Bioresource Technology 112 (2012) 111–115

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Comparison of the results of response surface methodology and artificial neural network for the biosorption of lead using black cumin

Deniz Bingöl [a,*], Merve Hercan [a], Sermin Elevli [b], Erdal Kılıç [c]

[a] Kocaeli University, Chemistry Dept., Kocaeli, Turkey
[b] Ondokuz Mayis University, Industrial Eng. Dept., Samsun, Turkey
[c] Ondokuz Mayis University, Computer Eng. Dept., Samsun, Turkey

ARTICLE INFO

Article history:
Received 11 January 2012
Received in revised form 15 February 2012
Accepted 17 February 2012
Available online 24 February 2012

Keywords:
Response surface methodology (*RSM*)
Artificial neural network (*ANN*)
Black cumin
Lead removal
Biosorption

ABSTRACT

In this study, Response Surface Methodology (*RSM*) and Artificial Neural Network (*ANN*) were employed to develop an approach for the evaluation of heavy metal biosorption process. A batch sorption process was performed using *Nigella sativa* seeds (black cumin), a novel and natural biosorbent, to remove lead ions from aqueous solutions. The effects of process variables which are pH, biosorbent mass, and temperature, on the sorbed amount of lead were investigated through two-levels, three-factors central composite design (*CCD*). Same design was also utilized to obtain a training set for *ANN*. The results of two methodologies were compared for their predictive capabilities in terms of the coefficient of determination-R^2 and root mean square error-*RMSE* based on the validation data set. The results showed that the *ANN* model is much more accurate in prediction as compared to *CCD*.

1. Introduction

Lead and lead compounds are generally toxic pollutants. Lead(II) salts and organic lead compounds are ecotoxicologically very harmful. Lead has the most damaging effects on human health by accumulating in organisms, sediments and sludge (http://www.lenntech.com/Periodic-chart-elements/Pb-en.htm). The current Environmental Protection Agency (*EPA*) and World Health Organization (*WHO*) drinking water standards for lead are 50 and 10 μg/L, respectively. The *EPA* standard for lead in wastewater is also 500 μg/L (Gupta and Rastogi, 2008; Shao et al., 2011). Lead can enter the human body through uptake of food (65%), water (20%), and air (15%) (http://www.lenntech.com/Periodic-chart-elements/Pb-en.htm); therefore, it must be removed before discharge. Many conventional methods have been used to remove metal ions from aqueous solutions, including oxidation, reduction, precipitation, membrane filtration, ion exchange, and sorption. Among these methods, the most promising process for removing heavy metals from aqueous solutions is sorption (Xu et al., 2008). In recent years, greater attention has been gained by biomaterials. Low-cost adsorbents obtained from plant waste have been reported to remove or recover heavy metals from aqueous solutions (Wan Ngah and Hanafiah, 2008; Shao et al., 2011). The seeds of the *Nigella sativa* plant, frequently called kalajira or black cumin, has been considered as a new biosorbent (http://www.en.wikipedia.org/wiki/Nigella_sativa). Black cumin which is an annual species of the family *Ranunculaceae*, is small and black and possesses an aromatic odor and taste. Black cumin has been extensively investigated in recent years and used in folk medicine as a natural remedy for a number of diseases such as asthma, hypertension, diabetes, inflammation, cough, eczema, fever and gastrointestinal disturbances (Suresh Kumar et al., 2010). However, there has been only one study of the absorptive effect of black cumin, although it has been studied for the removal of As (III) and arsenate (As (V)) from waste water (El-Said et al., 2009).

In recent years, multivariate statistical techniques have been preferred to identify the optimal combination of factors and interactions among factors, which are not possible to identify using the univariate method. In addition, these techniques are very useful tools to reduce the time and cost of studies. The experimental design involves estimation of the coefficients in a mathematical model, predicting the response, and checking the adequacy of the model. The most commonly used designs to determine response surfaces are factorial designs and the more complex response surface methodology (*RSM*) (Montgomery, 2008). In *CCD* which is one of the *RSM* tools, the response function-f largely depends on the nature of the relationship between the response and the independent variables. The response model may be expressed as follows:

$$y = f(X_1, X_2, X_3, \ldots, X_n) \pm \varepsilon \quad (1)$$

* Corresponding author. Tel.: +90 2623032030; fax: +90 2623032003.
E-mail addresses: deniz.bingol@kocaeli.edu.tr, denizbingol1@gmail.com (D. Bingöl).

0960-8524/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2012.02.084

where y is the response, f is the response function, X_i is the independent variables, and ε is the experimental error. *RSM* aims at approximating f by a suitable polynomial in some region of the independent process variables (Singh et al., 2010).

Although multivariate statistical techniques have been widely studied by many researchers for the optimization of various processes (Ferreira et al., 2007a, 2007b, 2007c; Bezerra et al., 2008; Stalikas et al., 2009), there isn't any study in the literature on response surface modeling of lead removal from aqueous solution by black cumin using an experimental design technique.

Recently an alternative modeling technique, artificial neural networks (*ANN*), have been used for representing non-linear functional relationships between variables. The ability of an *ANN* to learn and generalize the behavior of any complex and non-linear process makes it a powerful modeling tool. In the past, *ANN*s have been successfully used to model the biosorption of Pb(II) by Antep pistachio (*Pistacia Vera* L.) shells (Yetilmezsoy and Demirel, 2008), the removal of Laneset Red G on Chara contraria (Çelekli and Geyik, 2011), the biodegradation process (Huang et al., 2011), a full-scale waste water treatment plant (Lee et al., 2011) and the removal efficiency of Lanaset Red G on walnut husk (Çelekli et al., 2012).

Although there is already a considerable amount of research applied to different areas; such as modeling of extrusion process (Shihani et al., 2006), fermentation media optimization (Desai et al., 2008), modeling and optimization of heterogeneous photofenton process (Kasiri et al., 2008), modeling of a microwave-assisted extraction method (Moghaddam and Khajeh, 2011), by using both *RSM* and *ANN* techniques in the literature, there is only a few studies on the adsorption (Ranjan et al., 2011; Geyikçi et al., 2012). Hence, the main motivation behind this study is to develop an approach for the evaluation of heavy metal biosorption process by using both *RSM* and *ANN* techniques.

In this study, two-levels, three-factors *CCD* and a four-layer *ANN* models were developed to predict the relationship between experimental variables (pH, biosorbent mass and temperature) and response variable (sorbed amounts of lead). The other parts of the paper are organized as follows. The experimental procedure has been presented in Section 2, analysis of the experimental data and comparison of the results has been given in Section 3, and finally conclusion and suggestion have been presented.

2. Experimental

2.1. Material

Black cumin was used as a biosorbent. A commercial pack of black cumin was purchased from a local market in Kocaeli, Turkiye. The black cumin was crushed, ground and kept in an oven at 100 °C 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%, Ca0.36%, P 0.72% and Mg 0.25%. The energy was 4.18 kcal/g.

Stock solutions of 1000 mg/L lead in deionized water were made from $Pb(NO_3)_2$. A total of 10–20 mg/L lead working standard solutions were prepared for use in the experiments by dilution of 1000 mg/L stock solutions. 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. Analytical methods

A *Perkin Elmer Model AAnalyst 800* flame atomic absorption spectrophotometer (*FAAS*), fitted with a deuterium arc background corrector, was used for the analysis. The hollow cathode lamp for lead was set at 283.3 nm. The flame composition was air–acetylene and applied conditions were selected from the manufacture's method. A *Hanna pH 211 Microprocessor* pH-meter was used to adjust the pH values of the solutions. The pH-meter was standardized with *NBS* buffers before each measurement. Spectroscopic studies were conducted with a *Bruker Tensor 27* model FTIR spectrophotometer.

2.3. Batch biosorption studies

Batch experiments were performed for the removal of lead ions from aqueous solutions using black cumin in contact with the lead solutions. The equilibrium time dependence of lead biosorption was studied in the temperature range of 20 to 50 °C at pH 5, for a biosorbent mass of 500.0 mg, an initial concentration of lead of 20 mg/L and initial solution volume of 250 mL.

For lead, the effect of pH was studied in the range of pH 2–6 because lead occurs predominantly as Pb(II) species up to pH∼6.0 in aqueous solutions (Pavan et al., 2008; Singh et al., 2010; Xu et al., 2008). The equilibrium time (60 min), the initial solution volume (50 mL) and the initial lead concentration (20 mg/L) were selected on the basis of the results obtained for preliminary experiments. The equilibrated samples were taken out, and the aqueous solution phase was separated from the sorbent using a centrifuge. The residual concentrations of lead ions in solution were then directly determined using the FAAS. The absorbance was linear for the range of 5–20 mg/L of standard lead. The correlation coefficient was found to be 0.9997. The sorbed amounts of lead (q) were calculated as the difference between the initial and equilibrium metal concentrations:

$$q = (C_0 - C_e)\frac{V}{W} \quad (2)$$

where, C_0 and C_e are the initial and equilibrium liquid-phase concentrations of lead (mg/L), V is the volume of lead solution (L), and W is the mass of black cumin sample used (g). This equation represents the material mass balance at equilibrium.

3. Results and discussions

3.1. Modeling of biosorption process

3.1.1. Central composite design

CCD was used to understand the influence of the experimental factors and their interactions on the sorbed amount of lead (q) and to make predictions for different input values. Tests were performed to investigate the factors affecting the sorbed amount of lead on the black cumin.

The levels of the experimental factors and the design matrix which was also used as training set for *ANN* are given in Table 1. The *CCD* had six axial points ($\alpha = 1.68$), eight factorial (2^3), and six center points, all in two replicates, resulting in a total of 20 experiments used to optimize the chosen variables for the q. Experiments were performed in a random order, according to the below experimental plan to avoid systematic errors.

The experimental data was processed using *Minitab 16* Statistical Software. As can be seen from Table 2, some of the linear (X_1, X_2), square (X_1^2, X_2^2), and interaction coefficients (X_1X_3) were found as significant terms at the 5% probability level for the response q.

The biosorbent mass represented the most significant effect on q at the 5% significance level. The sorbed amount decreased due to a negative coefficient, for which biosorbent mass had a negative effect. The sorbed amount of lead decreased with the increase in biosorbent mass. The decrease in the sorbed amount of lead with the increasing biosorbent mass, as noted by Hasan et al. (2009), was due to a split in the flux or the concentration gradient between the lead concentration in the solution and the lead concentration

Table 1
Experimental data set for CCD and ANN.

Factors	Symbols	Levels of factors				
		−α (−1.68)	−1	0	+1	+α (+1.68)
Initial pH	X_1	2.0	2.8	4.0	5.2	6.0
Biosorbent mass, m (mg)	X_2	100.0	181.1	300.0	418.9	500.0
Temperature, T (°C)	X_3	20	26	35	44	50
Run	Actual and coded levels of variables					q (mg/g)
	pH (X_1)	m (mg) (X_2)		T (°C) (X_3)		
1	2.8(−1)	181.1(−1)		26(−1)		4.5464
2	5.2(+1)	181.1(−1)		26(−1)		4.9229
3	2.8(−1)	418.9(+1)		26(−1)		2.0129
4	5.2(+1)	418.9(+1)		26(−1)		2.0217
5	2.8(−1)	181.1(−1)		44(+1)		3.8535
6	5.2(+1)	181.1(−1)		44(+1)		2.1410
7	2.8(−1)	418.9(+1)		44(+1)		1.5610
8	5.2(+1)	418.9(+1)		44(+1)		0.8068
9	2.0(−1.68)	300.0(0)		35(0)		0.2567
10	6.0(+1.68)	300.0(0)		35(0)		2.6126
11	4.0(0)	100.0(−1.68)		35(0)		7.8453
12	4.0(0)	500.0(+1.68)		35(0)		1.4195
13	4.0(0)	300.0(0)		20(−1.68)		2.4279
14	4.0(0)	300.0(0)		50(+1.68)		1.8032
15	4.0(0)	300.0(0)		35(0)		2.6071

Table 2
Estimated coefficients for q (mg/g) at coded units.

Term	Coefficients	Standard error	T-value	P-value
Constant	2.7954	3.91198	0.715	0.480
pH (X_1)	3.5078	0.92684	3.785	0.001
m (X_2)	−51.9528	8.65856	−6.000	0.000
T (X_3)	0.1769	0.12991	1.362	0.183
pH∗pH (X_1^2)	−0.2965	0.08428	−3.518	0.001
m∗m (X_2^2)	50.2900	8.42802	5.967	0.000
T∗T (X_3^2)	−0.0022	0.00150	−1.499	0.144
pH∗m (X_1X_2)	0.5220	1.13118	0.461	0.648
pH∗T (X_1X_3)	−0.0336	0.01508	−2.228	0.033
m∗T (X_2X_3)	0.2131	0.15082	1.413	0.168
S = 0.6399 R-Sq = 87.95% R-Sq(adj)= 84.34%				
Values for the reduced model with significant coefficients.				
S = 0.2351 R-*Sq* = 97.97% R-*Sq(adj)*= 97.60% PRESS = 2.7220				

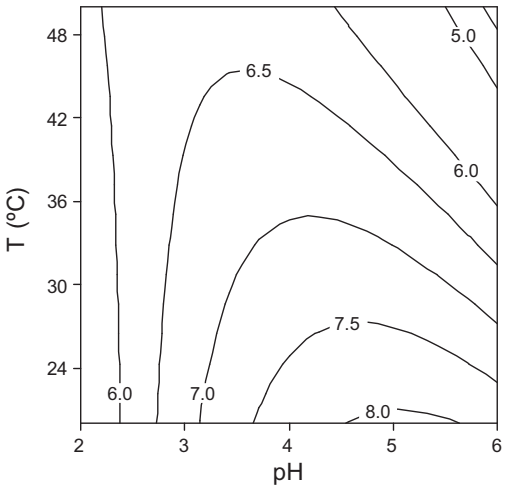

Fig. 1. The contour plot (hold value, biosorbent mass: 100.0 mg).

on the surface of the biosorbent, which finally reduced the sorbed amount of lead into the unit weight of biosorbent.

According to the reduced model which includes only the terms which were found as significant at 5% level in Table 2, the relationship between the sorbed amount of lead and the factors was obtained with coded variables as follows:

$$q(mg/g) = 2.8498 + 3.5641X_1 - 43.1600X_2 + 0.0836X_3 - 0.2840X_1^2 + 51.5442X_2^2 - 0.0336X_1X_3 \quad (3)$$

High correlation among the observed experimental results and the predicted values by using Eq. (6) demonstrates that the model is well fitted, considering the determination coefficient (R^2-adj = 0.9760), and only 2.40% (residuals) of total variation was not explained by the model.

Fig. 1 shows the combined effect of pH and temperature. It is clear from the figure that the biosorption improved as pH varied from 2.0 to 5.0. The sorbed amount of lead increased with the increase of pH due to the negative surface charge of black cumin at high pH values. In this case, electrostatic interactions and the adsorption of lead increased. The low adsorption that takes place in acidic solutions can be due to the competition between hydrogen and lead ions for active sites on the black cumin surface. At pH values higher than 5.0, the hydrolysis of lead ions could take place, leading to a decrease in the biosorption process, as already observed in other biosorbents containing carboxylic acids (Pavan et al., 2008; Xu et al., 2008). An increase in pH shows an increase in adsorption up to 5, at which the surface of black cumin is negatively charged and the sorbate species are also still positively charged. The increasing electrostatic attraction between positively charged sorbate species (Pb^{2+} and $Pb(OH)^+$) and negative surface sites will lead to increased adsorption of Pb(II) on black cumin (Hasan et al., 2009).

At high temperatures, the sorbed lead amount decreased with the increase of temperature, at a constant biosorbent mass of 0.100 g. The increase in uptake with decreasing temperature can be explained because the decrease of temperatures favors the sorbate transport within the pores of the sorbent (Hasan et al., 2009). By using a response optimizer, the predicted q, i.e., 8.08 mg/g, was obtained at pH 5.1, temperature 20 °C, and a biosorbent mass of 100.0 mg.

3.1.2. Artificial neural network

There are several *ANN* models such as feed-forward, Multi-Layer Perceptron (*MLP*) and the Radial Basis Function (*RBF*) have been used in engineering applications to model or approximate properties (Haykin, 1999). In this study a $3 \times 5 \times 9 \times 1$ feed-forward *MLP* (with tangent sigmoid transfer function (tansig) at hidden layers and a nonlinear function (logsig) at output layer were used as *ANN* network to predict the sorbed amount of lead (q) from aqueous solutions using biosorption process. The input- output patterns required for training were obtained from biosorption experimentation planned through *CCD*.

Different back-propagation (*BP*) algorithms were compared to select the best suited BP algorithm. The Marquardt–Levenberg learning algorithm with a minimum mean squared error (*MSE*) was found as the best. The *ANN* model and its parameters variation were determined based on the minimum value of the *MSE* of the training and prediction set. The training parameters are used as number of input nodes: 3, number of hidden neurons: 14, number of output node: 1, learning rule: Levenberg–Marquardt, number of epochs: 3500, error goal: 0.0001, Mu: 0.01 in this investigation.

3.1.3. Comparison of RSM and ANN models

RSM and *ANN* are modeling tools able to solve linear and nonlinear multivariate regression problems (Khayet et al., 2011). *RSM* and *ANN* models were used to investigate the biosorption of lead onto black cumin. At this stage, comparison criteria are needed to quantify the difference between values produced by the models and the actual values. To evaluate the performance of the constructed *ANN* and *RSM*, two statistical estimators which are the root mean squared error (*RMSE*) in Eq. (4) and coefficient of determination (R^2) in Eq. (5) were used:

$$RMSE = \left(\frac{1}{n}\sum_{i=1}^{n}(y_i - y_{di})^2\right)^{\frac{1}{2}} \quad (4)$$

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(y_i - y_{di})^2}{\sum_{i=1}^{n}(y_{di} - y_m)^2} \quad (5)$$

where n is the number of points, y_i is the predicted value, y_{di} is the actual value, and y_m is the average of the actual values.

For the validation purpose, experiments were conducted for 11 new trials, consisting of combinations of experimental factors, which do not belong to the training data set. The actual and predicted values are presented in Table 3.

The *RMSE* for *CCD* and *ANN* was found as 1.167 and 0.557. These results indicate that the *RSM*s prediction has a greater deviation than the *ANN*s prediction. R^2 values for *CCD* and *ANN* were found as 0.812 and 0.957 respectively. R^2 provides a measure of how well future outcomes are likely to be predicted by the investigated model. Both models were well fitted to experimental data. However, predictive power of *ANN* was found more powerful than that of *CCD*. On the other hand, *RSM* has the advantage of giving a regression equation for prediction and showing the effect of experimental factors and their interactions on response in comparison with *ANN*. However, the main limitation of *RSM* assumes only quadratic non-linear correlation. Since *ANN* can inherently capture almost any form of non-linearity, it can easily overcome limitation of *RSM* (Desai et al., 2008). Another advantage of *ANN* is that this methodology does not require a standard experimental design to build the model. In addition, an *ANN* model, unlike statistical models operates upon the experimental data without data transformations.

Table 3
Validation data.

Run	pH	m (*mg*)	T (°C)	q (mg/g)	CCD		ANN	
					Predicted	Residual	Predicted	Residual
1	5.0	100.0	20	7.704	8.081	−0.377	7.513	0.191
2	5.0	200.0	20	3.516	5.336	−1.820	4.272	−0.756
3	5.0	300.0	20	2.313	3.573	−1.260	2.170	0.143
4	5.0	400.0	20	1.791	2.863	−1.072	1.753	0.038
5	5.0	500.0	20	1.247	3.188	−1.941	1.490	−0.243
6	3.0	100.0	20	7.222	6.850	0.372	6.211	1.011
7	4.0	100.0	20	8.000	7.740	0.260	7.859	0.141
8	6.0	100.0	20	5.658	7.849	−2.191	4.372	1.286
9	5.0	100.0	30	7.389	7.224	0.165	7.200	0.189
10	5.0	100.0	40	7.058	6.392	0.666	7.011	0.047
11	5.0	100.0	50	6.985	5.546	1.439	6.870	0.115

3.2. Evaluation of biosorption process

The biosorption experiments were realized at different temperatures (20–50 °C) in a thermo-controlled (±1 °C) water bath shaker (Fig. 2). The results showed that the biosorption of lead (q) increased up to 60 min with increases in equilibrium time as temperature decreased, and then did not change. Therefore, the equilibrium time were selected as 60 min.

The FTIR analysis showed the presence of ionizable functional groups (i.e., carboxyl, amino, amide, and hydroxyl), able to interact with protons or Pb(II) ions, because of strong bands in the region 3500–3000 cm^{-1} stretching of hydrogen bonded O–H, N–H of secondary amides and NH_3^- and those around 2921–2852 cm^{-1} of the alkyl chain (Hasan et al., 2009). The carbonyl band (C = O) stretching of carboxylic acid was located at 1715 cm^{-1} (Pavan et al., 2008; Gupta and Rastogi, 2008). The absorbance of the peaks in the lead-treated black cumin was slightly sharper than that in the black cumin observed at the same frequencies. A similar result was also obtained from another study for the biosorption of lead (Hasan et al., 2009). It suggested that the Pb(II) ion binding could be preferentially ascribed to coordination with the oxygen atoms present in carboxyl groups. A simplified process of lead ion sorbed on biosorbent is shown in the reaction below, where R is the polymeric chain, which represents the whole biosorbent compound (Pavan et al., 2008):

$$2R - COOH + M^{2+}.H_2O \leftrightarrow 2R - COO^-M^+ + 2H^+nH_2O \quad (6)$$

In a certain pH range for Pb^{2+}, there may be number of species present in the solution, such as Pb^{2+}, $Pb(OH)^+$, $Pb(OH)_2$, etc. At a lower pH, the positively charged lead ion species may compete with H^+ and be sorbed at the surface of the black cumin by an ion exchange mechanism. With an increase in pH, lead ion species, mainly neutral, may be sorbed by a hydrogen bonding mechanism along with ion exchange. The chemical bonding results from the sharing of a free electron pair between the surface oxygen atom and the metal atom or the formation of an O–Pb(II) bond (Hasan et al., 2009).

There have been many reports on the biosorption of lead ions. Various materials have been investigated as biosorbents for the removal of lead. In Table 4, black cumin is compared with other sorbents reported in the literature, based on their lead biosorption capacity (q, mg/g). It is important to emphasize that a direct comparison of the q of black cumin with capacities of other biosorbent materials is difficult, because the experimental conditions applied are different (Calero et al., 2011). Nevertheless, the results demonstrate that the lead biosorption capacity is comparable to other corresponding biosorbents reported in the literature. However, the lead biosorption capacity of black cumin is relatively smaller than that of some other biomaterials. Black cumin was used without any previous treatment.

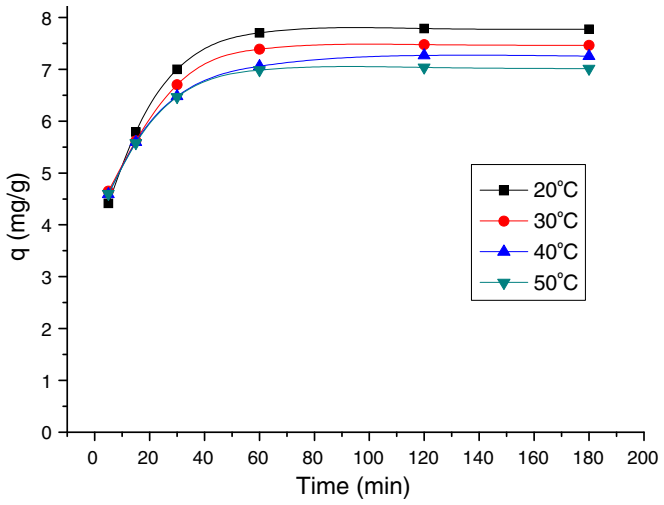

Fig. 2. The equilibrium time dependence of lead biosorption at different temperatures (pH 5, biosorbent mass 500.0 mg, initial lead concentration 20 mg/L, initial solution volume 250 mL).

Table 4
Comparison of black cumin with other biosorbents in literature.

Biosorbent	pH	Lead biosorption capacity (q, mg/g)	References
A sugar industry waste	5.0	2.50	Gupta and Ali, (2004)
Waste beer yeast	5.0–6.0	5.72	Han et al. (2006)
Rice husk	5.0	8.60	Zulkali et al. (2006)
Spirogyra sp.	5.0	140	Gupta and Rastogi, (2008)
Aeromonas hydrophila	5.0	122	Hasan et al. (2009)
Ponkan peel	5.0	112	Pavan et al. (2008)
Garcinia mangostana L. fruit shell	5.0	3.56	Zein et al. (2010)
Black cumin	5.1	8.08	This study

4. Conclusions

Black cumin was effectively used for the removal of lead ions from aqueous solutions as a potential biosorbent. The carboxyl, hydroxyl, and amine groups in the black cumin structure were effective in the biosorption process of lead onto black cumin surfaces. *CCD* and *ANN* models were used to predict the sorbed amounts of lead ions from aqueous solution by black cumin. The performance of the models, which was statistically measured by *RMSE* and R^2, indicated that *ANN* has better prediction capability than *RSM*. There exists a highly non-linear relationship between sorbed amount of lead and experimental factors.

References

Bezerra, M.A., Santelli, R.E., Oliveira, E.P., Villar., Escaleira, L.A., 2008. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. Talanta 76, 965–977.

Calero, M., Blázquez, G., Martín-Lara, M.A., 2011. Kinetic modeling of the biosorption of lead(II) from aqueous solutions by solid waste resulting from the olive oil production. J. Chem. Eng. Data 56, 3053–3060.

Çelekli, A., Geyik, F., 2011. Artificial neural networks (ANN) approach for modeling of removal of Lanaset Red G on *Chara contraria*. Biores. Tech. 102, 5634–5638.

Çelekli, A., Birecikligil, S.S., Geyik, F., Bozkurt, H., 2012. Prediction of removal efficiency of Lanaset Red G on walnut husk using artificial neural network model. Biores. Tech. 103, 64–70.

Desai, K.M., Survase, S.A., Saudagar, P.S., Lele, S.S., Singhal, R.S., 2008. Comparison of artificial neural network (ANN) and response surface methodology (RSM) in fermentation media optimization: case study of fermentative production of scleroglucan. Biochem. Eng. J. 41, 266–273.

El-Said, S.M., Alamri, M.B.S., El-Barak, Ali.-Bin.Saleh., Alsogair, O., 2009. Adsorptive removal of arsenite as (III) and arsenate as (V) heavy metals from waste water using *Nigella sativa* L. Asian J. Sci. Res. 2, 96–104.

Ferreira, S.L.C., Bruns, R.E., da Silva, E.G.P., dos Santos, W.N.L., Quintella, C.M., David, J.M., de Andrade, J.B., Breitkreitz, M.C., Jardim, I.C.S.F., Neto, B.B., 2007a. Statistical designs and response surface techniques for the optimization of chromatographic systems. J. Chromatogr. A 1158, 2–14.

Ferreira, S.L.C., Korn, M.G.A., Ferreira, H.S., da Silva, E.G.P., Araújo, R.G.O., Souza, A.S., Macedo, S.M., Lima, D.C., de Jesus, R.M., Amorim, F.A.C., Bosque-Sendra, J.M., 2007b. Application of multivariate techniques in optimization of spectroanalytical methods. App. Spectrosc. Rev. 42, 475–491.

Ferreira, S.L.C., Bruns, R.E., Ferreira, H.S., Matos, G.D., David, J.M., Brandão, G.C., da Silva, E.G.P., Portugal, L.A., dos Reis, P.S., Souza, A.S., dos Santos, W.N.L., 2007c. Box-Behnken design: an alternative for the optimization of analytical methods. Anal. Chim. Acta 597, 179–186.

Geyikçi, F., Kılıç, E., Çoruh, S., Elevli, S., 2012. Modelling of lead adsorption from industrial sludge leachate on red mud by using RSM and ANN. Chem. Eng. J.. doi:10.1016/j.cej.2011.12.019.

Gupta, V.K., Ali, I., 2004. Removal of lead and chromium from wastewater using bagasse fly ash–a sugar industry waste. J. Colloid Interface Sci. 271, 321–328.

Gupta, V.K., Rastogi, A., 2008. Biosorption of lead from aqueous solutions by green algae Spirogyra species: kinetics and equilibrium studies. J. Hazard. Mater. 152, 407–414.

Han, R., Li, H., Li, Y., Zhang, J., Xiao, H., Shi, J., 2006. Biosorption of copper and lead ions by waste beer yeast. J. Hazard. Mater. 137, 1569–1576.

Hasan, S.H., Srivastava, P., Talat, M., 2009. Biosorption of Pb(II) from water using biomass of *Aeromonas hydrophila*: central composite design for optimization of process variables. J. Hazard. Mater. 168, 1155–1162.

Haykin, S., 1999. Neural Networks: a Comprehensive Foundation, Second Edition. Prentice Hall International, Inc.

Huang, M., Ma, Y., Wan, J., Zhang, H., Wang, Y., Chen, Y., Yoo, C.K., Guo, W., 2011. A hybrid genetic–neural algorithm for modeling the biodegradation process of DnBP in AAO system. Biores. Tech. 102 (19), 8907–8913.

Kasiri, M.B., Aleboyeh, H., Aleboyeh, A., 2008. Heterogeneous photo-fenton process with response surface methodology and artificial neural networks. Environ. Sci. Technol. 42, 7970–7975.

Khayet, M., Cojocaru, C., Essalhi, M., 2011. Artificial neural network modeling and response surface methodology of desalination by reverse osmosis. J. Membrane Sci. 368, 202–214.

Lee, J.W., Suh, Changwen., Hong, Y.S.T., Shin, H.S., 2011. Sequential modelling of a full-scale waste water treatment plant using an artificial neural network. Bioproc. Biosyst. Eng. 34, 963–973.

Moghaddam, M.G., Khajeh, M., 2011. Comparison of response surface methodology and artificial neural network in predicting the microwave-assisted extraction procedure to determine zinc in fish muscles. Food Sci. Nutr. 2, 803–808.

Montgomery, D.C., 2008. Design and Analysis of Experiments, seventh ed. John Wiley & Sons, New York.

Pavan, F.A., Mazzocato, Ana.C., Jacques, Rosángela.A., Dias, Silvio.L.P., 2008. Ponkan peel: a potential biosorbent for removal of Pb(II) ions from aqueous solution. Biochem. Eng. J. 40, 357–362.

Ranjan, D., Mishra, D., Hasan, S.H., 2011. Bioadsorption of arsenic: an artificial neural networks and response surface Methodological Approach. Ind. Eng. Chem. Res. 50, 9852–9863.

Shao, W., Chen, L., Lü, L., Luo, F., 2011. Removal of lead (II) from aqueous solution by a new biosorption material by immobilizing Cyanex272 in cornstalks. Desalination 265, 177–183.

Shihani, N., Kumbhar, B.K., Kulshreshtha, M., 2006. Modeling of extrusion process using response surface methodology and artificial neural networks. J. Eng. Sci. Tech. 1, 3140.

Singh, K.P., Gupta, S., Singh, A.K., Sinha, S., 2010. Experimental design and response surface modeling for optimization of Rhodamine B removal from water by magnetic nanocomposite. Chem. Eng. J. 165, 151–160.

Stalikas, C., Fiamegos, Y., Sakkas, V., Albanis, T., 2009. Developments on chemometric approaches to optimize and evaluate microextraction. J. Chromatogr. A 1216, 175–189.

Suresh Kumar, T.V., Negi, P.S., Udaya Sankar, K., 2010. Antibacterial activity of *Nigella sativa* L. seed extracts. Br. J. Pharmacol. Toxicol. 1(2), 96–100.

Xu, D., Tan, X., Chen, C., Wang, X., 2008. Removal of Pb(II) from aqueous solution by oxidized multiwalled carbon nanotubes. J. Hazard. Mater. 154, 407–416.

Wan Ngah, W.S., Hanafiah, M.A.K.M., 2008. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. Biores. Tech. 99, 3935–3948.

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

Zein, R., Suhaili, R., Earnestly, F., Indrawati, E., Munaf, 2010. Removal of Pb(II), Cd(II) and Co(II) from aqueous solution using *Garcinia mangostana* L. fruit shell. J. Hazard. Mater. 181, 52–56.

Zulkali, M.M.D., Ahmad, A.L., Norulakmal, N.H., 2006. *Oryza sativa* L. husk as heavy metal adsorbent: Optimization with lead as model solution. Biores. Tech. 97, 21–25.

<http://www.lenntech.com/Periodic-chart-elements/Pb-en.htm>.

<http://en.wikipedia.org/wiki/Nigella_sativa>.