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Response Surface Methodology for Removal of Cobalt from Aqua Solutions Using Nevsehir and Kayseri Pumice Adsorbents

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The adsorption of cobalt ions from aqueous solutions onto Nevsehir and Kayseri pumice was investigated in this study. Pumice samples were activated at 873 K for 2 h before contact with cobalt ions. In order to develop the predictive regression models all experiments were performed according to statistical designs. The concentrations of cobalt ions were measured by UV-Vis spectrophotometer. The maximum removal efficiencies of 60 and 80 % have been obtained experimentally using Nevsehir pumice and Kayseri pumice, respectively. The goal of modeling was analyze the influence of sorbent dosage and initial cobalt concentration on sorption efficiency in case of Nevsehir and Kayseri pumice sorbent. The contour response surface plot was drawn for spatial presentation of regression equation. The experiments with radioactive ^{60}Co were performed to test Kayseri pumice ability to remove radioactive compounds. The results showed that Nevsehir and Kayseri pumice can be used as efficient sorption materials for cobalt ions.

Key Words: Nevsehir pumice, Kayseri pumice, Adsorption, Cobalt ions, Response surface methodology.

INTRODUCTION

Metal pollution usually derives from pigments, mining, fertilizers and metallurgical processes. Raising attention is being given to health hazards presented by the existence of heavy metals in the environment. Their accumulation in living tissues throughout the food chain, poses a serious health problem[1,2].

The presence of heavy metals in wastewater means that at the end of many industrial processes it is frequently necessary to use adsorbents to bring their concentration down to below the advised legal limit. The most commonly adsorbent used in the treatment of wastewater is still active carbon, though expensive and requiring the help of complexing agents[3,4]. The high cost would not be a problem if it was regenerated and reused many times. The regeneration is not suitable for use with

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contaminated adsorbents as returning heavy metals to water. The scientists focused on identifying efficient low-cost throw-away adsorbents in recently[4].

Pumice is a light, highly porous volcanic rock. Pumice stone has high silica content (generally 60-75 % SiO_2). It has a porous structure and a large surface area. The structure of pumice contains open channels that allow water and ions to travel into and out of the crystal structure. It is a valuable scouring, scrubbing and polishing material in pumice. Since the majority of internal pores, especially micropores, are not connected, pumice has a low permeability. The skeleton structure of pumice allows ions and molecules to reside and move within the overall framework. Pumice stone exhibit acidic or basic character. Pumice has been found to be effective for the removal of phosphate ions from aqua solutions[5-8].

Conventional methods of process investigation by changing one variable and maintaining other factors at constant levels does not describe properly the combined effect of all factors employed. This classical technique involves many experimental runs, which are time-consuming; ignores interaction effects between the considered operating parameters of the process and leads to a low efficiency in optimization. These restrictions of the classical method can be prevented by applying the response surface methodology (RSM) that involves statistical design of experiments in which all factors are varied together over a set of experimental runs[9-11].

The main objective of RSM is to settle the optimum operational conditions of the system or to determine a region that satisfies the operating specifications[10]. The implementation of statistical experimental design techniques in adsorption process development can result in enhanced product yields, diminished process variability, closer confirmation of the output response to target requirements and overall costs[11,12].

In this study, the adsorption of cobalt ions from aqueous solutions on Nevsehir and Kayseri pumice was investigated. The possibility of removal of ^{60}Co radionuclides from water by Kayseri Pumice sorbent was also investigated. The response surface methodology (RSM) was used as an efficient approach for predictive model building and optimization of adsorption process.

EXPERIMENTAL

Pumice samples were obtained from Suleyman Demirel University, Pumice Research and Implementation Center, Isparta, Turkey. The chemical composition of pumice powder samples determined by XRF is given elsewhere[5,6]. Prior to use in the experiments, pumice samples were crushed to get powder.

As a source of cobalt ions, cobalt(II) chloride hexahydrate $CoCl_2 \cdot 6H_2O$ (puriss) (m.w. = 237.93 g/mol) provided by Sigma-Aldrich was used for preparing of aqua solutions.

Nevsehir pumice and Kayseri pumice were activated at 873 K for 2 h prior to adding them into aqua solutions. Batch adsorption experiments have been carried out by mixing the activated powders of sorbents with synthetic wastewater solution of different initial cobalt concentrations. Samples were mixed for 24 h to reach the equilibrium state using an orbital shaker. The shaking speed was set up at 320 rpm to maintain the sorbent particles in suspension for all experiments. Afterwards, the suspensions were filtrated using a syringe filter (Whatmann Syringe Filter 25 mm diameter, 0.2 µm pore size). The resulted filtrate was analyzed for cobalt concentration *via* UV-Vis spectrometry method. In this respect, the concentrations of cobalt ions in filtrate solutions were measured by an analytical kit (HACH Permachem Reagents), based on a measurement of colour intensity (absorbance reading at a 620 nm wavelength) of the complex form in aqua solution. The reproducibility of the concentration measurement was within a maximum deviation of 5 % in all studied cases. By means of direct reading spectrophotometer UV-Vis (HACHDR/2000) the absorbance was recorded. The removal efficiency of cobalt ions from aqua solution by adsorption was determined as follows:

$$Y = \left(1 - \frac{C_f}{C_0}\right) \times 100 \qquad (1)$$

where C_0 is the initial concentration of cobalt in solution (mg/L) and C_f is the final concentration of cobalt after adsorption (mg/L).

For the adsorption experiments with radionuclides ^{60}Co, the radioactivity measurements were taken using a Polon Warszawa Analyzer (A-22p HT Power supply ZW N-21M HT Control 0/2000V). A volume of 10 mL sample was used for all liquid radioactivity measurements. For these experiments the decontamination factor (DF) was ascertained as:

$$DF = \left(\frac{A_0}{A_f}\right) \qquad (2)$$

where A_0 is the initial activity of cobalt solution (Bq/L) and A_f is the final activity of solution (Bq/L) after adsorption.

All experiments with non-active and radioactive solutions were carried out at room temperature and for a fixed pH of 5.70 ± 0.20.

RESULTS AND DISCUSSION

Adsorption studies dealing with non-active solutions: Recently, the search for low-cost adsorbents that have metal-binding capacities has increased. This has led many workers to search for cheaper alternates such as coal, silica gel, wool wastes, agricultural wastes and clay minerals[7,13].

The investigations of adsorption processes were carried out using the central composite design of experiments. The experimental data collected according to experimental designs were applied for statistical modeling using the response surface methodological approach. The response surface methodology (RSM) is generally used to improve and optimize the performance of a system that is subject to a set of controllable input variables called also design variables or factors. The first step in

RSM involves determining an appropriate functional form to explain the relationship between the response of interest (in present case the removal efficiency) and controllable input variables (factors). The most commonly used functional form in RSM is the polynomial regression model. For the experiments with non-active solutions the RSM tool has been applied to develop the polynomial regression models between the removal efficiency (metal uptake efficiency) and the experimental factors. The most important factors that influence the removal efficiency (response) are the initial concentration of cobalt ions in aqua solutions (C_0, mg/L) and the sorbent dose (SD, % w/v). It is noted that the sorbent dose of SD = 0.5 % w/v means 0.5 g of sorbent per 100 mL solution. For statistical calculations the actual values of factors were coded according to eqn. 3[9-11,14,15].

$$x_i = \frac{z_i - z_i^0}{h_i} \quad \forall i = \overline{1,\ n} \tag{3}$$

where z denotes the actual value of design variable; z^0 the center point of design variable (actual value); h-the interval of variation; x-the coded level of design variable (dimensionless value) and n-the number of variables (in present case n = 2). Thus, each variable consists of 3 different coded levels from low (-1), to medium (0) and to high (1).

For the case of 2 design variables (factors) the regression model of second-order with interaction given by RSM can be written in a general form as follows:

$$\hat{Y} = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 \tag{4}$$

where the regression coefficients that represent the components of the column matrix $\beta = [\beta_0\ \beta_1\ \beta_2\ \beta_{11}\ \beta_{22}\ \beta_{12}]^T$ were computed by means of regression analysis[9-11,14,15]:

$$\beta = (X^T \cdot X)^{-1} \cdot X^T \cdot Y \tag{5}$$

where: β-denotes the column matrix of the regression coefficients; X - the matrix of coded variables; Y- the column matrix of experimental values of response (removal efficiency).

The experimental designs used for investigation of adsorption processes with non-active solutions are given in Tables 1 and 2 for Nevsehir pumice and Kayseri pumice adsorbents, respectively.

Based on the data reported within experimental designs (Tables 1 and 2) the following statistical models have been constructed with coded and actual variables:

(1) Adsorption of cobalt ions from non-active solutions onto Nevsehir pumice;
- regression model with coded variables:

$$\hat{Y} = 14.5 + 6.817x_1 - 15.333x_2 - 20.113x_2^2 \tag{6}$$

subjected to: $-1 \le x_i \le +1$, $\forall i = 1,2$

(2) Adsorption of cobalt ions from non-active solutions onto Kayseri pumice;
- regression model with coded variables:

$$\hat{Y} = 14.542 + 7.967x_1 - 26.167x_2 + 22.611x_2^2 - 8.5x_1x_2 \tag{7}$$

subjected to: $-1 \le x_i \le +1$, $\forall i = 1,2$

TABLE-1
EXPERIMENTAL DESIGN FOR NON-ACTIVE MODEL SOLUTIONS OF COBALT IONS ADSORPTION ON NEVSEHIR PUMICE

Run No. (N)	Factors (controllable input variables)				Response : Removal efficiency
	Sorbent dosage		Initial cobalt concentration		
	SD (% w/v)	Level (x_1)	C_0 (mg/L)	Level (x_2)	Y (%)
1	0.500	1	100	1	24.0
2	0.250	-1	100	-1	14.0
3	0.500	1	10	1	60.0
4	0.250	-1	10	-1	40.0
5	0.500	1	55	1	20.0
6	0.250	-1	55	-1	9.1
7	0.375	0	100	0	20.0
8	0.375	0	10	0	50.0
9	0.375	0	55	0	14.5
10	0.375	0	55	0	16.4

TABLE-2
EXPERIMENTAL DESIGN FOR NON-ACTIVE COBALT IONS REMOVAL USING KAYSERI PUMICE ADSORBENT

Run No. (N)	Factors (controllable input variables)				Response: Removal efficiency
	Sorbent dosage		Initial cobalt concentration		
	SD (% w/v)	Level* (x_1)	C_0 (mg/L)	Level* (x_2)	Y (%)
1	0.500	1	100	1	14.0
2	0.250	-1	100	-1	8.0
3	0.500	1	10	1	80.0
4	0.250	-1	10	-1	40.0
5	0.500	1	55	1	14.5
6	0.250	-1	55	-1	12.7
7	0.375	0	100	0	11.0
8	0.375	0	10	0	70.0
9	0.375	0	55	0	16.4
10	0.375	0	55	0	20.0

*–1 = low value, 0 = center value, +1 = high value.

The significance of the coefficients was tested with the Student's t-test, on condition that the value of each coefficient should be greater than the significance level. Thus, in regression equations mentioned above only the meaningful coefficients were retained.

In order to test the estimated regression equations for the goodness of fit, the use is made of the Fisher F-test for the significance level of $p = 0.05$. In this respect one should compute the following statistical estimators. The error mean square (S_0^2) that has been found by using the repeated observations[14,15]:

$$S_0^2 = \frac{1}{n_0 - 1} \sum_{i=1}^{n_0} \left(Y_{0i} - \overline{Y}_0 \right)^2 \quad (8)$$

where n_0 is the number of experiments in center point (reproducibility), Y_{0i} denotes the values of response recorded in the center point and $\overline{Y}_0$ is the average value of Y_{0i}. The residual mean square (S^2_{res}) has been computed as[15]:

$$S_{res}^2 = \frac{1}{N - L} \sum_{j=1}^{N} \left(Y_j - \hat{Y}_j \right)^2 \quad (9)$$

where N is the number of observations (experimental runs), L is the number of significant coefficients in the regression equation, Y_j is the response (experimental value) and $\hat{Y}_j$ denotes the predictor of response according to regression equation. It is noted that the regression model is an adequate fit to the experiment if the F-ratio is smaller than the tabulated value of $F_{tab\ (p,\ f1,\ f2)}$[14,15]:

$$F = \frac{S_{res}^2}{S_0^2} < F_{tab\ (p, f_1, f_2)} \quad (10)$$

The outcomes of F-ratio test are focused in Table-3 for both regression models. According to the results from Table-3, the F-ratio is lower than tabulated value in both cases revealing the adequacy of the regression models.

TABLE-3
STATISTICAL ANALYSIS FOR REGRESSION EQUATIONS
(RESPONSE: REMOVAL EFFICIENCIES)

Model	Degree of freedom	F-ratio (computed value)	F-ratio (p=0.05) (tabulated value)	Model adequacy
Nevsehir pumice	$f_1 = N - L = 7$ $f_2 = n_0 - 1 = 1$	11.0	233.9	11.0 < 233.9 adequate
Kayseri pumice	$f_1 = N - L = 6$ $f_2 = n_0 - 1 = 1$	28.9	234.0	28.9 < 234.0 adequate

After testing the adequacy according to statistical analysis, the models have been applied for the prediction using the simulation techniques. In this respect the dependence between the removal efficiency (response) and factors have been ascertained by drawing the response surface plot and contour lines map. Such dependencies are shown in Figs. 1 and 2 for Nevsehir pumice and Kayseri pumice, respectively.

In case of cobalt removal from non-active solution using Nevsehir pumice sorbent, the response surface plot indicates the following. With the increasing of initial concentration of cobalt ions in solution the removal efficiency (response) is decreasing for the same amount of sorbent. The sorbent dosage has a positive main effect upon the removal efficiency (Fig. 1). By simulation techniques, the optimal condition

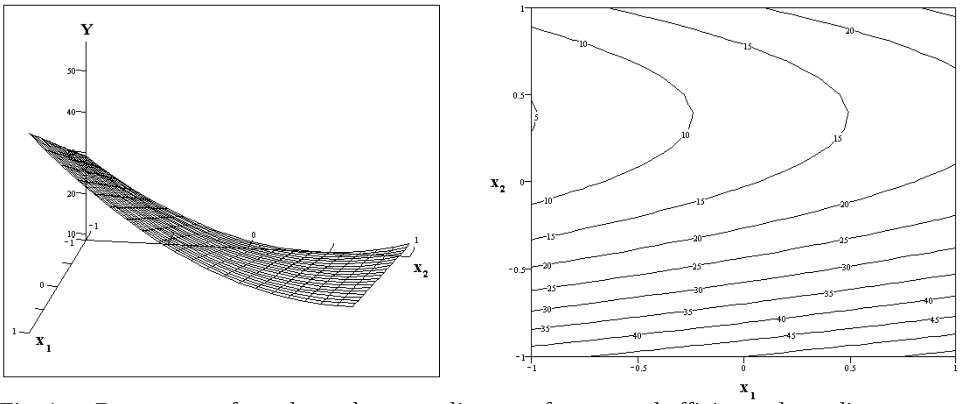

Fig. 1. Response surface plot and contour-line map for removal efficiency depending on x_1 (sorbent dosage) and x_2 (initial cobalt concentration). Sorbent: Nevsehir pumice

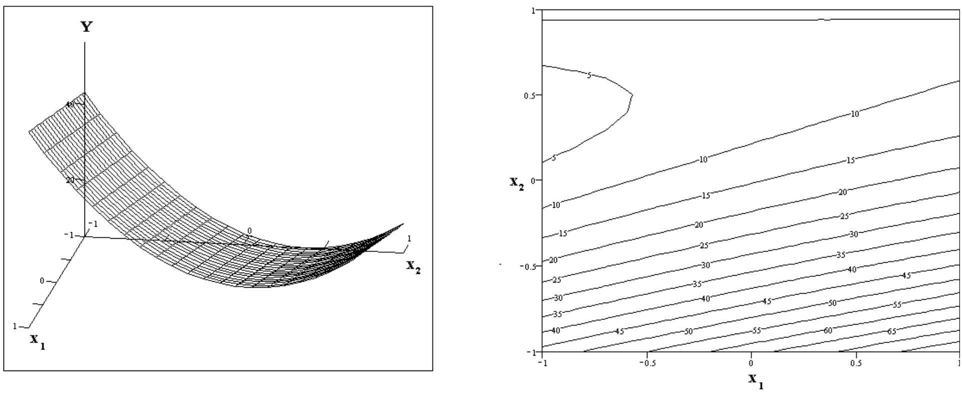

Fig. 2. Response surface plot and contour-line map for removal efficiency depending on x_1 (sorbent dosage) and x_2 (initial cobalt concentration). Sorbent: Kayseri pumice

of adsorption using Nevsehir pumice was found to be C_0 = 10 mg/L and SD = 0.5 % w/v. In these conditions a maximum removal efficiency of 56.8 % was computed (predicted value). The experimental value of response in such conditions corresponds to 60 %.

Fig. 2 shows the response surface plot for cobalt ions removal by adsorption using Kayseri pumice. The increasing of sorbent dosage leads to improve of response while the increasing of initial solute concentration conducts to the diminishing of removal efficiency. The optimal experimental condition of adsorption using Kayseri pumice was found by experimental design to be C_0 = 10 mg/L and SD = 0.05 % w/v. In this situation, the experimental value of removal efficiency of 80 % was obtained. The maximum removal efficiency of 79.8 % was computed.

Above results indicate that Kayseri pumice more efficient than Nevsehir pumice to remove cobalt ions from aqua solution.

Adsorption studies dealing with radioactive solutions: Kayseri pumice was used for adsorption experiments dealing with removal of ^{60}Co from radioactive model solutions. In this case the central composite design of experiment, resulting in 10 experimental runs was used. The experimental design is reported in Table-5.

TABLE-4
EXPERIMENTAL DESIGN FOR RADIOACTIVE COBALT ADSORPTION ON KAYSERI PUMICE

Run No. (N)	Factors (controllable input variables)				Response: Removal efficiency
	Sorbent dosage		Initial activity of solution		
	SD (% w/v)	Level (x_1)	A_0 (Bq/L)	Level (x_2)	DF
1	0.500	1	15200	1	52.6
2	0.250	-1	15200	1	41.8
3	0.500	1	7600	-1	89.7
4	0.250	-1	7600	-1	22.8
5	0.500	1	11400	0	67.7
6	0.250	-1	11400	0	54.1
7	0.375	0	15200	1	42.3
8	0.375	0	7600	-1	80.5
9	0.375	0	11400	0	86.9
10	0.100	0	11400	0	95.9

Based on the data obtained according to experimental design, the response surface model that describes the dependence between decontamination factor and design variables were developed using the regression analysis. The equations in terms of coded and actual variables may be written as follows after testing the significance of regression coefficients by means of Student's t-test.

- regression model with coded variables:

$$\hat{DF} = 79.635 + 15.217x_1 - 9.383x_2 - 15.102x_1^2 - 14.602x_2^2 - 14.025x_1x_2 \quad (11)$$

subjected to: $-1 \leq x_i \leq +1, \forall i = 1,2$

Regression model with actual variables: The statistical analysis of regression equation concerning F-ratio test is shown in Table-5. According to Fischer's test for a confidence level $p = 0.05$ the regression model is adequate and can be used for the prediction.

Fig. 3 illustrate the dependence between the decontamination factor (DF) and the design variables (factors of the adsorption process). With the increasing of sorbent dosage the decontamination factor is growing.

The optimal conditions of ^{60}Co removal from aqua solutions given by experimental design approach was found to be of SD = 0.5 % w/v and A_0 = 7600 Bq/L. In such conditions a maximal decontamination factor of 89.7 was found experimentally. The computational maximal decontamination factor of 88.6 was found.

All calculations and graphical illustration in this work were performed by means of Mathcad and Matlab software.

TABLE-5
STATISTICAL ANALYSIS FOR REGRESSION EQUATION
(RESPONSE: DECONTAMINATION FACTOR)

Model	Degree of freedom	F-ratio (computed value)	F-ratio (p=0.05) (tabulated value)	Model adequacy
Kayseri pumice	$f_1 = N - L = 5$ $f_2 = n_0 - 1 = 1$	125.3	230.1	125.3< 230.1 adequate

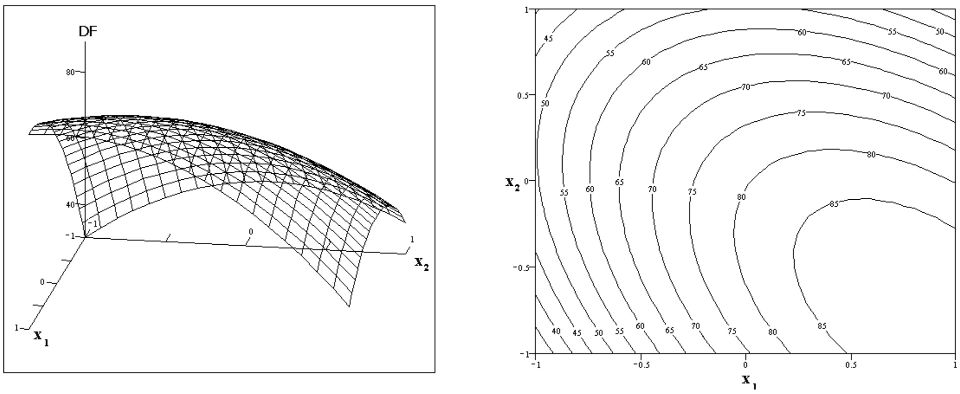

Fig. 3. Response surface plot and contour-line map for decontamination factor depending on x_1 (sorbent dosage) and x_2 (initial activity). Sorbent: Kayseri pumice

Conclusion

This study showed that the adsorption of Co^{2+} by Nevsehir pumice and Kayseri pumice is affected by the sorbent dosage and initial cobalt concentration. Response surface modeling was applied for Co^{2+} and ^{60}Co. We analyzed the influence of sorbent dosage and initial cobalt concentration on sorption efficiency in case of Nevsehir pumice and Kayseri pumice sorbent by response surface modeling for Co^{2+}. The influence of sorbent dosage and initial activity of feed solution on decontamination factor was analyzed by experimental and response surface modeling for ^{60}Co. The contours response surface plots demonstrated that response surface methodology was one of the suitable methods to optimize the operating conditions to maximize adsorption.

According to experimental design approach the optimal conditions that ensure the maximal removal efficiencies of 60 and 80 % have been obtained experimentally for Nevsehir pumice and Kayseri pumice, respectively. The minimum sorption percentages were found 9.1 and 8 % for Nevsehir pumice and Kayseri pumice, respectively for Co^{2+}.

The maximum sorption percentage is found 56.8 and 79.8 % for Nevsehir pumice and Kayseri pumice, respectively for Co^{2+} by modeling.

The maximum decontamination factor is found 89.7 and 88.6 experimental and modeling respectively, for ^{60}Co. The minimum decontamination factor is found 41.8 and 30.1 experimental and modeling, respectively, for ^{60}Co. These results indicate that the Kayseri pumice removal efficiency is higher than Nevsehir pumice for Co^{2+} both experimental and modeling studies.

Further studies are necessary to determination effects of pH, activation time and temperature on Co^{2+}, ^{60}Co adsorption.

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