

Investigation of strontium sorption onto Kula volcanics using Central Composite Design

Ceren Kütahyalı^{a,*}, Berkan Çetinkaya^a, M. Bahadır Acar^a, Nuray Olcay Işık^b, İrfan Cireli^c

^a Ege University, Institute of Nuclear Sciences, 35100 Bornova, İzmir, Turkey

^b Ege University, Engineering Faculty, Leather Engineering Department, 35100 Bornova, İzmir, Turkey

^c Celal Bayar University Kula Leather Training School, 45170 Manisa, Turkey

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ABSTRACT

In performance assessment studies, the uptake of the radioactive elements by rock formations play an important role in retarding their aqueous phase migration. Sorption studies of radionuclides have been conducted to obtain data on the distribution coefficient (K_d) that is as an input parameter in the performance assessment of the geological disposal of radioactive wastes. In this work, sorption experiments were studied in a batch sorption system using $\text{Sr}(\text{NO}_3)_2$ solution on non-treated and HCl-treated Kula volcanics. The distribution coefficient (K_d) values of Sr^{2+} derived from batch experiments were used to evaluate the migration behavior of Sr^{2+} . Central Composite Design was used in the experiments. Sr sorption was studied as a function of pH, temperature, initial concentration of adsorbate and contact time. The results show that the K_d values are higher at pH 7–9 which is the pH range of the natural waters. The kinetic data conformed better to the pseudo-second-order equation. Thermodynamic parameters ΔH° , ΔS° and ΔG° were estimated and these parameters show that adsorption is endothermic. The correlation coefficients indicate that the Langmuir model fits better for the strontium sorption onto non-treated and HCl-treated Kula volcanics with monolayer capacities as 2.04 and 1.72 mg/g, respectively.

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1. Introduction

Radionuclide migration in geologic media is an important part of the performance assessment studies for the radioactive waste disposal concepts to provide a long term safety [1–3]. Sorption is a main retardation mechanism of radionuclide migration in the surroundings of a deep geological disposal [4,5]. Safety analysis of nuclear waste repositories requires realistic prediction of the rates of migration of nuclides from the repository through the host geological medium to the accessible environment [6].

Laboratory sorption studies on natural soils and rocks have been conducted to obtain data on the radionuclide migration [7–10]. The distribution coefficient (K_d) values of nuclides derived from batch experiments are usually used to evaluate the migration behavior of radionuclides in environment [3]. These values can be used as an input parameter in the performance assessment of the geological disposal of radioactive wastes [2]. The K_d parameter, which is the most common and simplest model available, is a factor related to the distribution of a nuclide between the solid and aqueous phases [11]. Sorption modeling represents many functional data (thermodynamics, kinetics and sorption type) are able to predict

mechanism of how radionuclides migrate in the rock formations [5].

Ebner et al. [12] investigated the constant pH adsorption isotherms for nonradioactive Cs^+ , Sr^{2+} , and Co^{2+} on pure magnetite and an 80% (w/w) magnetite–silica composite at different pHs ranging from 5 to 9. All of the metal ions exhibited a positive dependence of the adsorption capacity with pH. At infinite dilution, the K_d s were strongly pH-dependent and ranged between 7 and 163; the values were also considerably higher for the 80% (w/w) magnetite–silica composite.

Nemes et al. [13] studied the surface reaction of strontium ions on rock samples with a radioactive tracer method. The distribution coefficient of montmorillonite, rectorite, illite, quartz and cristobalite was determined from the mineral composition and the distribution coefficient of samples with a linear model. The results showed that the minerals with similar structure generally have similar distribution coefficients.

Mell et al. [14] investigated the sorption properties of ^{60}Co , ^{85}Sr , ^{137}Cs and ^{125}I on samples originated from Boda (siltstone–) claystone formation (BCF) (Hungary) a candidate media for final disposal of HLW. The distribution of K_d values was determined in static batch experiments using natural groundwater. It was found that the order of sorption of isotopes was $\text{Co} > \text{Cs} > \text{Sr} > \text{I}$, where iodine exhibits sorption properties in a modest extent.

* Corresponding author. Tel.: +90 232 388 6466; fax: +90 232 388 6466.

E-mail address: ceren.kutahyalı@ege.edu.tr (C. Kütahyalı).

Tephra is a general term for fragments of volcanic rock and lava regardless of size that are blasted into the air by explosions or carried upward by hot gases in eruption columns or lava fountains. Tephra consists of a wide range of rock (size, shape, density and chemical composition), including combinations of pumice, glass shards and shattered rocks of all types (igneous, sedimentary and metamorphic). The largest pieces of tephra (greater than 64 mm) are called blocks and the smallest one (<2 mm) is called ash [15].

Tephra has porous structure because it contains a large amount of gas space formed by dissociation of evolved gases due to rapid cooling magma [16]. Accordingly, natural porous materials and their activated forms have been used for technical purposes, like water purification or as an adsorbent in final storage of nuclear waste [15].

The main constituents in the chemical structure of tephra are SiO_2 and Al_2O_3 and it is classified as acidic, neutral and basic according to its SiO_2 content. Kula volcanics used in this study is in Basaltic tephra type, since the SiO_2 content is 45% by weight [17].

In this study, Sr sorption onto the geological material typically found in the vicinity of a fracture in the granitic rock at the Manisa region was modeled. Strontium has 4 naturally occurring isotopes: ^{84}Sr (0.55%), ^{86}Sr (9.75%), ^{87}Sr (6.96%), and ^{88}Sr (82.74%). The other radioisotopes of strontium are between ^{80}Sr and ^{95}Sr . Only ^{90}Sr [half life ($t_{1/2}$) = 28.1 years], a fission product, is of concern in waste disposal operations and environmental contamination [11]. The distribution coefficients derived from batch experiments are used to evaluate the migration behavior of strontium and would contribute to the establishment of a database for transport models. Furthermore, since strontium is homolog of important species of radium [18], the results could provide information about its migration behavior. In this article, we briefly discuss to obtain data on the radionuclide migration. The significance of this research is due to the novel application of the Central Composite Design method on Kula volcanics.

2. Experimental

2.1. Chemicals

All chemicals used in this study were analytical grade. Granitic rock samples were taken from Manisa-Kula region in Turkey. Milli-Q water (resistivity of $18.2\text{ M}\Omega\text{ cm}$) was used in all experiments. $\text{Sr}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck) was used to prepare Sr(II) stock solutions (1000 mg L^{-1}). The working solutions were prepared by diluting the stock solutions to appropriate volumes. Considering the same chemical reactivity of radioactive and stable Sr^{2+} isotopes, natural isotope of strontium (^{88}Sr) was used instead of ^{90}Sr for economical and safety reasons.

2.2. Adsorbent preparation

Granitic rock samples were crushed and sieved in $\leq 0.125\text{ mm}$ particle size. Samples were then divided into two portions. The first portion was rinsed with Milli-Q water and dried in an oven at 60°C for 24 h; for removing moisture, sample was kept in a vacuum oven at 60°C for 2 h. This sample was named as non-treated Kula volcanics. The second portion was ultrasonically stirred with 1 M HCl for 5 min. The sample was then rinsed with Milli-Q water for several times to remove chloride ions. After dechlorination, sample was dried with same procedure as of the first portion. The second portion was named as HCl-treated Kula volcanics.

2.3. Characterization

Nitrogen adsorption and desorption isotherms were measured using the Micromeritics ASAP 2020 system at -196°C . Samples

Table 1
Specific surface area and pore size distribution of non-treated and HCl-treated Kula volcanics.

	BET (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
Non-treated	3.02 ± 0.038	29.20	0.013
HCl-treated	8.43 ± 0.073	21.30	0.020

were degassed at 130°C for 2 h under vacuum. Table 1 shows specific surface area and pore size distribution analyses results. The pore size distribution was calculated from the adsorption branch of the isotherm by Barrett–Joyner–Halenda (BJH) method. Increasing the cumulative pore volume from 0.013 to $0.020\text{ cm}^3/\text{g}$ by HCl treatment of Kula volcanics can be explained by the removal of metals accumulated in the pores by acid treatment. Average pore diameter reduces by acid treatment depending on cleaning of small closed pores on the structure. Specific surface area was obtained by the Brunauer–Emmett–Teller (BET) method. By acid treatment, surface area increases from 3.02 to $8.43\text{ m}^2/\text{g}$. This result can be explained that as well cleaning of pores by acid treatment. Fig. 1 shows the intra-structure of non-treated and HCl-treated volcanics obtained by scanning electron microscopy (SEM). From the picture different pore sizes may be observed.

Infrared spectroscopy has been frequently used to investigate the structural properties of clay minerals. These materials are hydrated aluminium silicates with a layered structure formed by tetrahedral sheets (containing Si(IV)) via shared oxygen atoms. Clay minerals are usually examined by using transmission infrared methods with a KBr disc. Clay minerals may be differentiated by their infrared spectra through a study of the bands due to the O–H

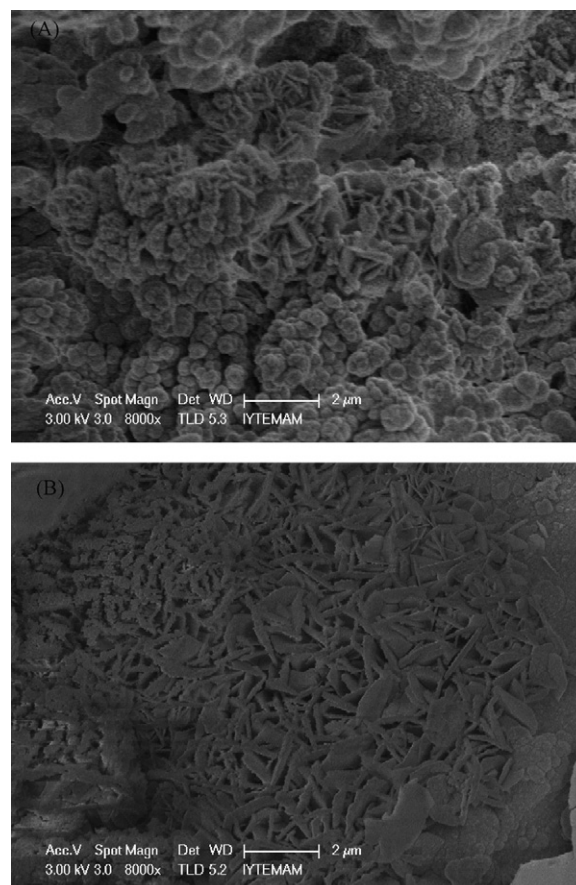


Fig. 1. SEM photographs of non-treated (A) and HCl-treated (B) Kula volcanics.

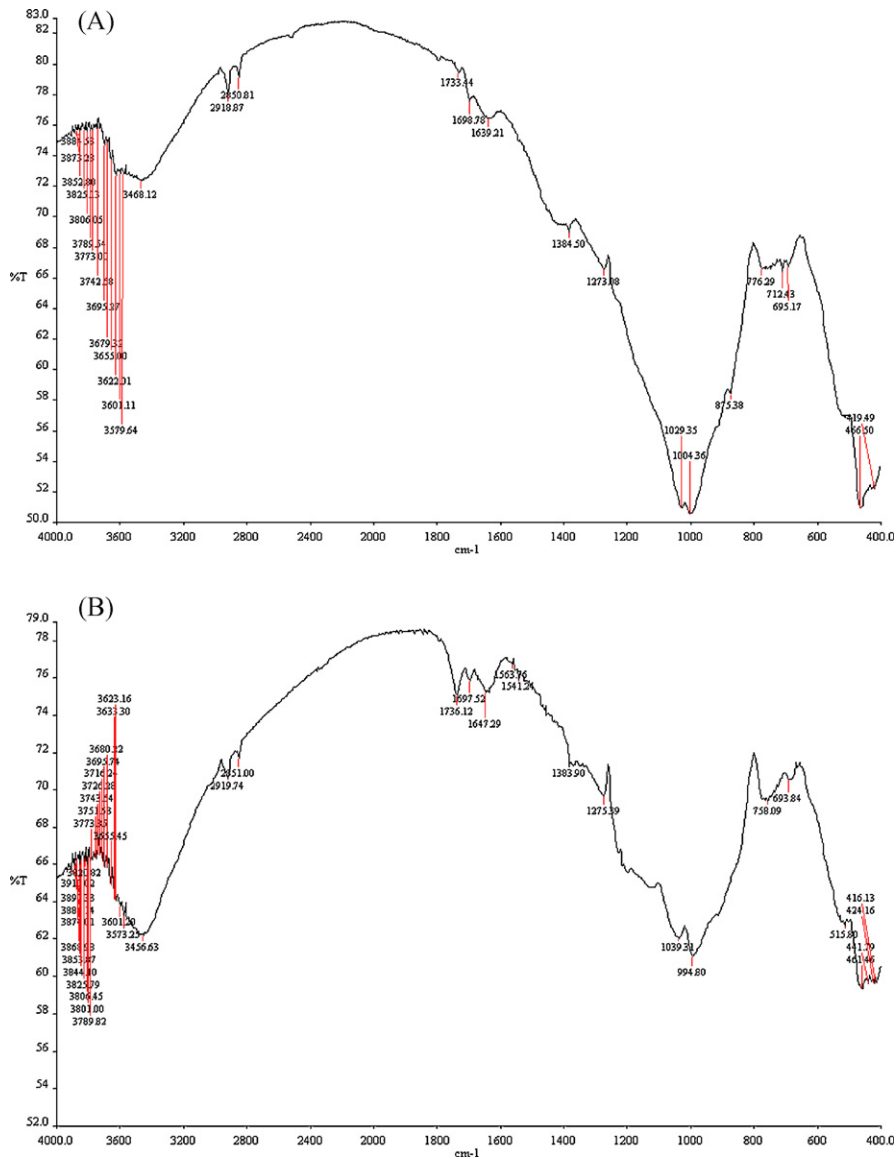


Fig. 2. FTIR spectroscopy of non-treated (A) and HCl-treated (B) Kula volcanics.

and Si–O groups. In the O–H stretching region, 3800–3400 cm^{-1} for clay minerals, there are a number of bands observed. The inner hydroxyl groups between the tetrahedral and octahedral sheets result in a band near 3620 cm^{-1} . The other three O–H groups at the octahedral surface form weak hydrogen bonds with the oxygens of the Si–O–Si bonds in the next layer and this result in stretching bands at 3669 and 3653 cm^{-1} . Where clays have most of their octahedral sites occupied by divalent central atoms such as Mg(II) or Fe(II), a single band in the O–H stretching region is often observed. In the 1300–400 cm^{-1} region, clay minerals show Si–O stretching and bending and O–H bending bands. The shape and position of the bands depend very much on the arrangement within the layers [19]. FTIR spectroscopy was used to understand the surface characteristics of volcanics. As can be seen in Fig. 2, the absorption bands observed in the region 450–1100 cm^{-1} was assigned to the Si–O bending and stretching vibrations. A broad absorption band due to O–H stretching vibration is observed around 3800–3200 and 1700–1600 cm^{-1} regions. Characteristic infrared bands of CO_3^{2-} at around 880–800 cm^{-1} , can be seen at the spectrum of the non-treated volcanics.

2.4. Sorption experiments

The experimental data in sorption can be expressed in terms of a distribution coefficient, K_d , defined as the ratio of the quantity of the adsorbate per gram of solid to the amount of the adsorbate remaining in solution at equilibrium:

$$K_d = \frac{\text{Mass of adsorbate sorbed (mg/g)}}{\text{Mass of adsorbate in solution (mg/mL)}} \quad (1)$$

Batch tests are commonly used to measure K_d values. The test is conducted by spiking a solution with the element of interest, mixing the spiked solution with a solid for a specified period of time, separating the solution from the solid, and measuring the concentration of the spiked element remaining in the solution. The concentration of element associated with the solid is determined by the difference between initial and final element concentrations. The primary advantage of the method is that such experiments can be completed quickly for a wide variety of elements and chemical environments [11].

2.5. Experimental design

In assessing the effects of multiple parameters on sorption efficiency, the use of an adequate experimental design is particularly important. To study the interactions of two or more variables, response surface methodology (RSM) has proved a useful tool [20]. It is a collection of mathematical and statistical techniques for designing experiments, building numerical models, evaluating the effects of variables and searching for the optimum combinations of factors. Experimental design methodology involves changing all variables from one experiment to the next. The reason for this is the variables can influence each other, and the ideal value for one of them can depend on the values of the others. This interaction between variables is a frequent phenomenon. RSM usually contains three stages: (i) design and experiment, (ii) response surface modeling through regression, and (iii) optimization. The main advantage of RSM is the reduced number of experiments needed to describe the effects of multiple parameters and their interactions [21].

In this study, the Central Composite Design (CCD) was employed to determine the optimum sorption conditions for non-treated and HCl-treated Kula volcanic samples, avoiding the traditional “one-factor-at-a-time” experiments. The CCD is an effective design method which is ideal for sequential experimentation and allows a reasonable amount of information for testing lack of fit while not involving an unusually large number of design points. CCD consists of 16 factorial points, 9 star points and 6 replicates.

According to the CCD, the optimization of Sr²⁺ removal was carried through four independent process variables: pH (X_1), temperature (X_2), initial Sr²⁺ concentration (X_3) and contact time (X_4) with seven replicates at centre points. The values of these variables are given in Table 2.

Table 2

The ranges and the levels of the investigated parameters.

Parameters		$-\alpha$	-1	0	$+1$	$+\alpha$
pH	X_1	3	4.5	6	7.5	9
Temperature (°C)	X_2	20	30	40	50	60
Initial Sr ²⁺ concentration (mg L ⁻¹)	X_3	10	30	50	70	90
Contact time (min)	X_4	15	55	95	135	175

The effects of the independent variables on Sr²⁺ sorption of non-treated and HCl-treated Kula volcanic samples were examined by batch tests. Batch sorption behavior of Sr ions on the volcanics was conducted by immersing 0.1 g volcanics in 10 mL of liquid phase. Shaking experiments were done in a temperature controlled environment at 135 rpm using a GFL 1086 water bath shaker equipped with microprocessor thermostat. After Sr²⁺ loading, samples were filtered by blue ribbon filter paper then obtained clear liquid phases were measured by Perkin Elmer Optima 2000DV ICP-OES.

Five “levels” were used for each variable: “+1”, the higher; “-1”, the lower; and “0” the central point, “ $-\alpha$ and $+\alpha$ ” as star points. The quadratic equation model for predicting the optimal point was expressed according to Eq. (2):

$$y_i = a_0 + \sum a_i X_i + \sum a_{ii} X_{ii}^2 + \sum a_{ij} X_i X_j \quad (2)$$

Four parameters varied, 14 coefficients has to be estimated, i.e. coefficients for the four main effects, four quadratic effects, six interactions and intercept term. y_i is the predicted response, a_0 is the intercept term, a_i is the i th linear coefficient term, a_{ii} is the i th quadratic coefficient term and a_{ij} is the interaction coefficients term

Table 3
Experimental data points used in CCD statistical design and predicted and actual responses.

No.	pH	Temp. (°C)	Sr conc. (mg L ⁻¹)	Contact time (min)	Non-treated		HCl-treated	
					K_d (mL/g) Actual	K_d (mL/g) Predicted	K_d (mL/g) Actual	K_d (mL/g) Predicted
1	1	1	1	1	43.35	39.47	37.10	39.79
2	1	1	1	-1	38.86	34.37	29.92	34.53
3	1	1	-1	1	129.07	134.88	119.43	120.89
4	1	1	-1	-1	98.36	116.58	97.25	108.05
5	1	-1	1	1	36.93	36.07	32.49	35.42
6	1	-1	1	-1	36.52	37.61	33.79	39.35
7	1	-1	-1	1	109.94	124.11	95.01	106.22
8	1	-1	-1	-1	105.05	112.45	102.71	102.57
9	-1	1	1	1	54.74	47.16	28.95	26.88
10	-1	1	1	-1	43.35	36.42	29.39	22.77
11	-1	1	-1	1	115.09	121.24	85.86	84.87
12	-1	1	-1	-1	96.62	97.30	78.31	73.18
13	-1	-1	1	1	53.60	42.62	31.93	25.70
14	-1	-1	1	-1	44.50	38.50	34.46	30.79
15	-1	-1	-1	1	105.01	109.32	80.21	73.39
16	-1	-1	-1	-1	80.89	92.01	69.00	70.90
17	α	0	0	0	67.33	52.14	100.42	82.05
18	$-\alpha$	0	0	0	31.25	39.40	21.47	37.46
19	0	α	0	0	54.96	54.50	47.80	46.61
20	0	$-\alpha$	0	0	52.41	45.82	41.15	39.96
21	0	0	α	0	59.31	82.65	41.11	43.69
22	0	0	$-\alpha$	0	261.96	231.57	169.86	164.90
23	0	0	0	α	63.23	63.19	45.28	45.37
24	0	0	0	$-\alpha$	47.79	40.78	40.10	37.62
25	0	0	0	0	66.71	59.51	45.22	44.58
26	0	0	0	0	62.25	59.51	38.76	44.58
27	0	0	0	0	56.87	59.51	47.07	44.58
28	0	0	0	0	57.36	59.51	44.97	44.58
29	0	0	0	0	62.69	59.51	44.09	44.58
30	0	0	0	0	54.21	59.51	47.01	44.58
31	0	0	0	0	56.48	59.51	44.95	44.58

for the model. Second-order polynomial equation can be presented as Eq. (3):

$$y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 + a_{44}X_4^2 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{14}X_1X_4 + a_{23}X_2X_3 + a_{24}X_2X_4 + a_{34}X_3X_4 \quad (3)$$

Experimental data points used in CCD statistical design and predicted and actual responses are given in Table 3.

3. Results and discussion

The relationship between independent variables and response was drawn by second-order polynomial equation. The regression equation coefficients were calculated and data were fitted to a second-order polynomial equations for removal of Sr^{2+} ions with non-treated (Eq. (4)) and HCl-treated (Eq. (5)) Kula volcanic samples.

$$y = 59.51 + 3.19 \times X_1 + 2.17 \times X_2 - 37.23 \times X_3 + 5.60 \times X_4 - 3.44 \times X_1^2 - 2.34 \times X_2^2 + 24.40 \times X_3^2 - 1.88 \times X_4^2 - 0.29 \times X_1X_2 - 5.33 \times X_1X_3 - 1.41 \times X_1X_4 - 1.84 \times X_2X_3 + 1.66 \times X_2X_4 - 3.30 \times X_3X_4 \quad (4)$$

$$y = 44.58 + 11.15 \times X_1 + 1.66 \times X_2 - 30.30 \times X_3 + 1.94 \times X_4 + 3.79 \times X_1^2 - 0.32 \times X_2^2 + 14.93 \times X_3^2 - 0.77 \times X_4^2 + 0.80 \times X_1X_2 - 5.78 \times X_1X_3 + 0.29 \times X_1X_4 - 2.58 \times X_2X_3 + 2.30 \times X_2X_4 - 1.90 \times X_3X_4 \quad (5)$$

On the basis of second-order polynomial equation of response surface methodology, the effect of independent variables: pH, temperature, initial Sr^{2+} concentration and contact time on the sorption of Sr^{2+} were analyzed. The efficiency values obtained as a result of 31 experiments determined at the Central Composite Design conditions were compared with the calculated efficiency values from the applied model. Table 4 represents analysis of variance (ANOVA) for the regression model for Sr^{2+} sorption capacity of non-treated and HCl-treated Kula volcanics. The value of R^2 was found 0.95 and 0.97 for strontium sorption on non-treated and HCl-treated Kula volcanics, respectively. Probability F values ($F < 0.05$) and high R^2 values ($R^2 \geq 0.95$) indicate that the model fits the experimental data well for each samples. The coefficients of independent variables, t and P values according to the investigated parameters (pH, temperature, initial Sr^{2+} concentration and contact time) are given in Table 5.

pH ($P = 9.07 \times 10^{-6}$), initial Sr^{2+} concentration ($P = 8.43 \times 10^{-12}$) were found significant, temperature and contact time ($P > 0.05$) were found non-significant for HCl-treated Kula volcanics. In the case of non-treated Kula volcanics, initial Sr^{2+} concentration ($P = 5.40 \times 10^{-10}$) was statistically significant, while pH, temperature and contact time were non-significant ($P > 0.05$).

The positive values of coefficients belong to pH ($X_1 = 11.15$), temperature ($X_2 = 1.66$) and contact time ($X_4 = 1.94$) indicate the positive effect, negative values of coefficients belong to initial Sr^{2+} concentration ($X_3 = -30.30$) indicate the negative effect on sorption of Sr^{2+} from aqueous solution by HCl-treated Kula volcanics. Similar behavior can be seen for non-treated Kula volcanics. pH ($X_1 = 3.19$), temperature ($X_2 = 2.17$) and contact time ($X_4 = 5.60$) show positive effect, Sr^{2+} concentration ($X_3 = -37.23$) shows negative effect on

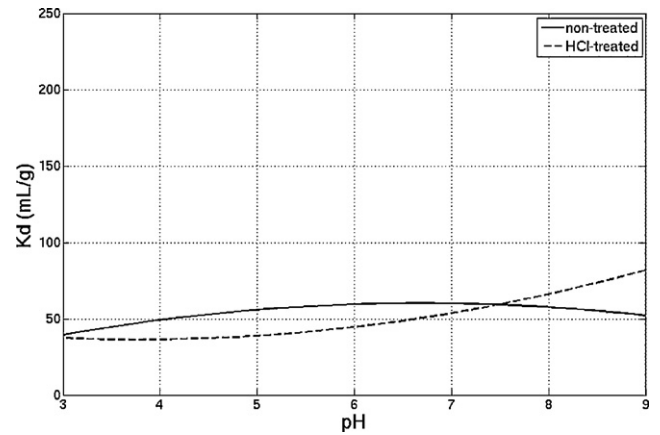


Fig. 3. Effect of solution pH on Sr^{2+} adsorption onto non-treated and HCl-treated Kula volcanics.

sorption of Sr^{2+} from aqueous solution by non-treated Kula volcanics.

The positive effect means the sorption of Sr^{2+} increases as the solution pH (Fig. 3), temperature (Fig. 4) or contact time increases (Fig. 6). On the other hand, negative values of coefficients belong to initial Sr^{2+} concentration for non-treated and HCl-treated Kula volcanics indicate that initial Sr^{2+} concentration has a negative effect on sorption of Sr^{2+} from aqueous solution by non-treated and HCl-treated Kula volcanics. It means that the sorption of Sr^{2+} decreases when initial Sr^{2+} concentration increases (Fig. 5).

Due to at lower pHs sorbent surface is mostly protonated the adsorption is not favored because the metal ions which are expected to be adsorbed are positively charged. Increasing pH the adsorbent surface becomes more negatively charged and therefore the adsorption of positively charged species is more favorable [22]. Fig. 3 shows that optimum pH is 6 and 9 for the non-treated and HCl-treated Kula volcanics, respectively. Decreasing Sr^{2+} sorption by increasing initial Sr^{2+} concentration can be explained as energetically less favorable sites become involved in sorption with increasing concentrations of the metals [23]. As can be seen from Fig. 5, maximum adsorption occurs at 10 ppm initial Sr^{2+} concentration. Temperature increase causes slight increase of the adsorption of Sr^{2+} until 40°C . It is not wrong to say that, almost no significant effect can be seen (Fig. 4). This behavior indicates that the process is endothermic in nature.

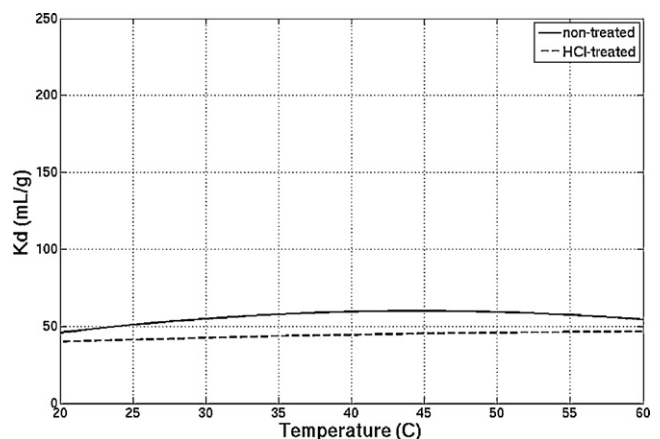


Fig. 4. Temperature effect of Sr^{2+} adsorption onto non-treated and HCl-treated Kula volcanics.

Table 4
Analysis of variance (ANOVA) for the regression model for Sr²⁺ distribution coefficient (K_d) of non-treated and HCl-treated Kula volcanics.

		df	SS	MS	F	Sig. F	R ²
Non-treated	Regression	14	54,127.84	3866.27	20.10	1.57×10^{-07}	0.95
	Residual	16	3077.43	192.34			
	Total	30	57,205.26				
HCl-treated	Regression	14	32,781.47	2341.53	32.00	4.98×10^{-09}	0.97
	Residual	16	1170.83	73.18			
	Total	30	33,952.29				

Table 5
Coefficients, *t* stat and *P*-values of the strontium sorption with non-treated and HCl-treated Kula volcanics.

	Non-treated			HCl-treated		
	Coefficients	<i>t</i> stat	<i>P</i> -value	Coefficients	<i>t</i> stat	<i>P</i> -value
Intercept	59.51	11.35	4.58×10^{-09}	44.58	13.79	2.68×10^{-10}
X ₁	3.19	1.13	2.77×10^{-01}	11.15	6.38	9.07×10^{-06}
X ₂	2.17	0.77	4.54×10^{-01}	1.66	0.95	3.55×10^{-01}
X ₃	-37.23	-13.15	5.40×10^{-10}	-30.30	-17.35	8.43×10^{-12}
X ₄	5.60	1.98	6.53×10^{-02}	1.94	1.11	2.84×10^{-01}
X ₁ X ₁	-3.44	-1.32	2.04×10^{-01}	3.79	2.37	3.06×10^{-02}
X ₂ X ₂	-2.34	-0.90	3.81×10^{-01}	-0.32	-0.20	8.42×10^{-01}
X ₃ X ₃	24.40	9.41	6.38×10^{-08}	14.93	9.33	7.13×10^{-08}
X ₄ X ₄	-1.88	-0.73	4.79×10^{-01}	-0.77	-0.48	6.37×10^{-01}
X ₁ X ₂	-0.29	-0.08	9.35×10^{-01}	0.80	0.37	7.13×10^{-01}
X ₁ X ₃	-5.33	-1.54	1.43×10^{-01}	-5.78	-2.70	1.57×10^{-02}
X ₁ X ₄	-1.41	-0.41	6.89×10^{-01}	0.29	0.13	8.95×10^{-01}
X ₂ X ₃	-1.84	-0.53	6.02×10^{-01}	-2.58	-1.20	2.46×10^{-01}
X ₂ X ₄	1.66	0.48	6.39×10^{-01}	2.30	1.07	2.98×10^{-01}
X ₃ X ₄	-3.30	-0.95	3.55×10^{-01}	-1.90	-0.89	3.88×10^{-01}

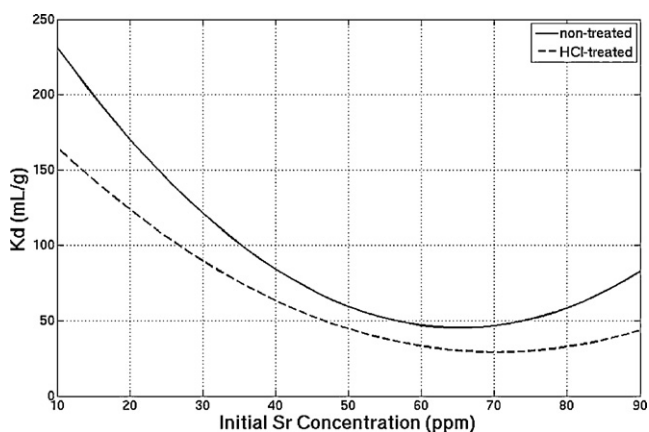


Fig. 5. Effect of initial Sr²⁺ concentration of the Sr²⁺ adsorption onto non-treated and HCl-treated Kula volcanics.

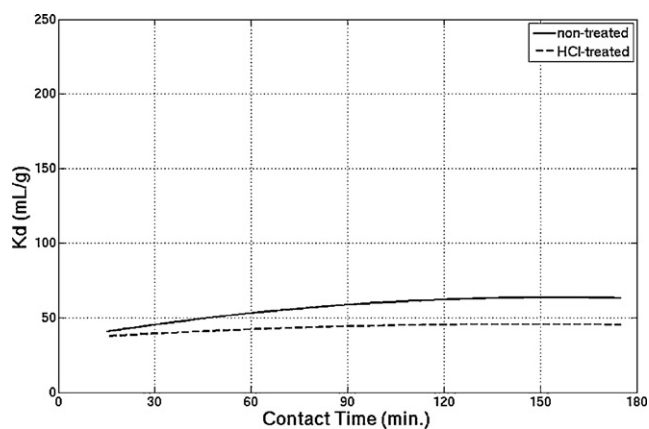


Fig. 6. Effect of contact time on Sr²⁺ adsorption on non-treated and HCl-treated Kula volcanics.

3.1. Non-treated Kula volcanics

Interactions between independent variables are shown in 3D surface plots with other variables being at fixed levels (Fig. 7A–F). Fig. 7A shows the dependence of adsorption on both pH (X_1) and temperature (X_2). Between 20 °C and 45 °C, sorption increases by increasing of temperature and after that decreases slightly by increasing of temperature. At a temperature of 45 °C and pH 6.6, maximum K_d (60.68 mL/g) is observed.

Fig. 7B and C shows the interactions between pH (X_1)–initial Sr²⁺ concentration (X_3) and pH (X_1)–contact time (X_4), respectively. Maximum K_d (245.5 mL/g) is observed at 10 ppm initial Sr²⁺ concentration and pH 9. At a 150 min contact time and pH 6.3, maximum K_d (63.77 mL/g) is observed.

Interaction between temperature (X_2) and initial Sr²⁺ concentration (X_3) is shown in Fig. 7D. Maximum K_d (235.1 mL/g) is observed at 10 ppm of initial Sr²⁺ concentration and 50 °C. Fig. 7E shows the interaction between temperature (X_2) and contact time (X_4). At 52 °C and 175 min contact time, maximum K_d (66.41 mL/g) is observed. Fig. 7F shows the interaction between initial Sr²⁺ concentration (X_3) and contact time (X_4). Maximum K_d (248.4 mL/g) is observed at 175 min contact time and 10 ppm initial Sr²⁺ concentration.

3.2. HCl-treated Kula volcanics

Interactions between independent variables are shown in 3D surface plots with other variables being at fixed levels (Fig. 8A–F). Fig. 8A shows the interaction between two independent variables of pH (X_1) and temperature (X_2). Maximum K_d (87.27 mL/g) is observed at 60 °C and pH 9. Fig. 8B shows the interaction between pH (X_1) and initial Sr²⁺ concentration (X_3). Maximum K_d (225.5 mL/g) is observed at 10 ppm initial Sr²⁺ concentration and pH 9. Fig. 8C shows the interaction between pH (X_1) and contact time (X_4). Maximum K_d (83.98 mL/g) is observed at 175 min contact time and pH 9. Fig. 8D shows the interaction between temperature

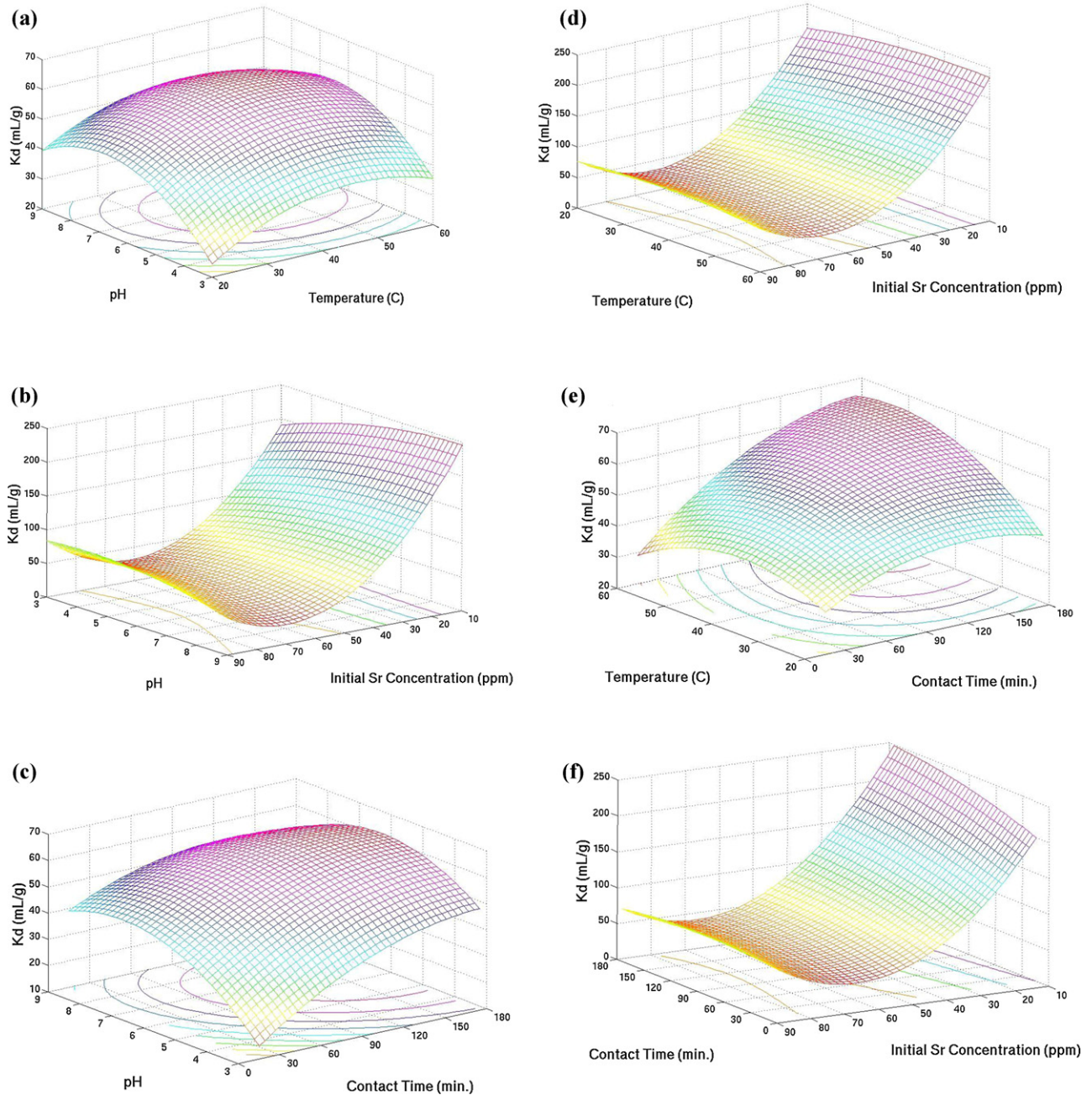


Fig. 7. (A–F) Response surface graphs for interactions of investigated parameters of Sr^{2+} adsorption onto non-treated Kula volcanics. (A) Effect of pH and temperature; (B) effect of pH and initial Sr^{2+} concentration; (C) effect of pH and contact time; (D) effect of temperature and initial Sr^{2+} concentration; (E) effect of temperature and contact time; (F) effect of contact time and initial Sr^{2+} concentration.

(X_2) and initial Sr^{2+} concentration (X_3). Maximum K_d (177.2 mL/g) is observed at 10 ppm initial Sr^{2+} concentration and 60 °C. Fig. 8E shows the interaction between temperature (X_2) and contact time (X_4). Maximum K_d (56.6 mL/g) is observed at 60 °C and 175 min contact time. Fig. 8F shows interaction between initial Sr^{2+} concentration (X_3) and contact time (X_4). Maximum K_d (173.3 mL/g) is observed at 175 min contact time and 10 ppm initial Sr^{2+} concentration.

3.3. Kinetic investigations

Various models can be used to analyze the kinetics of sorption process. Azizian [24] reported that when the initial concentration of solute is low, the pseudo second order model is suitable for analysis

of sorption kinetics, and when the initial concentration is high, the pseudo first order model becomes suitable.

The Lagergren first-order kinetic model equation is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

The plot of $\ln(q_e - q_t)$ against t provides a linear relationship from which k_1 , constant of pseudo-first-order adsorption (min^{-1}) and q_e , adsorption capacity at equilibrium (mg/g) are determined from the slope and intercept of the plot, respectively, given that q_t is the adsorption capacity at time t (mg/g).

The rate law for a pseudo second order system is expressed as

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (7)$$

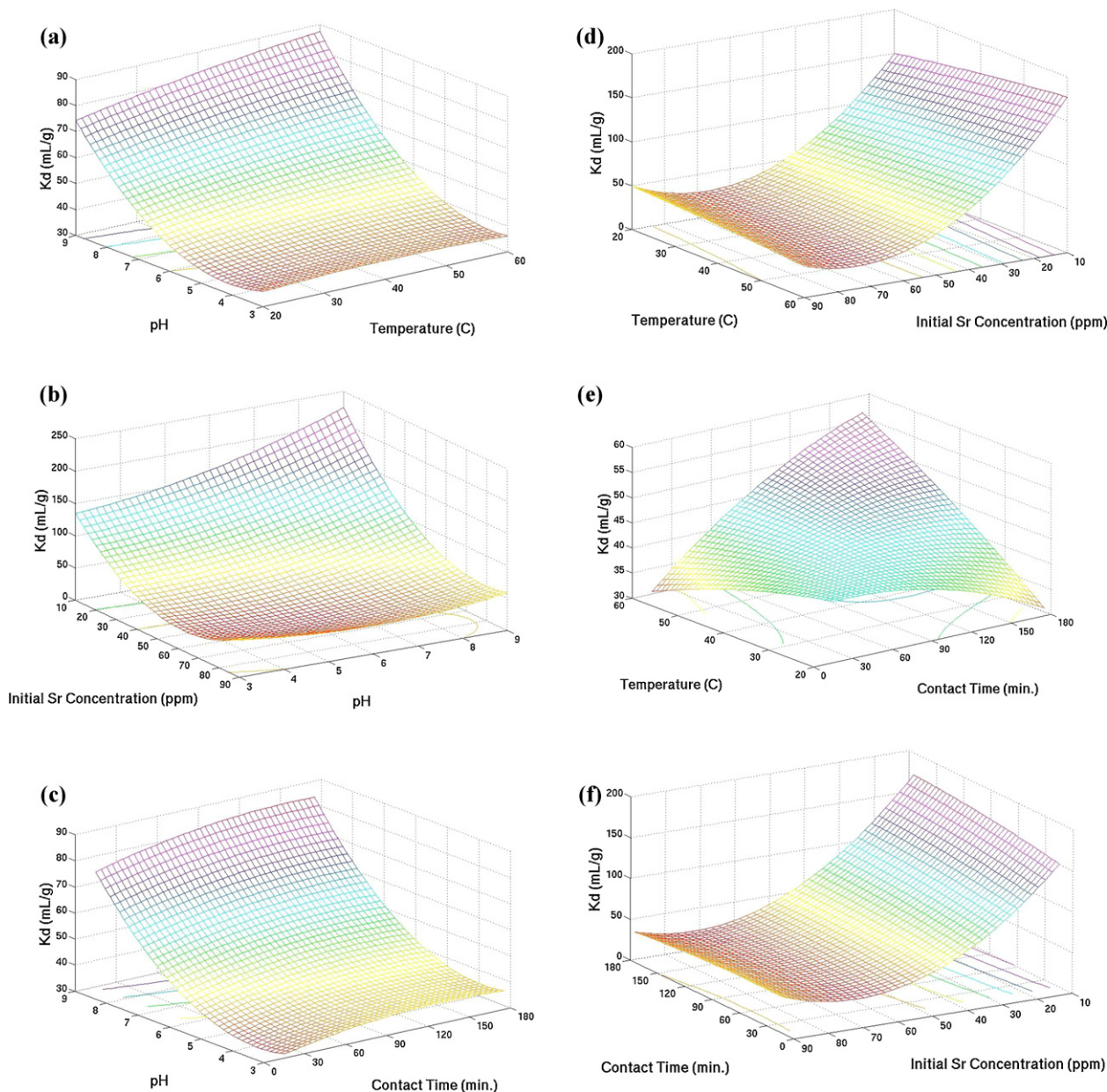


Fig. 8. (A–F) Response surface graphs for interactions of investigated parameters of Sr^{2+} adsorption onto HCl-treated Kula volcanics. (A) Effect of pH and temperature; (B) effect of pH and initial Sr^{2+} concentration; (C) effect of pH and contact time; (D) effect of temperature and initial Sr^{2+} concentration; (E) effect of temperature and contact time; (F) effect of contact time and initial Sr^{2+} concentration.

where q and q_e are the grams of solute sorbed per gram of sorbent at any time and at equilibrium, respectively, and k_2 is the rate constant of second order sorption. After integration to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

The plot of t/q_t versus t gives a straight line with slope of $1/q_e$ and intercept of $1/k_2 q_e^2$. Thus, the gram of solute sorbed per gram of sorbent at equilibrium (q_e) and sorption rate constant (k_2) could be evaluated from the slope and intercept, respectively. Kinetic investigation was performed under the following experimental conditions: 50 ppm initial Sr^{2+} concentration, pH 6, 40 °C temperature and time range as 15–175 min by 15 min time intervals. Then q values for non-treated and HCl-treated Kula volcanics are obtained by evaluation of Eqs. (4) and (5), respectively (Table 6). The correlation coefficients for the pseudo-second-order kinetic model were higher than that of the Lagergren first-order. Therefore, the

sorption system fits to the pseudo-second-order kinetic model. q_e values obtained from the pseudo-second-order kinetic model show that Sr^{2+} sorption is higher on non-treated Kula volcanics than HCl-treated. However, as k_2 values, faster adsorption occurs on HCl-treated Kula volcanics. It can be concluded that modification of Kula volcanics with HCl increases the sorption rate of Sr^{2+} ions. Correlation coefficient (R^2) values indicate that pseudo second order rate equation completely fits the sorption behavior of low concentrations of strontium ions onto non-treated and HCl-treated Kula volcanic samples.

3.4. Sorption isotherms

In order to understand the sorption capacity of the adsorbents, the equilibrium data were evaluated according to the Freundlich, Langmuir and D–R isotherms. Fig. 9 shows the experimental isotherm data (q_e versus C_e) for both adsorbents.

Table 6Grams of solute sorbed per gram of sorbent at equilibrium (q_e), Lagergren first order (k_1) and pseudo second order (k_2) rate constants and correlation coefficient values.

	Lagergren first-order			Pseudo-second-order		
	q_e (mg/g)	k_1 (min ⁻¹)	R_1^2	q_e (mg/g)	k_2 (g/mg min)	R_2^2
Non-treated	0.61	-0.01	0.9409	2.04	0.05	0.9994
HCl-treated	0.23	-0.01	0.8900	1.60	0.16	0.9998

The Langmuir equation, which has been successfully applied to many sorptions, is given by:

$$\frac{C_e}{q_e} = \frac{1}{bn_m} + \frac{C_e}{n_m} \quad (9)$$

where C_e is the equilibrium concentration (mg L⁻¹), q_e is the amount adsorbed at equilibrium (mg/g), n_m and b are the Langmuir constants related to monolayer capacity and energy of sorption. Langmuir isotherm models the monolayer coverage of the sorption surface. This model assumes that sorption occurs at specific homogeneous sorption sites within the adsorbent and intermolecular forces decrease rapidly with the distance from the sorption surface. The Langmuir sorption model further based on the assumption that all sorption sites are energetically identical and sorption occurs on a structurally homogeneous adsorbent [25].

The Freundlich equation, which was applied for the sorption of strontium is given as,

$$q_e = KC_e^n \quad (10)$$

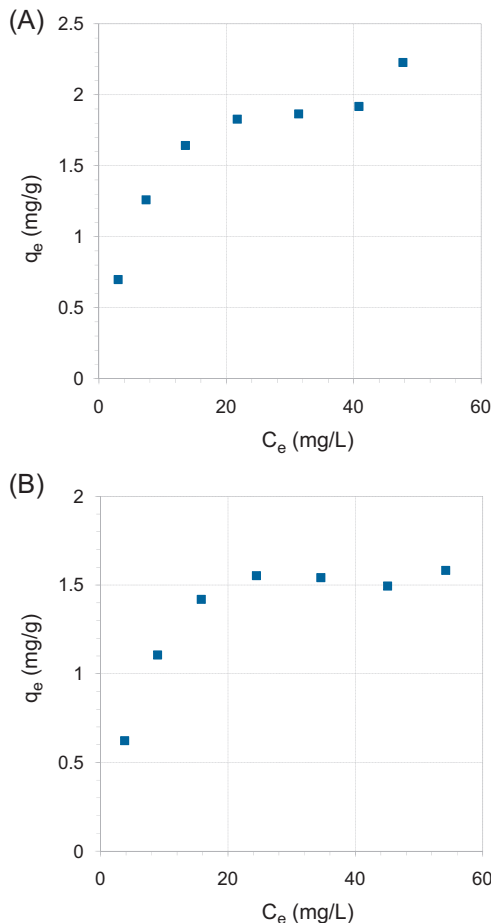


Fig. 9. Experimental isotherm data for non-treated (A) and HCl-treated (B) Kula volcanics.

Eq. (10) can be rearranged to linear form,

$$\log q_e = \log K + n \log C_e \quad (11)$$

where q_e is the amount of solute adsorbed per mass unit adsorbent, C_e is the equilibrium concentration, K and n are the Freundlich constants characteristic of a particular sorption isotherm and can be evaluated from the intercept and slope of the linear plot of $\log q_e$ versus $\log C_e$.

The experimental data were fitted using the Dubinin–Radushkevich (D–R) equation in order to understand the sorption type.

The linearised D–R equation can be written as,

$$\ln X = \ln X_m - K\varepsilon^2 \quad (12)$$

where ε is Polanyi potential and is equal to,

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (13)$$

X is the amount of metal adsorbed per unit mass of adsorbent, X_m is the theoretical sorption capacity, C_e is the equilibrium concentration of metal, K is the constant related to sorption energy, R is the universal gas constant and T is the temperature in Kelvin.

D–R isotherm constants K and X_m were evaluated from the slope and intercept of the plot $\ln X$ versus ε^2 , respectively. The mean free energy of sorption (E_{DR}) is the free energy change when 1 mol of a solute is transferred to the surface of the adsorbent from infinity in the solution, and that has been calculated by

$$E_{DR} = (-2K)^{1/2} \quad (14)$$

The magnitude of E_{DR} (kJ mol⁻¹) is useful for estimating the type of sorption reaction, and if it ranged between 8.0 and 16.0 the sorption should be taken place by ion exchange reaction.

For the sorption isotherm examination, initial Sr²⁺ concentrations ranging from 10 to 70 mg L⁻¹ (at pH 6, 40 °C temperature, and 95 min contact time) were chosen and q values for non-treated and HCl-treated Kula volcanics obtained by evaluation of Eq. (4). In the present case, the E_{DR} values obtained (12.58 and 13.36 kJ mol⁻¹, for non-treated and HCl-treated Kula volcanics, respectively) indicate ion exchange mechanism. The corresponding Freundlich, Langmuir and D–R parameters along with correlation coefficients are reported in Table 7. The correlation coefficients (R^2 0.99) indicate that the Langmuir model fits better than the Freundlich model for the strontium sorption onto non-treated and HCl-treated Kula volcanics.

3.5. Thermodynamic results

Sorption enthalpy was measured using the method based on the Van't Hoff plot. The values of ΔH° and ΔS° are calculated from the slopes and intercepts of the linear variation of $\ln K_d$ with reciprocal temperature, $1/T$, using the relation:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (15)$$

where ΔH° and ΔS° are the standard enthalpy and entropy changes of sorption, respectively. The results are given in Table 8. Positive ΔH° values for strontium sorption onto non-treated and

Table 7
Sorption isotherm constants for the sorption of strontium onto non-treated and HCl-treated Kula volcanics.

	Freundlich			Langmuir			Dubinin–Radushkevich			
	R^2	n	K	R^2	n_m (mg/g)	b (L/mg)	R^2	K (mol ² kJ ⁻²)	X_m (mol/g)	E_{DR} (kJ mol ⁻¹)
Non-treated	0.92	0.38	0.53	0.99	2.40	0.14	0.94	3.16×10^{-03}	8.59×10^{-05}	12.58
HCl-treated	0.83	0.32	0.49	0.99	1.72	0.21	0.86	2.80×10^{-03}	5.65×10^{-05}	13.36

Table 8
Thermodynamic parameters for strontium sorption onto non-treated and HCl-treated Kula volcanics.

	ΔH° (kJ mol ⁻¹)	ΔS° (J/(mol K))	ΔG° (kJ mol ⁻¹)			
			293 K	303 K	313 K	323 K
Non-treated	2.91	54.50	-15.97	-16.51	-17.06	-17.60
HCl-treated	3.50	53.61	-15.70	-16.24	-16.78	-17.31

HCl-treated Kula volcanics indicate that sorption of strontium is endothermic.

The free energy of specific sorption ΔG° is calculated using the equation:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (16)$$

The calculated negative values of ΔG° for all cases indicate that the sorption process of each is spontaneous and preferentially driven toward the products. Temperature change has no significant effect on ΔG° values for both non-treated and HCl-treated Kula volcanics. Temperature effect on strontium sorption onto both of non-treated and HCl-treated Kula volcanics was discussed previously in Section 3 and it was found that temperature had no significant effect on sorption. Thermodynamic results are in same sense and prove that conclusion.

4. Conclusions

In the present work, sorption behavior of Sr²⁺ onto Kula volcanic samples was investigated to obtain data on the radionuclide migration. The distribution coefficient (K_d) values of Sr²⁺ derived from batch experiments were used to evaluate the migration behavior of Sr²⁺. Central Composite Design was used in the experiments. Sr sorption was studied as a function of pH, temperature, initial concentration of adsorbate and contact time. The results show that the K_d values are higher at pH 7–9 which is the pH range of the natural waters. The kinetic data conformed better to the pseudo-second-order equation. Thermodynamic parameters ΔH° , ΔS° and ΔG° were estimated and these parameters show that adsorption is endothermic. The Langmuir, Freundlich and D–R adsorption models were used for mathematical description of the adsorption of the Sr²⁺ ions onto Kula volcanics. The correlation coefficients indicate that the Langmuir model fits better than the Freundlich model for the strontium sorption onto non-treated and HCl-treated Kula volcanics (correlation coefficients are 0.99).

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