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Assessment of Cr(VI) Biosorption from Aqueous Solution by Artificial Intelligence

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ABSTRACT

This work investigates the efficiency of date palm fiber as a biosorbent to the removal of Cr(VI) from aqueous solution. The effect of four main factors including, the initial pH, initial Cr(VI) concentration, biosorbent dosage, and time were assessed. The results revealed that, the maximum 89% removal of Cr(VI) at time 50 min, initial pH 3.2, initial Cr(VI) 181 ppm, and biosorbent dosage 0.8% (w/v) was obtained. The artificial neural network (ANN) model was developed to predict the Cr(VI) removal as a function of the studied variables. A number of data points were considered as test data to validate the model. The results indicated a high accuracy of the ANN modeling in estimating the target variable.

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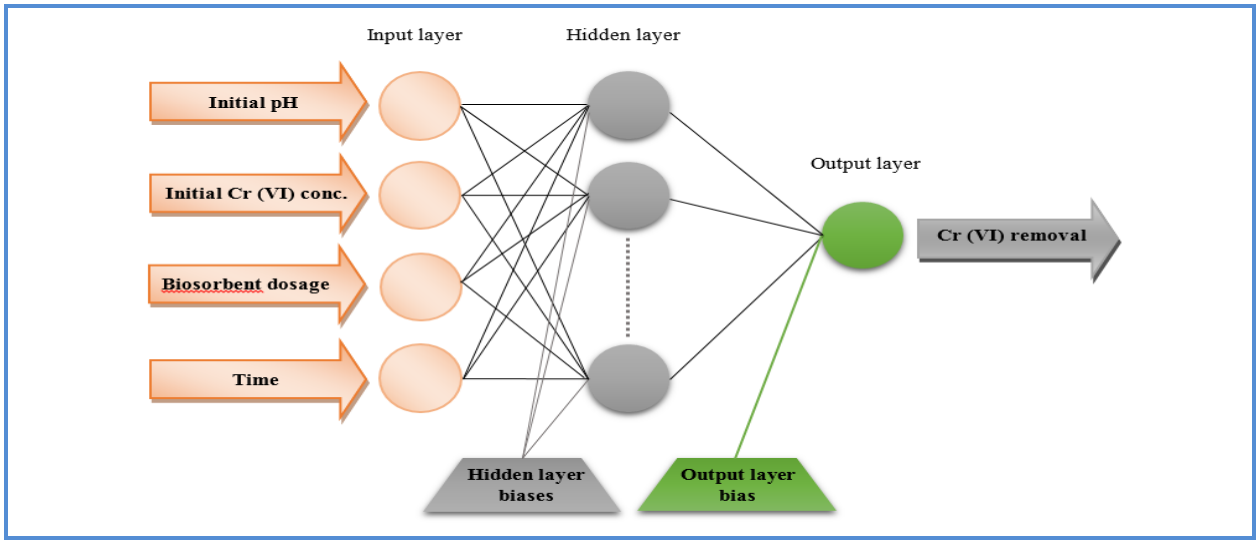
Graphical Abstract



Introduction

Chromium is one of the heavy metals and is commonly used in different industries including, metallurgical, fertilizers, mining, tanning, pigments, and electroplating [1]. Chromium exists in the wastewater could irreparably damage to the environment and ecosystems. Generally, there are two types of Cr in aqueous solutions including, hexavalent Cr(VI) and trivalent Cr (III) [2]. Cr(VI) can cause some disorders such as liver, kidney, lung, and gastrointestinal cancer [3]. Cr(VI) is much more toxic than Cr (III) and causes diseases like lung, kidney, liver, and gastrointestinal cancer [4]. The maximum tolerance limit of Cr(VI) in the effluent of industrial wastewater and potable water are 0.1 mg/L and 0.05 mg/L, respectively [5].

Therefore, the treatment of wastewater consisting of Cr(VI) is critical to environment. Various methods have been proposed for treatment of Cr(VI) including electro-coagulation, adsorption, photocatalyst, ion–exchange, membrane filtration, and precipitation [5-9]. However, considering a method with low production sludge, simplicity, robust and cost-efficient technology is necessary. Recently, using biosorbent such as plant leaves and different agricultural wastes have been used due to its low-cost and the availability [10-12]. One of the biomaterials is date palm fibre that has been extensively investigated as adsorbents for the removal of different heavy metals [13, 14]. They are highly abundant and have various functional groups that can bind heavy metal ions such as hydroxyl, amino carboxyl, and ether.

It has been reported in different studies that the date palm as a biomaterial has metal adsorption capacity compared to the other biomaterials [15, 16]. El Nemr *et al.*, reported that activated carbon developed from date palm seed was treated using sulfuric acid, could remove 100% of Cr(VI) [17]. The purpose of biomass treatment is to increase the surface porosity and adsorption capacity. Moreover, treatment of biomass results in protonation, which may displace the light metal ions from the binding sites like carboxylic and then increase the metal adsorption capacity [18, 19].

There are different effective parameters on the biosorption process which need to be optimized. Recently, artificial neural networks (ANNs) have traditionally a nonlinear approximation tool that can be applied to model the relatively complex systems. The purpose of this study is to provide a neural network model for an accurate prediction of the biosorption of Cr(VI) from an aqueous solution. ANN using its many parameters (weights and bias) is able to predict the output of the model with high accuracy. Delivering a model with high precision estimations will reduce the need for more laboratory data, allowing us to determine the optimal parameters for designing equipments.

Experimental

Material and methods

Preparation of Cr(VI) solutions

The potassium dichromate $K_2Cr_2O_7$ provided by Merck Company was used for preparing the Cr(VI) stock solution and stored at room temperature. The double distilled water was utilized to dilute the solution of chromium ion to prepare the condition of each experiment.

Preparation of biosorbent

Date palm fiber was taken from the Persian Gulf (Bandar Bushehr, Iran). Then the prepared sample was washed for several times with water to remove any mud and dirt. After drying, the sample was treated with 0.1 M HCl solution for 8.0 h at room temperature. The date palm fiber was then washed with the physiological saline solution and dried in an oven at 60 °C. Subsequently, it was ground and then sieved to obtain homogeneous particles and stored for further use.

Adsorption experiments

Design expert 7.0.1 software based on the response surface methodology (RSM) was used to design the experiments. RSM is essentially a particular set of mathematical and statistical methods for designing experiments, building models, evaluating the effects of variables, and searching optimum conditions of variables to predict targeted responses [20]. A central composite design (CCD) in RSM design was applied to assess the effects of main factors which diverse at five different levels. Additionally, analysis of variance (ANOVA) was used to determine the significant models and parameters.

Batch adsorption was studied in the 250 mL Erlenmeyer flask on a magnetic mixer rate with 300 rpm throughout the study. The influence of various parameters such as initial Cr(VI) concentration, biosorbent dosage, initial pH, temperature and time on the adsorption efficiency was examined. More details related to the RSM were presented in previous work [20]. All experiments were carried out twice and at the end of each experiment, the sample was filtered and the concentration of Cr(VI) ion was measured using atomic absorption spectrometer (AAS) (Model 929, Unicam). The removal efficiency of Cr(VI) was calculated according to the following Equation.

$$Cr\ removal\ efficiency\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

where C_i is the initial Cr(VI) concentration (mg/L) and C_f is the final Cr(VI) concentration (mg/L) after the biosorption experiment.

ANN modeling

In this study, an artificial neural network (ANN) model was developed to evaluate the Cr(VI) removal as a function of input variables including initial pH, initial Cr(VI) concentration, biosorbent dosage, and experiment time.

The ANN architecture consisted of an input and output layer and also a number of hidden layers which there are neurons in the layers. The number of neurons in the input and output neurons is equal to the input (independent) and output (dependent) variables, respectively. It is clear that four neurons are in the input and one is in the outlet layer of the studied network. The key process in the modeling is to determine the appropriate number of hidden layers as well as hidden neurons. Many hidden layers and neurons can lead to network complexity and overfitting [21]. Therefore, an ANN with one hidden layer was considered in which the number of hidden neurons was determined through the trial-and-error approach. In the trial-and-error method, a different number of hidden neurons were examined and the lowest number of neurons that results in proper accuracy was chosen as the optimum ANN.

The ANN includes weights (W) and biases (b) in the interconnected structure which leads to the final output (Y) as follows:

$$Y = F_p \left\{ \sum_{j=1}^{n} W_{kj} \left[F_t \left(\sum_{i=1}^{m} W_{ji} X_i + b_j \right) \right] + b_k \right\} \tag{2}$$

Where X is model input, n is the hidden neuron numbers, m is the number of input variables, ‘i’, ‘j’ and ‘k’ are related to input, hidden, and output layer, respectively. F is the transfer function which hyperbolic tangent sigmoid and linear transfer function were employed for hidden and output layer, respectively.

In this study, an ANN was developed to estimate the Cr(VI) removal from aqueous solution. The four input parameters include initial pH, initial Cr(VI) concentration, biosorbent dosage and time.

The Levenberg–Marquardt (LM) back propagation procedure was used for training the multi-layer perceptron neural network (MLP-NN) in which the ANN parameters iteratively adjust to reduce the error values according to the LM optimization technique [22]. All the data points were normalized at the range of 0-1 for more computing speed. The range of the input and output parameters is tabulated in Table 1. In addition, quarters of the data points were randomly selected for testing the validity of the model and were not used in the model training step.

Table 1. The range of studied variables

Variable	Range
pH	2 to 8
biosorbent dosage (%w/v)	0.1 to 4
time (min)	5 to 120
initial Cr Conc. (mg/L)	50 to 500
Cr removal (%)	8.01 to 100

Results and discussion

The effect of different factors on the Cr(VI) removal efficiency was investigated. The influence of contact time was studied when other parameters were initial Cr(VI) concentration of 200 mg/L, pH of 3, and biosorbent dosage of 0.8% (w/v). Results showed that rising the contact time to about 50 min increased the removal efficiency up to nearly 95% and then a little change of sorption rate is observed (Figure 1a). It revealed that, the adsorption of Cr(VI) was fast and the equilibrium was achieved during 50 min of contact time. Contact time of 50 min was chosen for further experiments [15]. Moreover, the interaction and the effect of initial pH and initial Cr(VI) concentration were shown in Figure 1b. The results revealed that, increasing the pH from 3.2 to 6.8 at constant initial Cr(VI) concentration of 181 ppm reduced the Cr(VI) removal efficiency from 89% to 34.7%. The higher removal efficiency in the lower pH was due to that in the lower pH the surface of date palm fiber positively charged with H^+ ions. This caused a significantly strong electrostatic attraction between the bioadsornet surface and anionic hexavalent chromium which resulted in increasing Cr(VI) removal efficiency [23]. In the 2.0 < pH < 6.0, the $HCrO_4^-$ reduced using the following reaction [24].

$$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \quad (3)$$

Cr^{3+} trivalent cations, can be adsorbed on surface functional groups of the adsorbent by the following reaction [28]:

$$\equiv M - OH + Cr^{3+} \rightarrow \equiv M - OHCr^{3+} \quad (4)$$

As seen in Figure 1b, the initial Cr concentration has a negative effect on Cr removal efficiency. At the pH constant of 3.2, with increasing the initial Cr concentration from 181 to 419 ppm the amount of removal efficiency decreased from 89% to 62.8%. The decrease in percentage removal can be explained by the fact that all the adsorbents have a limited number of active sites, which would have become saturated above a certain concentration [5].

The effect of bioadsorbent dosage is depicted in Figure 1c. The results indicated that, the amount of Cr(VI) removal was increased as the biosorption dosage enhanced from 0.3 to 0.8% (w/v) at a constant pH. The positive effect of increasing bioadsorbnet dosage on Cr removal efficiency is due to increasing availability of adsorbent surface area and hence more active sites to adsorption of Cr(VI) [18]. An artificial neural network with one hidden layer was developed to model Cr(VI) removal efficiency in the investigated system. The different numbers of neurons were investigated for the hidden layer to avoid model overfitting.

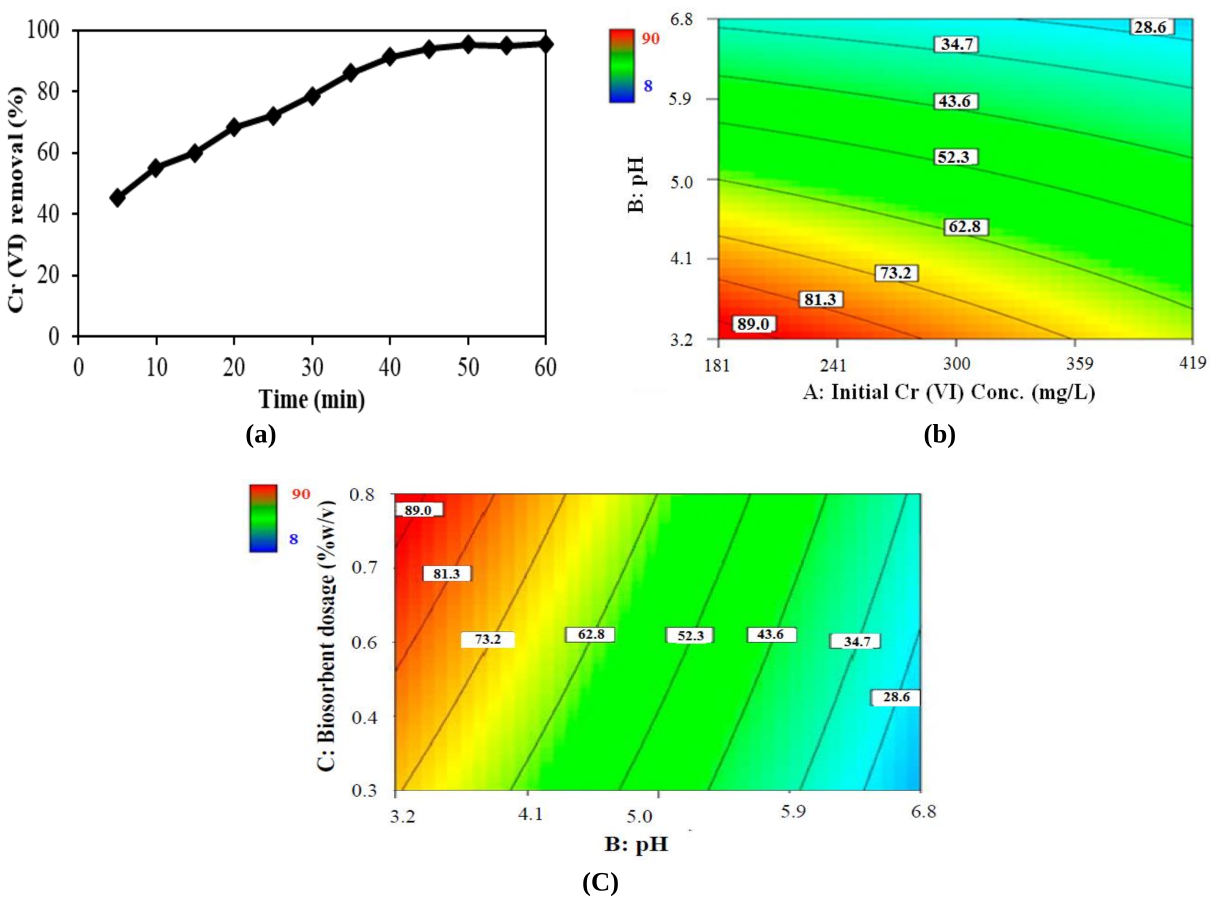


Figure 1. The effects of different parameters on the Cr(VI) removal efficiency

The errors employed to select the best ANN structure, are the mean square errors (MSE) and mean relative errors (MRE):

$$MSE = \frac{1}{N}\sum_{i=1}^{N}(r_i - e_i)^2 \tag{5}$$

$$MRE(\%) = \frac{100}{N}\sum_{i=1}^{N}\left(\frac{|r_i - e_i|}{r_i}\right) \tag{6}$$

Where N is the number of data points, r is the real (experimental) data, and e is the estimated (by model) data. As far as initial values of the ANN parameters (W and b) were considered randomly, 100 runs with different initial values were investigated and the best answer was selected. Table 2 reports the MRE and MSE values related to the developed ANNs with different hidden neurons. As specified in the table, five neurons have been chosen as the optimal number. The values of MRE and MSE of the ANN are 2.24% and 3.90, respectively.

Table 2. Deviations of the ANN with different number of hidden neurons

No. of neurons	MRE (%)	MSE
1	18.90	151.49
2	9.07	70.90
3	3.21	12.78
4	2.98	9.55
5	2.24	3.90
6	2.62	7.45
7	2.95	16.02
8	2.44	15.49

The related parameters of the optimum ANN with the structure of 4-5-1 are presented in Table 3. The output data (Cr removal efficiency) can be estimated with high precision using the reported weights and biases and applying Equation 2. The validation of the developed neural network was analyzed by a testing data set consisting of one-fours of the experimental data, which not previously employed in the training step. The error values (MRE and MSE) and absolute fraction of variance (R^2) related to the train and test data are presented in Table 4.

Table 3. Parameters (weights and biases) of the trained ANN

Neuron	W_{ji}				b_j	b_k=0.0652
	pH	Biosorbent dosage	Time	Initial Cr Conc.		W_{kj}
1	2.2691	3.2606	-3.2526	-1.0082	-1.4144	-0.3408
2	2.5543	2.3015	1.9804	1.5959	-4.2192	-0.3410
3	-0.1196	1.2806	0.1510	3.2547	-1.4790	0.7707
4	-1.8803	-1.2055	3.6459	-4.7538	1.4125	0.5544
5	-1.4405	-5.4262	3.5333	2.7303	-0.9882	-0.3094

Table 4. Deviations of the optimum ANN configuration (4-5-1) for train and test data set

Stage	Number of data points	MRE (%)	MSE	R^2
Training	32	1.77	2.89	0.9994
Testing	11	3.60	6.82	0.9983
Overall	43	2.24	3.90	0.9992

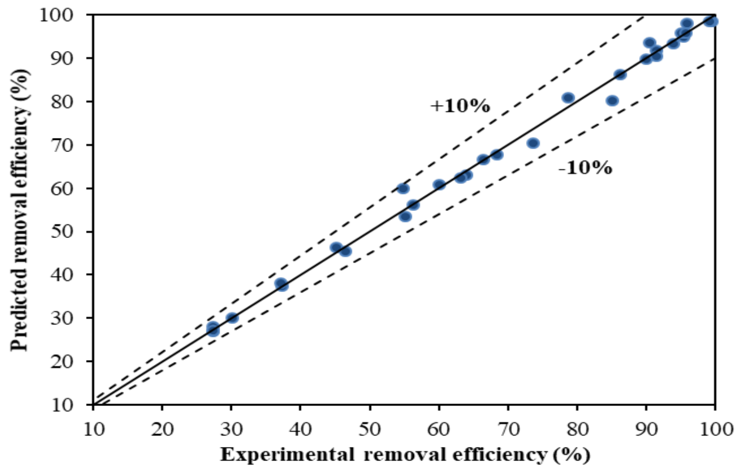


Figure 2. A comparison between the predicted Cr(VI) removal efficiency and empirical data for train data

The results indicated the acceptable testing deviations for approximating the Cr(VI) removal efficiency with MRE=1.77% and MSE=2.89. An assessment of the developed neural network model to estimate the train and test data group of experimental results are illustrated in Figures 2 and 3, respectively. As seen in Figures 2 and 3, the ANN estimation outputs are within ±10% deviation bands. Furthermore, low MRE and MSE of the test data group, and also an acceptable difference between obtained errors of the training and testing data confirm the validity of the model. It can be seen that the points are actually near the 45° line and the approximated data are in ±10% deviation bands.

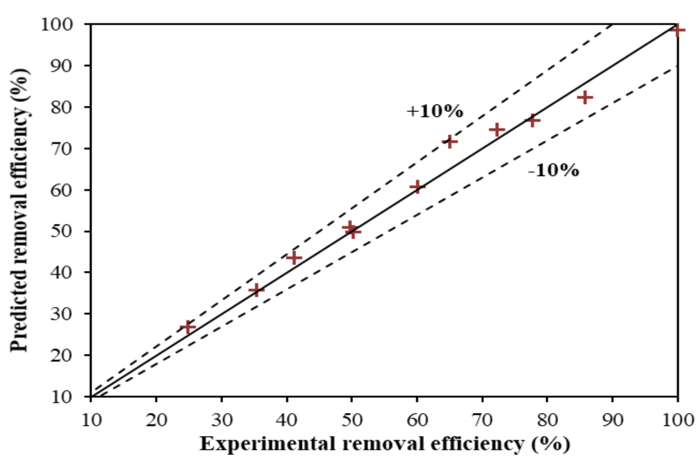


Figure 3. A comparison between the predicted Cr(VI) removal efficiency and empirical data for test data

Conclusions

In this work, the artificial neural network was developed for predict and model the Cr(VI) removal efficiency from the aqueous solution. An experimental setup was prepared to measure the Cr(VI) biosorbent using the date palm fibre. The variation of initial pH, initial Cr(VI) concentration, biosorbent dosage, and time on the removal efficiency was investigated. The structure of a three-layer feed forward ANN was optimized to estimate the Cr removal as a function of the four mentioned variables. The model outputs were found to be in good agreement with the experimental values. The mean relative error (MRE), mean square error (MSE), and the absolute fraction of variance (R^2) related to the test data set was 3.60 %, 6.82 and 0.9983, respectively. Also it was found that, the neural network is an appropriate and useful approach in Cr(VI) biosorbent modelling.

Conflict of Interest

We have no conflicts of interest to disclose.

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