



Investigation of Strontium (II) Ions Adsorption onto Long Chain Quaternary Amine Cationic-Volcanite: Modeling and Optimization by RSM

Uzun Zincirli Kuaterner Amin Katyonik-Volkanit Üzerine Stronsiyum (II) İyonlarının Adsorpsiyonununun Araştırılması: RSM ile Modelleme ve Optimizasyon

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Abstract

In this study, kula volcanite with alkaline basaltic structure and abundant abundance was used for strontium removal by increasing its adsorption capacity with hexadecyltrimethylammonium (HDTMA) organic cation. First, the adsorbent was characterized by XRF, FT-IR and SEM. Then, the adsorption of Strontium (II) ions from aqueous solutions was measured with the ICP device and the experiments were optimized by the surface response method (RSM). Central composite design (CCD) method was used for the study planning in the experiments. The theoretically adsorbed Strontium (II) at optimum values in the study was calculated as 31.978 mg/g. In addition, compatibility of various isotherms and thermodynamic parameters were evaluated in the study. According to the results, it was concluded that this cheap and abundant adsorbent material can be effective in the separation and purification of radioactive wastes, and this structure can also be used in protective containers for the transport of wastes.

Keywords: Adsorption, Strontium (II), Quaternary amine, Response surface method (RSM)

Öz

Bu çalışmada, alkali bazaltik yapıda ve bol miktarda bulunan kula volkaniti, hekzadesiltrimetilamonyum (HDTMA) organik katyonu ile adsorpsiyon kapasitesi artırılarak stronsiyum gideriminde kullanılmıştır. İlk olarak, adsorban XRF, FT-IR ve SEM ile karakterize edilmiştir. Daha sonra, sulu çözeltilerden Stronsiyum (II) iyonlarının adsorpsiyonu ICP cihazı ile ölçülmüş ve deneyler yüzey yanıt metodu (YYM) ile optimize edilmiştir. Deneylerdeki çalışma planlanması için merkezi kompozit tasarım (CCD) metodu kullanılmıştır. Çalışmada optimum değerlerde teorik olarak adsorbe edilen Stronsiyum (II) 31,978 mg/g olarak hesaplanmıştır. Ayrıca çalışmada, çeşitli izotermelerin uyumluluğu ve termodinamik parametreler değerlendirilmiştir. Sonuçlara göre, ucuz ve bol miktarda olan bu adsorban malzemenin radyoaktif atıkların ayrıştırılması ve arıtılmasında etkili olabileceği ve bu yapının aynı zamanda atıkların taşınması için koruyucu kaplarda da kullanılabilceği sonucuna varılmıştır.

Anahtar Kelimeler: Adsorpsiyon, Stronsiyum (II), Kuaterner amin, Yüzey yanıt metodu (YYM)

1. Introduction

Nowadays, when waste problems have reached great dimensions, studies on their removal from the environment and their recycling have increased. An important part of the work done in this area is the purification of metals from in-

dustrial wastewater. Particularly, radioactive and heavy metal wastes appear in different physical and chemical processes in many fields such as industry, medicine and scientific research in laboratories. Ion exchange, chemical precipitation, biosorption, adsorption etc. in the removal of heavy metals and radionuclides. methods such as these are still the most effective methods today. (Zhang et al. 2015; Shakur et al. 2016-a, b, c; Liu et al. 2016; Aghadavoud et al. 2016). Of these methods, the adsorption method has always been remarkable because it is cheap and effective to use, and the use of natural clays as inorganic adsorbent material. In order to increase the absorption of clays, the process of opening and

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modifying the pores with various substances has been applied. Especially by washing with acidic and basic solutions, the sorption capacity, the effect of inorganic cations and the organoclays formed by modifying with organic cations have been increased (Saitoh et al. 2016). Long chain quaternary amine cationic salts, a class of organic cations, become more hydrophobic for adsorption of metal ions when loaded on clays. However, the structure changes from the hydrophilic silica surface to the organophilic surface. Long chain organic cations used in surface modification are easily attached to the surface by the electrostatic forces between the positive charges in their structures and the negative charges on the adsorbent surface (Xi et al. 2007; Ryu and Yeo 2010).

There are many studies on organic cation modification, especially on bentonite structures. The removal of Pb^{2+} and phenol ions from the aqueous solution to the clay structure modified with HDTMA was carried out. (Richards and Bouazza 2010; Uddin, 2017; Lee et al. 2002). According to Majdan et al. (2010) investigated uranium adsorption on organo bentonite modified with HDTMA. Sprynsky et al. (2010) investigated the ability of natural and organic cation-modified diatomite (HDTMA-diatomite) to remove U(VI) ions. In another study, the maximum sorption capacities for radionuclide U(VI) on natural and modified diatomite were found to be 25.63 $\mu\text{mol/g}$ and 667.40 $\mu\text{mol/g}$, respectively.

Strontium has 16 known isotopes. Sr has four naturally occurring stable isotopes (Sr-84, -86, r-87 and r-88). The other 12 are radioactive isotopes. Only Sr-90 has a sufficiently long half-life (29 years). All other radionuclides have half-lives less than 65 days. 90-Strontium decays to 90-yttrium (^{90}Y) by emitting beta particles, and ^{90}Y decays to 90-zirconium with a half-life of 64 hours, emitting a larger energetic beta particle. The main health risks for strontium relate to the energetic beta particle emitted from ^{90}Y . Strontium is the 15th most abundant element on Earth, with a value of 0.01%. It is the 10th most abundant element in sea water, with a value of 0.0008%. The Sr^{90} isotope is a product of fission in uranium and plutonium reactors and weapons. In addition, strontium compounds have been used in electro-ceramics, superconductors, magnets, ship and aircraft construction, military materials, navy, fireworks, and signal lights. The strontium ion has a low toxic effect (Hong et al. 2016). The chemical and biological behavior of strontium is similar to that of calcium. In the human body, it accumulates in bones and teeth. In addition, Sr^{90} , which is the radioisotope of strontium and has a half-life of 29.1 years, similarly

settles in the body and causes cancer. Strontium oxide and strontium hydroxide have irritating effects on the skin, mucous membranes and especially the eyes. Strontium lactate is known to deactivate growth and reduce bone mineralization (Wu et al. 2012; Landstetter and Wallner 2006; Grahek and Maćefat 2005).

As a multivariate statistical and mathematical technique, the RSM method is generally used for system optimization. In this method, it directs the experimental studies to determine the experimental optimum conditions and for a high performance. Especially in many experimental chemistry fields, time saving, cost reduction and determination of optimum conditions for the effect of various factors have been widely used recently. (Cojocar and Zakrzewska-Trznadel 2007; Kunwar et al. 2011; Aralkumar et al. 2011).

In this study, it was aimed to increase the adsorption capacity of the Kula volcanic in alkaline basaltic structure by modifying it with HDTMA organic cation. Volcanic modified with HDTMA was made for the absorption of Sr^{2+} in aqueous media. XRF, FT-IR and SEM analysis of the adsorbent structure were performed for its physical and chemical characterization. In the study, conditions such as pH, Sr^{2+} concentration, temperature and time for strontium (II) adsorption were determined and optimized using RSM. In addition, adsorption isotherms and thermodynamic data were evaluated.

2. Materials and Methods

2.1. Materials

It is a volcanic alkali basalt structure used as an adsorbent in this study and was obtained from the volcanic region around Manisa-Kula. Kula volcanics are classified as basic according to their SiO_2 production rate and as basaltic according to their exit temperatures. Kula basaltic volcanics were chosen because they are abundant, cheap and accessible sorbent in nature. Cationic surfactants were prepared as a modified quaternary ammonium (alkyl aryl ammonium) compound from straight chain hexadecyltrimethylammonium (HDTMA)-bromide ($\text{C}_{19}\text{H}_{42}\text{NBr}$, MW: 364.46 g/mol, Sigma-Aldrich, 99%). Adsorption was carried out by the batch method and a thermostated GFL-1083 water bath agitator was used in the experiments.

2.2. Preparation of Organo-Volcanics

Before modification with organic cation, volcanic was taken from three different places in the extinct volcano region and thoroughly washed with pure water. After drying at 110 °C

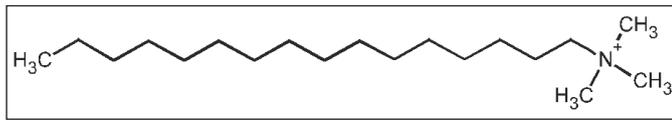


Figure 1. Structure of HDTMA organics molecule.

for 24 h, it is crushed in jaw crushers and lowered to the ground. Volcanics were prepared and dried by treating with 5, 10, 15 and 20 mM HDTMA salt solutions as an organic compound (organovolcanic). The molecular structure and surface binding types of HDTMA organic cation are shown in Figure 1. Structural characterization of organic modified volcanics was done with XRF, FT-IR and SEM/EDS.

2.3. Adsorption Studies

Adsorption of Sr²⁺ on modified volcanic samples was done using the batch method in a shaker. In this study, m (0.666 g) of modified volcanic sample adsorbent was shaken with 20 mL of Sr²⁺ solutions (20-100 mg/L) in test tubes (50 mL). And the supernatants were filtered. Sr²⁺ concentrations were determined before and after equilibration with ICP-OES (Perkin Elmer Optima 2000 DV). Single-element solutions containing individual Sr²⁺ were used to obtain the calibration curve. Q (mg/g) adsorption capacities of Sr²⁺ absorbed on HDTMA-Kula were determined by formula (1) at equilibrium and time.

$$Q = (C_0 - C_e) \times (V/m) \quad (1)$$

C₀: the early Sr²⁺ concentration; C_e: the concentration of Sr²⁺ at equilibrium; V: the volume (L); m: weight of dry adsorbent (g).

The sorption activity is defined by the ion distribution coefficient K_d (mL/g) determined using the formula (2).

$$K_d = \frac{(C_0 - C_e) \times V}{C_e \times m} \quad (2)$$

The sorption isotherms were studied by equilibration of 0.1 g HDTMA-organovolcanic with metal concentrations varying between 20 and 100 mg/L. The effect of tempera-

ture on Sr²⁺ sorption was investigated between 293 K and 313 K. ΔH°, ΔS° and ΔG° values were found.

2.4. Response Surface Methodology

RSM is a method, mathematical and statistical techniques that use quantitative data from symmetric experimental designs together to decide to run the conditions and regression model. In this method, RSM was used on the used response area to find a large number of sorption values. There are many methods for experimental design in RSM (Box Behnken Design “BBD”, Face Centered Design “CCF” and Central Composite Design “CCD”). CCD does the design for 5 different levels. In this study, the design of maximum Sr²⁺ adsorption was made by CCD method. For a quadratic surface, the CCD method is suitable. In this method, the active ingredients are optimized with the CCD method with a minimum number of experiments.

For a 2-level study, the total number of runs in this design is 2k+2k+n₀ (2k, factorial runs; 2k, axial work; k is given as the number of independent process variables and x₀, center runs). The effect of the factors (X₁: pH, X₂: Sr²⁺ concentration, X₃: temperature and X₄: amount of adsorbent) was investigated at 5 levels. The independent variables and their coded CCD design levels are given in table 1.

Each run was an average of three repetitions [24].

$$Y = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=2}^n b_{ij} x_i x_j + \epsilon \quad (3)$$

where Y is the answer; b₀, represents cutting; b_{ij}, coefficients; n, the amount of variable; x_i and x_j, arguments and ε represents error.

Optimum values of the variables, graphs and equation are found with RSM. The correlation coefficient (R²) of the study was found to be high (0.99). The importance of the RSM model was evaluated for probability value (Probe > F) and F value.[25]

Table 1. Independence factors and their coded levels used for optimization.

Factors	Factor code	Range and levels (coded)				
		-2	-1	0	+1	+2
Initial pH	X ₁	3	4	5	6	8
Sr ²⁺ Concentration (mg/L)	X ₂	20	40	60	80	100
Temperature (°C)	X ₃	20	30	40	50	60
Time (min)	X ₄	15	30	60	90	120

This works, the second-order polynomial equation can be given as followings: (4)

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4$$

Excel and Minitab 17 were used for the regression and graphical analysis of the data obtained in the study [26]

3. Result and Discussion

3.1. Characterization of HDTMA-Organo-Volcanics

According to Kula volcanic XRF results, the chemical composition of the original basaltic volcanic sample was SiO₂, Fe₂O₃, Al₂O₃, MnO, CaO MgO, Na₂O, TiO₂, K₂O and P₂O₅; 48.4% 8.648%; 17.66%; 0.085%; 6.234%; 8.538%; 3.989%; 1.85%, 2.881% and 0.625% respectively. Volcanics are divided into basalt groups according to the amount of SiO₂ (Fisher,1961).

Morphology as well as structural rearrangement of natural and modified volcanics are presented by SEM in Figure 1a and Figure 1b, respectively. SEM images of organic cation modified volcanites used as adsorbent were taken with QUANTA 400 F Field Emission-SEM and are given in Figure 2. EDS). Images are magnified 40000 times. It was

understood that the crystal sizes were in the micrometer scale. The carbon percentage in HDTMA organo-volcanic was calculated as 12.64%.

FT-IR spectra of crude and HDTMA-organovolcanics were recorded on a Perkin Elmer BX spectrometer operating in the 400-4000 cm⁻¹ range. The FT-IR spectra of the Kula volcanite are given in Figure 3. The peaks seen in the spectrum at 1031, 1390-1396 and 3385 cm⁻¹ are the frequency values of the stretching vibrations related to Si-O, C-N and O-H bonds respectively. Characteristic NH₂⁺, NH⁺ and N-H ammonium stretching vibrations are present around 2924 and 2845 cm⁻¹. IR data are in agreement with the literature (Majdan et al. 2010; Sprynskyy et. al. 2015).

The results obtained in this study were found to be compatible with the study obtained by other researchers (Sprynskyy et. al. 2015).

3.2. Experimental Design

3.2.1. The optimization of sorption parameters

Experiments were carried out under optimum conditions obtained with RSM. Effect of four different parameters (pH, Sr²⁺ concentration, temperature and time). Experimental planning in factorial order using the CCD method was determined by performing a total of 31 experiments,

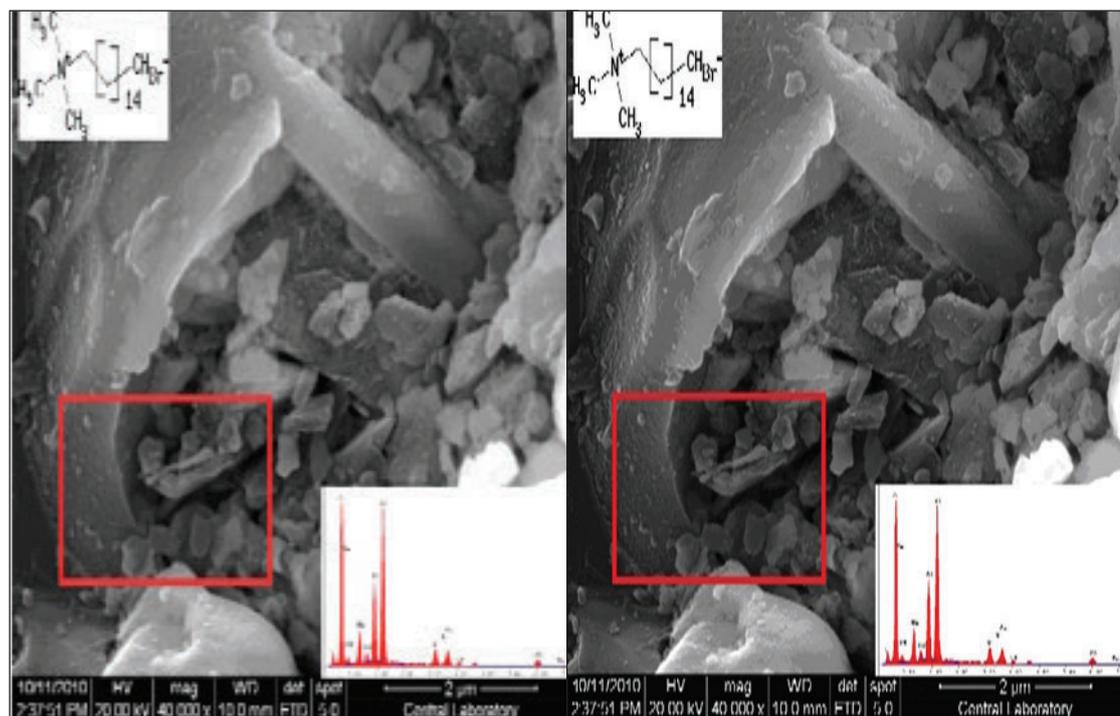


Figure 2. SEM images of the crude and HDTMA- organovolcanics and EDS distribution.

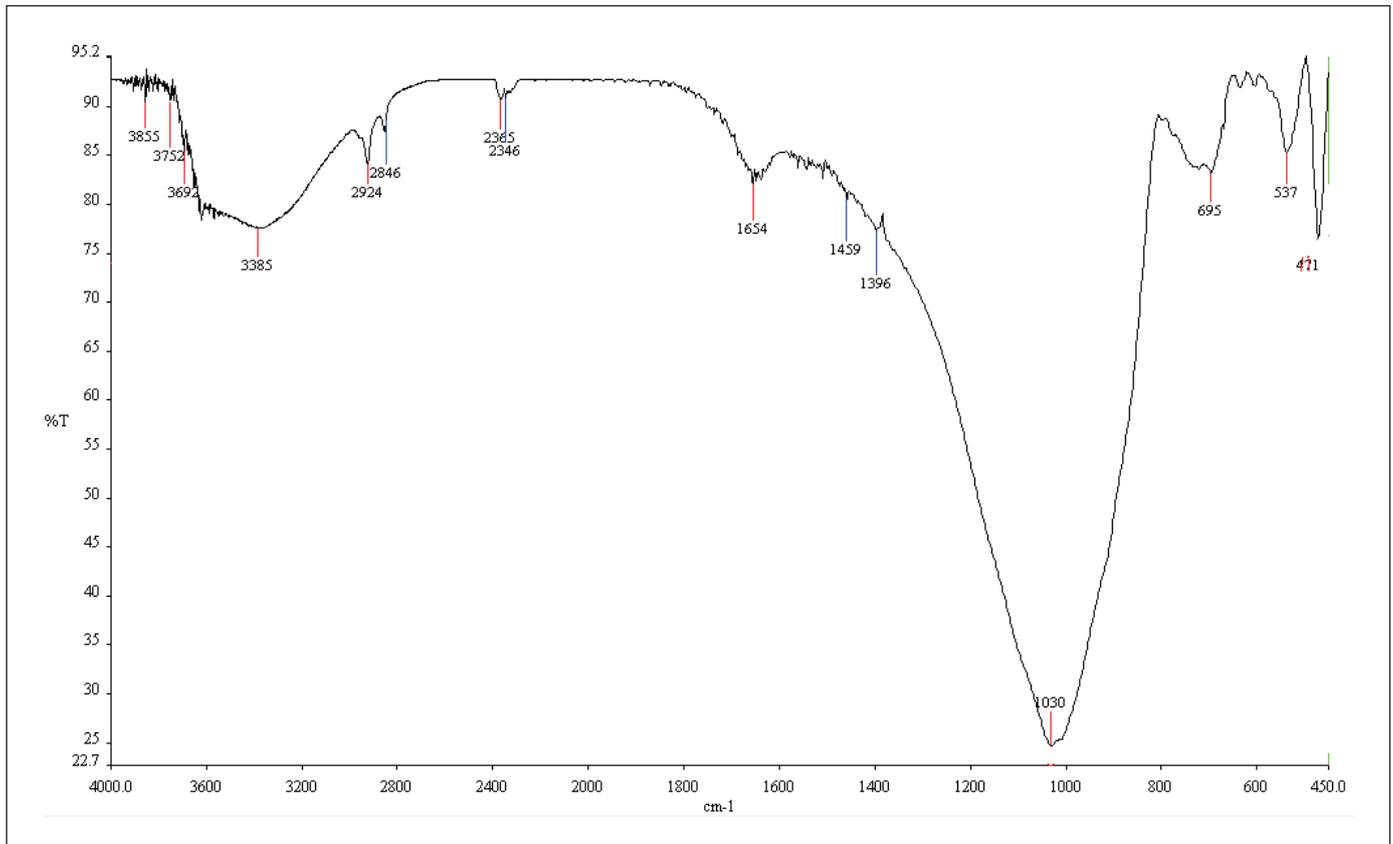


Figure 3. FT-IR spectra of HDTMA- organovolcanics.

some of which were at the central point, which is one of the RSM methods. The design matrix is shown in Table 2.

As a result of the evaluation of the obtained results, quadratic model (Eq.5) equality giving the amount of Sr^{2+} adsorbed is in the following.

Eq.5

$$Y \text{ (mg/g)} = 14.766 - 0.148 X_1 + 0.602 X_2 + 7.121 X_3 + 0.390 X_4 - 0.276 X_1 X_1 - 0.666 X_2 X_2 + 0.604 X_3 X_3 - 0.212 X_4 X_4 - 0.128 X_1 X_2 - 0.072 X_1 X_3 + 0.016 X_1 X_4 + 0.038 X_2 X_3 - 0.049 X_2 X_4 + 0.059 X_3 X_4$$

To check the statistical explanation of the above equation with a T-test, the second-order analysis of variance of the response surface (ANOVA) is given in Table 3. As the resulting F value was as large as 12.44, the experimental yields obtained by varying the factor levels were statistically significant at the 95% confidence limit. According to the result with probability value less than 0.0001, it is understood that the model is compatible. The R^2 and R^2_{adj} (0.96-0.92) values of the second order model calculated for the amount of adsorbed strontium (mg/g) are very close to 1. This result

shows that the experimental data are compatible with the values predicted by the model. Table 4 shows whether the coefficients of the model variables are significant, and the amount of strontium adsorbed (mg/g) is significant because the p value is less than 0.05 in the model (Sharma et al. 2009; Kaynar et al. 2015).

3.2.2 Response surface graphs

Three-dimensional surface graphs of the parameters affecting Sr^{2+} adsorption are given in Figure 4A-F.

When pH and time were evaluated together as three-dimensional surface graphs, it was observed that the amount of strontium adsorption on HDTMA organo-volcanic increased with increasing pH and decreased after a certain value (Figure 4A). The maximum value of adsorption capacity (Q) was determined as 15.22 mg/g in 95 minutes. A linear increase was observed when the changes in pH and initial strontium concentration were examined at constant temperature (40 °C) and adsorption time (67.5 min.). As seen in Figure 4B, it has been stated that it reaches 30 mg/g Q , especially at high concentrations. Changes depending on temperature and concentration at constant pH (5.5)

Table 2. Central Composite Cesign (CCD) model for Sr²⁺ adsorption by HDTMA-Organic- volcanics.

Run order	Coded values				Factors				Response (Y(mg/g))	
	X ₁	X ₂	X ₃	X ₄	pH	Conc.	Temp	Time	Observed value	Predicted value
1	1	1	1	1	6	80	50	90	22.85	22.05
2	1	1	1	-1	6	80	50	30	23.09	21.21
3	1	1	-1	1	6	80	30	90	6.86	7.75
4	1	1	-1	-1	6	80	30	30	7.10	7.16
5	1	-1	1	1	6	40	50	90	23.62	21.12
6	1	-1	1	-1	6	40	50	30	23.09	20.09
7	1	-1	-1	1	6	40	30	90	7.70	6.98
8	1	-1	-1	-1	6	40	30	30	7.97	6.19
9	-1	1	1	1	4	80	50	90	22.88	22.71
10	-1	1	1	-1	4	80	50	30	22.87	21.94
11	-1	1	-1	1	4	80	30	90	6.78	8.13
12	-1	1	-1	-1	4	80	30	30	7.05	7.60
13	-1	-1	1	1	4	40	50	90	22.98	21.27
14	-1	-1	1	-1	4	40	50	30	23.16	20.31
15	-1	-1	-1	1	4	40	30	90	6.92	6.84
16	-1	-1	-1	-1	4	40	30	30	6.96	6.11
17	2	0	0	0	8	60	40	60	10.31	13.37
18	-2	0	0	0	3	60	40	60	13.41	13.96
19	0	2	0	0	5	100	40	60	14.65	13.31
20	0	-2	0	0	5	20	40	60	5.95	10.90
21	0	0	2	0	5	60	60	60	26.31	31.43
22	0	0	-2	0	5	60	20	60	4.46	2.94
23	0	0	0	2	5	60	40	120	14.63	14.70
24	0	0	0	-2	5	60	40	15	9.61	13.14
25	0	0	0	0	5	60	40	60	14.97	14.77
26	0	0	0	0	5	60	40	60	14.64	14.77
27	0	0	0	0	5	60	40	60	14.98	14.77
28	0	0	0	0	5	60	40	60	14.75	14.77
29	0	0	0	0	5	60	40	60	14.75	14.77
30	0	0	0	0	5	60	40	60	14.62	14.77
31	0	0	0	0	5	60	40	60	14.66	14.77

Table 3. Analysis of variance (ANOVA) for the regression model for Sr²⁺ adsorption efficiency.

ANOVA	Df	SS	MS	F	Probability F
Regression	14	1259.28	89.95	12.44	4.7E-06
Residuals	16	115.674	7.23		
Total	30	1374.96			

Multiple R² = 0.96, Adjusted R² = 0.92

Table 4. Estimated regression coefficient and corresponding t and P values.

Regression	Coefficients	Standart error	T	P
Intercept	14.766	1.016	14.529	1.2E-10*
X ₁	-0.148	0.549	-0.269	0.7911
X ₂	0.602	0.549	1.098	0.2886
X ₃	7.121	0.549	12.974	6.5E-10*
X ₄	0.390	0.549	0.710	0.4878
X ₁ X ₁	-0.276	0.503	-0.549	0.5906
X ₂ X ₂	-0.666	0.503	-1.325	0.2039
X ₃ X ₃	0.604	0.503	1.202	0.2468
X ₄ X ₄	-0.212	0.503	-0.421	0.6795
X ₁ X ₂	-0.128	0.672	-0.191	0.8511
X ₁ X ₃	-0.072	0.672	-0.107	0.9157
X ₁ X ₄	0.016	0.672	0.024	0.9810
X ₂ X ₃	0.038	0.672	0.057	0.9553
X ₂ X ₄	-0.049	0.672	-0.073	0.9425
X ₃ X ₄	0.059	0.672	0.087	0.9314

*: Significant (p<0.05).

and time (67.5 min.) were performed in Figure 4C. Max. While the adsorption Q value was obtained at 40 degrees, the amount of adsorbed strontium increased proportional as the concentration increased (mg/g). According to the graph, the Q value was 29 mg/g. However, decreases were observed at higher temperatures. When the initial strontium concentration and adsorption time were evaluated together (Figure 4D), an increase in the amount of adsorption was detected for both parameters. The adsorption value was 31.8 mg/g at 95 mg/L strontium concentration (pH 5.5, temperature 40 °C). A peak occurred when pH and temperature were analyzed together at constant time (67.5 min) and initial strontium concentration (60 mg/g). observed to be max. strontium adsorption was 13.8 mg/g at 40 degrees and pH 5.8 (Figure 4E). When the temperature and time

were evaluated together for strontium adsorption (pH 5.5, concentration 60 mg/g), it was understood that the increase in temperature and time had a positive effect on adsorption (Figure 4F). According to the chart, the max. Q value of 15 mg/g was observed at 95 minutes.

3.3. Confirmation Rexpiriments

As comparative experiments of the RSM model, adsorption was determined as follows: pH 6.6, initial strontium concentration 72 mg/L, temperature 58.8 °C, and time 95 minutes. The theoretically adsorbed Sr²⁺ amount at these optimum values was calculated as 31.978 mg/g. In addition, this result was confirmed by experiments carried out under optimum conditions and the removal was found to be 28.32 mg/g. Essentially, HDTMA-Kula shows better adsorption

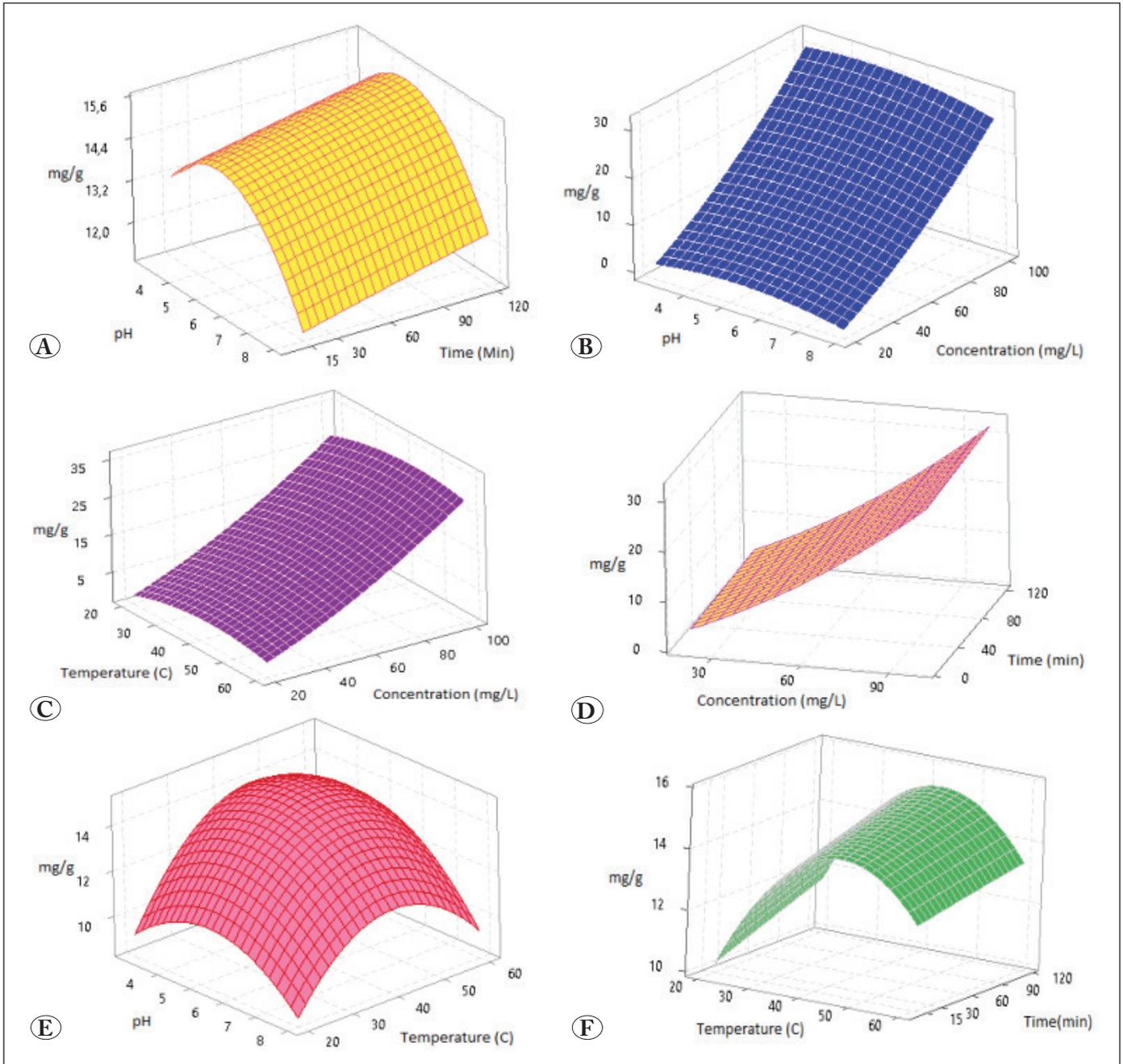


Figure 4. A-F) Response surface graphs for interactions of investigated parameters of Sr²⁺ adsorption onto HDTMA- organovolcanics.

performance for Sr²⁺ than the comparison listed in Table 5. In addition, the adsorption mechanism for Sr²⁺ is shown in Scheme 1.

3.4. Adsorption Isotherms

In this study, different isotherms were evaluated for the amount of sorbent and the concentration of adsorbate in the absorption in the interface medium. Different initial metal concentrations (20-100 mg/L) were used to evaluate the feasibility of adsorption processes.

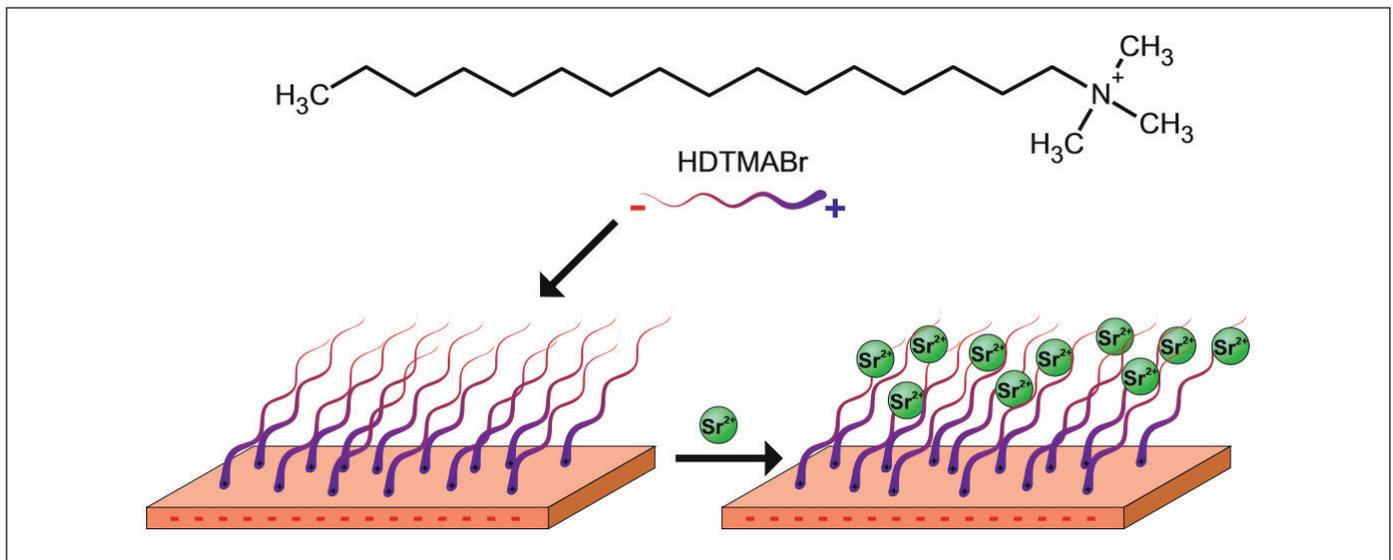
In our study, modeling of adsorption isotherms (Freundlich, Langmuir, Temkin, and DRK) was used to analyze the data. According to Langmuir equation;

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{C_e}{Q_0} \quad (6)$$

The value of b_L here is an adsorption equilibrium constant (L/mg) and Q_0 gives the adsorption capacity of the saturated monolayer (mg/g). The graph of C_e/q_e vs. C_e gives

Table 5. Comparison between the adsorption capacity (q_m , mg/g) of metals ions on various adsorbents.

Adsorbent	Metal Ions	Max. Ads. Capacity(mg/g)	References
HDTMA- Bentonide	U(VI)	17.39	Houhounea et al. 2016
HDTMA- Zeolite	Cr(VI)	39.47	Rosales-Landeros et al. 2013
Alginate microsphere	Sr(II)	17.8	Hong et al. 2016
Na- Montmorillonite	Sr(II)	10	Dos-Anjos et al. 2014
Natural clinoptilolite	Sr(II)	6.69	Smičiklas et al. 2007
Phosphorylated chitosan complex with cobalt (AP-CS-Co complex)	Sr(II)	3.4	Maranescu et al. 2017
HDTMA organo-montmorillonites	Sr(II)	3.91	Wu et al. 2012
Kula Volcanics		2.1	Current Study
HDTMA-Kula colcanics	Sr(II)	28.32	Current Study



Scheme 1. The mechanism of adsorption for Sr^{2+} onto surface of HDTMA- organovolcanics.

a straight line with a slope of $1/Q_0$ and intersects with $1/Q_0 B_L$.

The following Freundlich equivalence depends on adsorption on a heterogeneous surface. According to the equation:

$$q_e = k_f C_e^{1/n} \quad (7)$$

Eq.(7) can be converted into another linear form:

$$\log q_e = \log k_f + 1/n \log C_e \quad (8)$$

Here, k_f is the sorption capacity constant; $1/n$ is Freundlich's adsorption intensity constant.

The equation of the Temkin isotherm in the study is as follows:

$$q_e = B \ln A_T + B \ln C_e \quad (9)$$

where B: heat of adsorption constant (J/mol) and A_T : equilibrium binding coefficient (L/g).

Dubinin-Radushkevich isotherm generally refers to the adsorption mechanism on a heterogeneous surface with Gaussian energy distribution.

$$\ln q_e = \ln(q_s) - (K_{ad} \epsilon^2) \quad (10)$$

Where q_e : amount of adsorbate in the adsorbent at equilibrium (mg/g); q_s : theoretical isotherm saturation capacity (mg/g); K_{ad} : Dubinin-Radushkevich isotherm constant ($\text{mol}^2 / \text{kJ}^2$) and ϵ : Dubinin-Radushkevich isotherm

constant. The approach is generally applied to distinguish the physical and chemical adsorption of metal ions by their average free energies. The E per adsorbate molecule (for removing a molecule from its position in the sorption cavity forever) can be calculated by the relationship (11):

$$E = \left[\frac{1}{\sqrt{2B_{DR}}} \right] \quad (11)$$

Where B_{DR} is denoted as the isotherm constant. Meanwhile, the ϵ parameter can be calculated by Eq. (12) :

$$\epsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (12)$$

Here, R , T , and C_e represent gas constant (8.314 J/mol K), absolute temperature (K), and adsorbate equilibrium concentration (mg/L), respectively.

Freundlich, Langmuir, Temkin and DRK constants are shown, calculated according to R was Equation (6-12) and given in Table 6.

For Sr^{2+} sorption on HDTMA-Organovolcanic, Langmuir isotherm parameters congruences (Table 6) gave isotherms that were in good agreement with the detected behavior ($R^2 \geq 0.99$ for Sr^{2+}) (Figure 5). According to Langmuir, the maximum adsorption capacity for Sr^{2+} was 131.58 mg/g.

Table 6. Equilibrium isotherm parameters of sorption of Sr^{2+} by HDTMA-Organovolcanics.

Langmuir Isotherm				Freundlich Isotherm			
Q_m (mg/g)	K_L (Lm/g)	R^2		K_f (mg/g)	$1/n$	n	R^2
131.58	0.30	0.9920		4.72	0.41	2.43	0.8665
Temkin Isotherm				DRK Isotherm			
AT (L/mg)	b_T	B	R^2	q_s	K_{ad}	E	R^2
3.51	91.83	26.98	0.9655	104.03	-0.0005	31.62	0.9710

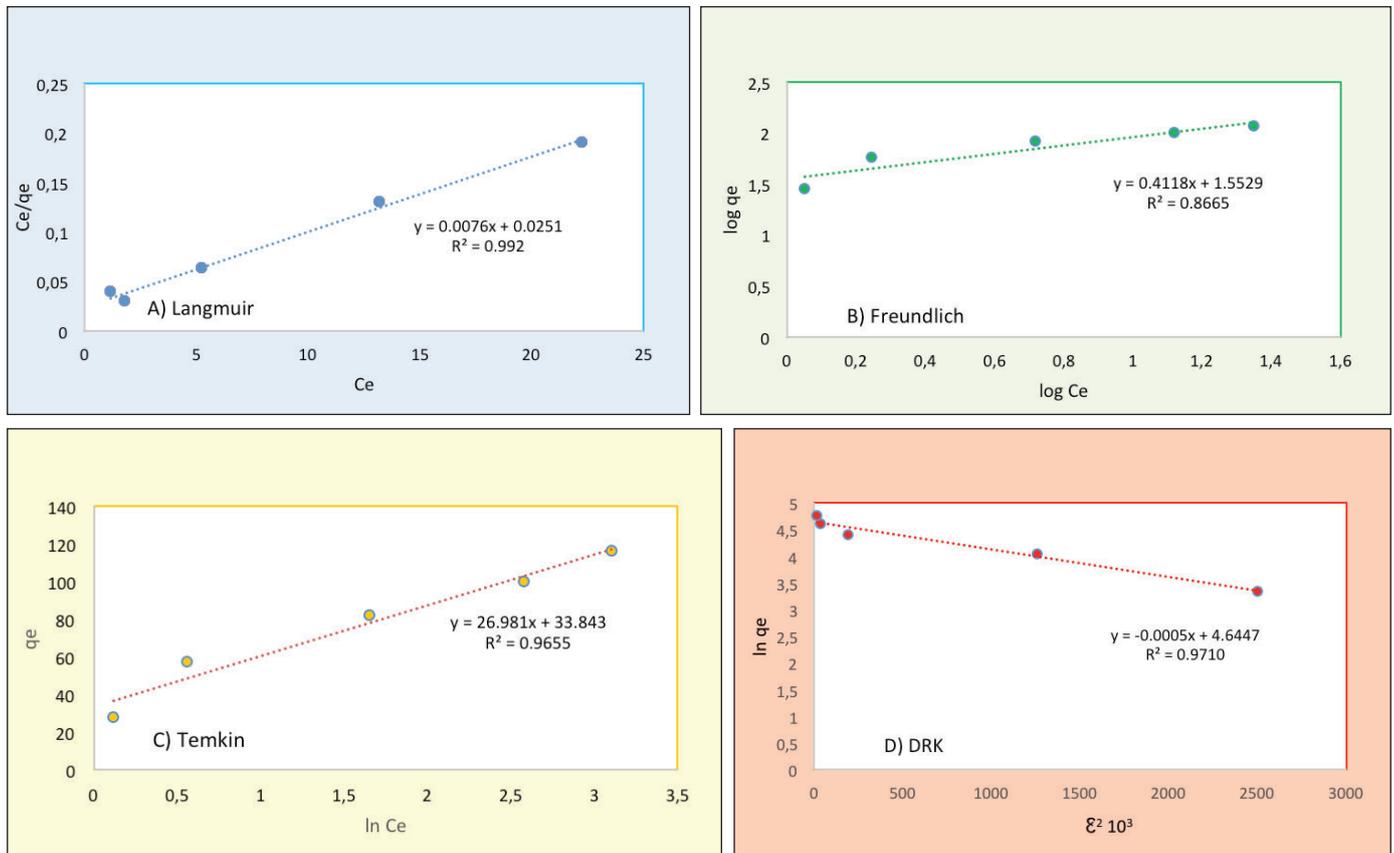


Figure 5. The adsorption isotherms for Sr^{2+} onto HDTMA- organovolcanics.

K_f and n values for Sr^{2+} were found to be 4.72 mg/g and 2.43, respectively. The Freundlich adsorption coefficient, K_p , was increased with temperature, so the sorption process was endothermic. $1/n$, ranging from 0 to 1, was a measure of sorption density or surface heterogeneity [33-34] Also, from the linear plot of the D-R model, q_s was determined as 104.3 mg/g, the mean free energy, E , is 31.62 KJ/g, indicating the chemical process. moles and R^2 was 0.9710 higher than Freundlich's. It is recommended that HDTMA-Organovolcanic be used effectively for Sr^{2+} adsorption in aqueous media.

3.5. Thermodynamic Studies

The sorption capacity of organovolcanics spontaneously has raised with the temperature from 293 to 313 K.

The entropy (ΔS°) and enthalpy (ΔH°) were determined according to the Van't Hoff formula:

$$\ln K_d = (\Delta S^\circ / R) - (\Delta H^\circ / RT) \quad (13)$$

Wherein, $\ln K_d$: coefficient distribution; T: temperature and R: gas constant.

The Gibbs free energy (ΔG°) were found by the formula:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

Adsorption experiments were carried out at various temperatures (293, 303, 313 K). When the thermodynamic parameters were examined, the adsorption ΔH , ΔG and ΔS for strontium adsorption to HDTMA-Kula were calculated as 7.6 kJ/mol, -19.05 kJ/mol and 0.08 kJ/Kmol, respectively. A positive value of ΔG indicates that the adsorption is endothermic. The fact that ΔG has smaller values with increasing temperature under optimum conditions indicates that the adsorption process proceeds spontaneously at high temperatures. All these data show that Sr^{2+} adsorption on HDTMA-Kula is physical adsorption (Shakur et al. 2016-b).

4. Conclusions

In this research, Sr^{2+} adsorption from aqueous solution was performed on HDTMA-Kula organovolcanite. All experiments were optimized with RSM. Regression analyzes show that all parameters in the study are important for Sr^{2+} adsorption. The agreement between the theoretical adsorption capacity values calculated in RSM and the actual values (0.96 for R^2) is quite high. also, the F values according to ANOVA (4.7E-06 for Sr^{2+}) show us that the study is statistically significant. The effects of process variables on

adsorption were investigated with reaction surface plots and significant effects of pH value, Sr^{2+} concentration, temperature and time on sorption were observed. Sr^{2+} adsorption capacity in HDTMA-Kula was obtained at 28.32 mg/g. Adsorption models (Langmuir, Freundlich, Temkin, and DRK) were used for the mathematical explanation of Sr^{2+} sorption on HDTMA-Kula. For Sr^{2+} sorption onto HDTMA-Kula, correlation coefficients (R^2 :0.9920) indicate that E is 31.62 KJ/mol, indicating a chemical process, and R^2 is 0.9710 higher than that of Freundlich. Thermodynamic parameters (ΔH° , ΔS° and ΔG°) were calculated and these parameters indicate that the adsorption is endothermic.

As a result, it has been understood that the natural adsorbent modified by the organic cation can be used as a good Sr^{2+} remover. Recently, there has been intense work on the use of economical adsorbents and increasing the adsorption capacity of activated adsorbents modified with different materials. The Kula volcanics, an indigenous resource, are readily available and in large quantities. A method in which the adsorption capacity of volcanics is increased by modifying them with ecologically harmless organic cations and these adsorbents are used to remove metal ion wastes, which are normally made at great cost, can provide many advantages. This method will benefit the country's economy and will prevent the problems and risks caused by such wastes.

5. References

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