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Artificial neural network (ANN) approach for modeling of Pb(II) adsorption from aqueous solution by Antep pistachio (*Pistacia Vera* L.) shells

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Abstract

A three-layer artificial neural network (ANN) model was developed to predict the efficiency of Pb(II) ions removal from aqueous solution by Antep pistachio (*Pistacia Vera* L.) shells based on 66 experimental sets obtained in a laboratory batch study. The effect of operational parameters such as adsorbent dosage, initial concentration of Pb(II) ions, initial pH, operating temperature, and contact time were studied to optimise the conditions for maximum removal of Pb(II) ions. On the basis of batch test results, optimal operating conditions were determined to be an initial pH of 5.5, an adsorbent dosage of 1.0 g, an initial Pb(II) concentration of 30 ppm, and a temperature of 30 °C. Experimental results showed that a contact time of 45 min was generally sufficient to achieve equilibrium. After backpropagation (BP) training combined with principal component analysis (PCA), the ANN model was able to predict adsorption efficiency with a tangent sigmoid transfer function (*tansig*) at hidden layer with 11 neurons and a linear transfer function (*purelin*) at output layer. The Levenberg–Marquardt algorithm (LMA) was found as the best of 11 BP algorithms with a minimum mean squared error (MSE) of 0.000227875. The linear regression between the network outputs and the corresponding targets were proven to be satisfactory with a correlation coefficient of about 0.936 for five model variables used in this study.

Keywords: Artificial neural networks; Adsorption; Modeling; Antep pistachio shells; Pb(II) removal

1. Introduction

Pollution of water by toxic heavy metals through the discharge of industrial wastewater is particularly intractable problem threatening the ecosystem. Rapid industrialization has seriously contributed to the release of toxic heavy metals to water streams [1]. Toxic metal compounds not only contaminate surface water sources (seas, lakes, ponds and reservoirs), but also contaminate underground water in trace amounts by leaching from the soil after rain and snow [2]. Increasing concentrations of these metals in the ecosystem constitute a severe health hazard due to their toxicity, accumulation and magnification throughout the food chain.

Lead has been recognized one of the hazardous heavy metals. Mining, acid battery manufacturing, metal plating, printing, textile, photographic materials, explosive manufacturing, ceramic and glass industries are the main sources of lead contamination [3]. Moreover, lead contanimation of drinking waters is often a result from corrosion of lead-containing piping material [4].

Lead poisoning causes various severe health problems in vital organs of humans, such as damage to the kidney, liver, blood composition, nervous system, reproductive system and retardation in mental function. Because lead is non-biodegradable and tends to bioaccumulate in cells of the living organisms, stricter environmental requirements and urgent treatment solutions are needed for lead removal from water and wastewater.

In recent years, adsorption techniques have been widely investigated for the removal of heavy metals from wastewaters. Adsorbent used in the adsorption processes are various materials including activated carbons prepared from some agricultural by-products, some cellulosic wastes and their carbonisation products, bituminous coal and commercial activated carbons [5]. However, the high cost of the activation process limits the use in wastewater treatment, particularly for the needs of developing countries. Therefore, over the last few years number of investigations have been conducted to test the low-cost adsorbents for heavy metal ion removal.

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Environmental preservation efforts and developments in the technology have resulted in stringent discharge standards. To achieve an optimum control and management, new concepts involving efficient operation and design should be developed and understood. Hence, a high quality representative model can provide a favourable solution in the process control and helps to explain the real process performance and to develop a continuous control strategy for this type of technologies.

Because of their reliable, robust and salient characteristics in capturing the non-linear relationships existing between variables (multi-input/output) in complex systems, it has become apparent that numerous applications of ANNs have been successfully conducted in various parts of environmental engineering field in the past decade, such as estimation of lead concentration in grasses [6], prediction of the bulking phenomenon in wastewater treatment plants [7], prediction of membrane fouling during nanofiltration of ground and surface water [8], assessing of ecosystem quality and community variations [9], modeling of H_2S and NH_3 component of biogas produced from anaerobic digestion [10], prediction of optimum body diameter of air cyclones [11], and predicting single droplet collection efficiency of countercurrent spray towers [12].

Although a number of investigations have been conducted on the removal of Pb(II) ion from aqueous solutions using various adsorbents, every special material needs to be given a particular focus for investigation. The present study describes the adsorption potential of Antep Pistachio (*Pistacia Vera* L.) shells in removal of Pb(II) ions from aqueous solutions. The effects of various operational parameters, such as adsorbent dosage, initial concentration of Pb(II) ions, initial pH, operating temperature, and contact time on Pb(II) adsorption were also investigated. On the basis of batch adsorption experiments, we proposed a three-layer ANN model using a backpropagation (BP) algorithm to predict the Pb(II) removal efficiency of pistachio shells used as adsorbent materials in this work. Following benchmark comparisons of BP algorithms, we conducted an optimization study to determine the optimal network structure. Finally, outputs obtained from the ANN modeling were compared with the experimental data, and advantages and further developments were discussed.

2. Materials and methods

2.1. Preparation of the adsorbent and synthetic wastewater

Antep Pistachio (*P. Vera* L.) shells used in the batch experiments were collected from lands near to Zohrecik Village (36°54′N, 37°52′E) of Gaziantep city in the southeastern part of Turkey. The surface area of the pistachio shells was determined by single point Brunauer, Emmett and Teller (BET) N_2 sorption procedure. Elemental analysis was performed with an elemental analyzer (EA 1108, Fisons Instruments). True density of pistachio shells was determined as outlined by Razavi et al. [13]. The results are summarized in Table 1.

Pb(II) analysis was done in raw pistachio shells according to EPA Method 3010 (acid digestion of extracts for total recoverable or dissolved metal analysis by FLAA or ICP spectroscopy). The result showed that there were no detectable lead levels present in raw pistachio shells to have an effect on the batch experiment data. This can be attributed to the fact that the lands near to Zohrecik Village, where the pistachio shells were collected, are quite away from urban freeways, as well as from industrial areas.

Table 1
Elemental composition and some physicochemical properties of pistachio shells used in the experiments

Component	Value
Elemental composition (wt.%)	
Moisture	4.22
Ash	0.2
Carbon	47.83
Hydrogen	5.32
Nitrogen	0.34
Total sulfur	0.19
Oxygen[a]	41.9
Physicochemical property	
True density (kg/m^3)	770
Natural color	Beige
Surface area (m^2/g)	0.41

[a] Oxygen content determined by difference.

Prior to batch adsorption tests, the shells were washed with distilled water to remove soluble and coloured components, and then dried in an oven (Nuve FN 500) at 80 °C for 24 h. The dried pistachio shells were sieved through a 1 mm sieve (Endecotts Ltd.) and stored in polythene bags.

A stock solution of 1000 ppm of Pb(II) was first prepared by dissolving analytical grade $Pb(NO_3)_2{\cdot}6H_2O$ (Merck Chemical Corp.) in distilled water. Then, synthetic wastewater samples were prepared to give Pb(II) concentrations of 5, 30, 50 and 100 ppm by diluting appropriate amounts of $Pb(NO_3)_2{\cdot}6H_2O$ stock solution with distilled water for batch adsorption experiments. The pH of synthetic samples was adjusted by the addition of 1N NaOH and 1N HCl solutions using a pH meter (WTW Multiline P4 model).

2.2. Batch adsorption tests

Series of batch adsorption experiments were conducted to determine the effect of adsorbent dosage, initial concentration of Pb(II) ions, initial pH, operating temperature, and contact time on adsorption performance of pistachio shells used as adsorbent materials in this study. Therefore, various adsorbent dosages of 0.5, 1 and 4 g were introduced into 250 mL flasks with 200 mL solution containing 5, 30, 50 and 100 ppm of Pb(II) ions. The flasks were then placed in an orbital shaker (Gallenkamp Orbital Incubator Shaker) and agitated up to a total contact time of 120 min at a fixed agitation speed of 250 rpm. Samples were taken at predetermined time intervals (5, 20, 45, 60, and 90 min) and then separated by centrifugation. Pb(II) ions concentrations of aqueous phases were analyzed by atomic absorption spectrometric procedure using a flame atomic absorption spectrometer (SpectrAA 220 Fast Sequential Atomic Absorption Spectrome-

Table 2
Data statistics of model variables

Variables	Data statistics	
	Range	Mean ± S.D.
Input layer [p]		
Adsorbent dosage (g)	0.5–4.0	1.23 ± 0.90
Initial lead concentration (ppm)	5–100	35.91 ± 22.62
Initial pH	2.0–9.0	5.37 ± 1.72
Temperature (°C)	30–60	35 ± 10
Contact time (min)	5–120	56.67 ± 39.64
Output layer [t]		
Adsorption efficiency (%)	26.45–98.7	84.6 ± 17.11

ter, Varian Inc.) with an air–acetylene flame and a hollow catode lamp [14].

Batch experiments were carried out in a pH range of 2.0–9.5 to determine the effect of initial pH on adsorption. Effects of various operating temperatures ranging from 30 to 60 °C were also investigated in batch studies. Temperature adjustments were conducted in the same orbital shaker. Each experiment was performed in duplicate to observe the reproducibility and the mean value was used for each set of values. Percentage of Pb(II) ions removal being the output parameter of the ANN model was considered as a measure of adsorption efficiency of pistachio shells. The efficiency of adsorption (%) was calculated as follows:

$$\% = (C_0 - C_e)100/C_0 \quad (1)$$

where C_0 and C_e are the initial and the equilibrium Pb(II) concentrations of the lead solution, respectively.

2.3. Definition of the ANN model

In this study, Neural Network Toolbox V4.0 of MATLAB® mathematical software was used to predict the adsorption efficiency. Sixty six experimental sets were used to develop the ANN model. Data statistics of model variables are presented in Table 2.

A three-layer ANN with tangent sigmoid transfer function (*tansig*) at hidden layer and a linear transfer function (*purelin*) at output layer was used. The data gathered from batch experiments was divided into input matrix [p] and target matrix [t].

Principal component analysis (PCA) was performed as an effective procedure for the determination of input parameters. We used principal components, which accounted for 99.9% of the variation were used. It was observed that there was no redundancy in the data set and size of the transformed data after the computation. The PCA analysis was followed by the division of the original data into training, validation and test subsets. One fourth of the data was taken for the validation set, one fourth for the test set and one half for the training set. Therefore 34, 16 and 16 samples were used for the training, validation and test subsets, respectively. The experimental data was loaded into the workspace at random for each subset.

In the next step, a number of benchmark comparisons of the various training algorithms were performed to select the best BP training algorithm. Following benchmark comparisons, an optimization was carried out as an important task between the neuron number and mean squared error (MSE) for the best BP algorithm. Then, the three-layer ANN was evaluated by the best BP algorithm for the optimal neuron number at hidden layer. Finally, some analysis of the network response was carried out. The entire data set was put through the network and a linear regression between the network outputs and the corresponding targets was performed.

3. Results and discussion

3.1. Selection of backpropagation (BP) algorithm

Eleven BP algorithms were compared to select the best suited BP algorithm. For all BP algorithms, a three-layer ANN with a tangent sigmoid transfer function (*tansig*) at hidden layer and a linear transfer function (*purelin*) at output layer were used. 10 neurons were used in the hidden layer for all BP algorithms. The LMA with a minimum MSE was found as the best of 11 BP (Table 3).

The benchmark comparison showed a loss on the optimality of the estimates/results produced by some BP training algorithms. The benchmark comparison study resulted that the LMA was able to provide smaller MSE compared to other BP algorithms such as the resilient backpropagation (RP)

Table 3
Comparison of 11 backpropagation (BP) algorithms with 10 neurons in the hidden layer

Backpropagation (BP) algorithms	Function	MSE	IN	R^2	BLE
Resilient backpropagation (Rprop)	*trainrp*	0.123026	20	0.864	$y = 0.719x + 23.6$
Fletcher–Reeves conjugate gradient backpropagation	*traincgf*	0.16533	14	0.822	$y = 0.742x + 20.8$
Polak–Ribiére conjugate gradient backpropagation	*traincgp*	0.148717	18	0.842	$y = 0.805x + 15.9$
Powell–Beale conjugate gradient backpropagation	*traincgb*	0.159847	13	0.812	$y = 0.698x + 25.0$
Levenberg–Marquardt backpropagation	*trainlm*	0.000398	11	0.930	$y = 0.946x + 4.05$
Scaled conjugate gradient backpropagation	*trainscg*	0.142747	19	0.888	$y = 0.846x + 12.6$
BFGS quasi-Newton backpropagation	*trainbfg*	0.072009	16	0.879	$y = 0.768x + 19.5$
One step secant backpropagation	*trainoss*	0.185715	20	0.826	$y = 0.724x + 22.6$
Batch gradient descent	*traingd*	0.618350	100	0.585	$y = 0.350x + 55.3$
Vairable learning rate backpropagation	*traingdx*	0.656301	38	0.499	$y = 0.265x + 62.8$
Batch gradient descent with momentum	*traingdm*	0.557397	100	0.608	$y = 0.390x + 51.5$

MSE, mean squared error; IN, iteration number; R^2, correlation coefficient; BLE, best linear equation.

algorithm and conjugate gradient algorithms. As shown in Table 2, the the smallest MSE was obtained about 0.000398 for *trainlm* function. This was followed by the *trainbfg* with a MSE of 0.072009. However, both *trainrp* and conjugate gradient algorithms such as *traincgf, traincgp and traincgb* produced greater error than the LMA. The loss on the optimality of the estimates/results produced by some BP training algorithms can be attributed to the combinatorial nature and non-linear structure of the experimental data. Hence, the complexity analysis of the problem was validated by the results of the various training algorithms used in the benchmark comparison.

3.2. Optimization of the ANN structure

The optimal architecture of the ANN model and its parameter variation were determined based on the minimum value of the MSE of the training and prediction set. In optimization of the network, two neurons were used in the hidden layer as an initial guess. With an increase in the number of neurons, the network gave several local minimum values and different MSE values were obtained for the training set. Fig. 1 illustrates the dependence between the neuron number and MSE for the LMA selected as the best BP algorithm.

Fig. 1 depicts that the MSE of the network was much higher for the 2 (MSE 0.151843) and 3 (MSE 0.0836682) hidden neurons than those with 4 (MSE 0.0441259), 5 (MSE 0.0439643), and 6 (MSE 0.0395008). With 7 hidden neurons, the MSE decreased significantly from 0.0395008 to 0.00502257. With a further increase in the number of neurons from 7 to 11, a gradual decrease was observed in the MSE. With 11 hidden neurons, the MSE reached its minimum value of 0.000227875. Hence, the neural network containing 11 hidden neurons (MSE 0.000227875) was chosen as the best case. When the number of neurons exceeded 11, the MSE showed a slight increase from 0.000227875 to 0.001100794 at 13 neurons. A further increase

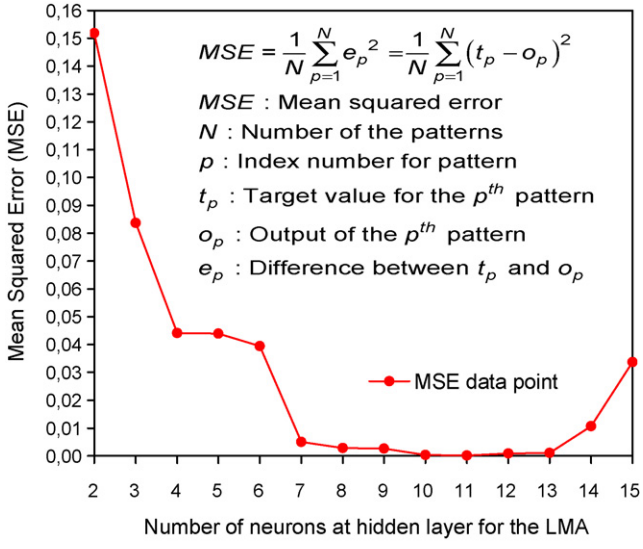

Fig. 1. Dependence between MSE and number of neurons at hidden layer for the LMA.

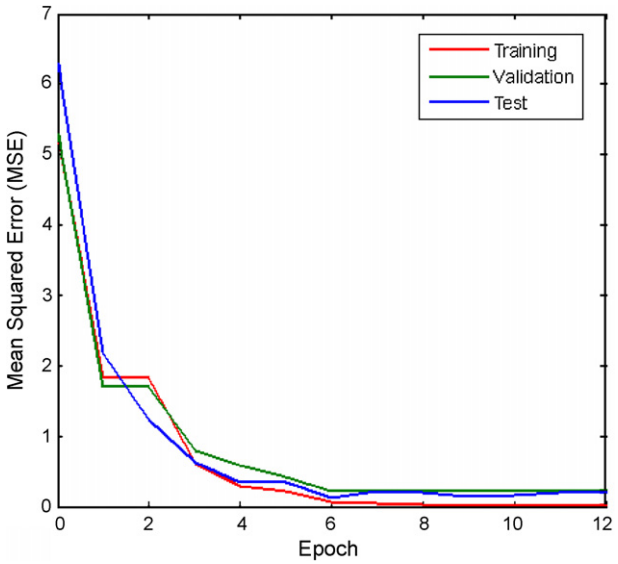

Fig. 2. Training, validation and test mean squared errors for the Levenberg–Marquardt algorithm.

in the number of neurons from 13 to 15 resulted a sharp increase in the MSE. This increment can be attributed to the characteristics of the MSE performance index and the input vector [p] used in this study.

The training was stopped after 12 iterations (TRAINLM, Epoch 12/100) for the LMA because the differences between training error and validation error started to increase. Fig. 2 illustrates training, validation and test mean squared errors for the LMA. Finally, the optimal ANN, together with a flowchart of the BP algorithm, is shown in Fig. 3: a three-layer ANN, with tangent sigmoid transfer function (*tansig*) at hidden layer with 11 neurons and a linear transfer function (*purelin*) at output layer.

A regression analysis of the network response between ANN outputs and the corresponding targets was performed. The graphical output of the network outputs plotted versus the targets as open circles is illustrated in Fig. 4. Taking into account the non-linear dependence of the data, linear regression shows a good agreement between ANN outputs (predicted data) and the corresponding targets (experimental data). The best linear fit was indicated by a solid red line and R^2 is almost 0.94. The performance control of ANN outputs was evaluated by estimating the correlation coefficient (R^2) which is defined as [15]:

$$R^2 = \frac{\sum_{p=1}^{N}(t_p - t_{\text{mean}})^2 - \sum_{p=1}^{N}(t_p - o_p)^2}{\sum_{p=1}^{N}(t_p - o_p)^2} \quad (2)$$

where R^2 is the correlation coefficient, N is the number of the patterns, p is the index number for pattern, t_p is the target value for the pth pattern, t_{mean} is the mean target value, o_p is the output of the pth pattern which is produced by the ANN model. Test outputs showed a very small deviation in efficiency values from the experimental data with an average value of about 3.18 (±2.79).

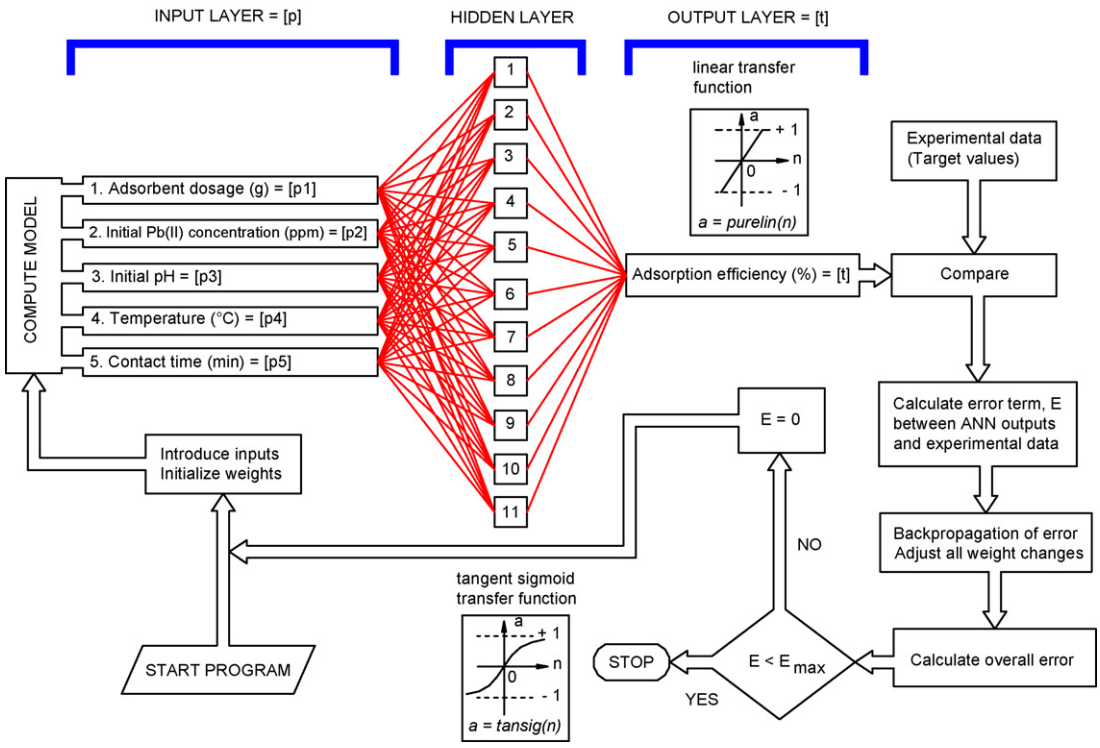

Fig. 3. Optimal ANN structure, together with a flowchart of the BP algorithm for the prediction of the adsorption efficiency.

3.3. Sensitivity analysis

In this study, a sensitivity analysis was conducted to determine the degree of effectiveness of a variable using the proposed ANN model. In the analysis, performance evaluation of various possible combination of variables were investigated. Therefore, performance of the groups of one, two, three, four, and five variables were tested by the optimal ANN structure using the LMA with 11 hidden neurons. The groups of input vectors were defined in this form: p_1, adsorbent dosage; p_2, initial Pb(II) ions concentration; p_3, initial pH; p_4, temperature; and p_5, contact time. Results of the performance evaluation of 30 combinations are summarized in Table 4.

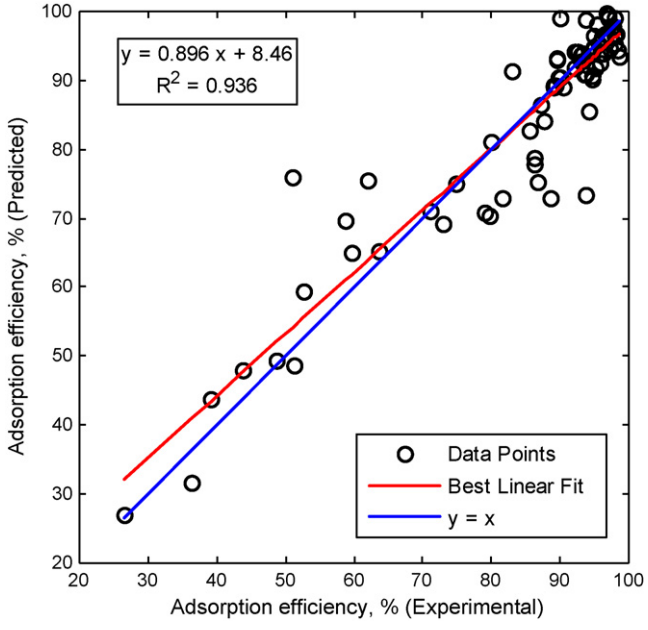

Fig. 4. The graphical output of the network outputs plotted versus the corresponding targets for the Levenberg–Marquardt algorithm.

Findings of the sensitivity analysis showed that p_3 (initial pH) was found to be the most effective parameter, among those considered in the group of one variable. As shown in Table 4, the MSE value (84.4549) significantly decreased when p_3 was used in combination with other variables in the subsequent group of two variables. The minimum MSE in the group of two variables was determined to be 0.123776 with a further contribution of p_5 (contact time). This was followed by the combination of p_2+p_3 with a MSE of 0.319334. The MSE value become smaller when the combination of p_3+p_5, the best case of group of two variables, was used together with p_2 (initial Pb(II) ions concentration). The minimum MSE in the group of three variables was determined to be 0.0631927 using the combination of $p_2+p_3+p_5$. With a further contribution of p_1 (adsorbent dosage), the MSE (0.0631927) decreased up to 0.0382589, which is the minimum value of the group of four variables. The MSE value significantly decreased from 0.0382589 to 0.000227875 when p_4 (temperature) was used in combination with other variables in the subsequent group of five variables. On the basis of the performance evaluation of combinations of input variables, best group performances according to number of parameters are listed in Table 5. The respective MSE values, as given in Table 5 show that MSE values decrease as the number of variables in the group increases. Furthermore, it can also be concluded that the relative increase in the perfor-

Table 4
Performance evaluation of combinations of input variables for the LMA with 11 neurons in the hidden layer for sensitivity analysis

CN	Combination	MSE	R^2	IN	Gradient	BLE
Group of one variable						
1	p_1	268.505	0.275	10	2.26912×10^{-8}	$y = 0.0759x + 78.5$
2	p_2	276.165	0.223	46	2.09286×10^{-5}	$y = 0.0495x + 80.8$
3	p_3	84.4549	0.842	12	3.11414×10^{-9}	$y = 0.709x + 24.7$
4	p_4	271.692	0.255	11	9.35531×10^{-10}	$y = 0.0649x + 79.5$
5	p_5	247.899	0.383	40	1.45941×10^{-11}	$y = 0.147x + 72.5$
Group of two variables						
6	$p_1 + p_2$	0.884074	0.404	4	1.30657×10^{-12}	$y = 0.175x + 68.7$
7	$p_1 + p_3$	0.349342	0.842	8	3.40497×10^{-14}	$y = 0.673x + 25.9$
8	$p_1 + p_4$	0.870325	0.428	6	2.26993×10^{-10}	$y = 0.201x + 65.7$
9	$p_1 + p_5$	0.744235	0.352	10	7.87679×10^{-14}	$y = 0.235x + 66.2$
10	$p_2 + p_3$	0.319334	0.861	6	1.80863×10^{-13}	$y = 0.749x + 19.2$
11	$p_2 + p_4$	0.925674	0.378	4	3.74868×10^{-12}	$y = 0.152x + 69.9$
12	$p_2 + p_5$	0.776596	0.349	8	9.87304×10^{-12}	$y = 0.154x + 69.5$
13	$p_3 + p_4$	0.355586	0.844	6	3.02331×10^{-11}	$y = 0.678x + 25.4$
14	$p_3 + p_5$	0.123776	0.869	8	3.07023×10^{-14}	$y = 0.886x + 10.6$
15	$p_4 + p_5$	0.77764	0.433	6	1.50819×10^{-13}	$y = 0.219x + 65.9$
Group of three variables						
16	$p_1 + p_2 + p_3$	0.307253	0.862	8	7.86722×10^{-15}	$y = 0.767x + 17.6$
17	$p_1 + p_2 + p_4$	0.669317	0.567	6	3.40328×10^{-13}	$y = 0.338x + 56.6$
18	$p_1 + p_2 + p_5$	0.623037	0.521	10	4.91802×10^{-8}	$y = 0.359x + 55.6$
19	$p_1 + p_3 + p_4$	0.331596	0.851	17	2.52168×10^{-14}	$y = 0.745x + 19.5$
20	$p_1 + p_4 + p_5$	0.616612	0.529	10	8.56887×10^{-8}	$y = 0.352x + 56.1$
21	$p_2 + p_3 + p_4$	0.313675	0.863	9	7.80873×10^{-12}	$y = 0.764x + 17.8$
22	$p_2 + p_3 + p_5$	0.0631927	0.921	13	3.95446×10^{-14}	$y = 0.804x + 16.6$
23	$p_2 + p_4 + p_5$	0.673288	0.528	7	1.45395×10^{-11}	$y = 0.280x + 60.8$
24	$p_3 + p_4 + p_5$	0.109178	0.896	12	4.90824×10^{-14}	$y = 0.863x + 11.5$
Group of four variables						
25	$p_1 + p_2 + p_3 + p_4$	0.28744	0.865	12	6.6532×10^{-9}	$y = 0.740x + 20.4$
26	$p_1 + p_2 + p_3 + p_5$	0.0382589	0.922	11	7.62405×10^{-8}	$y = 0.845x + 12.2$
27	$p_1 + p_2 + p_4 + p_5$	0.40297	0.687	13	1.0443×10^{-13}	$y = 0.502x + 43.8$
28	$p_1 + p_3 + p_4 + p_5$	0.0710054	0.843	14	2.85766×10^{-9}	$y = 0.744x + 20.6$
29	$p_2 + p_3 + p_4 + p_5$	0.0525177	0.904	13	1.21999×10^{-9}	$y = 0.855x + 10.9$
Group of five variables						
30	$p_1 + p_2 + p_3 + p_4 + p_5$	0.000227875	0.936	12	0.466008×10^{-10}	$y = 0.896x + 8.46$

CN, combination no; MSE, mean squared error; IN, iteration number; R^2, correlation coefficient; BLE, best linear equation; INF, infinity; p_1, adsorbent dosage; p_2, initial Pb(II) ions concentration; p_3, initial pH; p_4, temperature; p_5, contact time.

mance due to inclusions of p_5 is larger than the contribution of others.

3.4. Effect of initial pH on the adsorption efficiency

The pH of a suspension is an important factor that can affect the form and the quantity of Pb(II) in water, the form and quantity of a mineral's surface sites, and the interaction of the mineral and Pb(II) [16]. Effect of initial solution pH on adsorption was determined by mixing 1.0 g of adsorbent with 200 mL of solution containing Pb(II) concentration of 30 ppm at various pH values ranging from 2.0 to 9.5.

Findings of batch experiments showed that the initial pH of the solution was found to be an important parameter affecting the adsorption performance. Percentage of Pb(II) ions removal was relatively low at pH 2.0 compared to higher pH values.

Table 5
Best group performances according to number of parameters

CN	Combination	MSE	R^2	IN	Gradient	BLE
3	p_3	84.4549	0.842	12	3.11414×10^{-9}	$y = 0.709x + 24.7$
14	$p_3 + p_5$	0.123776	0.869	8	3.07023×10^{-14}	$y = 0.886x + 10.6$
22	$p_2 + p_3 + p_5$	0.0631927	0.921	13	3.95446×10^{-14}	$y = 0.804x + 16.6$
26	$p_1 + p_2 + p_3 + p_5$	0.0382589	0.922	11	7.62405×10^{-8}	$y = 0.845x + 12.2$
30	$p_1 + p_2 + p_3 + p_4 + p_5$	0.000227875	0.936	12	0.466008×10^{-10}	$y = 0.896x + 8.46$

CN, combination no; MSE, mean squared error; IN, iteration number; R^2, correlation coefficient; BLE, best linear equation; INF, infinity; p_1, adsorbent dosage; p_2, initial Pb(II) ions concentration; p_3, initial pH; p_4, temperature; p_5, contact time.

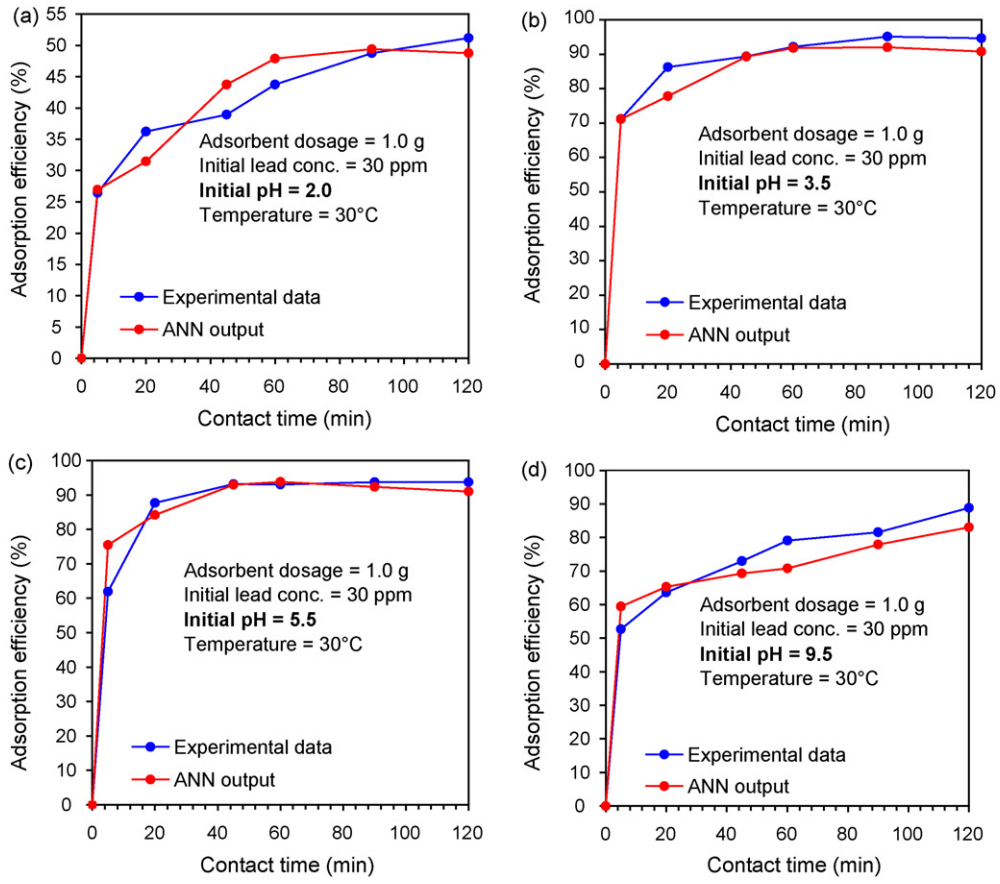

Fig. 5. Agreement between ANN outputs and experimental data as a function of initial pH (adsorbent dosage = 1.0 g, initial lead concentration = 30 ppm, and temperature = 30 °C).

This can be attributed to the fact that a high concentration of H^+ ions compete with Pb(II) for active sites at low pH ($\leq$2.0), with an apparent preponderance of H^+ ions, resulting in the supression of Pb(II) adsorption on the surface of pistacho shells [17]. Therefore, increasing the initial concentration of proton in aqueous solutions resulted in the decrease of Pb(II) removal. Chen and Wang [16] and Inglezakis et al. [18] observed similar phenomena in removal of Pb(II) ions from aqueous solutions using palygorskite clay and natural minerals, respectively.

At pH 9.5, a moderate efficiency of Pb(II) ions removal was observed with a maximum value of 88.8% for 120 min of contact time. Experimental results showed that adsorption of Pb(II) ions decreased when the pH was high (>7.0). This can be ascribed that high pH conditions reduce the mobility of Pb(II) due to the decrease in the exchangeable form, resulting in a decrease in the contact probability between adsorbent and adsorbate [16]. At high pH values (pH 9.5), no interference of lead hydroxide precipitation was observed in this study.

A similar trend was observed for pH 3.5 and pH 5.5 on Pb(II) adsorption. The maximum efficiency of Pb(II) ions removal was found to be 95.1% at pH 3.5 for a total contact time of 90 min. For the same agitation period, the efficiency of Pb(II) ions removal was found to be about 93.8% at pH 5.5. However, percentage of Pb(II) ions removal decreased from 95.1 to 89.3% at pH 3.5 when the contact time was decreased from 90 to 45 min. For the same decrease in contact time at pH 5.5, a negligible decrease from 93.8 to 93.2% was observed in the efficiency of Pb(II) ions removal. Taking into account the cost of energy consumed in agitation, pH 5.5 was found as the optimal initial pH for further batch experiments investigating the effects of other operational parameters on the efficiency of Pb(II) ions removal. The agreement between the ANN model predictions and the experimental data as a function of initial pH is shown in Fig. 5. From this plot it can be seen that obtained results from the proposed ANN model are in good agreement with the experimental data.

3.5. *Effect of adsorbent dosage on the adsorption efficiency*

Adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate [19]. Effect of adsorbent dosage on adsorption was determined by mixing 200 mL of solution containing Pb(II) concentration of 30 ppm with various adsorbent dosages ranging from 0.5 to 4.0 g at an initial pH of 5.5.

Experimental results generally showed that as the adsorbent mass increased from 0.5 to 1.0 g, the percentage of Pb(II) ions removed also increased up to a total contact time of 45 min. This can be attributed to the fact that the number of adsorption sites or surface area increases with the weight of adsorbent, resulting in a higher percent of metal removal at a high dose [3]. However, a further increase in the adsorbent mass from 1.0 to 4.0 g, did not yield a significant difference in the efficiency

of Pb(II) ions removal after a total contact time of 20 min, basically due to reaching the equilibrium adsorption capacity at higher adsorbent dosage.

The maximum efficiency of Pb(II) ions removal was found to be 98.7% with an adsorbent dosage of 0.5 g for 120 min of contact time. Batch experiments resulted that the effect of adsorbent dosage on the percentage of Pb(II) ions removal was negligible after 45 min of contact time. For a total agitation period of 45 min, no striking differences in the efficiency of Pb(II) ions removal were observed for adsorbent dosages of 1.0 and 4.0 g. The percentage of Pb(II) adsorbed was obtained to be about 93.2% with an adsorbent dosage of 1.0 g for 45 min of contact time. Almost 95% of Pb(II) ions removal was found with adsorbent dosages of 0.5 and 4.0 g for a total contact time of 60 min. However, the cost of energy consumed in agitation was apparently high for the second choice. For shorter contact times, high efficiency values were obtained at high adsorbent dosages. However, high amounts of adsorbent were needed in this case. Both taking into account the mass of adsorbent required and the cost of energy consumed in agitation, 1.0 g of adsorbent dosage was selected as the optimal dosage for further batch experiments. Fig. 6 shows a comparison between the ANN model predictions and the experimental data as a function of adsorbent dosage. It can be seen that the ANN model satisfactorily predicts the trend of the experimental data.

3.6. Effect of initial concentration of Pb(II) ions on the adsorption efficiency

Effect of initial concentration of Pb(II) ions on adsorption was determined by mixing 1.0 g of adsorbent with 200 mL of solution containing various Pb(II) concentrations ranging from 5 to 100 ppm at an initial pH of 5.5.

Batch experiments apparently showed that the percentage of Pb(II) ions removal increased when the initial concentration of Pb(II) ions per 200 mL of solution was increased from 5 to 50 ppm for each agitation period. However, a small decrease was observed in the percentage of Pb(II) ions removal for the solution containing 100 ppm of Pb(II) ions. This was basically due to the saturation of adsorbent above an initial Pb(II) ions concentration of 50 ppm.

Adsorption characteristics indicated that percentage of Pb(II) ions removal was fairly dependent on the initial concentration of Pb(II) ions. Horsfall and Spiff [20] reported that adsorption sites take up available metal more quickly at low concentrations. However, at high concentrations metals need to diffuse to the adsorbent surface by intraparticle diffusion and greatly hydrolyzed ions will diffuse at a slower rate. Experimental results showed that the adsorption process reached equilibrium in about 45 min of agitation period for all initial concentrations of Pb(II) ions in this study. However, for initial Pb(II) ions concentrations of 30, 50 and 100 ppm, adsorption equilibrium percentages were determined to be higher than the initial Pb(II) ions concentration of 5 ppm. For initial Pb(II) ions concentrations of 30, 50 and 100 ppm, results indicated that there were no significant differences in the removal efficiency after desired time. Hence, 30 ppm of Pb(II) ions concentration was selected as the optimal initial concentration for further batch experiments. The experimental data and ANN calculated outputs for various initial Pb(II) ions concentration values are shown in Fig. 7. It can be seen that the ANN model shows a good performance on prediction of the experimental data.

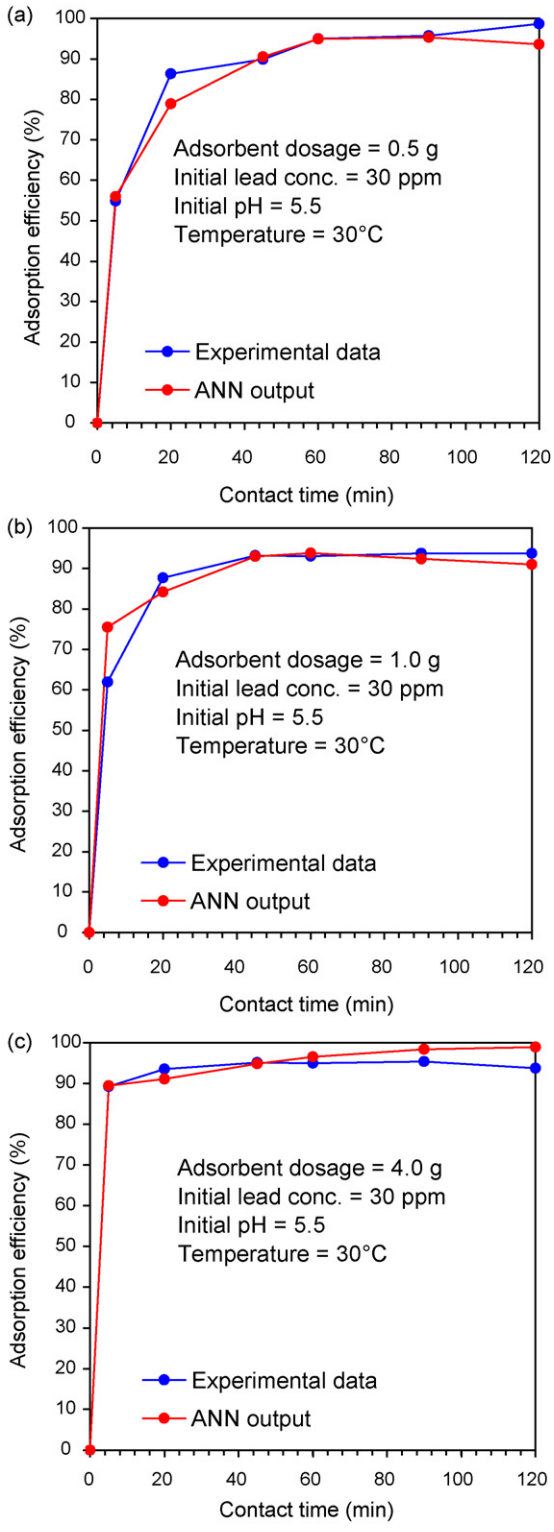

Fig. 6. Agreement between ANN outputs and experimental data as a function of adsorbent dosage (initial pH = 5.5, initial lead concentration = 30 ppm, and temperature = 30 °C).

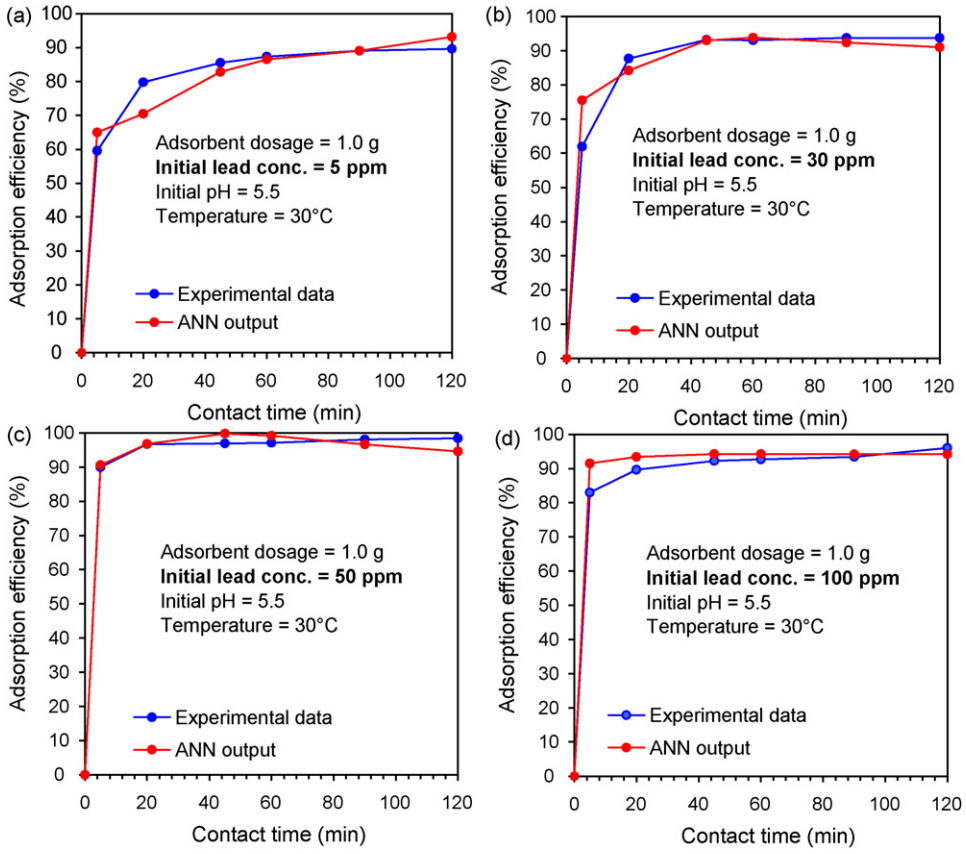

Fig. 7. Agreement between ANN outputs and experimental data as a function of initial lead concentration (adsorbent dosage = 1.0 g, initial pH 5.5, and temperature 30 °C).

3.7. Effect of temperature on the adsorption efficiency

Effect of temperature on the adsorption of Pb(II) ions onto pistachio shells was studied by mixing 1.0 g of adsorbent with 200 mL of solution containing Pb(II) concentration of 30 ppm at pH 5.5 for temperature values ranging from 30 to 60 °C.

Experimental results showed that adsorption of Pb(II) ions onto pistachio shells was fairly dependent on the temperature until the contact time of 45 min. The adsorption of Pb(II) onto pistachio shells increased up to about 98.1%, when the temperature was increased from 30 to 50 °C. However, the magnitude of such an increase continued to decline as the temperature was increased from 50 to 60 °C. This can be attributed to the fact that the attractive forces between adsorbent surface and metal ions are weakened and the adsorption decreases above a certain temperature threshold [21]. Similarly, Aksu and Kutsal [22] commented on that the thickness of the boundary layer decreases at relatively high temperatures, due to the increased tendency of the metal ion to escape from the adsorbent surface to the solution phase, which results in a decrease in adsorption.

The ambient temperature was about 30 °C during the spring season when the batch experiments were carried out. We conducted additional heating to investigate the effect of temperature on the adsorption of Pb(II) ions for temperatures above the ambient temperature. However, no significant differences in the efficiency of Pb(II) ions removal were observed depending on the temperature above 45 min of agitation period. Therefore, both taking into account the cost of energy consumed in heating and the magnitude of such a decrease in the adsorption of Pb(II) ions at high temperature, an operating temperature of 30 °C (ambient conditions) was generally found to be sufficient for further batch experiments. The agreement between the ANN model predictions and the experimental data as a function of operating temperature is depicted in Fig. 8. From this plot it can be seen that there is a good agreement between predictions of the ANN model and the experimental data.

3.8. Effect of contact time on the adsorption efficiency

The batch experimental data obtained from the adsorption of Pb(II) ions onto the pistachio shells showed that a contact time of 45 min was generally sufficient to achieve equilibrium and the adsorption did not change significantly with further increase in contact time. In some cases, equilibrium was almost attained in 5 or 20 min, depending on the values of operating variables. These results indicate that the adsorption process can be considered very fast. To summarize, taking into account the cost of energy consumed in agitation, longer contact times (>45 min) unnecessarily prolonged the process to obtain similar result.

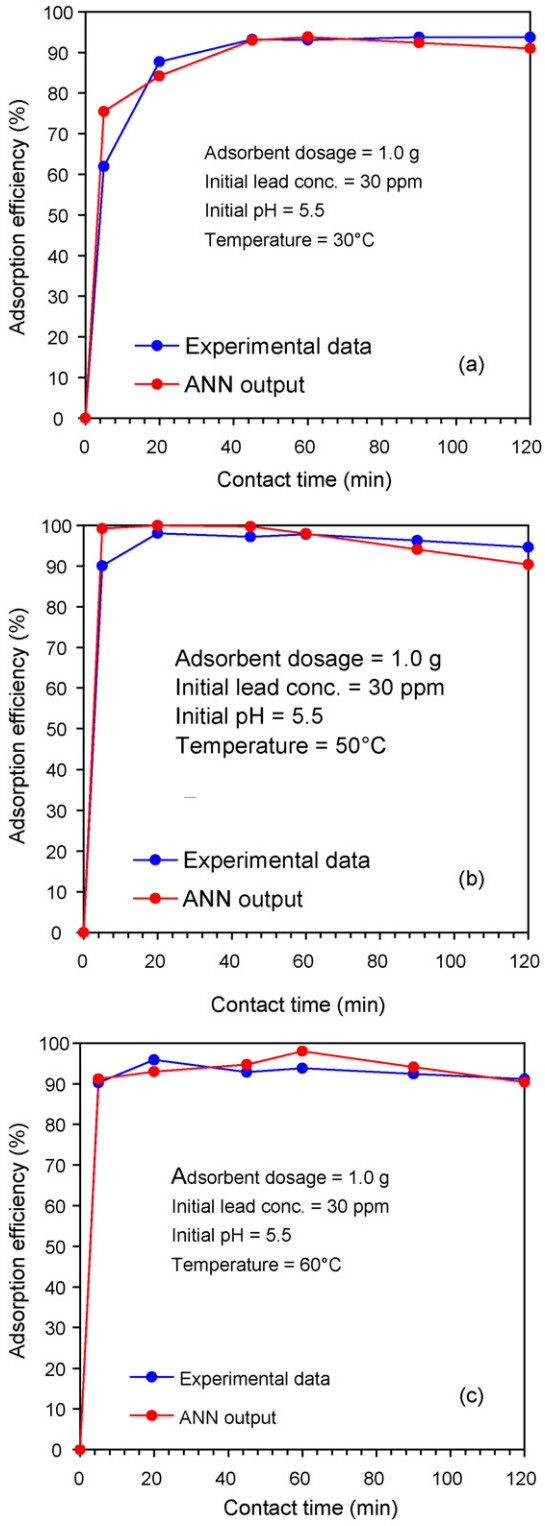

Fig. 8. Agreement between ANN outputs and experimental data as a function of temperature (adsorbent dosage = 1.0 g, initial pH 5.5, and initial lead concentration = 30 ppm).

3.9. Comparisons with literature data

Table 6 summarizes performance data concerning the comparison of batch experiments conducted with various materials and operating conditions on removal of Pb(II) ions from aqueous solutions. The performance data figures out that a wide range of operating conditions have been conducted in removal of Pb(II) ions using low-cost materials. On the basis of maximum Pb(II) removals, the present data seems to be in agreement with those reported by others. The performance data shows that optimum initial pH has been investigated between 2 and 12. Effect of various amounts of sample materials, ranging from 0.01 to 4.0 g have been examined. Most of studies, including the present study, have been carried out at an operating temperature above 20 °C. A wide range of contact time, from 1 min to 120 h (5 days), has been studied at various agitation speeds up to 3500 rpm. Performance data obviously indicated that the removal of Pb(II) ions from aqueous solutions could be effectively improved up to about 100% by using low-cost sample materials [18,23,30,31]. Differences in performances can be attributed to the different characteristics and amounts of sample materials, initial pH of solutions, concentration of Pb(II) ions, operating temperatures and also contact times.

In this study, the adsorption data were also described by well-known Freundlich and Langmuir isoterms models as a function of equilibrium Pb(II) concentration (C_e) and the corresponding equilibrium adsorption capacity (q_e). Results showed that the Langmuir model represented the adsorption process better than the Freundlich model, and the maximum adsorption capacity of the pistachio shell in Pb(II) removal was found to be 27.1 mg/g. Maximum adsorption capacities (q_0) obtained for adsorption of Pb(II) onto other materials as low cost adsorbents reported in the literature are listed in Table 7. As seen from Table 7, pistachio shell is a better adsorbent compared to some of low cost adsorbents reported by others. This result indicates that the studied pistachio shell possesses a good adsorption capacity, so that this material can be useful in removing Pb(II) from aqueous solutions. Higher values of q_0 have also been reported by some workers. However it should be noted that differences are due to the properties of each adsorbent such as structure, functional groups and surface area.

3.10. Economical discussion

The removal of heavy metals from water and wastewater has recently become the subject of considerable interest due to more strict legislations introduced in many countries to control water pollution [3]. Precipitation of heavy metals the metal hydroxides or sulfides has been practiced as the prime method of treatment for heavy metals in industrial wastewater for many years. However, this process leads to a special problem of sludge handling and costly disposal. Although membrane filtration and electrochemical process are proven techniques, their high costs limit their use in pratice. Similarly, activated carbon is regarded as an effective adsorbent for removal of metal ions from water [39,40]. However, due to its high cost and about 10–15% loss during regeneration, unconventional adsorbents like fly ash, peat, lignite, bagasse pith, wood, saw dust, etc. have attracted the attention of several investigations [41].

The pistachio shell used as an adsorbent in this study is an agricultural by-product produced in very large quantities partic-

Table 6
Comparison of batch experiments conducted with various materials and operating conditions for removal of Pb(II) ions from aqueous solutions

Material	Range of operating parameters and maximum removals							Reference and region
	Initial pH	Material dosage (g)	Initial Pb(II) concentration (ppm, mg/L, meq/L or mM)	Temperature (°C)	Contact time (min or h)	Agitation speed (rpm)	Maximum removal (%)	
Antep pistachio shells (*Pistachia Vera* L.)	2.0–9.5	0.5–4.0	5–100 ppm	30–60	5–120 min	250	Up to 99	Present study, Turkey
Clinoptilolite and bentonite (clay)	4.0	2.0	1.036 ppm	28–60	1–120 min	0–500	Up to 100	Inglezakis et al. [18] Greece
Modified alginic acid (MMA)	5.81	0.6	297 mg/L	Room temp.	10–180 min	NS	Up to 100	Jeon et al. [23], Korea
Washed biomass (dry basis)	3.6–9.0	1.1–5.5	25–150 mg/L	30	16–72 h	120	96	Ray et. al. [24], India
Mexican clinoptilolite	4.0–12.0	1.5	15–30 meq/L	25	18 h	30	>97	Vaca-Mier et al. [25], Mexico
Tree leaves	5.42	2.0	49 mg/L	Room temp.	2 h	300	96	Adeyiga et al. [26], Virginia
Phosphatic clay	2.0–8.0	0.5	50 mg/L	25 ± 3	Up to 120 h	30 ± 1	Up to 99	Singh et al. [27], USA
Kaolinite clay	2.0–8.0	0.1	3.4 mg/L	25	10–90 min	3500	85	Kamel et al. [28], Egypt
Modifed clay	5.5 ± 0.01	1.0	50–1500 ppm	23	24 h	10	93	Park and Shin [29], Korea
Natural goethite	3.0–5.0	1.0	5–750 ppm	27 ± 1	8 h	120	Up to 100	Abdus-Salam and Adekola [30], Nigeria
Waste brewery biomass	4.5–8.0	0.95–1.2	0.1–1.0 mM	30	96 h	150	Up to 100	Marques et al. [31], Portugal
Peat moss	3.0–6.0	0.01–0.06	10 mg/L	23 ± 1	5–180 min	125	95.5	Akinbiyi [32], Regina

NS, not specified.

Table 7
Maximum adsorption capacities (q_0) obtained for adsorption of Pb(II) onto various adsorbents (Langmuir isoterm model)

Adsorbent	q_0 (mg/g)	Reference and region
Antep pistachio shells	27.1	Present study, Turkey
Saw dust	3	Shukla et al. [33], USA
Tree barks	21	Martin-Dupoint et al. [34], France
Tea waste	65	Amarasinghe and Williams [3], UK
Rice husk	11	Chuah et al. [35], Malaysia
Sago waste	47	Quek et al. [36], Birmingham
Kaolinite	11.52	Gupta and Bhattacharyya [37], India
Coffee residue	20	Boonamnuayvitaya et al. [38], Thailand

ularly in the southeastern part of Turkey. The main advantages of Pb(II) removal by using pistachio shells is that it is in abundance and easy availability. This makes it a strong choice in the investigation of an economic way of Pb(II) removal. From the economical point of view, pistachio shells can be used as an alternative media to activated carbon, to gain an understanding of the adsorption process.

Further investigations may be needed for desorption studies, economically feasible regeneration of the adsorbent and application of the adsorbent for real industrial wastewater. However, in many parts of the world where pistachio shells are available at no cost, regeneration is not required and the metal laden biomass can be disposed by incineration. The remaining ash after incineration will be highly enriched with lead and has to be ultimately disposed of in a secure landfill [32]. Consequently, acceptance of pistachio shell as a sustainable, low-cost, and renewable resource is expected to contribute to its universal appeal for removal of Pb(II) from aqueous solutions, particularly for the needs of developing countries.

4. Conclusions

The pistachio shell used as a low-cost adsorbent showed a good adsorption performance for removal of Pb(II) ions from aqueous solutions. The effect of various operational parameters on the adsorption of Pb(II) ions onto pistachio shells was investigated and optimized. Batch adsorption experiments showed that optimal operating conditions were determined to be an initial pH of 5.5, an adsorbent dosage of 1.0 g, an initial Pb(II) concentration of 30 ppm, and a temperature of 30 °C. A contact time of 45 min was found to be sufficient to achieve equilibrium. Findings of the experimental study clearly indicated that the removal of Pb(II) ions from aqueous solutions could be effectively improved up to about 99% by using pistachio shells. The maximum adsorption capacity of the pistachio shell in Pb(II) removal was found to be 27.1 mg/g.

On the basis of batch adsorption experiments, an important objective was to obtain an ANN model that could make reliable prediction on the percentage of Pb(II) ions removal. A three-layer ANN with a tangent sigmoid transfer function (*tansig*) at hidden layer and a linear transfer function (*purelin*) at output layer were proposed to predict the efficiency of Pb(II) ions removal. The benchmark comparisons conducted with 10 hidden neurons resulted that the LMA was able to provide smaller MSE compared to other 11 BP algorithms with a MSE of 0.000398. The optimal neuron number for the LMA was determined to be 11 hidden neurons with MSE of 0.000227875. The proposed ANN model showed a precise and an effective prediction of the experimental data with a satisfactory correlation coefficient of 0.936 for five operating variables. The sensitivity analysis showed that MSE values decreased as the number of variables used in the ANN model increased. The relative increases in the performance due to inclusions of p_5 (contact time) was found to be larger than the contribution of others. To conclude, a simulation based on the ANN model can provide a further contribution to develop a better understanding of the dynamic behaviour of process where still some phenomena cannot be explained in all detail.

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