}^{i} X_i W_{ij} + b_j \quad \text{(Eq. 2)}$$

Where y_i is the net input to node j in hidden or output layer, w_{ij} is the weights representing the strength of connection between the i^{th} node and j^{th} node, x_i is the inputs to node j (or the outputs of the previous layer), b_j and i are the bias associated with node j and the number of nodes. Each neuron has a transfer function expressing an internal activation level. The output from a neuron is determined by transforming its input applying a suitable transfer function [19].

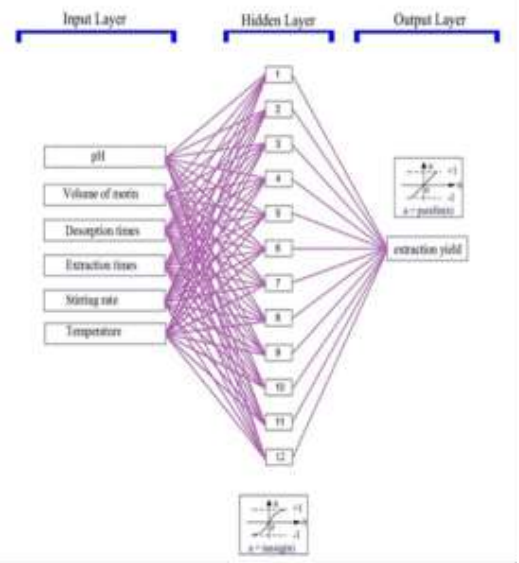

Fig. 1. Optimal artificial neural network structure.

2.7. Definition of the ANN model

Each neuron has a transfer function expressing an internal activation level. Using a suitable transfer function is transformed input to output data. Generally transfer functions for functions approximation (regression) consists of sigmoidal function (logistic), hyperbolic tangent (tansig) and linear (purelin) function [18].

The transfer (activation) function acts on the weighted sum of the neuron's inputs and most generally applied transfer function is the logistic (sigmoid) function [20, 21].

The equation of this function is indicated as Eq. 3 [18].

$$Z_j = 1/(1 + e^{-Y} y) \quad \text{(Eq. 3)}$$

Where z_j is the output of node j, is also an element of the inputs to the nodes in the next layer.The logistic is bounded between 0 and 1. Therefore the input and output values should be normalized in the range between 0 and 1 [19]. Weights are randomly chosen in during the initial training of the neural network. If one input consists of a large number and another consists of a small number, but both show a similar amount of variance. So, the network may ignore the small input due for the large contribution from the other input [22]. So, scaling (normalization) of data with special range (e.g. 0-1) is essential to avoid data by larger magnitude from overriding the smaller ones. Similarly, it is necessary to avoid a premature saturation of the hidden nodes, as this impedes the learning process. The development of an ANN model can be made more effective if the preprocessing step, normalization, is considered for the network inputs and the output data [13]. The network inputs and outputs and output data have been normalized before training. In this study, normalization of the data to the range of 0-1 was performed as follows [23]:

$$x_{norm} = (x - x_{min})/(x_{max} - x_{min}) \quad \text{(Eq.4)}$$

Where x_{norm}, x, x_{max} and x_{min} are the normalized value, the actual value, the maximum value and the minimum value respectively. The values of the interconnection weights are obtained with the training process applying a set of data. To find the value of the weight that minimizes the error is the aim [19]. An often-employed performance of the proposed network was evaluated using the mean squared error (MSE) and the coefficient of determination (R^2) as follows:

$$MSE = (1/n)\sum_{i=1}^{n}(y_i - y_{di})^2 \quad \text{(Eq. 5)}$$

$$R^2 = 1 - [\sum_{i=1}^{n}(y_i - y_{di})^2/[\sum_{i=1}^{n}(y_{di} - y_m)^2]] \quad \text{(Eq. 6)}$$

Where n, y_i, y_{di} and y_m are the number of points, the predicted obtained from the neural network model, the actual value and the average of the actual values respectively.

3. RESULT AND DISCUSSION

3.1. ANN modeling

The application of an ANN depends on the data set for its training. Here, we divided the

experimental values into three subsets of 69% for the training set, 15.5% for the validation and the test sets (Table 1). A three layer ANN by tansig transfer function at hidden layer and a purelin at output layer were utilized. It was applied to transform input data consisted of absorption and desorption time, pH, stirring rate, temperature, and volume of ligand (morin) into desired response (extraction yield of copper). Seven experimental values were selected as the validation data set to check the generality of network prediction and to prevent the over-fitting phenomenon. For each subset, the experimental data were loaded into the workspace at random.

The number of neurons in hidden layer was obtained by training several FFNNs of various topologies and choosing the optimal one based on minimization of performance function (mean squared errors; MSE) and improving the generalization ability of the topology. The obtained optimal topology of ANN includes sex inputs, one hidden layer with 12 neurons and one output layer. The optimal topology of the developed ANN model is showed in Fig. 2.

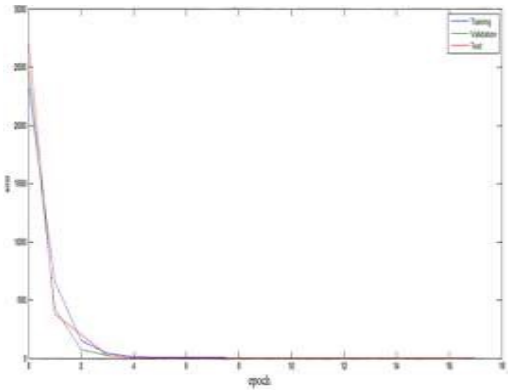

Fig. 2. Training, validation and testing mean squared errors for the Levenberg- Marquardt algorithm.

The neurons in the hidden layer consist of tansig transfer function and the output layer neuron consists of purelin transfer function. To minimize to MSE, training was performed by adjusting the weights and biases of the entire NN. Each neuron in the training set receive the signals of input, aggregates with applying the weights and biases and finally passes the results after suitable transformation as output. To finish at the point where the MSE becomes sufficiently small, the training was forced. Fig. 3 depicts the evaluation of the MSE during training phase by using Levenberg-Marquardt Algorithm (LMA). The training process was successfully terminated.

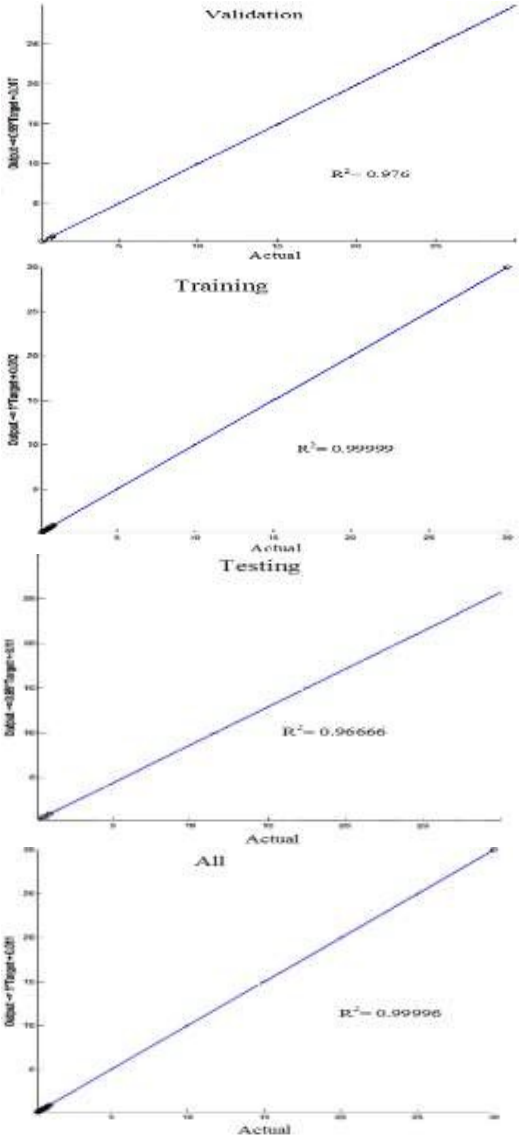

Fig. 3. Predicted extraction efficiency index by artificial neural network versus experimental validation, testing and all data sets.

This figure also shows a regression analysis between ANN outputs and experimental data. The R^2 values were determination as 0.9999, 0.975, 0.96666 for training, validation and testing data, respectively. MSE between the actual and predicted values were determined as 0.0009, 0.0032 and 0.0030 for training, validation and testing sets respectively. The MSE and R^2 for all data sets were obtained 0.0016 and 0.99996. The goodness of fit was carried out between the experimental data the predictive data. The results indicate which the predictive accuracy of the model is high. The results of this literature showed the network consisted of three layers: input, hidden and output with 12 nodes in hidden

layer has produced the best performances. As shown in Table 1, the predicted values of the best model for the training, validation and testing set. The scatter plots of the ANN model predicted versus actual values using LM algorithm for the training validation, testing and all data sets are presented in Fig. 3. As can be seen, the predicted model well fitted to the actual values for the training, validation, testing and all data set.

3.2. Comparing experimental data and ANN modeling prediction

The experimental values and ANN output were described in Fig. 4 that shows an enough agreement between experimental values and ANN predicted.

Table 1. Experimental values (training, validation and testing data set), actual and model predicated of extraction yield of copper by MIPSB.

Number	Temperature C°/	pH	Stirring rate / rpm	Volume of morin / µL	Desorption time / min	Absorption time/ min	Extraction yield	
							Actual	Predict
Training set								
1	45	2.5	700	500	30	20	0.2300	0.3102
2	45	3.0	700	500	30	20	0.5000	0.4528
3	45	3.5	700	500	30	20	0.6500	0.6427
4	45	4.0	700	500	30	20	0.8000	0.8647
5	45	5.5	700	500	30	20	1.0000	0.9798
6	45	6.0	700	500	30	20	0.6600	0.6686
7	45	6.5	700	500	30	20	0.5500	0.5512
8	45	7.0	700	500	30	20	0.3000	0.2999
9	45	7.5	700	500	30	20	0.2400	0.2403
10	45	8.0	700	500	30	20	0.2000	0.1998
11	45	5.5	700	500	30	5	0.5000	0.5439
12	45	5.5	700	500	30	10	0.8500	0.8597
13	45	5.5	700	500	30	15	0.9400	0.9606
14	45	5.5	700	500	5	20	0.3000	0.3001
15	45	5.5	700	500	10	20	0.4500	0.4477
16	45	5.5	700	500	20	20	0.7600	0.7626
17	45	5.5	700	100	30	20	0.4000	0.4010
18	45	5.5	700	300	30	20	0.8200	0.8111
19	45	5.5	700	350	30	20	0.8600	0.8689
20	45	5.5	700	400	30	20	0.9100	0.9165
21	45	5.5	700	500	30	20	1.0000	1.0077
22	45	5.5	150	500	30	20	0.2400	0.2992
23	45	5.5	200	500	30	20	0.3000	0.2832
24	45	5.5	350	500	30	20	0.4900	0.5530
25	45	5.5	400	500	30	20	0.5900	0.5812
26	45	5.5	550	500	30	20	0.8400	0.8342
27	45	5.5	600	500	30	20	0.8800	0.9196
28	25	5.5	700	500	30	20	0.5500	0.5425
29	30	5.5	700	500	30	20	0.6400	0.6422
30	35	5.5	700	500	30	20	0.7000	0.7516
31	40	5.5	700	500	30	20	0.9400	0.9377
Validation set								
32	45	2.0	700	500	30	20	0.2000	0.2108
33	45	4.5	700	500	30	20	0.8500	0.9724
34	45	5.5	700	500	25	20	0.8800	0.8882
35	45	5.5	700	250	30	20	0.7700	0.7407
36	45	5.5	250	500	30	20	0.3600	0.4146
37	45	5.5	450	500	30	20	0.6700	0.6351
38	45	5.5	500	500	30	20	0.7700	0.7273
Testing set								
39	45	5.0	700	500	30	20	0.9500	0.8452

40	45	5.5	700	500	15	20	0.6500	0.6088
41	45	5.5	700	150	30	20	0.5100	0.5421
42	45	5.5	700	200	30	20	0.6200	0.6531
43	45	5.5	700	450	30	20	0.9500	0.9541
44	45	5.5	300	500	30	20	0.4400	0.5102
45	45	5.5	650	500	30	20	0.9300	0.9663

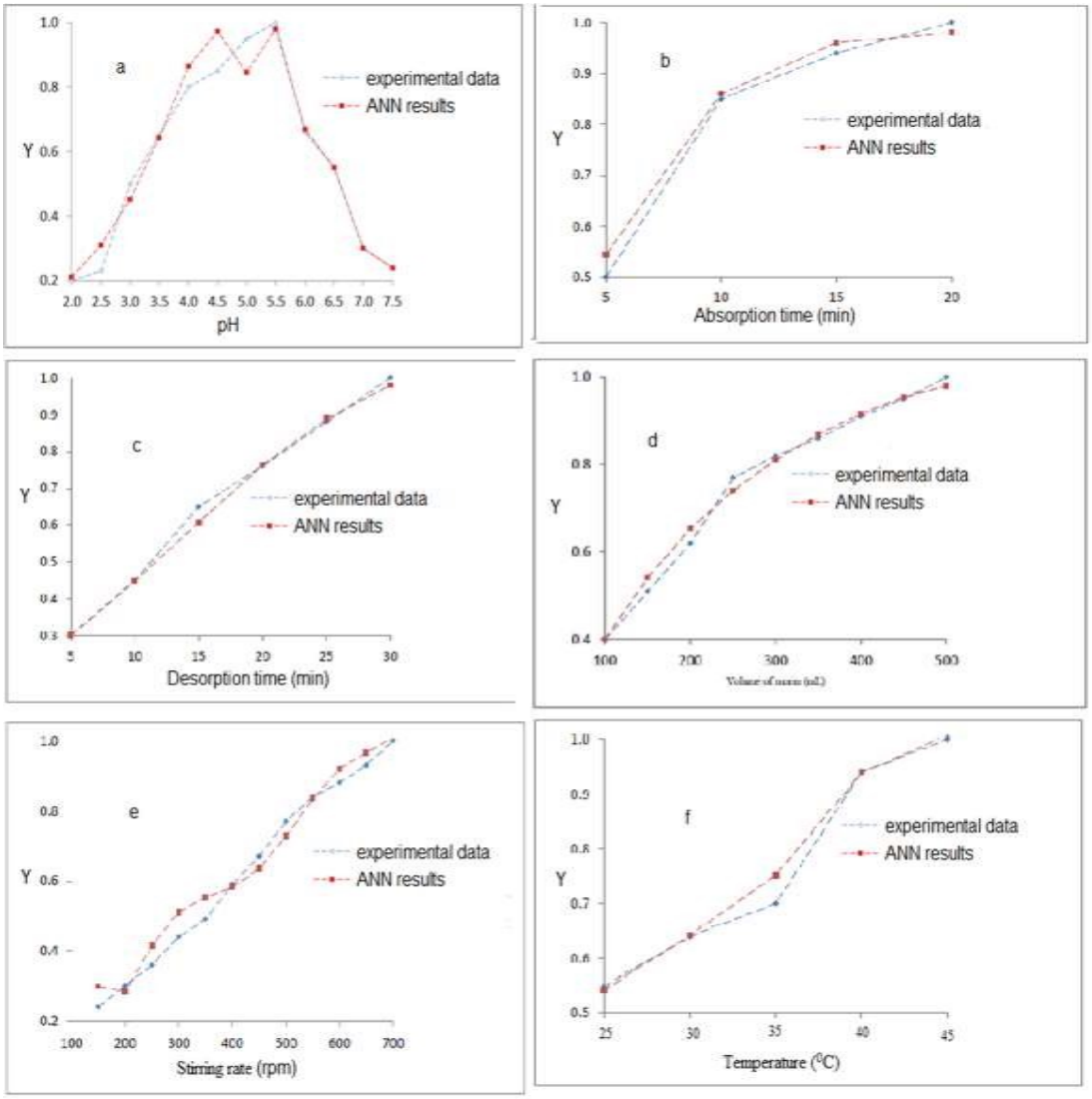

Fig. 4. Comparing ANN output and experimental data, effect of pH, absorption and desorption time, stirring rate, temperature and volume of ligand.

3.2.1. Effect of pH

The effect of pH value on the absorption of Cu-morin complex on SBSE was studied in the range of 2.0 to 7.5. In Fig. 4a experimental data and ANN output are showed for this study. The results illustrates that the extraction efficiency was at the highest point at a pH of 5.5 (experimental data and ANN results). So, pH 5.5 was selected for further works.

3.2.2. Effect of adsorption and desorption time

Extraction recovery of Cu-morin complex increases as the adsorption time increases and reaches to a maximum at 20 min. The percent elution of adsorbed Cu^{+2}-morin complex from MIPSB occurred after 30 min by 10% V/V acetic acid solution. The Effect of adsorption and desorption time on the recovery of Cu-morin

(experimental data) and ANN output are showed in Fig. 4b and Fig. 4c, which both of them indicate that the best adsorption and desorption times are 20 and 30 min, respectively. Hence, these values were chosen for further work.

3.2.3. Effect of volume of morin

To study the optimum volume of morin on the recovery of Cu^{+2} by MIP sorbent, ion extraction was conducted with changing the volume of morin from 100 to 500 µL. Fig. 4d shows that quantitative enrichment of adsorbed analyte on the MIPSB can be found using volumes of morin greater than 500 µL (both experimental data and ANN prediction). So, next extraction runs were performed with the volume of 500 µL of morin.

3.2.4. Effect of stirring rate

The effect of stirring rate on the recovery of the complex was also investigated. The experimental and ANN observations expressed that the percent extraction increased by an increase of stirring rate up to 700 rpm. So, a rate of 700 rpm was chosen in subsequent studies (Fig. 4e).

3.2.5. Effect of temperature

Both experimental and ANN results showed that desorption of copper morin complex from the MIPSB sorbent increased by increasing temperature and became constant after 45 ^{0}C (Fig. 4f).

3.3. Linear range, detection limit and preconcentration factor

In the optimum values of extraction, the calibration graph was plotted and found to be linear between 5 and 1000 µg L^{-1} and the least square equation was $A = 0.3378 \times C(\mu g L^{-1}) + 0.0014$ (R^2= 0.999); in which C=concentration of copper-morin complex and A=response of FAAS. The limit of detection (LOD) achieved by using $3S_d$ m^{-1} criteria was calculated as 0.38 µg L^{-1} (S_d=the standard deviation of 10 following determinations of the blank and m=the slope of the calibration graph). In order to achieve a high enrichment factor (EF), the influence of the volume of sample on the response of FAAS of copper was investigated between 25 and 500 mL. The extraction efficiency of the complex was excellent (>97%) in a volume of sample between 25 and 250 mL and then decreased. Since the optimum volume of sample was 250 mL, and percent extraction was 98%, enrichment factor is 48 folds.

3.4. Interference studies

Interference investigations were carried out in 500 µg L^{-1} of Cu and various concentrations of interference ions. Among the foreign ions investigated, pb^{2+}, Ag^{+} and Au^{+} (ion/ Cu (w/w%=1000) and Co^{2+}, Cd^{2+}, Fe^{3+}, Zn^{2+}, Ni^{2+} and Cr^{3+} (ion/Cu (w/w%=200) did not interfere with copper determination. Because of the Cl^{-}, NO_3^{-} and SO_4^{-2} ions in combined by above ions were used in the research without any interference, so, these anions have not interference.

3.5. Real sample

The suggested procedure was employed for sorptive extraction of Cu from 25 mL of three various real samples taken from tap water, a well and a local mineral water source. Samples were spiked at four levels and observations shown that protocol can be successfully employed for enrichment and determination of the complex of copper-morin. Reproducibility as relative standard deviation was between 0.56 and 5.3% (Table 2).

Table 2. Results of determination of copper in three real samples.

Sample	Spiked amount (mg L^{-1})	Recovery (%)	RSD (%)
Tap water	-	-	-
	0.80	98.8	5.3
	0.50	98.0	1.9
	0.10	97.0	0.56
	0.05	99.2	2.5
Well water	-	-	-
	0.80	97.5	0.88
	0.50	97.6	2.6
	0.10	98.0	3.5
	0.05	98.8	3.5
Mineral water	-	-	-
	0.80	97.5	0.88
	0.50	98.0	2.4
	0.10	96.0	0.63
	0.05	96.0	3.5

4. CONCLUSION

Molecularly imprinted stir bar sorptive extraction was successfully utilized for the preconcentration and extraction of copper-morin complex from water samples before its FAAS determination. MIPSB showed good chemical and physical stability and revealed high affinity and selectivity towards its copper-morin. These experimental data were compared to the data acquired from an ANN model that could reliably predict the extraction efficiency of copper ions from water samples. A three layer (input, hidden and output layers) ANN with tansig and purelin at hidden layer and output layer was applied for this purpose. The evaluation of the MSE was obtained during training phase using LMA. MSE and correlation coefficient between the experimental

data and the ANN predictions were determined as 0.0009 and 0.9999 for training, 0.0032 and 0.976 for validation, 0.0030 and 0.96666 for testing and 0.0016 and 0.99996 for all data sets. An optimal number of 12 neurons were obtained in the hidden layer. The experimental data and ANN modeling prediction was compared and the results showed that a network accurate in predicting the extraction yield of copper ions in water samples.

REFERENCES

[1] N.L. Nemerow, Industrial waste treatment: contemporary practice and vision for the future, *Elsevier Inc*., Burlington, USA. (2010).

[2] N.L. Nemerow and F.J. Agardy, Strategies of industrial and hazardous waste management, Van Nostrand Reinhold, New York, USA (1998).

[3] N. Pechishcheva and K.Y. Shunyaev, Application of luminescence to the determination of trace copper, *J. Anal. Chem*. 63 (2008) 412-423.

[4] G.F. Lima, M.O. Ohara, D.N. Clausen, D.R. Nascimento, E.S. Ribeiro, M.G. Segatelli, M.A. Bezerra and C.R. Tarley, Flow injection on-line minicolumn preconcentration and determination of trace copper ions using an alumina/titanium oxide grafted silica matrix and FAAS, *Microchim. Acta* 178 (2012) 61-70.

[5] M. Csuros and C. Csuros, Environmental sampling and analysis for metals, 1st edition, *CRC Press*, NY, USA (2016) p. 20.

[6] W.B. Mills, D.B. Porcella, M. Ungs, S. Gherini and K. Summers, Water-quality assessment: a screening procedure for toxic and conventional pollutants in surface and ground water (1985).

[7] H. Hashemi, M. Khajeh and M. Kaykhaii, Molecularly imprinted stir bar sorptive extraction coupled with atomic absorption spectrometry for trace analysis of copper in drinking water samples, *Anal. Methods* 5 (2013) 2778-2783.

[8] N. Zhang and B. Hu, Cadmium (II) imprinted 3-mercaptopropyltrimethoxysilane coated stir bar for selective extraction of trace cadmium from environmental water samples followed by inductively coupled plasma mass spectrometry detection, *Anal. Chim. Acta* 723 (2012) 54-60.

[9] S.H. Hashemi, M. Kaykhaii, A.J. Keikha, Z. Sajjadi and M. Mirmoghaddam, Application of response surface methodology for silver nanoparticle stir bar sorptive extraction of heavy metals from drinking water samples: a Box-Behnken design, *Analyst* 144 (2019) 3525-3532.

[10] S.H. Hashemi, M. Kaykhaii and F. Tabehzar, Molecularly imprinted stir bar sorptive extraction coupled with high performance liquid chromatography for trace analysis of naphthalene sulfonates in seawater, *J. Iran Chem. Soc*. 13 (2016) 733-741.

[11] S. Mandal, P. Sivaprasad, S. Venugopal and K. Murthy, Artificial neural network modeling to evaluate and predict the deformation behavior of stainless steel type AISI 304L during hot torsion, *Appl. Soft Comput*. 9 (2016) 237-244.

[12] M. Khayet and C. Cojocaru, Artificial neural network modeling and optimization of desalination by air gap membrane distillation, *Sep. Purif. Technol.* 86 (2012) 171-182.

[13] M. Khayet, C. Cojocaru and M. Essalhi, Artificial neural network modeling and response surface methodology of desalination by reverse osmosis, *J. Membrane Sci.* 368 (2011) 202-214.

[14] D. Baş and İ.H. Boyacı, Modeling and optimization II: Comparison of estimation capabilities of response surface methodology with artificial neural networks in a biochemical reaction, *J. Food Eng*. 78 (2007) 846-854.

[15] M.A. Akcayol and C. Cinar, Artificial neural network based modeling of heated catalytic converter performance, *Appl. Therm. Eng.* 25 (2005) 2341-2350.

[16] Y.X. Jin, H.Z. Cheng, J.Y. Yan and L. Zhang, New discrete method for particle swarm optimization and its application in transmission network expansion planning, *Electr. Power Syst. Res.* 77 (2007) 227-233.

[17] M. Hussain, M.S. Rahman and C. Ng, Prediction of pores formation (porosity) in foods during drying: generic models by the use of hybrid neural network, *J. Food Eng*. 51 (2002) 239-248.

[18] E. Jorjani, S.C. Chelgani and S. Mesroghli, Application of artificial neural networks to predict chemical desulfurization of Tab as coal, *Fuel* 87 (2008) 2727-2734.

[19] M.A. Razavi, A. Mortazavi and M. Mousavi, Dynamic modelling of milk ultrafiltration by artificial neural network. *J. Membrane Sci.* 220 (2003) 47-58.

[20] J.S. Torrecilla, L. Otero and P. Sanz, Optimization of an artificial neural network for thermal/pressure food processing: Evaluation of training algorithms, *Comput. Electron. Agric.* 56 (2007) 101-110.

[21] A. Ghaffari, H. Abdollahi, M. Khoshayand, I.S. Bozchalooi, A. Dadgar and M. Rafiee-

Tehrani, Performance comparison of neural network training algorithms in modeling of bimodal drug delivery, *Int. J. Pharm*. 327 (2006) 126-138.

[22] M. Khare and S.S. Nagendra, Artificial neural networks in vehicular pollution modelling, Springer-Verlog Berlin Heidelberg (2007).

[23] Y. Erzin, B.H. Rao and D. Singh, Artificial neural network models for predicting soil thermal resistivity, *Int. J. Therm. Sci*. 47 (2008) 1347-1358.

کاربرد شبکه عصبی مصنوعی در پیشگویی بازده استخراج کمپلکس مس- مورین از محیط‌های آبی با بکارگیری مولکول نگاری پلیمری پوشش‌دار شده روی میله همزن

سید حسین هاشمی[1،*]، مسعود کیخوائی[2]، محمد شاکری[3]

۱. گروه شیمی دریا، دانشکده علوم دریایی، دانشگاه دریانوردی و علوم دریایی، چابهار، ایران

۲. گروه شیمی، دانشکدهٔ علوم، دانشگاه سیستان و بلوچستان، زاهدان

۳. گروه شیمی، دانشکدهٔ علوم، دانشگاه زابل، ایران

تاریخ دریافت: ۲ اسفند ۱۳۹۸ تاریخ پذیرش: ۲۷ اسفند ۱۳۹۸

چکیده

در این تحقیق، یک روش جدید مدل سازی با شبکه عصبی مصنوعی سه لایه‌ای برای پیشگویی بازده استخراج کمپلکس مس- مورین از نمونه‌های آبی توسط استخراج بر روی میلهٔ همزن پوشش‌دار شده با مولکول نگاری پلیمری بکار رفت. داده‌های ورودی مدل شبکه عصبی مصنوعی، pH، زمان جذب و واجذب، سرعت هم‌زدن، دما و مقدار لیگاند بودند و خروجی آن بازده استخراج یون‌های مس بود. نتایج نشان داد که شبکهٔ با ۱۲ نرون مخفی صحت بالائی در پیشگویی بازده استخراج کمپلکس مس- مورین در نمونه‌های آبی دارد. میانگین خطای مربعات و ضریب همبستگی بین داده‌های تجربی و پیشگویی‌های ۰/۰۰۰۹ و ۰/۹۹۹۹ برای آموزش، ۰/۰۰۳۲ و ۰/۹۷۶ برای ارزیابی و ۰/۰۰۳۰ و ۰/۹۶۶۶۶ برای داده‌های آزمایش تعیین شد. در شرایط بهینه، گسترهٔ خطی دینامیکی ۵/۰ تا ۱۰۰۰/۰ میکروگرم بر لیتر با حدّ تشخیص ۰/۳۸ میکروگرم بر لیتر به دست آمد و انحراف استاندارد نسبی کمتر از ۵/۳٪ بود. این روش با موفقیّت برای پیش تغلیظ و تعیین مس در چند نمونهٔ حقیقی بکار گرفته شد.

واژه‌های کلیدی

شبکه عصبی مصنوعی؛ استخراج مس؛ میلهٔ همزن پوشش‌دار شده با مولکول‌نگاری پلیمری؛ تجزیهٔ آب.