# Original Article

### Prediction of the Experimental Data for Removal of Organic Pesticides by Carbon Nanoparticle Synthesized from Pomegranate Peel using Artificial Neural Networks

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(Received: 19 Jan. 2017; Revised: 2 Jul. 2017; Accepted: 24 Oct. 2017)

#### Abstract

*Background and purpose:* The present study is aimed to investigate the prediction of the experimental data for the removal of agricultural pesticides including three herbicides Trifluralin, Glyphosate, and 2,4-Dichlorophenoxyacetic acid from aqueous solution by carbon nanoparticles synthesized from pomegranate peel using artificial neural network.

*Materials and Methods:* Removal studies were conducted under the different experimental conditions in pH = 4-8, contact time of 0-25 minutes, and the initial concentrations in the range of 50-250 mg/L. In the present study, artificial neural network, back propagation algorithm, and Levenberg Marquardt training approach were used.

*Results:* The results showed that the removal of agricultural pesticides Trifluralin, Glyphosate and 2,4D depended on pH such that the optimal removal efficiency observed for pesticides Trifluralin, Glyphosate, and 2,4D in pH=8 was 92.6, 78, and 92%, respectively. The optimal adsorbent weight was also found to be 0.5 g for pesticides Trifluralin, Glyphosate, and 2,4D so that the removal efficiency was equal to 97, 98.8 and 98.4% within 20 minutes. In the initial concentration of 50 mg/L, the removal efficiency was respectively equal to 88, 94, and 92% for Trifluralin, Glyphosate, and 2,4D. The results also showed that the experimental data followed from both isotherm models.

**Conclusions:** The artificial neural network successfully predicts the data, and there is a good agreement between experimental and predicted data.

**Keywords:** Removal Efficiency; Artificial Neural Networks; Isotherm Models *Citation*: **Yousefi F**<sup>\*</sup>. Prediction of the Experimental Data for Removal of Organic Pesticides by Carbon Nanoparticle Synthesized from Pomegranate Peel using Artificial Neural Networks 2018; 6 (1):43-57

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## 1. Introduction

of Contamination water with toxic agricultural pesticides is becoming a severe environmental and public health problem (1-2). To avoid the contamination of environment by these wastewaters and remove these contaminants, providing a suitable strategy could be of great importance in maintaining a healthy environment. In order achieve to environmental detoxification. various techniques like adsorption, precipitation, ion exchange, reverse osmosis, oxidation, and biosorption processes with removal efficiency of 43%, 55.3%, 68.4% 70.26% ,76.57 % and 84%, respectively, are extensively applied (3-5). Among these, adsorption is a conventional but efficient technique to remove toxic metal ions from water. Development of novel and costeffective nanomaterials for environmental remediation, pollution detection and other applications has attracted considerable attention. Recent advances suggest that many of the issues involving water quality could be resolved using nanoparticles, nanofiltration, or other products resulting from the development of nanotechnology (6-7). Many studies have been done in this field using artificial neural networks and nanoparticles. Pirsaheb et al. (8) studied batch removal of diazinon and 2,4dichlorophenoxyacetic acid (2,4-D) from aqueous solution by granular-activated carbon. The required concentrations of toxins were prepared by appropriate dilution of the stock standard solution. The obtained results showed a significant relationship between chemical oxygen demand (COD) and toxins concentration, and that COD was measured instead of direct analysis of toxins. For all the investigated concentrations, removal

Iran J Health Sci 2018; 6(1): 44

efficiency increased by increasing the contact time for both toxins. The highest removal efficiency was 90% for 2,4-D and 88% for diazinon obtained in 50-min contact time. Also, the highest value of toxin removal for both toxins occurred at pH=6.

Simkovic studied the application of iron nanoparticles to remove selected specific synthetic substances including ghexachlorobutadiene,

pentachlorobenzene, hexachlorobenzene, lindane, and heptachlor (9). Experimental measurements were performed in order to evaluate the effectiveness of the removal of substances and their specific removal rate. Evaluation of the results showed that nanoiron oxide was a convenient reactant for the removal of heptachlor, lindane, and hexachlorobenzene; while for pentachlorbenzene and hexachlorobutadiene removal, longer contact times were necessary to obtain significant removal efficiencies. The results of Amouei study showed that any increase in pH level, contact time, and adsorbent dose caused increasing efficiency of removal cadmium from aqueous solutions. The results were modeled using biosorption kinetics and a neural network with four hidden neurons, including bias which was able to predict the concentration dependency of data very accurately. Based on the results, it could be said that sunflower residues act as a cost-effective and efficient biosorbent for the treatment of wastewater with Cadmium. The prediction of the Artificial Neural Network Model also fit the experimental data very precisely. In the present study, removal of organic pesticides by carbon nanoparticle synthesized from pomegranate peel and prediction of the data using artificial neural

networks have been investigated. Since organic pomegranate peel contains compounds, such 4.6as gallagylglucosellagitannins (Ets), Gallic acid, polyphenols, and so on, it can be used to produce activated carbon with an average pore diameter and high volume that has the ability to adsorb organic contaminants effectively. It should also be noted that providing easy access to vast resources of pomegranate can facilitate the production of activated carbon from pomegranate peel with low cost.

# 2. Materials and Methods

# 2.1 Artificial neural network modeling

Neural network consists of a network of simple processing elements (neurons) which can declare a predetermined overall complex behavior of the relationships between processing elements and element parameters. The main and the most inspiring source for this technique derives from the conducted experiment on central nervous system and neurons (axons, dendrite and synapse) which is one of the most significant components of Neural Information Processing Systems (NIPS) (12). The third phase refers to testing neural networks using previous data not used in the training of network (12). In the present study, a two-layer neural network consisting of a hidden layer of neurons in different output layers in addition to a threelayer neural network consisting of two hidden layers of neurons in different and output layers were used. Training data were given to the network in training algorithms and the network repeatedly updated the weights and orientations in order to conform the predicted values to the desired values. Back Propagation Levenberg-Marquardt learning algorithm (BP-LM) was also employed in the current study. At the same time, pH, initial concentration, time and adsorbent weight were considered as input, and removal efficiency as output for the neural network in this research (Figure1).



Figure1. The schematic of the used multilayer perceptron neural network.

Mean Square Error (MSE) in addition to Coefficient of Determination  $(R^2)$  were used to evaluate the obtained results (12):

$$MSE = \frac{1}{N} \sum_{i=1}^{N} (E_i^{Exp} - E_i^{ANN})^2$$
(1)

 $R^2$ 

$$=\frac{\sum_{i=1}^{N}(E_{i}^{Exp}-\bar{E})^{2}-\sum_{i=1}^{N}(E_{i}^{Exp}-E_{i}^{ANN})^{2}}{(E_{i}^{Exp}-\bar{E})^{2}}$$
(2)

Where N is the number of experimental data,  $E_i^{Exp}$  is the experimental data dedicated to removal efficiency, and  $E_i^{ANN}$  is the removal efficiency predicted by neural network. Moreover,  $\overline{E}$  is the mean value of removal efficiency and  $\overline{E}$  is the mean value of error.

# 2.2 Synthesis of carbon nanoparticles adsorbent

First pomegranate peel was thoroughly washed with distilled water 10 times, and then was heated for 24 hours in an oven at  $80 \degree$  C. Finally, it was powdered and sieved

by a sieve with mesh number 50. Then, 100 g of raw material was put in the oven with a temperature of 650 °C for 3 hours and was cooled in a desiccator (13). The obtained carbon particles mass was 21.6 g. Afterward, the obtained carbon was sieved using a sieve with mesh number 150. Chemicals used in this study were Trifluralin, Glyphosate, and 2,4-Dichlorophenoxyacetic acid purchased from Iprochem Company Limited.

# 2.3 Adsorption experiments

Initially, 0.1 gr of carbon nanoparticles was added to a beaker containing 0.1 lit of trifluralin solution with the concentration of 50 mg in 0.1 liter of water. At the same time that the contents were stirred by the agitator, sampling was done in 0, 5, 10, 20, and 25 minutes intervals, and during sampling, 0.005 liter of sample was removed by pipette and centrifuged (to separate the adsorbent powder). Then, 0.001 liter of the sample was removed by pipette and the volume increased to 0.01 liter and COD of the residual pesticide was measured. The same experiment was repeated for pesticides glyphosate and 2,4D. The different adsorbent doses in the range of 0.1-0.5 gr were separately added to liter of wastewater containing 0.01 pesticides trifluralin, glyphosate, and 2,4D with the concentration of 50 mg/L. Sampling was done in 0, 5, 10, 20, 25 minutes intervals, and during the sampling, 0.005 liter of sample was removed by pipette and centrifuge (to separate the adsorbent powder). Then, 0.001 liter of the sample was removed by pipette and the volume increased to 0.01 liter and COD of the residual pesticide was measured. To investigate the effect of pH after pouring 0.2 g of adsorbent into 0.1 liter of wastewater containing 0.5 g of each pesticide, pH of the solution became constant in three different values of 4, 6, and 8, and sampling was done after 20 minutes. Later on, COD of the residual solution was measured. To investigate the effects of different initial concentrations on the presence of 0.2g of carbon nanoparticles synthesized from pomegranate peel, 0.1 liter of agricultural pesticides solutions each with concentration of 50, 150, 200, and 250 ppm adsorption obtained. Then, were experiments were performed on carbon nanoparticles, and the remaining COD in the solutions was measured.

To calculate the removal efficiency of each pesticide onto the nano-adsorbent as the equilibrium value (qe) in terms of mg / g and removal efficiency of these compounds (R%), equations (3) and (4) were respectively used (10).

$$q_e = (C_0 - C_t) \times \frac{v}{m}$$
(3)

$$\%R = \frac{C_0 - C_t}{C_0} \times 100$$
 (4)

Where  $C_0$  and  $C_t$  are the concentration of pesticide in initial solution and after exposure to nano-adsorbent in terms of mg /L, respectively. V is the volume of initial solution in liters and m is the mass of adsorbent added to the beakers in g. The concentration of pesticide at different time intervals was also determined by measuring the absorbance at 272 nm using a UV–Vis spectrophotometer.

# 2.4. Adsorption isotherms2.4.1 Langmuir model

In this model, adsorption occurs uniformly on the active sites of the adsorbent, and once the active sites are occupied by adsorbates, the adsorption is naturally terminated at this site. The non-linear Langmuir equation is (14):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{5}$$

where  $K_L$  is the equilibrium constant (L mg-1), q max is the maximum adsorption capacity (mg g-1) of adsorbent, C is the equilibrium concentration (mg L-1), and q is the amount of metals adsorbed at equilibrium (mg g-1).

The linear Langmuir model is given by the following equation:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} \cdot \frac{1}{C_e} \tag{6}$$

where  $q_m$  and b are the saturated monolayer adsorption capacity and the adsorption equilibrium constant. A plot of C<sub>e</sub>/qe versus C<sub>e</sub> would then result in a straight line. From the slope and intercept, the maximum adsorption capacity and bond energy of adsorbates can be calculated.

# 2.4.2 Freundlich isotherm

The Freundlich equation is an empirical model allowing for multilayer adsorption on sorbent. The non-linear form of Freundlich Model is [14]:

$$q_e = K_F C_e^n \tag{7}$$

The linear form of Freundlich Model can be expressed as:

$$ln(q_e) = ln(K_F) + \left(\frac{1}{n}\right) lnCe$$
(8)

 $q_e$  is loading of adsorbate on adsorbent at equilibrium (mg g-1); K<sub>F</sub> is indicator of sorption capacity (mg1-n Ln g-1), n is adsorption energetics and C<sub>e</sub> is aqueous concentration of adsorbate at equilibrium (mg L-1).

# 3. Results and Discussion3.1 Scanning electron microscopy of carbon nanoparticles

To study the successful synthesis, SEM images of carbon nanoparticles synthesized from pomegranate peel were taken. Figure 2 (a, b) represents the SEM images of nanoparticles. As seen in the Figure, the adsorbents have high adsorption capacity due to the porosity. After the adsorption, pores are filled by adsorbate. The synthesized nanoparticles provide high specific surface area, more capacity, and faster uptake kinetics. As Figure 2 shows, nanoparticles have an average size of approximately 30-50 nm. Particle size distribution is equal and homogeneous, and shows the good synthesis of nanoparticles with the same size.





Figure 2 (a, b). SEM images of carbon nanoparticles synthesized from pomegranate peel

### **3.2 Effect of adsorbent dosage**

Initially, 0.1-0.5 gr of adsorbent of carbon nanoparticles synthesized from pomegranate peel was separately added to 0.1 lit of the solution containing Trifluralin, Glyphosate and 2,4D with a concentration of 500 mg/land. The sampling was done in 0, 5, 10, 20, 25 minutes intervals, and during the sampling, 0.005 lit of sample was removed by pipette and centrifuged (to separate the adsorbent powder). Then, 0.001 lit of the sample was removed by pipette, and the volume increased to 0.01 lit, and COD of the residual pesticide was measured. As shown in Tables 1 and 2, the optimal time is 20 minutes, and optimal adsorbent weight is 0.5 g, so that the highest adsorption for glyphosate is 99.2 percent. In general, using an adsorbent to adsorb organic pesticides is explained by

electrostatic and van der Waals interactions .Electrostatic interaction is related to the surface charges created on the adsorbent surface, while van der Waals interaction is related to the coordination of the functional groups with the contaminants.

Saifuddin et al. (15) studied to prepare silver nanoparticles embedded in chitosan, which is a non-toxic and biodegradable polymer. using microwave natural irradiation for the removal of pesticides from water. A sharp increase in percent reduction of the pesticide content was observed in water as the adsorbent dose was increased from 0.5 to 2.0 g. At 2.0 g dosage of cross-linked chitosan-silver nanoparticle composite micro-beads, 98% removal was also observed for 1 L of pesticide solution at 1 ppm concentration (1 mg/lit).

1		
0.3 g adsorbent		
Trifluralin		
IIIIuiaiiii		
20.4		
83		
87.6		
98.4		
98.6		
h		

**Table 1.** Adsorption versus time for pesticides Glyphosate, 2,4D and Trifluralin for 0.1, 0.2 and 0.3 gof adsorbent

 Table 2. Adsorption versus time for pesticides Glyphosate, 2,4D and Trifluralin for 0.4 and 0.5 g of adsorbent

0.4 g adsorbent				0.5 g adsorbent		
Time(min)	Glyphosate	2,4- Dichloroph enoxyacetic acid	Trifluralin	Glyphosate	2,4- Dichloroph enoxyacetic acid	Trifluralin
0	23	33.6	25.8	26.6	37.8	29.4
5	81.2	88.6	86.4	85.8	89	90.4
10	90.8	93	89.6	93.2	94.4	91.8
20	97.2	98	98.6	98.2	97.2	96.4
25	99	98.4	98.6	99.2	98.6	99

# 3.3 Effect of pH

Solution pH plays an important role in the process of adsorption and especially in the adsorption capacity. In this study, optimization was performed on the solution containing the pesticides with the concentration of 500 mg/l. Solutions pesticides with containing the concentration of 500 mg/l which were into contact with 0.2 g of carbon nanoparticles adsorbent were stirred on a shaker with 200 rpm for 20 minutes. Then, the solution containing the adsorbent was filtered by paper, and the concentration of residual pesticides was determined by COD device. Finally, the removal efficiency of the

value, according to Figure 3, for the removal of 92, 80 and 92% of pesticides trifluralin, glyphosate and 2,4D by carbon nanoparticles adsorbent was considered to be 8, 6, and 8, respectively. As is seen in Figure 3, the removal property depends on the number of hydroxyl groups on the surface of nanoparticles, and adsorption property depends on the physicochemical characteristics of macromolecules and the composition of dissolved ions. Bv increasing the pH value of hydroxyl functional groups, the surface is negatively charged and attracts positive ions, and as a result, the removal efficiency is increased.

pesticides was calculated. The optimal pH

 $pH_{pzc}$  of adsorbent depends on many variables, such as aging, doping of impurities, nature of crystallinity, temperature, degree of hydration, and synthetic processes (16). At different pH

values, these functional groups may be dissociated as their dissociation remains constants, and therefore, the groups could take part in the surface complexation (17).



**Figure 3.** Adsorption percent versus pH for triflouralin, glyphosate, and 2,4D (0.2 g of adsorbent, initial concentration of pesticides 500 ppm and adsorption time 20 minutes)

Table 3 shows the adsorption power of agricultural pesticides onto the carbon nanoparticles in various concentrations. The amount of adsorption is reduced with increasing the initial concentration of pesticides. As the number of active sites of adsorption on the adsorbent surface

decreases, adsorption capacity in higher concentrations is filled. Adsorption of pesticides in quantities of less than 100 ppm is relatively good. At the same time, with increasing concentration, pesticide residues concentration in the solution will slightly increase.

Pesticide	COD level in 50 ppm	COD level in 150 ppm	COD level in 200 ppm	COD level in 250 ppm		
Trifluralin	6	11	25	36		
Glyphosate	3	5	9	13		
2,4D	4	6	14	19		

**Table 3.** Effect of initial concentration of pesticides on the adsorption rate (adsorbent weight 0.2 g,<br/>adsorption time 30 minutes)

In Tables 4 -6, values obtained from the isotherm equations and their constants are shown. As can be seen, the experimental

data agree well with the data of Langmuir and Freundlich Models.

	qe(Langmuir)	q <sub>e</sub> (Freundlich)	qe(Experimental)	Ce	Co
1	27.06	27.06	21.5	6	50
	46.98	45.19	69.5	11	150
	87.83	87.88	87.5	25	200
	111.03	118.08	107	39	250

Table 4. The Langmuir and Freundlich isotherms for trifluralin

**Table 5.** The Langmuir and Freundlich isotherms for glyphosate

qe(Langmuir)	q <sub>e</sub> (Freundlich)	q <sub>e</sub> (Experimental)	Ce	C <sub>0</sub>
28.3	28.48	23.5	3	50
45.45	50.05	72.5	5	150
76.27	91.73	95.5	9	200
103.17	134.125	118.5	13	250

Table 6.The Langmuir and Freundlich isotherms for 2,4D

qe(Langmuir)	q <sub>e</sub> (Freundlich)	qe(Experimental)	Ce	Co
31.17	32.41	23	4	50
45.73	47.26	72	6	150
81.01	83.051	94.5	14	200
125.98	138.06	115.5	19	250



Figure 4. The desired number of inputs and outputs used in the removal of pesticides

In the present study, feed-forward neural network with two layers and post-propagation training algorithm of Levenberg-Marquardt (BP-LM) was used for modeling. Parameters including pH, initial concentration, adsorbent weight, and time were considered as input parameters and removal efficiency as the output. One of the parameters that requires sensitivity test in neural networks is the number of neurons in the hidden layer. For this purpose, the number of neurons in hidden layer was examined using trial and error. As it is clear from the figure, the network with 10 neurons in the hidden layer has the best performance (Figure 4). In addition, more than 10 neurons for the model are not evaluated because the increase in the number of neurons of the model increases the runtime, as well as the likelihood of error in the model. Of course, better results can sometimes be achieved by increasing the number of neurons.

In some cases, however, the accuracy is close to the number of neurons 10 but has a non-normal distribution of error. As is seen in Figure 5, the correlation coefficient obtained for removal efficiency is 0.9871, and all obtained data are around the diameter line. Correlation coefficient is one of the important prediction factors that is much closer to 1, and the prediction will be more successful. We can clearly see that the experimental data and the predicted data are very close to each other, which shows the successful prediction by the network with 10 neurons.



Figure 5. The obtained correlation coefficients for the removal efficiency data of pesticides

In Figure 5, the error difference between the experimental data and the data predicted by the neural network is illustrated on the x-axis and y-axis. The number of samples dedicated to training, validation, testing, and all data (blue, green and red) are also shown in Figure 6. The highest and lowest difference for the data of removal efficiency was 0.99 and 0.75. As is seen in the figure, the training data is close to the line Zero Error, and this shows that the data

dedicated to the testing and validation has been successfully predicted. Of the 12 successive repetitions for removal efficiency data, the best result is obtained by 6 repetitions. As can be observed in Figure 6, the validation data, which is shown by green color, is on the best line (Zero Error) and by increasing the number of repetitions, data becomes away from this line, and good result is not achieved.



Figure 6. The results obtained from the error difference between the predicted values and the experimental data for removal efficiency of pesticides



Figure 7. The results of mean square error for removal efficiency data of pesticides

Figure 7 shows the mean square error for removal efficiency data of pesticides. As illustrated in the figure, the desired level is 0.0019122. Also, Table (7) shows the values obtained for the mean square error.

As is observed there, the best result is obtained by 10 neurons with 2 layers, and the smaller mean square error leads to more successful prediction.

Number of	Number of neurons in each	MSE
hidden layers	hidden layer	
1	2	2.10e-05
1	4	4.0432e-003
1	6	1.7436e-04
1	8	3.562e003
1	10	4.527e-004
2	2	5.896e-04
2	4	3.6754e-03
2	6	2.254e-05
2	8	3.5161e04
2	10	1e0.0028182

Table 7.	The results	obtained for	or the mean so	quare error

### 4. Conclusion

Adsorption experiments were performed on pesticides trifluralin, glyphosate, and 2,4D, and the effects of parameters, such as adsorption time, initial concentration of pesticides, different weights of nanoadsorbent, and pH of solution on removal of pesticides were measured. In general, the following conclusions were obtained:

The optimum pH for the removal of pesticides trifluralin, glyphosate, and 2,4D by carbon nanoparticles adsorbent synthesized from the pomegranate peel with 500 mg/l of each pesticides and

adsorption time of 20 minutes was respectively 8, 6, and 8. The more adsorbent dose in solution results in an increase in the removal efficiency because of the increase in the adsorption active sites on the adsorbent surface.

Adsorption isotherms equations are very important in the design of an adsorption system. There are several equations. In the present study, the experimental data obtained with initial concentrations of 50-250 mg/l and temperature of 25°C under the optimal conditions was investigated using Langmuir and Froundlich isotherms.

The removal efficiency decreased with an increase in the initial concentration of pesticides. The optimal removal efficiency of pesticides triflourine, 2,4D and glyphosate was obtained at the initial concentrations of 50-250 mg/l, the adsorbent weight of 0.2 g and adsorption time of 30 minutes.

In order to demonstrate the adsorption equilibrium successfully, it is important to distribution have а satisfactory of adsorption rate in the state of equilibrium between the two phases as an equation. Langmuir Model assumes that the adsorption of adsorbate on the homogeneous surface occurs through adsorption in a single layer, without any interaction between the adsorbed species. It should be noted that there was observed a good agreement between the experimental data with the data obtained from Freundlich and Langmuir models. Because according to the calculations, the conclusion is that the adsorption has followed isotherm models of Langmuir and Freundlich.Chemical properties of adsorbate and adsorbent vary by changing the pH. The solution pH affects the degree of ionization of various contaminants, leading to changes in

reaction kinetics and equilibrium characteristics of the adsorption process.

In the modeling, the perceptron artificial neural network, back propagation algorithm and Levenberg– Marquardt method are used. For the investigation of prediction of the removal efficiency using perceptron artificial neural networks, removal data, pH, initial concentration, adsorbent weight and time were taken as input parameters, and removal efficiency was considered as output. The results of the study showed that in the case of using four input variables and the 10 neurons, the best results are achieved so that the correlation coefficient and root mean square error are very normal.

### Acknowledgments

The author would like to thank Nano Technology Institution, Islamic Azad University of Saveh, and also Mr. Aghayari whose helpful comments helped the author to improve the quality of this manuscript.

## **Conflict of Interest**

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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