Appl Water Sci (2015) 5:191–199
DOI 10.1007/s13201-014-0180-z

ORIGINAL ARTICLE

Modeling of biosorption of Cu(II) by alkali-modified spent tea leaves using response surface methodology (RSM) and artificial neural network (ANN)

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Received: 22 October 2013 / Accepted: 14 March 2014 / Published online: 5 April 2014

Abstract In the present work, spent tea leaves were modified with $Ca(OH)_2$ and used as a new, non-conventional and low-cost biosorbent for the removal of Cu(II) from aqueous solution. Response surface methodology (RSM) and artificial neural network (ANN) were used to develop predictive models for simulation and optimization of the biosorption process. The influence of process parameters (pH, biosorbent dose and reaction time) on the biosorption efficiency was investigated through a two-level three-factor (2^3) full factorial central composite design with the help of Design Expert. The same design was also used to obtain a training set for ANN. Finally, both modeling methodologies were statistically compared by the root mean square error and absolute average deviation based on the validation data set. Results suggest that RSM has better prediction performance as compared to ANN. The biosorption followed Langmuir adsorption isotherm and it followed pseudo-second-order kinetic. The optimum removal efficiency of the adsorbent was found as 96.12 %.

Keywords Biosorption · Cu(II) · $Ca(OH)_2$-modified spent tea leaves · Response surface methodology · Central composite design · Artificial neural network

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Introduction

Over the past several decades, the exponential population and social civilization expansion, sharp modernization and metropolitan growth, and continuing progress of the industrial and technologies has largely contributed to the contamination of groundwater and other water resources by toxic heavy metals (Foo and Hameed 2010a, b). Copper is one of the most widely used heavy metals. Copper and its compounds are extensively used in various important industrial applications such as electrical wiring, plumbing, gear wheel, air conditioning tubing, and roofing (Chowdhury and Saha 2011). Its potential sources in industrial effluents include metal cleaning and plating baths, fertilizer, refineries, pulp, paper board mills, printed circuit board production, wood pulp production, wood preservatives, paints and pigments, municipal and storm water run-off, etc. (Chowdhury and Saha 2011). Intake of excessively large doses of copper by human beings leads to severe mucosal irritation and corrosion, stomach upset and ulcer, wide spread capillary damage, hepatic and renal damage, central nervous system irritation followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney (Yao et al. 2010). Chronic copper poisoning can also result in Wilson's disease leading to brain and liver damage (Jaman et al. 2009). Therefore, removal of copper from effluents is essential not only to protect the water sources but also for the protection of human health.

Various treatment technologies exist for the removal of Cu(II) from wastewater, including precipitation, ion exchange, evaporation, oxidation, electroplating and membrane filtration (Yao et al. 2010; Ajmal et al. 1998; Wang and Qin 2007). However, application of such technologies is restricted because of technical or economical

constraints (Wang and Qin 2007; Rangsayatorn et al. 2004; Meunier et al. 2003). Biosorption as an alternative and effective technology has been widely studied over recent years, because of its wide range of target pollutants, high sorption capacity, excellent performance, eco-friendly nature and low operating cost (Farooq et al. 2010; Sud et al. 2008). A number of inexpensive biosorbents (prepared by utilizing different types of waste materials particularly agro-industrial wastes) have been used to remove heavy metal ions from waste water (Sud et al. 2008; Bhatnagar and Sillanpaa 2010; Ghosh and Saha 2012; Ghosh et al. 2013).

Tea is an aromatic beverage consumed by the largest number of people in the world. Nearly 18–20 billion cups of tea are drunk daily on our planet (Hameed 2009). India is the largest producer and consumer of tea in the world (Goel et al. 2001). Tea is prepared instantly by hot water extraction of *Camellia sinensis* leaves, and the producers face a problem in disposing of the spent tea leaves after the extraction (Hameed 2009). Utilization of this waste as biosorbent is an attractive alternative which formed the motivation of this present study. Recently, it has been reported that alkali treatment improves the biosorption property of tea leaves (Nasuha and Hameed 2011). Therefore, in this study, spent tea leaves were modified with alkali and used as biosorbent for the removal of Cu(II) from aqueous solutions. Nowadays, response surface methodology (RSM) and artificial neural network (ANN) methods are jointly applied by researchers worldwide to predict the adsorption/biosorption behavior in solid–liquid systems (Geyikci et al. 2012; Bingol et al. 2012). The concurrent application of both techniques allows researchers to compare the results of different modeling approaches and to better understand their process under investigation (Geyikci et al. 2012). Thus, in the present study, a two-level three-factor (2^3) full factorial central composite design (CCD) in RSM and ANN-based models were developed to predict the relationship between the experimental variables (pH, biosorbent dose and contact time) on the biosorption efficiency (response variable). Finally, the optimal solutions offered by RSM and ANN were statistically compared by the root mean square error (RMSE) and absolute average deviation (AAD) based on the validation data set.

Materials and methods

Biosorbent: preparation and characterization

Spent tea leaves (STL) were collected from a tea-making shop located in the cafeteria. The collected leaves were washed with distilled water to remove any adhering dirt. Then it was boiled with distilled water several times until the leaves gave no color. The leaves were then dried in an oven at 373 ± 1 K for 24 h. The dried leaves were immersed in 0.05 M $Ca(OH)_2$ solution for 8 h. The leaves were then washed thoroughly with distilled water until they were neutralized and dried in the oven at 373 ± 1 K for 24 h. Finally, the resulting biosorbent—alkali-modified spent tea leaves (MSTL)—was stored in air-tight glass bottles for further use in biosorption experiments.

Surface morphology of the biosorbent was studied using a scanning electron microscope (S-3000 N, Hitachi, Japan) at an electron acceleration voltage of 25 kV. Prior to scanning, the biosorbent was mounted on a stainless steel stab with double stick tape and coated with a thin layer of gold in a high vacuum condition. The Brunauer–Emmett–Teller (BET) surface area, pore volume and pore size of the biosorbent were measured by a surface area and porosity analyzer (NOVA 2200, Quantachrome Corporation, USA). A gas mixture of 22.9 mol % nitrogen and 77.1 mol % helium was used for this purpose. FTIR analysis was performed using FTIR spectrophotometer (Perkin-Elmer Spectrum BX-II Model) in the wavenumber range 4,000–500 cm^{-1} at 4 cm^{-1} spectral resolution.

Cu(II) solutions

Stock solution of Cu(II) (500 mg L^{-1}) was prepared by dissolving required quantity of $CuSO_4 \cdot 5H_2O$ (analytical reagent grade) in double-distilled water. Experimental Cu(II) solutions of different concentrations were prepared by diluting the stock solution with suitable volume of double-distilled water. The initial pH was adjusted with 0.1 M HCl and 0.1 M NaOH solutions using a digital pH meter (ELICO) calibrated with standard buffer solutions.

Batch biosorption studies

Batch biosorption experiments were carried out in 250 mL glass-stoppered Erlenmeyer flasks by adding a weighed amount of biosorbent to an initial solution volume of 100 mL containing 100 mg L^{-1} Cu(II) at desired pH. The flasks were agitated at a constant speed of 150 rpm in an incubator shaker (Innova 42, New Brunswick Scientific, Canada) at a constant temperature of 303± K for a prefixed time period. Samples were collected from the flasks at predetermined time intervals for analyzing the residual concentration of Cu(II) in the solution. The residual amount of Cu(II) in each flask was investigated colorimetrically using UV/VIS spectrophotometer (U–2800, Hitachi, Japan). 1 % w/v sodium diethyl dithiocarbamate solution (0.2 mL) and 1.5 N ammonia solution (20 mL) were added to the test sample (1 mL). The absorbance of the resulting yellow colored solution was determined at λ_{max} of 460 nm.

The percent (%) removal of Cu(II) was calculated using the following equation:

$$\% \text{ Removal} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where C_i is the initial Cu(II) concentration (mg L^{-1}) and C_e is the equilibrium Cu(II) concentration in solution (mg L^{-1}).

Experimental design

The present study involves the optimization of different parameters affecting the adsorption of copper solution using the MSTL. Generally, by varying one parameter and keeping the other variables constant, the optima for a given process are analyzed. But the problem is that it does not include the interactive effects among the different variables and as a net result, the true optima are not possible to achieve. To overcome this, optimization studies have been studied using RSM. RSM is an affective statistical technique for optimizing complex processes. It reduces the number of experimental trials which will require evaluating multiple parameters and their interactions. It is less laborious and time-consuming than other approaches. A number of factors such as solution pH, biosorbent dose and contact time can significantly affect the metal removal efficiency. Therefore, a standard RSM design (CCD) was used to identify the relationship between the response function (% removal) and the process variables (pH, biosorbent dose and contact time). Other RSM design models are also available (Box–Behnken method). The advantage of CCD analysis is that, in CCD analysis high range prediction can be possible within the design range as well as outside the design range. But in case of Box–Behnken method, fewer experiments are needed than the CCD analysis but the optimization can be possible within the range only. The treatment condition in this case is at the midpoint of the edges and one at the center point and this method has limited capability than the CCD design. The experimental range of the selected process variables with their units and notation is given in Table 1. The response variable can be expressed as a function of the independent process variables according to the following response surface quadratic model:

Table 1 Experimental range and levels of independent process variables

Variable	Unit	Notation	Range and levels (coded)				
			$-\alpha$	-1	0	$+1$	$+\alpha$
pH		*A*	2.81	3.50	4.50	5.50	6.18
Biosorbent dose	g L^{-1}	*B*	3.18	10.00	20.00	30.00	36.81
Time	min	*C*	29.65	45.00	67.50	90.00	105.34

Table 2 CCD for three independent variables used in this study along with the observed response

Run no.	Coded values			Real values			% Removal
	A	*B*	*C*	*A*	*B*	*C*	
1	+1	+1	+1	5.50	30.00	90.00	84.67
2	+1	+1	−1	5.50	30.00	45.00	86.82
3	+1	−1	+1	5.50	10.00	90.00	90.95
4	−1	+1	−1	3.50	30.00	45.00	91.61
5	+1	−1	−1	5.50	10.00	45.00	94.23
6	−1	−1	+1	3.50	10.00	90.00	90.60
7	−1	+1	+1	3.50	30.00	90.00	92.97
8	−1	−1	−1	3.50	10.00	45.00	90.23
9	$-\alpha$	0	0	2.81	20.00	67.50	92.94
10	$+\alpha$	0	0	6.18	20.00	67.50	89.22
11	0	$-\alpha$	0	4.50	3.18	67.50	93.13
12	0	$+\alpha$	0	4.50	36.81	67.50	89.15
13	0	0	$-\alpha$	4.50	20.00	29.65	88.85
14	0	0	$+\alpha$	4.50	20.00	105.34	87.14
15	0	0	0	4.50	20.00	67.50	89.96
16	0	0	0	4.50	20.00	67.50	90.07
17	0	0	0	4.50	20.00	67.50	89.99
18	0	0	0	4.50	20.00	67.50	89.82
19	0	0	0	4.50	20.00	67.50	89.91
20	0	0	0	4.50	20.00	67.50	89.76

$$\% \text{ Removal} = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1} \sum_{j=1+1} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

where β_0 is the constant coefficient, $\beta_i, \beta_{ii}, \beta_{ij}$ are the coefficients for the linear, quadratic and interaction effect, respectively, x_i and x_j are the independent variables and ε is the error.

A total of 20 experiments were performed in triplicate according to the CCD matrix in Table 2 and the average values were used in data analysis. The experimental data were analyzed by the software, Design Expert Version 7.1.6 (Stat-Ease, USA). The adequacy of the developed model and statistical significance of the regression coefficients were tested using the analysis of variance (ANOVA). The interaction among the different independent variables and their corresponding effect on the response were studied by analyzing the response surface contour plots.

ANN model

ANN, inspired by the structural and/or functional aspect of biological neural network, has attracted increasing attention in recent years, particularly for process modeling. It is now used as a very powerful tool to predict the behavior of

a given system, to design new processes and to analyze existing processes (Cavas et al. 2011). The basic ANN architecture consists of an input layer (independent variables), a number of hidden layers and an output layer (dependent variables). Each of these layers consists of a number of inter-connected processing units called neurons. These neurons interact by sending signals to one another along weighted connections (Aghav et al. 2011). Each neuron is connected to all neurons in the preceding and following layers by links. The input layer receives information from external sources and passes this information to the hidden layer for processing. Before entering the hidden layer, the input values are weighted individually (Ozdemir et al. 2011). The hidden layer then does all the data processing and produces output based on the sum of the weighted values from the input layer modified by a sigmoid transfer function (Giri et al. 2011).

In the present study, the inputs to the ANN model were identical to the factors considered in RSM approach, namely, pH, biosorbent dose and contact time. Similar to RSM modeling, the % removal of Cu(II) was considered as response (target) for ANN modeling. The input–output patterns required for training were obtained from batch adsorption experimentation planned through CCD. A tan-sigmoid transfer function (tansig) at hidden layer and a linear transfer function (purelin) at output layer were applied. The Levenberg–Marquardt back-propagation algorithm was used for network training. All ANN calculations were carried out using Neural Network Toolbox of MATLAB Version 7.9 (R2009b).

Results and discussion

Using MSTL it was observed that adsorption capacity of copper increased 20 times more than using untreated tea leaves (UTL). The reason may be that surface of the spent tea leaves after treatment had higher negative charge resulting higher attraction for copper ions. So, the further study was performed using MSTL.

Characterization of MSTL

The SEM micrograph of MSTL (Fig. 1a) shows a porous irregular surface structure suggestive of the expected biosorption of Cu(II) onto the surface of the biosorbent. The BET surface area, total pore volume and average pore diameter of the biosorbent were measured to be 7.2 $m^2\ g^{-1}$, 0.007 $cm^3\ g^{-1}$ and 71 Å, respectively.

The FTIR study of MSTL showed significant peak at 3,500, 2,800, 1,750, 1,000 nm^{-1} (Fig. 1b) which was due to the presence of alcohol or phenolic group, alkane, ester or carboxylic acid group in MSTL.

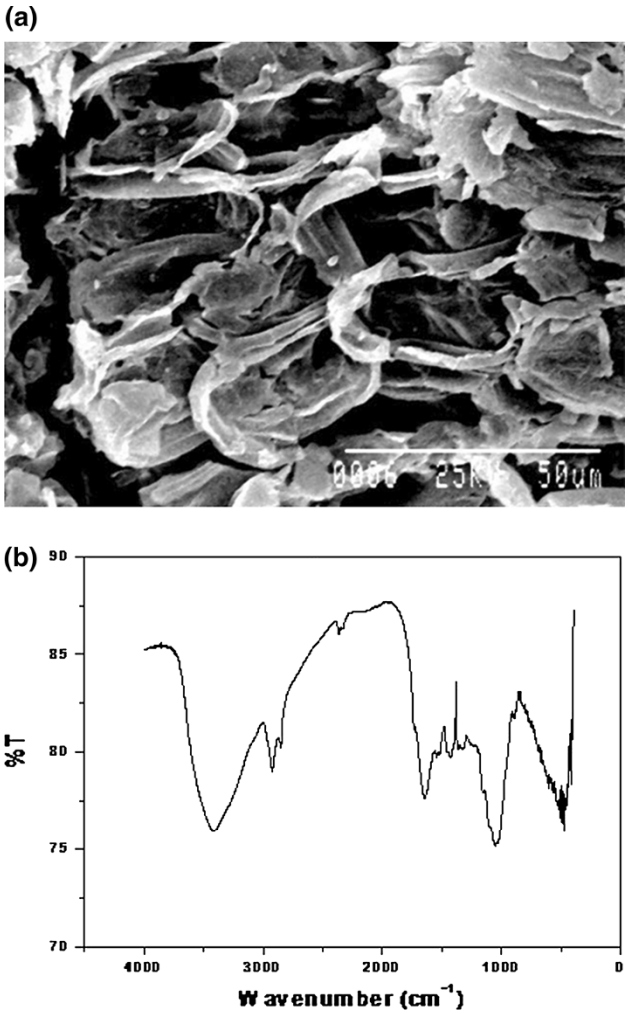

Fig. 1 **a** SEM micrograph of MSTL **b** FTIR analysis of MSTL

RSM model

Results obtained by performing the biosorption experiments according to the CCD matrix are presented in Table 2. The quadratic model equation relating the response function to the tested independent variables as developed by the software is given by Eq. (3).

$$\begin{aligned}\text{Removal}\ (\%) = {} & 73.815 + 1.906 \cdot A + 0.592 \cdot B + 0.304 \cdot C \\ & - 0.217 \cdot A \cdot B - 0.040 \cdot A \cdot C + 0.00011 \cdot B \cdot C \\ & + 0.452 \cdot A^2 + 0.00048 \cdot B^2 - 0.00013 \cdot C^2 \end{aligned} \quad (3)$$

The analysis of variance (ANOVA) is considered to be useful to test the statistical significance of the response surface quadratic model. The ANOVA results (Table 3) of the quadratic model suggest that the model was highly significant, as it is evident from the Fisher's F value (higher F value, i.e., 661.91) with a low probability value ($p < 0.0001$). The goodness of fit of the model was further checked by the correlation coefficient (R^2) between the

Table 3 ANOVA for the response surface quadratic models for biosorption of Cu(II) by MSTL

Source	Sum of squares	Degree of freedom (*df*)	Mean square	*F* value	Probability > *F*	Remarks
Model	98.15	9	10.91	661.91	<0.0001	Significant
A	16.44	1	16.44	997.67	<0.0001	Significant
B	20.28	1	20.28	1,231.05	<0.0001	Significant
C	3.32	1	3.32	201.65	<0.0001	Significant
AB	37.93	1	37.93	2,302.32	<0.0001	Significant
AC	6.55	1	6.55	397.69	<0.0001	Significant
BC	0.50	1	0.50	30.35	0.0003	
A^2	2.94	1	2.94	178.63	<0.0001	Significant
B^2	3.30	1	3.30	200.21	<0.0001	Significant
C^2	5.69	1	5.69	345.19	<0.0001	Significant
Residual	0.16	10	0.016			
Lack of fit	0.11	5	0.023	2.23	0.1996	Not significant
Pure error	0.051	5	0.010			
Total	98.31	10				

experimental and model predicted values of the response variable. A fairly high R^2 value of 0.9983 implies that the regression model was statistically significant and only 0.17 % of the total variations was not explained by the model. The predicted correlation coefficient (pred. $R^2 = 0.987$) also shows good agreement with the adjusted correlation coefficient (adj. $R^2 = 0.990$). A coefficient of variance (C.V.) of 1.14 % suggests better precision and reliability of the data obtained by performing the experiments while a non-significant lack of fit value (more than 0.05) implies validity of the quadratic model (Chowdhury and Saha 2012). The main and the square effects of the independent process variables were highly significant ($p < 0.0001$). Also the interaction effect of pH and biosorbent dose as well as pH and contact time was highly significant ($p < 0.0001$). Overall, the ANOVA analysis indicates the applicability of the model for simulation of the biosorption process of Cu(II) by MSTL within the limits of the experimental factors.

To study the interaction among the different independent variables and their corresponding effect on the response, contour plots were drawn (Figs. 2, 3). A contour plot is a graphical representation of a three-dimensional response surface as a function of two independent variables, maintaining all other variables at fixed level. These plots can be helpful in understanding both the main and interaction effects of the independent variables on the response (Jain et al. 2011).

The combined effect of pH and biosorbent dose on the response function is shown in the contour plot of Fig. 2a. The biosorption yield significantly decreased with increasing biosorbent dose which may be due to saturation of biosorption sites owing to particulate interaction such as aggregation (Chakraborty et al. 2011). Such aggregation leads to a decrease in total surface area of the biosorbent and increase in diffusional path length (Chakraborty et al. 2011). On the other hand, the interaction effect of pH and contact time on the biosorption efficiency is depicted in the contour plot of Fig. 2b. Maximum removal of Cu(II) is observed at lower contact times which may be explained by increased availability in the number of active binding sites on the biosorbent surface. Contrary to the usual notion, pH did not significantly affect the biosorption process within the experimental range as it was observed from the study.

The contour plot of Fig. 3 suggests that there is a negative correlation between the biosorbent dose and reaction time to achieve the maximum removal efficiency.

ANN model

In the present study, an ANN-based model was also developed for describing the biosorption removal of Cu(II) by MSTL. A three-layer ANN, as illustrated in Fig. 4a, was used for this purpose. The data generated from the experimental design planned through CCD (Table 2) were used to figure out the optimal architecture of ANN. The original data set (comprising of 20 data points) was divided into three subsets—training (12 data points), validation (4 data points) and test sets (4 data points). The splitting of data into training, validation and test subsets was carried out to estimate the performance of the neural network for prediction of "unseen" data that were not used for training. In this way, the generalization capability of ANN model can be assessed.

The number of hidden layers and neurons was established by training different feed-forward networks of various topologies and selecting the optimal one based on minimization of the performance function—mean square

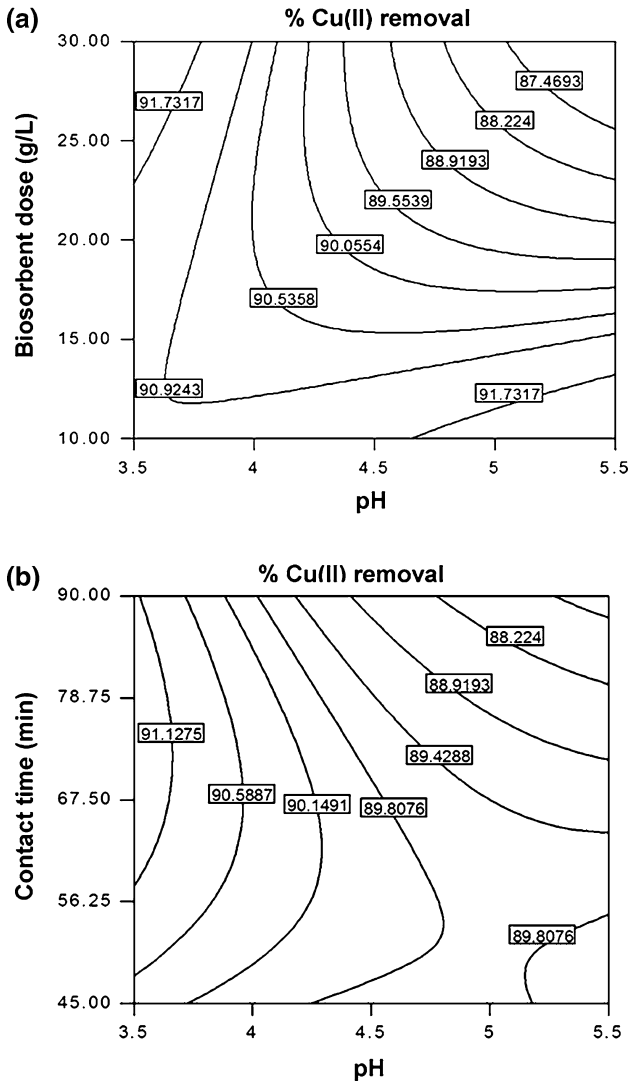

Fig. 2 **a** Contour plot showing the combined effect of pH and biosorbent dose on the % removal of Cu(II) by MSTL. **b** Contour plot showing the combined effect of pH and contact time on the % removal of Cu(II) by MSTL

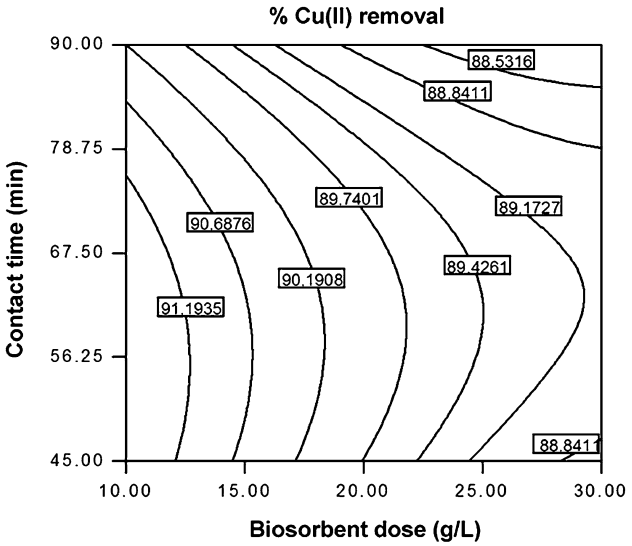

Fig. 3 Contour plot showing the combined effect of biosorbent dose and contact time on the % removal of Cu(II) by MSTL

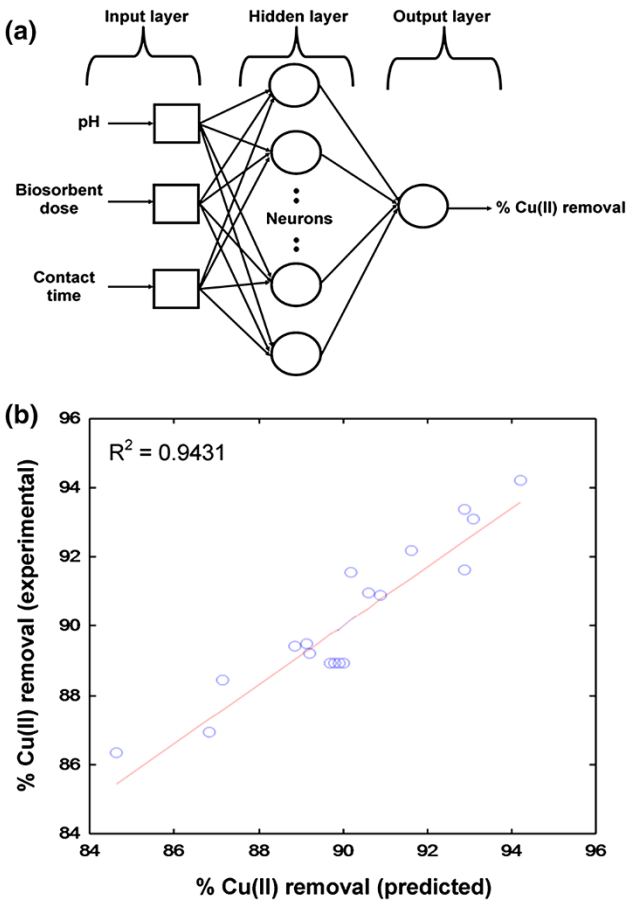

Fig. 4 **a** Topology of the ANN architecture. **b** Comparison of the experimental data with those predicted by the ANN model

error (MSE). The obtained optimal architecture (topology) of ANN model for the present problem involved a feed-forward neural network with three inputs, two hidden layers (one layer with ten neurons and another with four neurons) and one output layer (including one neuron). This feed-forward network topology is denoted as multilayer perception, MLP (3:10:4:1), referring to the number of inputs and the number of neurons in the hidden and output layers, respectively. To figure out the optimal values of weights and biases, the network MLP (3:10:4:1) was trained using back-propagation method (BP) based on Levenberg–Marquardt algorithm.

The goodness-of-fit between the experimental and the predicted response given by the ANN model is shown in Fig. 4b. The % removal of copper using MSTL showed the relation between the experimental and predicted removal as:

Table 4 Validation data set

Run	pH	Biosorbent dose (g L^{-1})	Time (min)	% Removal	RSM		ANN	
					Predicted	Residual	Predicted	Residual
1	3.50	20.00	67.50	93.58	91.50	2.08	89.82	3.76
2	3.50	30.00	90.00	94.14	93.01	1.13	91.87	2.27
3	3.50	36.81	105.34	92.52	94.15	−1.63	88.78	3.74
4	4.50	30.00	90.00	90.14	88.42	1.71	93.70	−3.56
5	4.50	10.00	45.00	90.16	91.74	−1.57	94.95	−4.79
6	5.50	20.00	67.50	88.12	89.37	−1.24	86.66	1.46
7	5.50	3.18	29.65	96.12	97.61	−1.48	93.64	2.48
8	5.50	36.81	105.34	82.87	81.69	1.17	80.50	2.37

$$y = 0.726x + 24.79$$

where y is the % Cu removal (experimental) and x is the % Cu removal (ANN model).

A correlation coefficient of 0.9431 suggests the reliability of the developed ANN model.

Comparison of RSM and ANN models

In this study, RSM and ANN methods were applied for modeling and optimization of the biosorption process of Cu(II) by MSTL. To test the validity of RSM and ANN results, experiments were conducted for eight new trials, consisting of combinations of experimental factors, which do not belong to the training data set. The actual and predicted values together with the residuals (the difference between actual and predicted values), for both approaches are shown in Table 4. The fluctuations of the residuals are relatively small and regular for RSM compared to ANN. The ANN model shows greater deviation than the RSM model.

The performance of the constructed ANN and RSM models was also statistically measured by the root mean squared error (RMSE) and absolute average deviation (AAD) as follows:

$$\text{RMSE} = \left(\frac{1}{n}\sum_{i=1}^{n}\left(\%R_{\text{predict}} - \%R_{\text{exp}}\right)^2\right)^{1/2} \quad (4)$$

$$\text{AAD} = \left|\frac{1}{n}\sum_{i=1}^{n}\left(\frac{\%R_{\text{predict}} - \%R_{\text{exp}}}{\%R_{\text{exp}}}\right)\right| \times 100 \quad (5)$$

where n is the number of points, $\%R_{\text{predict}}$ is the predicted value, and $\%R_{\text{exp}}$ is the actual value. The RMSE for RSM and ANN was determined as 1.536 and 3.217 while AAD was found as 0.038 and 1.038 for RSM and ANN, respectively. These results show a clear superiority of RSM over ANN for both data fitting and estimation capabilities. This finding is opposed to the usual notion that ANN has better prediction performance than RSM (Hameed 2009; Jain et al. 2011). RSM has the advantage of giving a regression equation for prediction and showing the effect of experimental factors and their interactions on the response in comparison with ANN. ANN would require more number of experiments than RSM to build an efficient model.

Adsorption isotherms

Two adsorption isotherms were used to evaluate the adsorption using treated tea leaves. These isotherms were:

$$\text{Langmuir}: \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L\, q_m} \quad (6)$$

$$\text{Freundlich}: \log\, q_e = \log\, K_F + \left(\frac{1}{n}\right) \log\, C_e \quad (7)$$

Using experimental results, it was observed that copper removal using treated tea leaves followed the Langmuir model which confirmed that the adsorption was monolayer, and the interaction of sorbate–sorbate was negligible. The monolayer adsorption capacity as obtained from the Langmuir isotherm was found as 7.813 mg g^{-1}, and K_L was 0.783 L mg^{-1} (Fig. 5). The K_F values from Freundlich equation was 0.398 (mg g^{-1})(L mg^{-1})$^{1/n}$ and n was 7.63 ($n > 1$) indicated that adsorbate was favorable and the n value suggesting the stronger adsorption intensity.

Adsorption kinetics

Lagergren's pseudo-first-order and Ho-Mc Kay's pseudo-second-order models were applied to the experimental data to determine the kinetic parameter for the adsorption study.

$$\text{Pseudo-first-order}: \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (8)$$

$$\text{Pseudo-second-order}: \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (9)$$

From R^2 values, it was observed that the adsorption of copper using the adsorbent followed pseudo-second-order

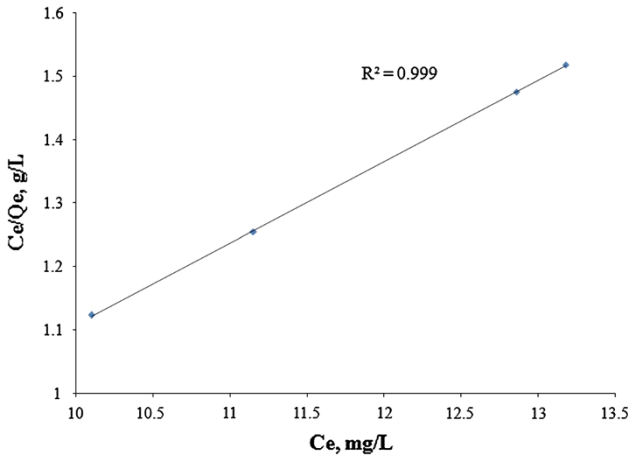

Fig. 5 Langmuir adsorption isotherm analysis of the adsorption of copper using MSTL

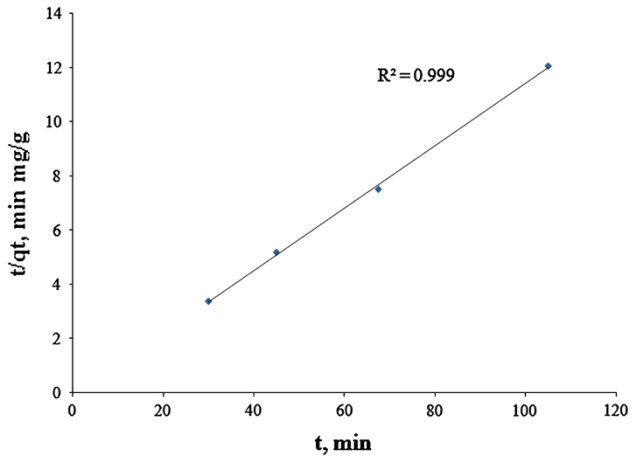

Fig. 6 Pseudo-second-order kinetic model of the adsorption of copper using MSTL

kinetics (due to higher R^2 values for pseudo-second-order reaction). K_2 was found as 0.162 g mg^{-1} min^{-1} (at 310 K) (Fig. 6).

Conclusion

In this study, STL were modified with $Ca(OH)_2$ and used as an effective biosorbent for the removal of Cu(II) from aqueous solution. RSM based on a 2^3 full factorial CCD and a feed-forward multilayer ANN trained using back-propagation algorithm were applied for modeling and optimization of the biosorption process. Three independent process parameters, namely pH, biosorbent dose and contact time were selected as input variables while the % biosorption removal was considered as response. The effect of the operating factors was investigated by analyzing response surface contour plots. The most important effect on the biosorption performance was found to be of biosorbent dose followed by contact time. The effect of pH was negligible within the experimental range. The predicted biosorption removals were in good agreement with the experimental results for both ANN and RSM techniques. Finally, RMSE and AAD were used together to compare the prediction performance of RSM and ANN based on the validation data set. The results indicate that the prediction accuracy of the RSM model was better than the ANN model. Based on the findings, it is worth mentioning that there exists a non-linear quadratic relationship between the biosorption efficiency and the experimental factors. From kinetic and isotherm study, it was observed that adsorption experiment followed pseudo-second-order kinetics and Langmuir adsorption isotherm.

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