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Evaluation of artificial neural network and multiple regression model for Cd(II) sorption on activated carbons

Manoharan Hema[1] and Krishnamoorthy Srinivasan[2]

[1]Department of Chemistry, College of Engineering, Anna University, Salem-636011, India.

[2]Gnanamani College of Technology, Namakkal 636018, India.

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ABSTRACT

A multi layer artificial neural network (ANN) and multiple regression (mathematical) models were developed for the investigation of cadmium removal efficiency of powered activated carbons of coconut oilcake, neem oilcake and commercial carbon. Levenberg-Marquardt (LM) Back-propagation algorithm is used to train the network. The network topology was optimized by varying number of hidden layers and number of neurons in hidden layers. The effective parameters on the removal of cadmium (%R) by adsorption process, which included the pH, contact time (T), distinctiveness of activated carbon (Cn), amount of activated carbon (Cw) and initial concentration of cadmium (Co) were investigated. The model was developed in terms of training; validation and testing of experimental data, the test subsets that each of them contains 60%, 20% and 20% of total experimental data, respectively. Standard deviation (SD) with respect to experimental output was calculated for outputs of ANN and regression model. The experimental data were best fitted with the artificial neural network model.

Introduction

Industrial effluents of metallurgical alloying, ceramics, electroplating, photography, pigment works, textile, printing, chemical industries, Cd/Ni batteries and lead mine drainage containing toxic metal such as cadmium (Wesley Eckenfelder Jr, 2000; Cheremisinoff, 1995). Higher concentration of cadmium causes gastrointestinal discomforts, kidney damage, nausea, vomiting, and diarrhea, destruction of red blood cells, renal disorder, itai-itai disease and high blood pressure (Drush, 1993). Stricter environmental regulations on cadmium discharge proclaim due to their toxicological and bioaccumulation tendency of cadmium. In India, the permissible limit for cadmium discharge into inland surface (IS: 1991) is 2.0 mg/L and for drinking water (ISI: 1982) is 0.01 mg/L. This necessitates the removal of cadmium from wastewater before its discharge into the environment.

The removal of cadmium from aqueous system is effectively done by adsorption technique using activated carbon as an adsorbent (Srinivasan, and Balasubramanian, 2003). Selecting suitable operating conditions for adsorption of Cd(II) from wastewater requires many experimental studies involving many functional parameters. Factors influencing the Cd(II) removal efficiency of activated carbon is quite complex in nature. But once a model is developed, it simplifies the tremendous work. Numerous reports are available with respect to multiple regression equation (Manju, and Anirudhan, 1997; Raji, and Anirudhan, 1997; Babu, and Ramakrishna, 2002) and artificial neural network (ANN), applications for wide range of problems in water and wastewater treatment purposes (Prakash, *et.al*., 2008; Fagundes-Klen, *et.al*., 2007; Salari, *et.al*., 2005; Abbaspour, and Baramakeh, 2005; Arzu Sencan, *et.al*., 2006; Ivo M. Raimundo Jr. and Narayanaswamy, 2003). ANN has already been used to develop a model for complex adsorption system of metal removal using activated carbon (Alireza Khataee, and Ali Khani, 2005).

A neural network is a powerful data modeling tool that is able to capture and represent complex input/output relationships. An artificial neural network is similar to biological neural system. ANN is composed by simple elements operating in parallel. The unit element of a network is the neuron; a simple mathematical function is associated with the so-called intra-neural connections. The ANN mathematically transforms an input vector in to an output vector through a suitable transfer functions (Simon Haykin, 2008). The model prediction with ANN is made by learning of the experimentally generated data by changing the connection weights. Each neuron receives the information in the form of inputs that occurred at the previous neurons. This information is processed together with the weights values of each connection of this neuron with previous one and the transfer function.

The most common neural network model is the multilayer perceptron (MLP) is known as a supervised network (Rojas, 1996). MLP network requires a desired output along with input in order to learn. The predicted model correctly maps the input to the output using historical data so that the model can then be used to produce the output, when the desired output is unknown. The back-propagation algorithm is used in layered feed-forward ANN. The artificial neurons are organized in layers and signals, are forwarded and then the errors are propagated backwards. There may be one or more intermediate hidden layers. The back-propagation algorithm uses supervised learning (http://rxiv.org) and it computes the network with the given input and output data. The algorithm comparing the simulated output data with the actual/given output data and the error is calculated. The error is reduced by the algorithm until the ANN learns training data by changing the connection weights between layers.

Tele:
E-mail addresses: srini_vasank@hotmail.com

Regression analysis is one of the commonly used empirical model based on statistical technique for investigating and modeling the relationship between variables. Generally regression equations are valid only over the region of the regressor variables contained in the observed data. An important objective of regression analysis is to estimate the unknown parameters in the regression model, known as model fitting to data. Building a regression model is an iterative process. Usually several analysis are required as improvements in the model structure and flaws in the data are discovered. The output of the model is dependent (or) response variable and the inputs are known as independent/predictor (or) regressor variable (Douglas C.Montgomery *et.al.,* 2007). Multiple linear regression models help us to approximate the relationships between a response variable and a number of explanatory variables by a linear function.

In the present study, ANN and multiple regression models were developed for the removal of cadmium from wastewater by using COCAC, CAC and NOCAC in batch mode adsorption process. The ANN modeling is carried out in three steps; such as optimization of the network topology, train and validates the network with data and test the network with data. The output of the ANN model was compared with output of multiple regression equation and was statistically analyzed.

Materials and methods

Adsorption studies: Adsorption by using activated carbon is most popular treatment method for cadmium removal from wastewater. Removal of Cd(II) from wastewater was carried out by using activated carbons derived from coconut oilcake (COCAC), neem oilcake (NOCAC) and commercial activated carbon (CAC). The method of preparation of activated carbons were reported earlier (Srinivasan, and Hema, 2009) and the results of batch adsorption studies for the removal of cadmium from wastewater was deliberated.

Removal of Cd(II) from wastewater by batch adsorption process is affected by the various factors, among these process variables, pH, contact time (T), distinctiveness of activated carbons (Cn), weight of activated carbons (Cw), and cadmium ion concentration in wastewater (Co) are considered. These five variables are used as the input vectors and the percent removal of Cd(II) (%R) as output for developing and training the network topology. The experimental conditions for these studies are shown below:

pH	: 2.0-10.0 ± 0.2
Contact time (min)	: 5, 10, 15, 20, 25, and 30.
Initial concentration of Cd(II) in each reagent bottles (mg/L)	: 9, 15, 30, 45, 60, and 75.
Weight of activated carbon in each reagent bottles (mg / 100mL)	: 100, 250, 500, 750, 1000, 1250, and1500.
Activated carbon used	: COCAC, CAC and NOCAC.

Particle size (120-200 ASTM) and temperature (30° C) were maintained constant.

An experimental design for the sorption of Cd(II) using three different powdered activated carbons (COCAC, NOCAC and CAC) has been developed by assigning three different experimental modes as listed here.

pH	Initial Cd(II) concentration (75 mg/L) and Weight of activated carbon (500 mg)	pH of the wastewater and Contact time (5-30 min)
Weight of activated carbon	Initial Cd(II) concentration (75 mg/L) and pH of the wastewater (optimum pH of 7± 0.2)	Weight of activated carbon and Contact time (5-30 min)
Initial metal ion concentration	pH (7± 0.2) and Weight of activated carbons (optimum dosage for COCAC and CAC – 500 mg/100mL and for NOCAC - 1000 mg/100mL).	Initial Cd(II) concentration and Contact time (5-30 min)

ANN Modeling: ANN modeling was performed using MATLAB version 7.5.0.342 (R2007b) software with the ANN toolbox version 5.1. In the present work, the Levenberg-Marquardt (Train LM) back-propagation learning algorithm was used in a feed-forward multilayer network. The training algorithm was repeatedly applied until satisfactory training was achieved. The functions used to train the network are shown in table 1. The data were randomly divided for test subsets such as 60% for training, 20% for validation and 20% for testing the network. In the present ANN, transfer functions used for hidden layers are tansig (figure 1(A)) and for the output layer is purelin (figure 1(B)).

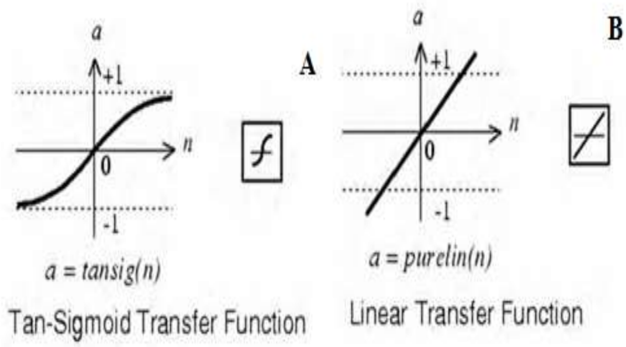

Fig. 1- TANSIG (A) and PURELIN (B) transfer functions used to build ANN

ANN model was developed using 396 sets of data of percent removal of Cd(II) by using COCAC, CAC and NOCAC activated carbons. Out of these, 238 data were used for training the network and the network was adjusted according to its error. Validation was performed with 79 data sets; these are used to measure network generalization, and to halt training when generalization stops improving. Testing of the generated network with the remaining untrained 79 data sets, therefore provide an independent measure of network performance during and after training.

Multiple linear regression modeling: Minitab the statistical computer software was used to develop the multiple linear regression model for the removal of Cd(II) from wastewater by using COCAC, CAC and NOCAC. The regression model was developed for the results of batch experiments for each carbon separately. Totally three regression models have been developed. Percent removal of Cd(II) from wastewater (%R) is dependent (or) response variable and the operating functions such as pH, contact time (T), weight of activated carbon (Cw), and initial Cd(II) concentration (Co) are called as independent/ predictor (or) regressor variable.

Result and discussions

ANN modeling: The topology of an ANN is determined by the number of layers, number of neurons in each layer and type of training algorithm used. Levenberg-Marquardt back-propagation algorithms (Kaan Yetilmezsoy and Sevgi Demirel, 2008) show better performance for the modeling of metal adsorption process using activated carbon. Optimization of ANN topology is probably the important step in the development of a model. The number of input and output neurons is fixed by the nature of the problem. The proper number of neurons in the hidden layer and number of hidden layer was investigated by trial and error method by training ANN with different architectures. The parameter used to evaluate the different ANN performance was the *mse* (mean squared error) value obtained for the test samples set. The *mse* measures the networks performance according to the following equation

$$mse = \frac{1}{Q}\sum_{k=1}^{Q}(t(k) - a(k))^2$$

Where Q is the number of data point, $t\ (k)$ is the network prediction and $a\ (k)$ is experimental response and k is an index of data.

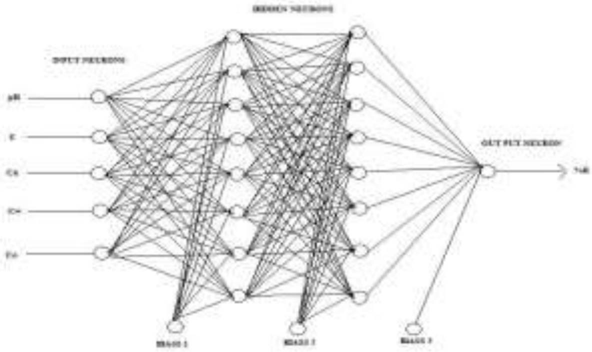

Fig. 2- Optimized network topology of ANN

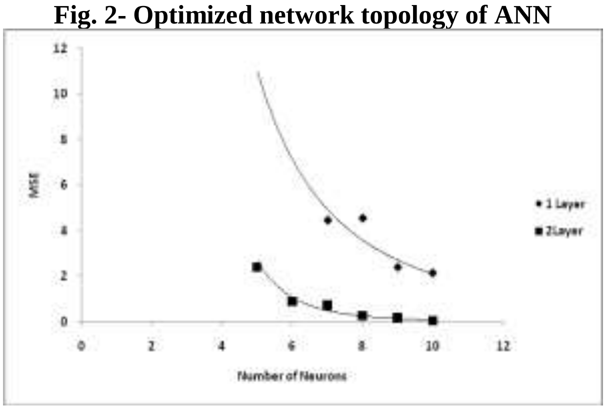

Fig. 3- Dependence between mse and number of neurons in hidden layer for Train LM algorithms

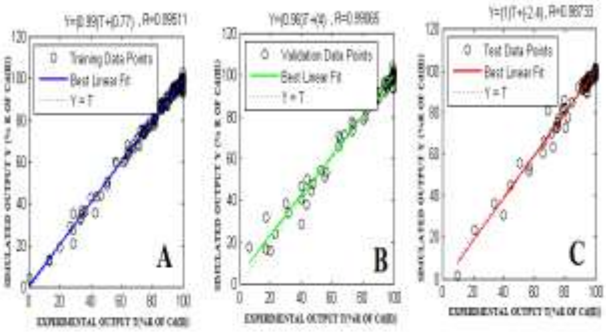

Fig. 4 - Comparison of simulated output with experimental output of Cd(II) removal from wastewater, (A) Training set, (B) Validation set, (C) Testing set.

Figure 3 shows the plot of *mse* against with varying number of neurons in hidden layer. It clearly indicates the minimum *mse* for percent removal of Cd(II) from wastewater occurred when eight neurons are in hidden layer. The hidden layers act like feature detectors; there can be more than one hidden layer. Increasing the number of hidden layer shows much more decreasing of *mse* of the model developed.

Figure 2 shows one of the optimum topology of ANN with five input neurons and two hidden layers with eight neurons each and one output layer. If the number of neurons in the hidden layer is more, the network becomes complicated. Results probably indicate that the present problem (predicting the percent removal of Cd(II) by three different powdered activated carbons) is not too complex to have a complicated network routing. Hence, the results were satisfactorily achieved by keeping the number of neurons in the hidden layer at one of the optimum number of eight.

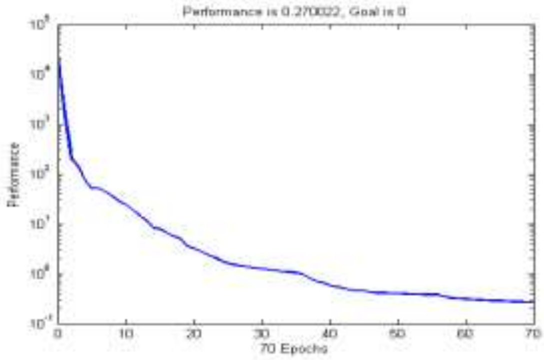

Fig. 5 - Effect of increaing hidden neurons on *mse* of the training results of Train Lm algorithms

Fitting model to the data: The simulated results of the percent removal of Cd(II) have been compared with the experimental results, are shown in figure 4. The R^2 value obtained in this case is > 0.98 which shows best fitting of model to data. These results substantiate that the ANN model reproduces the output (percent removal of Ni(II)) of cadmium adsorption system, within the experimental ranges adopted in the model fitting. Figure 5 shows the decrease of the *mse* during the training process. The statistical analysis of simulated output of 5 – 8 – 8 - 1 multilayer network topology with the experimental output values are listed in table 2. The SD used in the present study is determined using the following formula.

$$SD = \sqrt{\frac{\sum(x - y/x)^2}{(n-1)}}$$

Were x is the experimental data, y is the calculated data and n is number of observations. The SD less than 1.0 shows good agreement between experimental and predicted outputs. Then the higher value (>1) of SD may be due to the insufficient data to train the network when the experimental conditions of low pH and maximum dosage of activated carbons added to the adsorption system.

Multiple Regression modeling: A mathematical model was developed for Cd(II) removal from wastewater by using three different powered activated carbons. Regression analysis is widely employed tool for data analysis. In multiple linear regression, the regression co-efficient as well as the variance of the errors, are usually unknown and have to be estimated from observations by using least-squares criterion. A multiple regression equation for cadmium removal with respect to COCAC, CAC and NOCAC are listed in table 3 along with the regression co-efficient (R^2) and probability (P) values. Table 3 shows the value of P for three carbons as 0, since the P value is less than 0.01 the model is used for prediction (Douglas C.Montgomery, *etal.*, 2007).

The accuracy of the prediction is determined using standard deviation (SD) calculated with respect to the actual data. Table 4 shows that SD of the mathematical model was higher when compared with ANN model with respect to experimental data. It indicates that the output of the present problem from ANN was well fitted with the experimental data than predicted by multiple linear regression model.

Conclusions: ANN with two hidden layers of eight neurons each was developed for the adsorption system of Cd(II) removal from wastewater using COCAC, CAC and NOCAC. The simulated data are better correlated with the experimental one. The application of modeling technique to describe the sorption process is very effective and can provide a useful estimate of the cadmium removal efficiency by these activated carbons under the specific range of operating parameters tested. Multiple regression model for the same system shows higher SD when compared with ANN model. Therefore the predicted ANN model will be very much useful in predicting the more suitable operating conditions to treat Cd(II) containing industrial wastewater.

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Table 1-Functions used for building ANN

SL.No	Parameters	Choice
01	Number of Input	5
02	Number of hidden layers	2
03	Number of neurons	8, 8
04	Number of output	1
05	Maximum number of epochs	1000
06	Learning	Supervised
07	Training time	Infinite
08	Training style	Batch
09	Stopping Criteria	
	i)	Maximum number of epochs is reached.
	ii)	The performance gradient falls below MINGRAD (1e-10).
	iii)	Performance has been minimized to the GOAL (0)
	iv)	Validation performance has increased more than MAX_FAIL times (50)
	v)	MU exceeds MU_MAX (1e10).
For optimization		
01	Number of Neurons	7-10
02	Number of hidden layers	1, 2.

Table 2- Statistical analysis of simulated results of percent removal of Cd(II) from wastewater with experimental results.

Sl.No Set	% Removal of Ni(II) (Experimental)	% Removal of Ni(II) (Simulated)	Standard Deviation	Relative Error
01 Validation	99.21	99.83	0.43	0.62
02 Test	23.25	21.07	1.54	-2.18
03 Validation	99.49	99.93	0.31	0.44
04 Train	99.60	99.93	0.23	0.33
05 Validation	24.48	23.33	0.81	-1.15
06 Test	99.58	99.91	0.23	0.33
07 Validation	80.45	81.60	0.81	1.15
08 Train	99.97	99.99	0.01	0.02
09 Test	98.68	99.65	0.68	0.97
10 Validation	65.88	64.44	1.01	-1.44
11 Test	51.76	56.67	3.47	4.91
12 Train	85.14	85.60	0.32	0.46
13 Validation	44.72	46.67	1.37	1.95
14 Test	76.99	76.00	0.70	-0.99
15 Train	75.40	74.67	0.51	-0.73
16 Test	91.08	91.00	0.05	-0.08
17 Train	27.49	28.67	0.83	1.18
18 Validation	87.26	87.73	0.33	0.47
19 Test	95.57	93.51	1.45	-2.06
20 Train	63.58	64.67	0.77	1.09

Table 3- Multiple regression equations for the removal of Cd(II) from wastewater by using three different powdered activated carbons.

Sl.No	Carbon	Multiple regression equation	R^2	P
01	COCAC	%R = 47.1 + 7.13 pH + 0.035 T + 0.00841 Cw - 0.0917 Co	0.52	0
02	CAC	%R = 0.04 + 8.09 pH + 0.108 T + 0.00654 Cw + 0.286 Co	0.88	0
03	NOCAC	%R = - 8.80 + 9.01 pH + 0.150 T + 0.0274 Cw + 0.0088 Co	0.85	0

Table 4 - Statistical analysis of calculated results (output of multiple regression model) of percent removal of Cd(II) from wastewater with experimental and simulated output results.

Sl.No	Carbon	pH	T	Cw	Co	%R (Exp)	%R (Calc)	%R (Simu)	SD (Cal Vs EXP)	SD (Sim Vs Exp)	Relative error
1	COCAC	2	30	500	75	21.07	59.73	23.25	27.34	1.54	-38.66
2		4	20	500	75	96.77	73.64	97.45	16.35	0.48	23.12
3		6	20	500	75	98.77	87.90	97.55	7.68	0.86	10.86
4		7	30	500	15	99.60	100.88	98.98	0.91	0.43	-1.28
5		7	20	500	60	99.97	96.41	98.18	2.51	1.26	3.55
6		7	30	1500	75	99.91	103.79	93.31	2.74	4.66	-3.88
7		7	10	250	75	99.39	92.58	95.17	4.81	2.98	6.80
8		7	10	500	9	99.33	100.73	98.66	0.99	0.47	-1.40
10	CAC	2	20	500	75	42.67	43.10	35.76	0.30	4.88	-0.43
11		5	25	500	75	81.33	67.91	77.79	9.48	2.50	13.42
12		10	10	500	75	99.31	106.74	98.98	5.25	0.23	-7.43
13		8	5	100	75	80.20	87.40	72.92	5.09	5.14	-7.20
14		8	10	1000	75	94.67	93.83	96.13	0.59	1.03	0.84
15		8	15	500	45	90.00	82.52	88.46	5.28	1.08	7.48
16		8	20	500	45	90.22	83.06	88.15	5.06	1.46	7.16
17		8	25	500	15	74.67	75.02	75.40	0.24	0.51	-0.35
18		8	20	500	9	70.00	72.76	68.35	1.95	1.16	-2.76
19	NOCAC	4	20	500	75	50.67	44.60	55.60	4.29	3.48	6.07
20		5	10	500	75	56.67	52.11	53.92	3.22	1.94	4.56
21		9	10	500	75	99.68	88.15	97.76	8.15	1.35	11.53
22		8	20	100	75	30.00	69.68	38.58	28.05	6.06	-39.68
23		8	25	250	75	78.67	74.54	81.05	2.92	1.68	4.13
24		8	5	1000	75	94.35	92.09	89.67	1.59	3.30	2.26
25		8	20	1250	75	96.32	101.19	95.97	3.44	0.24	-4.87
26		8	30	1000	30	94.27	95.44	96.82	0.83	1.80	-1.17
27		8	5	1000	15	92.87	91.56	93.26	0.92	0.27	1.30
28		8	20	1000	9	97.00	93.75	93.51	2.29	2.46	3.24