

Design and Optimization of Cu(II) Adsorption Conditions from Aqueous Solutions by Low-Cost Adsorbent Pumice with Response Surface Methodology

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Received: 26 February 2015

Accepted: 22 March 2015

Abstract

The adsorption of Cu(II) by pumice was investigated in a batch system. Optimization of medium conditions was studied through experimental design. Response surface methodology – including central composite design – was successfully applied to develop a response surface to optimize medium conditions. The most influential medium parameters were determined as initial Cu(II) concentration, pH, temperature, and adsorbent dosage. The optimum conditions were evaluated to be 47.14 mg/L, 5.31, 38.30°C, and 3.14 g for initial Cu(II) concentration, pH, temperature and adsorbent dosage, respectively. At these optimum points, the adsorption yield and adsorption capacity were calculated as 95.10% and 1.43 mg/g, respectively.

Keywords: adsorption, central composite design, pumice, response surface methodology

Introduction

Heavy metal pollution is increasing as a result of rapid industrialization and increasing human population. Heavy metals such as lead (Pb), chromium (Cr), copper (Cu), cadmium (Cd), nickel (Ni), and zinc (Zn) are toxic and have negative effects on the environment and public health, even at low concentrations [1]. It has been proved that metal ions such as Pb(II), Cd(II), Hg(II), Ni(II), and Cu(II) can inhibit the metabolic function of aquatic life by specifically binding proteins and small metabolites in living cells, which causes severe health problems [2]. Copper is among the potentially toxic heavy metals. Major sources releasing Cu are industries such as fertilizer manufacturing, copper polishing, electroplating, paper industry, battery industry, etc.

Although copper is a micronutrient, excessive intake can lead to liver disease and kidney defects, and damage human psychology.

Many processes, including ion exchange, solvent extraction, ultrafiltration, chemical precipitation, reverse osmosis, electro dialysis, and adsorption, exist to remove metal pollutants from aqueous environments. Of these, there are significant advantages of adsorption such as regeneration of adsorbents, very effective removal, high selectivity, lower operating costs, and environmentally friendly processes for wastewater treatment [3]. Adsorption has been the most common process in industry, and is still the most widely used method [4-9].

In recent years, various adsorbents have been used for the removal of Cu(II), including chitosan-zeolite composite [10], fly ash [11], *Spirodela polyrhiza* (L.) Schleiden [12], rice straw [13], coconut dreg residue [14], alginate-immu-

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bilized bentonite clay [15], and eggshell [16]. However, new economic adsorbents that are locally available and have high adsorption capacity, are still needed [3]. Pumice is a light, porous igneous volcanic rock produced by the release of gases during the solidification of lava [7]. It has high silica content (70.90% SiO₂), providing durable features to the material, so it is appropriate as an adsorbent against aggressive external factors [3].

Traditional methods can be used for adsorption of heavy metals from aqueous solutions, but these methods include changing one independent variable parameter, like temperature, pH, or heavy metal concentration, while maintaining all others at a constant level. Thus traditional methods cause additional chemical consumption for each parameter, involving excessive human power requirements and time. To solve this problem, many statistical programs have been developed. Among them, Response Surface Methodology (RSM) has been commonly used in recent years [3, 17, 18]. RSM is a collection of mathematical and statistical techniques useful for analyzing the effects of several independent variables. The main advantage of RSM is the decreased number of experimental trials required to interpret multiple parameters and their interactions. In order to determine a suitable polynomial equation to describe the response surface, RSM can be employed to optimize the process [19].

The objective of this present work is to remove Cu(II) with pumice in batch experiments and optimize the adsorption conditions (initial Cu(II) concentration (mg/L, C_o), pH, temperature (°C), and adsorbent dosage(g)) via RSM.

Material and Methods

Preparation of Adsorbent

Pumice, which was used as an adsorbent, was collected from the foot of Mount Ararat, Turkey. Samples were washed with distilled water several times to remove impurities and then dried in an oven at 120°C for 24 h. Subsequently, they were ground with a mill and sieved to obtain the desired particle size. Then the pumice was stored in desiccators for further use without any pretreatment. Pore volume, pore radius, Bruner-Emmet-Teller (BET) surface area, energy dispersive x-ray spectroscopy (EDX) and x-ray diffraction (XRD) analyses for pumice samples were completed in our previous study [3]. XRD spectrograms show that pumice consists mainly of silica glass (SiO₂) with smaller amounts of Al₂O₃, MgO, Na₂O, CaO, and K₂O supported by EDX.

Cu(II) Solutions

The Cu(II) stock solution (1000 mg/L) was prepared by dissolving Cu(NO₃)₂ (purity ≥99, Sigma Aldrich) in 250 mL of distilled water. Required dilutions were made from the stock solution to prepare solutions in the range of desired concentrations. The solutions were adjusted to the desired pH by adding 0.1 M HNO₃ and 0.1 M NaOH solutions before adsorption.

Batch Adsorption Experiments

All experiments were carried out in 250 mL erlenmeyer flasks containing 100 mL Cu(II) solution on a temperature-controlled magnetic stirrer (at fixed contact time of 120 min.). The concentrations of unadsorbed Cu(II) in filtrate solutions were determined using a flame atomic absorption spectrophotometer (AAS) (THERMO Solar AA Series spectrometer, USA) after the separation of adsorbent by filtration. The removal efficiency was calculated using Eq. 1:

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

C_o and C_e are the initial and equilibrium concentrations (mg/L) of Cu(II) solution, respectively. After filtration, filter paper and glass were washed with 0.1 M HNO₃ several times. The amount of Cu(II) in the washing solution was determined with AAS and found to be lower than the detection limit of the AAS, which is 0.0001 mg/L. Therefore, this loss of Cu(II) concentration was ignored in the measurements.

Experimental Design and Optimization

Optimization of Adsorption Conditions with Central Composite Design (CCD)

In RSM, CCD is the most popular choice to fit a second-order model [3]. The CCD was applied using Design-Expert 8.0.7.1 (trial version). The total number of experiments with four independent variables were determined as 30 ($= 2k + 2^k + 6$) where k is the number of independent variables. Thirty experiments were applied with six replications at the center values (zero level) to evaluate the experimental error.

In the optimization process, the response can be related to the chosen variables by linear or quadratic models [3]. A quadratic model is given as Eq. 2:

$$\hat{y}_n = \beta_o + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{ii} x_i^2 + \sum_{i=1}^3 \sum_{j=i+1}^3 \beta_{ij} x_i x_j \quad (2)$$

...where \hat{y}_n is the response; β_o is the constant coefficient; x_i ($i = 1-3$) are non-coded variables; and β_i is the linear, β_{ii} the quadratic, and β_{ij} (i and $j = 1-3$) the second-order interaction coefficients. The residuals, ϵ_n , for each experiment were computed as the difference between y_n and \hat{y}_n , which are the residual of the n th experiment, observed response and predicted response, respectively.

Experimental data were evaluated with Design-Expert 8.0.7.1 (trial version) including ANOVA (Analysis of variance) in order to obtain the interaction between the processed variables and the response. The quality of the fit of the polynomial model was expressed by the coefficient of determination (R^2) and the statistical significance was checked by the F-test using the same program.

Determination of Maximum Points

The second-order model determined from Eq. 2 is adequate for the optimal points. A general mathematical solution can be obtained from Eq. 3 for the location of the stationary point [3, 19].

Writing the second-order model in matrix notation, we have:

$$y = \beta_0 + x'b + x' Bx_s \tag{3}$$

...where:

$$X_s = \begin{bmatrix} X_1 \\ X_2 \\ \vdots \\ X_k \end{bmatrix}, \quad b = \begin{bmatrix} \beta_1 \\ \beta_2 \\ \vdots \\ \beta_k \end{bmatrix} \text{ and}$$

$$B = \begin{bmatrix} \beta_{11} & \beta_{12}/2 & \beta_{1k}/2 \\ \text{Sym.} & \beta_{22} & \beta_{2k}/2 \\ \text{Sym.} & \text{Sym.} & \beta_{kk} \end{bmatrix}$$

That is, *b* is a (*kx*₁) vector of the first order regression coefficient and *B* is a (*kxk*) symmetric matrix whose main diagonal elements are the pure quadratic coefficients (β_{ii}) and whose off-diagonal elements are one-half of the mixed quadratic coefficients (β_{ij} , $i \neq j$). The stationary points (*X_s*) are the solution of Eq. 4.

$$x_s = -\frac{1}{2} B^{-1} b \tag{4}$$

Results and Discussion

Optimization of Cu(II) Adsorption Conditions

Optimization of the removal of Cu(II) ions from aqueous solutions for four parameters (*C_o*, pH, temperature, and adsorbent dosage) were carried out with CCD. CCD experiments for optimization of these parameters were performed to locate the maximum removal of Cu(II) by Design Expert 8.0.7.1 trial version. Together with six replications conducted at the center values (zero level) to evaluate the pure error, a total of 30 experiments were completed for optimization. The order of the experiments and levels of each parameter in coded, - α , -1, 0, +1, + α , and uncoded form and the observed responses are shown in Table 1. The model equation for uncoded (real) values of the quadratic model fitting experimental results was presented in Eq. 5.

$$\begin{aligned} \% \text{ Removal} = & -136.83764 + 0.42459 [C_o] + 32.8977 \\ & [\text{pH}] + 4.00174 [\text{Temperature}] + 36.8073 [\text{Adsorbent} \\ & \text{Dosage}] + 0.099267 [C_o \cdot \text{pH}] - 4.472\text{E-}003 \\ & [C_o \cdot \text{Temperature}] + 0.075075 [C_o \cdot \text{Adsorbent Dosage}] - \\ & 0.062933 [\text{pH} \cdot \text{Temperature}] - 0.79875 [\text{Adsorbent} \\ & \text{Dosage} \cdot \text{pH}] - 0.26795 [\text{Temperature} \cdot \text{Adsorbent Dosage}] - \\ & 0.010785 [C_o]^2 - 3.07287 [\text{pH}]^2 - 0.03412 [\text{Temperature}]^2 \\ & - 4.10762 [\text{Adsorbent Dosage}]^2 \end{aligned} \tag{5}$$

Table 1. CCD results for Cu(II) adsorption onto pumice.

Run	<i>C_o</i> (X ₁ , mg/L)	pH (X ₂)	Temperature (X ₃ , °C)	Adsorbent Dosage (X ₄ , g)	% Removal (Y)
1	80.0 (+1)	6.0 (+1)	20.00 (-1)	4.5 (+1)	83.29
2	27.5 (- α)	4.5 (0)	32.50 (0)	2.5 (0)	75.91
3	55.0 (0)	4.5 (0)	46.25 (+ α)	2.5 (0)	65.79
4	30.0 (-1)	6.0 (+1)	20.00 (-1)	0.5 (-1)	40.13
5	30.0 (-1)	6.0 (+1)	20.00 (-1)	4.5 (+1)	71.65
6	55.0 (0)	4.5 (0)	32.50 (0)	2.5 (0)	95.00
7	55.0 (0)	4.5 (0)	32.50 (0)	2.5 (0)	97.89
8	30.0 (-1)	3.0 (-1)	20.00 (-1)	4.5 (+1)	75.60
9	80.0 (+1)	3.0 (-1)	20.00 (-1)	0.5 (-1)	6.890
10	55.0 (0)	4.5 (0)	32.50 (0)	0.3 (- α)	50.81
11	30.0 (-1)	6.0 (+1)	45.00 (+1)	0.5 (-1)	75.25
12	30.0 (-1)	3.0 (-1)	45.00 (+1)	0.5 (-1)	57.85
13	55.0 (0)	6.15(+ α)	32.50 (0)	2.5 (0)	88.97
14	80.0 (+1)	3.0 (-1)	45.00 (+1)	4.5 (+1)	63.32
15	80.0 (+1)	6.0 (+1)	45.00 (+1)	4.5 (+1)	80.93
16	55.0 (0)	4.5 (0)	32.50 (0)	4.7 (+ α)	63.52
17	55.0 (0)	2.85(- α)	32.50 (0)	2.5 (0)	48.39
18	30.0 (-1)	6.0 (+1)	45.00 (+1)	4.5 (+1)	72.83
19	80.0 (+1)	6.0 (+1)	20.00 (-1)	0.5 (-1)	20.56
20	55.0 (0)	4.5 (0)	32.50 (0)	2.5 (0)	97.96
21	55.0 (0)	4.5 (0)	18.75 (- α)	2.5 (0)	75.40
22	55.0 (0)	4.5 (0)	32.50 (0)	2.5 (0)	97.50
23	30.0 (-1)	3.0 (-1)	20.00 (-1)	0.5 (-1)	10.63
24	30.0 (-1)	3.0 (-1)	45.00 (+1)	4.5 (+1)	75.88
25	80.0 (+1)	6.0 (+1)	45.00 (+1)	0.5 (-1)	49.80
26	55.0 (0)	4.5 (0)	32.50 (0)	2.5 (0)	97.05
27	82.5 (+ α)	4.5 (0)	32.50 (0)	2.5 (0)	61.87
28	80.0 (+1)	3.0 (-1)	20.00 (-1)	4.5 (+1)	43.39
29	55.0 (0)	4.5 (0)	32.50 (0)	2.5 (0)	92.20
30	80.0 (+1)	3.0 (-1)	45.00 (+1)	0.5 (-1)	21.52

The statistical significance of the quadratic model evaluated with ANOVA is shown in Table 2. The low p value shows that the second-order quadratic model for observed results is significant [3]. The value of the coefficient of determination ($R^2=0.85$) indicates that 85% of the variability in the response is explained by the model. The plot of observed removal of Cu(II) versus those obtained

Table 2. The analysis of variance (ANOVA).

Source	Sum of Squares	dF	Mean Square	F-value	p-value
Model	16847.43	14	1203.39	6.16	0.0006
X_1 (C_o , mg/L)	855.93	1	855.93	4.38	0.0538
X_2 (pH)	1837.96	1	1837.96	9.40	0.0078
X_3 (Temperature, °C)	984.57	1	984.57	5.04	0.0403
X_4 (Adsorbent Dosage)	4828.87	1	4828.87	24.70	0.0002
X_1, X_2	221.71	1	221.71	1.13	0.3037
X_1, X_3	31.25	1	31.25	0.16	0.6949
X_1, X_4	225.45	1	225.45	1.15	0.2998
X_2, X_3	22.28	1	22.28	0.11	0.7403
X_2, X_4	91.87	1	91.87	0.47	0.5034
X_3, X_4	717.97	1	717.97	3.67	0.0745
X_1^2	169.74	1	169.74	0.87	0.3662
X_2^2	178.60	1	178.60	0.91	0.3543
X_3^2	106.19	1	106.19	0.54	0.4725
X_4^2	1008.61	1	1008.61	5.16	0.0383

from Eq. 5 is shown in Fig. 1. The figure proves that the predicted response from the empirical model is in agreement with the observed ones.

Fig. 2 shows the simultaneous effects of adsorbent dosage and temperature on Cu(II) removal by pumice. It is clear from Fig. 2 that temperature has a positive effect on Cu(II) adsorption. Removal of Cu(II) ions by pumice slowly increased with temperature and reached its maximum value around 38°C. The increase in uptake of metal ions with temperature may be due to the desolvation of the sorbing species and the change in the size of the pores [20]. Also, other researchers have suggested that increasing adsorption with an increase in temperature indicates an

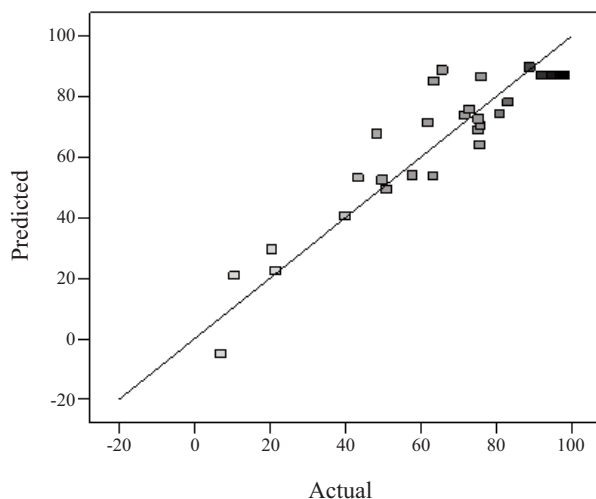


Fig. 1. Observed Cu(II) removal versus predicted Cu(II) removal.

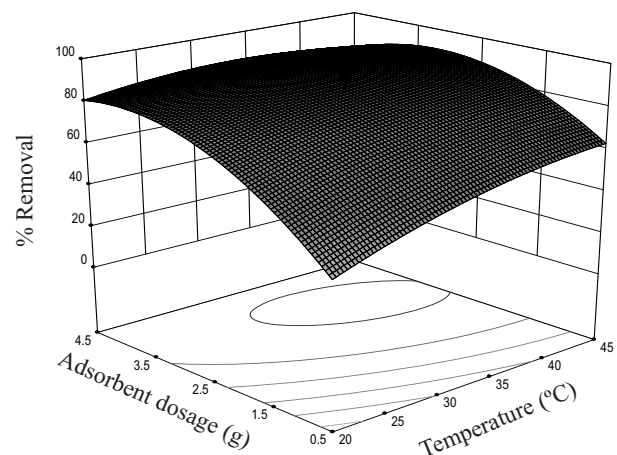


Fig. 2. Simultaneous effects of adsorbent dosage and temperature on Cu(II) removal at fixed pH 2.50 and initial concentration 55.00 mg/L.

increase in the mobility of large metal molecules with increasing temperature and the ongoing adsorption process is endothermic [21]. In addition, increasing temperature may cause a swelling effect within the internal structure of the adsorbent, enabling metal ions to penetrate further [22]. The adsorption capacity of Cu(II) ions onto pumice decreased at temperatures higher than 38°C. This decrease may be due to a tendency for the Cu(II) ions to escape from the solid phase to the stack phase with the increase in the temperature of the solution. The removal capacity of pumice rapidly increased when the adsorbent dosage increased from 0.50 g to 3.00 g and roughly reached a max-

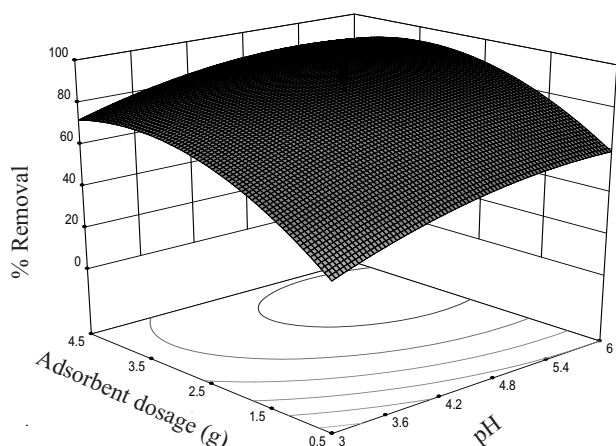


Fig. 3. Simultaneous effects of adsorbent dosage and pH on Cu(II) removal at fixed initial concentration of 55.00 mg/L at 32.50°C.

imum at 3.00 g. The increase in removal of Cu(II) ions with increasing adsorbent dosage can be explained by the increase in active sites in the higher amount of adsorbent, thus providing easier penetration of metal ions to active sites. Similar observations are reported in the literature [23, 24]. Then removal of Cu(II) ions decreased by increasing adsorbent dosage from 3.00 to 4.50 g. This is due to the fact that at higher adsorbent dosage, the ion concentration of the solution drops to a lower value and the system reaches equilibrium at lower values adsorbed per unit weight of adsorbent, indicating that the adsorption sites remain unsaturated [25]. Similar observations are reported by Li et al. [26].

As is clearly shown in Fig. 3, although removal of the Cu(II) ions increased sharply when pH rose from 3.00 to 5.40, removal capacity decreased above this pH. Maximum removal was approximately observed at pH 5.40. The pH dependence of metal uptake is related to both the functional groups on the adsorbent surface and the metal chemistry in solution, which affects the surface charge of the adsorbent and the degree of ionization of the adsorbate [27, 28]. Surface charge density is related to pH of the media. The point of zero charge (PZC) is an important factor to explain the effects of pH on adsorption. At PZC, the charges from cations and anions are equal and total charge of adsorbent is zero. The pH_{pzc} for pumice was calculated [3] according to a method in the literature [29] as ≈ 4.00 . With this method, the pH_{pzc} was identified as the pH where 0.1M HNO_3 titration curves of different adsorbent masses (0.10, 0.20, and 0.30 g suspended in 0.03M NaNO_3 at pH 12.0) converged with that of the reactive blank solution. Accordingly, when pH increases from 3.00 to 5.40, the high adsorption efficiency is probably due to the fact that at pH above the pH_{pzc} 4.00, the pumice surface is mostly negatively charged with deprotonated surface sites. Similar observations are available in the literature [30, 31]. An adsorption mechanism for high pH can be explained by Eqs. 6 and 7 [3].

At pH below pH_{pzc} 4.00, the low adsorption capacity is due to the increase in positive charge density on the surface

sites, and thus electrostatic repulsion occurs between the metal ions ($\text{M}^{2+}:\text{Cu}^{2+}$) and the edge groups with positive charge (Si-OH_2^+) on the surface (Eq. 8) [3].

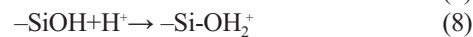
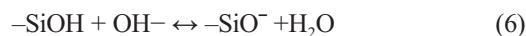


Fig. 4 shows the adsorption capacity of pumice rapidly increased with increasing C_o from 30.00 to 40.00 mg/L and roughly reached a maximum at 45.00 mg/L. Then it did not change by further increasing C_o . This result can be explained because of the interaction of Cu(II) ions and adsorbent. At the lower Cu(II) concentration, the ratio of number of moles of metal ion to the available adsorption sites is low, and therefore the amount adsorbed per unit adsorbent increases slowly [32, 33]. With increasing metal ion concentration, there is an increase in the amount of metal ion adsorbed due to increased driving force of the metal ions toward the active sites on the adsorbent [34, 35]. In our study, when C_o was between 40.00 and 50.00 mg/L, the metal uptake reached equilibrium and all sites were saturated with metals. This phase is the gradual adsorption stage and the rate of increment of adsorption capacity gradually slows with increasing C_o , and finally the metal uptake reaches equilibrium. In the C_o range from 50.00 to 80.00 mg/L, the available pores become insufficient to adsorb further metal ions and many ions are left in suspension. Similar observations are reported in the literature [35].

Fig. 5a shows normal % probability *versus* residuals. As the points on the plot follow a straight line, it can be concluded that the residuals are normally distributed and data transformation is not required. Therefore, it concluded that the prediction of the experimental data obtained from developed quadratic model for the adsorption of Cu(II) by pumice is quite satisfactory.

It is usually necessary to check the fitted model to ensure that it provides an adequate approximation to the

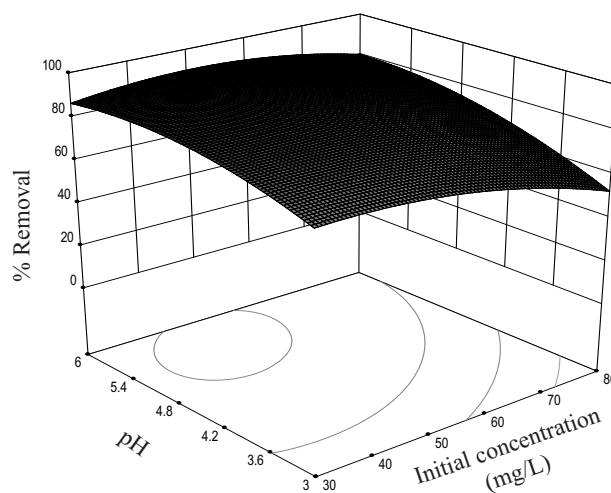


Fig. 4. Simultaneous effects of and pH and initial concentration (C_o) on Cu(II) removal at fixed adsorbent dosage 2.50 g and 32.50°C.

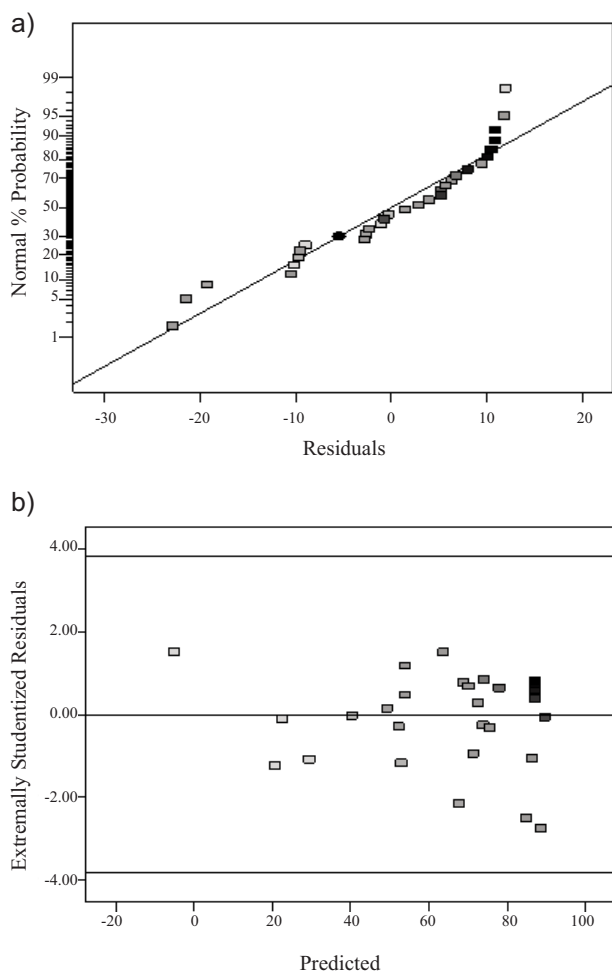


Fig. 5. a) Validation of the prediction of Cu(II) adsorption residuals versus normal percentage probability, b) studentized residuals versus predicted values.

real system. Unless the model shows an adequate fit, proceeding with investigation and optimization of the fitted response surface will likely give poor or misleading results. The residuals play an important role in judging model adequacy. Fig. 5b shows that the residuals were randomly scattered around ± 2 . According to this result, it can be concluded that the experimental data fit with the predicted ones evaluated from Eq. 5 [19].

Determination of the Optimum Values for Adsorption Conditions

The optimum points of the most important parameters to maximize the adsorption of Cu(II) were evaluated by application of Eq. 4. X_s , b , and B matrixes in Eq. 4 were arranged according to Eq. 5, which includes uncoded values of the parameters. X_s , b , and B matrixes were formed as follows [17, 19]:

$$X_s = \begin{bmatrix} X_1(C_o) \\ X_2(pH) \\ X_3(T) \\ X_4(Dosage) \end{bmatrix}, \quad b = \begin{bmatrix} 0.42459 \\ 32.8977 \\ 4.00174 \\ 36.8073 \end{bmatrix} \text{ and}$$

Table 3. Comparison between pumice and other adsorbents investigated in the literature.

Adsorbent	% Removal	References
Unmodified coir	29.44	[36]
Oxidized coir	75.71	
Fe ₃ O ₄ magnetic nano-particles	98.30	[37]
Tamarind fruit shell	99.20	[38]
Perlite	80.00	[39]
Cotton boll	78.30	[40]
Snake fruit (<i>Salacca sumatrana</i>) seed powder	90.69	[41]
Biopolymeric cross-linked pectin and alginate beads	92.40	[42]
Pumice	95.10	This work

$$B = \begin{bmatrix} -0.010785 & 0.0496335 & -2.24E-03 & 3.75E-02 \\ 0.0496335 & -3.07287 & -0.03145 & -0.399375 \\ -2.24E-03 & -0.0314665 & -0.03412 & -0.133975 \\ 3.75E-02 & -0.399375 & -0.133975 & -4.10762 \end{bmatrix}$$

From the solution of the above matrixes with Eq. 4, the optimum values for Cu(II) removal were 47.14 mg/L, 5.31, 38.30°C, and 3.14 g for C_o , pH, temperature, and adsorbent dosage, respectively. At these optimum points, the adsorption efficiency and adsorption capacity were calculated as approximately 95.10% and 1.43 mg/g, respectively. These results were confirmed by experiments.

Table 3 shows a comparison between the adsorption capacity of pumice and other adsorbents in the literature. As can be seen from Table 3, pumice is a native adsorbent having a high adsorption capacity for Cu(II) ions comparable to other adsorbents.

Conclusions

RSM was successfully used to optimize the adsorption conditions for Cu(II) removal onto pumice samples that were collected from the Mount Ararat region, Turkey. CCD was used to determine the optimum values of the effective factors, which are C_o , pH, temperature, and adsorbent dosage. A quadratic model obtained from CCD matched the experimental data. Based on the quadratic model, the optimum adsorption conditions for removal of Cu(II) ions from an aqueous environment were evaluated to be 47.14 mg/L, 5.31, 38.30°C, and 3.14 g for C_o , pH, temperature, and adsorbent dosage, respectively. Under these optimum conditions, the maximum amount of Cu(II) adsorbed and removal efficiency were 1.43 mg Cu(II)/g pumice and 95.10%, respectively. Considering the results, it can be concluded that RSM is an efficient statistical method for optimization of experimental condi-

tions, and pumice is a convenient adsorbent for the removal of Cu(II) from aqueous environments due to its significant adsorption capacity, natural abundance, and low cost.

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