



# Artificial neural network modeling in competitive adsorption of phenol and resorcinol from water environment using some carbonaceous adsorbents

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## ABSTRACT

This paper illustrates the application of artificial neural network (ANN) for prediction of performances in competitive adsorption of phenol and resorcinol from aqueous solution by conventional and low cost carbonaceous adsorbent materials, such as activated carbon (AC), wood charcoal (WC) and rice husk ash (RHA). The three layer's feed forward neural network with back propagation algorithm in MATLAB environment was used for estimation of removal efficiencies of phenol and resorcinol in bi-solute water environment based on 29 sets of laboratory batch study results. The input parameters used for training of the neural network include amount of adsorbent (g/L), initial concentrations of phenol (mg/L) and resorcinol (mg/L), contact time (h), and pH. The removal efficiencies of phenol and resorcinol were considered as an output of the neural network. The performances of the developed ANN models were also measured using statistical parameters, such as mean error, mean square error, root mean square error, and linear regression. The comparison of the removal efficiencies of pollutants using ANN model and experimental results showed that ANN modeling in competitive adsorption of phenolic compounds reasonably corroborated with the experimental results.

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## 1. Introduction

Phenols and its derivatives as Phenolic compounds are included in EPA's priority water pollutants list. These compounds are present in effluents of the petroleum refining, coke oven batteries, coal gasification plant, ply board manufacturing industries, etc. The average phenol concentration in some of the industrial wastewater is given in Table 1 [1].

Phenolic compounds are very harmful to organisms even at very low concentration due to its toxicity, foul odour and carcinogenic properties [2]. The health effects following repeated exposure to low levels of phenol in water include liver damage, diarrhoea, mouth ulcers, dark urine and hemolytic anemia [3]. Ministry of Environment and Forest (MOEF), Govt. of India, New Delhi and United States Environmental Protection Agency (US EPA) has listed phenol and phenolic compounds under priority pollutants list. As per the Bureau of Indian Standards, New Delhi, India, the allowable limit of phenol in drinking water is 1 mg/L while MOEF (Govt. of India) has set a maximum concentration level of 1 mg/L of phenol in the industrial effluents for safe discharge into inland surface water and 5 mg/L for safe discharge into public sewers and marine

coastal areas. The world health organization (WHO) recommended 0.001 mg/L as the permissible phenolic concentration in potable water. It is therefore necessary to reduce or to eliminate phenols from water and wastewater before discharge or reuse.

Various treatment methods are available for removal of phenolic compounds which include adsorption, ion exchange, reverse osmosis, chemical oxidation, precipitation, distillation, gas stripping, solvent extraction, complexation and even bioremediation [4]. However, adsorption process is considered to be the cost effective method for treating phenol containing water and wastewater potentially of low concentration level. The activated carbon (AC) is widely used for removal of a variety of organics from water, but the disadvantage associated with it is the higher regeneration cost and generation of carbon fines due to the brittle nature of carbon [5]. The challenge is now to find an alternative adsorbent of comparable efficiency with lower cost. The use of agricultural byproducts and lignocellulosic residue as adsorbents has been extensively studied [2–6]. The feasibility of using such materials as adsorbents without subjecting them to complex and expensive pretreatment makes them as one of the interesting alternative to the use of AC. Such materials do not need regeneration because of their availability at much cheaper cost.

There may be rarely a situation in which only a single solute would be adsorbed in a treatment process. Raw water supplies contain a variety of organic compounds that would be adsorbed

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**Table 1**  
Industrial sources and concentrations of phenol.

Industry	Concentration (mg/L)
Coking plant	
Weak ammonia liquor without dephenolization	58,010
Weak ammonia liquor after dephenolization	4–332
Wash oil still wastes	30–150
Oil refineries	
Sour water	80–185
General wastewater	10–100
APF separator effluent	0.3–6.8
Petrochemical	
Benzene refinery	210
Tar distillation	300
Nitrogen works	250
Orean manufacturing	100–150
Plastic factory	600–2000
Phenolic resin production	1600
Fiberboard factory	150
Fiberglass manufacturing	40–400
Aircraft maintenance	200–400

at different rates and at different sites on adsorbents like commercial AC. This is usually considered to be a competitive situation. The components of a mixture of adsorbate in bi-solute or multi-solute condition may mutually enhance adsorption which acts relatively independently or inhibitionally interfere with one another. Mutual reduction of both adsorption capacities and adsorption rates can be expected if the affinities of the adsorbate do not differ by order of magnitude and if there are no specific interactions among them which can enhance adsorption. This is because the adsorption of more than one substance generally reduces the number of surface sites preferentially available. For diffusion, controlled rates of adsorption by porous adsorbents, very slowly diffusion species in mixed adsorbate systems can depress rates of uptake of those which diffuse more rapidly. Thus, the degree of mutual inhibition of competing adsorbate is related to the relative sizes of molecules being adsorbed, relative adsorptive affinities and relative concentrations of the solutes and also depending on adsorption mechanism.

The adsorption capacity will be less with a single compound. Weber and Morris [7] cited difference between the break-through curves for adsorption of a solute from its pure solution and from a mixture of solutes in column of AC. It was evident that the presence of other solutes in the mixture adversely affects the adsorption of the first leading to much rapid breakthrough of this material. Jain and Snoeyink [8] investigated competitive adsorption on commercial AC from aqueous bi-solute solutions of p-nitrophenol, p-bromophenol and sodium benzenesulfonate using batch studies. They reported that a modified model of original Langmuir equation can reasonably be predicted for competitive adsorption. Srivastava and Tyagi [9] studied competitive adsorption of 4-nitrophenol, 2,4,6-trinitrophenol, 4-chlorophenol and 1,3-dihydroxy-benzene on AC obtained from fertilizer waste slurry in single and bi-solute system using Langmuir model and Jain and Snoeyink modified model. Khan et al. [10] investigated adsorption isotherms for five organic phenolic compounds on AC for single and bi-solute systems. They stated that for multi-component system, the adsorption of a solute in presence of other solutes is controlled by molecule size, solubility and polarity. Mihalache et al. [11] presented competitive adsorption on AC of three aqueous bi-solute system (phenol/p-nitrophenol, phenol/p-chlorophenol, p-nitrophenol/p-chlorophenol) and tri-solute system (phenol/p-nitrophenol/p-chlorophenol). Lee et al. [12] investigated competitive adsorption for phenol and 4-nitrophenol in binary system using commercial AC. They reported that the stronger-adsorbing species (4-nitrophenol) were more rapidly adsorbed than the weaker-adsorbing species (phenol).

Singh and Yenkie [13] carried out competitive adsorption of phenol, o-cresol, p-nitrophenol, m-methoxyphenol, benzoic acid and salicylic acid from their aqueous solution onto granular AC column as single, bi and tri-solute systems. They reported that in multi-solute system; initially all the adsorbates were taken up by the GAC surface, but near breakthrough point, more absorbable solute was able to desorb the less adsorbable one. The initial breakthrough in multi-solute adsorption in an adsorbent column occurs earlier as compared to their breakthrough times from single solute adsorption system. Also, the total amount of solute adsorbed from solution was greater in multi-component system than in single solute system. Alam et al. [14] used waste tyre rubber granules for competitive adsorption of phenol and 2,4-D using batch study for single and bi-solute aqueous systems. They found that Freundlich model fitted well with the experimental data and predicted amount of adsorbed well in bi-solute system. Wei and Nakato [15] conducted competitive adsorption of phenol, 2-chlorophenol and 2,4-dichlorophenol in binary and tertiary solute systems on organically modified hexaniobate  $K_4Nb_6O_{17}$ . They reported that uptake of each solute was reduced by the presence of other solutes and reduction in multi-solute systems depended on the hydrophobicity of the adsorbates co-existed in the solution. For the adsorbent modified with 2C<sub>18</sub>2MeN, uptake of the solutes were enhanced by the presence of each other at low equilibrium concentrations in comparison with single solute solutions because of competitive adsorption. The prediction of the competitive adsorption behavior of phenols with Freundlich-based Sheindorf–Rebuhn–Sheintuch (SRS) model gave good results.

ANN is one of data based non-traditional tools for modeling the adsorption process. ANN modeling has been successfully used for adsorption process in the past decade. Sundaram [16] developed a three layer ANN model using modified version of back-propagation algorithm for pressure swing adsorption (PSA) processes *i.e.*, four-step PSA cycle for H<sub>2</sub>–CO separation, six-step PSA cycle for H<sub>2</sub> production from natural gas and four-step PSA/Vacuum swing adsorption (VSA) cycle for the production of N<sub>2</sub> from air. Singh et al. [17] predicted the adsorption capacity of cadmium (Cd) by hematite using the adapted neural fuzzy model. Initial concentrations of Cd, agitation rate, temperature, pH and particle size of the hematite were used as input parameters for the training of the model. The value of coefficient of correlation ( $R^2$ ) between experimental and predicted values was worked out as 0.9607. Dabhade et al. [18] studied the effect of flow rate, influent concentration and solids loading for phenol degradation in spouted bed contactor and modeling was carried out using ANN. The performance of ANN model was measured using mean square error (MSE) as  $9.318e-12$ . Their results showed that ANN model prediction is better than multiple regression model. Yetilmezsoy and Demirel [19] developed a three layer ANN for prediction of Pb (II) removal efficiency from aqueous solution using Antep pistachio (*Pistacia Vera L.*) as an adsorbent. They used Levenberg–Marquardt algorithm (LMA) for training of ANN model in MATLAB environment. The performance of the formulated ANN model was measured using MSE of  $2.27875 \times 10^{-4}$  and correlation coefficient of 0.936. Kumar et al. [20] constructed and tested a three layer feed-forward neural network to analyze the kinetic dye uptake of batch adsorption study using AC. The input to ANN model was contact time, initial dye concentration, agitation speed, temperature, initial solution pH and AC mass. The reported value of correlation coefficient of formulated model was 0.98. Kumar and Porkodi [21] formulated a three-layer feed forward neural network to analyze the second order kinetics of dye *i.e.*, auramine O sorption onto AC under different experimental conditions. The values of parameters used in experiments include the following:

Experiment 1:  $C_0 = 200$  mg/L, agitation speed: 800 rpm, mass of AC: 1 g, volume of solution: 1.5 L, initial pH: 8, temperature: 305 K.

Experiment 2:  $C_0 = 200$  mg/L, agitation speed: 800 rpm, mass of AC: 2 g, volume of solution: 1.5 L, initial pH: 8, temperature: 305 K.

The values of coefficient of determination ( $R^2$ ) between experimental data and predicted kinetics ( $q$ ) using ANN were 0.99 for the two experiment and the values of MSE were 183.49 and 7.233, respectively. Khataee and Khani [22] carried out modeling of nitrate adsorption on GAC using ANN tool box of MATLAB 6.5 software. They found that ANN based model is a good and precise method to predict the extent of adsorption of nitrate on GAC under different conditions. An important feature of ANN is the ability to approximate arbitrarily complex relationship without detailed knowledge of the underlying process [23]. The objective of ANN model is to compute the output values from input values by some internal manipulated calculations. These models have three layers, such as input, hidden and output layers. Each of these layers contains nodes, and these nodes are connected to nodes at adjacent layer(s). The hidden layer(s) contain two processes *i.e.*, weighted summation functions and transformation function. Both these functions rationalized values from input data to the output measures. The weighted summation function is typically used in a feed-forward/back propagation neural network model. The removal efficiency of the adsorbent is to be considered as an output layer of the ANN model.

The pollutant removal efficiency is one of the important parameters in case of wastewater treatment using adsorption. The pollutant removal efficiency depends on various factors, such as adsorbent dose, adsorbent characteristics, initial concentration of adsorbate, solution pH, contact time, and agitation speed. The accuracy in prediction of pollutant removal efficiency will be beneficial for better process control of wastewater treatment system.

The investigative work on the competitive adsorption of phenolic compounds using low cost carbonaceous adsorbents is not very much exhaustive as per the literature survey. Also, limited work has been carried out on ANN modeling of the competitive adsorption process. The objective of the present work was to develop an ANN model of competitive adsorption to predict the removal efficiencies of phenol and resorcinol from water environment as bi-solute conditions using AC, wood charcoal (WC), and RHA.

## 2. Materials and methods

### 2.1. Materials

All chemicals and reagents used were of analytical grade supplied by E-Merck India. All experiments were conducted using double distilled water. Stock solutions were prepared in accordance with the "Standard Methods" [24] using double distilled water. Fresh stock solutions were made after every 10 days. To prepare the stock solution, first 1 g of phenol/resorcinol was diluted to 1000 mL of boiled and cooled distilled water. The strength of the solution was 1000 mg/L. Samples for required predetermined strength were prepared by adding required volume of stock solution to the distilled water for necessary dilution.

GAC carbon (E-Merck, India make) was procured and pulverized to different sizes (425–600  $\mu\text{m}$ ). The materials with varying sizes were kept in a desiccator at room temperature until it was used. The geometric mean sizes of materials used in all the studies ranged from 425  $\mu\text{m}$  to 600  $\mu\text{m}$ . WC was procured from the local market and pulverized into different sizes (425–600  $\mu\text{m}$ ). WC was pretreated with hot distilled water using 1 N  $\text{HNO}_3$  solution. After being soaked for 24 h, WC was separated from the solution and thereafter thoroughly washed several times using distilled water. Then, it was dried in a hot air oven at 105–110  $^\circ\text{C}$  for 24 h and stored in desiccators at room temperature before using it.

**Table 2**  
Characteristics of adsorbents.

Parameter	AC	RHA	WC
Surface area, $\text{m}^2/\text{g}$ (BET)	950–1050	480–600	200–260
Bulk density, $\text{kg}/\text{m}^3$	750.82	350.36	220
Moisture, %	1–2	5.13	8.00
Ash, %	0.5–8.0	29.5	33.0
Chemical composition			
SiO <sub>2</sub> , %	8.00	6.35	0.47
Al <sub>2</sub> O <sub>3</sub> , %	ND	0.41	0.06
CaO, %	ND	0.41	1.54
Fe <sub>2</sub> O <sub>3</sub> , %	ND	0.20	0.07
MgO, %	ND	0.45	0.08

ND: not detectable.

Rice is one of the major crops grown throughout the world and upon its separation from the paddy; one-third of its mass remains agricultural waste materials. The husk is generated in the milling process while the grain is separated from the outer covering (husk). The bulk quantity of RHA was obtained by burning in uncontrolled conditions in a muffle furnace at  $700 \pm 25$   $^\circ\text{C}$ . RHA was then pretreated with hot distilled water followed by washing with 1 N  $\text{HNO}_3$  solution. After being soaked for 24 h, RHA was separated from the above solutions and thereafter thoroughly washed several times using distilled water. Then, it was dried in a hot air oven at 105–110  $^\circ\text{C}$  for 24 h and stored in a desiccator at room temperature. The physico-chemical characteristics of these three test adsorbents are presented in Table 2.

### 2.2. Methodology

#### 2.2.1. Experimental methodology

All the experiments were conducted at room temperature. The test samples were agitated in reciprocating type horizontal shaker (Remi, India) at a speed of 140 rpm. The pH, adsorbent dose and initial phenol/resorcinol concentration were studied for their effects on removal of phenol and resorcinol. A set of IS Sieves was used for sieving purpose. pH measurement was carried out using a pH meter (Electronics, Model 101E) in all the experiments. Chemito make Gas Chromatography (model GC 1000) was used for measurement of residual adsorbate concentration of phenol and resorcinol mixture (1:1) at fixed conditions, such as fixed oven temperature (60  $^\circ\text{C}$ ); fixed injector temperature (250  $^\circ\text{C}$ ) and fixed FID detector temperature (250  $^\circ\text{C}$ ).

#### 2.2.2. Determination of adsorbate concentration

For bi-adsorbate solution *i.e.*, (1:1) mixture of phenol and resorcinol, 50 mL of standard solution (20 mg/L) of both phenol and resorcinol were taken into a conical flask and concentrations of phenol and resorcinol were reduced to 10 mg/L. The bi-solute adsorbate solution was then placed in a shaking machine for batch kinetic study keeping speed of the machine at 140 rpm.

Residual concentrations of phenol and resorcinol in 1:1 mixture solution after shaking and filtration were determined in GC with FID using capillary column. For such detection, no chemical or reagent was required to be added to filtrate obtained from the shake mixture of phenol and resorcinol. The filtrate was directly injected to GC for estimation of the residual sorbate concentrations *i.e.*, phenol and resorcinol against standard Chromatogram of phenol–resorcinol. Eq. (1) was used to calculate phenol/resorcinol removal efficiency (PRE) (%).

$$\text{PRE} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where  $C_0$  is initial concentration of phenol (mg/L) and  $C_e$  is concentration of phenol (mg/L) at time  $t$ . All the tests were performed in triplicate.

### 2.2.3. Modeling technique

2.2.3.1. ANN. ANN simulates the working principle of human brain and performs learning and prediction [25]. The architecture of ANN consists of input layer, one or more hidden layers and output layer. Each layer of the network consists of a number of an inter-connected processing element called neurons. These neurons interact with each other with the help of the weight. Each neuron is connected to all the neurons in the next layer. The data are presented to the neural network in the input layer. The output of the neural network is given by the output layer for the given input data. The hidden layers enable these networks to compute complicated relations between inputs and outputs.

The number of hidden layers is to be selected depending on the complexity of the problem. Generally one hidden layer is sufficient for investigation of most of the problems. The number of neurons in the hidden layer is selected by trial and error method starting from minimum and then increased depending on the nature of problem. The training of neural network is carried out by presenting a series of input data and target output values. The parameters affecting output should be selected as input parameters. The back propagation training algorithm has been widely used to model various problems in environmental engineering. In backpropagation training algorithm, neurons in the hidden layer and output layer processes its inputs by multiplying each input by its weight, summing the product, and then processing the sum using a nonlinear transfer function, also called activation function. The most common transfer function used is sigmoid function. The learning in neural network takes place by modifying weights of the neurons according to the error between the values of actual output and target output. The changes in weights are proportional to the negative of the derivative of the error.

The back propagation is essentially a gradient descending method to minimize the network error function (Eq. (2)):

$$E = \sum_{j=1}^k \sum_{i=1}^n (e_i(j) - t_i(j)) \quad (2)$$

where  $e_i(j)$  and  $t_i(j)$  are the estimated and targeted value, respectively. 'n' is the number of output nodes and 'k' is the number of training samples.

Before starting the training of ANN, weights are initially randomized. Based on the error propagation, the weights are adjusted as indicated in Eq. (3)

$$\Delta W_{ij}(n) = \alpha \frac{\partial E}{\partial W_{ij}} + \eta \Delta W_{ij}(n-1) \quad (3)$$

where  $\Delta W_{ij}(n)$  and  $\Delta W_{ij}(n-1)$  are weights increment between nodes  $i$  and  $j$  during adjacent iteration,  $\alpha$  and  $\eta$  are learning rate and momentum factor. Careful selection and appropriate adjustments of the learning rate are very much necessary for successful training of back propagation neural network.

The training of ANN model is carried out by presenting the complete input data set to the network and continued till the average MSE is minimized. After the training is over, the trained neural network deemed to reproduce the target output values for the training data. Weights of the trained neurons are then stored in the memory of neural network. The testing of the trained network is carried out by presenting the set of test data and then comparing the output of the network with the actual values of the output. The performance of formulated ANN model can be measured by several statistical parameters such as coefficient of determination ( $R$ ), mean error (ME), MSE, root mean square error (RMSE). A well-trained model should have  $R$  value close to 1 and values of error terms should be minimal.

The numbers of input and output neurons are fixed according to the nature of the problem. In present study, only one hidden

**Table 3**  
Range of variables.

Sl. no.	Variables	Ranges
1	Amount of adsorbent dose (g/L)	10–100
2	Initial concentration of phenol (mg/L)	10–100
3	Initial concentration of resorcinol (mg/L)	10–100
4	pH	3–9
5	Contact time (h)	0.5–6
6	Phenol/resorcinol removal efficiency (%)	0–100

layer was selected. The number of neurons in the hidden layer was selected from 2 to 14. The input to the neural network includes amount of adsorbent dose (g/L), concentration of phenol (mg/L), concentration of resorcinol (mg/L), pH, and contact time (h). The percentage removal of phenol and resorcinol was selected as targets. The range of variables used is given in Table 3.

### 2.2.4. Data preprocessing

The input and output variables in the present study had different characteristics and importance level resulting into varied response to the neural network. The ANN model training would be more efficient if preprocessing steps are performed on the input and target data, and thus the preprocessing exercise is used in real application. The input parameters were scaled in the range of 0.2–0.8. The preprocessing of the data could be performed by the algorithm as given in Eq. (4).

$$X_i(\text{net}) = 0.2 + 0.6 \frac{(X_{im} - \min(X_i))}{\max(X_i) - \min(X_i)} \quad (4)$$

where  $X_i(\text{net})$  is the normalized value of the  $i$ th variable;  $X_{im}$  is the observed value of the  $i$ th variable;  $\min(X_i)$  is the minimum value of the  $i$ th observed variable in the training data-set; and  $\max(X_i)$  is the maximum value of the  $i$ th observed variable in the training data-set.

After preprocessing of the training set-data, new inputs are fed into the trained networks, and then be processed with the minimum and maximum vectors that are computed for the training set. In order to compare the results of neural network with the observed values, the rescaled output needs to be converted back within the same range for the original target. The algorithm as given in Eq. (5) was used for this purpose:

$$Y_{i(p)} = \text{Min}Y_i + \frac{(\text{Max}Y_i - \text{Min}Y_i)}{0.6} \times (X_i(\text{net}) - 0.2) \quad (5)$$

where  $Y_{i(p)}$  is the predicted value of the  $i$ th output variable;  $X_i(\text{net})$  is the normalized value of the  $i$ th output variable;  $\text{Min}Y_i$  is the minimum value of the  $i$ th observed variable in the training data-set; and  $\text{Max}Y_i$  is the maximum value of the  $i$ th observed variable in the training data-set.

Total data generated in the batch experiment was divided for training (15 data sets), validation (7 data sets) and testing (7 data sets).

### 2.2.5. ANN software

The training, validation and testing of the ANN model was carried out using MATLAB 7 software with ANN tool box. A three layer feed forward neural network with tansig transfer in the hidden layer and purelin transfer function in the output layer was used. The Levenberg–Marquardt algorithm was used for the ANN model training.

### 2.2.6. Performance of developed ANN model

In order to measure the pollutant removal efficiency and performance of all the three ANN models developed for competitive adsorption, different types of statistical parameters can be used to estimate the generalization error. In the present work, ME, MSE

**Table 4**  
Data-set for Phenol–Resorcinol–AC ANN model training.

Sl. no.	Phenol conc. (mg/L)	Resorcinol conc. (mg/L)	AC (g/L)	Time (h)	pH	% Phenol removal efficiency	% Resorcinol removal efficiency
1	10	10	60	0.5	7	24.3	43.8
2	10	10	60	1.5	7	41.2	61.6
3	10	10	60	2.5	7	51.4	70.3
4	10	10	10	4.0	7	66.8	79.9
5	30	30	30	4.0	7	24.3	40.2
6	80	80	60	4.0	7	43.7	63.4
7	10	10	80	4.0	7	55.8	75.8
8	10	10	60	4.0	7	61.5	79.9
9	10	10	60	4.0	7	71.5	90.1
10	30	30	60	4.0	7	67.2	84.6
11	50	50	60	4.0	7	62.8	80.3
12	80	80	60	4.0	7	61.0	76.9
13	10	10	60	4.0	3	74.8	86.3
14	10	10	60	4.0	7	78.8	87.6
15	10	10	60	4.0	9.2	58.8	67.9

and RMSE were selected to measure the network performance of Models 'A', 'B' and 'C'. Further in order to investigate the network response in more details, a linear regression analysis was also carried out with respect to network predicted values and actual experimental values of pollutant removal efficiencies for all the three developed models.

### 3. Results and discussion

#### 3.1. Binary adsorption kinetics for removal of phenol and resorcinol

Adsorption of phenol and resorcinol individually in bi-solute systems was conducted with initial concentrations of phenol and resorcinol in the aqueous solutions varying from 10 to 100 mg/L (10, 20, 30, 40, 50, 60, 80, and 100 mg/L) with a 1:1 molar ratio of phenol and resorcinol mixtures. The phenol and resorcinol removal efficiency for AC were found 71 and 90%, respectively, for initial concentration of phenol and resorcinol as 10 mg/L each with contact time of 4 h, pH 7 and adsorbent dose = 60 g/L. Similarly, the removal efficiency for phenol and resorcinol for WC was found 69 and 85%, respectively. The removal efficiency for phenol and resorcinol for RHA was observed 75 and 87%, respectively. The absorbability of resorcinol was found more than that of phenol for AC, WC and RHA. The adsorption of adsorbate depends on compound's solubility, pH, ionic density and the presence and position of the hydroxyl group on the aromatic ring.

**Table 5**  
Data-set for Phenol–Resorcinol–WC ANN model training.

Sl. no.	Phenol conc. (mg/L)	Resorcinol conc. (mg/L)	WC (g/L)	Time (h)	pH	% Phenol removal efficiency	% Resorcinol removal efficiency
1	10	10	60	0.5	7	6.8	24.1
2	10	10	60	1.5	7	16.5	43.3
3	10	10	60	2.5	7	25.4	58.8
4	10	10	10	4.0	7	41.5	68.5
5	30	30	30	4.0	7	15.8	21.9
6	80	80	60	4.0	7	28.3	44.2
7	10	10	80	4.0	7	34.5	65.5
8	10	10	60	4.0	7	39.8	70.5
9	10	10	60	4.0	7	68.6	84.6
10	30	30	60	4.0	7	65.9	81.0
11	50	50	60	4.0	7	62.8	75.3
12	80	80	60	4.0	7	57.9	70.0
13	10	10	60	4.0	3	72.5	73.2
14	10	10	60	4.0	7	76.9	86.0
15	10	10	60	4.0	9.2	43.4	61.6

#### 3.2. ANN model developments in competitive adsorption of phenol and resorcinol

Three models were developed for the competitive adsorption of phenol and resorcinol for the following combinations:

- Model 'A': AC and Phenol–Resorcinol System;
- Model 'B': WC and Phenol–Resorcinol System;
- Model 'C': RHA and Phenol–Resorcinol System.

Total 29 data sets were available for each adsorption system. These data were divided into 50% for training set (15), 25% for validation set (7) and 25% for testing data set (7). The training set was used to develop the neural network. The validation data-set was used to determine when the network's general performance was maximized through early stopping and the testing data set was used to evaluate the generalization ability of the trained network. Basheer and Najjar [26] used 36 data sets for training and 5 data sets for testing, Isha et al. [27] used 19 data sets for training and 5 data sets for testing, Shetty et al. [28] used 24 data sets for training, 4 data sets for validation and 3 data sets for testing of the ANN model respectively (see Tables 4–6).

During the training process, small weights were assigned to the connection between neurons in a random way. The weights were modified until the error between the predicted and experimental values of adsorption efficiency are minimized. It is desired that the difference between the predicted and observed values should be as small as possible. During the testing process, the network was tested for its generalization ability with the observed output after

**Table 6**  
Data-set for Phenol–Resorcinol–RHA ANN model training.

Sl. no.	Phenol conc. (mg/L)	Resorcinol conc. (mg/L)	Wood charcoal (g/L)	Time (h)	pH	% Phenol removal efficiency	% Resorcinol removal efficiency
1	10	10	60	0.5	7	13.8	38.4
2	10	10	60	1.5	7	28.7	54.2
3	10	10	60	2.5	7	41.0	63.3
4	10	10	10	4.0	7	56.8	76.5
5	30	30	30	4.0	7	11.4	31.5
6	80	80	60	4.0	7	28.7	54.3
7	10	10	80	4.0	7	44.2	68.9
8	10	10	60	4.0	7	51.5	73.5
9	10	10	60	4.0	7	74.9	86.8
10	30	30	60	4.0	7	70.5	83.5
11	50	50	60	4.0	7	68.6	77.1
12	80	80	60	4.0	7	65.0	74.5
13	10	10	60	4.0	3	53.5	69.2
14	10	10	60	4.0	7	75.9	84.6
15	10	10	60	4.0	9.2	23.3	63.9

the training process is completed. When the neural networks are tested successfully, it can be used for prediction. The neural networks are sensitive to the number of neurons in the hidden layers. Insufficient neurons may cause under fitting. Also, too many neurons might lead to over fitting. When such network is presented with a new data set, the network would likely to give incorrect output since the new data might exhibit random noise different from random noise of the developmental data-set. The over fitting problem can be prevented with generalization improving techniques, such as regularization or early stopping. Another problem in neural network training is the selection of the most appropriate learning rate. A too large learning rate might result in unstable learning, while a too small learning rate could also lead to long training time. For the training of nonlinear multilayer ANN, a learning rate of 1.0 normally can produce good result.

The feed forward backpropagation (BP) algorithm with Levenberg–Marquardt (LM) training was applied for development of all three ANN models. The BP is an approximate steepest descent algorithm with MSE used as performance function. In the neural network development, different number of hidden layers, number of neurons in each layer, and type of transfer function for each neuron were analyzed with a learning rate of 1.0 and training goal of  $10^{-5}$ . Then, the trained networks were tested using the testing data sets and MSE method by modifying the network weights. It was found that network with one hidden layer of neurons is successful. It was observed that Models 'A', 'B' and 'C' took 12, 25 and 30 epochs, respectively, to train the 15 data sets. The tansig transfer function was used in the hidden layer and linear transfer function in the output layer. The training of the network was carried out with different number of neurons in the hidden layer with training goal of  $10^{-5}$ . It was observed that the best network for all the models has 8 neurons in the hidden layer.

The LM training algorithm used was one of the fast training BP methods *i.e.*, Levenberg–Marquardt algorithms. The LM algorithm is designed to approach second-order training speed without computing the Hessian matrix. This algorithm uses the approximation to the Hessian matrix as given in Eq. (6).

$$X_{k+1} = X_k - [J^T + \mu I]^{-1} J^T e \quad (6)$$

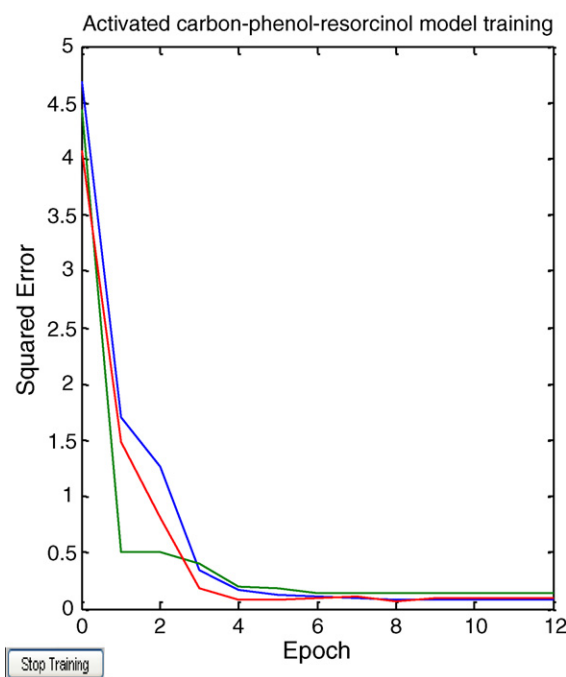
The LM algorithm is appeared to be the fastest method for training moderate-sized feed forward neural networks (up to several hundred weights). It has better performance than the other methods for function approximation problems. The training of the ANN models formulated is shown in Figs. 1–3. The comparison of the ANN model's results and experimental values of phenol/resorcinol removal efficiencies for all the three models formulated is presented in Tables 7–9. The statistical analysis of the results of the

network performance is presented in Table 10. The performance of the three models developed is shown in Figs. 4–6.

The results of the linear regression analysis for the three models developed are shown in Figs. 7–9. The values of R for all the three models are closer to 1. The values of slope (*M*) for all the three models are closer to 1. Also, the values of Y-intercept for all the three models are closer to 1. The values of ME, MSE and RMSE of these three models are on lower side. It was found that the predicted values of phenol and resorcinol removal efficiency by ANN model are very close to the experimental values for all data sets in test series for Models A, B and C.

### 3.3. Effect of contact time, adsorbent dose, pH and initial concentration of phenol and resorcinol on competitive adsorption

The adsorptions of phenol and resorcinol (1:1 mix) onto AC, WC and RHA were studied as a function of contact time in order to determine the time required to reach the equilibrium. The efficiency of an adsorbent depends on the rapid uptake and quick establishment of



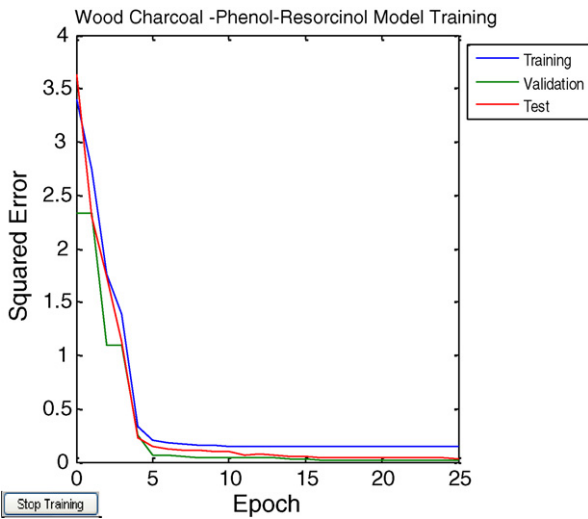
**Fig. 1.** ANN model training for prediction of phenol and resorcinol removal efficiency.

**Table 7**  
Comparison of ANN Model 'A' output and experimental values for test data.

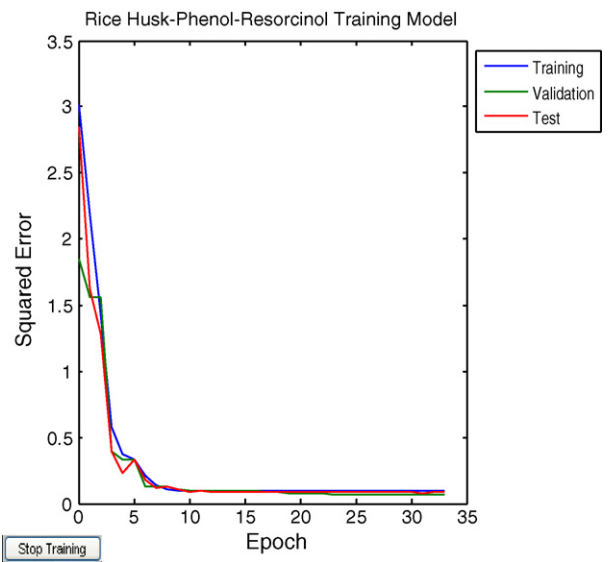
Sl. no.	Phenol removal efficiency (%)		Resorcinol removal efficiency (%)		Error (%)	
	Experimental values	ANN predicted values	Experimental values	ANN predicted values	Phenol	Resorcinol
1	34.6	32.8	54.2	52.5	1.8	1.7
2	57.5	57.2	73.9	74.1	0.3	-0.2
3	34.5	29.9	57.1	46.8	4.6	10.3
4	59.8	63.0	77.6	80.3	-3.2	-2.7
5	68.4	70.7	90.0	85.8	-2.3	4.2
6	60.8	61.1	77.4	77.8	-0.3	-0.4
7	73.1	74.6	83.2	86.3	-1.5	-3.1

**Table 8**  
Comparison of ANN Model 'B' output and experimental values for test data.

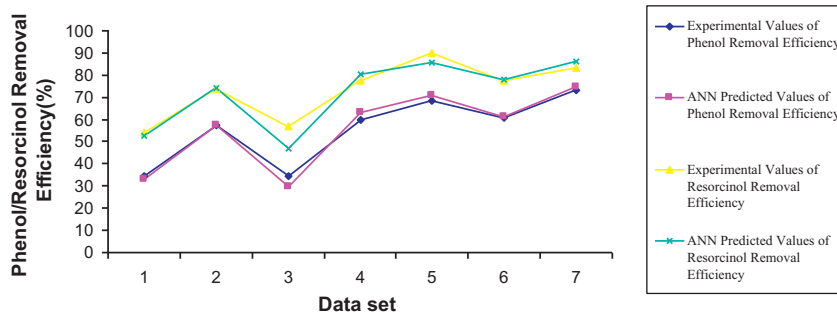
Sl. no.	Phenol removal efficiency (%)		Resorcinol removal efficiency (%)		Error (%)	
	Experimental values	ANN predicted values	Experimental values	ANN predicted values	Phenol	Resorcinol
1	11.6	11.7	36.4	33.9	-0.1	2.5
2	30.8	34.0	63.1	66.2	-3.2	-3.1
3	23.4	22.5	37.5	33.8	0.9	3.7
4	36.6	38.7	67.9	73.4	-2.1	-5.5
5	67.2	67.2	82.6	82.6	0	0
6	60.9	60.9	74.0	73.6	0	0.4
7	65.9	72.0	69.4	77.0	-6.1	-7.6



**Fig. 2.** ANN Model 'B' training for prediction of phenol and resorcinol removal efficiency.



**Fig. 3.** ANN Model 'C' training for prediction of phenol and resorcinol removal efficiency.



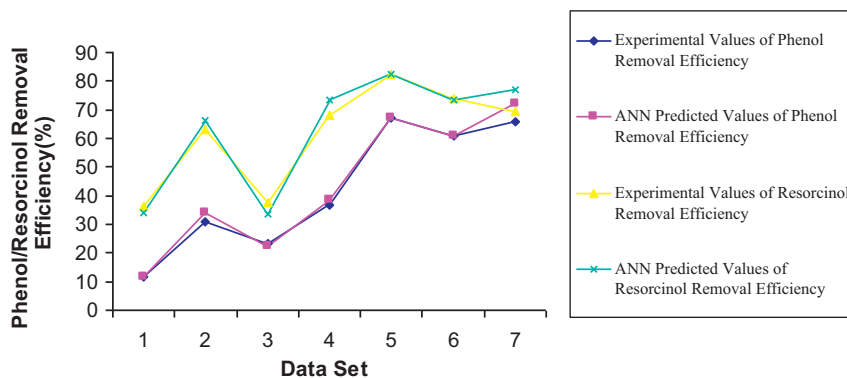
**Fig. 4.** Simulation results for Model 'A'.

**Table 9**  
Comparison of ANN Model 'C' output and experimental values for test data.

Sl. no.	Phenol removal efficiency (%)		Resorcinol removal efficiency (%)		Error (%)	
	Experimental values	ANN predicted values	Experimental values	ANN predicted values	Phenol	Resorcinol
1	21.0	22.4	47.4	46.4	-1.4	1.0
2	45.4	48.3	67.4	69.7	-2.9	-2.3
3	21.0	21.1	45.7	45.1	-0.1	0.6
4	48.8	59.7	70.1	77	-10.9	-6.9
5	71.0	70.0	85.7	84.0	1.0	1.7
6	67.7	67.5	75.5	75.9	0.2	-0.4
7	72.7	58.5	72.8	74.6	14.2	-1.8

**Table 10**  
Comparison of performance statistics of neural network models.

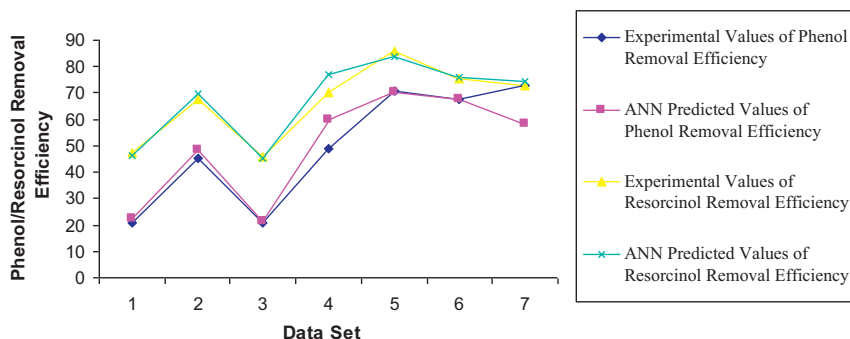
Pollutant removal efficiency model		ME	MSE	RMSE	Coefficient of determination	Slope	Y-axis intercept
Model 'A'	Phenol	0.08	6.0	2.4	0.96	0.98	0.01
	Resorcinol	1.4	20.5	4.5	0.95	1.0	0.00
Model 'B'	Phenol	1.5	7.5	2.7	0.93	0.89	0.06
	Resorcinol	1.3	16.2	4.0	0.97	0.98	0.01
Model 'C'	Phenol	0.01	47.4	6.8	0.95	0.90	0.05
	Resorcinol	-1.1	8.6	2.9	0.96	0.98	0.01



**Fig. 5.** Simulation results for Model 'B'.

equilibrium time. Initially, a large number of vacant sites are available for adsorption for which the rate of adsorption is very fast that increases the amount of phenol and resorcinol adsorbed on the surface of carbon within the first stage of 4 h of adsorption. In this study, marginal decrease in phenol removal was observed where as the resorcinol removal enhanced slightly. The percentage removal of phenol for AC, WC and RHA was found as 67, 44 and 60%, respectively. The percentage removal of resorcinol for AC, WC and RHA was found 82, 72 and 79%, respectively.

The adsorption of phenol and resorcinol on AC, WC and RHA were also carried out at different adsorbent dose (10–100 g/L) by keeping other parameters constant. The percentage removal of phenol and resorcinol increased with an increase in the adsorbent dose while loading capacity (amount of phenol and resorcinol loaded per unit weight of adsorbent) gradually decreased for the same. The increase in loading capacity is due to the availability of higher number of solutes (phenol/resorcinol) per unit mass of adsorbent. These experiments were carried out with initial con-



**Fig. 6.** Simulation results for Model 'C'.



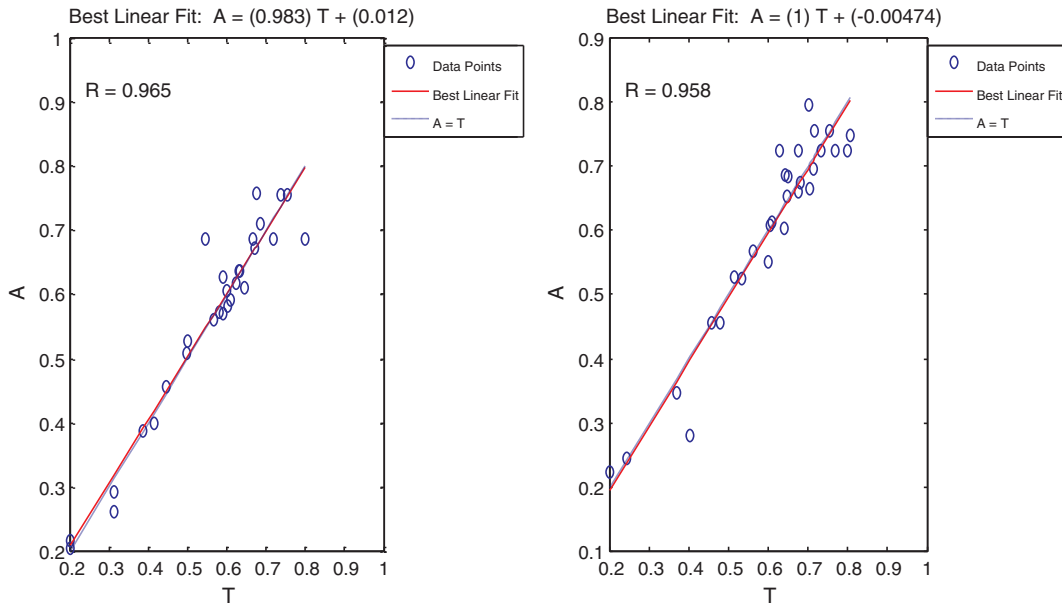


Fig. 7. Regression analysis for AC and Phenol-Resorcinol System. (Note: A = simulated values, T = experimental values.)

centrations of phenol and resorcinol, 10 mg/L of solutes and neutral pH of the solution. It has been found that phenol/resorcinol binding with adsorbent increases more rapidly in the initial stages and after some point, the adsorption is marginal which becomes almost constant.

The pH of adsorption medium is one of the most important factors affecting the adsorption process. Effect of initial pH on adsorption of phenol and resorcinol was studied with an initial concentration of 10 mg/L and optimum dose of 60 g/L. In the alkaline range, the pH was varied using 1 N NaOH, whereas in the acidic range, pH was varied using 1 N HCl. The experiments for the uptake of phenol and resorcinol on AC, WC and RHA were carried out in the pH range of 3, 4, 7, 8 and 9.2. It has been found that the relative amount of phenol and resorcinol adsorbed was significantly affected by pH. The maximum adsorption of phenol and resorcinol occurs at neutral pH. Significant decline in removal efficiency

of phenol and resorcinol was observed for further increase in pH, which may be due to formation of phenolate anions.

The phenol and resorcinol removal percentage was found to decrease with increase in initial concentration of phenol and resorcinol from 10 mg/L to 100 mg/L at same equilibrium condition. The amount of phenol and resorcinol adsorbed per unit AC mass increases with the increase in initial phenol and resorcinol concentration due to the decrease of uptake resistance of solute from solution of phenol and resorcinol. At initial concentration of 10 mg/L for phenol and resorcinol, the percentage phenol uptake for AC, WC and RHA was found as 71, 69 and 75%, respectively, and resorcinol uptake by AC, WC and RHA was found as 90, 85 and 87%, respectively. At the maximum initial concentration of 100 mg/L, the percentage uptake of phenol adsorbed by AC, WC and RHA was found as 60, 55, and 62% and resorcinol adsorbed by AC, WC and RHA was found as 73, 67 and 70%, respectively.

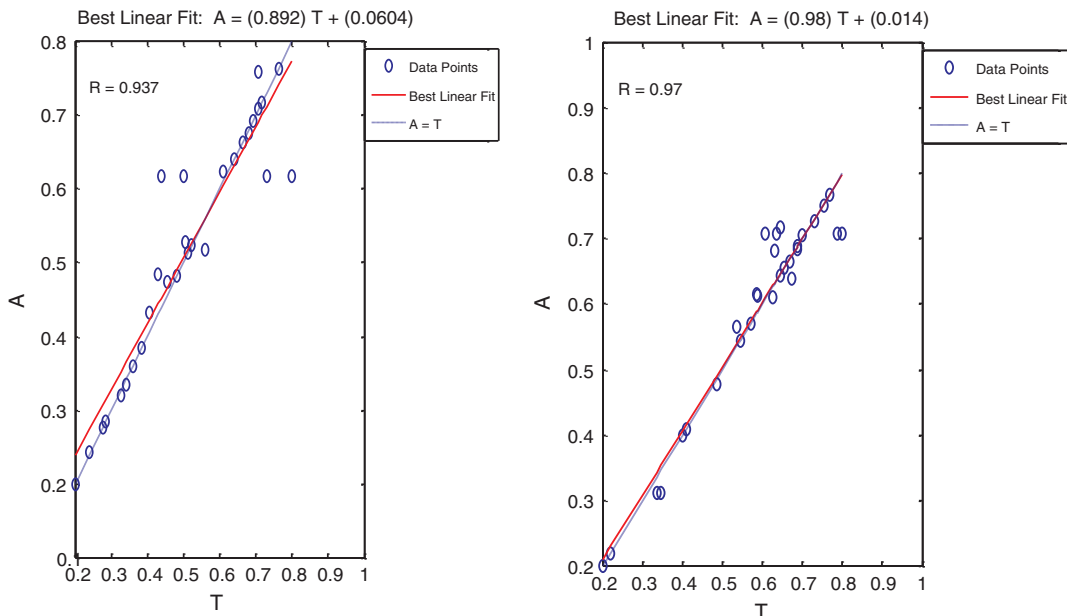


Fig. 8. Regression analysis for WC and Phenol-Resorcinol System. (Note: A = simulated values, T = experimental values.)

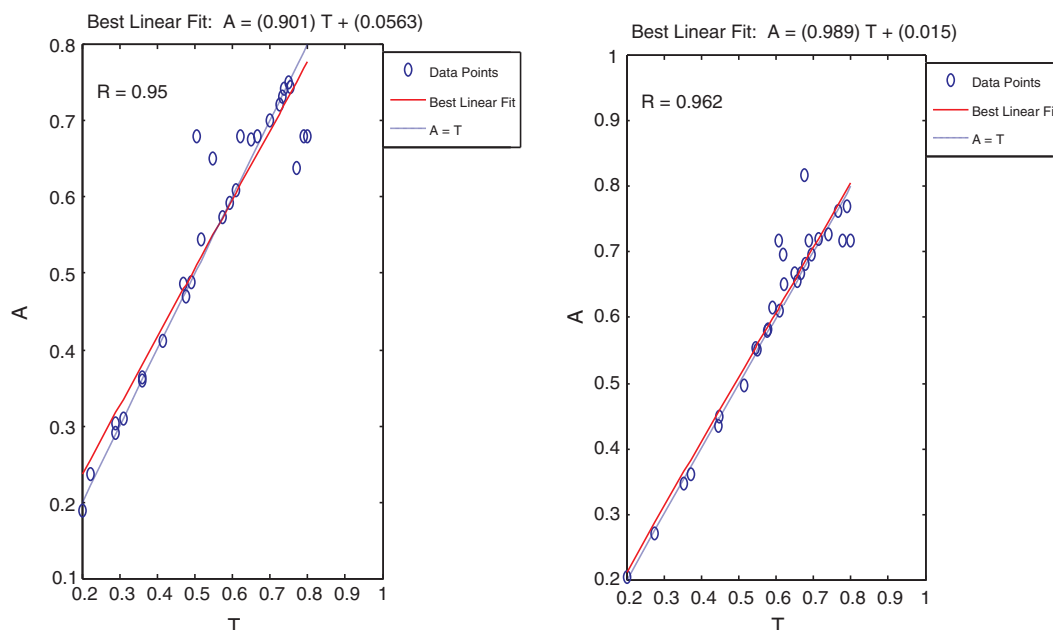


Fig. 9. Regression analysis for RHA and Phenol-Resorcinol System. (Note: A = simulated values, T = experimental values.)

#### 4. Conclusion

Batch study results showed that the equilibrium time was achieved after a contact period of 4.0 h at a buffer pH of 7 corresponding to initial phenol and resorcinol concentrations of 10 mg/L each. At equilibrium time, phenol and resorcinol removal efficiencies were found to be 79 and 88%, respectively, for AC. In case of WC under identical conditions, removal efficiencies were observed as 77 and 86% while for RHA, it was 76 and 85%. The above results exhibited initial concentrations of 10 mg/L of both phenol and resorcinol in solution. The differences in adsorbing capacity of various adsorbents were very marginal (within 5%). Hence, RHA can be used as a low cost carbonaceous adsorbing material for removal of phenol-resorcinol from bi-solute water environment up to a concentration of 10 mg/L. The experimental data derived from batch kinetic studies was subsequently utilized in prediction of pollutant removal efficiencies for competitive adsorption of phenol and resorcinol in the water environment as a bi-solute pollutant using ANN technique. With the experimental data of batch adsorption study of phenol and resorcinol mix (1:1) using AC, WC and RHA, three feed-forward networks with a backpropagation learning algorithm were developed to facilitate the modeling approach. Based on experimental results, the error of ANN model output (Tables 7–9) was well within 10%. Table 10 also demonstrated that the co-efficient of determination ( $R$ ) above 0.95 and slope ( $m$ ) approaching 1 with  $Y$  intercept value closer to zero. The three ANN models were successfully trained and tested which could forecast pollutant removal efficiency in bi-solute mix of phenol and resorcinol reasonably. The study also indicated that the ANN technique has a great potential in prediction of pollutant removal efficiency in competitive adsorption process.

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