Factor Analysis and Response Surface Optimization for Copper Removal from Aqueous Solutions

Burcu Çağlar Gençosman
Industrial Engineering Department
Uludag University, Gorukle, Bursa 16059, Turkey

Âli Yurdun Orbak
Industrial Engineering Department
Uludag University, Gorukle, Bursa 16059, Turkey

İlkün Orbak
Industrial Engineering Department
Maltepe University, Maltepe, Istanbul 34857, Turkey

Abstract

Since its introduction in agriculture, experimental design methodology has been used in various research areas including industrial and chemical engineering. In this paper, factor analysis and response surface optimization approaches were used for copper removal from aqueous solutions. The factors affecting removal of copper (II) ions from aqueous solutions were investigated depending on pH, initial metal concentration and solution temperature. Activated carbon used in the experiments was produced from Tunçbilek lignite by physical activation method. The analysis of important factors is established by using the design of experiments method. The effect and the interaction among the investigated factors are evaluated using the analysis of variance method. Together with regression analysis, response surface optimization is also utilized to obtain optimum conditions for best copper removal within the experimental limits.

Keywords
Design of experiments, response surface optimization, activated carbon, adsorption, copper

1. Introduction

Factor analysis and experimental design techniques have been used in many different study fields, in order to understand the nature of systems, affecting parameters and how to improve the performance of a system [1]. It can be used to determine the best facility design in a manufacturing system [2], or to analyze a heuristic approach for a simulation-based meta-modeling of manufacturing systems [3]. In this paper, experimental design approach is used for analyzing copper removal process and to determine the optimal compound of parameters.

Wastewater discharged by industrial activities is often contaminated by a variety of toxic or otherwise harmful substances which have a negative effect on the water environment [4]. Numerous metals such as chromium Cr (III) and Cr (VI), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), cadmium (Cd), etc, are known to be significantly toxic. Though copper is not generally considered to be a threat to public health (it is an essential mineral in trace amounts), its presence at high concentrations in the body has been linked to kidney damage and other ailments [5]. The undesirable effects of hazardous chemicals can be prevented by removal of heavy metals by using various methods. The removal methods of metallic species from wastewater include chemical precipitation, electro flotation, ion exchange, reverse osmosis and adsorption [6]. The process of adsorption implies the presence of an 'adsorbent': solid that efficiently binds molecules by means of physical attractive forces, ion exchange or chemical binding. It is recommended that the adsorbent is available in large quantities, of free or very low cost and easily regenerable [7]. Activated carbon was especially known for the effectiveness in removing organic chemicals from wastewater, it is also known for the effectiveness in removing inorganics and heavy metal pollutants [8, 9].

Netzer and Hughs [10] demonstrated that powdered activated carbon could be used effectively for the removal of lead and copper from aqueous solutions. In general, carbon adsorption is not nearly effective at removing metals and inorganic pollutants as it is in removing organic compounds [11].

The goal of this research is to evaluate the adsorptive capacity of Tunçbilek Lignite for heavy metals. The adsorption of copper(II) was studied in steady-state batch tests. The Superfund Amendments and Reauthorization Act (SARA), Clean Water Act (CWA), and the Safe Drinking Water Act (SDWA) all specify limits on copper release concentrations. Copper standards in current EPA regulations are summarizes in Table 1 [12].

Table 1: EPA copper discharge limits

EPA Regulation	**Limit**
CWA (daily)	3.39 mg/l
CWA (30-day average)	2.07 mg/l
SDWA	1.3 mg/l
SARA	4.5 kg/year

The experimental tests were carried out according to a full 2^3 factorial design where factors were chosen as temperature, pH and concentration. After the experiments were completed a regression analysis was provided to investigate the most effective factors. As a last step for analysis response surface optimization is used to determine the optimum conditions for maximum copper removal.

2. Experimental Procedure

Activated carbon sample produced from Tunçbilek lignite with physical activation method was used in this study. The preparation procedure and the textural and chemical properties are given in [13].

The batch adsorption experiments were performed by varying the parameters of pH (2.0 – 6.0), initial Cu(II) ion concentration (25 – 1000 mg/L) and temperature (298 K, 308 K and 323 K). Initial and final concentrations of Cu(II) ions were determined by atomic absorption spectrometry. Blank solutions were treated similarly (without having adsorbent) and the concentration of this solution was taken as the initial concentration. Active carbon sample was contacted with the Cu(II) ion solutions for 24 h at which the equilibrium is reached. The pH was adjusted using dilute hydrochloric acid or sodium hydroxide solutions.

3. Mathematical Modeling and Analysis

Experiments were performed using different levels of factors as seen in Table 2. Each factor has two different levels and thus full 2^3 factorial design were chosen for analysis [1]. Design of experiments and gathered results can be found in Table 3.

Table 2: Controllable factors and their levels

Factors	**-1**	**+1**
A – Temperature (K)	298	323
B - Concentration	100	1000
C - pH	2	6

Table 3: Experimental results

Temperature (A)	**Concentration (B)**	**pH (C)**	**Cu q_e Value**
-1	-1	-1	1.28
1	1	-1	9.24
1	-1	1	3.52
-1	-1	1	2.68
1	1	1	24.99
-1	1	-1	6.67
1	-1	-1	2.04
-1	1	1	22.03

According to full 2^3 factorial designs [1], there have been at least 8 experiments as seen in Table 3. If a researcher decides to provide experiments in 3 replications, it means 24 different experiments for full factorial designs. Although more than one replication may produce more powerful results, in this study, as each experiment takes too long time to produce, only one replication is chosen. In order to eliminate lack of freedom, 3-way interactions are excluded from the analysis.

Main effects plot in Figure 1 indicates that concentration is the most effective factor and temperature has the least effect. The interactions plot in Figure 2 further indicates that concentration and pH have an interaction, and temperature with concentration or pH interactions are not important for copper removal process.

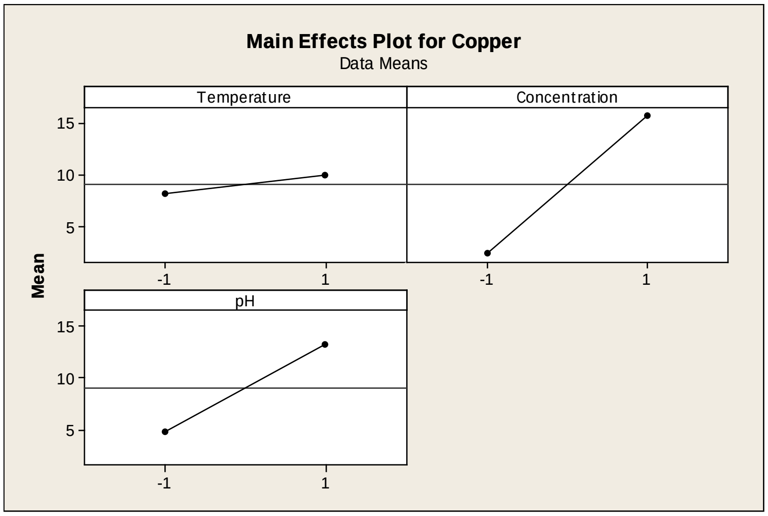

Figure 1: Main effects plot

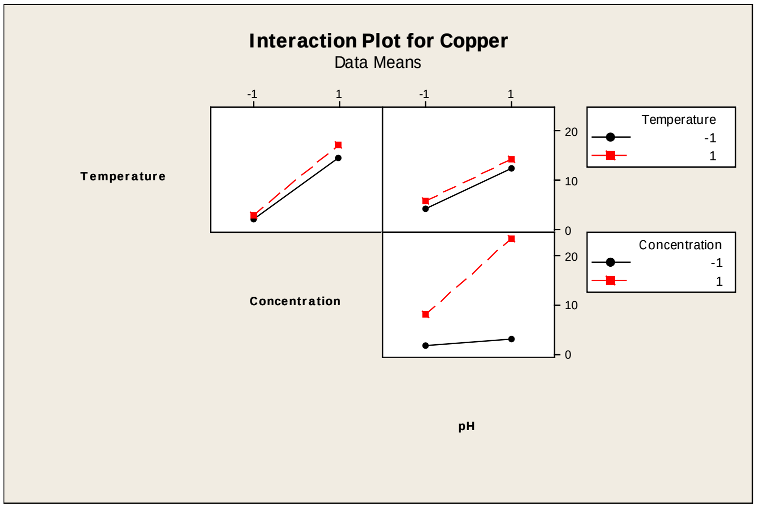

Figure 2: Interaction plot.

Normal plot of the standardized effects which can be seen in Figure 3, confirms that concentration, pH and their interactions have significant effects on experiment results.

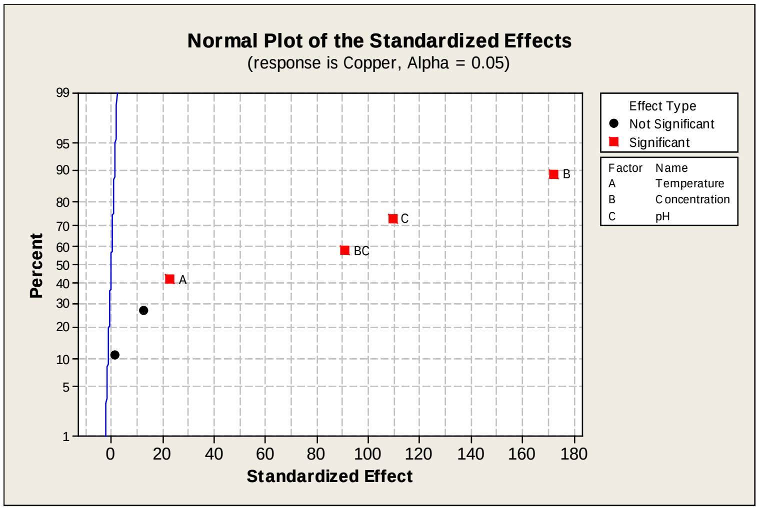

Figure 3: Normal plot of the standardized effects

After the above analysis a linear regression correlation was developed between adsorption amount, $q_{e,}$ and the operating parameters using Minitab 16 software and it is given below:

$$q_e = 9.06 + 0.891 * A + 6.68 * B + 4.25 * C + 0.491 * AB + 3.53 * BC \quad (1)$$

The Minitab output of the factorial fits is also given in Figure 4. This figure indicates that the regression equation provides a 99.98% fit for the given experimental values. The confidence intervals of the regression coefficients were also calculated to confirm the validity of the regression equation. This calculation is provided in Figure 5.

Factorial Fit: Copper versus Temperature, Concentration, pH

Estimated Effects and Coefficients for Copper (coded units)

Term	Effect	Coef	SE Coef	T	P
Constant		9.0563	0.04977	181.98	0.000
Temperature	1.7825	0.8912	0.04977	17.91	0.003
Concentration	13.3525	6.6762	0.04977	134.16	0.000
pH	8.4975	4.2488	0.04977	85.38	0.000
Temperature*Concentration	0.9825	0.4912	0.04977	9.87	0.010
Concentration*pH	7.0575	3.5287	0.04977	70.91	0.000

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S = 0.140757    PRESS = 0.634
R-Sq = 99.99%   R-Sq(pred) = 99.90%   R-Sq(adj) = 99.98%
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Figure 4: Factorial fit of the experimental data.

Estimated Regression Coefficients for Copper using data in uncoded units

Term	Coef
Constant	9.05625
Temperature	0.891250
Concentration	6.67625
pH	4.24875
Temperature*Concentration	0.491250
Concentration*pH	3.52875

Predicted Response for New Design Points Using Model for Copper

Point	Fit	SE Fit	95% CI	95% PI
1	1.2600	0.121899	(0.7355, 1.7845)	(0.4588, 2.0612)
2	9.3375	0.121899	(8.8130, 9.8620)	(8.5363, 10.1387)
3	3.5000	0.121899	(2.9755, 4.0245)	(2.6988, 4.3012)
4	2.7000	0.121899	(2.1755, 3.2245)	(1.8988, 3.5012)
5	24.8925	0.121899	(24.3680, 25.4170)	(24.0913, 25.6937)
6	6.5725	0.121899	(6.0480, 7.0970)	(5.7713, 7.3737)
7	2.0600	0.121899	(1.5355, 2.5845)	(1.2588, 2.8612)
8	22.1275	0.121899	(21.6030, 22.6520)	(21.3263, 22.9287)

Figure 5: Confidence intervals of the regression coefficients

Next analysis step is the addition of center points to check the curvature effect. For this purpose experiments were conducted in the center points (Factor A = 308K, Factor B = 500 and Factor C = 5) and the results are given in Table 4. ANOVA analyses are also conducted for this second case with center points (see Figure 6). The analysis indicated that the curvature is indeed effective. The same analysis as above provides a valid regression equation (with R^2 (adj.) = 99.83 %) as follows:

Table 4: Experimental results at center point

q_e value	10.68	9.95	10.05	10.65

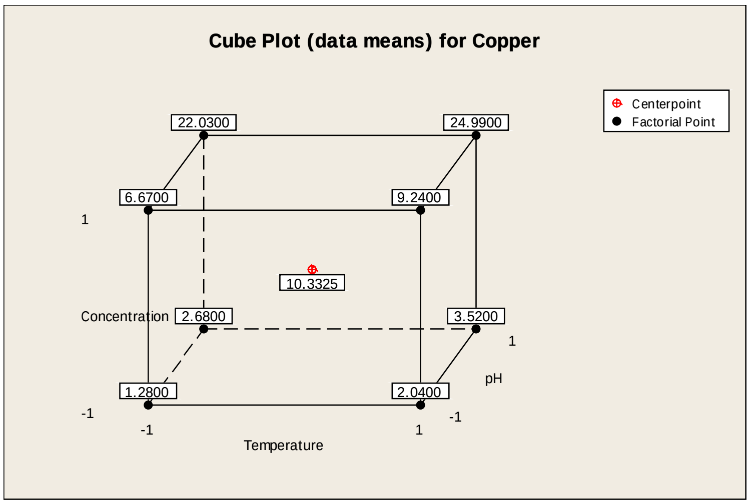

Figure 6: Design of experiments with center points

$$q_e=10.33+0.891{*}A+6.68{*}B+4.25{*}C-1.28{*}A^2+0.491{*}AB+3.53{*}BC \qquad (2)$$

Now response surface methodology is used to obtain the optimum values for the factors to attain best copper removal. The surface plots of the design are shown in Figure 7 with Figure 7(a) being the surface with pH value hold, and Figure 7(b) being the surface with Temperature value hold.

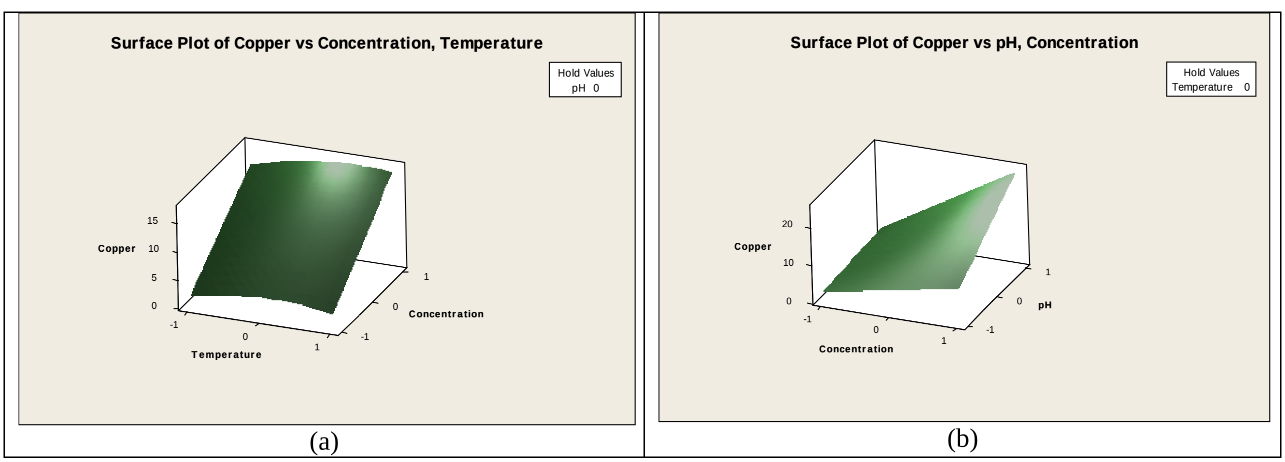

Figure 7: Surface plots (a) pH is the hold value, (b) temperature is the hold value

Using Minitab 16 software the optimum values for controllable factors are found and interpolated as shown in Table 5. With these values the maximum q_e value will be 25.1606.

Table 5: Surface response optimization results

	Optimum Values	
Factor	**Coded**	**Interpolated**
A = Temperature (K)	0.5354	316
B = Concentration	1	1000
C = pH	1	6

4. Conclusion

In this study, the effects of the initial Cu(II) concentration, adsorption temperature, and solution pH on adsorption were investigated on the basis of the active carbon. The mineral matter contents of the sample might affect the cupper ions uptake. It is obvious that increasing the initial Cu(II) concentration from 25 mg/L to 1000 mg/L causes an increase in adsorption capacity. Similarly, pH of the solution has a positive effect. The maximum adsorption capacity is found at the temperature of 316K. This study shows that, experimental design techniques can be successfully used to improve performance of experiments in very different research fields, such as the copper removal process. Using these analyses, researchers can explore the impact of parameters, the interactions of parameters and their effects on the process results.

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