Al-Khwarizmi Engineering Journal

Al-Khwarizmi Engineering Journal,Vol. 12, No. 3, P.P. 1- 9 (2016)

Modeling the removal of Cadmium Ions from Aqueous Solutions onto Olive Pips Using Neural Network Technique

Ayad A.H. Faisal* **Zahraa Saud Nassir****

*,** *Environmental Engineering Department / University of Baghdad*

*Email: ayadabedalhamzafaisal@yahoo.com

**Email: Zahraa_saud@yahoo.com

(Received 20 December 2015; accepted 17 April 2016)`

Abstract

The uptake of Cd(II) ions from simulated wastewater onto olive pips was modeled using artificial neural network (ANN) which consisted of three layers. Based on 112 batch experiments, the effect of contact time (10-240 min), initial pH (2-6), initial concentration (25-250 mg/l), biosorbent dosage (0.05-2 g/100 ml), agitation speed (0-250 rpm) and temperature (20-60ºC) were studied. The maximum uptake (=92 %) of Cd(II) was achieved at optimum parameters of 60 min, 6, 50 mg/l, 1 g/100 ml, 250 rpm and 25ºC respectively.

Tangent sigmoid and linear transfer functions of ANN for hidden and output layers respectively with 7 neurons were sufficient to present good predictions for cadmium removal efficiency with coefficient of correlation equal to 0.99798. The sensitivity analysis for outputs of ANN signified that the relative importance of initial pH equal to 38 % and it is the influential parameter in the treatment process, followed by initial concentration, agitation speed, biosorbent dosage, time and temperature.

Keywords: *Neural network, Adsorption, Olive pips, Modeling, Equilibrium.*

1. Introduction

One of the most widely and rapidly spreading problems in the field of conservation and protection of water resources is water pollution with heavy metals. It is closely associated with several human activities such as mining, the metal processing industry, petroleum industry, power industry and on a smaller scale by electroplating wastes, metal-based pigments and numerous other industrial wastes, besides the high exhaust emissions in urban regions from car engines, burning of hospital wastes and domestic solid waste, as well as wasteland-landfills [1]. There are several methods to treat the metal contaminated effluent, but the selection of the adequate method is based on the concentration of pollutant and the cost of treatment [2]. These methods include chemical precipitation, electroplating, ion exchange, and reverses osmosis which are expensive and inefficient especially for low metal concentration as cited by many studies [3-5].

Adsorption technique is considered a promising method and this can be attributed to its simplicity in design and operation, low cost, and insensitivity to toxic materials. Investigation the usage of low cost sorbents for treating large quantities of wastewater has become a substantial issue. In this concern, olive pips as an example for wastes generated from forestry activities and industrial agriculture acquired a great importance in the removing of metal ions [6].

Modeling of adsorption process is a topic of interest for the prediction of the metal partitioning between the aqueous solution and the solid surface, and its subsequent application to the design of adsorption treatment units [7]. Adsorption isotherm models such as Langmuir, Freundlich, Elovich, Temkin and others are used mostly for description the equilibrium relationship between the adsorbate concentration in the fluid phase and the adsorbate concentration in the adsorbent particles at a given temperature [8]. Hence, there is a need to use a more representative model that can identify the equilibrium/ non-equilibrium biosorption process for different values of temperature. Consequently, ANN technique has drawn great attention as an alternative approach in the determination of complex relationship between operating parameters.

ANN based predictive models are powerful in terms of learning the nonlinear relationships to understand and solve and thereby achieving ability to predict accurately [9]. So, the present study aimed to characterize the non-equilibrium/equilibrium non-isotherm cadmium removal from aqueous solutions onto olive pips using ANN model in comparison with batch experimental results for different operational conditions.

2. Description of ANN

The working basis of ANN is inspired from the biological neurons of natural network. Neuron, or node, is represented the principle core of this network. The neuron impulse or the output of a node is determined as weighted sum of the input signals from the proceeding neuron, altered by the transfer function. The learning capability of a neuron is accomplished by adjusting the weights in conformity to chosen learning algorithm. Basically, the topology of ANN is consisted of input, hidden and output layers and the number of neurons is depended on the number of input and output parameters. The significant step in the solution procedure using ANN is finding the number of neuron at a hidden layer and this can be achieved by trial and error [17].

3. Experimental Work

3.1. Materials

The olive pips were collected from the olive oil industry and the dirt particles were removed from these pips by washing with deionized water. They were then air-dried, ground in a mechanical grinder and sieved to obtain the desired size between 125-710 μm size particles.

The simulated water was contaminated with Cd(II) by dissolved $Cd(NO_3)_2$ (manufactured by BDH, England) and kept at temperature of the room (25ºC). The pH of the prepared solution was adjusted by using 0.1 M NaOH or 0.1 M HNO_3 as required and this stock solution was used to prepare any required concentration of Cd(II).

3.2. Batch Tests

The effect of contact time (t), initial pH, initial concentration (C_o) of Cd(II), olive pips dosage, agitation speed and temperature (T) on the performance of sorbent material was investigated based on batch biosorption tests. Adsorbent dosages varied from 0.05 to 2 g were introduced into 250 ml flasks with 100 ml solution containing 50 mg/l of metal ions. These flasks were agitated using an orbital shaker (Edmund Buhler SM25, German) with t equal to 60 min and agitation speed of 250 rpm. Samples were withdrawn at specified time intervals ranged from 10 to 240 min and then passed through filter paper. Cd(II) concentrations in the samples were analyzed by atomic absorption spectrophotometer (AAS) (Shimadzu, Japan).

Tests were carried out in a pH range of 2-6 to determine the effect of initial pH on biosorption. While effects of operating temperatures ranged from 20 to 60 ºC were investigated. Removal efficiency (R) of Cd(II), which is represented the predicted value of ANN model, was calculated as follows:

$$R = \frac{(C_o - C_e)}{C_o} \times 100 \qquad \dots(1)$$

where C_e is the equilibrium concentration of cadmium remaining in the solution at the end of the test.

4. Results and Discussion

4.1. Developing and Optimization of the ANN Model

ANN model with Levenberg–Marquardt backpropagation (LMA) training algorithm for correlating the removal efficiency of cadmium ions from aqueous solution by biosorption method was developed. This algorithm was calculated using Matlab program version 7.10.0.499 (R2010a). The experimental data was divided into training, validation and test subsets with corresponding proportions of 60, 20 and 20% respectively. This step is very important in the development of optimized topology for ANN.

The training data is the biggest set and is used by neural network to learn pattern presented in the data by updating the network weights. The testing data is used to evaluate the quality of the network. The final check on the performance and generalization ability of the trained network is made using validation data. Transfer functions of tangent sigmoid (tansig) at hidden layer and linear (purelin) at output layer were applied in the present study. The input variables to the feed forward neural network were; biosorbent dosage, t, initial pH, Co, agitation speed and T. In addition, the removal efficiency was chosen as output variable.

Figure 1 illustrates best topology for ANN and the variation of parameters was calculated depended on the minimum mean square error (MSE) of the training and prediction sets. The solution procedure was beginning with two neurons in the hidden layer for optimization of the network. Table 1 illustrates the dependence between the neuron number and MSE for the LMA algorithm.

It seems from Table 1 that the MSE of the network was the highest (= 0.0015) for 2 hidden neurons and it is decreased significantly to minimum value of 0.000335 with 7 neurons. Hence, the 7 hidden neurons were adopted as the best case. When the neurons changed from 7 to 16, MSE was increased and this behavior can be attributed to the properties of performance index and the input parameters [9]. The training was stopped after 30 epochs for the LMA because the differences between training error and validation error started to increase.

Figure 2 presents the MSE for subsets described previously with LMA and the best regression was set in Figure 3. It can be seen that the correlation coefficient for training, validation, testing and all data was 0.99795, 0.99874, 0.99793 and 0.99798 respectively.

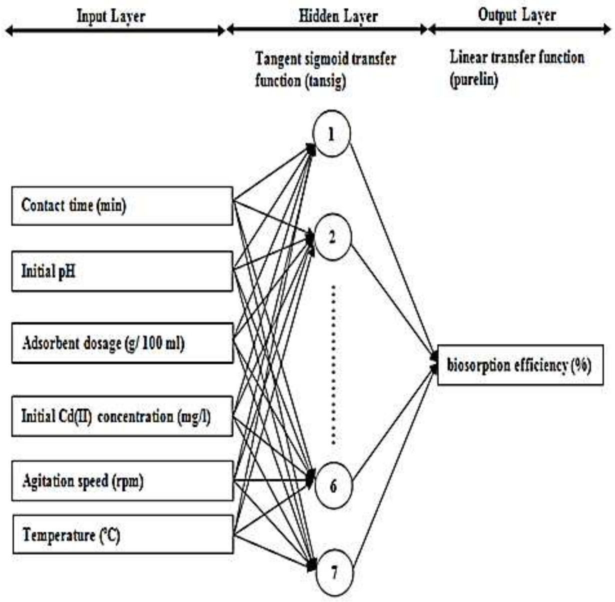

Fig. 1. The optimal architecture of ANN.

Table 1,
MSE values of the training set for Cd(II) on the olive pips.

No. of neurons	MSE ($\times 10^{-3}$)
2	1.500
3	0.963
4	0.838
5	0.972
6	0.552
7	0.335
8	0.711
9	0.560
10	0.840
11	0.678
12	0.431
13	0.453
14	0.349
15	0.452
16	0.788

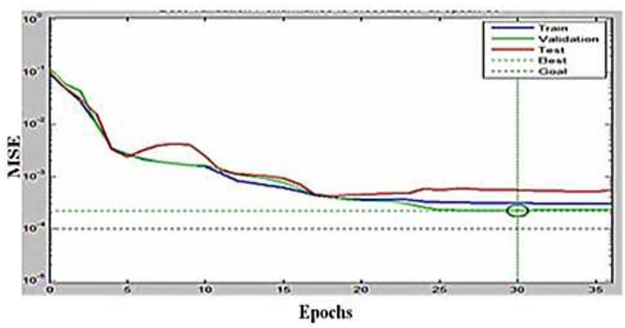

Fig. 2. MSE of training, validation and test for the LMA algorithm.

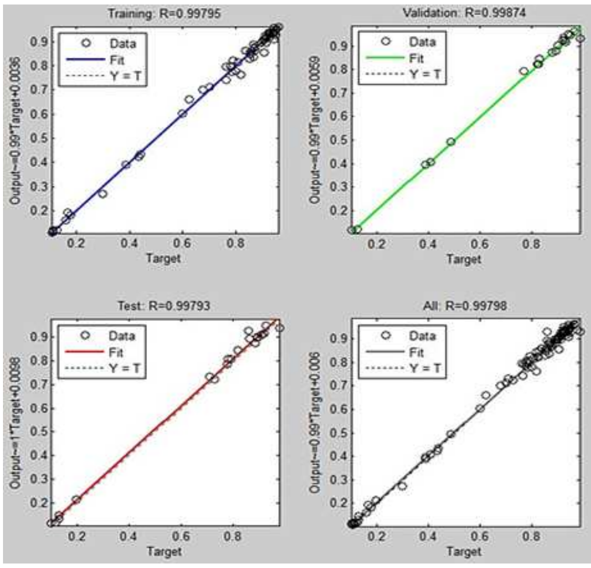

Fig. 3. Training, validation and testing regression for the LMA algorithm.

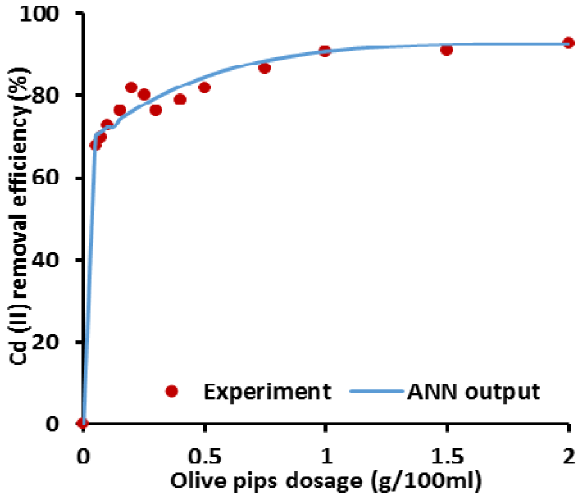

Fig. 4. Variation of ANN outputs and experimental results with biosorbent dosage (*t*= 60 min, initial pH= 6, C_o =50 mg/l, agitation speed = 250 rpm and *T* = 25 °C).

4.2. Biosorbent Dosage

One of the important parameters that strongly affect the sorption capacity is the biosorbent dosage. This effect was studied by adding different boisorbent dosages into 100 ml of solution contaminated with 50 mg/l of Cd(II) and pH of 6 as shown in the Figure 4. These tests were conducted with agitation speed of 250 rpm, *t* of 60 min and *T* of 25ºC.

This figure signified that the removal efficiency was changed from 70 to 92 % in response to the variation of olive pips dosage from 0.05 to 1 g/ 100 ml at conditions described previously. This can be resulted from the increasing of biosorption sites, i.e. surface area, prepared for contact with dissolved contaminant due to increase of biosorbent dosage [10]. Due to reaching the equilibrium sorption, additional increment in the biosorbent dosage do not cause any significant change in the removal efficiency and, so, 1 g/ 100 ml was considered the best choice for further experiments to investigate the influences of other parameters. Figure 4 states a good agreement between the predictions and experimental data with correlation coefficient of 0.994.

4.3. Contact time and initial pH of solution

The sorption uptake is varied rapidly in the first minutes and, then, remains approximately stabilized as a function of contact time until achieved the equilibrium state as illustrated in Figure 5. This can be explained on the basis of availability large number of binding sites for metal ions which are decreased with time. This decrease can be caused slowed down in the sorption uptake due to generation of repulsive forces [11].

In addition, results proved that the removal efficiencies of metal ions were approximately low at pH of 2 and this may be due to high concentration of H^+ ions which are competed with Cd(II) ions for binding sites. The higher values of pH means low concentrations of hydrogen ions and this reduces the competition between these ions and ions of pollutant, i.e. reduce of positive surface charge, resulting in the rapidly increment of removal efficiency from 11 to 92 % as pH changed from 2 to 5 [12]. The results showed that the efficiency was decreased in response to any further increase of pH and this may be due to generation of soluble hydroxyl complexes which are precipitated from the liquid phase making studies of true sorption impossible [13]. The experimental results signified that the equilibrium can be achieved at *t* of 60 min. Also, Figure 5 explains that obtained results from the proposed ANN model and experimental data are in good agreement with correlation coefficient not less than 0.985.

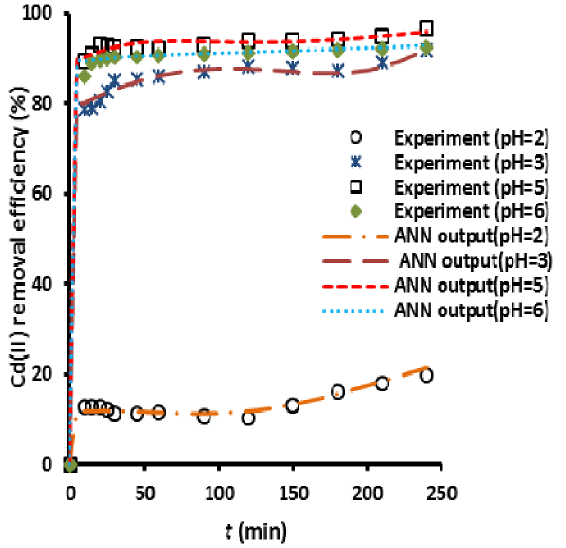

Fig. 5. Variation of ANN outputs and experimental results with *t* for different values of initial pH (dosage =1g/100 ml min, C_o =50 mg/l, agitation speed = 250 rpm and *T* = 25 °C).

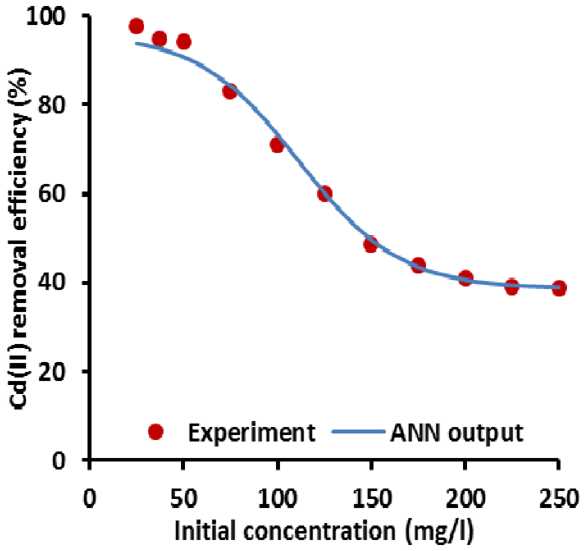

Fig. 6. Variation of ANN outputs and experimental results with C_o (dosage =1g/100 ml min, *t* =60 min, initial pH= 6, agitation speed = 250 rpm and *T* = 25 °C).

4.4. Initial concentration

Figure 6 shows that the removal efficiency of Cd(II) onto the olive pips decreased from higher values (≈ 97 %) to lower values (≈ 38 %) as a function of metal concentration. This trend is logical because of the lack of sufficient binding sites that are required for sorption much more Cd(II) ions present in the liquid phase. Conversely, the results explained that the removal efficiencies were higher with lower concentrations because all ions in aqueous phase can interact with the binding sites. As a result, the treatment yield can be increased by diluting the wastewaters containing high metal ion concentrations [14]. It is clear that there is a good agreement between outputs of ANN and experimental data with correlation coefficient of 0.997.

4.5. Agitation speed

Approximately 10 % of the Cd(II) was sorbed onto olive pips at agitation speed of zero and the uptake increases with the increase of agitation speed up to 250 rpm at which maximum contaminant removal can be achieved as illustrated in Figure 7. Increasing of agitation speed can be improved the diffusion of pollutants towards the biosorbent and the sufficient contact can be developed between the solutes and active sites [15]. Figure 7 shows that agitation with 150 rpm is sufficient and there is no substantial change in removal efficiency beyond this value. However, this figure stated that the ANN model presents a good prediction for the experimental data with correlation coefficient of 0.996.

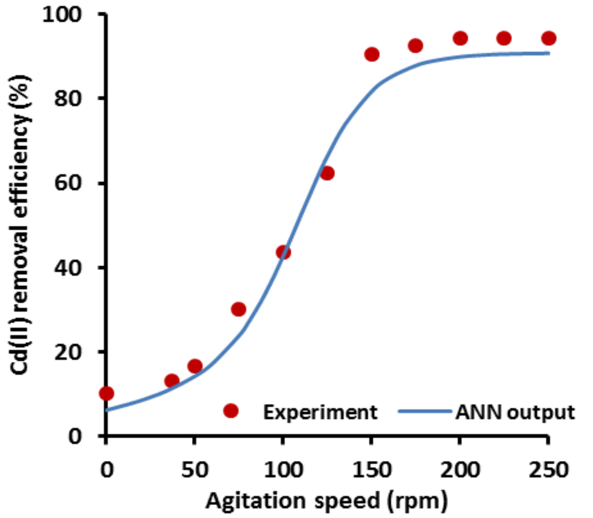

Fig. 7. Variation of ANN outputs and experimental results with agitation speed (dosage =1g/100 ml min, t =60 min, initial pH= 6, C_o= 50 mg/l and T = 25 °C).

4.6. Temperature

Table 2 signifies that the sorption uptake of Cd(II) ions onto olive pips was varied from 85 to 96 %, when the corresponding temperature was changed from 20 to 60 ºC. This may be due to increasing the diffusion rate of the contaminant ions across the external boundary layer and the internal pores of the sorbent particles. This shows that the adsorption process is an endothermic process [12]. However, optimization between the cost of heating energy and the achieved increase of biosorption efficiency at high temperatures, temperature with value of 25 ºC was very suitable for batch tests. The results of Table 2 signified that the predictions are approaching from the measured values with correlation coefficient 0.9.

Table 2,
Experimental and ANN output values of Cd(II) ions removal efficiency as a function of temperature (dosage = 1 g/100ml, t= 60 min, initial pH= 6, C_o= 50 mg/l, and agitation speed= 150 rpm).

Temp. (ºC)	Removal efficiency (%)	
	Exp.	ANN
20	85.84	87.54
25	92	90.77
30	94.3	92.5
40	95.12	92.47
50	95.52	94.62
60	96.3	95.75

4.7. Biosorption characteristics

The biosorption data (Figure 8) were also described by ANN model in the terms of equilibrium concentration (C_e) and the corresponding equilibrium sorption capacity (q_e). A good agreement can be recognized between the predicted and measured values with maximum sorption capacity equal to 10 mg/g.

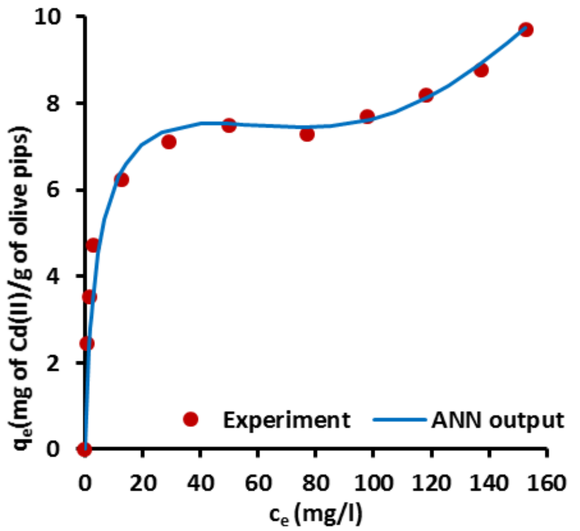

Fig. 8. Comparison of the experimental results with the q_e values obtained by ANN model.

4.8. Sensitivity analysis

The sensitivity analysis was aimed to calculate the relative importance of the input parameters based on the neural net weight matrix and Garson equation. Garson (1991) proposed an equation based on the partitioning of connection weights as follows (Faisal, 2015):

$$I_j = \frac{\sum_{m=1}^{m=Nh}\left(\left(\frac{|W^{ih}_{jm}|}{\sum_{k=1}^{Ni}|W^{ih}_{km}|}\right)\times|W^{ho}_{mn}|\right)}{\sum_{k=1}^{k=Ni}\left\{\sum_{m=1}^{m=Nh}\left(\frac{|W^{ih}_{km}|}{\sum_{k=1}^{Ni}|W^{ih}_{km}|}\right)\times|W^{ho}_{mn}|\right\}} \quad \text{...(2)}$$

where I_j is the relative importance of the j^{th} input parameter on the output parameter, Ni and Nh are the numbers of input and hidden neurons respectively, $W's$ are connection weights, the superscripts i, h and o refer to input, hidden and output layers, respectively, and subscripts k, m and n refer to input, hidden and output neurons, respectively.

The results proved that the most influential parameter is initial pH of aqueous phase with relative importance equal to 38% for biosorption process under consideration (Figure 9). This parameter is followed by C_o (17%), agitation speed (15%), dosage (14%), *t* (8 %), and the last rank is temperature with relative importance of (7%). However, the experimental ranges used for fitting ANN model, as proved by many researchers, are specified the influential variable and influence of each variable [16].

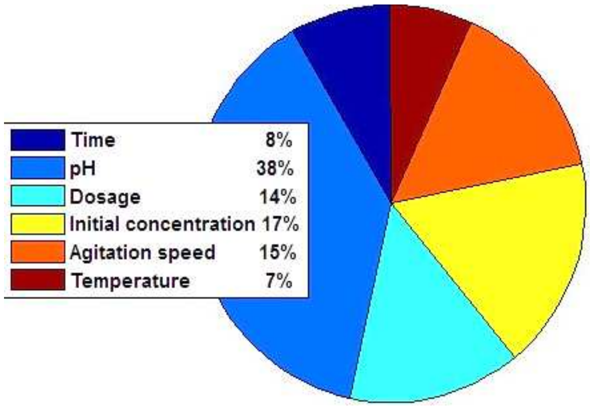

Fig. 9. Sensitivity analysis using artificial neural network.

5. Conclusions

Best operating parameters for biosorption of Cd(II) ions from simulated wastewater onto olive pips were specified depended on batch tests and these values are; *t* of 60 min, initial pH of 6, biosorbent dosage of 1 g/ 100 ml, C_o of 50 mg/l, agitation speed of 150 rpm and *T* of 25 ºC. The results proved that the achieved maximum uptake and biosorbent capacity of 92 % and 10 mg/g respectively.

The ANN of three layers with transfer functions consisted of tangent sigmoid at the hidden layer and linear at the output layer is very efficient in the description of Cd(II) biosorption process onto olive pips with coefficient of correlation equal to 0.99798 and MSE of 0.00033. Finally, the results of sensitivity showed that the initial pH of aqueous phase is the most influential parameter governed this process with relative importance of 38 %.

6. References

[1] M. A. Hashim, S. Mukhopadhyay, J. N. Sahu and B. Sengupta,"Remediation technologies for heavy metal contaminated groundwater". J. of Environmental Management, vol. 92, pp. 2355-2388, 2011.

[2] N. M. Hilal, I. A. Ahmed and R. E. El-Sayed," Activated and Nonactivated Date Pits Adsorbents for the Removal of Copper(II) and Cadmium(II) from Aqueous Solutions. International Scholarly Research Network ISRN Physical Chemistry, 2012.

[3] A. Dabrowski, Z. Hubicki, P. Podkoscielny and E. Robens," Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method", Chemosphere, vol. 56, pp. 91-106, 2004.

[4] E. S. Z. El-Ashtoukhy, N. K. Amin, and O. Abdelwahab," Removal of lead(II) and copper(II) from aqueous solution using pomegranate peel as a new adsorbent", Desalination, vol. 223, pp. 162-173, 2008.

[5] B. Volesky, and A. Leusch,"The influence of film diffusion on cadmium bio-sorption by marine biomass. J. Biotechnology", vol. 43, pp. 1-10, 1995.

[6] S. E. Samra, B. Jeragh, A. M. EL-Nokrashy and A. A. El-Asmy,"Biosorption of Pb2+ from Natural Water using Date Pits: A Green Chemistry Approach", Mod. Chem. Appl., vol. 2, no. 13, 2014.

[7] A. A. Faisal,"Modeling of Cd(II) removal from simulated wastewater by adsorption on eggshell using artificial neural network", Journal of the Association of Arab Universities for Basic and Applied Sciences, vol. 21, no. 2, pp. 1-20, 2015.

[8] O. Hamdaoui and E. Naffrechoux,"Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon", J. Hazard. Mater., vol. 147, pp. 381–394, 2007.

[9] K. Yetilmezsoy and S. Demirel,"Artificial neural network (ANN) approach for modeling of Pb(II) adsorption from aqueous solution by Antep pistachio (Pistacia Vera L.) shells", J. Hazard. Mater., vol. 153, pp. 1288–1300, 2008.

[10] B. M. W. P. K. Amarasinghe, R. A. Williams, "Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater", Chem. Eng. J., vol. 132, pp. 299–309, 2007.

[11] G. O. El-Sayed, H. A. Dessouki and S. S. Ibrahim,"Biosorption of Ni(II) and Cd(II) ions from aqueous solutions onto rice straw", Chem. Sci. J., vol. 9, 1–11, 2010.

[12] M. Alkan, B. Kalay, M. Doğan, Ő. Demirbaş,"Removal of copper ions from aqueous solutions by kaolinite and batch design", J. Hazard. Mater., vol. 153, pp. 867–876, 2008.

[13] C. Raji, G. N. Manju, T. S. Anirudhan, "Removal of heavy metal ions from water using sawdust-based activated carbon", Indian J. Eng. Mater., vol. 4, pp. 254-260, 1997.

[14] H. J. Rao, G. Kalyani, K. V. Rao, T. A. Kumar, K. Mariadas, Y. P. Kumar, P. Vijetha, P. Pallavi, B. Sumalatha and K. Kumaraswamy, "Kinetic studies on bio-sorption of lead from aqueous solutions using eggshell powder", International Journal of Biotechnology and Biochemistry, vol. 6, no. 6, pp. 957-968, 2010.

[15] J. Anwar, W. Zaman, U. Shafique, M. Salman, A. Dar and S. Anwar, "Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana", Bio-resource Technology, vol. 101, pp. 1752-1755, 2010.

[16] Y. Yang, X. Lin, B. Wei, Y. Zhao, and J. Wang, "Evaluation of adsorption potential of bamboo biochar for metal-complex dye: equilibrium, kinetics and artificial neural network modeling", Int. J. Environ. Sci. Technol., 2013.

[17] J. Kabuba and A. M. Bafubiandi, "Comparison of equilibrium study of binary system Co-Cu ions using adsorption isotherm models and neural network", International Conference on Mining, Mineral Processing and Metallurgical Engineering, Johannesburg (South Africa). April 15-16, 2013.

نمذجة ازالة ايونات الكادميوم من المحاليل المائيه على نوى الزيتون باستخدام تقنيه الشبكه العصبيه الاصطناعيه

اياد عبد الحمزه فيصل*   زهراء سعود ناصر**

**، ** قسم الهندسة البيئية / كلية الهندسة/ جامعة بغداد*

* البريد الالكتروني: ayadabedalhamzafaisal@yahoo.com

** البريد الالكتروني: Zahraa_saud@yahoo.com

الخلاصة

تم نمذجة امتزاز ايونات الكادميوم عللى نوى الزيتون بأستخدام الشبكه العصبيه الاصطناعيه المتكونه من ثلاث طبقات. اعتماداً على ١١٢ تجربة بطريقة الدفعة ، تم دراسة تأثير زمن التماس (١٠-٢٤٠) دقيقة، الدالة الحامضية للمحلول (٢-٦) ، التركيز الابتدائي (٥٠-٢٥٠) ملغم/ لتر، كمية المادة المازه (٠.٠١-١٥) غم/١٠٠مل ، سرعة الاهتزاز(٠-٢٥٠) دوره/ثانية و درجة الحرارة (٢٠-٦٠) سيليزية . تم الحصول على اعلى امتزاز للكادميوم (= ٩٢%) من خلال الظروف المثلى الاتية:٦٠ دقيقة،٥٠ملغم/لتر،١غم/١٠٠مل،٢٥٠ دورة/دقيقة،٢٥سيليزية.وقد وجد ان Tangent sigmoid ودوال التحويل الخطية للشبكه العصبيه الاصطناعية لكل من الطبقة المخفية والخارجية على التوالي مع ٧ عصبات كافية لايجاد توقعات جيدة لكفاءة ازالة الكادميوم مع معامل ارتباط يساوي ٠.٩٩٧٩٨ أظهر تحليل الحساسية أن الدالة الحامضية الابتدائية تمتلك التاثير الاكبر على عملية المعالجة وبنسبة تصل الى ٣٨% يليها التركيز الابتدائي ثم سرعة الاهتزاز ثم كمية الماده المازه ثم الوقت واخيرا درجة الحرارة.