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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

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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).

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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 photo-fenton 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$\sim$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 (α = 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