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Central composite design optimization and artificial neural network modeling of copper removal by chemically modified orange peel

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ABSTRACT

The ability to remove Cu^{2+} ions from aqueous solution using calcium oxide ($Ca(OH)_2$) treated orange peel was investigated in the present study. Response Surface Methodology (RSM) was applied for the optimization of the process parameters responsible for the reduction of metal ion effect and to evaluate the effects and interactions of the process variables. The optimum reduction of copper was 93.4253% at pH 4.75, 55.5 mg/l copper concentration and 33.91 min of contact time. The deviation between experimental and RSM model equation was very less. Computational simulated artificial neural network (ANN) was formulated to get a good correlation between the input parameters responsible for copper removal and the output parameters (% removal) of the process. The correlation coefficient (R) of ANN is 0.967. The optimization process shows a close interaction between the observational and modeled values of copper removal.

Keywords: Copper; Adsorption; Orange peel; Calcium oxide; Response surface methodology; Optimization

1. Introduction

Very quick urbanization and industrialization cause environmental contamination due to heavy metal which is a serious and common problem throughout the whole world [1]. These heavy metals in effluent do not undergo biodegradation, causes bioaccumulation and biomagnifications. Copper is one such a heavy metal which is an essential trace element, but higher concentration of copper may cause hazard to the animals and plants. High copper intake may cause kidney, brain, and liver damage and also damage marine life, soil microbial pollution [2–4].

Copper is present in industrial effluents such as metal cleaning and plating baths, pulp, paper board mills, wood pulp production, the fertilizer industry, electroplating, microelectronics, battery manufacture, dyestuff, chemical, metallurgical, pharmaceutical industry [5,6]. There are some formal methods to remove copper (II) from waste water like precipitation, electrolysis, adsorption with activated carbon, reverse osmosis, ultrafiltration etc. But these methods require high costs, high energy and also suffer from incomplete removal in some cases [7].

Various types of natural and artificial adsorbents have been studied by various researchers for the removal of different heavy metals. Different agro-waste or plant derived materials, such as rice husk,

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wheat shell, cereal husk, sawdust, pine bark, fruit peel etc., can be used to remove heavy metals [6,8–11]. The process is low cost and does not require any energy for the operation.

Orange peel is one of the agro-waste matters. It is one of the common wastes generated by maximum households during winter. So, it is a municipality waste matter cheap, and easily available. Orange peel is the rind of the citrus fruit named orange. Orange peel contains citral, aldehyde, cellulose, pectin, hemicellulose, lignin, chlorophyll pigments, and other low molecular weight hydro-carbons [12,13]. The texture of orange peel resembles the bumpy surface. Outer surface color of the peel is orange; whereas inner surface is white in color. Some researchers used orange peel as adsorbent, without processing, for removal of metal ions from wastewater [12–14]. Also several researches used orange wastes as different metal ions adsorbent, after different chemical modification such as pre-treatment with NaOH, $CaCl_2$ or by hydrolysis, xanthation process etc. [15–20].

However, raw plant wastes can bring some constraint in the adsorption process, such as low adsorption capacity, high BOD, high COD, high TOC for releasing soluble organic compounds contained in the plant materials [20]. For better adsorption capacity, plant wastes need to be chemically modified. This study is focused on copper removal from aqueous solution using calcium hydroxide treated orange peel as an adsorbent. For making large surface area and porous structure of the adsorbents lime treatment was performed. Orange peel contains methyl esters which do not bind metal ions effectively [12]. The methyl esters can be modified to carboxylate ligands by a base treatment, which can improve the metal binding capacity to the surface of chemically modified orange peel [12].

Formal batch adsorption studies depends on different process parameters, such as initial solution pH, initial adsorbate concentration, adsorbent dose, agitation, temperature etc. which are constant at unspecified levels [20]. But, this approach does not determine the combined effect of all the process parameters. For scale-up studies, conventional batch process is time consuming and to determine the optimum levels (which may be unreliable) requires a large number of experiments and thereby, increase the overall cost of the process.

These problems can be mitigated and minimized by optimizing all the process parameters by statistical experimental design analysis process, such as response surface methodology (RSM).

RSM is a combination of computational, mathematical, and statistical process which is used for developing and optimizing the processes parameters and evaluates their complex interactions [21,22].

The application of statistical methods for optimizing adsorption process involves less treatment time, low costs and higher percentage yields [23]. The mutual interactions between variables are described by the graphical representation of the equations called response surfaces [24,25].

Design-Expert 7.0.0 software (Stat Ease, USA) was used for this study. In this study, 2^3 full factorial central composite design (CCD) was employed with 20 experiments, including six replicates using RSM was employed. Artificial neural network (ANN) was used for designing the process modeling.

2. Experimental

2.1. Preparation of the adsorbents

At first Orange peel was collected from local fruit juice shop and dried at 70°C. Then, it was treated with 0.05(M) calcium hydroxide solution for 18 h. Then, it was washed repeatedly for 5–6 times with distilled water, until the orange color was removed from the washed water. Then it was dried in a hot air oven at 80°C for 24 h. The adsorbents mesh size was approximately 2 mm. The adsorbents were kept in an air tight glass bottle for further use in the adsorption experiments. Orange peel is common waste of every house-hold during winter and it is easily available. So the process of copper removal using treated orange peel is cost-effective.

2.2. Preparation of the adsorbate solution

A stock solution of copper was prepared using copper sulfate pentahydrate ($CuSO_4$,$5H_2O$), by dissolving in distilled water. 1,000 mg l^{-1} Cu(II) stock solution was prepared ($CuSO_4$,$5H_2O$ obtained from Merck). Using this stock solution different copper concentration solutions were prepared. For pH adjustment 0.1(N) HCl and 0.1(N) NaOH solutions were added, using a digital pH meter (ELICO).

2.3. Experimental setup

Copper solution was kept in conical flask and placed in incubator rotary shaker and required amount of (20 g/l) adsorbent was added to the solution. After predefined time intervals, sample was collected and centrifuged at 6,000 rpm for 10 min. Supernatant fractions were analyzed and copper concentration was determined spectrophotometrically at 460 nm by using sodium diethyl dithiocarbamate as the complexing agent [26,27]. Copper reduction by this process was obtained by using the following formula:

$$\% \text{ reduction} = \{(C_0 - C_1)/C_0\} \times 100 \quad (1)$$

where C_0 is initial copper concentration (mg/l) and C_1 is remaining copper concentration.

2.4. Optimization of adsorption process

A two-level three-factor (2^3) full factorial CCD was used for this copper removal study. Design Expert Version 7.0.0 (Stat Ease, USA) was used for the optimization of the process variables, and to evaluate the effects and complex interactions of each process variables. The effect of adsorption parameters, initial pH 3.5–5.5, copper concentration 15–50 mg/l, and contact time 45–90 min on percentage removal of copper was studied using statistically designed experiments and optimization by RSM. The ranges and levels of variables investigated in the research are given in Table 1.

The quadratic equation model for predicting the optimal point was expressed according to Eq. (2):

$$Y = \beta_0 + \sum_{i=1}^{K} \beta_i X_i + \sum_{i=1}^{K} \beta_{ii} X_i^2 + \sum_{i=1} \sum_{j=i+1} \beta_{ij} X_i X_j + \in \quad (2)$$

where Y was the predicted response, X_i, X_j refers to the independent variables, β_0, β_i, β_{ii}, β_{ij} are the regression coefficients and ε is the statistical error.

Percentage removal of copper was studied with a standard RSM design called the CCD. Twenty experiments were conducted consisting of factorial points (coded to the usual ±1 notation), axial points (±α), and six replicates at the centre points (0), and each of the experiment was conducted in duplicates in Table 2.

Design Expert Version 7.0.0 (Stat Ease, USA) was used for graphical analysis and regression of the data obtained. The optimum values of the selected parameters were found by solving the CCD equation of actual factors and by examining the response surface contour plots.

2.5. ANN description

Artificial neurons basically consist of inputs, outputs and mathematical functions which determine the activation of the neurons. ANNs combine artificial neurons in order to process information and validate a model. An ANN is a combination of mathematical and computational model, which is inspired by the structure and operational aspects of biological neural networks like synapses [28].

ANN has been used successfully for modeling copper removal. MATLAB 7 (The Mathworks, Inc., Ver. 7.0.1) was chosen to develop the ANN model using neural network toolbox from the data. In this present study, a three-layer feed-forward backpropagation neural network with a linear transfer function was developed for modeling of copper removal, using treated orange peel. Generally, ANN has three layers: an input layer which represents the independent variables, the output layer which gives the dependent variables (Response), and one or more hidden layer which act as a collection of feature detectors. As we have chosen pH, copper concentration (mg/l), and contact time (min) as independent variables and percentage removal of copper from the solution as dependent variables, network model with three neurons in the input layer and one neuron in the output layer, describes the ANN. Fig. 1 presented the ANN picture in this study.

The complexity of model of a neural network is determined by the number of hidden nodes in the network model. Though, presence of too many neurons in the hidden layer may also cause over fitting of the model data [29].

3. Results and discussion

3.1. Response surface estimation for maximum removal of copper

The empirical relationship between the response and the independent variables had been expressed by the following quadratic models

Table 1
Experimental range and levels of independent process variables

Independent variables	Range and levels (coded)				
	−α	−1	0	+1	+α
pH (*A*)	2.81821	3.50	4.50	5.50	6.18179
Initial copper concentration, mg/l (*B*)	3.06863	15	30.00	50	61.9314
Time, min (*C*)	29.6597	45.00	67.50	90.00	105.34

Table 2
2^3 factorial experimental setup and percent removal response

Run	Initial solution pH (*A*)	Initial copper concentration, mg/l (*B*)	Time (*C*), min	Response (% removal)
1	5.50	50	45	93.07
2	3.50	50	90	96
3	4.50	32.50	67.50	93
4	4.50	32.50	67.50	93
5	3.50	15	90	91
6	4.50	61.93	67.50	93.8
7	4.50	32.50	67.50	92.9
8	6.18	32.50	67.50	91.6
9	4.50	32.50	67.50	92.8
10	3.50	50.00	45.00	92.7
11	4.50	32.50	67.50	92.9
12	4.50	32.50	29.66	91.24
13	4.50	3.07	67.50	85.5
14	4.50	32.50	105.34	96
15	5.50	50.00	90	94.16
16	3.50	15.00	45	85.9
17	5.50	15.00	45	88.2
18	5.50	15.00	90	91.2
19	4.50	32.50	67.50	92.9
20	2.82	32.50	67.50	91.4

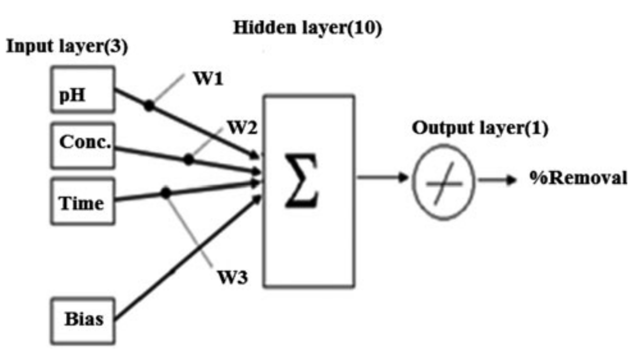

Fig. 1. Artificial neural network.

$$R_1 = 92.92 + 0.10A + 2.46B + 1.50C - 0.50AB - 0.54AC - 0.46BC - 0.50A^2 - 1.15B^2 + 0.25C^2 \tag{3}$$

$$R_1 = 57.63661 + 7.1092A + 0.59192B + 0.14533C - 0.028357AB - 0.023944AC - 0.00117778BC - 0.49681A^2 - 0.00375799B^2 + 0.0004992C^2 \tag{4}$$

where A is pH, B is concentration in mg/l, C is time in minutes.

Eq. (3) is in terms of coded factors and Eq. (4) is in terms of actual factors.

The percent removal of copper was taken as the response of the system.

The design expert 7.0.0 software was used for regression analysis of the data obtained and to estimate the coefficient of the regression equation. The equations were validated by the statistical tests called the ANOVA, to determine the significance of each term in the equations fitted and to estimate the goodness of fit in each case (Table 3). Response surfaces were drawn for the experimental results, obtained from the effect of different variables on the percentage removal of copper, in order to determine the individual and cumulative effects of these variables and the mutual interactions between them.

The Fisher's F value (1344.10) with a low probability ($p < 0.0001$) showed that the model was significant. The multiple corelation coefficient (R^2) demonstrated the goodness of the model (Table 4). Moreover, R^2 value is 0.9992 implied that more than 99% of the data deviation could be explained by the developed quadratic model, and the predicted R^2 values were in agreement with adjusted R^2, which means all the terms depicted in the model were significant. In this case, the non-significant lack-of-fit, 0.9992 (more than 0.05) showed the quadratic model was valid for this process [30,31].

Table 3
Analysis of variance for the response surface quadratic model for copper removal

Source	Sum of squares	Degree of freedom (df)	Mean square	*F* value	Probablity > F
Model	143.10	9	15.90	1344.10	<0.0001
Residual	0.12	10	0.012		
Lack of fit	0.090	5	0.018	3.18	0.1153
Pure error	0.028	5	0.005667		
Cor total	143.22	19			

Table 4
Regression analysis by using CCD

Model term	Coefficient estimate	Standard error	*F* value	*P* value
A	0.10	0.029	11.56	0.0068
B	2.46	0.029	6983.38	<0.0001
C	1.50	0.029	2600.07	<0.0001
AB	−0.50	0.038	166.54	<0.0001
AC	−0.54	0.038	196.29	<0.0001
BC	−0.46	0.038	145.44	<0.0001
A^2	−0.50	0.029	300.68	<0.0001
B^2	−1.15	0.029	1613.58	<0.0001
C^2	0.25	0.029	77.81	0.0003

Note: $R^2 = 0.9992$; adjusted $R^2 = 0.9984$; predicted $R^2 = 0.9949$.

3.2. Effect of initial solution pH and initial copper concentration

The effect of different levels of initial solution pH and initial copper concentration on adsorption using the $Ca(OH)_2$ modified orange peel can be predicted from the contour plot as shown in Fig. 2. The possible goals were: within range (for three independent variables pH, initial copper concentration), minimize (time) and maximize (for responses only) and set to an exact value (factors only). From the contour plot, it can be observed that copper removal percentage increased with increase of pH and initial copper concentration.

Solution pH affected the chemistry of the metal ions, the activity of ions on the adsorbent surface, as well as competition of copper ions with hydrogen ions for the binding sites [32,33]. The surface of adsorbent were protonated at pH values lower than 3.5, and thereby restricted the approach of positively charged copper (Cu(II) cations to the surface of the adsorbent). In the pH range of 3.5–5.5, these groups were negatively charged and the sorption process of copper then proceeded because of electrostatic attraction between the positively charged copper cations and the negatively charged adsorbent surface [34].

3.3. Effect of initial copper concentration and time

The combined effect of initial copper concentration and contact time on copper removal was shown in the contour plot of Fig. 3. The number of copper cations adsorbed at higher concentrations was more than that removed from less concentrated solutions. Higher copper concentrations enhanced the mass transfer driving force and increased the copper cations adsorption. From the results it was observed that a maximal removal efficiency of 93.4253% was achieved at pH 4.7533, 55.5 mg/l copper concentration, and 33.9162 min of contact time.

3.4. Effect of initial solution pH and contact time

The combined effect of initial solution pH and contact time on copper removal was shown in the contour plot of Fig. 4. It was observed that initially % removal increased with increasing pH. At minimum contact time the % removal was maximum. The maximum copper removal efficiency of 93.4253% was obtained from pH 4.7533 and contact time 33.9162 min, when copper solution concentration was fixed at 55.5 mg/l. It was evident from contour plots that both the independent variables had a strong influence on the copper biosorption process.

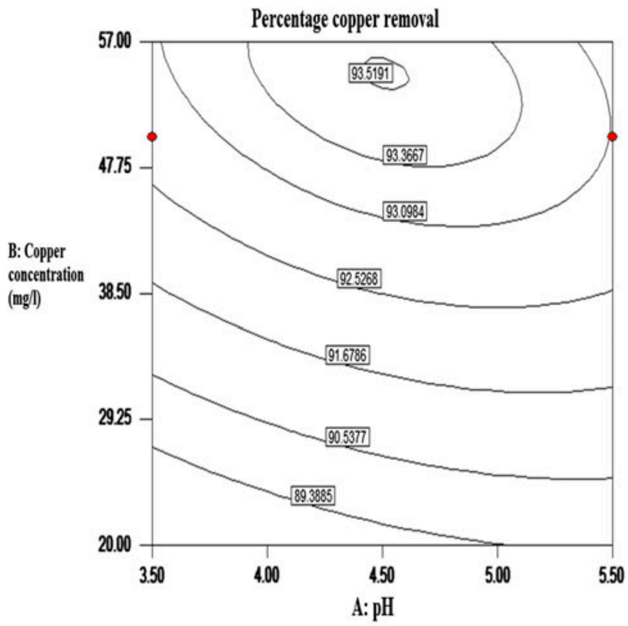

Fig. 2. The contour plot shows the relationship between pH and initial copper concentration with the percentage copper removal.

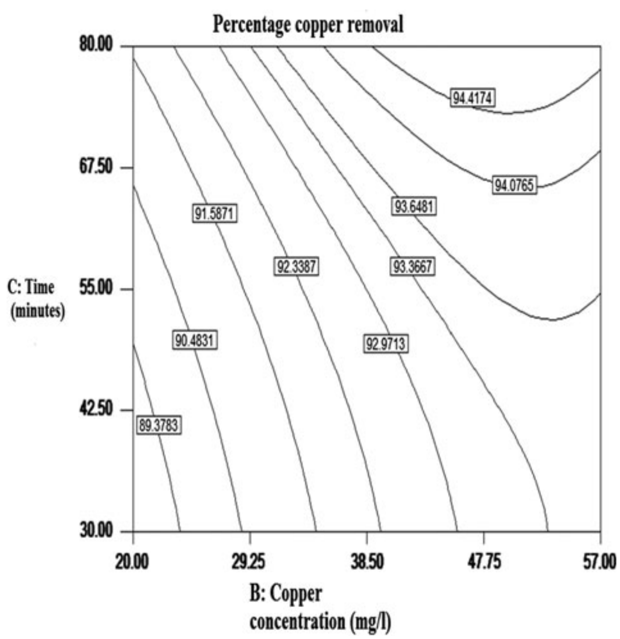

Fig. 3. The contour plot shows the relationship between initial copper concentration and time with the percentage copper removal.

3.5. Comparison between theoretical and experimental data

The CCD equation of actual factors was solved by partial differential calculus for obtaining the optimum value of A, B, C [35].

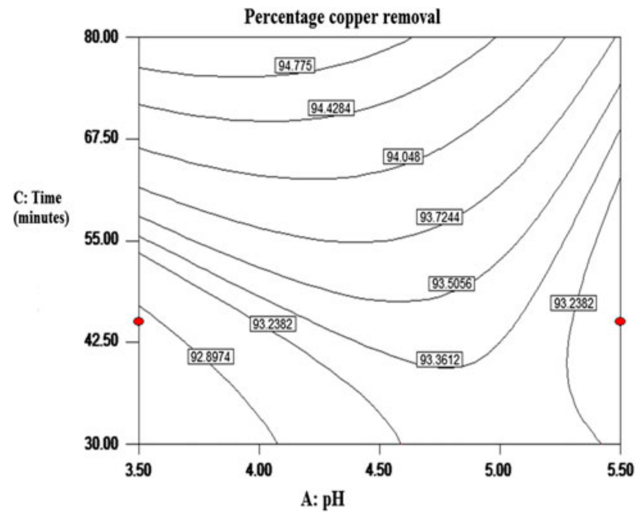

Fig. 4. The contour plot shows the relationship between pH and the time with the percentage copper removal.

CCD equation of actual factors:

$$\begin{aligned} R_1 = {} & 57.63661 + 7.1092A + 0.59192B + 0.14533C \\ & - 0.028357AB - 0.023944AC - 0.00117778BC \\ & - 0.49681A^2 - 0.00375799B^2 + 0.0004992C^2 \end{aligned} \quad (4)$$

$$\begin{aligned} \partial R_1/\partial A = {} & 7.10920 - 0.99362A - 0.028357B \\ & - 0.023944C \end{aligned} \quad (5)$$

$$\partial^2 R_1/\partial A^2 = -0.99362 \quad (6)$$

$$\begin{aligned} \partial R_1/\partial B = {} & 0.59192 - 0.028357A - 0.00751598B \\ & - 0.00117778C \end{aligned} \quad (7)$$

$$\partial^2 R_1/\partial B^2 = -0.00751598 \quad (8)$$

$$\begin{aligned} \partial R_1/\partial C = {} & 0.14533 - 0.023944A - 0.00117778B \\ & + 0.000998412C \end{aligned} \quad (9)$$

$$\partial^2 R_1/\partial C^2 = 0.000998412 \quad (10)$$

The Eqs. (5), (7) and (9) are first-order-partial differential equations and these equations were equated with zero for solving, and the solutions were:

A (pH) = 4.7533,
B (conc.) = 55.5097 mg/l,
C (time) = 33.9162 min.

Eqs. (6), (8) and (10) are second-order-partial differential equations.

Table 5
The algorithm used in the study

Algorithm for hidden layer	Function for output layer	Transfer function	Transfer function	Correlation efficient (R)
Levenberg-Marquardt backpropagation	Trainlm	Poslin	Purelin	0.967

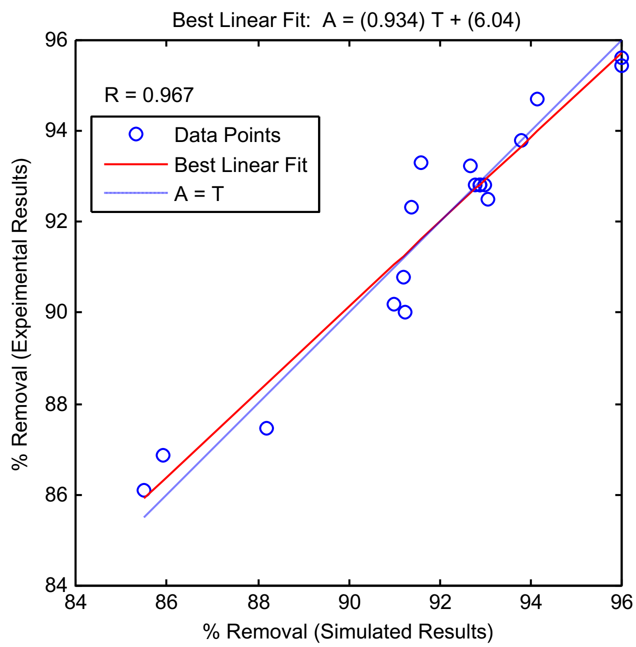

Fig. 5. Regression plot (experimentally vs. predicted) using three input variables, ten processing elements in hidden layer, and one output variable using ANN model.

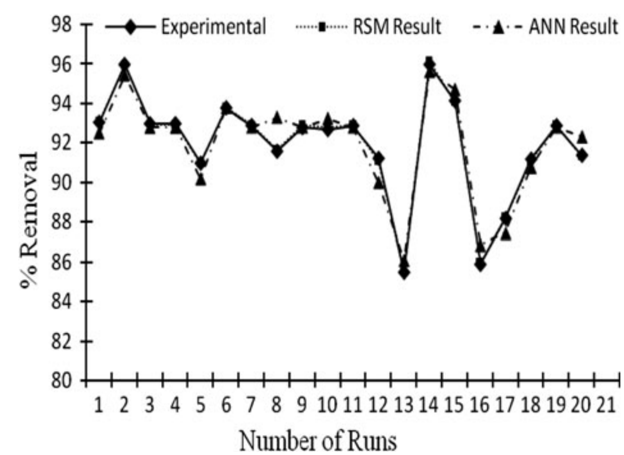

Fig. 6. Plot of experimental and theoretical results of RSM and ANN model.

Table 6
Comparison of RSM and ANN models

Parameters	RSM	ANN
RMSE	0.0766	0.6857

Eqs. (6) and (8) showed negative values indicating absence of local maximum and applicability of maximization, and Eq. (10) showed positive values, indicating the local minimum and applicability of minimization of process time.

Theoretical R_1 (%removal) = 93.4253%.

Experimental removal R_1 was 93.4506% obtained at A (pH) = 4.75, B (conc.) = 55.5097 mg/l, C (time) = 33.9162 min.

The % deviation of experimental and theoretical was 0.02708%.

Using the CCD equation theoretical response was calculated at twenty different sets of the A, B, C values. Table 5 showed the comparison between experimental data and theoretical data.

3.6. ANN training

The data generated from the experimental design planned through CCD was used to figure out the optimal architecture of ANN by using MATLAB7 software. After testing, it was observed that 10 neurons produced minimum value of error of the training and validation sets. ANNs are used to the copper adsorption optimization studies to develop and validate the model that can predict the copper removal efficiency. The experimental dataset (consisting of 20 data points) was separated into three subsets—training (12 data points), validation (4 data points) and test sets (4 data points). The total copper reduced from the solution was chosen as the experimental response or output variable. The network which gave a coefficient of correlation (R) 0.967 which is near to 1 considered to be a perfect model and hence, was selected. Majority of ANN architectures are feed-forward networks, which were mostly trained from the input data using error backpropagation algorithm. Linear transfer function "POSLIN" (being a positive linear transfer function) was chosen for the input to hidden layer mapping,

Table 7
Validation set

Run	pH (*A*)	Conc. (*B*) (mg/l)	Time (*C*) (min)	Experimental response (% removal)	Predicted response (from CCD equation)	Residual (RSM)	Predicted (from ANN equation)	Residual (ANN)
1	5.5	50	45	93.07	93.08615	0.017354514	92.5175	−0.5525
2	3.5	50	90	96	95.95234	−0.049674559	95.4475	−0.5525
3	4.5	32.5	67.5	93	92.91596	−0.090450799	92.8150	−0.185
4	4.5	32.5	67.5	93	92.91596	−0.090450799	92.8150	−0.185
5	3.5	15	90	91	90.9683	−0.03484417	90.1962	−0.8038
6	4.5	61.93	67.5	93.8	93.79717	−0.003020222	93.8	0
7	4.5	32.5	67.5	92.9	92.91596	0.017173342	92.815	−0.085
8	6.18	32.5	67.5	91.6	91.67909	0.086270853	93.3089	1.7089
9	4.5	32.5	67.5	92.8	92.91596	0.124797483	92.815	0.015
10	3.5	50	45	92.7	92.80099	0.108829275	93.2525	0.5525
11	4.5	32.5	67.5	92.9	92.91596	0.017173342	92.815	−0.085
12	4.5	32.5	29.66	91.24	91.10693	−0.146059237	90.0101	−1.2299
13	4.5	3.07	67.5	85.5	85.52436	0.028484179	86.1007	0.6007
14	4.5	32.5	105.34	96	96.1546	0.160783804	95.6198	−0.3802
15	5.5	50	90	94.16	94.08254	−0.08233611	94.7125	0.5525
16	3.5	15	45	85.9	85.96196	0.072075953	86.8606	0.9606
17	5.5	15	45	88.2	88.23211	0.036390267	87.4487	−0.7513
18	5.5	15	90	91.2	91.08349	−0.127912475	90.784	−0.416
19	4.5	32.5	67.5	92.9	92.91596	0.017173342	92.815	−0.085
20	2.82	32.5	67.5	91.4	91.34244	−0.063016211	92.321	0.921

while a purely linear transfer function "PURELIN" was chosen for the hidden layer to the output layer mapping. The values of correlation coefficient (*R*) were calculated among the best of 10 repeated run. The regression plot of the trained network was shown in Fig. 5. The trained network in this figure gave a correlation coefficient of 0.967. A high correlation coefficient of this plot signified the reliability of the neural model with the experimental data. Table 5 showed that the "Levenberg–Marquardt backpropagation (Trainlm)" algorithm with "poslin" transfer function, with a minimum mean squared error, (MSE) gave a most satisfactory result [36]. The CCD of three independent variables and ANN analysis with copper reduction experimentally, as responses, was presented in Fig. 6. It was observed that the deviation in both of the cases were very low.

The performance of the constructed ANN and RSM models were also statistically measured by the root mean squared error (RMSE) as follows [37,38]:

$$\mathrm{RMSE} = \left(1/n \sum_{i=1}^{n} \left(R_{\mathrm{predicted}} - R_{\mathrm{experimental}}\right)^2\right)^{1/2} \quad (11)$$

where n is the number of points, $R_{\mathrm{predicted}}$ is the predicted value, $R_{\mathrm{experimental}}$ is the actual value.

Tables 6 and 7 present the statistical comparison of RSM and ANN models. The RMSE for RSM and ANN was determined as 0.0766 and 0.6857 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 [37,38]. 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.

4. Conclusion

The present study was taken with the aim of scale-up of the copper adsorption process using the $Ca(OH)_2$ modified orange peel and to investigate the combined effect of various process parameters on copper removal using RSM. The initial solution pH, initial copper concentration, and contact time significantly influenced the copper removal efficiency. Optimization conditions for the maximum removal efficiency of copper were obtained by applying a desirability function in RSM. Based on the statistics analysis the optimum conditions were obtained from pH 4.75, initial copper concentration 55.5 mg/l, contact time 33.9162 min, and the copper removal was 93.4253%. This adsorbent is an agro-waste material and so the process of removal of copper from waste water is very cost-effective process.

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