

Use of artificial neural network for modeling of simultaneous adsorption of cyanide and phenol on granulated activated carbon

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ABSTRACT

In this study, a three layer artificial neural network was used to predict the simultaneous adsorption efficiency of phenol and cyanide on granular activated carbon. The input layer consisted of 5, 15, 2 neurons in input layer, hidden and output neurons respectively. Five operating variables namely pH, contact time, adsorbent dosage, temperature and initial concentration of phenol/cyanide was used as input to the constructed neural network to predict the adsorption efficiency of phenol and cyanide. A comparison between the experimental and predicted values by using neural network showed high correlation coefficient of 0.984 and 0.988 for phenol and cyanide respectively. Results indicated that contact time is the most influential parameter on output variable (23.57%) followed by initial concentration of phenol/cyanide (21.16%), adsorbent dosage (20.79%) and pH (19.44%). © 2013 Trade Science Inc. - INDIA

KEYWORDS

Artificial neural network;
Adsorption;
Cyanide;
Phenol;
Granular activated carbon.

INTRODUCTION

Water pollution has been a major problem for over decades. Due to growing public concern, removal of toxic pollutants like phenol and cyanides from industrial wastewater has become a major focus of research and policy debate. Due to poor degradability, high toxicity and ecological aspects, wastewater containing phenol presents a serious discharge problem. Phenols are present in wastewater generated from coke plant (620-1150 mg/l), refineries (10-100 mg/l), petrochemicals (50-600 mg/l), coal gasification (207-4900 mg/l) etc. Industries associated with manufacture of pulp and paper, metals, resins, plastics, rubber proofing, disinfectant, paint and steel also contribute significantly towards phenols in wastewater^[1]. Exposure to phenol can cause gastrointestinal irritation, tissue erosion, protein degen-

eration, systemic effects such as respiratory distress, methaemoglobinaemia, neurological effect and finally death^[2]. Due to its toxicity, European Union has set limits for phenol in potable and mineral water as 0.5 µg/l, wastewater emissions as 0.5 mg/l and sewerage system as 1 mg/l (law no. 152/2006).

Another toxic compound being released in environment, in large concentrations, as a result of industrial activities is cyanide. Cyanides are discharged mainly from wastewaters of coke plant (100-1000 mg/l), gold and silver extraction^[3,4] and plating industries (4000-100000 mg/l)^[5,6]. For the protection of environment, many countries and environmental protection agencies have imposed limiting standards for the discharge of wastewater containing cyanide to sewers. In India, Central Pollution Control Board (CPCB) has set a minimal national standard (MINAS) limit for cyanide in ef-

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fluent as 0.2 mg/l^[7]. The US Environmental Protection Agency (USEPA) has proposed a limit on total cyanide concentration in drinking and aquatic-biota waters as 200 and 50 µg/l respectively, where total cyanide refers to free and metal-complexed cyanides^[8]. Exposure to lower levels of cyanide may result in breathing difficulties, heart pains, vomiting, blood changes, headaches, and enlargement of the thyroid gland. Exposure to high levels of cyanide harms the brain and heart and may cause coma and ultimately death. Cyanide has been found in at least 471 of the 1662 National Priorities List sites identified by the Environmental Protection Agency^[9].

Considering the above regulations it is necessary to treat wastewater containing phenol and cyanides. Conventional methods of treatment of phenol containing wastewaters include distillation, liquid-liquid extraction, adsorption, membrane extraction, ozonation, photocatalytic oxidation, etc.^[1] The methods employed for cyanide removal are oxidation by hydrogen peroxide, oxidation by ozone, photo oxidation, biological degradation, oxidation by Caro's acid, oxidation by SO₂/air (INCO process), electrochemical processes and adsorption on activated carbon^[10]. Of the above reported methods, activated carbon adsorption is effective for the removal of several compounds and has gained popularity. Abatement of single components using activated carbon adsorption has been reported, however this method is impractical for large scale applications owing to high costs of activated carbon. Therefore, study of simultaneous removal of more than one component is essential since industrial effluents contain many components.

A very limited literature is available on the adsorption in multi-component systems, for e.g. adsorption in multi-component system of 2-methylphenol/2-nitrophenol/2-chlorophenol^[11], phenol, p-chlorophenol and p-nitrophenol^[12], p-cresol and p-nitrophenol^[13], phenol and m-cresol^[14], phenol and resorcinol^[15], phenol and aniline, phenol and nitro-phenol^[16]. However application of simultaneous adsorption of phenol and cyanide has not been reported yet. For adsorption to be put in practical use, it is necessary to model the adsorption rate and to establish the time dependency of adsorption systems under various process conditions. Selecting the optimum operating conditions for the ad-

sorption process requires the information about adsorption kinetics. It is important to know the adsorption behavior under various operating variables like pH regimes, contact time, effluent concentration, temperature, etc.

Artificial neural network (ANN) could be an effective tool in solving the complex relationship between multi-input variables and outputs. ANNs are non linear mapping structures which acts like a human brain. It can identify and learn correlated patterns between input data sets and corresponding target values. It has been successfully applied to predict the adsorption of solid-liquid systems^[17-19]. Aghav et al. 2011^[20] has used ANN to predict the adsorption of phenol and resorcinol from water environment using some carbonaceous adsorbents. A three layers feed forward neural network with back propagation algorithm in MATLAB has been used for estimation of removal efficiencies of phenol and resorcinol in bi-solute water environment. Singh et al. predicted the adsorption capacity of cadmium by hematite using the adapted neural fuzzy model^[21]. To the best of our knowledge, no studies have been reported so far on the use of ANN for the prediction of removal efficiency of phenol and cyanide using granular activated carbon. In the present study, a three layer ANN model was used on the basis of batch adsorption experiments to determine simultaneous removal efficiency of phenol and cyanide. Finally outputs obtained from the models are compared with the experimentation data.

EXPERIMENTAL

Granular Activated Carbon AR was washed several times with distilled water to remove any attached impurities. It was then soaked in 0.5 M H₂SO₄ in the ratio of 1:2 for 24 h. The treated GAC was again washed several times with distilled water, dried in an oven at 110 °C for 48 h and stored in air tight plastic containers. TABLE 1 shows the characteristic of GAC used for adsorption. BET surface area and pore density of GAC used was estimated using surface area analyser (model micrometrics chemisorb 2720).

The adsorption of phenol and cyanide on GAC was studied using batch experiments. Phenol stock solution of concentration 1000 mg (Phenol)/l was prepared by

dissolving 1 g of pure phenol crystal in 1 l of distilled water. Similarly cyanide stock solution of concentration 1000 mg (Cyanide)/l was prepared by dissolving 1.89 g of NaCN in 1 l of distilled water. The working solutions (50-350 mg/l) were prepared by diluting the stock solutions. Optimization studies were carried out as described here. Initial pH was varied from 3 to 11 to know its effect on adsorption. pH was maintained by the addition of required amount of 0.1 M H₂SO₄ and 0.1 M NaOH. The temperature was varied from 20 °C to 45 °C. The adsorbent dosage was varied from 10 g/l to 50 g/l. The initial concentration of phenol and cyanide was varied from 50 mg/l to 350 mg/l. The contact time was studied by sampling at an interval of 6 h for 72 h. All batch experiments were conducted in conical flasks with 1:1 ratio of phenol and cyanide at shaking speed of 120 rpm. The flasks were kept into an incubator cum orbital shaker (Metrex Scientific Instruments, New Delhi) for 24-72 h. The concentration of phenol and cyanide remaining in the simulated wastewater after the attainment of equilibrium was measured using colorimetric 4-aminoantipyrene method and colorimetric picric acid method respectively by measuring the absorbance at 510 nm and 520 nm respectively on a UV-VIS spectrophotometer, Hach® USA according to American standards^[22].

TABLE 1 : Characteristics of GAC

Characteristics	Value
Particle size	4-5 mm
BET surface area	228.6375 m ² /g
Pore volume	0.1151 m ³ /g
Bulk density	0.4 g/ml

The removal efficiency of adsorption was calculated as follows:

$$R_{em} \% = \frac{100(C_i - C_e)}{C_i} \quad (1)$$

where C_i and C_e are the initial concentration and equilibrium concentration in the solution respectively.

Modeling approach

ANN has been developed as generalizations of mathematical models of biological nervous system. The basic elements of a neural network are neurons interconnected to each other. A neural network has to be configured to produce the desired set of output on the

application of a set of input. The training of a neural network is performed by feeding teaching patterns to it and letting it change its weights according to some learning rule. The neurons receive impulses from either input cells or other neurons and perform some kind of transformation of the input and transmit the outcome to other neurons or to output cells. The layers of neurons are interconnected so that one layer receives input from the preceding layer of neurons and passes the output on to the next layer. An ANN architecture consist of number of hidden layers, hidden nodes, input nodes, output nodes, etc. (figure 1). The data is given to neural network in the input layer whereas the output layer provides the output for given set of input data for a trained network. The complicated relation between input layer and output layer is solved by hidden layers.

Generally a neural network with one hidden layer is sufficient for approximating any continuous function. The number of neurons in the hidden layer is determined by trial and error method starting from minimum and increasing it. Many researchers have used back propagation training algorithm for modeling of various problems which uses supervised training. Each input is multiplied by its weight and then added and processed using an activation function. Sigmoid function is most commonly used transfer function. The training samples are fed as input vectors through a neural network, calculating the error of the output layer and then adjusting the weights of the network to minimize the error. The performance of trained network is measured by statistical parameters like coefficient of determination (R²), mean square error (MSE), etc. A model should have its R² value as close as possible to 1 and its MSE value should be minimal.

In this work MATLAB 7.6.0 (R2008a) is used to predict simultaneous adsorption efficiency of phenol and cyanide on GAC. A three-layer ANN, an input layer with 5 neurons (initial pH, contact time, temperature, adsorbent dosage and initial concentration of phenol and/or cyanide), a hidden layer and an output layer with 2 neurons (removal efficiency of phenol and cyanide) was used to predict the removal efficiency of phenol and cyanide. The training of network was done using Levenberg-Marquardt back propagation method. The number of neurons was varied from 1-20. TABLE 2 shows the architecture of ANN used for modeling.

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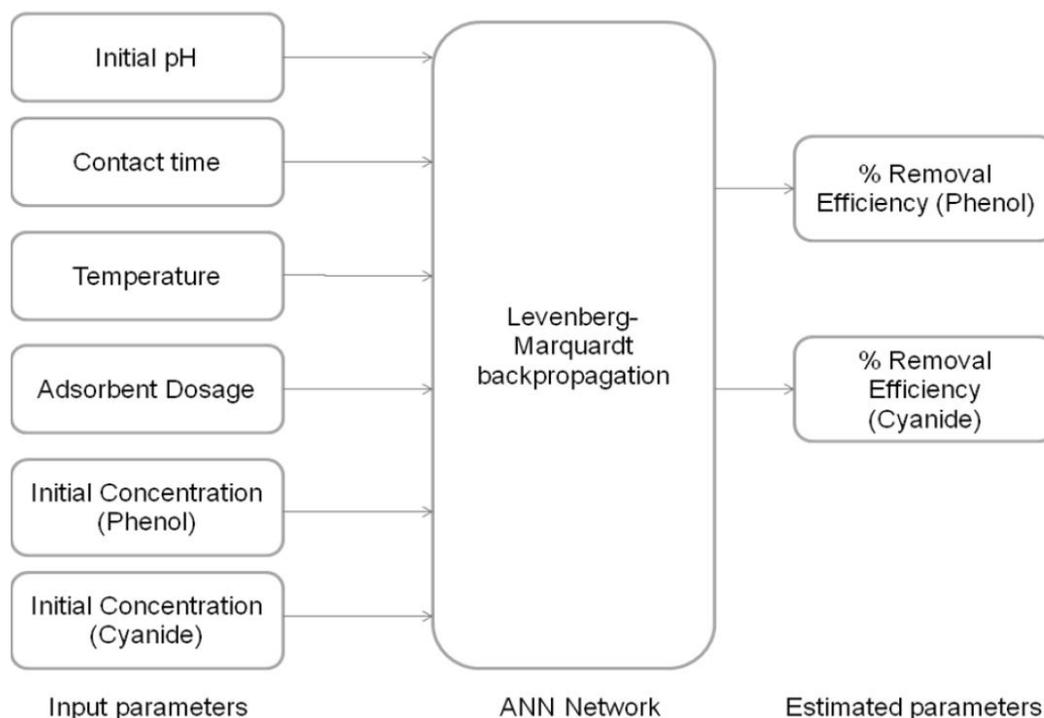


Figure 1 : Structure of artificial neural network

TABLE 2 : Details of trained artificial neural network for the simultaneous removal of phenol and cyanide on granular activated carbon

Type	Value/ Comment
Input layer	5
Hidden Layer	1-20
Output layer	2
Type of algorithm	Levenberg-Marquardt Backpropagation method
Number of data used for training	49
Number of data used for validation	17
Number of data used for testing	17

RESULTS AND DISCUSSION

Data preprocessing

To improve the learning and training process of neural network, it is necessary to normalize the input and output data using equation (2) and equation (3) respectively.

$$Y_i = L_{\min} + (L_{\min} - L_{\max}) * \frac{(X_i - X_{\min})}{(X_{\max} - X_{\min})} \quad (2)$$

where Y_i is the normalized value of X_i , X_i is the input or

output of the network, L_{\min} and L_{\max} define the limit of the range where we want to scale X_i and X_{\max} and X_{\min} are the maximum and minimum values of X_i . The input and output data was normalized between 0.2 - 0.8. The outputs were converted back to original state after modeling using equation 3.

$$X_i = X_{\min} + \frac{(Y_i - L_{\min})}{(L_{\min} - L_{\max})} * (X_{\max} - X_{\min}) \quad (3)$$

where Y_i is the normalized value of X_i , X_i is the predicted value of an output of the network, L_{\min} and L_{\max} define the limit of the range of X_i and X_{\max} and X_{\min} are the maximum and minimum values of X_i in the training data set.

Data division

In this study, a total of 84 experiment sets were used to train and test the performance of ANN for modeling of simultaneous adsorption of phenol and cyanide on GAC. Out of 84 experiment sets, 49 were selected for training, 17 for validation and rest for testing of the network. The experiment sets were selected for training, validation and testing on random basis. Aghav et al., 2011^[20] used 15 data sets for training and 7 each for validation and testing. Shetty et al., 2008^[23] used 24 data sets for training, 4 data sets for validation and 3

data sets for testing. The training was done using Levenberg-Marquardt backpropagation algorithm. Number of neurons in the hidden layer is an important factor of neural network. Lack of sufficient neuron causes under fitting of the network whereas too many neurons might lead to over fitting. This over-fitting occurs when the neural network adapt to a specific noisy

training data. It occurs when the difference between training error and test error rises with increase in the number of hidden neurons. In this study the number of neurons in hidden layer was varied from 1-20. The optimum number of hidden neurons was found to be 15 because training error and testing error start to diverge after 15 as seen from figure 2.

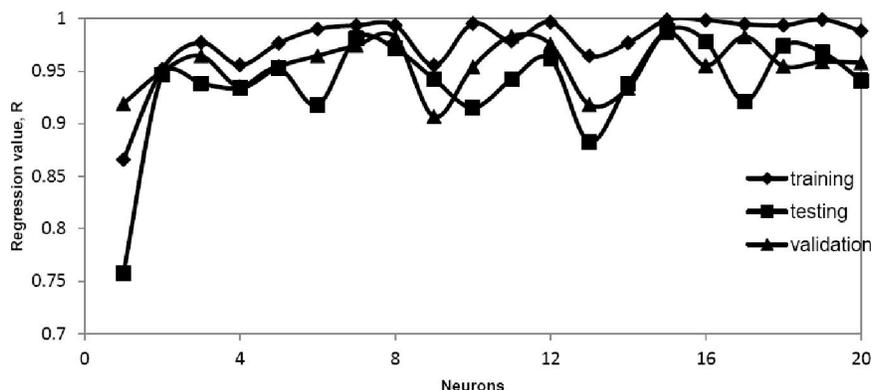


Figure 2 : Variation of training, testing and validation regression with increasing neurons in the hidden layer

Simulation result of ANN model

The training of data automatically stops when generalization stops improving as indicated by an increase in the mean square error of the validation samples. The Mean Squared Error (MSE) is the average squared difference between outputs and targets. It should be as low as possible. A MSE of zero means no error. The regression (R^2) value measures the correlation between outputs and targets. An R^2 value of one refers to a close relationship whereas zero a random relationship. The ANN model used here has sum of square error (SSE) of 2.210744, mean square error (MSE) of 4.887388, average relative error (ARE) of 2.540766 and Chi-square statistic as 8.001271 for phenol and SSE of 2.297312, MSE of 5.27764, ARE of 3.135181 and Chi square statistic as 26.83004 for cyanide. It shows

that ANN modeling performance is good to predict the removal efficiency of phenol and cyanide by adsorption using GAC. The regression value for training data is 0.99867, validation data is 0.98663 and testing data is 0.9886. A comparison between the experimental and predicted values using ANN is shown in figure 3 and 4 for phenol and cyanide respectively. The correlation coefficient (R^2) is 0.984 and 0.988 for phenol and cyanide respectively. This is in close agreement with the findings of previous studies^[17, 24-26]. It was found that ANN can predict the removal efficiency of cyanide better than phenol since the correlation coefficient for cyanide is greater than that of phenol. The percentage error between predicted and experimental values is more than 10% for percentage removal efficiency less than 35%. Therefore experiment sets pertaining to removal efficiency greater than 35% were selected.

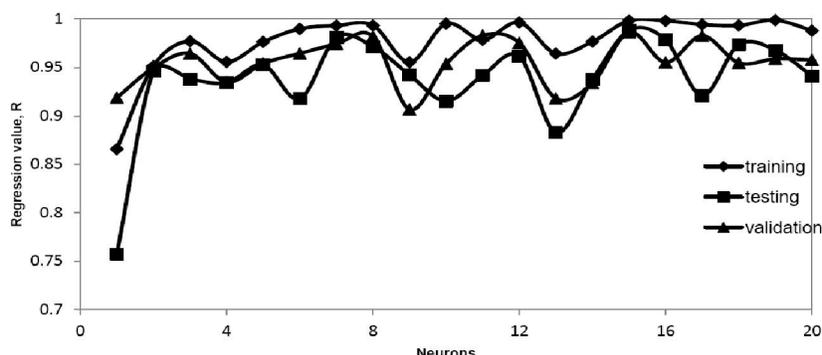


Figure 3 : Comparison of experimental removal efficiency with removal efficiency predicted by ANN for phenol

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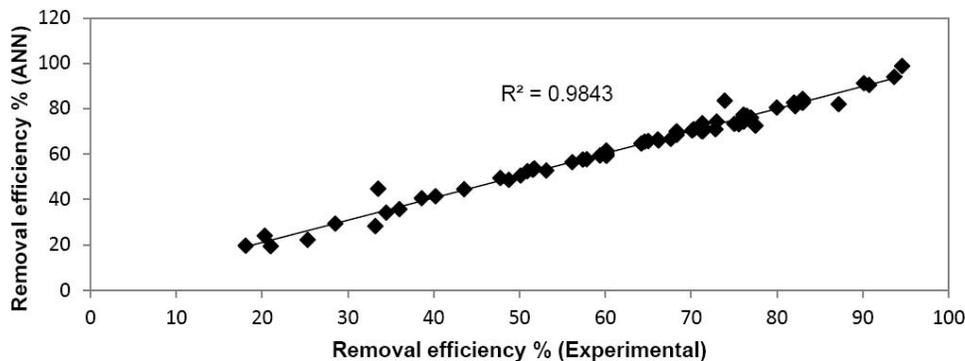


Figure 4 : Comparison of experimental removal efficiency with removal efficiency predicted by ANN for cyanide

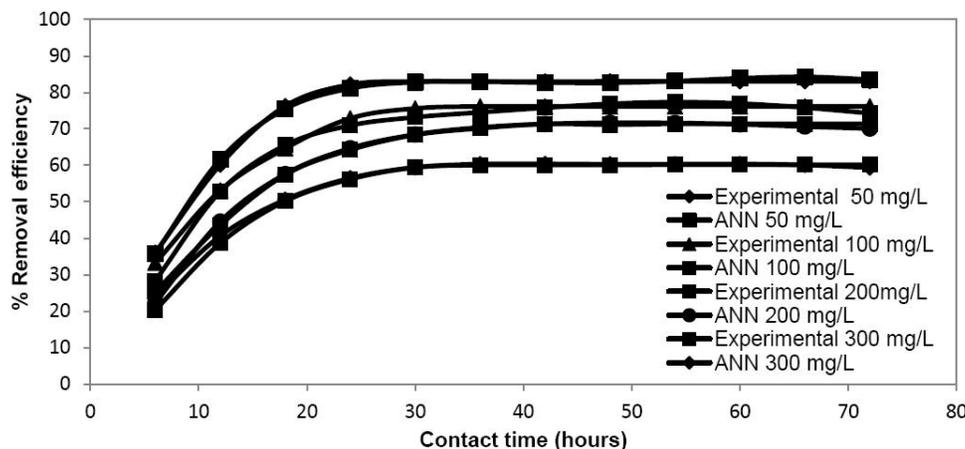


Figure 5 : Experimental removal efficiency and ANN removal efficiency of phenol for different initial concentration of phenol/cyanide

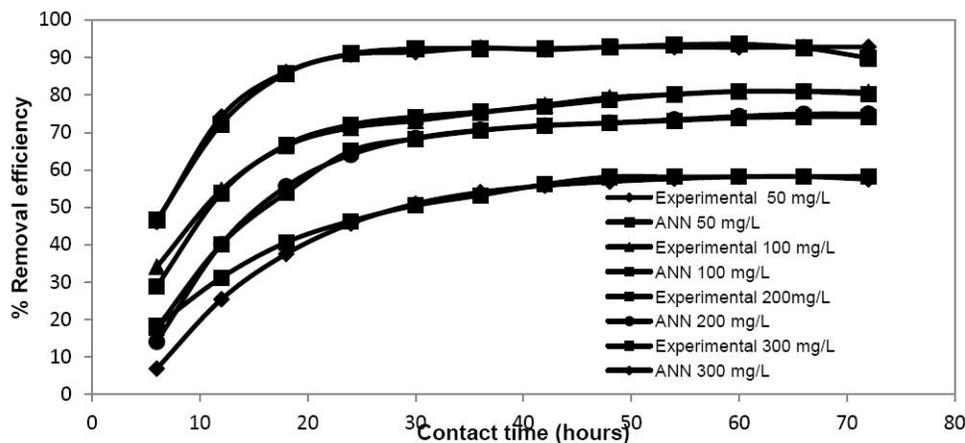


Figure 6 : Experimental removal efficiency and ANN removal efficiency of cyanide for different initial concentration of phenol/cyanide

Figure 5 and 6 shows the percentage removal efficiency of phenol and cyanide for different initial concentration of phenol/cyanide. The neural net weight matrix was used to find the relative importance of input variables on the output variables. The equation used was based on the partitioning of connection weights^[27]. It was found that contact time has the maximum effect on the removal efficiency (23.57%) followed by initial

concentration (21.16%), adsorbent dosage (20.79%) and pH (19.44%). The relative importance of temperature on removal efficiency was 15.04%.

Aleboye et al., 2008^[28] found initial concentration of H_2O_2 to be the most influential parameter in the decolorization process followed by contact time. The initial concentration appeared to be the most influential parameter in the biosorption process followed by pH,

temperature and time for Acid Black 172 metal-complex dye whereas for Congo Red, temperature was most influential and initial concentration was least influential. TABLE 3 shows the comparison of results of the present

study with that from the literature. The values of parameters obtained from pseudo second order kinetic modeling were used to predict the amount of phenol and cyanide adsorbed on GAC.

TABLE 3 : Comparison of effect of various input variables on output variables of this study with other studies

	This study	Khataee et al., 2010 ^[18]	Aleboyeh et al., 2008 ^[28]	Yang et al., 2011 ^[25]	
				Acid Black 172	Congo Red
Time	23.57	40.33	21.00	15.95	24.30
pH	19.44	16.00	11.61	23.45	29.83
Temperature	15.04	20.55	-	19.17	36.76
Adsorbent dosage	20.79	10.78 ^a	48.89 ^b	-	-
Initial concentration	21.16 ^c	12.34 ^d	18.50 ^d	41.43	9.11

^a Initial concentration of phenol/cyanide; ^b Initial concentration of H₂O₂; ^c Amount of algae; ^d Initial concentration of dye

TABLE 4 shows the comparison of amount of phenol and cyanide adsorbed on GAC with those predicted by ANN and pseudo 2nd order. Both the model had well fitting to experimental data. However in the case of amount of phenol adsorbed on the GAC, ANN was found to be more accurate than pseudo second order modeling. In the case of cyanide, ANN was found to have same accuracy as pseudo second order modeling. This is in agreement with previous studies^[19,24,25] that ANN had well fitting results to describe the experimental data.

TABLE 4 : Comparison of amount of phenol and cyanide adsorbed on GAC with those predicted by ANN and pseudo 2nd order GAC at pH=8, Contact time = 72 h, Temperature=35 °C, Adsorbent dosage = 30 g/l

C _i (mg/l)	Phenol			Cyanide		
	q _{exp}	q _{predict} (ANN)	q _{predict} (Pseudo 2 nd Order)	q _{exp}	q _{predict} (ANN)	q _{predict} (Pseudo 2 nd Order)
50	1.38	1.38	1.41	1.55	1.54	1.57
100	2.54	2.48	2.60	2.69	2.52	2.74
200	4.76	4.69	4.91	4.94	4.71	4.36
300	6.01	6.03	6.23	5.82	5.40	6.04

CONCLUSION

In this paper, prediction of removal efficiency of phenol and cyanide using granular activated carbon by artificial neural network was studied. A three layer neural network with 5 neurons in input layer, 15 neurons in hidden layer and 2 neurons in output layer was used.

The ANN model has sum of square error (SSE) of 2.210744, mean square error (MSE) of 4.887388, average relative error (ARE) of 2.540766 and Chi-square statistic as 8.001271 for phenol. The ANN model has SSE of 2.297312, ARE of 3.135181, MSE of 5.27764 and Chi square statistic as 26.83004 for cyanide. It was found that prediction of removal efficiency was better for cyanide than phenol. The percentage error of removal efficiency of phenol and cyanide predicted by ANN with experimental value less than 35% was more than 10%. All the input variables had important effect on the output variables. Contact time was found to be most influential parameter (23.57%) followed by initial concentration of phenol/cyanide (21.16%), adsorbent dosage (20.79%) and pH (19.44%). The comparison of experimental amount of phenol and cyanide adsorption on GAC was found to be better predicted by ANN than pseudo second order modeling in case of phenol whereas in cyanide it was found to have same prediction as of pseudo second order modeling.

ACKNOWLEDGEMENT

This study was supported by a research grant from the Ministry of Human Resource and Development, India.

NOMENCLATURE

C_e : equilibrium concentration in the solution, mg/l

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C_i : initial concentration in the solution, mg/l
 L_{\min}, L_{\max} : limit of the range of X_i
 MSE : mean square error
 R^2 : coefficient of determination
 R_{em} : Removal Efficiency, %
 X_i : input or output of the network
 X_{\max}, X_{\min} : maximum and minimum values of X_i
 Y_i : normalized value of X_i

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