DOI:10.25092/baunfbed. 1330185 **J. BAUN Inst. Sci. Technol., 26(1), 124-138, (2024)**

Modelling and optimization of copper removal from water using carbon nanotubes with RSM and ANN

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Geliş Tarihi (Received Date): 20.07.2023
Kabul Tarihi (Accepted Date): 02.10.2023

Abstract

In this study, it was aimed to remove heavy metal copper from aqueous solutions by using MWCNT-OH, which is a multi-walled carbon nanotube. Modelling and optimization were performed using the Response Surface Method (RSM) and Artificial Neural Networks (ANN). Model equations were derived by both methods. ANOVA analyses were performed with RSM to determine the significance of the parameters on removal efficiency and adsorption capacity. Contour graphs showing the binary parameter interactions were obtained. Optimization was carried out to obtain the maximum removal efficiency and maximum adsorption capacity using both RSM and ANN. Using RSM and ANN, the maximum copper removal efficiencies were obtained at 45.1% and 39.1%, while the maximum adsorption capacities were found to be 16.7 mg/g and 17.12 mg/g, respectively. In addition, test experiments and modelling methods were compared, revealing that the modelling capability of ANN was superior to that of RSM.

Keywords: *Copper, carbon nanotubes, adsorption, response surface methodology, artificial neural networks.*

Karbon nanotüpler kullanılarak sulardan bakır gideriminin YYY ve YSA ile modelleme ve optimizasyonu

Öz

Bu çalışmada çok duvarlı karbon nanotüplerden olan MWCNT-OH kullanılarak ağır metallerden bakırın sulu çözeltilerden giderimi hedeflenmiştir. Çalışmada modelleme ve optimizasyon için Yanıt Yüzey Yöntemi (YYY) ile Yapay Sinir Ağları (YSA) kullanılmıştır. Her iki yöntemle model denklemleri türetilmiştir. YYY ile ANOVA analizi yapılarak

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parametrelerin giderim verimi ve adsorpsiyon kapasitesi üzerindeki anlamlılıklarını belirlenmiştir. İkili parametre etkileşimlerinin görüldüğü contour grafikler elde edilmiştir. YYY ve YSA ile maksimum giderim verimi ve maksimum adsorpsiyon kapasitesini elde etmek amacıyla optimizasyon yapılmıştır. RSM ve YSA kullanılarak, maksimum bakır giderim verimleri %45,1 ve %39,1 olarak elde edilirken, maksimum adsorpsiyon kapasiteleri sırasıyla 16,7 mg/g ve 17,12 mg/g olarak bulunmuştur. Ayrıca test deneyleri ile modelleme yöntemleri karşılaştırılmıştır. YSA'nın modelleme kabiliyetinin YYY'ye göre daha iyi olduğu görülmüştür.

Anahtar kelimeler: *Bakır, karbon nanotüpler, adsorpsiyon, yanıt yüzey metodolojisi, yapay sinir ağları.*

1. Introduction

Copper is one of the earliest metals used by humans since the beginning of civilization [1]. Copper is widely used in industries such as electrical cables, air conditioning pipes, plumbing, roofing, etc. owing to its high thermal and electrical conductivity, ease of fabrication and installation, resistance to corrosion, high recyclability, pleasing appearance, etc. [2]. The majority of copper pollution originates from activities such as metal plating, electroplating, etching and engraving printing, pulp and paper manufacturing, cardboard production, wood preservative factories, and the fertilizer industry [3,4]. While copper (Cu^{2+}) is an essential trace element required for enzyme synthesis, tissue and bone development in humans, it can become toxic and carcinogenic when consumed above the recommended limits [5]. Various treatment methods have been employed to remove Cu^{2+} from water and wastewater, including chemical precipitation [6,7], ion exchange [8,9], membrane filtration [10,11], flotation [12], electrochemical treatment [13,14], coagulation/flocculation [15,16], and adsorption. Among these, adsorption is the most commonly used method due to its ease of application and low investment cost [2,17].

Carbon nanotubes (CNT) are composed of cylindrical sheets of graphite (an allotropic form of carbon) wrapped in a tube-like structure [18]. CNTs are classified as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) based on the number of layers they possess. MWCNTs offer several advantages over SWCNTs, including bulk synthesis capability, catalyst-free production, and low production cost [19]. CNTs are used for heavy metal (Pb, Cu, Hg, Cd, Ag, Ni, etc.) removal from wastewater due to their large surface area and chemical stability [20–25]. In order to increase the adsorption capacity of CNTs for metal ions, oxygen-containing functional groups are introduced through oxidation [26].

In this study, modeling and optimization of copper removal using MWCNT-OH from multi-walled carbon nanotubes as adsorbent by RSM and ANN were aimed.

2. Material and methods

In the studies, MWCNT-OH, a multi-walled carbon nanotube obtained from Nanography Nano Technology, was used as an adsorbent for copper removal from synthetic solutions. Copper solutions were prepared using $CuSO_4.5H_20$ salt obtained from Horasan Kimya.

A stock solution of 1000 mg/L was prepared from $CuSO_4.5H_2O$ salt, and samples were prepared through dilutions from the stock solution. 0.1 N HCl and NaOH solutions were used for pH adjustments. Copper was determined by volumetric analysis. Preliminary experiments indicated that the equilibrium time was 30 minutes.

RSM is used for experimental design, particularly when the process inputs (factors) affect the process outputs. One of the significant advantages is its cost-effectiveness and time-efficiency due to the limited number of experiments required [27,28]. Central composite design (CCD), a type of RSM designs, is a standard method that that minimizes the number of experiments needed to establish correlations between inputs and outputs [29,30]. The mathematical expression of the second-order central composite RSM is given in Equation (1).

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

In this equation, Y represents the second-order polynomial, β_0 is the model constant, βi, βii and β_{ij} are the coefficients to be calculated [31,32].

For the experimental design of copper adsorption on MWCNT-OH as an adsorbent, the CCD method of RSM was applied using Minitab 19 program. Based on the results of preliminary experiments, four independent variables and their corresponding levels were determined. Solid/liquid ratio (S/L), initial copper concentration, temperature and stirring speed (SS) were determined as independent variables. The dependent variables are removal efficiency and adsorption capacity. The experimental design consisted of four factors, three levels, and seven center-point experiments for these factors, resulting in a total of 31 sets of experiments. The factors and levels used in the experimental design for copper adsorption with MWCNT-OH are presented in Table 1.

Table 1. Experimental design factors and levels.

Factor	-1	0	+1
A- Solid/Liquid (S/L) (g/L)	1	2	3
B- Concentration (mg/L)	25	50	75
C- Temperature (˚C)	20	30	40
D- Stirring speed (SS) (rpm)	100	200	300

100 mL of copper samples were taken and placed in polyethylene bottles, and the adsorption process was carried out in the shaker for 30 minutes under the conditions determined in the experimental design. At the end of the equilibrium adsorption time, the samples were passed through a 0.2 µm pore diameter syringe tip filter, and the copper concentration was determined. Removal efficiency (%) and q_e values, determined as independent parameters were calculated according to Equation (2) and Equation (3), respectively.

$$R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{3}$$

where C_o describes initial concentration of contaminants in the solution (mg/L), C_e defines equilibrium concentration of contaminants in the solution (mg/L), V demonstrates the solution volume (L), m stands for adsorbent quantity (g).

Artificial neural network (ANN) is a method inspired by human learning and responding abilities by studying the function and structure of the nervous system in the human brain. For this reason, they have a high success rate in the field of analyzing or modelling data [33]. While forming the ANN model, it is not necessary to know the process in all the details of the process or conduct various technical analyses. As a result of selecting the network structure compatible with the available data, models with high accuracy can be created. During the training of the network, the feed-forward back propagation artificial neural network (FFBPANN) structure is formed as a result of updating the weights determined by propagating the error rate obtained between the actual result in the dataset and the model result backward [34]. The error rate obtained between the actual result in the dataset and the model result is propagated backward during the training of the network, leading to the creation of the FFBPANN model as a result of updating the determined weights. Thus, by determining the most appropriate weights, the error rate between the model result and the actual results is reduced to a minimum level, maximizing the accuracy. In this study FFBPANN model was used.

The factors and levels given in Table 1 were also used in the ANN studies. In this study, two different ANN equations were obtained by modeling the removal efficiency (%) and q_e values as independent variables using the 'nntool' toolkit of the Matlab program. For copper removal, an ANN model with an input layer consisting of 4 factors (S/L ratio, initial copper concentration, temperature and stirring speed), a hidden layer consisting of 5 neurons and an output layer consisting of removal efficiency and adsorption capacity was created. ANN experiments were carried out following the same procedure as the RSM experiments.

3. Results and Discussion

The removal efficiency (%) and adsorption capacity (q_e) values, calculated according to the experimental design (RSM) and experimental results in copper adsorption studies with MWCNT-OH, are given in Table 2.

Table 2. Experimental design and results for copper adsorption with MWCNT-OH.

No.	S/L (g/L) A	Copper Conc. (mg/L) B	Temperature (˚C) C	Stirring Speed (rpm) D	Removal Efficiency (%)		q_e (mg/g)	
					Exp. Results	RSM Model Results	Exp. Results	RSM Model Results
1	1	25	20	100	15.79	17.44	3.81	5.18
2	3	25	20	100	31.58	30.50	2.54	2.56
3	1	75	20	100	19.66	18.82	14.61	13.47
4	3	75	20	100	26.50	26.12	6.57	6.36

Table 2. (continued)

5	1	25	40	100	18.42	17.06	4.45	3.95
6	3	25	40	100	31.58	32.05	2.54	2.03
7	1	75	40	100	17.95	19.46	13.34	13.99
8	3	75	40	100	28.21	28.69	6.99	7.58
9	1	25	20	300	21.05	19.22	5.08	4.28
10	3	25	20	300	36.84	36.39	2.97	2.46
11	1	75	20	300	17.95	18.53	13.34	14.01
12	3	75	20	300	29.91	29.93	7.41	7.69
13	1	25	40	300	21.05	22.49	5.08	5.44
14	3	25	40	300	42.11	41.59	3.39	4.32
15	1	75	40	300	23.08	22.82	17.16	16.92
16	3	75	40	300	36.75	36.16	12.53	11.31
17	1	50	30	200	20.51	19.62	10.17	9.81
18	3	50	30	200	30.77	32.82	5.08	5.69
19	2	25	30	200	26.32	28.00	3.18	2.82
20	2	75	30	200	26.50	25.97	9.85	10.46
21	2	50	20	200	30.77	33.09	7.62	7.95
22	2	50	40	200	37.18	36.01	9.21	9.14
23	2	50	30	100	33.33	32.88	8.26	7.99
24	2	50	30	300	35.90	37.51	8.90	9.41
25	2	50	30	200	33.33	32.29	8.26	8.01
26	2	50	30	200	33.33	32.29	8.26	8.01
27	2	50	30	200	30.77	32.29	7.62	8.01
28	2	50	30	200	34.62	32.29	8.58	8.01
29	2	50	30	200	33.33	32.29	8.26	8.01
30	2	50	30	200	30.77	32.29	7.62	8.01
31	2	50	30	200	33.33	32.29	8.26	8.01

The correlation coefficient (R^2) value for the removal efficiency of copper adsorption with MWCNT-OH was found to be 0.9664. The equation derived from the model for the removal efficiency is given in Equation (4). Using this equation, removal efficiency values can be calculated without performing experiments by entering the desired variables.

$$\begin{aligned}
\mathrm{Re}\,movalEfficiency(\%) &= 4.77 + 30.25A + 0.935B - 1.542C \\
&-0.1306D - 6.07A*A - 0.00849B*B + 0.0226C*C \\
&+0.000290D*D - 0.0576A*B + 0.0485A*C \\
&+0.01028A*D + 0.00102B*C - 0.000207B*D \\
&+0.000912C*D
\end{aligned} \tag{4}$$

The results of ANOVA analysis to determine the effect of independent variables on the removal efficiency (%) for copper adsorption on MWCNT-OH are presented in Table 3.

Table 3. ANOVA analysis for removal efficiency of copper adsorption with MWCNT-OH.

	DF	Adj SS	Adj MS	F-Value	P-Value	p<0,05
Model	14	1380.56	98.61	32.86	0.000	Significant
Linear	4	936.95	234.24	78.05	0.000	Significant
S/L (g/L)	1	783.83	783.83	261.19	0.000	Significant
Copper Conc. (mg/L)	1	18.49	18.48	6.16	0.025	Significant
Temperature (˚C)	1	38.34	38.34	12.78	0.003	Significant
Stirring Speed (rpm)	1	96.29	96.29	32.09	0.000	Significant
Square	4	371.07	92.77	30.91	0.000	Significant
S/L (g/L)*S/L (g/L)	1	95.64	95.63	31.87	0.000	Significant
Copper Conc. (mg/L)*Copper Conc. (mg/L)	1	73.06	73.06	24.34	0.000	Significant
Temperature (˚C)*Temperature (˚C)	1	13.29	13.29	4.43	0.052	
Stirring Speed (rpm)*Stirring Speed (rpm)	1	21.88	21.88	7.29	0.016	Significant
2-Way Interaction	6	72.54	12.09	4.03	0.012	Significant
S/L (g/L)*Copper Conc. (mg/L)	1	33.22	33.22	11.07	0.004	Significant
S/L (g/L)*Temperature (˚C)	1	3.76	3.76	1.25	0.279	
S/L (g/L)*Stirring Speed (rpm)	1	16.90	16.89	5.63	0.031	Significant
Copper Conc. (mg/L)*Temperature (˚C)	1	1.04	1.04	0.35	0.565	
Copper Conc. (mg/L)*Stirring Speed (rpm)	1	4.31	4.30	1.43	0.248	
Temperature (˚C)*Stirring Speed (rpm)	1	13.32	13.32	4.44	0.051	

When evaluating the p-values ($p<0.05$) given in Table 3, it can be observed that the model exhibited significance for copper removal on MWCNT-OH, as well as for the parameters S/L, copper concentration, temperature, and SS. Additionally, the binary parameters S/L*S/L, Copper Concentration*Copper Concentration, SS*SS, S/L*Copper Concentration and S/L*SS were found to be effective.

Contour graphs illustrating the effect of the other two parameters on the removal efficiency of copper adsorption with MWCNT-OH, while keeping the two parameters constant, are presented in Figure 3.

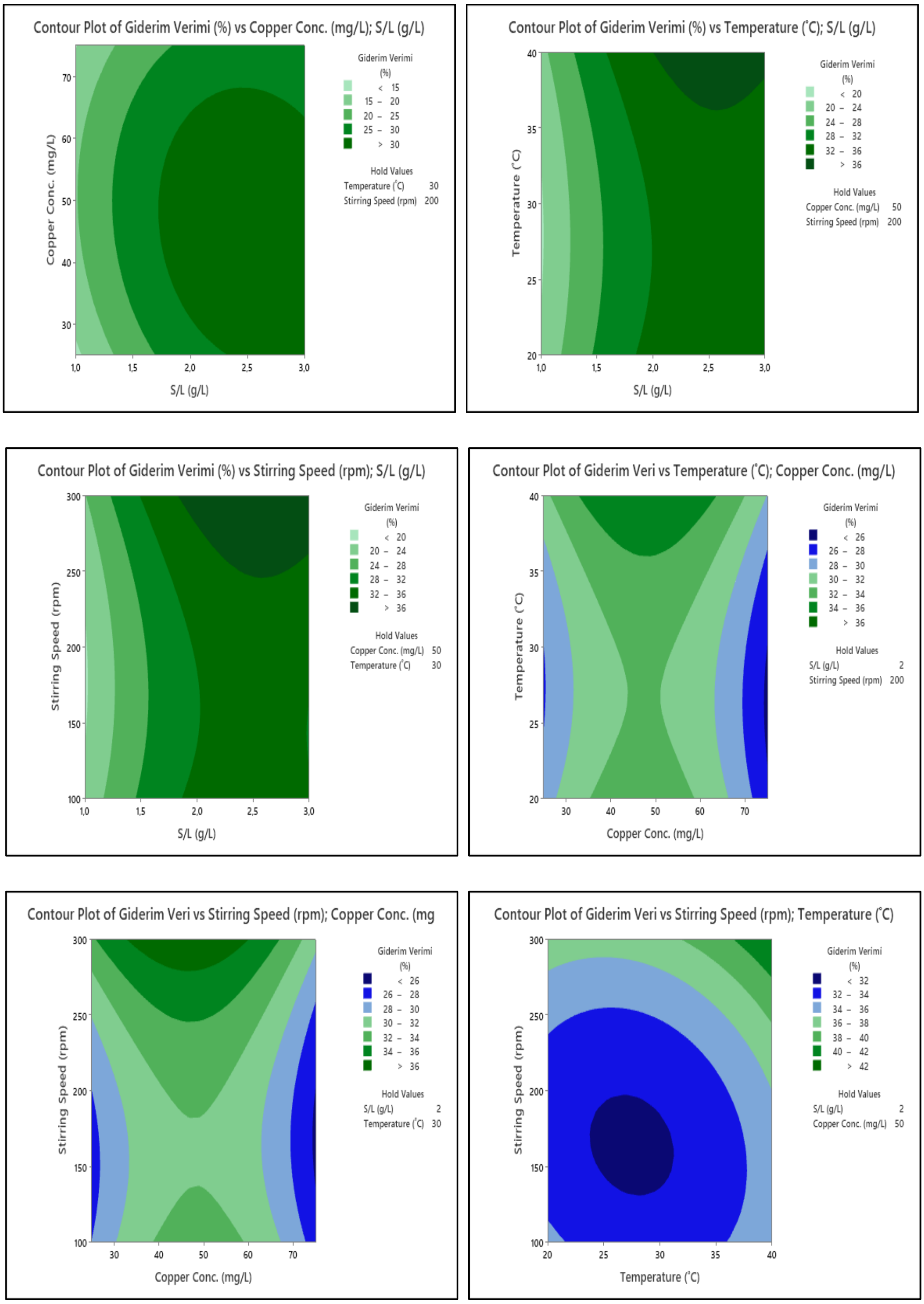

Figure 3. Contour plots for removal efficiency (%) in copper adsorption with MWCNT-OH.

The R^2 value for copper adsorption with MWCNT-OH was found to be 0.9733, and the equation derived from the model for q_e value is given in Equation (5).

$$
\begin{aligned}
& q_e(mg/g) = 7.28 + 0.32A + 0.3813B - 0.501C \\
& -0.0496D - 0.263A*A - 0.0022B*B \\
& +0.00531C*C + 0.000069D*D - 0.04493A*B \\
& +0.0174A*C + 0.00201A*D + 0.001755B*C \\
& +0.000144B*D + 0.000598C*D
\end{aligned} \tag{5}
$$

The results of the ANOVA analysis to determine the effect of independent variables on q_e (mg/g) for copper adsorption on MWCNT-OH are presented in Table 4.

Table 4. ANOVA analysis for adsorption capacity (q_e) of copper adsorption with MWCNT-OH.

	DF	Adj SS	Adj MS	F-Value	P-Value	p<0,05
Model	14	392.879	28.063	41.64	0.000	Significant
Linear	4	354.299	88.575	131.44	0.000	Significant
S/L (g/L)	1	76.174	76.174	113.04	0.000	Significant
Copper Conc. (mg/L)	1	262.703	262.703	389.84	0.000	Significant
Temperature (˚C)	1	6.399	6.399	9.50	0.007	Significant
Stirring Speed (SS) (rpm)	1	9.023	9.023	13.39	0.002	Significant
Square	4	6.404	1.601	2.38	0.096	
S/L (g/L)*S/L (g/L)	1	0.180	0.180	0.27	0.613	
Copper Conc. (mg/L)*Copper Conc. (mg/L)	1	4.908	4.908	7.28	0.016	Significant
Temperature (˚C)*Temperature (˚C)	1	0.732	0.732	1.09	0.313	
SS (rpm)*SS (rpm)	1	1.235	1.235	1.83	0.195	
2-Way Interaction	6	32.176	5.363	7.96	0.000	Significant
S/L (g/L)*Copper Conc. (mg/L)	1	20.186	20.186	29.96	0.000	Significant
S/L (g/L)*Temperature (˚C)	1	0.485	0.485	0.72	0.409	
S/L (g/L)*SS (rpm)	1	0.643	0.643	0.95	0.343	
Copper Conc. (mg/L)*Temperature (˚C)	1	3.081	3.081	4.57	0.048	Significant
Copper Conc. (mg/L)*SS (rpm)	1	2.066	2.066	3.07	0.099	
Temperature (˚C)*SS (rpm)	1	5.715	5.715	8.48	0.010	Significant

According to the p values given in Table 4, it is evident that the model is significant in copper adsorption on MWCNT-OH. The S/L ratio, copper concentration, temperature, and SS, along with the binary parameters Copper Concentration*Copper Concentration, S/L*Copper Concentration, Copper Concentration*Temperature, Temperature*SS are found to be effective.

Contour graphs illustrating the effect of the other two parameters on copper adsorption with MWCNT-OH, while keeping the two parameters constant for q_e are given in Figure 4.

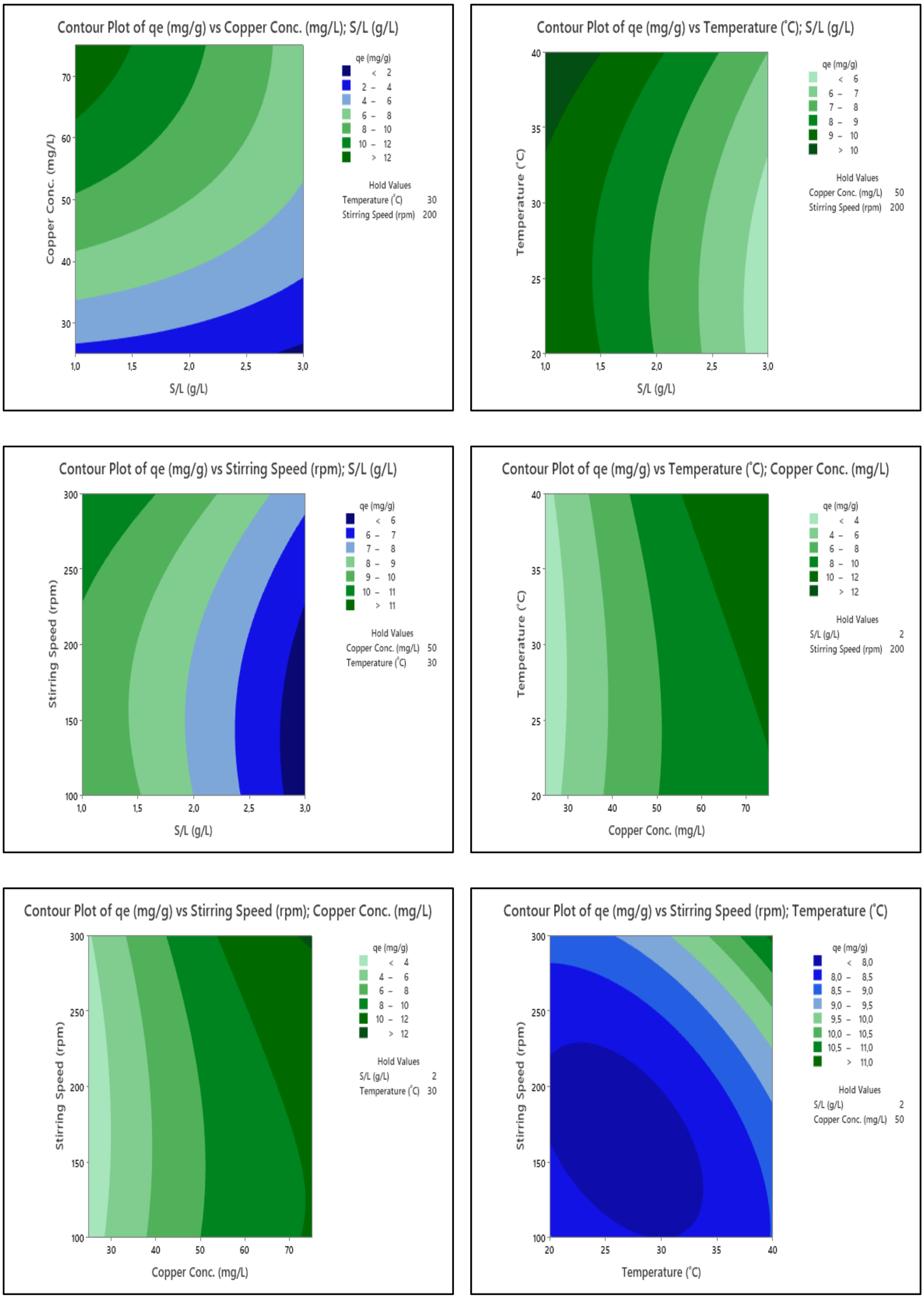

Figure 4. Contour plots for q_e in copper adsorption with MWCNT-OH.

In copper adsorption with MWCNT-OH, the conditions that maximized the removal efficiency (%) and adsorption capacity were determined, and the average results of three repeated experiments performed under these conditions are given in Table 5 and Table 6, respectively.

Table 5. Optimum conditions and results for copper removal efficiency (%).

Optimum Conditions				RSM Model Removal Efficiency (%)	Exp. Result Removal Efficiency (%)
S/L (g/L)	Concentration (mg/L)	Temperature (˚C)	SS (rpm)		
2,7	45	40	300	42.2-47.9	45.1

Table 6. Optimum conditions and results for copper adsorption capacity (q_e).

Optimum Conditions				RSM Model q_e (mg/g)	Exp. Result q_e (mg/g)
S/L (g/L)	Concentration (mg/L)	Temperature (˚C)	SS (rpm)		
1	75	40	300	15.5-18.3	16.7

As shown in Table 5 and Table 6, when the results of the experiments are compared with the results predicted by the RSM, it is seen that the results are in agreement with the model and are within the acceptable limit.

The ANN model for copper adsorption with MWCNT-OH was obtained using the experimental design and results given in Table 7. The removal efficiency (%) and adsorption capacity (q_e) values calculated from this model are also given in Table 7.

Table 7. Experimental design and ANN model results for copper adsorption with MWCNT-OH.

No	S/L (g/L) A	Copper Conc.(mg/L) B	Temperature (˚C) C	SS (rpm) D	Removal Efficiency (%)		q_e (mg/g)	
					Exp. Result	ANN Model Result	Exp. Result	ANN Model Result
1	1	25	20	100	15.79	15.79	3.81	3.81
2	3	25	20	100	31.58	31.58	2.54	2.55
3	1	75	20	100	19.66	19.66	14.61	14.61
4	3	75	20	100	26.50	26.50	6.57	6.57
5	1	25	40	100	18.42	18.42	4.45	4.45
6	3	25	40	100	31.58	31.58	2.54	2.55
7	1	75	40	100	17.95	17.95	13.34	13.34
8	3	75	40	100	28.21	28.21	6.99	6.99
9	1	25	20	300	21.05	21.05	5.08	5.08
10	3	25	20	300	36.84	36.84	2.97	2.96
11	1	75	20	300	17.95	17.95	13.34	13.34
12	3	75	20	300	29.91	29.91	7.41	7.41
13	1	25	40	300	21.05	21.05	5.08	5.08
14	3	25	40	300	42.11	42.10	3.39	3.39
15	1	75	40	300	23.08	23.08	17.16	17.15
16	3	75	40	300	36.75	36.75	12.53	12.53
17	1	50	30	200	20.51	20.51	10.17	10.17
18	3	50	30	200	30.77	30.77	5.08	5.07
19	2	25	30	200	26.32	26.32	3.18	3.18

Table 7. (continued)

20	2	75	30	200	26.50	26.50	9.85	9.85
21	2	50	20	200	30.77	30.77	7.62	7.62
22	2	50	40	200	37.18	37.18	9.21	9.21
23	2	50	30	100	33.33	33.33	8.26	8.26
24	2	50	30	300	35.90	35.90	8.90	8.90
25	2	50	30	200	33.33	32.78	8.26	8.26
26	2	50	30	200	33.33	32.78	8.26	8.12
27	2	50	30	200	30.77	32.78	7.62	8.12
28	2	50	30	200	34.62	32.78	8.58	8.12
29	2	50	30	200	33.33	32.78	8.26	8.12
30	2	50	30	200	30.77	32.78	7.62	8.12
31	2	50	30	200	33.33	32.78	8.26	8.12

The removal efficiency and adsorption capacity ANN model was found and the mean-squared error (MSE) values were reduced to 0.408 and 0.025 as a result of 100 iterations, respectively. The R^2 value, which represents the correlation coefficient of the model obtained from training, was found to be 0.99. The graph drawn to visualize the compatibility between the experimental results of removal efficiency (%) and adsorption capacity (q_e) and the results obtained from the ANN model is presented in Figure 5.

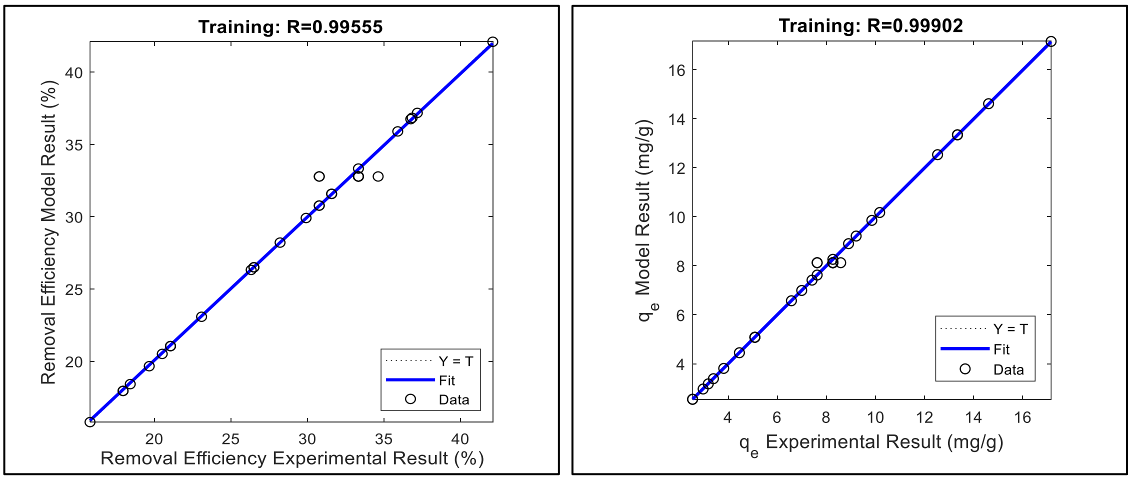

Figure 5. Training plot of ANN model for removal efficiency and adsorption capacity in copper adsorption with MWCNT-OH.

To test and compare the accuracy of ANN and RSM models in copper removal with MWCNT-OH, experiments were carried out under operating conditions not included in the experimental design. The graphs comparing the results obtained are shown in Figure 6 and it is evident that the error rate of the ANN model in the test results is lower than the RSM model.

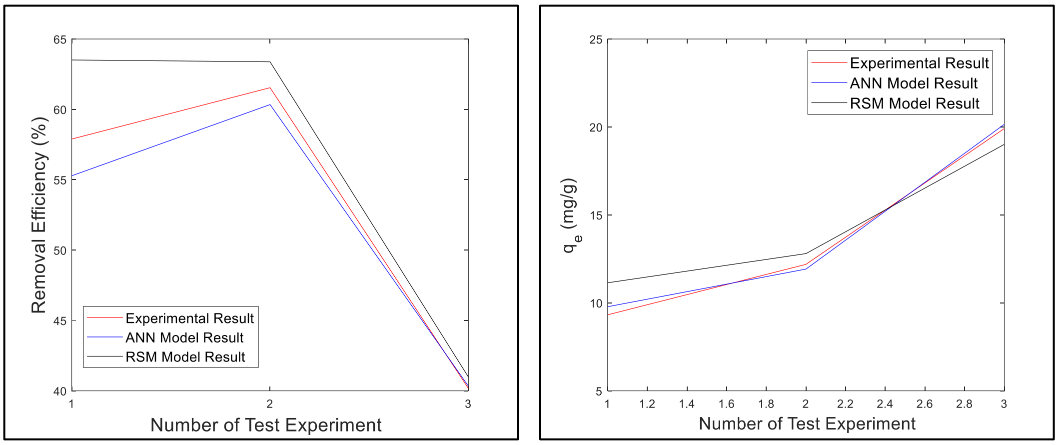

Figure 6. Test experiments for removal efficiency and qe in copper adsorption with MWCNT-OH.

The copper adsorption with MWCNT-OH, the removal efficiency (%) and adsorption capacity were optimized by ANN, and the optimum conditions and the average of the experimental results with three repetitions are given in Table 8 and Table 9, respectively.

Table 8. Optimum conditions and results derived from ANN model for copper removal efficiency (%).

Optimum Conditions				ANN Model Removal Efficiency (%)	Exp. Result Removal Efficiency (%)
S/L (g/L)	Concentration (mg/L)	Temperature (˚C)	SS (rpm)		
2.95	25	40	300	42.1	39.1

Table 9. Optimum conditions and results derived from ANN model for copper adsorption capacity (mg/g).

Optimum Conditions				ANN Model q_e (mg/g)	Exp. Result q_e (mg/g)
S/L (g/L)	Concentration (mg/L)	Temperature (˚C)	SS (rpm)		
1	75	32	300	17.11	17.12

4. Conclusion

In this study, considering the lack of copper removal studies with multi-walled carbon nanotubes with different structures in the literature, copper removal from synthetic solutions using MWCNT-OH was studied. Utilizing CCD in experimental design, both RSM and ANN models were developed based on the experimental results. In copper removal studies using MWCNT-OH, the R^2 values of RSM for removal efficiency (%) and adsorption capacity were found to be 0.9664 and 0.9733, respectively. The R^2 values of ANN model are calculated as 0.9955 and 0.9990 for removal efficiency (%) and adsorption capacity. The accuracy of both models was verified through test experiments. It was proven via these models, more results can be predicted with high accuracy without experiments. Finally, the optimal conditions, aiming for maximum removal efficiency (%) and adsorption capacity, were determined. The optimal results provided by RSM and ANN for the maximum copper removal percentage were 45.1% and 39.1%, respectively. Additionally, for adsorption capacity (q), the values obtained were 16.7 mg/g for RSM and 17.12 mg/g for ANN. Experimental studies confirmed that both model results closely matched the experimental results. However, ANN demonstrated greater effectiveness compared to RSM, attributed to its higher regression coefficient and modeling capability.

Acknowledgement

This study is based on a PhD thesis authored by Elif ÇALGAN under the supervision of Assist. Prof. Dr. Elif ÖZMETİN.

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