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Artificial Neural Network (ANN) approach to copper biosorption process

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ABSTRACT

This paper demonstrates use of artificial neural network (ANN) model for the evaluation of copper biosorption process using black cumin. The experimental variables (temperature, biosorbent mass, initial copper concentration, initial pH) were used as the input to the constructed neural network to predict the adsorbed amounts of copper at any time as the output. The high R^2-values, 0.89 and 0.93 for training and testing data sets, respectively; between the network prediction and the corresponding experimental data prove that modeling the biosorption process using artificial neuron network is a satisfactory method. Thermodynamic parameters such as Gibbs free energy ($\Delta G°$), the enthalpy ($\Delta H°$) and the entropy change of sorption ($\Delta S°$) were also evaluated. It was found that the biosorption process was spontaneous, favorable and exothermic in nature. The equilibrium sorption of copper ions was determined from the Langmuir equation and found to be 16.13 mg/g at 293 K. A comparison between the model results and experimental data showed that the ANN model is able to predict the removal of copper using black cumin.

Keywords: artificial neural network (ANN), black cumin, copper, biosorption

Bakır biyosorpsiyon işlemine Yapay Sinir Ağı (ANN) yaklaşımı

ÖZ

Bu makale, çörek otu kullanılarak bakır biyosorpsiyon işleminin değerlendirilmesi için yapay sinir ağı (ANN) modelinin kullanımını göstermektedir. Deneysel değişkenler (sıcaklık, biyosorbent kütlesi, başlangıç bakır derişimi, başlangıç pH'ı) çıkış olarak, herhangi bir zamanda adsorplanan bakır miktarını tahmin etmek için kurulan sinir ağında girdi olarak kullanılmıştır. Ağ tahmini ve ilgili deneysel veriler arasındaki yüksek R^2-değerleri, eğitim ve test veri setleri için sırasıyla 0,89 ve 0,93, yapay nöron ağını kullanarak biyosorpsiyon işleminin modellemede yeterli bir yöntem olduğunu kanıtlamaktadır. Gibbs serbest enerji ($\Delta G°$), entalpi ($\Delta H°$) ve sorpsiyonun entropi değişimi ($\Delta S°$) gibi termodinamik parametreler de değerlendirildi. Biyosorpsiyon işleminin gerçekte kendiliğinden, istemli ve ekzotermik olduğu bulunmuştur. Bakır iyonunun denge sorpsiyonu, Langmuir denklemine göre belirlenmiştir ve 293 K'de 16,13 mg/g olarak bulunmuştur. Model sonuçları ve deneysel veriler arasındaki karşılalaştırma çörek otu kullanılarak bakırın giderilebileceğini göstermektedir.

Anahtar Kelimeler: yapay sinir ağı (ANN), çörek otu, bakır, biyosorpsiyon

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1. INTRODUCTION

Copper is a metallic element that is essential to human health. Copper can be found in many kinds of food, in drinking water and in air. Too little is unhealthy and too much can lead to copper poisoning. People that live in houses that still have copper plumbing are exposed to higher levels of copper than most people, because copper is released into their drinking water through corrosion of pipes. The current Environmental Protection Agency (EPA) drinking water standards has proposed a maximum contaminant level of 1.3 mg/L for copper [1]. Many conventional methods have been used to remove copper ions from aqueous solutions, including precipitation, ion-exchange, electrolysis, sorption, etc. Among these methods, the most promising process for removing copper ions from aqueous solutions is sorption. In recent years, there is a growing interest in the search of low-cost, easily available and environment friendly biomaterials suitable for the efficient removal of heavy metal ions. The physico-chemical phenomenon of metal biosorption, based on sorption, ion-exchange, complexation and/or microprecipitation, is relatively rapid and can be reversible [2].

In recent years, considerable attention has been focused on the removal of copper ions from aqueous solution using adsorbents derived from low-cost biomaterials. Several biosorbents, such as teak leaves powder [3], *Tectona grandis* L.f. leaves powder [4], *Ulva fasciata* sp. [5], *Enteromorpha prolifera* [2], dried yeast biomass [6], Cinnamomum camphora leaves powder [7], Spirulina platensis [8], cassava peel [9], red macroalgae [10], Lyngbya putealis [11], cashew nut shell [12], spent-grain [13], Uncaria gambir [14], have been reported to remove or recover copper from aqueous solutions, The black cumin, has been considered as a new biosorbent for removal of copper ions. However, there are only two studies on the removal of As (III) and arsenate (As (V)) from waste water [15] and the removal of lead from aqueous solutions [16] for the absorptive effect of black cumin. In present study, a sorption process was modeled, and was evaluated with a different perspective.

In the last decades an alternative modeling technique, artificial neural networks (ANN) approach, one of the well-known types of evolutionary computation methods, has been successfully applied to model the nonlinear relationships inherent in complex chemical processes such as adsorption [17–22]. ANN is an information-processing paradigm that is inspired by the way the human brain processes information [23]. The ability of an ANN to learn and generalize the behaviour of any complex and non-linear process makes it a powerful modelling tool.

ANN methodology does not require a standard experimental design to build the model. Hence, we can use ANN modeling technique to avoid experimental costs. Because of these reasons, in this study, an ANN model developed from experimental data was applied to predict relationship between experimental variables (temperature, biosorbent mass, initial copper concentration and initial pH) and the response variable (adsorbed copper amounts). In addition, equilibrium sorption isotherms and thermodynamics of sorption were also investigated.

2. EXPERIMENTAL

2.1. Material

A commercial pack of black cumin used as biosorbent was purchased from a local market in Kocaeli, Turkey. The black cumin was crushed, ground and kept in an oven at 373 K for 2 h for the removal of moisture, and then it was stored in desiccators. The chemical composition of black cumin on dry weight basis was: carbohydrate 15.57%, lipid 28.91%, fiber 21.98%, ash 4.00%, protein 22.00%, moisture 5.54%, Ca 0.36%, P 0.72%, Mg 0.25%, and the energy was 4.18 kcal/g [16].

A stock solution of copper (1.0 g/L) in deionized water were made from $Cu(NO_3)_2.2.1/2H_2O$. Copper working standard solutions in the range of 5–100 mg/L were prepared for use in the experiments by dilution of 1.0 g/L stock solution. All the chemicals used in the study were of analytical reagent grades. All the glassware materials were cleaned by soaking them in diluted HNO_3 (1 + 9) and were rinsed with distilled water prior to use.

2.2. Methods

Flame atomic absorption spectrophotometer (FAAS) with a deuterium arc background corrector (A Perkin Elmer Model AAnalyst 800) was used for the analysis. The hollow cathode lamp set at 324.8 nm was used for copper. The air-acetylene was selected as flame composition. pH-meter was used to measure the pH values of the solutions (Hanna pH 211 Microprocessor). The pH-meter was standardized with NBS buffers before each measurement. ARE model magnetic stirrer and Elektromag M815P model centrifuge device were used to biosorption experiments and solid-liquid separation, respectively. FTIR analyses were conducted with a Bruker Tensor 27 model FTIR spectrophotometer.

2.3. Batch Biosorption Study

Batch biosorption study was performed for the removal of copper ions from aqueous solutions using black cumin. Depending on the equilibrium time to copper biosorption

was studied in the temperature range of 293 to 323 K (pH: 5.60, biosorbent mass: 0.500 g, initial concentration of copper: 5 mg/L, initial solution volume: 250 mL). After each certain time interval, 2 mL solution was taken to determine copper concentration by FAAS.

The pH effect was investigated at pH range of 2.0–6.0 since copper precipitation as its hydroxide at a pH above 6.0. The pH was adjusted by appropriate amounts of HCl solution (0.1 N) added to the solution. According to preliminary experiments, equilibrium time and initial solution volume were selected as 60 min and 50 mL, respectively. To analyze copper ions remaining in solution, samples were centrifuged 5 min at 1000 rpm for solid/liquid seperation. Copper ions in solution were determined using FAAS. Calibration graph was linear for the range of 1–5 mg/L of standard copper solutions and correlation coefficient was found as 0.9994. The adsorbed amounts of copper (q_e) were calculated as the difference between the initial and equilibrium copper concentrations:

$$q_e = (C_o - C_e)x\frac{V}{m} \quad (1)$$

where, C_o and C_e are the initial and the equilibrium concentrations of copper (mg/L), V is the volume of copper solution (L), and m is the mass of black cumin sample used (g).

2.4. Artificial Neural Network (ANN)

ANN, which consist of an input layer, hidden layers and one output layer, are mathematical models used for computation. They are usually used to model complex relationships between inputs and outputs or to find patterns in data. An ANN is an adaptive system having the ability to learn from existing data and adopt to map a set of input parameters into a set of output parameters, without knowing the intricate relationship among them. In literature, one can see many ANN models and architectures that have been used in engineering applications to model or approximate properties. The most widely used one is the multi-layer perceptron (MLP) [24].

A MLP based feed-forward ANN, which makes use of the Marquardt-Levenberg learning algorithm, was applied for modeling. The performance of the ANN model was statically measured by root mean squared error (RMSE) in Eq. 2 and the coefficient of determination (R^2) in Eq. 3.

$$RMSE = \left(\frac{1}{n}\sum_{i=1}^{n}(q_{e,pred} - q_{e,\exp})^2\right)^{\frac{1}{2}} \quad (2)$$

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(q_{e,pred} - q_{e,\exp})^2}{\sum_{i=1}^{n}(q_{e,\exp} - \overline{q}_{e,\exp})^2} \quad (3)$$

where n is the number of points, $q_{e,pred}$ and $q_{e,exp}$ is the predicted and experimental q_e,-values, respectively, and is the average of the experimental values.

3. RESULTS AND DISCUSSION

3.1. Equilibrium Sorption Study

In the sorption systems, the equilibrium sorption isotherms are very important from fundamental point of view. Sorption isotherms give the relationship between the concentration and the amount of matter adsorbed by the adsorbent at constant temperature. It is critical in optimizing the use of adsorbent. The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the sorption mechanism and the surface properties and affinity of the sorbent [6]. The most frequently employed models, Freundlich and Langmuir isotherm models were used in this study.

The sorption experiments for isotherms were carried out in the temperature of 293 K at pH 5.60, for a biosorbent mass of 0.100 g, initial concentration range of copper ions of 20–100 mg/L and initial solution volume of 50 mL.

3.1.1. Langmuir sorption isotherm

The Langmuir isotherm model is valid for monolayer sorption onto a homogeneous surface and it is represented by the following equation:

$$C_e/q_e = (1/K_L q_m) + (1/q_m)C_e \quad (4)$$

where C_e is copper ion concentration (mg/L) at equilibrium, q_e is amount adsorbed (mg/g) at equilibrium time, and q_m is monolayer biosorption capacity of adsorbent (mg/g), and K_L is Langmuir biosorption constant (L/mg) relating free energy of sorption. The plot of C_e/q_e versus C_e is linear.

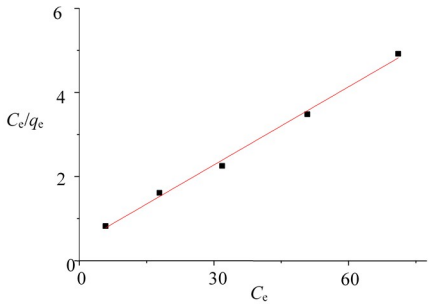

Figure 1. Langmuir isotherm plots for biosorption of copper ions onto black cumin

3.1.2. Freundlich sorption isotherm

The Freundlich equation is purely empirical based on sorption on a heterogeneous surface. It is commonly described by the following equation:

$$\log q_e = \log K_F + 1/n \log C_e \quad (5)$$

where C_e is equilibrium concentration (mg/L), q_e is amount of metal adsorbed (mg/g) at equilibrium time, and K_F and n are Freundlich constants. n gives an indication of the favourability and K_F the capacity of adsorbent. The Freundlich isotherm constants K_F and $1/n$ are evaluated from the intercept and the slope respectively, of the linear plot of $\log q_e$ versus $\log C_e$.

Figures 1 and 2 indicate the linear relationship between the amounts of copper ions sorbed (mg) per unit mass of black cumin (g) against the concentration of copper ions remaining in solution (mg/L).

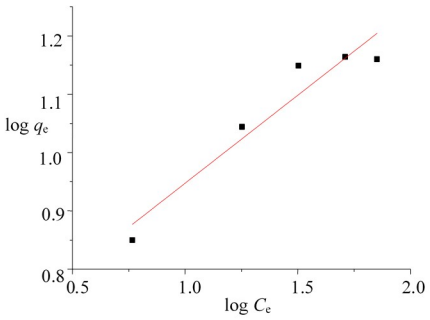

Figure 2. Freundlich isotherm plots for biosorption of copper ions onto black cumin

The comparison of the Langmuir and Freundlich adsorption constants obtained from adsorption isotherms of copper ions at 293 K was given in Table 1. The coefficients of correlation R^2 indicate that the Langmuir isotherm fitted the adsorption data of copper on black cumin better than the Freundlich isotherm. As shown from Table 1, the maximum biosorption capacities (q_m) 16.13 mg/g.

The removal of copper and the adsorbed amounts of copper (q_e) were approximately 70% and 7.0 mg/g, respectively, in the sorption experiments carried out in the temperature of 293 K at pH 5.60, for a biosorbent mass of 0.100 g, initial concentration range of copper ions of 20 mg/L and initial solution volume of 50 mL.

Table 1. The comparison of the Langmuir and Freundlich adsorption constants

Ion	Langmuir constants			Freundlich constants		
	q_m	K_L	R^2	n	K_F	R^2
Copper	16.13	0.146	0.994	1.331	4.426	0.897

3.2. Sorption thermodynamics

In this study, an alternative use of black cumin as untreated sorbents was also proposed for the removal of copper ions from aqueous solutions. The biosorption experiments were carried out at different temperatures (293–323 K) in a thermo-controlled magnetic shaker (Figure 3). The results showed that the adsorbed amounts of copper (q_e) increased up to 60 min with increases in contact time as temperature decreased, and then qe did not change. Biosorption equilibrium time was observed in 60 min.

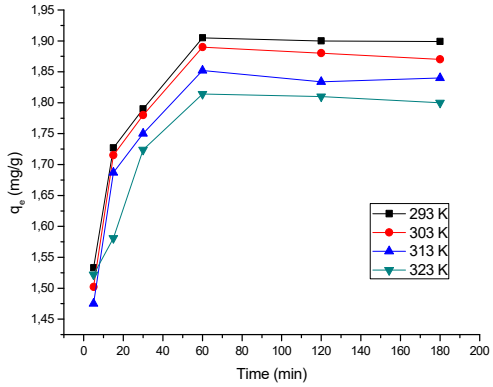

Figure 3. The contact time dependence of copper biosorption at different temperatures

The thermodynamic parameters, including the free energy changes ($\Delta G°$), the standard enthalpy changes ($\Delta H°$) and the standard entropy changes ($\Delta S°$) related to the adsorption process, can be used to understand the adsorption mechanism. For a thermodynamic study, the standard enthalpy change was estimated by applying the Van't Hoff equation:

$$\ln K_d = -\frac{\Delta G^o}{RT} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad (6)$$

$$K_d = \frac{C_o - C_e}{C_e} x \frac{V}{W} = \frac{q_e}{C_e} \quad (7)$$

where $\Delta H°$ and $\Delta S°$ are changes in standard enthalpy (kJ/mol) and standard entropy (J/mol.K) of adsorption, respectively. The values of $\Delta H°$ and $\Delta S°$ can be calculated from the slopes and intercepts of the linear variation of ln K_d with reciprocal temperature, $1/T$. T is absolute temperature (K), K_d is distribution coefficient of metal ions between aqueous phase and solid phase, and R is gas constant (8.314 J/mol.K). The free energy change, $\Delta G°$, of adsorption is calculated using the following equation:

$$\Delta G° = \Delta H° - T\Delta S° \quad (8)$$

The thermodynamics of biosorption of the copper onto the black cumin biosorbent was evaluated using Eq. 8. The negative enthalpy, $\Delta H°$ (–5.17 kJ/mol) and negative free energy, ΔG^o (–1.35, –1.22, –1.08, –0.42 kJ/mol, at temperatures 293, 303, 313 and 323 K, respectively) reflect the exothermic, feasible and spontaneous nature of biosorption, respectively. In addition to, $\Delta G°$ values at all temperatures were negative and increased as temperature increase, which suggests that the process was spontaneous in nature and the spontaneity decreases with rising temperature.

In addition, the value of $\Delta S°$ (–13.05 J/mol.K) was found to be negative due to the exchange of metal ions with more mobile ions present on the active sites of the biosorbent, which would cause a decrease in entropy during the adsorption process [14,25]. The negative value of $\Delta S°$ suggests that the adsorption process is enthalpy driven [21]. The thermodynamic parameters thus indicate that this adsorption process can be used for the removal of copper ions by black cumin.

3.3. FTIR Analysis

FTIR spectroscopy was used to investigate the functional groups on the surface of the black cumin. In Figure 4, the strong band in the region 3500–3000 cm^{-1} indicates the existence of free and intermolecular bonded OH groups. The peaks assigned to aliphatic C–H groups were observed at 2921–2852 cm^{-1}. A peak at 1715 cm^{-1} represents the stretching of carboxyl groups associated with carboxylic acids. The black cumin's surface has several functional groups, namely hydroxyl, carboxyl, carboxylate, etc., which are able to attach to the metal ions [16, 26].

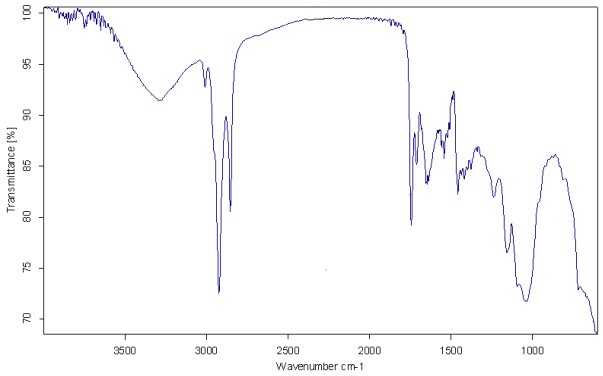

Figure 4. The FTIR spectrum of black cumin [26]

3.4. ANN Modeling

Copper biosorption process was modeled from experimental data using ANN. The network was trained using experimental results obtained at four variables such as temperature, biosorbent mass, initial copper concentration and initial pH. Different back-propagation (BP) algorithms and various topologies (from 2 to 24 hidden neurons) were examined to select the best suited BP algorithm. Decision on the optimum topology given Table 3 was based on the Marquardt-Levenberg learning algorithm with a minimum mean squared error (MSE). The network consists of an input layer, two hidden layers and an output layer. The inputs for the network include biosorbent mass (g), C_o (mg/L), initial pH and temperature; output is the amount of q_e (mg/g). There are many continuously differentiable activation functions in literature but the tangent sigmoid transfer (tansig) and nonlinear function (logsig) at hidden layers were preferred in this study. The linear activation function is also used as the output activation function. The algorithm used to train ANN in this study is the Marquardt-Levenberg and the number of the training data is 30. Marquardt recommendation is used to the choice of the damping parameter in the algorithm. Each topology was repeated ten times to avoid random correlation due to the random initialization of the weights. After repeated trails, an ANN model with two layers including 12 hidden neurons produced the best performance and its parameters variation was determined. Validation error is used for algorithm stopping criteria. In order to avoid network memorizing problem, firstly a regression model was built by using experimental data to increase the number of data (i.e., 1000), then the data obtained was splitted into 3 pieces (60% for training, 20% for validation, 20% for test). Lastly, over-training was prevented by finalizing the training process as the result of the cross-validation. We have made and acquired the success rates 87.10% for training, 89.30% for validation, and 92.75% for test data. Table 2 and Table 3 illustrate the data normalized between zero and one used to train ANN and the performance of the ANN, respectively.

Table 2. The range of the data

Parameters	Training Data		Validation Data		Testing Data	
	Min	Max	Min	Max	Min	Max
T (K)	293	323	293	323	303	323
Biosorbent mass (g)	0.100	0.450	0.100	0.450	0.150	0.400
C_o (mg/L)	5.0	100.0	5.0	100.0	5.0	100.0
pH	2.0	6.0	3.0	6.0	2.0	6.0

A relationship between the estimation results of the designed ANN model and experimental data has been normally establish to evaluate the success of ANN modeling used as an effective tool [27]. A regression analysis of the network response between ANN outputs (predicted, q_e) and the corresponding targets (experimental, q_e) shows high determination coefficients (R^2) of 0.89 and 0.93 for training and testing data sets, respectively. The high R^2-values between the network prediction and the corresponding experimental data prove that modeling the biosorption process using ANN is a satisfactory method.

Table 3. Statistical measures and performance of Marquardt-Levenberg learning algorithm

The best architecture	RMSE		R^2	
	Training Validation	Testing	Training Validation	Testing
4-7-5-1	0.051 0.053	0.035	0.89 0.87	0.93

The experimental results and the predicted results by the model were given in Figure 5 for comparison. The experimental results and the predicted results by the model with the ANN were found to be highly compatible with each other.

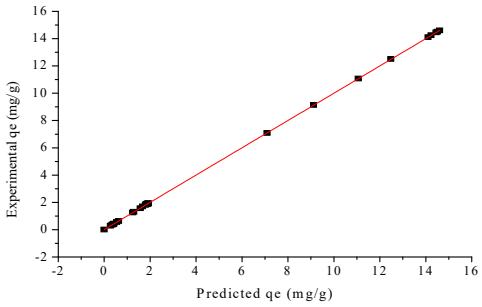

Figure 5. Comparison of the experimental and predicted results by the model.

3.5. Comparison of black cumin and various biosorbents

There have been many reports on the biosorption of copper ions. Different materials have been investigated as biosorbents for the removal of copper. Table 4 shows the biosorption capacity of copper, qm on other biomaterials in the literature. Black cumin can be considerable potential for the removal of copper ions from aqueous solution.

Table 4. Comparison of maximum adsorption capacities of copper ions on some biosorbent

Biosorbent	q_m, mg/g	References
Teak leaves powder	95.40	[3]
Tectona grandis L.f. leaves powder	15.43	[4]
Ulva fasciata sp.	26.88	[5]
Spent-grain	10.47	[13]
Enteromorpha prolifera	57.14	[2]
Dried yeast biomass	2.59	[6]
Cinnamomum camphora leaves powder	16.76	[7]
Spirulina platensis	67.93	[8]
Cassava peel	41.77	[9]
Red macroalgae	105.20	[10]
Lyngbya putealis	28.17	[11]
Cashew nut shell	20.00	[12]
Uncaria gambir	9.95	[14]
Black cumin	16.13	This study

4. CONCLUSION

ANN model was developed from experimental data to predict the relationship between four experimental variables (temperature, biosorbent mass, initial copper concentration and initial pH) and a response variable (q_e). The high R^2-values, 0.89 and 0.93 for training and testing data sets, respectively; between the ANN models predicted results and the experimental data prove that modeling the biosorption process using ANN is a satisfactory method. Equilibrium data fitted very well in the Langmuir isotherm equation confirming the monolayer biosorption capacity of copper ions onto black cumin with a monolayer biosorption capacity of 16.13 mg/g at 293 K in pH 5.60 and biosorbent mass 0.100 g within 60 min-contact. Thermodynamic parameters indicated that the biosorption process was spontaneous, favorable and exothermic. Thus, it was proposed an alternative use of black cumin, without any treatment or any other modification for the removal of copper ions from aqueous solutions as an eco-friendly process.

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