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Prediction of Co(II) and Ni(II) ions removal from wastewater using artificial neural network and multiple regression models

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Abstract: In this research, carboxymethyl chitosan-bounded Fe_3O_4 nanoparticles were synthesized and used for removal of Co(II) and Ni(II) ion metals from wastewater. The capability of magnetic nanoparticles for metal ions removal was investigated under different conditions namely pH, initial concentration of metal ions and adsorbent mass. The assessment of adsorbent performance for metal ions removal under different conditions requires cost and time spending. In this regard, the capability of artificial neural network (ANN) and nonlinear multi-variable regression (MNLR) models were investigated for predicting metal ions removal. The values of operational parameters such as pH, contact time, initial concentration of metal ions and adsorbent mass were applied for simulation by means of ANN and MNLR. A back propagation feed forward neural network, with one hidden layer (4:8:2), was proposed. Two criteria, including mean square error (MSE) and coefficient of determination (R^2) were used to evaluate the performance of models. The results showed that two models satisfactorily predicted the adsorbed amount of metal ions from wastewater. However, the ANN model with higher R^2 and lower MSE than the MNLR model had better performance for predicting the adsorbed amount of metal ions from wastewater.

Keywords: *artificial neural network, nonlinear multi-variable regression, heavy metals, adsorption*

Introduction

Discharge of industrial wastes containing heavy metals into the environment is a serious environmental problem, due to contamination of aquatic environment by heavy metal ions (Yurdakoc et al., 2005). It has been desired that a heavy metal level can be reduced in industrial and municipal effluents before ultimate repository in the ecosystem. Several methods have been employed to remove metal ions from aqueous solutions. These methods include coagulation (El Samrani et al., 2008), flotation (Zouboulis et al., 1997), chemical precipitation (Esalah et al., 2000), ion exchange (Papadopoulos et al., 2004) and membrane processes (Qdaisa and Moussab, 2004).

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Some of these methods have disadvantages and limitations such as a low efficiency in the removal of some toxic metal ions, high operation cost, low selectivity (Esalah et al, 2000; Papadopoulos et al., 2004; Yurdakoc et al., 2005; El Samrani et al., 2008). Adsorption provides an attractive alternative treatment to other removal methods because it is more economical and readily available (Kara et al., 2003; Jiang et al., 2010).

An appropriate adsorbent should have important properties such as large surface area, proper pore size, mechanical stability, ease of regeneration, cost effectiveness and high selectivity (Marković et al., 2015). Therefore, researchers have been developed polymer materials such as chitosan and its modifications that have higher adsorption capacity for heavy metal ions than some traditional adsorbents (Reddy and Lee, 2013). Despite of a good performance of chitosan adsorbent for removal of metal ions, it has structural defects, low thermal stability and low acid stability (Guibal, 2004). In this regards, researchers have used either physical or chemical modification to increase the adsorption properties of adsorbents for removal of metal ions (Gérente et al., 2010; Liu et al., 2012).

Carboxymethylchitosan has a higher metal ion binding capacity than chitosan because its chain flexibility and concentration of chelating groups is improved with chemical modification (Muzzarelli et al., 1989; Guibal, 2004). After the adsorption process, it is difficult to recover chitosan-based adsorbents from aqueous effluents using traditional methods such as sedimentation and filtration, because adsorbents may be discarded with the process sludge. Therefore, magnetic adsorbents have been developed to overcome the problems of separation and regeneration of adsorbents (Reddy and Lee, 2013).

Artificial neural network (ANN) is the most commonly used method for developing predictive models that can be used to perform nonlinear statistical modeling. Neural networks (NNs) can be applied to optimize complex non-linear systems and to predict the output of new sets of data (Li and Yu, 2009).

In recent years, ANNs have been used as a powerful modeling tool in various processes such as flotation (Allahkarami et al., 2017), liquid-liquid extraction (Giri et al., 2011), arsenic biosorption (Chouai et al., 2000) and many other fields of mineral processing (Acharya et al., 2006; Jorjani et al., 2007). The conventional adsorbents for treating heavy metals containing wastewaters are palygorskite (He et al., 2011), sepiolite (Kara et al., 2003), activated carbon (Hasar, 2003), natural kaolinite clay (Jiang et al., 2010) and etc. Recently, the use of magnetic chitosan-based adsorbents has received particular attention (Monier et al., 2010).

The aim of this work is to investigate the capability of using carboxymethyl chitosan-bounded Fe_3O_4 nanoparticles for removal of Co(II) and Ni(II) ions from aqueous solutions. In this study, adsorption of Co(II) and Ni(II) ions by magnetic chitosan-based nanoparticles was studied as a function of the initial metal ions concentration, pH, adsorbent mass and contact time. Finally, the adsorption process of cobalt (II) and Nickel (II) on carboxymethyl chitosan-bounded Fe_3O_4 nanoparticles with using artificial neural network and nonlinear multi-variable regression based on operation parameters such as pH, adsorbent mass, metal ion concentration and contact time, was modelled.

Materials and methods

Reagents

All reagents were of analytical grade (Merck, Germany). Stock solutions of cobalt and nickel (500 mg/dm^3) were prepared by dissolving desired quantity of cobalt nitrate and nickel nitrate (Merck, Germany) in deionized water, respectively. The desired concentrations of cobalt and nickel ions were prepared by successive dilutions of the stock solution. The pH of solution was adjusted by using either 0.1 M NaOH or 0.1 M H_2SO_4. The values of desired concentration and pH in the experiments are given in Table 1.

Table 1. The summary statistics for input and output variables

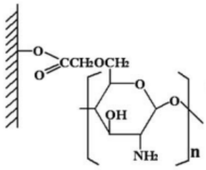
Variable	Index	Range	Standard deviation
pH	pH	4, 6, 8	2
Adsorbent (mg)	ads	30, 75, 120	45
Time (min)	time	20, 40, 60	20
Metal concentration (ppm)	conc	43, 100, 157	57
Amount adsorbed (Ni)	q_e-Ni	[6.657, 84.377]	2.926
Amount adsorbed (Co)	q_e-Co	[5.840, 80.033]	2.883

Preparation of adsorbent

First, Fe_3O_4 nanoparticles were prepared by co-dissolution of Fe^{2+} and Fe^{3+} ions [Fe^{2+}: Fe^{3+}= 1:2] in about 10 cm^3 HCl 0.1 M, and then drop-wising NaOH solution at temperature of 70 ^{o}C for 30 minutes. Then, these magnetic nanoparticles were decanted by a magnet and cleaned by water several times (Kang et al., 1996).

Briefly, 10 g chitosan and 10 g sodium hydroxide were added into a 100 cm^3 mixture of isopropanol/water (50/50) at 50 ^{o}C to swell and alkalize for 1 hour. Then, 20 cm^3 solution of chloroacetic acid (0.75 g/ cm^3) was added into the mixture in drops. After 4 h, the reagent of ethyl alcohol was added into the mixture to stop the reaction. To get Na salt carboxymethyl chitosan (CC), the solid was filtered, rinsed with ethyl alcohol (80%) and vacuum dried. Then, 1 g of Na-CC was suspended in 100 cm^3 ethyl alcohol aqueous solution (80%), and stirred for 30 min. Finally, 10 cm^3 hydrochloric acid (37%) was added and stirred to desalt (Zhu, 2008).

Binding of carboxymethyl chitosan (CCs) was conducted according to the method of Chang and Chen (2005). First, Fe_3O_4 nanoparticles were added to 2 cm^3 of buffer solution (0.003 M phosphate, pH 6, 0.1 M NaCl). Then, after adding 0.5 cm^3 of carbodiimide solution, the reaction mixture was sonicated for 10 min. Eventually, the 2.5 cm^3 of carboxymethyl chitosan solution was added and the reaction mixture was sonicated for 60 min. The chitosan-bounded Fe_3O_4 (Fig. 1) nanoparticles were recovered from the reaction mixture by a magnetic bar, and washed with water and ethanol.



Fe_3O_4-CMCH

Fig. 1. Carboxymethyl chitosan-bounded Fe_3O_4 nanoparticles (Chang et al., 2006)

Experimental methods and measurements

Adsorption studies were done by batch process. 25 cm^3 of wastewater containing Ni^{2+} and Co^{2+} ions were added to magnetic nanoparticles. This mixture was agitated in a temperature-controlled shaking water bath, at a constant speed (100 rpm) for all experiments. All experiments were conducted at ambient temperature. The concentration of metal ions after adsorption was measured by Atomic absorption spectroscopy (AAS). The amount adsorbed of nickel and cobalt ions (in mg/g) was calculated using the following equation:

$$q_e = (C_0 - C_e)\cdot V/m \tag{1}$$

where C_0 and C_e are concentration of metal ions before and after adsorption in the solution (in mg/cm^3), respectively, V and m are the solution volume (in dm^3) and the mass of magnetic nanoadsorbent (in g), respectively.

The effect of pH on the amount adsorbed of metal ions was determined in the pH range from 4 to 8. The effect of mass adsorbent on adsorption capacity was determined in the mass adsorbent range from 30 to 120 mg. Different amounts of metal ions in the range of 43 to 157 ppm were used to examine the effect of a metal concentration on adsorption of magnetic nanoparticles. Finally, the effect of time on the amount adsorbed of metal ions was determined.

Theory

Nonlinear multi-variable regression description

Analysis of nonlinear multi-variable regression (MNLR) is a statistical method that examines cause-effect relationships between dependent and independent variables. In non-linear regression, procedures determine values of the parameters that minimize the sum of the squares of the distances of the data points to the curve. If value of each data point is called Y_{data} and the y value of the curve is Y_{curve}, the goal is to minimize the residual sum of squares (SS):

$$SS = \sum_{\mathrm{i}=1}^{\mathrm{n}} (Y_{\text{data}} - Y_{\text{curve}})^2. \tag{2}$$

Because this criterion minimizes the sum of the square of the distances, it is called a least squares method (Seber and Wild, 2003).

In this paper, the multi non-linear regression is applied to fit a predictive model to an observed data set of dependent variable Y and k independent variables or predictors X_i (i=1, 2, …, k). The independent variable is controlled by the experimenter, while the dependent variable is measured. The relationship between the variables x and Y can be described by an equation that includes either one or more parameters, which are called pr_0, pr_1, pr_2 and etc. The used regression function is defined as follow:

$$Y = pr_0 + pr_1 x_1 + pr_2 x_2 + pr_3 x_3 + pr_4 x_4 + pr_5 x_1^2 + pr_6 x_2^2 + pr_7 x_3^2 + pr_8 x_4^2 \tag{3}$$

where Y is the predicted value corresponding to the response, pr_0 is the intercept, x_1, x_2, x_3 and x_4 are predictors, and pr_1 and pr_8 are the regression coefficients of x_1, x_2, x_3 and x_4.

The model performance was evaluated by applying various standard statistical performance evaluation criteria. The coefficient of determination (R^2) and mean square error (MSE) were the statistical measures. Two evaluation criteria were calculated according to the following equations:

$$R^2 = 1 - \frac{\sum_{\mathrm{i}=1}^{\mathrm{n}} (Y_i - X_i)^2}{\sum_{\mathrm{i}=1}^{\mathrm{n}} (Y_i - X_m)^2} \tag{4}$$

$$\mathrm{MSE} = \frac{1}{\mathrm{n}} \sum_{\mathrm{i}=1}^{\mathrm{n}} (X_i - Y_i)^2 \tag{5}$$

where X and Y are the predicted and experimental values, n is number of data sets and X_{m} is the average of experimental values. In this study, the regression analysis was performed using the train and test data which were then applied in neural network data.

Artificial neural network

The artificial neural network employs very powerful computational techniques for modeling complex non-linear relationships (Smith, 1994). The neural network usually consists of a structure of three types of layers described as input, hidden, and output layers. The most popular ANN is the feed forward multi-layer ANN which uses the back propagation learning algorithm (Jorjani et al., 2007). Back propagation learning works by adjusting weight values starting at the output layer, then moving backward through the hidden layer of the network. This training procedure essentially aims at obtaining an optimal set of network connection weights that minimizes a pre-specified error function (Rumelhart et al., 1986).

The consecutive steps of artificial neural network modeling are summarized as follows:

- giving the pre-processed data to the network
- determining the train and test sets,
- determining the number of hidden layer(s) nodes
- training the neural network by iterative process
- comparison of the output of network and measured data (testing the network)
- repeating step 2-5 until an optimal model is obtained,

A total of 54 datasets were used in the prediction by the ANN method; 41 and 13 datasets were applied for training and testing the network, respectively, for estimation of the adsorbed amount of Ni^{2+} and Co^{2+} ions. Usually, the optimum number of hidden layers and neurons in each layer is found via a trial and error method (Anderson and McNeill, 1992).

In the current study, pH, contact time, initial concentration of metal ions and adsorbent mass were considered as inputs to the network and also the amount adsorbed of Ni(II) and Co(II) were considered as the network output. Table 1 presents the summary statistics for each input and output variable.

Data pre-processing can be effective in the process of training the neural network (Demuth and Beale, 2002). To have a successful training process, the data were normalized, and then fed to NN for the training phase. Finally, these data changed in the range of 0.1 and 0.9. The normalized value (X_N) for each raw input/output dataset was calculated using the following equation:

$$X_N = 0.8\frac{X-X_{min}}{X_{max}-X_{min}} + 0.1 \tag{6}$$

where X_N is the normalized value of each input or output variable, X is an original value of a variable, and X_{max} and X_{min} are the maximum and minimum original values of the variables, respectively.

A correlation matrix was produced to study the strength of the linear relationships between the input and output variables. In the correlation analysis, Pearson's correlation coefficients between amount adsorbed of Ni(II) and Co(II) and the other selected operating conditions were calculated according to the following equation:

$$R = \frac{n\sum_{i=1}^{n}(X_iY_i)-(\sum_{i=1}^{n}X_i)(\sum_{i=1}^{n}Y_i)}{\sqrt{[n\sum_{i=1}^{n}X_i{}^2-(\sum_{i=1}^{n}X)^2]\times[n\sum_{i=1}^{n}Y_i{}^2-(\sum_{i=1}^{n}Y)^2]}} \tag{7}$$

and the results are given in Table 2. The sign of the correlation indicates the direction of the relationship, and its absolute value indicates the strength, with larger absolute values indicating stronger relationships. A negative value for the correlation implies either negative or inverse association, where a positive value means a positive association. Therefore, according to Table 2, it can be concluded that the adsorbed amount of metal ions has strong relationship with adsorbent mass and metal ion concentration. There is a very poor relationship between time and response variables. Also, there is a positive correlation coefficient between the adsorbed amount of metal ions and pH.

Table 2. Correlation matrix for original dataset

	pH	ads	Time	conc	q_e-Ni	q_e-Co
pH	1.000	-	-	-	-	-
ads	-0.067	1.000	-	-	-	-
time	0.073	-0.002	1.000	-	-	-
conc	0.077	0.067	-0.004	1.000	-	-
q_e-Ni	0.236	-0.709	-0.057	0.503	1.000	-
q_e-Co	0.242	-0.723	-0.037	0.471	0.996	1.000

Results and discussion

Experimental work

Figures 2-3 show the 3D surface plot of the relationship between the operation parameters and the adsorbed amount of metal ions. The results indicate that the operation parameters affect the response variables in the sequence of the adsorbent mass, metal ion concentration, pH and time. The pH of solution plays a vital role in the adsorption process and the adsorption capacity by modification of the ionization level of chitosan derivatives (Dinu and Dragan, 2010). The decrease in unit adsorption with increasing the adsorbent mass is basically due to adsorption sites remaining unsaturated during the adsorption process.

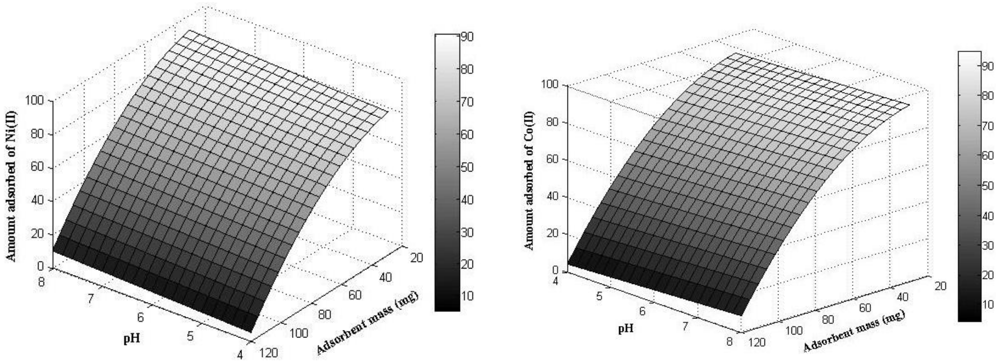


Fig. 2. Correlation between pH and adsorbent mass with adsorbed amount of metal ions

Time as a parameter has very poor relationship with the adsorbed amount of metal ions, because the initial adsorption is very fast and the maximum adsorption was reached within 30 min for metal ions. The effect of initial metal ion concentration on adsorption of Co(II) and Ni(II) using the carboxymethyl chitosan-bounded Fe_3O_4 nanoparticles was examined with results shown in Fig. 6, where increasing in the initial metal ion concentration from 43 to 157 ppm resulted in a decrease in the metal ions adsorbed.

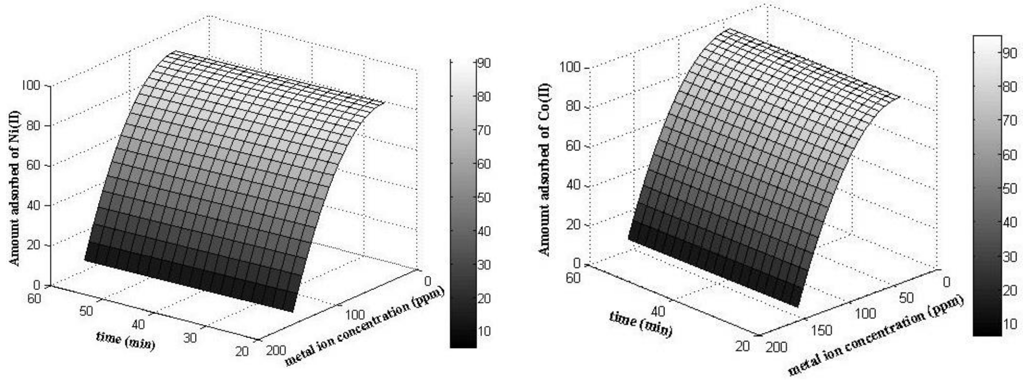


Fig. 3. Correlation between time and metal ion concentration with adsorbed amount of metal ions

Structure and chemical composition

The binding of carboxymethyl chitosan on magnetic nanoparticles was demonstrated by the analyses of Fourier transform infrared (FTIR) spectroscopy. Figure 4 shows the FTIR spectra of (a) pure Fe_3O_4, (b) Fe_3O_4-chitosan, and (c) Fe_3O_4– carboxymethyl chitosan nanoparticles. The peak at 570 cm^{-1} in Fig. 2a relates to Fe–O group where this peak shifted to lower amounts for Fe_3O_4 – carboxymethyl chitosan nanoparticles. Furthermore, peaks at 1555 and 1408 cm^{-1} are related to Fe_3O_4–carboxymethyl chitosan nanoparticles. This revealed that carboxymethyl chitosan was adsorbed on the magnetite nanoparticles.

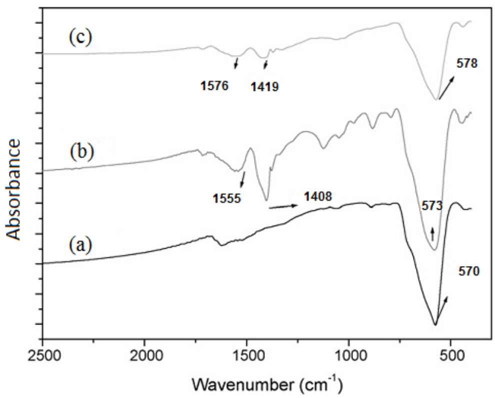


Fig. 4. FTIR spectra of (a) pure Fe_3O_4, (b) Fe_3O_4-chitosan and (c) Fe_3O_4– carboxymethyl chitosan nano-adsorbents

Figure 5 shows the H-NMR spectrum of carboxymethyl chitosan. The peak at 2 ppm can be related to hydrogen in acetamide groups and another one at 3.14 ppm can be related to hydrogen linked to C2 in glucosamine groups. To more precise, very small peaks from 4.26 ppm to 4.5 ppm can indicate the carboxymethyl protons replacing (-O-CH_2-COOD) groups in carboxymethyl chitosan. From data given it is clear that the maximum response from the protons is related to the amino groups at 3.29 ppm.

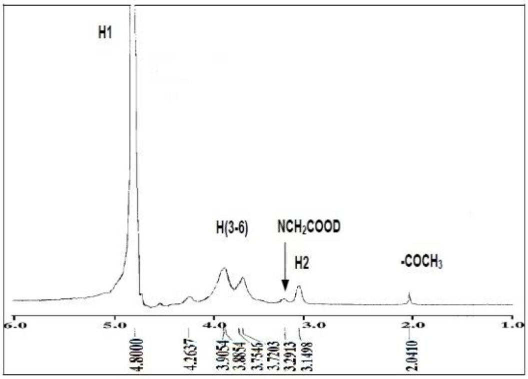


Fig. 5. H-NMR spectrum of carboxymethyl chitosan

Statistical technique

In these tests, the regression analysis was performed to determine the relationship between 4 variables and 2 response functions. The response functions representing the adsorbed amount of nickel and cobalt ions could be expressed as function of pH, contact time (min), initial concentration of metal ions (mg/dm^3) and adsorbent mass (mg). The relationship between responses (adsorbed amount of nickel and cobalt ions) was obtained with SPSS 16.0 as follows:

$$\begin{gathered}\text{Amount adsorbed of nickel (II)ion} = q_e - \text{Ni} = 93.43 - 12.92 \cdot \text{pH} \\ -1.3 \cdot \text{ads} - 0.46 \cdot \text{time} + 0.52 \cdot \text{conc} + 1.21 \cdot \text{pH}^2 + 5.52\text{E}^{-3} \cdot \text{ads}^2 \\ +4.75\text{E}^{-3} \cdot \text{time}^2 - 1.06\text{E}^{-3} \cdot \text{conc}^2 \end{gathered} \tag{8}$$

$$\begin{gathered}\text{Amount adsorbed of cobalt (II)ion} = q_e - \text{Co} = 99.59 - 14.00 \cdot \text{pH} \\ -1.33 \cdot \text{ads} - 0.53 \cdot \text{time} + 0.48 \cdot \text{conc} + 1.31 \cdot \text{pH}^2 + 5.71\text{E}^{-3} \cdot \text{ads}^2 \\ +5.64\text{E}^{-3} \cdot \text{time}^2 - 9.87\text{E}^{-4} \cdot \text{conc}^2. \end{gathered} \tag{9}$$

The correlation between observed and predicted values of the testing stage is presented in Figure 6. The performance evaluation factors (MSE and R^2) of the statistical models are listed in Table 3. The results show that the predictive capability of the developed models (high R^2) is reasonably good.

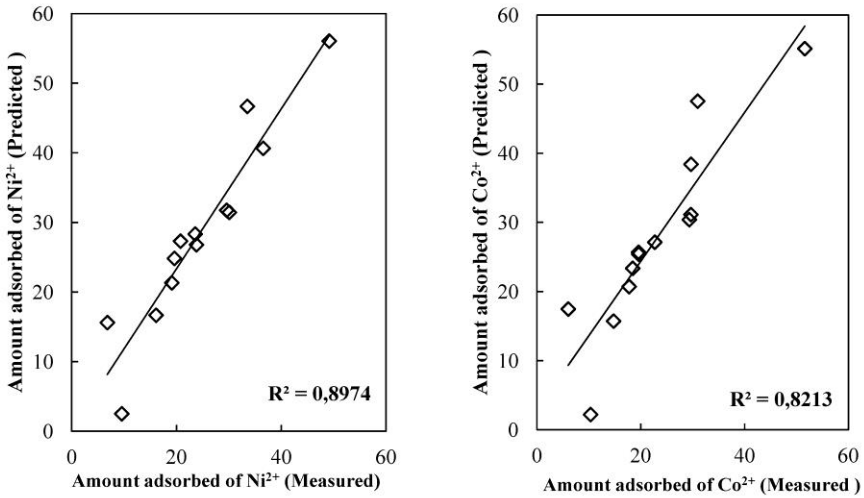


Fig. 6. Measured vs. predicted values of adsorbed amount of metal ions
in the testing stage using the MNLR model

Table 3. Comparison of MSE and R^2 values of MNLR and ANN in training and testing stages

Method	Amount adsorbed of Ni^{2+}				Amount adsorbed of Co^{2+}			
	Training stage		Testing stage		Training stage		Testing stage	
	R^2	MSE	R^2	MSE	R^2	MSE	R^2	MSE
MNLR	0.9192	55.89	0.8974	36.81	0.9213	52.58	0.8212	53.09
ANN	0.9996	0.2338	0.9702	4.3256	0.9951	0.1741	0.9673	4.4664

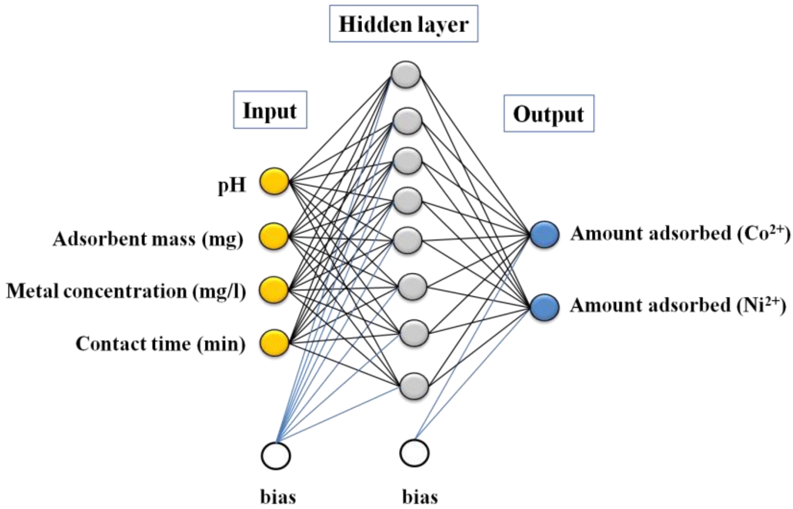


Fig. 7. Neural network structure of this study

Results of artificial neural network

A back propagation feed forward neural network, with one hidden layer (4:8:2), was developed. As mentioned above, the optimum number of neurons was selected via the trial and error method. Finally, the best structure and geometry of ANN in this work was attained 4:8:2 arrangements (Fig. 7). In each step of training (iteration), an error between the estimated and measured values travelled backward from the output neurons towards the input neurons through neurons of the hidden layer. This work continued until the convergence criterion was met (Demuth and Bale, 2002). Finally, the coefficient of determination (R^2) values in the training stage for the amount adsorbed of nickel (II) and cobalt (II) ions were 0.99 and 0.99, respectively (Fig. 8).

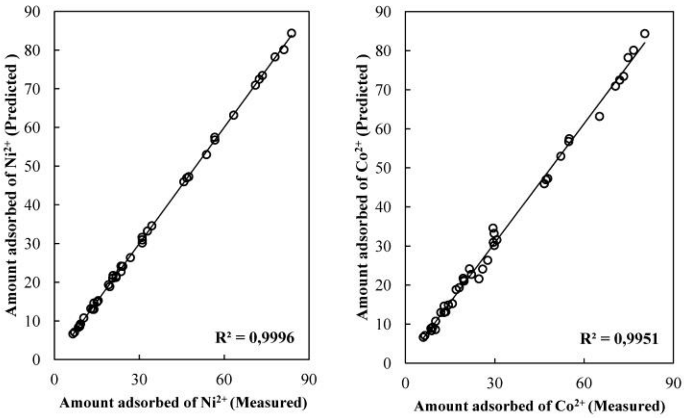


Fig. 8. Correlation between observed and predicted values in the training stage using the ANN model for nickel (left) and cobalt (right) ions

After the training stage, the network was tested for its prediction capability. In this regard, 13 new data sets that were unfamiliar to network were fed to the neural network. In fact, these data sets were not included in the training stage. The assessment of testing stage of NN showed that the model can quite satisfactorily predict the adsorbed amount of Co^{2+} and Ni^{2+} ions from wastewaters. It can be seen from Fig. 9 that the coefficient of determination (R^2) values in the testing stage for the adsorbed amount of Co^{2+} and Ni^{2+} ions were 0.96 and 0.97, respectively. It was observed that the ANN model can predict the adsorbed amount of metal ions simultaneously. The attained results of R^2 and MSE values from two models for training and testing stages are given in Table 3. Figure 10 shows a comparison of predicted values using ANN and MNLR models and measured values. Apparently, it was observed that both models can predict the adsorbed amount of metal ions in within a very good acceptance limit (Fig. 10). However, the network more fitted with the data collected than the MNLR model and showed the least variation error in predicting the adsorbed amount of metal ions in the testing stage.

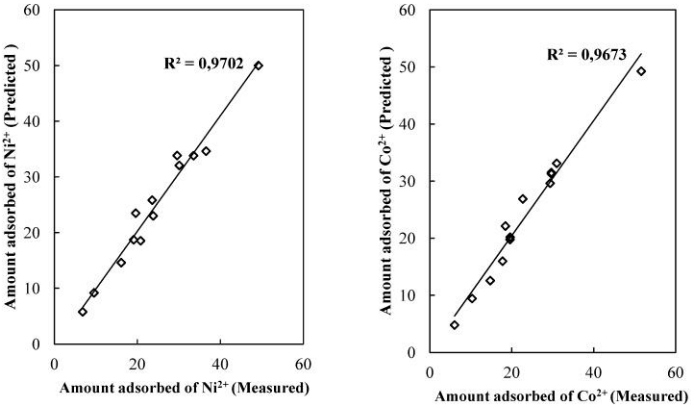


Fig. 9. Correlation between observed and predicted values in the testing stage using ANN model for nickel (left) and cobalt (right) ions

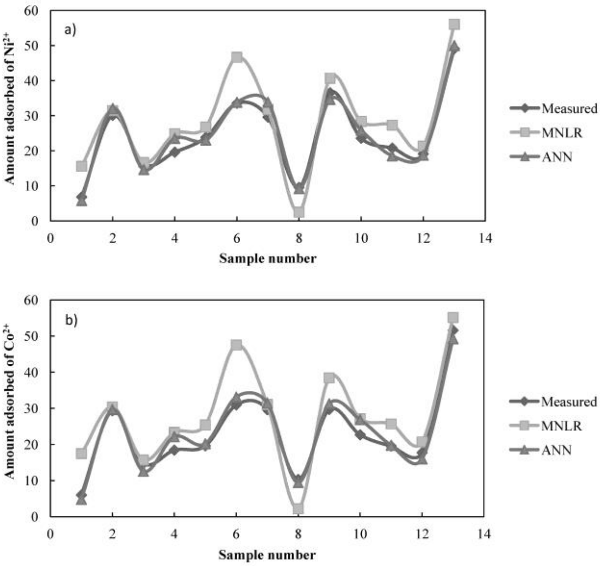


Fig. 10. Comparison of predicted and measured values for MNLR and ANN models in testing stage, (above figure) adsorbed amount of Ni^{2+} (a) Co^{2+} (b) ions

Conclusions

On the basis of batch adsorption experiments, an important objective was to obtain either an ANN model or a regression equation that could make reliable prediction on the adsorbed amount of Ni(II) and Co(II) ions. Therefore, MNLR and ANN were investigated. Modeling was performed based on 54 experimental data under various operating conditions such as pH, contact time, initial concentration of metal ions and adsorbent mass. The non-linear regression and a three layer back propagation NN model with tangent sigmoid (tansig) and linear (purelin) functions in the hidden and output layers were constructed for predicting the adsorbed amount of metal ions. The optimum structure of ANN was determined by the trial and error procedure. Two criteria, including mean square error (MSE) and coefficient of determination (R^2) were used to evaluate the performance of models, which was then tested by using new datasets. From the obtained results it was concluded that all two models satisfactorily predicted the adsorbed amount of metal ions from wastewater. However, the ANN model outperformed the MNLR model. Based on the obtained results, ANN indicated superiority in assessing the quality in terms of accuracy.

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