

Adsorption of Uranium (VI) on organic cation-modified kula volcanite and optimization with surface response method (RSM)

Ümit H. Kaynar*¹, Sermin Çam Kaynar²

¹ Department of Fundamental Sciences, Faculty of Engineering and Architecture, Izmir Bakırçay University, Menemen, 35030, Izmir, Turkey

<https://orcid.org/0000-0002-3321-0341>

*corresponding author: umit.kaynar@bakircay.edu.tr

² Department of Physics, Faculty of Arts and Sciences, Manisa Celal Bayar University, Muradiye, 45010, Manisa, Turkey

(Received: 15.03.2023, Accepted: 18.10.2023, Published: 23.11.2023)

Abstract: First of all, the structural characteristics of the prepared HDTMA-volcanite. such as XRF, SEM and BET surface area were examined, then uranium U(VI) adsorption from aqueous solutions was optimized by surface response method (RSM), which is widely used in industrial research. Effective experimental conditions on adsorption efficiency: pH (3-8), time (30-150 minutes), uranium concentration (20-80 mg/L) and temperature (20-60 °C) were selected. The best possible combinations of these parameters were obtained by the surface response method (RSM). The central composite design (CCD) was chosen for the design of the experimental conditions. According to the RSM results, it was determined that the experimental design fit the quadratic model, and the R^2 and R^2_{adj} values, which are the parameters showing the model fit, were 0.98 and 0.95, respectively. HDTMA-Volk at optimum conditions. Adsorption capacity was obtained as 4.41 mg/g for the HDTMA-Volcanics at optimum conditions. The compatibility of the obtained data with adsorption isotherms was investigated, and thermodynamic parameters were calculated.

Key words: Adsorption, Uranium (VI), Volcanit, Response Surface Methodology (RSM)

1. Introduction

One of the most significant issues with nuclear technology is the removal, recovery, and storage of waste, which results in high expenditures. The elimination of pollution, especially caused by the expansion of the nuclear sector, is an important situation and is seen as a necessity for development today. Moreover, radioactive wastes that are generated in a variety of industries and sectors, including research, industry, and medicine, can be found in a variety of physical and chemical states. Chemical precipitation, coagulation, adsorption, ion exchange, biosorption [16], and other processes are the most efficient ways to remove radioactive materials and heavy metals. Due to the abundance of clays in our nation and the fact that they may be used to purify metals using the adsorption method, clays are often used as inorganic adsorbent materials. Modifying clays with long-chain quaternary amine cationic salts from organic cations increases their hydrophobicity, leading to improved adsorption of metal ions. This modification alters the structure from a hydrophilic silica surface to an organophilic surface, and the organic cation can easily bond to the adsorbent surface through electrostatic forces between the positive charges of the long-chain organic cations and the

negative charges on the adsorbent surface [1]. Several adsorbents that are modified with organic cations are used as adsorbents in the literature [2-4].

In the environment, uranium (U) is typically found in its hexavalent form and is considered a toxic heavy metal due to its radioactive properties. It can be found in rocks, soils, and water, and can enter the environment through various sources, such as scientific research, industry, nuclear power plants, medicine, and weapons. The US EPA has classified uranium as a confirmed human carcinogen (group A) [3], and the tolerable limit for its carcinogenic risk is 0.5 µg/kg body weight (or 35 µg for a 70 kg adult) [4]. While soluble uranium salts are toxic, their toxicity is generally less severe compared to other heavy metals such as mercury or lead. The kidneys are the organ most affected by uranium toxicity [4-9]. In a research conducted by Kutahyalı et al. [10], they determined that the sorption of strontium ions on untreated and HCl-treated Kula volcanic samples yielded calculations of 2.04 and 1.72 mg/g, respectively. In a study examined by Xi et al. (2009) [11], the adsorption capacity of 3.54 mg/g was shown under optimum conditions by using U(IV) solution in the adsorption of uranium on Hematite. In a different study, uranium adsorption was carried out on nano-MgO particles obtained by Kaynar et al. (2018b) ignition method. In the study, it was observed that the adhesion had multilayer adsorption and a sorption capacity of 128.4 mg/g [12].

The production of dangerous rays like alpha, beta, and gamma from the breakdown of atomic nuclei in radioactive materials like thorium and uranium can seriously affect both living things and the environment. Radioactive contamination has the potential to harm genetic material, impair immunological function, hasten the progression of cancer, and possibly result in fatalities [13].

The RSM (Response Surface Methodology) is a technique that utilizes statistical and mathematical modeling to evaluate the correlation between diverse observations obtained from different factors. Through the optimization of independent and dependent variables, RSM analyzes the theoretical and experimental data to investigate this correlation [14]. This methodology is extensively employed across various fields for enhancing and optimizing the process and obtaining a better understanding of how different variables impact the system under study [15,16].

This study focused on enhancing the adsorption capacity of the abundant and cost-effective alkali basaltic Kula volcanite by modifying it with an organic cation, HDTMA, for the removal of U(VI) from aqueous solutions. The effectiveness of the HDTMA-modified volcanite was evaluated and RSM for the adsorption of U(VI) from aqueous solutions. The goal was to investigate the feasibility of using organic-loaded volcanites in the removal and separation of U(VI) from aqueous solutions. Overall, this research aimed to develop a practical and cost-effective method for U(VI) removal and separation from aqueous solutions using modified volcanites.

2. Material and Method

The alkali basalt structure of the Kula volcanite used as an adsorbent in this study was derived from the volcanic zone surrounding Demirköprü Dam (Manisa). The study's chemical reagents were all analytical quality. The structure-modified quaternary ammonium (alkyl aryl ammonium) compound containing cationic surfactants utilized was straight chain hexadecyltrimethylammonium (HDTMA)-bromide (C₁₉H₄₂NBr, MA: 364.46 g, Sigma-Aldrich, purity: 99%). A thermostatic water bath shaker with the

model number GFL-1083 was used to conduct the batch method adsorption investigations.

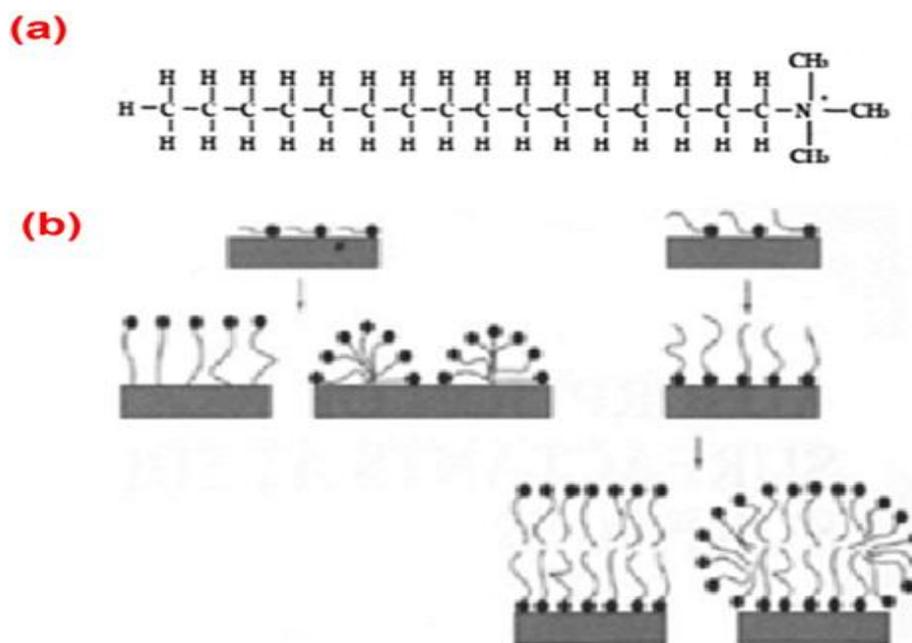


Figure 1. HDTMA molecule (a) and surface binding types (b)

2.1. Preparation of organo-volcanics

The volcanics were collected from three different locations around the Demirköprü dam extinct volcano region and washed thoroughly with pure water before undergoing organic cation modification. Subsequently, they were dried at 110 °C for 24 hours and crushed using jaw crushers. The volcanics were then treated with HDTMA salt solutions of 5, 10, 15, and 20 mM concentrations as organic matter and dried to prepare the modified organo-volcanites. The optimal concentration of 5 mM was chosen. The molecular structure and surface binding types of the organic cation HDTMA are depicted in Figure 1. The modified organo-volcanites were characterized using XRF, SEM, and BET surface area analysis.

2.2. Adsorption studies of uranium(VI)

For the uranium uptake studies from aqueous solutions, dilutions were made from a stock solution of 1000 ppm $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. The modified Kula volcanic materials with HDTMA (5 mM) were used for the batch experiments. In each experiment, 0.375 g of modified volcanic material was mixed with 20 mL of uranium solution in a 50 mL tube. After centrifugation at 4500 rpm for 10 minutes, the supernatant was analyzed using ICP-OES (Perkin-Elmer Optima 2000 DV model Inductively Coupled Plasma-Optic Emission Spectrometry) to determine the remaining uranium concentration in the solution after adsorption.

2.3. Mathematical modeling of the experimental system

Response Surface Methodology

RSM is an analytical technique that employs statistical and mathematical models to investigate the relationship between multiple observations obtained under varying conditions [14]. By optimizing the values of independent and dependent variables, RSM allows for the comparison of theoretical and experimental data. Its application is widespread, as it enables the optimization and enhancement of processes, as well as the examination of the interrelationships between different variables that impact the system being studied [16].

Experimental design

The impact of each factor can be represented by a mathematical model derived from the scanning design and optimization. In addition to the experimental results, predicted outcomes can also be obtained. The statistical experimental design data is analyzed using multiple linear regression analysis, and response variables are described by polynomial functions. Subsequently, it is verified if the expected outcomes can be achieved experimentally.

$$y = b_0 + \sum_1^k b_i x_i + \sum_1^k b_{ii} x_i^2 + \sum_{i < j}^k b_{ij} x_i x_j + \varepsilon \quad (1)$$

In this study, the relationship between the response variable (y) and the independent variables (x1, x2, ..., xk) was expressed using a polynomial function that includes coefficients (b1, b2, ..., bk) determined by regression analysis. The interaction between factors was taken into account by including terms (bijxixj), and the curvature of the model was defined by including quadratic terms (biixi²). The error term (ε) was also included in the model. The optimal values of the independent variables were determined using the Minitab program.

Table 1. Independence Factors and their Coded Levels Used for Optimization.

| Parameters | Code | -2 | -1 | 0 | 1 | 2 |
|-----------------|------|----|----|----|-----|-----|
| pH | X1 | 3 | 4 | 5 | 6 | 8 |
| Concentration | X2 | 20 | 40 | 50 | 60 | 80 |
| Temperature (C) | X3 | 20 | 30 | 40 | 50 | 60 |
| Time (t) | X4 | 30 | 60 | 90 | 120 | 150 |

3. Results

3.1. Characterization of adsorbents

The original basaltic volcanic sample analyzed in this study was found to have a chemical composition consisting of various elements, including SiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, TiO₂, P₂O₅, and other trace elements. The percentages of each element were measured, with SiO₂ being the most abundant at 48.4%, followed by Al₂O₃ at 17.66%, and Fe₂O₃ at 8.648%. Other elements found in smaller quantities included MnO at 0.085%, MgO at 8.538%, CaO at 6.234%, Na₂O at 3.989%, K₂O at 2.881%, TiO₂ at

1.85%, P_2O_5 at 0.625%, and other trace elements at 1.09% [17]. The analysis of the chemical composition provided important information about the properties of the original basaltic volcanic sample and informed the subsequent modification and use of the material in the study.

The SEM images of the volcanic adsorbent modified with organic cation were obtained using the QUANTA 400 F Field Emission-SEM and are presented in Figure 2. The EDS was also utilized to examine the elements in the pore structure and their percent distributions. The images are magnified x3000 times, and the crystalline dimensions appear to be in the micro-meter scale. The images indicate that the organic cation-modified surface completely covers the volcanic surface. Compared to normal volcanite, an increase in carbon percentage of 6.32% was observed in HDTMA-volcanite. The surface area changes of the raw and HDTMA modified volcanic samples were determined, and the results are presented in Table 2. The HDTMA modification increased the surface area of Kula volcanite to 3,689 (m^2/g).

Table 2. Surface area changes of unmodified and HDTMA modified -volcanite samples.

| | Unmodified volcanite | HDTMA-volcanite |
|--------------------------|----------------------|-----------------|
| Surface area (m^2/g) | 1,265 | 3,152 |

3.2. Experimental design results

The study aimed to optimize the amount of uranium (VI) adsorbed (mg/g) by using RSM and optimizing certain parameters including pH, temperature, initial U(VI) concentration (mg/L), and time. The optimal conditions were determined through RSM, and subsequent experiments were conducted to assess the effect of these parameters using the central composite design (CCD) method, a type of RSM method. A total of 31 experiments were conducted, with seven at the center point. The results obtained from the designed experimental conditions are presented in Table 3.

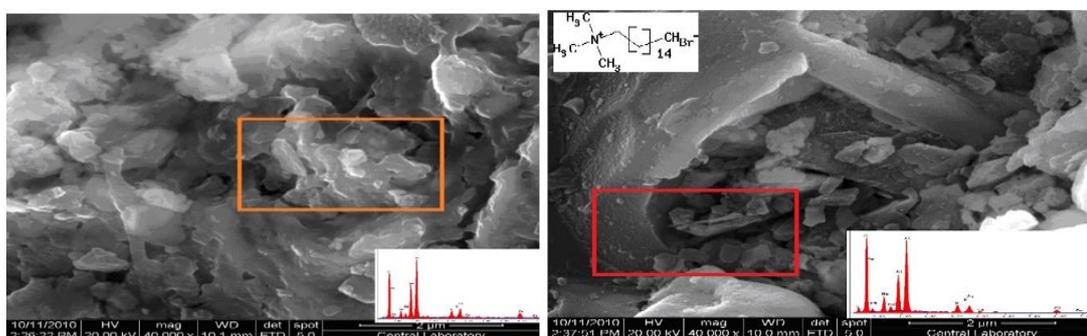


Figure 2. SEM image (x40000) and EDS distribution of raw and HDTMA-volcanics

Table 3. Central composite design model for U(VI) adsorption by HDTMA-Volcanics

| Run Order | x_1 | x_2 | x_3 | x_4 | pH | Const | Temp | Time | Response (mg/g) | |
|-----------|-------|-------|-------|-------|----|-------|------|------|------------------------|-----------------------|
| | | | | | | | | | Predicted value (mg/g) | Observed value (mg/g) |
| 1 | 1 | 1 | 1 | 1 | 6 | 60 | 50 | 120 | 3,20 | 3,15 |
| 2 | 1 | 1 | 1 | -1 | 6 | 60 | 50 | 60 | 3,25 | 3,15 |
| 3 | 1 | 1 | -1 | 1 | 6 | 60 | 30 | 120 | 3,04 | 3,04 |
| 4 | 1 | 1 | -1 | -1 | 6 | 60 | 30 | 60 | 3,07 | 3,02 |
| 5 | 1 | -1 | 1 | 1 | 6 | 40 | 50 | 120 | 1,99 | 2,07 |
| 6 | 1 | -1 | 1 | -1 | 6 | 40 | 50 | 60 | 2,01 | 2,11 |
| 7 | 1 | -1 | -1 | 1 | 6 | 40 | 30 | 120 | 1,92 | 2,07 |
| 8 | 1 | -1 | -1 | -1 | 6 | 40 | 30 | 60 | 1,92 | 2,06 |
| 9 | -1 | 1 | 1 | 1 | 4 | 60 | 50 | 120 | 3,22 | 3,11 |
| 10 | -1 | 1 | 1 | -1 | 4 | 60 | 50 | 60 | 3,20 | 3,15 |
| 11 | -1 | 1 | -1 | 1 | 4 | 60 | 30 | 120 | 3,15 | 3,15 |
| 12 | -1 | 1 | -1 | -1 | 4 | 60 | 30 | 60 | 3,12 | 3,08 |
| 13 | -1 | -1 | 1 | 1 | 4 | 40 | 50 | 120 | 1,97 | 2,12 |
| 14 | -1 | -1 | 1 | -1 | 4 | 40 | 50 | 60 | 1,92 | 1,97 |
| 15 | -1 | -1 | -1 | 1 | 4 | 40 | 30 | 120 | 1,99 | 2,13 |
| 16 | -1 | -1 | -1 | -1 | 4 | 40 | 30 | 60 | 1,93 | 2,07 |
| 17 | 2 | 0 | 0 | 0 | 8 | 50 | 40 | 90 | 2,53 | 2,47 |
| 18 | -2 | 0 | 0 | 0 | 3 | 50 | 40 | 90 | 2,56 | 2,49 |
| 19 | 0 | 2 | 0 | 0 | 5 | 80 | 40 | 90 | 3,84 | 4,11 |
| 20 | 0 | -2 | 0 | 0 | 5 | 20 | 40 | 90 | 1,44 | 1,04 |
| 21 | 0 | 0 | 2 | 0 | 5 | 50 | 60 | 90 | 2,60 | 2,64 |
| 22 | 0 | 0 | -2 | 0 | 5 | 50 | 20 | 90 | 2,45 | 2,28 |
| 23 | 0 | 0 | 0 | 2 | 5 | 50 | 40 | 150 | 2,52 | 2,42 |
| 24 | 0 | 0 | 0 | -2 | 5 | 50 | 40 | 30 | 2,51 | 2,49 |
| 25 | 0 | 0 | 0 | 0 | 5 | 50 | 40 | 90 | 2,63 | 2,68 |
| 26 | 0 | 0 | 0 | 0 | 5 | 50 | 40 | 90 | 2,63 | 2,53 |
| 27 | 0 | 0 | 0 | 0 | 5 | 50 | 40 | 90 | 2,63 | 2,66 |
| 28 | 0 | 0 | 0 | 0 | 5 | 50 | 40 | 90 | 2,63 | 2,68 |
| 29 | 0 | 0 | 0 | 0 | 5 | 50 | 40 | 90 | 2,63 | 2,52 |
| 30 | 0 | 0 | 0 | 0 | 5 | 50 | 40 | 90 | 2,63 | 2,61 |
| 31 | 0 | 0 | 0 | 0 | 5 | 50 | 40 | 90 | 2,63 | 2,41 |

The quadratic equation that predicts the amount of uranium adsorbed (mg/g) was derived from the evaluation of the obtained results.

$$Q \text{ (mg/g)} = 2,629 - 0,007X_1 + 0,6X_2 + 0,039X_3 + 0,003X_4 - 0,021X_1X_1 + 0,003X_2X_2 - 0,026X_3X_3 - 0,028X_4X_4 - 0,01 X_1X_2 + 0,024 X_1X_3 - 0,016 X_1X_4 + 0,022 X_2X_3 - 0,009 X_2X_4 - 0,005 X_3X_4$$

Table 5 shows the second-order analysis of variance (ANOVA) of the response surface, which is used to test the statistical significance of the equation using the F-test. The obtained F-value of 23.04 indicates that the experimental results obtained by varying the factor levels are highly significant at a 95% confidence level. The model is considered compatible since the probability (P) value is less than 0.0001. The close proximity of R^2 and R^2_{Adj} (0.98-0.95) values for the quadratic model obtained for

adsorbed uranium amount (mg/g) indicates that the predicted values by the model and the experimental values are in excellent agreement. The significance of the coefficients in front of the model variables was assessed using p-values in Table 4, where p-values less than 0.05 indicate that the first-order effect of increasing uranium initial concentration is significant in predicting the amount of adsorbed uranium (mg/g) using the model.

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

| Regression | Coefficients | Standart error | T | P |
|------------|--------------|----------------|--------|----------|
| Intercept | 2,629 | 0,062 | 42,217 | 7,74E-18 |
| x1 | -0,007 | 0,034 | -0,200 | 0,8438 |
| x2 | 0,600 | 0,034 | 17,851 | 5,48E-12 |
| x3 | 0,039 | 0,034 | 1,150 | 0,2670 |
| x4 | 0,003 | 0,034 | 0,102 | 0,9197 |
| x1^2 | -0,021 | 0,031 | -0,677 | 0,5079 |
| X2^2 | 0,003 | 0,031 | 0,104 | 0,9185 |
| X3^2 | -0,026 | 0,031 | -0,837 | 0,4149 |
| X4^2 | -0,028 | 0,031 | -0,899 | 0,3818 |
| X1X2 | -0,010 | 0,041 | -0,231 | 0,8202 |
| X1X3 | 0,024 | 0,041 | 0,572 | 0,5751 |
| X1X4 | -0,016 | 0,041 | -0,392 | 0,7005 |
| x2x3 | 0,022 | 0,041 | 0,522 | 0,6086 |
| x2x4 | -0,009 | 0,041 | -0,213 | 0,8341 |
| x3x4 | -0,005 | 0,041 | -0,117 | 0,9085 |

Table 5. Analysis of variance (ANOVA) for the regression model for U(VI) adsorption efficiency.

| ANOVA | Df | SS | MS | F | Probability F |
|--------------------------------|----|------|------|-------|---------------|
| Regression | 14 | 8,76 | 0,63 | 23,04 | 5,77E-08 |
| Residuals | 16 | 0,43 | 0,03 | | |
| Total | 30 | 9,19 | | | |
| $R^2 : 0.98, R^2_{adj} : 0.95$ | | | | | |

Three-dimensional surface graphs of the parameters affecting the U(VI) adsorption are given in Figure 3. In the adsorption of U(VI) on HDTMA-volcanic, according to the three-dimensional surface graphics; In Figure 4a, changes depending on the time and concentration, which are the adsorption parameters at constant pH (5.5) and temperature (40 °C), are seen. When the effect of concentration was examined as a parameter, it was observed that the best adsorption occurred at 80 mg/L and the amount of adsorbed U(VI) increased proportionally as the concentration increased. According to the graph, the maximum amount adsorbed reached 3.9 mg/g. When pH and initial U(VI) concentration (mg/L) were evaluated together, an increase in the amount of adsorption was observed for both parameters. At a concentration of 80 mg/L U(VI) at pH 5.5, it reached 4.13 mg/g adsorption values (time 90 min.; temperature 40 °C). When the changes in pH and time at constant temperature (40 °C) and concentration (50 mg/L) were examined, it was determined that the adsorption amount reached 2.55 mg/g in pH

5.5 and 120 minutes. In adsorption, temperature and pH were found to have positive effects on adsorption and it is shown in Figure 3 (d). When the time and temperature were evaluated together, the amount of adsorption increased with the increase in time and a decrease was observed after a certain value (Figure 3 e). With the increase of the adsorption time, it reached the maximum adsorption values of 2.52 mg/g at 120 min and pH 5.5. When the concentration and temperature are evaluated together in a constant time (90 min) and pH environment, both have a positive effect on the increase, and the maximum U(VI) adsorption was observed as 4.16 mg/g at 58°C (Figure.3-f).

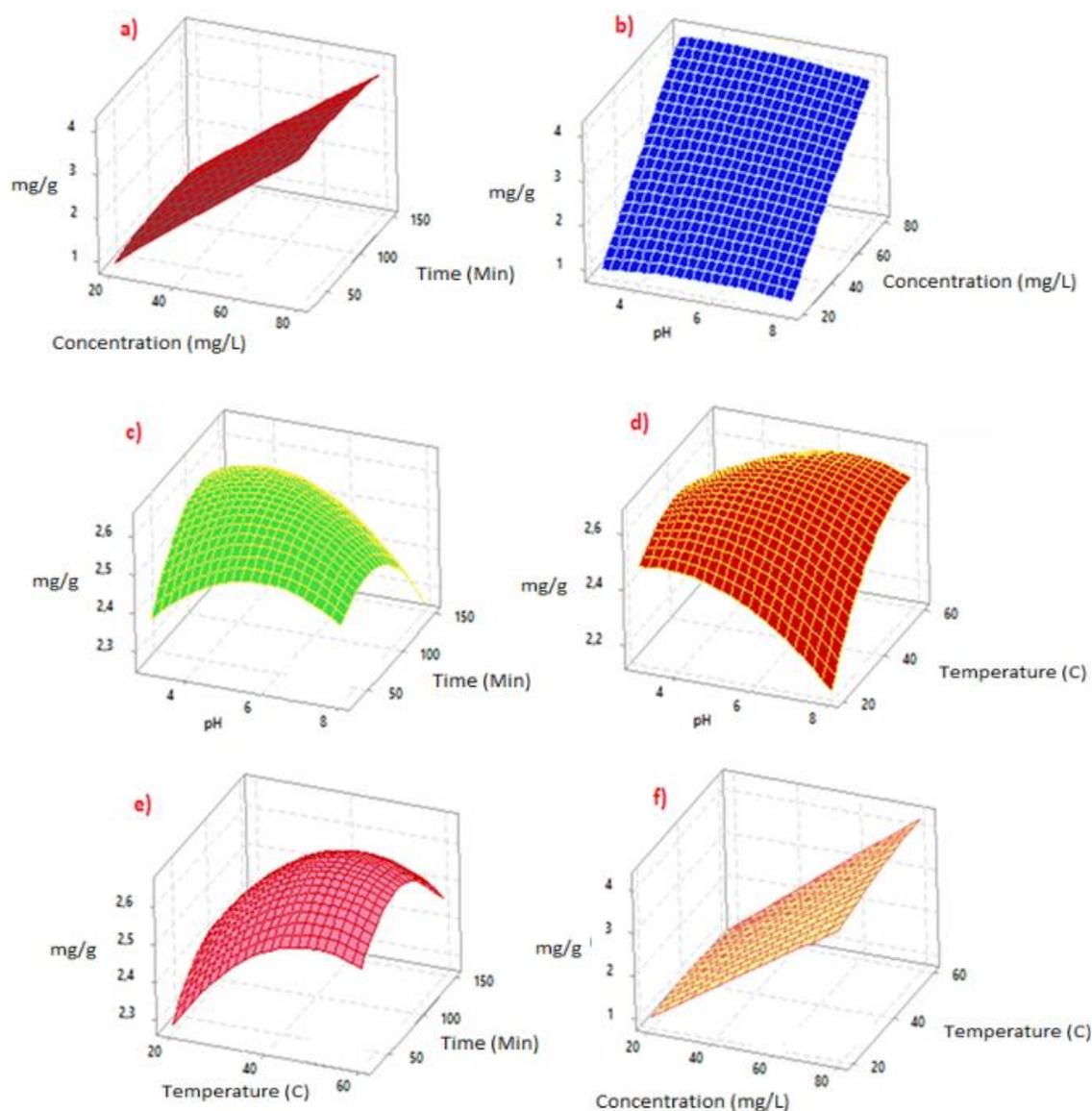


Figure 3. (a-f) Response surface graphs for interactions of investigated parameters of U(VI) adsorption onto HDTMA- volcanics

Optimum conditions for maximum adsorption were determined by conducting comparison experiments with the model. The optimal values were found to be pH 5.75, initial uranium concentration of 80 mg/L, temperature of 59.8 °C, and a duration of 40 minutes. The model predicted that the amount of adsorbed uranium at these optimum points would be 3,918 mg/g. In the experiments performed under these optimum conditions, the adsorption of U(VI) on HDTMA-volcanite was found to be 4.41 mg/g.

When the literature is examined, it is seen that HDTMA-Volcanite is a good adsorbent for U(VI) (Table 6).

Table 6. U(VI) uptake capacities of different adsorbents

| Adsorbents | q(mg/g) | pH | References |
|--------------------------|---------|------|------------|
| Hematite | 1.63 | 7 | [18] |
| Talc | 2.19 | 5 | [19] |
| DEEA organo-volcanics | 2.2 | 5 | [20] |
| HDTMA-modified volcanite | 4,41 | 5,75 | This study |

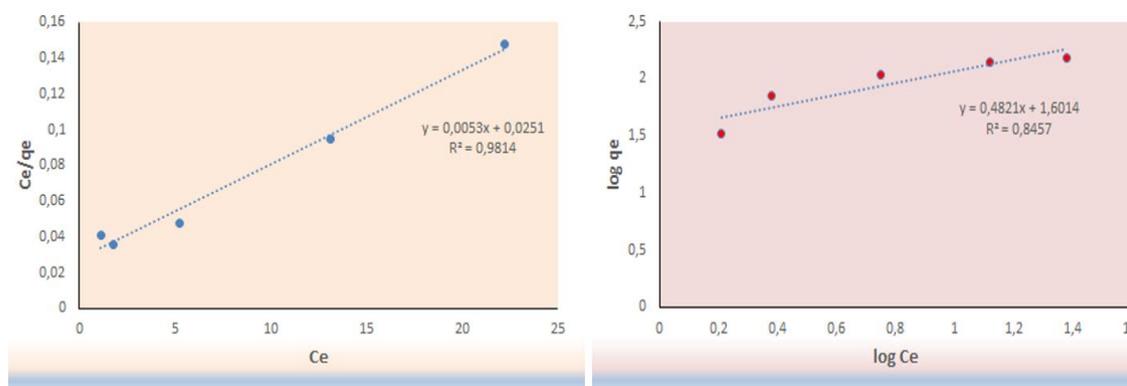


Figure 4. Langmuir and Freundlich adsorption isotherm for U(VI)

Based on the experimental data obtained from uranium adsorbed from aqueous solutions using organic cationic volcanic adsorbent, it was found that the adsorption isotherms followed Langmuir type adsorption ($R^2 = 0.9814$) (Figure. 4). Furthermore, when the thermodynamic parameters were analyzed, it was determined that the adsorption enthalpy (ΔH) was 3.5 kJ/mol, the free energy change (ΔG) was -18.07 kJ/mol, and the entropy change (ΔS) was 0.07 kJ/Kmol for the adsorption of uranium on HDTMA-volcanite. The positive value of ΔH indicates that the adsorption is endothermic. The observation that the free energy exchange ΔG has smaller values with increasing temperature under optimal conditions suggests that the adsorption process is spontaneous at high temperatures. Based on this information, it can be concluded that the uranium adsorption onto HDTMA-volcanite is a physical adsorption process. These findings have important implications for the use of HDTMA-volcanite in the removal and separation of U(VI) from aqueous solutions.

4. Results and discussion

The elimination of radionuclide pollution resulting from the nuclear industry is not only vital but also challenging and expensive. Advanced facilities and technologically applicable, economical methods are required for the removal, purification, and separation of radioactive elements from the environment, especially from uranium and thorium mining. In this study, it was found that a natural adsorbent called Kula volcanite, modified with an organic cation, can be a useful U(VI) remover. This

adsorbent is locally sourced, readily available in large quantities, and can be modified with ecologically harmless organic cations to increase its adsorption capacity. Thus, it offers many advantages as a viable method for the removal of radionuclides that are costly to eliminate as waste. The development of Kula volcanite's features for the removal of hazardous metal ion wastes from the environment is significant for both the country's economy and the elimination of potential dangers and problems resulting from such wastes in the environment.

References

- [1] Upson, R. T., Burns, S. E. 2006. Sorption of nitroaromatic compounds to synthesized organoclays. *J. Colloid Interface Sci.* 297, 70–76.
- [2] Ryu, C. H., Yeo, S. D. 2010. Vapor phase adsorption of trichloroethane using organically modified montmorillonite. *J. Ind. Eng. Chem.* 377, 441-449.
- [3] Majdan, M., Pikus, S., Gajowiak, A., Gladysz-Plaska, A., Krzyzanowska, H., Zuk, J., Bujacka, M. 2010. Characterization of uranium(VI) sorption by organobentonite. *Appl. Surf. Sci.* 256-17, 5416-5421.
- [4] Shen, Y. H. 2004. Phenol sorption by organoclays having different charge characteristics. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 232, 143–149.
- [5] Benedict B, Pigford TH, Levi HW (1981) *Nuclear chemical engineering*. Mc Graw-Hill, New York
- [6] Xie SB, Yang J, Chen C, Zhang XJ, Wang QL, Zhang C (2008) *J Environ Radioact* 99:126
- [7] U.H. Kaynar, M. Ayvacikli, S.C. Kaynar et al., Removal of uranium(VI) from aqueous solutions on nanoporous ZnO by manufactured microwave-assisted combustion synthesis. *J. Radioanal. Nucl. Chem.* 299, 1469–1477 (2014).
- [8] US Environmental Protection Agency (1992) *Integrated Risk Assessment System*. Retrieval for metals, 9/14/92. Micromedex Inc, Denver
- [9] Shuibo X, Chun Z, Xinghuo Z, Jing Y, Xiaojian Z, Jingsong W (2009) *J Environ Radioact* 100:162
- [10] C. Kutahyalı, C. Cetinkaya, B. Acar M.B. Investigation of strontium sorption on Kula volcanic using central composite design. *J. Hazard. Mater.* 201–202, 115–124 (2012).
- [11] Xi, S., Zhang, C., Xinghuo, Z., Jing, Y., Xiaojian, Z., Jingsong, W. 2009. “Removal of uranium (VI) from aqueous solution by adsorption of hematite”, *J. Environ. Radioact*, 100: 162-166
- [12] Kaynar, U.H. 2018b. “A Modeling and Optimization Study by Response Surface Methodology (RSM) on UO_2^{2+} Ions Adsorption Using Nano-MgO Particles” *Inorganic and Nano-Metal Chemistry*, 48-3: 187-195
- [13] Hollriegel, V., Greiter, M., Giussani, A., Gerstmann, U., Michalke, B., Roth, P., Oeh, U. 2007. Observation of changes in urinary excretion of thorium in humans following ingestion of a therapeutic soil. *J. Environ. Radioact.* 95, 149–160.
- [14] S., Malik, A., Satya, S. 2009. Application of response surface methodology (RSM) for optimization of nutrient supplementation for Cr(VI) removal by *Aspergillus lentulus* AML05. *J. Hazard. Mater.* 164, 1198–1204.
- [15] Cao, J., Wu, Y., Jin, Y., Yilihan, P., Huang, W. 2014. Response surface methodology approach for optimization of the removal of chromium (VI) by NH_2 -MCM-41. *J. Taiwan Inst. Chem. Eng.* 45, 860–868.

- [16] Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S., Escaleira, L. A. 2008. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta*, 76, 965–977.
- [17] Helvacı, C. and Erkül F. 2001. Volcaniclastic rocks. Formation, general characteristics and classification. DEÜ, Engineering Faculty Publications, No: 285, Izmir (in Turkey),s: 93.
- [18] Sprynskyy, M., Kovalchuk, I., Buszewski, B., 2010. The separation of uranium ions by natural and modified diatomite from aqueous solution. *J. Hazard. Mat.*181, 700–707.
- [19] Liu, Y., Liu, Y., Cao, X., Hua, R., Wang, Y., Pang, C., Hua, M., Li, X. 2011. Biosorption studies of uranium (VI) on cross-linked chitosan: isotherm, kinetic and thermodynamic aspects. *J. Radioanal. Nucl. Chem.* 290(2), 231-239.
- [20] Zhao, D., Wang, X., Yang S. et al., 2012. Impact of water quality parameters on the sorption of U(VI) onto hematite. *J. Environ. Radioact.* 103, 20–29.
- [21] Sprynskyy, M., Kowalkowski, T., Tutu, H. et al., 2011. Adsorption performance of talc for uranium removal from aqueous solution. *Chem. Eng. J.* 171, 1185–1193.
- [22] KAYNAR, U.H., HIÇSÖNMEZ, U., ÇAM -KAYNAR, S., KOÇAK, S. 2018. Sorption of uranium (VI) from aqueous solutions by DEEA- organovolcanic: Isotherms and thermodynamic studies, *Nucl. Sci. Techn.* 29:30,
- [23] Zhang, Z., Zhou, Y., Liu, Y. H., Cao, X. H., Zhou, Z. W., Han, B., Liang, P., Xiong, G. 2014. Removal of thorium from aqueous solution by ordered mesoporous carbon CMK-3. *J. Radioanal. Nucl. Chem.*, 302(1), 9–16.
- [24] Ilaiyaraja, P., Deb, A.K.S., Sivasubramanian, K., Ponraju, D., Venkatraman, B. 2013. Removal of thorium from aqueous solution by adsorption using PAMAM dendron- functionalized styrene divinyl benzene, *J. Radioanal. Nucl. Chem.* 297, 59–69.