

## Prediction of Ionic Cr (VI) Extraction Efficiency in Flat Sheet Supported Liquid Membrane Using Artificial Neural Networks (ANNs)

Eyupoglu, V.<sup>1\*</sup>, Eren, B.<sup>2</sup> and Dogan, E.<sup>3</sup>

<sup>1</sup>Sakarya University, Department of Chemistry, Esentepe Campus, 54187 Sakarya, Turkey

<sup>2</sup>Sakarya University, Department of Environmental Engineering, Esentepe Campus, 54187 Sakarya, Turkey

<sup>3</sup>Sakarya University, Department of Civil Engineering, Esentepe Campus, 54187 Sakarya, Turkey

Received 4 Nov. 2009;

Revised 15 March 2010;

Accepted 22 March 2010

**ABSTRACT:** Artificial neural networks (ANNs) are computer techniques that attempt to simulate the functionality and decision-making processes of the human brain. In the past few decades, artificial neural networks (ANNs) have been extensively used in a wide range of engineering applications. There are only a few applications in liquid membrane process. The objective of this research was to develop artificial neural networks (ANNs) model to estimate Cr (VI) extraction efficiency in feed phase. Data set (413 experiment records) were obtained from a laboratory scale experimental study. Various combinations of experimental data, namely % (w/w) extractant Alamine 336 concentration in membrane phase, stirring speed in feed and stripping phase, flat sheet support type, stripping phase NaOH concentration, feed phase pH, diluents type, % (w/w) diluents concentration, polymer support type, extractant type, and time are used as inputs into the ANN so as to evaluate the degree of effect of each of these variables on Cr (VI) extraction efficiency in feed phase. The results of the ANN model is compared with multiple linear regression model (MLR). Mean square error (MSE), average absolute relative error (AARE) and coefficient of determination ( $R^2$ ) statistics are used as comparison criteria for the evaluation of the model performances. Based on the comparisons, it was found that the ANN model could be employed successfully in estimating the Cr (VI) extraction efficiency.

**Keywords:** Artificial neural networks, multiple linear regression models, supported liquid membrane, chromium (VI) extraction, solvent extraction

### INTRODUCTION

The extensive use of chromium in leather tanning, metallurgy, electroplating spraying anticorrosion coatings, dyeing in textile, welding and cutting stainless steel, and other industries has resulted in the release of aqueous chromium to the subsurface at numerous sites. While chromium oxidation states range from  $-2$  to  $+6$  (Cotton, *et al.*, 1988), the  $+3$  and  $+6$  states are most prevalent in the environment. The hexavalent chromium anions chromate ( $\text{CrO}_4^{2-}$ ), bichromate ( $\text{HCrO}_4^-$ ) and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) are not strongly sorbed in many soils under alkaline condition to slightly acidic conditions (Kabir and Ogbeide, 2008; Abdullahi *et al.*, 2009). Chromium (VI) is recognized to be much more toxic than Cr (III), and is found to be toxic to bacteria, plants, animals and people. Human toxicity includes lung cancer, as well as kidney, liver, and gastric damage. Therefore, the level of chromium in discharged wastewater should be reduced. Its concentrations in industrial wastewaters range from  $0.5$  to  $270,000$  mg  $\text{L}^{-1}$ . Many countries have regulations of the maximum permissible

concentration of Cr (VI) in natural or drinking water. The tolerance limit for Cr (VI) for discharge into inland surface waters is  $0.1$  mg/L and in potable water is  $0.05$  mg/L. Thus, the removal of Cr (VI) from industrial effluents is important before discharging them into aquatic environments or onto land (Kumbasar, 2009). Various methods have been developed for the removal of chromium (VI) from industrial waste waters. It includes chemical precipitation, ion exchange, solvent extraction, reverse osmosis, diffusion dialysis, adsorption, etc. (Palmer *et al.*, 1988). The conventional and the most commonly used method for chromium (VI) removal is chemical precipitation (Young *et al.*, 1986). In this method, the Cr (VI) is first reduced to Cr (III) which is then precipitated for removal. But the process is very tedious requiring a large amount of chemicals (Sahmoune *et al.*, 2009; Biati *et al.*, 2010).

In recent years, a remarkable increase of the applications of liquid membranes in separation processes is observed. These membranes include bulk liquid membranes (BLMs), emulsion liquid membranes

\*Corresponding author E-mail: chemist49@gmail.com

(ELMs), and flat sheet supported liquid membranes (FSSLMs). Two papers (Zouhri *et al.*, 1995; Zouhri *et al.*, 1999) deal with applications of BLMs for Cr (VI) removal using dicyclohexane-18-crown-6 as ion carrier. Several results of the concentration and separation of chromium (VI) with ELM process have been also reported. Tertiary amines, such as tri-*n*-dodecylamine (Mori *et al.*, 1999), and Alamine 336 (Kumar *et al.*, 1994) were used as the ion carriers. Quaternary ammonium salt, such as Aliquot 336 was also applied as an ion carrier in ELMs (Salazar *et al.*, 1992; Banerjee *et al.*, 2000). The applications of FSSLMs for chromium (VI) concentration and separation with tertiary amines and quaternary ammonium salts as the most widely used ionic carriers have been shown in two papers (Chiarizia, 1991; Wang *et al.*, 1998). Recently, in this papers reported the use of the commercially available phosphine oxide [Cyanex 923] (Alguacil *et al.*, 2000). A common problem for FSSLMs is the loss of membrane, diluents and/or carrier to the both aqueous phases, and as the result the FSSLM-based processes have not been exploited industrially due to their poor durability. Recently, published papers, which deal with chromium (VI) transport across ELMs (Bhowal and Datta, 2001) and FSSLMs (Alguacil *et al.*, 2001; Park *et al.*, 2001). The FSSLM technology offers an attractive alternative to the conventional liquid-liquid (L-L) extraction by combining the extraction and stripping in a single step operation. An FSSLM usually consists of an organic solution immobilized in the pores of a hydrophobic macro porous membrane that contains an extractant agent (carrier) that selectively binds one of the components from the feed solution. The FSSLM separates, by means of two interfaces, the aqueous solution containing the species that diffuse (feed) and the solution into which the species will diffuse (strip). The species are accumulated in the strip phase at a concentration generally greater than that in the feed phase. The permeation of the species is due to a chemical potential gradient (the driving force of the process) that exists between the opposite sides of the FSSLM. High enrichment factors (EFs) can be achieved when using FSSLM in hollow fiber (HF) configuration which has several additional advantages like the high feed to stripping volume ratio leading to higher enrichment of the analyte and easy coupling to the sensitive analytical techniques (Cezary and Walkowiak, 2002; Asraf and Mian, 2006).

The present work has been undertaken in an attempt to simulate the Cr (VI) extraction efficiency in feed phase using artificial neural network model. ANN has a vast range of applications in fields of agriculture, weather forecasting, finance and economics, medicine, robotics, material science, chemistry and chemical engineering, etc (Naik and Manjapp, 2010). Appli-

cations of ANNs to the chemical engineering have increased significantly since 1988. One of the first applications was by Hoskins and Himmelblau (Hoskins and Himmelblau, 1988; Jalili Ghazi Zade and Noori, 2008), who applied ANN to fault diagnosis. Since then the number of research publications on ANN applications in chemical engineering has risen astronomically. Recently artificial neural networks have been used for modeling of liquid-liquid extraction column (Chouai *et al.*, 2000), vapor-liquid equilibrium data analysis for mixed solvent (Iliuta *et al.*, 2000) and for modeling of transportation and dispersion of tracers in complex terrain (Podnar *et al.*, 2002).

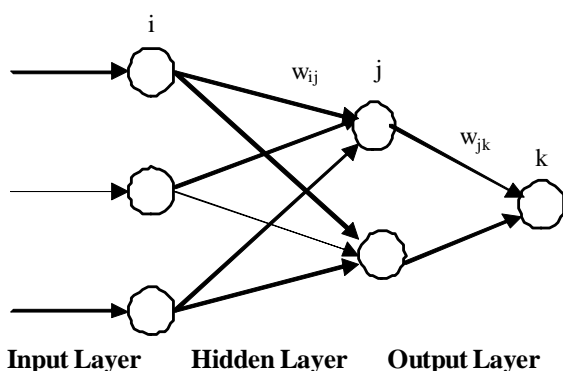
The objective of the present study is to develop and train a network of suitable architecture for simulation of Cr (VI) extraction efficiency in feed phase. Experimental data from laboratory analysis have been used to train the network employing the back-propagation learning algorithm. The predicted values of Cr (VI) extraction efficiency in feed phase are found to be in good agreement with the experimental results.

## MATERIALS & METHODS

Artificial Neural Networks (ANNs) consist of large number of processing elements with their interconnections. ANNs are basically parallel computing systems similar to biological neural networks. They can be characterized by three components:

- Nodes
- weights (connection strength)
- An activation (transfer) function

ANN modeling is a nonlinear statistical technique. It can be used to solve problems that are not amenable to conventional statistical and mathematical methods. In the past few years there has been constantly increasing interest in neural networks modeling in different fields of chemical engineering (Abilov and Zehra, 2000; Rajasimman *et al.*, 2009). The basic unit in the artificial neural network is the node. Nodes are connected to each other by links known as synapses, associated with each synapse there is a weight factor. Usually neural networks are trained so that a particular set of inputs produces, as nearly as possible, a specific set of target outputs. The most commonly used ANN is the three-layer feed-forward ANN. In feed-forward neural networks architecture, there are layers and nodes at each layer. Each node at input and inner layers receives input values, processes and passes to the next layer. This process is conducted by weights. Weight is the connection strength between two nodes. The numbers of neurons in the input layer and the output layer are determined by the numbers of input and output parameters, respectively. In the present feed-forward artificial neural networks are used. The model is shown in Fig. 1.



**Input Layer      Hidden Layer      Output Layer**  
**Fig. 1. A typical three-layer feed forward ANN**

In the Fig. 1, i, j, k denote nodes input layer, hidden layer and output layer, respectively.  $w$  is the weight of the nodes. Subscripts specify the connections between the nodes. For example,  $w_{ij}$  is the weight between nodes i and j. The term “feed-forward” means that a node connection only exists from a node in the input layer to other nodes in the hidden layer or from a node in the hidden layer to nodes in the output layer; and the nodes within a layer are not interconnected to each other. Commonly, neural network modeling follows these steps: database collection; analysis and preprocessing of the data; training of the neural network. The latter includes the choice of architecture, training functions, training algorithms and parameters of the network; testing of the trained network; and using the trained neural network for simulation and prediction. The model developed here has adopted these steps. Multiple linear regression attempts to model the relationship between two or more explanatory variables and a response variable by fitting a linear equation to observed data. Every value of the independent variable  $X$  is associated with a value of the dependent variable  $Y$ . If it is assumed that the dependent variable  $Y$  is affected by  $m$  independent variables  $X_1, X_2, \dots, X_m$  and a linear equation is selected for the relation among them, the regression equation of  $Y$  can be written as:

$$y = a + b_1x_1 + b_2x_2 + \dots + b_mx_m \quad (1)$$

$y$  in this equation shows the expected value of the variable  $Y$  when the independent variables take the values  $X_1 = x_1, X_2 = x_2, \dots, X_m = x_m$ .

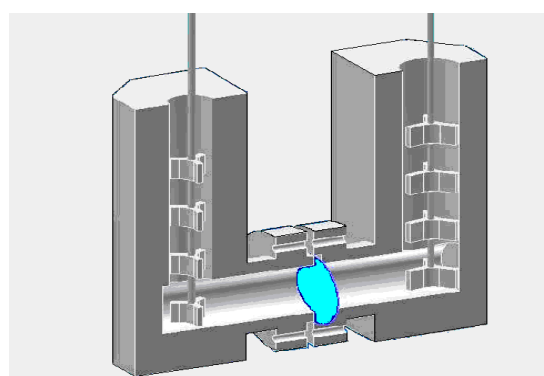
The regression coefficients  $a, b_1, b_2, \dots, b_m$  are evaluated, similar to simple regression, by minimizing the sum of the  $e_{yi}$  distances of observation points from the plane expressed by the regression equation.

$$\sum_{i=1}^N e_{yi}^2 = \sum_{i=1}^N (y_i - a - b_1x_{1i} - b_2x_{2i} - b_mx_{mi})^2 \quad (2)$$

In this study, the coefficients of the regressions were determined using least square method. The FSSLM were impregnated with carrier (Alamine 336) solutions containing the extractant dissolved in chloroform, car-

bon tetrachloride, n-decanol, toluene, cycloheksan and immersed for 12 hour and then leaving it to drip for a few seconds before being placed in the transport cell.

Batch FSSLM measurements were performed in a two-compartment permeation cell was showed (Fig. 2) which consisted of a feed phase (250 mL) separated from a stripping phase chamber (200 mL) by a FSSLM having an effective membrane area of 19.63 cm<sup>2</sup>. The feed and stripping phases were mechanically stirred at various rpm. Samples were taken each an hour while phases were being stirring.



**Fig. 2. Experiment Apparatus**

Membrane permeabilities were determined by monitoring Cr (VI) concentration by AAS (Shimadzu AA-6701GF spectrophotometer) in the feed and stripping phase as a function of time. The chromium concentration in the various phases was found to be reproducible within  $\pm 4\%$ .

Cr (VI) extraction efficiency in feed phase ( $E_o$ ), time, initial concentration, % (w/w) extractant, extractant type, % (w/w) diluents, diluents type, support type, pH, stirring speed in feed phase, stirring speed in stripping phase, NaOH concentration in stripping phase data sets obtained from the laboratory experiments were used in the study. The matching of experimental parameters with number is given below Table 1. The statistical parameters of each data are given in Table 2. In this table,  $x_{mean}, S_x, C_v, C_{sx}, x_{min},$  and  $x_{max}$  denote the mean, standard deviation, variation, skewness coefficient, minimum and maximum of the data, respectively. It is clearly seen from Table 2 the mostly varied ( $C_v=0.831$ ) data is time. Its minimum value is 1.00 while its mean and maximum values are 5.039 and 49.00, respectively. The highest correlation coefficient with the  $E_o$  (0.0616) belongs to the support type.

**RESULTS & DISCUSSION**

In this study, before the training of the model both input and output variables were normalized within the range 0.1 to 0.9 as follows:

**Table 1. The matching of experimental parameters with the numbers**

No.	Experimental Parameters
1	Time
2	Initial Concentration
3	%(w/w) Extractant
4	Extractant Type
5	%(w/w) Diluents
6	Diluents Type
7	Support Type
8	pH
9	Stirring Speed in Feed Phase
10	Stirring Speed in Stripping Phase
11	NaOH Concentration in Stripping Phase

$$x_i = 0.8 \frac{(x - x_{min})}{(x_{max} - x_{min})} + 0.1 \quad (3)$$

where  $x_i$  is the normalized value of a certain parameter,  $x$  is the measured value for this parameter;  $x_{min}$  and  $x_{max}$  are the minimum and maximum values in the database for this parameter, respectively.

To develop an ANN model for estimating  $R_o$ , the available data set was partitioned into a training set and a test set according to station. About 63% (261 laboratory data set) of the available record was selected for training while the remaining 37% (152 for laboratory data set) was used for testing. For all created neural networks the general structure of input, one hidden and one output layer was used. In order to determine the optimal architecture, several neural networks were trained with different iteration number (epoch) and number of nodes in the hidden layer. For all cases a “log sigmoid transfer function (logsig)” was used in the hidden and output layers. When the logsig was applied, the inputs and the outputs were normalized to within the range 0-1. The most accurate estimations of

the ANN’s were obtained with log sigmoid transfer function.

The selection of the input parameters is a very important aspect for the neural network modeling. In order to use ANN structures effectively, input variables in the phenomenon must be selected with a great care. This highly depends on the better understanding of the problem. In a firm ANN architecture, in order not to confuse training process key variables must be introduced and unnecessary variables must be avoided. For this purpose, a sensitivity analysis can be used to find out the key parameters. Also sensitivity analysis can be useful to determine the relative importance of the parameters when sufficient data are available. The sensitivity analysis is used to determine the effect of changes and to determine relative importance or effectiveness of a variable on the output. The input variables that do not have a significant effect on the performance of an ANN can be excluded from the input variables, resulting in a more compact network. Then, it becomes necessary to work on methods like sensitivity analysis to make ANN work effectively.  $E_o$  depends on the some independent parameters and those can be given in this form:  $E_o = f(\text{time, initial concentration, \% (w/w) extractant, extractant type, \% (w/w) diluents, diluents type, support type, pH, stirring speed in feed phase, stirring speed in stripping phase, NaOH concentration in stripping phase})$ . The eleven ANN models were established using each independent parameter separately. Sensitivity analysis applied for finding the most effective input parameters. Sensitivity analysis determination coefficient ( $R^2$ ) of the parameters involved in the phenomenon is given in Table 3. It is clearly seen from Table 3 that the most effective parameter is determined as time.

One of the problems that occur during neural network training is called over fitting. Over fitting is sug-

**Table 2. The statistical parameters of each data set**

Data Set	$\bar{x}_{mean}$	$S_x$	$C_y(S/\bar{x}_{mean})$	$C_{sx}$	$x_{min}$	$x_{max}$	Correlation with $E_o$
Time	5.039	4.185	0.831	5.007	1.000	49.00	0.00032
Initial concentration	442.0	8.500	0.019	2.992	100.0	1200	0.00044
%(w/w) Extractant	8.242	0.166	0.020	0.284	0.000	20.00	0.00008
Extractant type	1.041	0.012	0.012	6.612	1.000	3.000	0.00532
%(w/w) Diluents	91.38	0.110	0.001	1.006	90.00	95.00	0.00002
Diluents type	1.218	0.038	0.031	3.769	1.000	5.000	0.00824
Support type	1.162	0.034	0.029	4.485	1.000	5.000	0.06158
pH	0.906	0.046	0.051	2.672	0.500	5.000	0.04736
Stirring speed in feed phase	1188	5.708	0.005	-2.847	600.0	1500	0.00039
Stirring speed in stripping phase	1188	5.708	0.005	-2.847	600.0	1500	0.00038
NaOH concentration in stripping phase	2.668	0.028	0.011	-1.745	0.500	3.000	0.01333
Chromium extraction Efficiency ( $E_o$ )	57.16	1.391	0.024	-0.134	100.0	0.552	1.00000

**Table 3. The sensitivity analysis of each input parameters using ANN**

Data Set	R <sup>2</sup>
Time	0.4838
Initial concentration	0.0757
%(w/w) Extractant	0.0261
Extractant type	0.0000
%(w/w) Diluents	0.0000
Diluents type	0.0289
Support type	0.0944
pH	0.0453
Stirring speed in feed phase	0.0007
Stirring speed in stripping phase	0.0002
NaOH concentration in stripping phase	0.0143

gested when the error on the training set is driven to a very small value, while for the test data presented to the network the error is large. That means the network has memorized the training examples, but it has not learned to generalize to new situations. In order not to over fit training data, appreciate epoch number, number of hidden layers and node number of hidden layer must be chosen by trial and error process. Networks are sensitive to the number of nodes in their hidden layers. Too few nodes can lead to under fitting and too many nodes can result in over fitting. In order to reach an optimum amount of hidden layer nodes 2, 5, 8, 12, 16, 20, 25, 35, 45 and 50 nodes are tested. The results are shown in Table 4. The first column in this table denotes the nodes of each layer for the ANN models. Accordingly, an ANN structure like ANN (i,j,k) indicates a network architecture with i, j and k nodes in input, hidden and output layers, respectively. In this case the input layer covers time, initial concentration, % (w/w) extractant, extractant type, % (w/w) diluents, diluents type, support type, pH, stirring speed in feed phase, stirring speed in stripping phase, NaOH concentration in stripping phase and the output layer consists of the Cr (VI) extraction efficiency in feed phase (E<sub>o</sub>). It can be seen from the Table 4 that the ANN (11,45,1) model with 2000 iterations has the R<sup>2</sup> value of 0.938 and MSE value of 39.890 is the best model.

It appears that while assessing the performance of any model for its applicability in estimating E<sub>o</sub>, it is not only important to evaluate the average prediction error but also the distribution of prediction errors. The statistical performance evaluation criteria employed so far in this study are global statistics (R<sup>2</sup> and MSE) and do not provide any information on the distribution of errors. Therefore, in order to test the robustness of the model developed, it is important to test the model using some other performance evaluation criteria such as average absolute relative error (AARE). The AARE not only gives the performance index in terms of predicting E<sub>o</sub> but also shows the distribution of the prediction errors.

These criteria can be computed as:

$$AARE = \frac{1}{N} \sum_{p=1}^n |RE| \quad (4)$$

in which,

$$RE = \frac{t_p - o_p}{t_p} \cdot 100 \quad (5)$$

where RE is the relative error in forecast expressed as percentage, t<sub>p</sub> is the observed E<sub>o</sub> for the p<sup>th</sup> pattern; and o<sub>p</sub> is the computed E<sub>o</sub> for the p<sup>th</sup> pattern which is produced by ANN; and N is the total number of the testing patterns. Clearly the smaller the value of AARE is the better performance. The performance control of the ANN output was evaluated by estimating the determination coefficient (R<sup>2</sup>) which is defined as:

$$R^2 = \frac{E_{ot} - E_{os}}{E_{os}} \quad (6)$$

where:

$$E_{ot} = \sum_{p=1}^n (t_p - t_{mean})^2 \quad (7)$$

where, t<sub>mean</sub> is the mean E<sub>o</sub>.

The mean Square error (MSE) is defined as,

$$E_{os} = \sum_{i=1}^n (t_p - o_p)^2 \quad (8)$$

MSE=

$$\frac{1}{N} \sum_{i=1}^N (t_p - o_p)^2 \quad (9)$$

Time is used as the common parameter for the rest of the sensitivity analysis. Performance evaluation of all possible combination of variables such that each and every combination includes time, was also investigated. The findings are listed in Table 5. As can be seen from Table 3, the most effective parameter is determined as time. However, it is clearly seen from Table 5 adding other parameters into model increases the models' performances. Based on the findings, as depicted in Table 5 the ANN model has eleven inputs (time, initial concentration, % (w/w) extractant, extractant type, % (w/w) diluents, diluents type, support type, pH, stirring speed in feed phase, stirring speed in stripping phase, NaOH concentration in stripping phase) gives the best estimation. Sensitivity analysis determination coefficient (R<sup>2</sup>) of the parameters involved in the phenomenon is given in Table 6. It is clearly seen from Table 6 that the most effective parameter is determined as support type. The performance criterion for the test results of the MLR model is given in Table 7. The MLR estimates are demonstrated in Fig. 3.

As can be seen from Table 7, the most effective parameter is determined as support type. However, it is

**Table 4 . Determination coefficient according to the number of inputs, hidden layer neurons and iteration numbers**

ANN structure (number of nodes in layers)	Iteration number (Epoch)	Coefficient of Determination ( R <sup>2</sup> )	Mean Square Error ( MSE )
ANN(1 1, 2, 1)	2000	0.852	95.678
ANN(1 1, 5, 1)	2000	0.912	56.809
ANN(1 1, 8, 1)	2000	0.919	52.484
ANN(1 1, 12, 1)	2000	0.937	40.269
ANN(1 1, 16, 1)	2000	0.936	41.142
ANN(1 1, 20, 1)	2000	0.931	44.691
ANN(1 1, 25, 1)	2000	0.931	44.077
ANN(1 1, 35, 1)	2000	0.930	44.749
ANN(1 1, 45, 1)*	2000*	0.938*	39.890*
ANN(1 1, 50, 1)	2000	0.932	43.683
ANN(1 1, 2, 1)	1000	0.853	95.322
ANN(1 1, 5, 1)	1000	0.903	62.870
ANN(1 1, 8, 1)	1000	0.922	50.762
ANN(1 1, 12, 1)	1000	0.933	43.323
ANN(1 1, 16, 1)	1000	0.923	50.107
ANN(1 1, 20, 1)	1000	0.937	40.647
ANN(1 1, 25, 1)	1000	0.925	48.153
ANN(1 1, 35, 1)	1000	0.923	49.571
ANN(1 1, 45, 1)	1000	0.931	44.498
ANN(1 1, 50, 1)	1000	0.933	43.206

**Table 5. Performance evaluation of the effective parameters for sensitivity analysis**

Performance	1	1-2	1-2-3	1-2-3-4	1-2-3-4-5	1-2-3-4-5-6
AARE (%)	31.92	26.14	22.00	17.65	14.35	11.97
MSE	336.6	273.0	197.6	147.7	109.7	64.67
R <sup>2</sup>	0.484	0.577	0.693	0.770	0.830	0.899
Performance	1-2-3-4-5-6-7	1-2-3-4-5-6-7-8	1-2-3-4-5-6-7-8-9	1-2-3-4-5-6-7-8-9-10	1-2-3-4-5-6-7-8-9-10-11*	
AARE (%)	11.35	11.39	9.752	8.397	8.564	
MSE	64.47	57.15	54.12	44.70	41.37	
R <sup>2</sup>	0.899	0.912	0.916	0.931	0.937	

\*The explanation of the numbers is given in Table 2

**Table 6. The sensitivity analysis of each input parameters using MLR**

Data Set	R <sup>2</sup>
Time	0.00032
Initial concentration	0.00044
% (w/w) Extractant	0.00008
Extractant type	0.00532
% (w/w) Diluents	0.00002
Diluents type	0.00824
Support type	0.06158
pH	0.04736
Stirring speed in feed phase	0.00039
Stirring speed in stripping phase	0.00038
NaOH concentration in stripping phase	0.01333

clearly seen from Table 7 adding other parameters into model increases the models' performances. Based on the findings, as depicted in Table 7 the MLR model has eleven inputs (time, initial concentration, % (w/w) extractant, extractant type, % (w/w) diluents, diluents type, support type, pH, stirring speed in feed phase, stirring speed in stripping phase, NaOH concentration in stripping phase) gives the best estimation. The performance of the MLR and selected neural network model in predicting of E<sub>o</sub> is demonstrated in Fig. 3 and Fig.4 for the test data set, respectively. The MLR has poor estimates. It is a drawback for the MLR. The comparison of the Table 5 and Table 6 also showed that the phenomenon is a non-linear problem. As can be seen from Fig. 4. the ANN estimates follow the corresponding experimental measured data with a significantly high R<sup>2</sup> value of 0.938. Furthermore ANN significantly outperforms MLR model in terms of E<sub>o</sub> estimation.

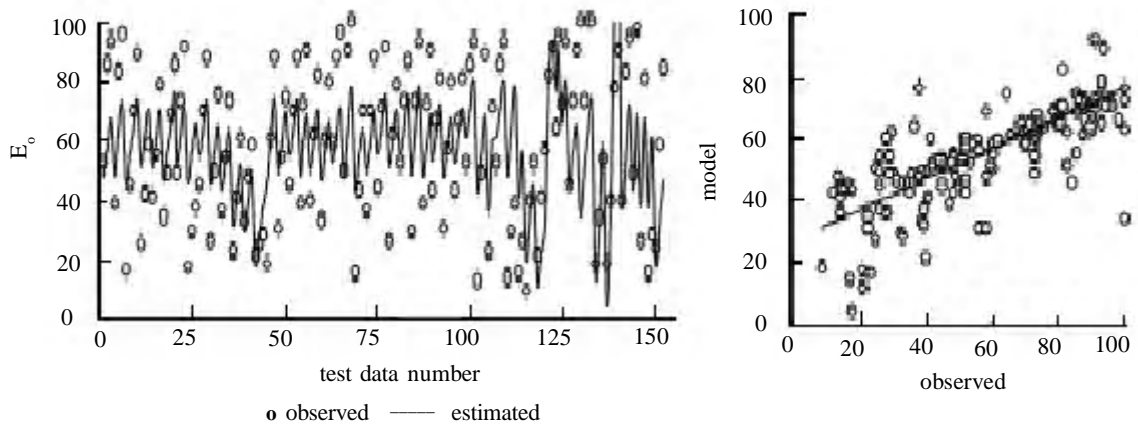


Fig. 3. Comparison of MLR results and observed  $E_o$  depending on each input parameters

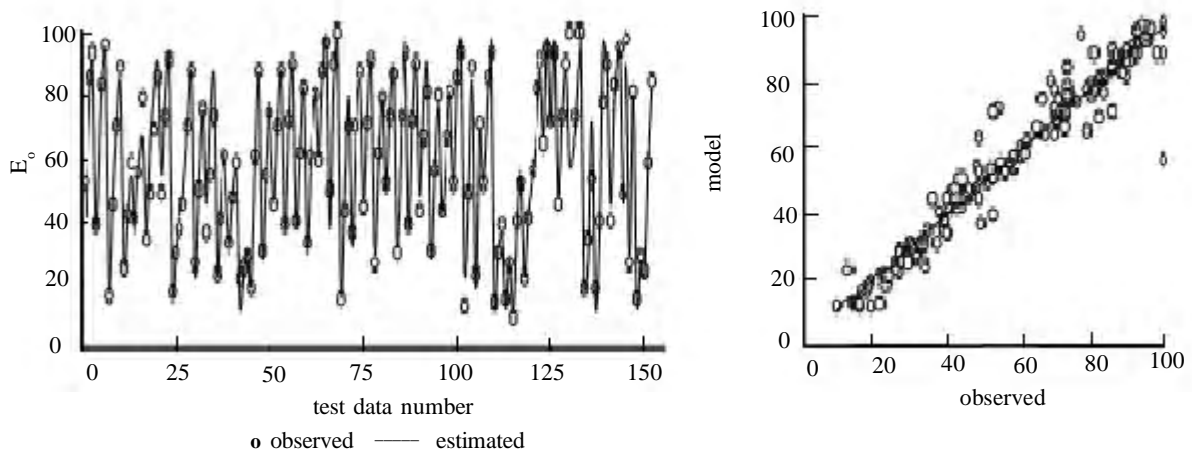


Fig. 4. Comparison of ANN results and observed  $E_o$  depending on each input parameters

Table 7. The performances of the MLR in the test period

Performance	7	7-8	7-8-11	7-8-11-6	7-8-11-6-4	7-8-11-6-4-2
AARE (%)	54.69	52.36	52.34	52.19	51.75	51.20
MSE	605.9	567.4	566.5	568.0	562.1	559.1
$R^2$	0.062	0.117	0.119	0.116	0.125	0.129
Performance	7-8-11-6-4-2-9	7-8-11-6-4-2-9-10	7-8-11-6-4-2-9-10-1	7-8-11-6-4-2-9-10-1-3	7-8-11-6-4-2-9-10-1-3-5*	
AARE (%)	51.23	51.24	35.19	35.12		34.8
MSE	559.9	560.0	360.0	359.1		345.0
$R^2$	0.128	0.128	0.445	0.447		0.469

\*The explanation of the numbers is given in Table 2

**CONCLUSION**

The present study demonstrates the capabilities of artificial neural network model (ANN) for  $E_o$  modeling, however the choice of ANN architecture and input parameters are crucial for obtaining good estimate accuracy. Thus, sensitivity analysis had been conducted to determine the degree of effectiveness of the variables by using various performance statistics. From the results, an ANN model appears to be a useful tool for prediction of the  $E_o$ . The results showed that the input variable time was found to be more effective on  $E_o$  estimation by using ANN. Remaining parameters

were used one by one in estimating  $E_o$ . The models whose inputs are the time, initial concentration, % (w/w) extractant, extractant type, % (w/w) diluents, diluents type, support type, pH, stirring speed in feed phase, stirring speed in stripping phase, NaOH concentration in stripping phase have the best performance criteria among the input combinations tried in the study. This indicates that all these variables are needed for better  $E_o$  modeling. The MLR is also used for  $E_o$  estimation. However, MLR has poor estimates. It is a drawback for the MLR. Based on the comparison results, the ANN technique was found to be significantly superior to the MLR technique.

## ACKNOWLEDGEMENT

The authors wish to express their gratitude for the support extended by the authorities of Sakarya University, Adapazari, Turkey in carrying out the research work in chemistry research laboratory, Department of Chemistry.

## REFERENCES

- Abdullahi, M. S., Uzairu, A. and Okunola, O. J. (2009). Quantitative Determination of Heavy Metal Concentrations in Onion Leaves. *Int. J. Environ. Res.*, **3**(2), 271-274.
- Abilov, A. and Zehra, Z. (2000). Use of neural network for modeling of non-linear process integration technology in chemical engineering. *Chem. Eng. Process.*, **39**(5), 449-458
- Alguacil, F.J., Coedo, A.G., Dorado, M.T. and Sastre, A.M. (2001). Uphill permeation of chromium (VI) using Cyanex 921 as ionophore an immobilized liquid membrane, *Hydrometallurgy*, **61**, 13.
- Alguacil, F.J., Coedo, A.G. and Dorado, M.T. (2000). Transport of chromium (VI) through a Cyanex 923-xylene flat-sheet supported liquid membrane, *Hydrometallurgy*, **57**, 51.
- Asraf, W. and Man, A. (2006). Selective separation and preconcentration studies of chromium (VI) with Alamine 336 supported liquid membrane, *Toxic. & Env. Chem.*, **88**(2), 187-196
- Banerjee, S., Datta, S. and Sanyal, S.K. (2000). Mass transfer analysis of the extraction of Cr(VI) by liquid surfactant membrane, *Sep. Sci. Technol.*, **35**, 483
- Bhowal, A. and Datta, S. (2001). Studies on transport mechanism of Cr(VI) extraction from an acidic solutions using liquid surfactant membranes. *J. Membr. Sci.*, **188**, 1.
- Biati, A., Moattar, F., Karbassi, A. R. and Hassani, A. H. (2010). Role of Saline Water in Removal of Heavy Elements from Industrial Wastewaters. *Int. J. Environ. Res.*, **4**(1), 177-182.
- Cezary, A. K. and Walkowiak W. (2002). Removal of chromium (VI) from aqueous solutions by polymer inclusion membranes, *Water Research*. **36**, 4870-4876.
- Chiarizia, R. (1991). Application of supported liquid membranes for removal of nitrate, technetium (VII) and chromium (VI) from groundwater, *J. Membr. Sci.*, **55**, 39.
- Chouai, A., Cabassud, M., Le Lann, M.V., Gourdon, C. and Casamatta, G. (2000). Use of neural networks for liquid-liquid extraction column modeling: an experimental study, *Chem. Eng. Process*. **39**, 171.
- Cotton, A.F. and Wilkinson, G. (1988). *Advanced Inorganic Chemistry*, 5th edn., John Wiley and Sons, New York, 680.
- Hoskins, J.C. and Himmelblau, D.M. (1988). Artificial neural network models of knowledge representation in chemical engineering, *Comput. Chem. Eng.*, **12**, 881.
- Iliuta, M.C., Iliuta, I. and Larachi, F. (2000). Vapour-liquid equilibrium data analysis for mixed solvent electrolyte systems using neural network models, *Chem. Eng. Sci.*, **55**, 2813.
- Jalili Ghazi Zade, M. and Noori, R. (2008). Prediction of Municipal Solid Waste Generation by Use of Artificial Neural Network: A Case Study of Mashhad. *Int. J. Environ. Res.*, **2**(1), 13-22.
- Kabir, G. and Ogbeide, S.E. (2008). Removal of Chromate in Trace Concentration Using Ion Exchange From Tannery Wastewater. *Int. J. Environ. Res.*, **2**(4), 377-384.
- Kumar, S.V., Ravindram, M., Chandra, M. and Mudakavi, J. R. (1994). Heavy metal removal using liquid membrane, *Indian J. Chem. Technol.*, **1**, 131.
- Mori, Y., Uemae, U., Hibino, S. and Eguchi, S.E. (1990). Proper condition of the surfactant liquid membrane for the recovery and concentration of chromium (VI) from aqueous sulfuric acid solution. *Int. Chem. Eng.*, **30**, 124.
- Naik, V. K. and Manjapp, S. (2010). Prediction of Dissolved Oxygen through Mathematical Modeling. *Int. J. Environ. Res.*, **4**(1), 153-160.
- Palmer, S.A.K., Breton, M.A., Nunno, T.J. and Sullivan, D.M. (1988). *Supernatant Metal/Cyanide Containing Water Treatment Technologies*. Noyes Data Corporation, Millroad, Park Ridge, New Jersey (07656).
- Park, S., Kim, G., Kim, S. and Sohn, J. (2001). Facilitated transport of Cr (VI) through supported liquid membranes with trioctylmethylammonium chloride as a carrier, *Sep. Sci. Technol.*, **36**, 2309.
- Podnar, D., Koracin, D. and Panorska, A. (2002). Application of artificial neural networks to modeling the transport and dispersion of tracers in complex terrain, *Atmos. Environ.* **36**, 561.
- Rajasimman, M., Govindarajan, L. and Karthikeyan, C. (2009). Artificial Neural Network Modeling of an Inverse Fluidized Bed Bioreactor. *Int. J. Environ. Res.*, **3**(4), 575-580.
- Kumbasar, R. A. (2008). Studies on extraction of chromium (VI) from acidic solutions containing various metal ions by emulsion liquid membrane using Alamine 336 as extractant, *J. Mem. Sci.*, **325**, 460-466.
- Sahmoune, M.N., Louhab, K. and Boukhiar, A. (2009). Biosorption of Cr (III) from Aqueous Solutions Using Bacterium Biomass *Streptomyces rimosus*. *Int. J. Environ. Res.*, **3**(2), 229-238.
- Salazar, E., Ortiz, M.I., Urtiaga, A. M. and Irabien, J. (1992). Kinetics of the separation-concentration of chromium(VI) with emulsion liquid membranes, *Ind. Eng. Chem. Res.*, **31**, 1523.
- Wang, Y., Thio, Y.S. and Doyle, F. M. (1998). Formation of semi-permeable polyamide skin layers on the surface of supported liquid membranes, *J. Mem. Sci.*, **147**, 109.
- Young, K. and Robert, W. (1986). The effect of weak chelating agents on the removal of heavy metals by precipitation process. *Environ. Prog.*, **5**, 147.
- Zouhri, A., Burgard, M. and Lakkis, D. (1995). The use of dicyclohexanol8-crown-6 as an extractant-carrier for the recovery chromic acid. *Hydrometallurgy*, **38**, 299.
- Zouhri, A., Ernst, B. and Burgard, M. (1999). Bulk liquid membrane for the recovery of chromium (VI) from a hydrochloric acid medium using dicyclohexano-l8-crown-6 as extractant-carrier, *Sep. Sci. Technol.*, **38**, 1891.