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Artificial neural network (ANN) approach for modeling Zn(II) adsorption in batch process

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Abstract−Artificial neural networks (ANN) were applied to predict adsorption efficiency of peanut shells for the removal of Zn(II) ions from aqueous solutions. Effects of initial pH, Zn(II) concentrations, temperature, contact duration and adsorbent dosage were determined in batch experiments. The sorption capacities of the sorbents were predicted with the aid of equilibrium and kinetic models. The Zn(II) ions adsorption onto peanut shell was better defined by the pseudo-second-order kinetic model, for both initial pH, and temperature. The highest R^2 value in isotherm studies was obtained from Freundlich isotherm for the inlet concentration and from Temkin isotherm for the sorbent amount. The high R^2 values prove that modeling the adsorption process with ANN is a satisfactory approach. The experimental results and the predicted results by the model with the ANN were found to be highly compatible with each other.

Keyworlds: Artificial Neural Network (ANN), Kinetics and Isotherm Study, Zn(II) Ions, Peanut Shell

INTRODUCTION

Heavy metal contamination of water resources from various sources, including mining and mineral processing, electroplating, pesticides, galvanizing plants, manufacture of batteries, textile, tannery operations, pigment and chemical manufacturing, car and aeronautic industries, poses significant ecological, public and environmental health risks [1]. The term "heavy metal" is collectively applied to a group of metals (and metal-like elements) with density greater than 5 g/cm^3 and atomic number above 20 [2]. Heavy metals such as Cu^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} are toxic to human beings and other living organisms if their concentrations exceed threshold values.

Zinc is the 23rd most abundant element in the Earth's crust and its concentrations are rising through human activities [3]. Although zinc is an essential element for human health as it participates in metabolism, stimulates the enzymes and plays an important role in functioning of immunologic system, it becomes toxic at intake levels of 100-500 mg/day [4]. Most important sources of zinc are general industry and mining, plating, fertilizers, paper products and fibers [5].

Conventional methods for removal of heavy metals in aqueous solutions include precipitation, flotation, electrodialysis, ion exchange, ultrafiltration, membrane filtration and adsorption. However, the high costs, operational difficulties and low removal efficiencies associated with conventional adsorbents such as activated carbon restrict their large-scale application, especially in developing countries. Natural materials that exist in large quantities or certain waste from agricultural processes may have potential to be used as low cost adsorbents, as they represent unused resources, widely existing and are environment friendly.

The use of biological molecules rather than physical and chemical methods for the removal of metals from industrial waste is an alternative and very effective method. Applications of biological molecules for the removal of metals include biosorption, adsorption and phytoremediation methods. Biosorption, is the uptake of metal ions from aqueous environments by the biomass. Dissolved substances on the surface of biosorbent biomass should pass through the film of its surrounding liquid solvent.

Biological materials are organisms like bacteria, algae, fungi, molds etc. Besides, during the last twenty years, several biomass sorption characteristics have been examined. Biomass contains various functional groups such as carboxyl, sulfate, phosphate and amino groups. Among these biomasses, the common ones are biomass fom the microbiological production, wastes from sugar production, crab shell, nuts shells, tea leaf wastes, rice husks etc [6].

Biomass can be obtained from the organisms contained in industrial waste or nature. In the biosorption process, the necessary physiological conditions for living organisms are not required [7]. Since it does not require expensive nutrients to ensure the development of biomass nutrient solution, the working environment is no longer nutrients or metabolic by-products are not available. Death biomass acts as an ion exchanger and thus the event takes place in a short time [6]. Since the cells are dead, occurrence of the event is not limited to certain conditions. Thus, biosorption may occur in a broad pH, concentration and temperature ranges. Biosorption is also a quite low-cost process as compared to other chemical processes applied to control environmental pollution [8].

On the other hand, the progress of biological processes is limited in biosorption since metabolic activities are not carried out in dead cells [7]. Quick equilibrium may cause some problems [8]. Biosorption nay require some optimal conditions for the process.

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It is influenced by physicochemical factors such as the metal ion type, amount and type of biomass, concentration, temperature and pH of the solution. In present study, the most important researches related to the removal of zinc from aqueous solutions by biosorption were reviewed.

By-products of biomaterial production activities are a cheap source of biosorbents. Several researches and experimental studies were conducted about the removal of zinc by adsorption on various biosorbents like carrot residues [3], coffee husks [9], apple wastes [10], cocoa shell [11], corn stalks [12], grape pomace [13], potato peels [14], and banana peels [15], sawdust and water hyacinth [16], orange waste [17] and olive stone waste [18].

In the present study, the ability of peanut shell as a sufficient biosorbent for Zn(II), ion removal from aqueous solutions was studied. Effects of the initial pH, Zn(II) concentrations, temperature, contact duration and and adsorbent dosage were determined in batch experiments. The sorption capacities of the sorbent were predicted with the aid of equilibrium and kinetic models. The interactions of peanut shell with metal ions were analyzed by scanning electron microscopy (SEM), energy dispersive X-Ray analysis (EDX), Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) spectrum and atomic force microscopy (AFM). Based on batch adsorption experiments, ANN model was also developed to predict Zn(II) removal efficiency of peanut shell used as a low cost adsorbent. Model outputs were compared with the experimental data. There are several studies about Zn removal with different absorbents. But, in the present study, peanut shell, which has not been experimented before, was used as an absorbent and Zn removal efficiency of intermittent system was modeled with artificial neural network (ANN) methodology. It was concluded that ANN models could be used in intermittent absorption processes.

Sorption experiments were performed in triplicate and the average values of samples were presented. Also, blank samples were used to compare the results through all batch procedures. Data were presented in mean values from the experiments, standard deviation (Zn(II)≤5%) and error bars were indicated in the figures.

MATERIAL AND METHODS

1. Preparation of Sorbent

All the sorbents were washed thoroughly with deionized water and dried at 105 °C for 24 hours. Dried peanut shells were made active through immersing into 1% H_2SO_4 solution for 24 hours. Sorbents were washed again with distilled water to remove the residual acids and dried at 105 °C for 24 hours. Peanut shells were crushed and sieved through 0.30 mm sieve.

2. Preparation of Solutions

The stock solutions of Zn(II) were prepared at concentration of 1,000 mg/L by dissolving 4.40 g of zinc sulfate heptahydrate salt ($ZnSO_4 \cdot 7H_2O$) in 1,000 mL distilled water. The required initial concentration of Zn(II) standard solution was prepared by appropriate dilution of the above stock Zn(II) solution.

3. Characterization of Sorbent

The characterization of peanut shell before and after adsorption was determined by FTIR, SEM, EDX, XRD, and AFM analyses. The morphology of the particles was observed with a scanning electron microscope (SEM).

4. Batch Sorption Experiments

The effects of pH, contact duration, temperature, concentration and sorbent dose on adsorption efficiency were studied to determine the optimal values of these factors in the sorption mechanism. All experiments were in 250 mL Erlenmeyer flasks in an intermittent system by using 100 mL zinco solutions and biosorbent. The pH of the solutions for Zn(II) varied within the range of 3 to 7. The pH arrangements were conducted in a pH meter using a 1 M HCl or 1 M NaOH solution. The effects of experimental parameters such as, initial Zn^{2+} ion concentration (5-50 mg/L), pH (3.0-7.0), adsorbent dosage (0.05-0.5 g/L) and temperature (25-55 °C) on the removal of Zn(II)ions were studied. Various concentrations of Zn(II)solutions (25 mg/L) at a constant initial pH value (5.0), temperature (25, 35, and 45), adsorbent dosage (0,3 g/L) were used for the kinetic experiments. The batch units were agitated in an orbital incubator shaker (Gerhardt) for a contact durations varied in the range 0-60 min at a speed of 125 rpm at 25 °C. The time at which biosorbent added to metal solution was assumed to be t=0, and analyses were performed at certain intervals. Free Zn(II)ions in samples were read from a Merck NOVA60 spectrophotometer. During the tests, pH values were read by Thermo Orion - STARA2145 brand pH meter. Two parallel experiments were conducted for each experimental condition, and the average values of experimental results were used in the calculations.

Biosorption capacity (q_e) and percent removal efficiency (yield) were calculated by using the following equations:

$$q_e = \frac{V \cdot (C_o - C_e)}{X} \quad (1)$$

$$(E)\% = \frac{(C_o - C_e)}{C_o} \cdot 100 \quad (2)$$

where q_e (mg/g) is the concentration of the substances bound over adsorbent; X (g) is the amount of adsorbent used in tests; V (mL) is the solution volume; C_o (mg/L) is the initial concentration of the solution; C_e (mg/L) is the final concentration of the solution.

Compliance of the experimental data with Langmuir, Freundlich, Temkin and D-R isotherm models was researched. However, sorption kinetics of Zn(II)ions on the peanuts shell were analyzed using four kinetic models for fitting sorption kinetic data: pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich models. Equations for the kinetic models and isoterms are presented in Table 1.

where (Eq. Langmuir), q_e and Q_o are the amount of equilibrium adsorption capacity and the maximum adsorption capacity (mg/g), respectively; C_e is the equilibrium solution concentration (mg/L); b is the Langmuir constant (L/mg) [19]. Dimensionless RL (dispersion) coefficient was calculated to find the availability of biosorption; a value between 0 and 1 indicates the availability of the adsorption [26].

Freundlich isotherm: K_F and (1/n) are the Freundlich constant and adsorption intensity, respectively. K_F is called as adsorption capacity and the term 1/n is called as heterogeneity factor [27].

Temkin model: "A" is Toth constant (dm^3/g). When this equa-

Table 1. List of mathematical equations used in the study

Mathematical model	Equations	
Equilibrium isotherm models		
Langmuir isotherm	$q_e=\frac{Q_o\cdot b\cdot C_e}{1+b\cdot C_e}\quad R_L=\frac{1}{1+b\cdot C_o}$	[19]
Freundlich isotherm	$q_e=K_F C_e^{(1/n)}$	[20]
Temkin isotherm	$q_e=B\ln A+B\ln C_e$	[21]
Dubinin ve Radushkevich (DR) isotherm	$\ln q_e=\ln q_{max}-\beta\varepsilon^2$ $\varepsilon=RT\ln\left(1+\frac{1}{C_e}\right)$	[22]
Kinetics models		
Pseudo first-order model	$\log(q_e-q_t)=\log(q_e)-\frac{k_1}{2.303}\cdot t$	[23]
Pseudo second-order model	$\frac{t}{q_t}=\frac{1}{k_2\cdot(q_e)^2}+\frac{1}{q_e}\cdot t$	[24]
Inter-particle diffusion (Weber-Morris) model	$q_t=k_{id}\cdot(t)^{0.5}+C$	[25]

tion is linearized and the term (RT/b) in this equation is expressed as B, Equation is obtained [21]. The values of A and B can be calculated from the linear plot of q_e versus ln (C_e).

The constants obtained from Langmuir and Freundlich isotherms do not provide any information about the physical and chemical characteristics of biosorption. The Dubinin-Radushkevich (D-R) isotherm was used to determine the nature of the adsorption process. The amount adsorbed (q_e, mol/g) is related to maximum sorption capacity (qD-R, mol/g), average adsorption energy (E) and relevant activity coefficient (β, mol^2/J^2) and is a function of Polanyi potential (ε).

Pseudo first-order kinetic model: "k_1" is rate constant (1/min), "q_e" is adsorption capacity (mg/g), "q_t" is adsorbed material concentration at time t (mg/g). When the graph of log (q_e-q_t) versus t is drawn according to equation, the slope of the line provides k_1/2.303 and y-axis interception point provides log (q_e).

Pseudo second-order rate equation: "k_2" is pseudo second-order rate constant (g/mg·min), "q_e" is the amount of adsorbed material at equilibrium (mg/g), "q_t" is the material concentration adsorbed at time t (mg/g). When the graph of (t/q_t) vs t is drawn according to equation, slope of the line provides $1/q_e$ and y-axis interception point provides $1/k(q_e)^2$ value [28].

Inter-particle diffusion (Weber-Morris) model: "k_{id}" (mg/g min0.5), "t" is time (minute) and C are the rate constant of intra-particle diffusion model and the intercept, respectively. When the graph of qt versus $t^{0.5}$ is drawn, the slope of the line provides k_{id} adsorption constant.

Elovich kinetic model (developed by Zeldowitsch in 1934) is proper to define second-order kinetics assuming that the actual solid surfaces are energetically heterogeneous. Therefore, the model defines the rate of chemical adsorption on energetically heterogeneous surface [29]. Elovich parameters are provided in Eq. (3).

$$q_t=\frac{1}{\beta}\ln(\alpha\beta)+\frac{1}{\beta}\ln t \tag{3}$$

where α is the initial adsorption rate (mg/g·min) and β is the desorption rate constant (g/mg).

Thermodynamic tests: The study of thermodynamics presumes that the energy in an isolated system cannot be lost or gained when the entropy change is the driving force [30]. Thermodynamic parameters are provided in Eqs. (4)-(5).

$$\Delta G^0=\Delta H^0-T\Delta S^0 \tag{4}$$

where ΔG^0: Gibbs free energy (kJ/mol), ΔH^0: Enthalpy exchange (kJ/mol), ΔS^0: Entropy exchange (kJ/mol K), T: Absolute temperature (Kelvin).

$$\ln K_c=\frac{\Delta G^0}{R}+\frac{\Delta H^0}{RT} \tag{5}$$

Gibbs free energy value of adsorption process carried out at a certain temperature was calculated with K_c by using the equation $\Delta G^0=-RT\ln K_c$ (R= 8.314 J/mol K). Then the graph of $\ln K_c$ versus 1/T was drawn and ΔH^0 and ΔS^0 were calculated by using the slope and interception point. Negative values of ΔG^0 and ΔH^0 indicate that adsorption was spontaneous, feasible, and exothermic [31]. The positive value of ΔS^0 shows that randomness increased at the solid-liquid interface during adsorption [32].

5. Artificial Neural Network (ANN) Modeling

The progression of empirical models using numerical estimation techniques such as artificial neural network (ANN) can be considered as powerful options for predicting the adsorption system [33]. An ANN was used for modeling the adsorption studies based on the application of the experimental data at different operating conditions. A simple ANN architecture is presented in Fig. 1 where inputs are indicated by x_1, x_2, … x_n and weight coefficients of each input are indicated by W_{k1}, W_{k2}, … W_{kn}. Thus, xn represents input signals and W_{kn} represents weight coefficients of these signals. The core gives the weighted sum of entire input signals. The results from the thresholding function of the network are indicated by Y [34].

Back-propagation algorithm is a training algorithm commonly used because of high training capacity and simple algorithm. There

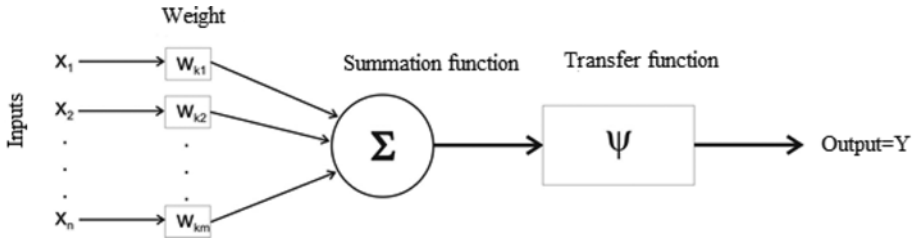

Fig. 1. Artificial Neural Network (ANN) cell pattern.

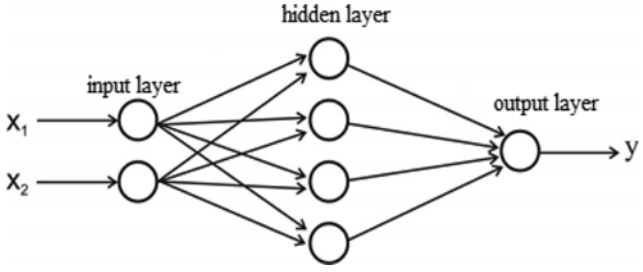

Fig. 2. Simple architecture of back-propagation algorithm of ANN.

are three layers of back-propagation network algorithm model as of input, hidden and output (Fig. 2). It is possible to increase the number of hidden layers in ANN based on the nature of the problem. Computer-aided software MATLAB was used for ANN calculations [35].

RESULTS AND DISCUSSION

1. Characterization of the Sorbent

FT-IR is an important tool for analyzing the functional groups

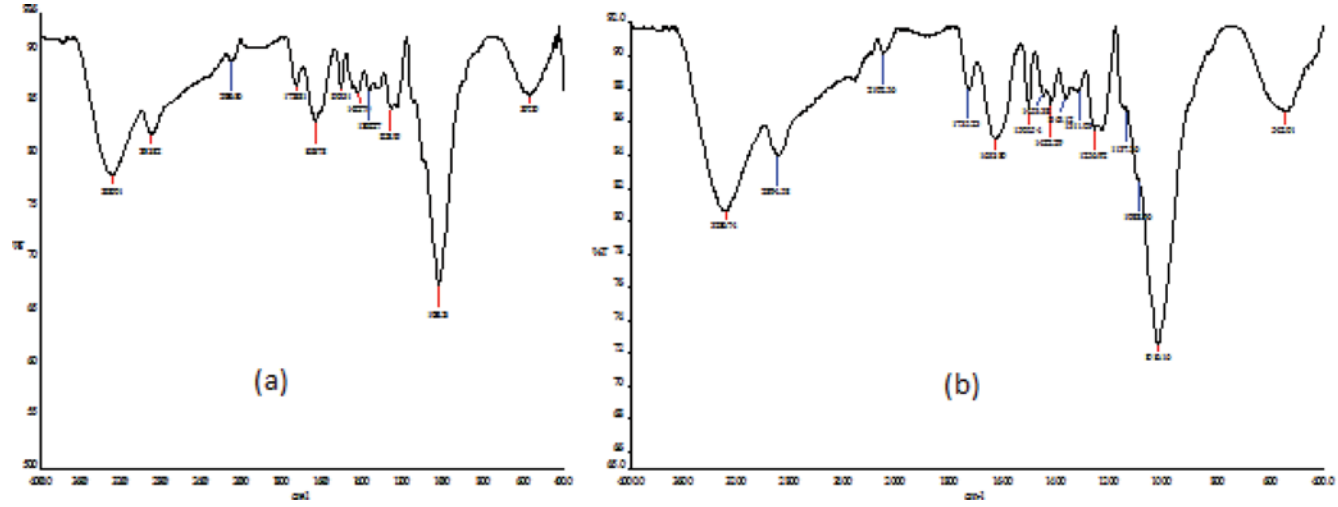

Fig. 3. FTIR spectra of peanut shell before (a) and after (b) adsorption.

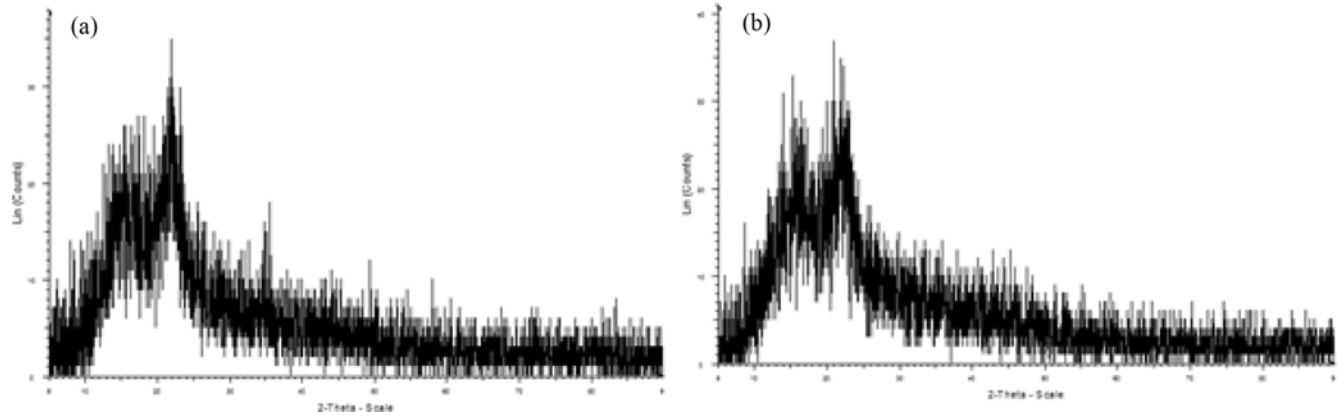

Fig. 4. XRD spectra of peanut shell before (a) and after (b) adsorption.

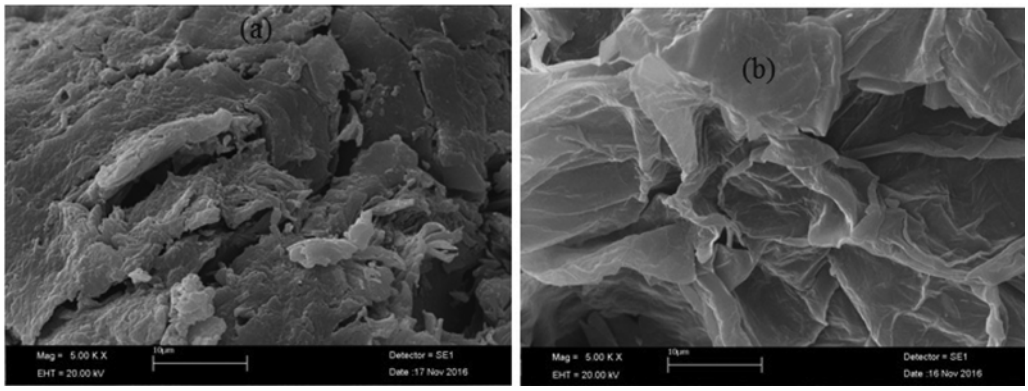

Fig. 5. SEM spectra of peanut shell before (a) and after (b) adsorption.

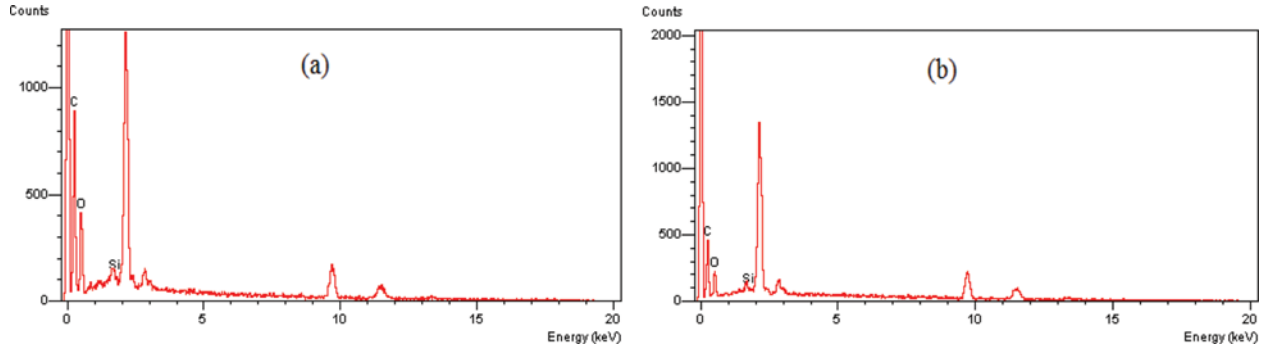

Fig. 6. EDX spectra of peanut shell before (a) and after (b) adsorption.

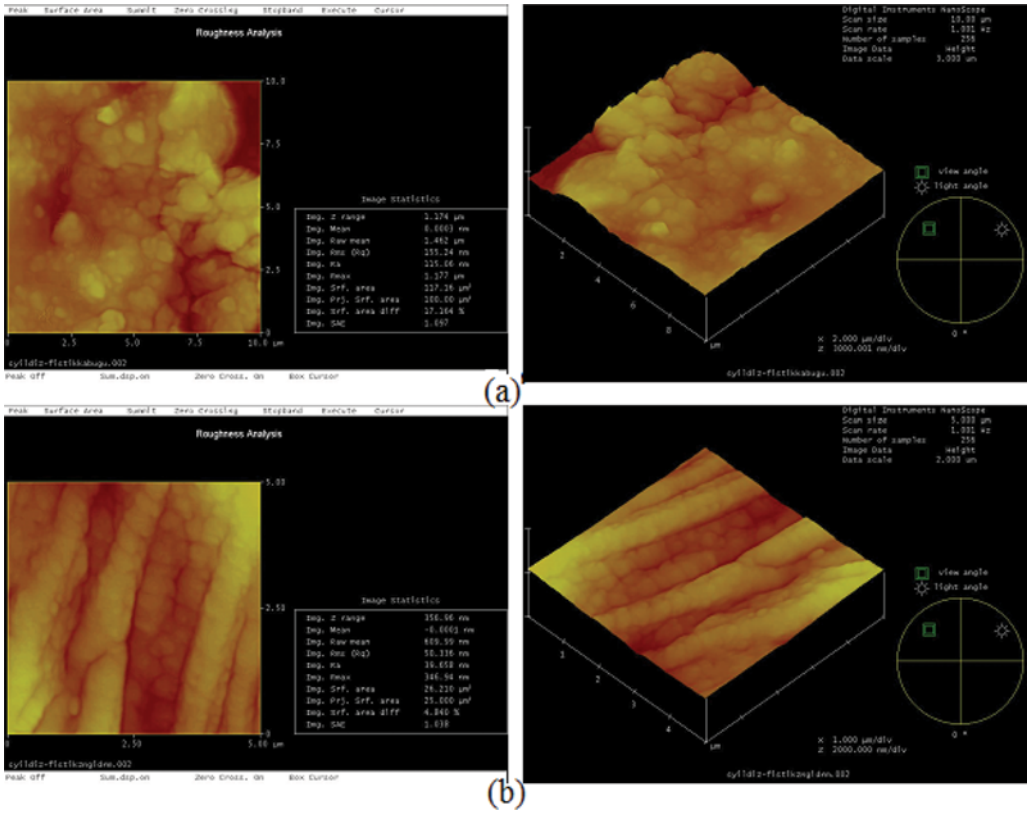

Fig. 7. AFM spectra of peanut shell before (a) and after (b) adsorption.

on the surface of the adsorbent material [36]. When the FTIR of the peanut shell was examined, it was seen that it contained peaks similar to other biomass sources of the lignocellulosic structure [37]. To determine the peanut shell changes before and after the adsorption, the spectrum of the peanut shell was obtained by FTIR and the results are presented in Fig. 1. Based on the qualification of the peaks in Fig. 1, the adsorption at 3,287 and 3,286 cm^{-1} indicated the tensile vibration of the hydroxyl groups [38]. The peaks at 1633,4 and 1633,8 cm^{-1} can be designated to C=O stretching [39]. It was observed that peanut shells had quite similar peaks before and after absorption. The peaks at 3,287 and 1,633 cm^{-1} showed a significant decrease in peak density after Zn(II) loading. The above changes in FTIR spectra indicated that the hydroxyl and carboxyl groups were related in Zn(II) adsorption by surface complexation [40].

The XRD spectrum in Fig. 4 shows sharp peaks for peanut shells. There are similar peaks at 16° and 21° in peanut shell. It was not structurally distorted during the adsorption. Scanning electron micrographs (SEM) of the prepared samples are presented in Fig. 5. It is clear that the outer surface of samples was rough and contained abundant porous structures of different size and shapes. The interior cavities in porous structures provide new sites for accommodation of Zn(II) ions.

To highlight the mechanism of ion exchange in biosorption of Zn onto peanut shell, EDX analyses were released before and after biosorption through the comparisons of the peaks density of exchangeable ions (Fig. 6).

To observe the morphological properties such as surface porosity, roughness and texture, micrographs of the surface and cross-section of the adsorbents were taken by using AFM. Surface characterization includes micro-porosity, roughness and macro-pores size distribution using AFM before and after adsorption (Fig. 7). Fig. 7 shows that surface roughness decreased after adsorption. Surface roughness was reduced by ion adsorption.

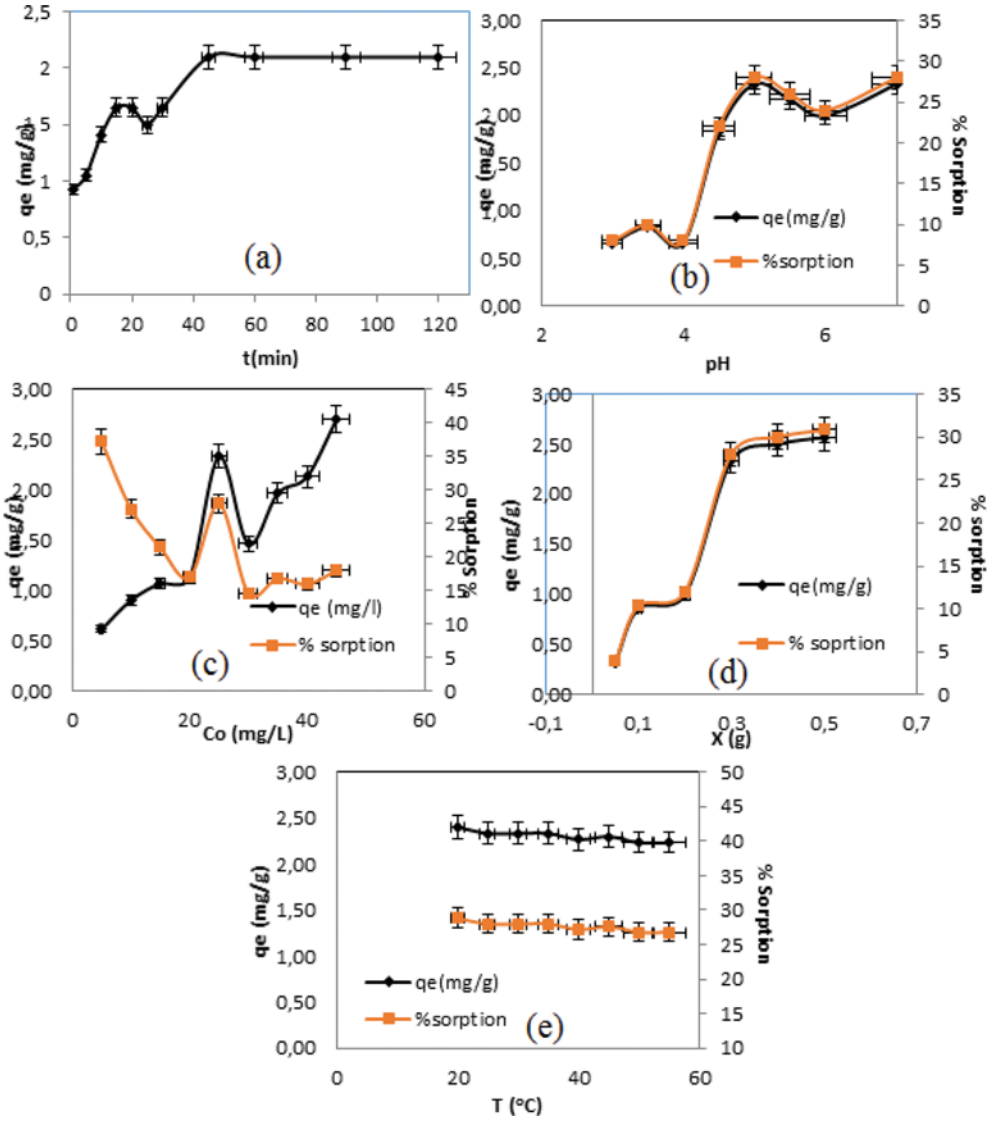

Fig. 8. Effect of various parameters for the removal of Zn(II) using peanut shell (a) contact time, (b) initial pH (c) initial concentration, (d) adsorbent dosage, (e) temperature.

2. Experimental Results

The analyses were performed for 120 minutes to determine the equilibrium duration of the sorption. Initial concentration (C_o) was selected as 25 mg/L to determine the equilibrium duration. Other ambient conditions were set as biosorbent dose (X)=0.3 g, shaking rate=125 rpm, pH=7. Resultant outcomes are presented in Fig. 8(a). The highest biosorbent capacity was achieved in 60 minutes. Later, significant changes were not observed; therefore, equilibrium duration was determined to be 60 minutes.

The pH is an significant controlling parameter in all adsorption processes. Previous adsorption tests revealed that pH had significant impacts on biosorption capacity [28,41,42]. Fig. 8(b) shows that the removal of metal ions increased with increasing pH. The pH effect on the adsorption of Zn(II) was researched with optimized experimental parameters by varying pH in the range 3.0-7.0. The adsorption of Zn(II) increased from 8.0 to 28% when the pH value of the solution was enhanced from 3.0 to 7.0.

The effect of initial metal concentration on the removal of Zn(II) is shown in Fig. 8(c). The adsorption efficiency of peanut shell highly depended on initial concentrations of metal ions. The con-

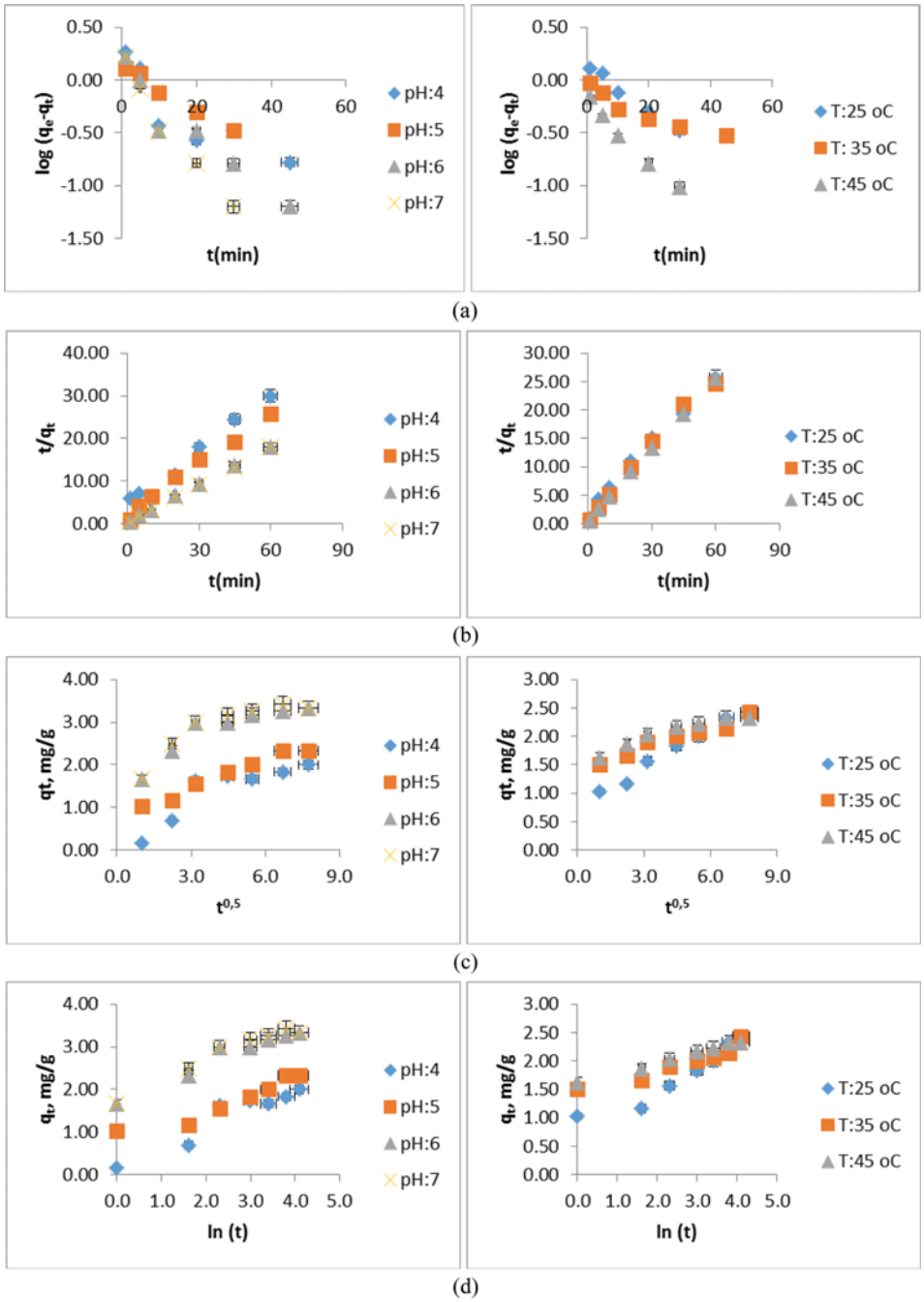

Fig. 9. Graphs of pseudo first-order kinetic models (a), pseudo second-order kinetic models (b), Weber-Morrisi (c) and Elovich for biosorption of Zn(II).

centration increased from 0.62 to 2.80 mg g^{-1} with an increase in the inlet concentration from 5 to 50 mg L^{-1} of Zn(II), respectively. The increase in the adsorption capacity was due to the availability of more amount of adsorbate per unit amount of adsorbent. The decrease in percentage adsorption of Zn(II) ions from their solutions was due to saturation of binding sites at particular concentration, and added metal ions remained in the solution. Such a case caused to have lower percentage adsorption [43].

Fig. 8(d) shows the effect of adsorbent dosage on the removal of Zn(II). The effect of sorbent dose was studied for doses between 0.05 g and 0.5 g. It was observed that the adsorption capacity increased rapidly with the increasing sorbent amounts. This result is expected because the increase of adsorbent dose leads to greater surface area.

Tests were carried out at temperatures in between 20-55 °C to determine the effects of temperature on biosorption (Fig. 8(e)). Biosorption capacity (q_e) varied between 2.40-2.23 mg/g and yield values varied between 29-27% at temperatures in between 20-55 °C. While some previous studies indicated linear increases in biosorption capacities with increasing temperatures [44], others indicated decreasing biosorption capacities with increasing temperatures [41]. Some others indicated that temperature did not have any significant effects on biosorption process [28]. Similarly, significant effects of temperature on biosorption system were not observed in this study.

3. Kinetic Studies

The mechanism of the adsorption process depends on the physical and chemical characteristics of the adsorbent [44]. Kinetic tests were carried out at pH levels of 4-5-6-7, temperature of 25-35-45 °C and for durations of 1-60 minutes (Fig. 9). Compliance of data with pseudo first-order (Fig. 9(a)) and pseudo second-order (Fig. 9(b)) kinetic models, inter-particle diffusion model (Fig. 9(c)) and Elovich model (Fig. 9(d)) was assessed. The pseudo first- and second-order rate constants (k_1 and k_2), amount of Zn(II) adsorbed by a unit biosorbent at equilibrium (q_e, exp), initial sorption rate (h; mg/g·dk), inter-particle (Weber-Morris model) diffusion rate constant k_i (mg/g·dk0.5) and α-β value for Elovich model are provided in Table 2.

The Zn(II) ion adsorption onto peanut shell was better defined by the pseudo second-order kinetic model for both initial pH, and temperature since the regression coefficients (R^2) of this model had the highest values (Table 2). This was also confirmed by the

Table 2. Kinetic constant (for pH and temperature)

pH	q_e (exp) mg/g	Pseudo-first-order			Pseudo-second-order			Weber-Morris		Elovich		
		k_1	q_e	R^2	k_2	q_e	R^2	k_{id}	R^2	α	β	R^2
4	2.00	0.048	0.84	0.73	0.463	2.29	0.97	0.246	0.77	0.719	2.201	0.90
5	2.33	0.048	0.735	0.98	0.078	2.501	0.98	0.211	0.96	3.902	2.861	0.91
6	3.33	0.067	0.809	0.91	0.157	3.408	0.99	0.222	0.79	28.70	2.423	0.94
7	3.33	0.107	0.703	0.96	0.194	3.453	0.99	0.226	0.76	28.70	2.340	0.94
T(C°)												
25	2.33	0.048	0.73	0.98	0.078	2.51	0.98	0.211	0.96	3.902	2.861	0.91
35	2.43	0.024	0.80	0.90	0.153	2.39	0.98	0.123	0.94	214.7	4.882	0.90
45	2.30	0.066	0.65	0.98	0.310	2.37	0.99	0.102	0.92	1365	5.527	0.99

Table 3. İsotherm parameters for the adsorption of Zn(II) ions (for C_o and x)

Model	Equation		Parameters	
			C_o	X (g)
Langmuir	$1/q_e=(1/Q_{max}\cdot K_a)\cdot(1/C_e)+(1/Q_{max})$	R^2	0.6086	0.6485
		Ka (L/mg)	33.27	17.768
		Q_{max} (mg/g)	0.1317	0.0071
		R_L	0.0012	0.0022
Freundlich	$\ln q_e=\ln K_F+(1/n)\cdot\ln C_e$	R^2	0.9173	0.8712
		K_F (L/g)	1.7306	1624.89
		1/n	0.5731	5.5693
Temkin	$q_e=B\ln A+B\ln C_e$	R^2	0.7857	0.9979
		A (L/g)	2.3183	25.415
		B	0.8087	6.7761
D-R	$\ln q_e=\ln q_{max}-\beta\varepsilon^2$	R^2	0.5497	0.8128
		β (mol^2/j^2)	−2.5149	190.09
		q_{max} (mg/g)	1.7672	12.3752
		E (kj/mol)	0.4458	0.051

values of qe from pseudo second-order kinetic equation that were very close to the experimental values (qexp e, mg/g) [42]. This means that in case of Zn(II) adsorption onto peanut shell, the rate restraint step of the adsorption involves chemical interactions (ion exchange and/or sharing of electrons) between Zn(II) ions from aqueous solution and functional groups of adsorbent [45].

4. The Isotherm Model

The Langmuir, Freundlich, Temkin and D-R models were applied to fit the equilibrium data. The isotherm study was carried out for concentration (C_o) and sorbent amount (x). The regression coefficients (R^2) and isotherm parameters are listed in Table 3.

As seen in Table 3, the highest R^2 value in isotherm studies was obtained from the Freundlich isotherm (R^2=0.9173) for the inlet concentration and from the Temkin isotherm (R^2=0.9979) for the sorbent amount. This indicates that the data was perfectly compatible with the models.

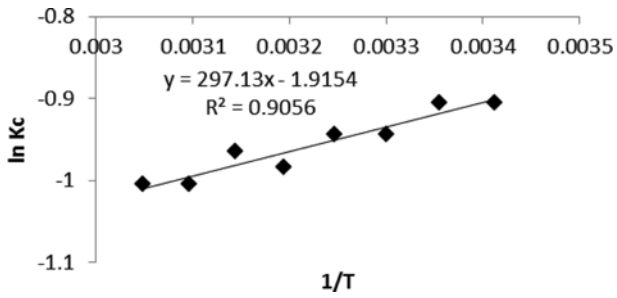

Fig. 10. Van t'Hoff graph of Zn(II) adsorption.

Table 4. Thermodynamic parameters

ΔH^o (kj/mol)	ΔS^o (kj/mol)	ΔG^o (kj/K·mol)							
		293 K	298 K	303 K	308 K	313 K	318 K	323 K	328 K
2.47	−0.015	2.20	2.42	2.37	2.41	2.56	2.54	2.69	2.74

Table 5. Adsorption capacity of several biosorbents for zinc adsorption

Biosorbent	q_{max} (mg/g)	T (C^o)	pH	Ref.
Waste activated sludge	408.3	55	6	[51]
Thiobacillus ferrooxidans (bacteria)	172.4	40	6	[52]
Aphanothece halophytica (bacteria)	133	25	7	[53]
Flammulina velutipes (fungus)	95.2	27	6	[54]
Thiobacillus ferrooxidans (bacteria)	82.6	25	6	[55]
Pseudomonas aeruginosa at18 (bacteria)	77.5	30	7	[56]
Bacillus cereus (bacteria)	66.6	30	6	[57]
Escherichia coli (bacteria)	65.9	28	7	[58]
Aerobic- anaerobic activated sludge	64.9	30	5	[59]
Inactivated Funalia Trogii (fungus)	54	25	6	[60]
Shewanella Putrefaciens (bacteria)	34	22	6.5	[61]
Azadirachta İndica bark	33.4	30	6	[62]
Sunflower Stalks	30.7	25	5	[63]
Maıze Stalks	30.3	24	7	[12]
Cashew Nut Shell	24.9	30	5	[64]
Cashew Peduncle	19.4	28	5	[65]
Sugar Beet Pulp	17.7	20	5.5	[66]
Tectona Grandis L.f. Leaves	16.4	30	5	[67]
Rice Husk Ash	14.3	30	5	[68]
Tea Factory Waste	14.2	25	4.2	[69]
Rice Bran	14.1	30	5	[70]
Papaya Wood	13.5	25	5	[71]
Gelidium (red algae)/ Algal Waste	13/7.1	20	5.3	[72]
Sawdust - Groundnut shells	10.9 -7.6	35	5.9	[73]
Hizikia Fusiformis (sea vegetable)	10.5	--	4	[74]
Wheat Hull	9	25	6.7	[75]
Coir	8.6	25	5.6	[76]
Coffee Residues	8	25	5	[77]
Banana peel- Orange peel	5.8-2.9	30	5	[78]
Peanut Shell	2.3	25	7	This study

In the Langmiur model, Q_{max} (mg/g) for concentration and sorbent amount were, respectively, calculated as 0.1317 mg/g and 0.0071 mg/g; R_L values, respectively, as 0.0012 and 0.0022 and Ka, respectively, as 33.27 L/mg and 17.768 L/mg.

The Freundlich constant (1/n) involves the adsorption density of the adsorbent. If $0.1<1/n\leq0.5$, adsorption is easy; if $0.5<1/n\leq1$, adsorption is difficult, and if $1/n>1$, adsorption is quite difficult [46]. For concentration and sorbent amount, it was 0.5731 and 5.5693, respectively.

In D-R model, adsorption energies (E) for concentration and sorbent amount were, respectively, calculated as 0.4458 kj/mol and 0.051 kj/mol; qmax values as 1.7672 mg/g and 12.3752 mg/g and β values as -2.5149 mol^2/j^2 and 190.09 mol^2/j^2. The E values of between 8-16 kj/mol indicate that sorption was mainly realized through ion exchange. An "E" value below 8 kj/mol indicates that sorption mechanism could be explained thorough physical interactions [47]. Here, E values were below 8 kj/mol, and such values defined that sorption could be explained with physical interactions.

5. Thermodynamics Studies

Fig. 10 shows a graph of ln K_c-1/T (van't Hoff graph) obtained at different temperatures. Thermodynamic parameters are given in Table 4. The negative values of Gibbs energies (ΔG^o) at various temperatures show that the biosorption process was spontaneous. Positive value indicates nonspontaneous biosorption, and a value equal to zero indicates biosorption equilibrium [48]. In this study, Gibbs energy (ΔG^o) values for Zn ions were identified as positive (+); thus it was identified that biosorption was nonspontaneous.

Positive values for biosorption enthalpy (ΔH^o) define that the system absorbed energy from surroundings (endothermic) [49] and negative values for ΔS^o indicate more regular state of metal ion over the biosorbent surface [50].

Table 5 shows the sorbents and removal capacities used for zinc removal.

6. ANN Performance

An alternative modeling technique, the artificial neural networks (ANN) approach, has been successfully applied to model the nonlinear relations peculiar to complex chemical processes such as adsorption [79].

This study demonstrated the use of artificial neural network (ANN) model for the evaluation of Zn(II) adsorption process with peanut shells. Fig. 11 shows the recommended optimum ANN type. The ANN consists of three layers: input, hidden, and output. The experimental variables (sorbent amount, initial concentration and initial pH) were used as the input to the constructed neural network to predict the adsorbed amounts of zinc. Training, validation and test data of the best forecaster ANNs model are presented in Fig. 12.

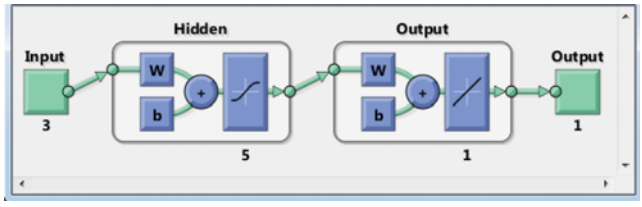

Fig. 11. Recommended ANN structure.

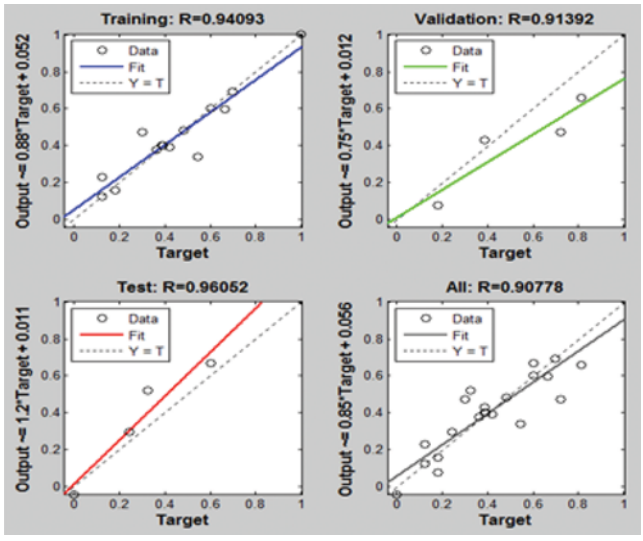

Fig. 12. Comparison of model predicted and target value of percent Zn(II) removal.

A relation between the estimation results of the designed ANN model and experimental data was established to evaluate the success of ANN modeling. The performance of the ANN can further be improved by normalizing the existing experimental data set. Therefore, the available data points were normalized to a certain level. Once the new data points were attained, the developed network was trained again by using these new data sets.

The high R^2 values prove that modeling the adsorption process with ANN was a satisfactory approach (R^2=training (0.94), validation (0.91), test (0.96)). The decision about the efficiency of ANN model is based on the maximization of R^2 value and reducing the MSE value of the testing set (1-20 neurons correspond to hidden layer) [80]. The minimum mean squared error (MSE) against the number of epochs for optimal ANN models (Fig. 13), showed that the method performance did not change significantly after 16 epochs. It can be seen from Fig. 13 that the network was successfully trained by using resilient backpropagation algorithm.

In Fig. 14, the experimental results and the predicted results

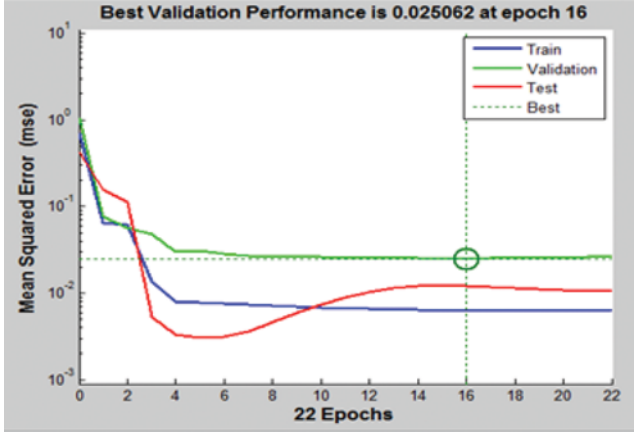

Fig. 13. MSE against the number of epochs for Zn(II).

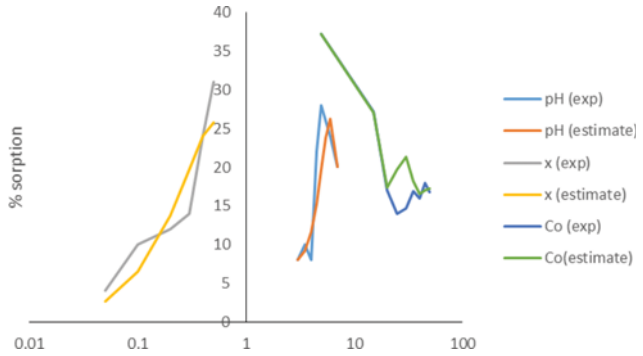

Fig. 14. Comparison of the experimental and predicted results by the model.

were compared (initial pH, sorbent amount "x" and initial concentration "C_o"). The experimental results and the predicted results by the model with the ANN were found to be highly compatible with each other.

CONCLUSIONS

Adsorption of Zn^{2+} ions in aqueous solutions to peanut shell was investigated. Based on batch adsorption experiments, an ANN model was also developed to predict Zn(II) removal efficiency of peanut shells used as a low cost adsorbent. The pseudo-first-order, pseudo-second-order, Weber-Morris and Elovich kinetic models were applied to test the experimental data. Zn(II) ions adsorption onto peanut shell was better defined by the pseudo-second-order kinetic model, for both initial pH, and temperature. The equilibrium data were evaluated using Langmuir, Freundlich, Temkin and D-R isotherms. The highest R^2 value in isotherm studies was obtained from Freundlich isotherm (R^2=0.9173) for inlet concentration and from Temkin isotherm (R^2=0.9979) for the sorbent amount. The Zn(II) removal efficiency was successfully described through the neural network. According to resilient backpropagation algorithm, the optimal number of neurons required for the hidden layer of the developed network was found to be 16. The high R^2 values prove that modeling the adsorption process using ANN is a satisfactory approach (R^2=training (0.94), test (0.96)). Both the results obtained by ANN and with the experimental design were compatible with each other.

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