



Removal of Strontium Ions by Synthetic Nano Sodalite Zeolite from Aqueous Solution

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ABSTRACT

In this article, a novel nano sodalite zeolite was synthesized and characterized by X-ray diffraction, scanning electronic microscopy (SEM) and infrared spectroscopy and evaluated in order to facilitate the sorption of strontium ions from aqueous solutions in batch operations onto acid treated zeolite with dilute H₂SO₄ solutions. The optimum conditions of sorption were found as follows: a sorbent amount of 0.25 g in 100 mL of strontium solution (50 mg/L), contact time, pH and temperature of 80 min, 6 and 20 °C, respectively. To study the kinetics of removal process, three equations, i.e. Morris–Weber, Lagergren (pseudo first order) and pseudo second order were used. The strontium sorption process was well described by the pseudo second order (type 2) kinetic model. The Langmuir, Freundlich, Dubnin-Randkovich (D-R) and Temkin models were subjected to sorption data to estimate sorption capacity, intensity and energy. An evaluation of the thermodynamic parameters including ΔH , ΔS and ΔG was done. It was found out from thermodynamic parameters that the sorption of strontium onto zeolite was feasible, spontaneous and endothermic under studied conditions.

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1. INTRODUCTION

The elemental forms of strontium in the environment are ⁸⁹Sr and ⁹⁰Sr with half-lives of 51 days and 29 years, respectively. It is synthesized as a waste fission product from nuclear power plants and during the nuclear fuels reprocessing phase [1]. Sr-90 is regarded as the main species that is a soft β -emitter of 0.5460 MeV energy. Most of the ⁹⁰Sr present in the environment can deposit alone with rain or other condensed moisture. Radio strontium goes through decomposition while β -radiation and forms ⁹⁰Y with a half-life of 64 h which is a very strong β -emitter. Strontium-90 is comparatively mobile and can move down to underlying soil layers along with percolating water and into groundwater around the world due to the fallout from past atmospheric nuclear weapons tests. Strontium preferably sticks to soil particles. Typically, the content of the sandy soil is around 15 times more than that of the interstitial water.

Clay has rather higher ratios of concentration [2]. From a chemical perspective, strontium is similar to calcium. It is adsorbed via the gastrointestinal tract, accumulates in the body, becomes part of the bone marrow tissue and damages the blood-producing cells. It easily forms into bone and continues to expose the localized tissues to radiation with the gradual development of bone sarcoma and leukemia. Therefore, ⁹⁰Sr, among all other fission products, is regarded as one of the most high-risk elements. Thus, the high content of Sr, as a heat-generator, is undesirable especially for the vitrification of high level liquid waste (HLLW). Regarding the safety, the removal of Sr from the radionuclides is really necessary before the final disposal of HLLW [1, 3, 4]. Zeolites make up a favorable class of advanced crystalline microporous inorganic materials with amazing properties which make them ideal for applications such as the molecular sieving, ion-exchange and shape-selective catalytic processes [5]. They have strongly organized microporous channel systems and high surface areas that is advantageous in

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comparison with the other classical support materials that hold particular interest for the adsorbent [6, 7]. Sodalite is considered as one of the most typical artificial zeolites that is regarded as a traditional zeolite primarily produced by the hydrothermal crystallization method [8]. It comes with a small pore size (2.8 Å) and high ion exchange capacity. Also, it attracted a lot of attention in industry and is employed in applications such as optical material [9], hydrogen storage [10] and catalyst support [11]. To remove strontium, various methods such as treatment via adsorption [12, 13], membrane filtration [14], biological treatment [15] and ion exchange treatment [16] were utilized. Each method has its pros and cons. Among the others, the adsorption process provides one of the most efficient physical methods for the elimination of pollutants from the environment because the technique uses readily available equipments that are energy efficient and easy to use. Therefore, it provides a cost-effective treatment [17-19]. Many factors such as strontium concentration, adsorbent amount, temperature, pH, etc affect the adsorption process; however, adsorbent and the type of adsorbent is of great importance [12, 13, 20]. In the work of Sabriye and Sema [12], a PAN/Zeolite was used for the elimination of strontium from aqueous solutions and the effect of various parameters such as the function of initial strontium concentration, solution pH, contact time and temperature on the removal of strontium was studied. In another research, the possibility of using zeolite A for the sorptive elimination of Cs^+ and Si^{2+} ions from aqueous solutions using batch and fixed bed column method was examined [21]. To remove cesium and strontium from water, zeolite P was utilized as sorbent and the effect of various operating variables on the sorption of strontium onto zeolite P and also the equilibrium isotherm of this sorption process were studied [22]. In this study, synthetic sodalite zeolite adsorbent was prepared and the adsorption of strontium from aqueous solution was studied onto acid treated zeolite. The effects of various operational parameters such as initial pH, adsorbent dosage, contact time and initial strontium concentration were also studied on the elimination of strontium during the batch adsorption experiments. Some isotherm and kinetic models were used to evaluate the sorption process and this led to a better understanding of the adsorption characteristics.

2. MATHEMATICAL MODEL

2. 1. Reagents and Chemicals

The two formulations, i.e. sodium metasilicate ($\text{Na}_2\text{O}_3\text{Si}\cdot 5\text{H}_2\text{O}$) and sodium aluminate that are of analytical reagent grade were provided by Merck Co. Strontium was purchased as strontium chloride from the same

company. Dissolving $\text{SrCl}_2\cdot 6\text{H}_2\text{O}$ in distilled water yields stock solutions of the test reagents.

2. 2. Instrumentation

In this study, X-ray diffraction (XRD) patterns were used with a GBC MMA diffractometer equipped with $\text{CuK}\alpha$ radiation. Scans were compiled in the angular range of 5° to 70° . To study the sodalite zeolite surface, the Scanning Electron Microscope (SEM) model S3400, Hitachi, Japan was used. Using a sputter coater, the sample was coated with gold and palladium. It contained conductive materials to improve the image quality. The coating thickness and the density were 30.00 nm and 19.32 g/cm^3 , respectively. The sodalite infrared spectra (IR) was provided by FTIR Spectrometer (Shimadzu 4100) in order to detect the sodalite functional groups. Using a spectrometer and KBr pellets, spectra were collected. In each case, using mortar and pestle, 1.0 mg of dried sodalite and 100 mg of KBr were homogenized and later pressed into a transparent tablet at 200 kg/cm^2 for 5 min. The pellets characterization was done using a FTIR spectrometer in the transmittance (%) mode with a scan resolution of 4 cm^{-1} in the range of 4200–500 cm^{-1} .

2. 3. Batch Adsorption Experiments

The effect of various parameters (pH, contact time, adsorbent dosage and initial concentration) was studied to determine the conditions that lead to the maximum amount of strontium sorption in the batch method at room temperature. Isotherm, kinetics and thermodynamics evaluations were also conducted in this part of the study. Batch sorption experiments were performed at a constant temperature of 20°C on a magnetic mixer at 400 rpm. Through the dilution of 1 g/L stock solutions, 100 mL of the strontium solution was prepared for each adsorption test. Using the diluted solution of hydrochloric acid or sodium hydroxide, the initial pH was adjusted to variable values. The suspension was filtered at the end of the predetermined time intervals and the filtrate was analyzed for any residual strontium. Each experiment was conducted two times with the purpose of observing the reproducibility and the mean value used for each set of values. The clear liquid phases obtained during these experiments were diluted to reach an appropriate concentration range for the elemental analysis using the Atomic Absorption Spectrophotometer (Buck scientific model VGP 210). Each experiment was performed in duplicate so that we could observe the reproducibility and the mean value used for each set of values. The experimental error was below 4%. The removal efficiency of strontium and/or the percent removal was obtained as follows:

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

where C_i is the initial concentration (mg/ L) and C_f is the final concentration (mg/ L); q is the adsorption capacity that indicates the amount of ions adsorbed per specific amount of adsorbent (mg/g). The sorption capacity at time t was calculated as follows:

$$q_t = (C_i - C_t) \times \frac{V}{m} \quad (2)$$

where q_t is the amount of adsorbed strontium at time t (mg/g); V is the solution volume (L); C_i denotes the initial concentration and C_t indicates the concentration at time t (mg/L); and m is the adsorbent weight (g). The adsorption capacity at state of equilibrium, q_e , was given as the following (Equation (3)):

$$q_e = (C_i - C_e) \times \frac{V}{m} \quad (3)$$

where C_e (mg/L) is the concentration of strontium at equilibrium.

2. 4. Synthesis of Sodalite Zeolite

Sodalite nano zeolite was provided by hydrothermal crystallization method using sodium metasilicate ($\text{Na}_2\text{O}_3\text{Si} \cdot 5\text{H}_2\text{O}$) and sodium aluminate (NaAlO_2) as a silica and aluminum sources, respectively. In a standard synthesis, solution A was prepared by dissolving 18.235 g $\text{Na}_2\text{O}_3\text{Si} \cdot 5\text{H}_2\text{O}$ (43 % H_2O , 29 % Na_2O , 28 % SiO_2) in 8 mL double distilled water at 80 °C. Also, solution B was prepared by dissolving 3.097 g NaOH in 12 mL double distilled water. The solution was used for solving 1.837 g of NaAlO_2 . Then, solution A was added to solution B drop wise under vigorous stirring and kept under stirring for 1 h before hydrothermicity is achieved. The molar composition of the above reactants was as follows: 1.0 Al_2O_3 :3.8 SiO_2 :2.1 Na_2O :50 H_2O . Subsequently, the above gel was transferred to Teflon-lined stainless steel autoclaves and heated at 100 °C for 20 h under static condition. At the end of the process, the product was separated via centrifuge (5,000 rpm), washed several times with double distilled water until the pH value of the solution was about 8.0 and dried overnight at 80 °C.

2. 5. Acid Treated Zeolite

Five grams of sodalite zeolite was stirred in 100 mL of 0.06 N H_2SO_4 at 87 °C for 2 h. The solid was washed with deionized water several times, and dried at 110°C overnight [23].

3. RESULTS AND DISCUSSION

3. 1. Characterization of Sodalite Zeolite

The characterization of synthesized sodalite zeolites was done using XRD, SEM and FTIR. The XRD powder pattern of synthesized sodalite nanozeolite is presented in Figure 1[24]. The crystallization products matched the characteristic peaks of sodalite nanozeolite at 2θ values of 14.1°, 20.1°, 22.4°, 24.5°, 27.7°, 31.9°,

34.9°, 37.9°, 43.1°, 45.7° and 48.1° that were reported by Treacy and Higgins [25], suggesting successful synthesis of sodalite nanozeolite with good crystallinity. This result is in agreement with previous works [10, 26]. Figure 2 shows the morphology of synthesized zeolite. It can be seen from the figure that the morphology of synthesized sodalite zeolite has a spherical structure and its mono dispersed particle size equals 40-70 nm. The sodalite structure has come under scrutiny by means of the FTIR technique as shown in Figure 3. The band located at 719.3 cm^{-1} matching the vibration of Al–O fragment and the strong broad band at 989.3 cm^{-1} is related to the T–O band (T = silica or aluminum) and its sharpness is indicative of an appropriate crystallization of the zeolitic product [27]. The peak at 1648.8 cm^{-1} is related to the bending vibration of free water. The strong broad band at 3400-3700 cm^{-1} (centered at 3513 cm^{-1}) indicates the stretching of water molecules adsorbed on OH groups [28, 29].

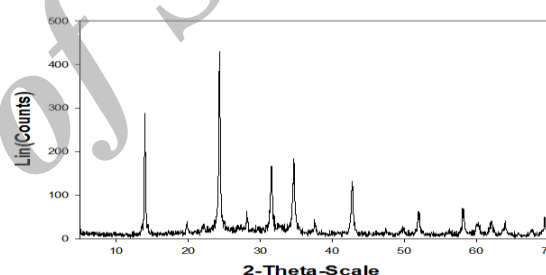


Figure 1. X-ray diffraction of synthesized sodalite zeolite.

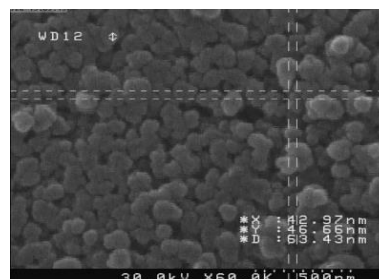


Figure 2. Scanning electron micrographs of sodalite zeolite

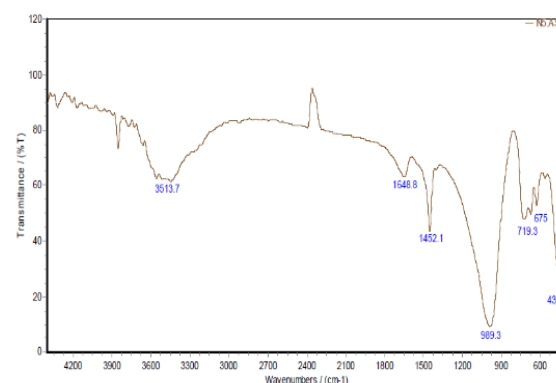


Figure 3. FTIR spectrum of sodalite zeolite

3. 2. Effect of pH on Strontium Sorption

Experiments were carried out with 100 mL of a 50 mg/L strontium solution containing 0.25 g of the sorbent at different pHs in the range of 2–8 at 20 °C to study the effect of initial pH on the removal efficiency (Figure 4). As can be seen from Figure 4, increasing the pH leads to an increase in the strontium adsorption amount. This increase gradually reached a maximum value at pH 6 and then decreased. It is also evident that the zeolites structures are affected by mineral acids. Within the zeolite framework, the Si-O-Al is weaker than Si-O-Si and can easily be attached by H⁺ ions that affect the zeolite structure. This shortcoming is more evident in the case of zeolites with low Si/Al ratios such as zeolite A, X types and sodalite zeolite [30]. The acids pH has an effect on the extent of damage imposed on their structure. The zeolites structures especially those with low Si/Al ratios may collapse in the presence of acids with pH lower than 5.0 but the severity could be much lower than a pH value of 3.0. As a matter of fact, pH above 5.0 is recommended for zeolites [31]. Thus, all future sorption experiments in this research were conducted at initial pH value of 6.0.

3. 3. Effect of Contact Time The effect of contact time on the sorption of strontium was studied by acid treated zeolite (0.25 g in 100 mL) with initial strontium concentration of 50 mg/L, pH 6 and temperature of 20 °C (Figure 5). It is clear that the amount of strontium sorption increased by every increase in contact time. Under the above conditions, Figure 4b shows that the adsorption amount reaches the maximum value after 80 min and a subsequent little change of sorption occurs (i.e., remains constant thereafter).

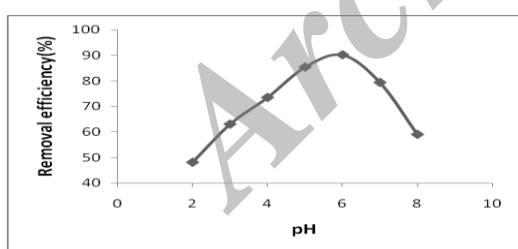


Figure 4. The effect of pH on the removal efficiency

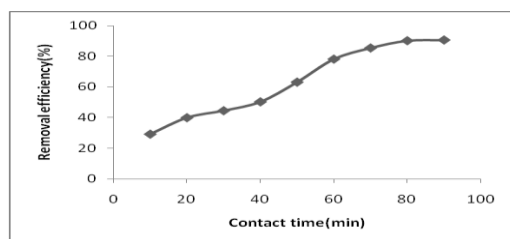


Figure 5. The effect of contact time on the removal efficiency

3. 4. Kinetics of Sorption

Most of adsorption processes in various solid phases depend on the time element. Knowledge of the kinetics of these processes is important to understand the dynamic interactions of strontium with acid treated zeolite and predict the rate of adsorption with time [32, 33]. Some kinetic models, i.e. Morris–Weber, Lagergren and pseudo second order models were used for their validity with the experimental adsorption data for the adsorption of strontium onto acid treated zeolite. These models were supposed to offer no mass transfer (both external and internal external) resistance to the overall adsorption process. A study was conducted on the adsorption kinetics and the findings suggest that these rates along with the solute uptake rate control the residence time of adsorbate uptake at the solid–solution interface including the diffusion process [33, 34]. The kinetic data of strontium sorption onto acid treated zeolite was used in Morris–Weber (Equation (4)) to examine the change in the concentration of sorbate onto sorbent with contact time [35]:

$$q_t = K_{id}(t)^{0.5} + C \quad (4)$$

where q_t is the sorbed concentration of strontium at time 't'. The Morris-weber transport (K_{id}) rate constant value is calculated from the slope of the linear plot of this graph ($K_{id} = 2.2227 \text{ min}^{-1}$) with a correlation factor of 0.9501. The result of the Morris-weber equation is presented in Table 1.

In Lagergren [36, 37], a pseudo-first-order equation was suggested for the sorption of liquid/solid system based on solid capacity. It is assumed in this equation that the rate of change of sorbate uptake with time is proportionate to the difference in the saturation concentration and the amount of solid uptake with time. The Lagergren equation is mostly used in liquid phase sorption. The general equation is given as:

$$\log(q_e - q_t) = \log q_e - \left(\frac{K}{2.303} \right) t \quad (5)$$

where q_e is the sorbed concentration at equilibrium and K is the first order rate constant. The linear plot of $\log(q_e - q_t)$ against time 't' reveals the applicability of the above equation for strontium sorption onto the sodalite zeolite. The rate constant $K = 0.0573 \text{ min}^{-1}$ was calculated from the slope of the straight line using the correlation factor of 0.8264. The result of the Lagergren equation is given in Table 1.

The sorption of strontium onto acid treated zeolite following pseudo-second-order kinetics is expressed as Equation (6):

$$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{t}{q_e} \quad (6)$$

where q_t denotes the amount of strontium adsorbed at time t and q_e shows that amount at equilibrium (mg/g). Also, k_2 (g/mg.min) is the pseudo-second-order rate constant for the adsorption process. There are four

different forms of linearization for this equation. The different linear forms of the pseudo second-order equation are presented in Table 1.

It can be understood from the results that the adsorption of strontium by acid treated zeolite will be fit using types (1-4) pseudo second-order model. Results suggested that type 2 equation offers the best correlation factor. The kinetic data showed that the adsorption process was controlled by pseudo-second-order (type 2) equation. Based on the above assumption, the strontium uptake process occurs due to chemisorptions. The fact that the rate-limiting step might be chemisorption involving valence forces through sharing or exchanging of electrons between adsorbent and adsorbate forms the assumption of pseudo-second order kinetic model. The strontium molecules behavior in system is strongly dependent upon the concentration and the properties of other species, pH of the solution, physical and chemical properties of both the adsorbent and adsorbate. The adsorption kinetic form and its related coefficients in the system were influenced by both the interaction and competition effects among the strontium [38].

3. 5. Effect of Adsorbent Dosage The effect of acid treated zeolite dose was studied at the dose between 0.05 and 0.3 g in 100 mL aqueous solution. The experiments were performed at 20°C, pH 6 and the initial strontium concentration of 50 mg/L. It was found out that increasing the zeolite dose increases the amount of adsorbed strontium (Figure 6). Shortly after, it was discovered that the availability of larger surface area and more adsorption sites increases with every increase in the adsorbent dose. Increasing the zeolite at higher concentrations of sorbate did not cause the equilibrium uptake to increase significantly.

3. 6. Effect of Initial Concentration of Strontium

The effect of initial strontium concentration on adsorption was studied at concentrations ranging from 50 mg/L to 150 mg/L with 0.25, 80, 6 of adsorbent dose, contact time and pH, respectively at ambient temperature (20°C) (Figure 7). Results suggested that the percentage removal of strontium decreased from 90.18% to 42.23% when the initial concentration increased from 50–150 mg/L. It was found out that there is a reduction in strontium adsorption due to the lack of available active sites needed for the high initial concentration of strontium. The higher uptake of strontium at low concentration may be ascribed to the availability of more active sites on the surface of the adsorbent for lesser number of adsorbate species.

In order to fit different isotherm models, i.e., Langmuir, Freundlich, Temkin and Dubinin-Randkovich (D-R), the data of Figure 7 were used.

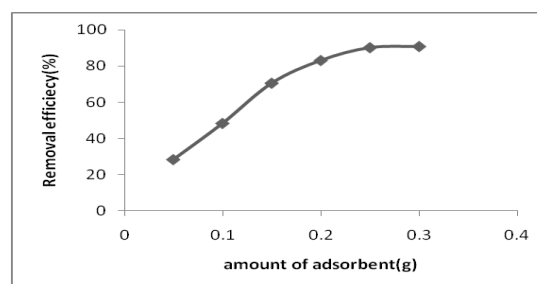


Figure 6. The effect of amount of adsorbent on the removal efficiency

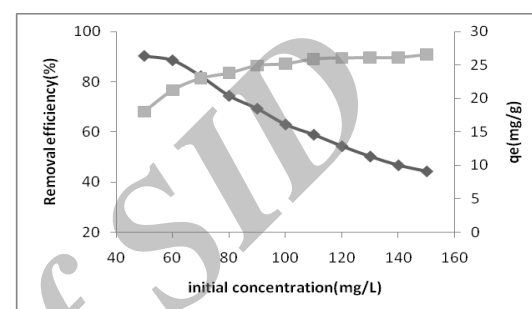


Figure 7. The effect of initial concentration on the removal efficiency

TABLE 1. Kinetic constants for strontium adsorption

Morris-Weber equation	$K_{ad}(\text{min}^{-1})$	R^2	
	2.2227	0.9501	
Pseudo-first order kinetic model	$K(\text{min}^{-1})$	$q_e(\text{mg/g})$	R^2
	0.0573	46.978	0.8264
Pseudo- second order kinetic model			
Type 1	$\frac{t}{q_i} = \frac{1}{k_2 q_e} + \frac{1}{q_e} t$	$q_e(\text{mg/g})$	R^2
		28.169	0.9109
Type 2	$\frac{1}{q_i} = \frac{1}{q_e} + \left(\frac{1}{k_2 q_e}\right) \frac{1}{t}$	20.833	0.9681
Type 3	$q_i = q_e - \left(\frac{1}{k_2 q_e}\right) \frac{q_i}{t}$	23.103	0.8285
Type 4	$\frac{q_i}{t} = k_2 q_e^2 - k_2 q_e (q_i)$	25.233	0.8285

3. 7. The Isotherm Model The assumption that every adsorption site is equal and independent of adjacent sites occupation or lack of occupation is the ground on which the adsorption isotherm is based [39]. The relationship between strontium concentrations in solution can be easily understood from the presence of isotherms and the amount of strontium sorbed on a specific sorbent at a constant temperature.

3. 7. 1. The Langmuir Isotherm Model In this model, the assumption is that the adsorption occurs in a monolayer and the absorption sites located on the surface of the adsorbent are uniform and all of them

have the same absorbing capacity. This isotherm model is often suggested in the form of Equation (7) [40-43]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

where q_e denotes the strontium adsorbed per specific amount of adsorbent; C_e is the concentration of the strontium solution (mg/ L) at equilibrium and q_m , indicates the maximum amount of adsorption strontium (mg g⁻¹). The rearrangement of the Langmuir equation leads to four various linear types which are presented in Table 2. Compared to the other types, the best match was obtained by the Langmuir type 1. Regarding the dimensionless constant separation factor or equilibrium parameter R_L , the basic features and practicality of the Langmuir isotherm are defined as Equation (8) [44]:

$$R_L = \frac{1}{1 + K_L C_i} \quad (8)$$

where K_L is the Langmuir constant and C_i the initial concentration of strontium. The desired value of absorption is specified somewhere between 0 and 1.

3. 7. 2. The Freundlich Isotherm Model

The Langmuir isotherm is based on the assumption that the enthalpy of adsorption is independent of the amount adsorbed while the empirical Freundlich equation is based on sorption on heterogeneous surface that can be obtained assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites. Based on sorption on heterogeneous surface, the Freundlich equation is completely empirical and is expressed by Equation (9) [44]:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (9)$$

where K_F and $(1/n)$ are the Freundlich constants corresponding to the adsorption capacity and adsorption intensity, respectively. The equilibrium constants obtained from the intercept and the slope of the linear plot of $\log q_e$ versus $\log C_e$ are based on the experimental data. In logarithmic terms, the Freundlich equation can be linearized as Equation (10) to determine the Freundlich constants:

$$\log(q_e) = \log(K_F) + \frac{1}{n} \log C_e \quad (10)$$

The slope and the intercept are related to $(1/n)$ and K_F , respectively. It was found out that the plot of $\log q_e$ vs. $\log C_e$ gives a straight line. Results are given in Table 2.

3. 7. 3. The Temkin Isotherm Model

There is a factor in the isotherm model that provides the possibility of including the interactions between adsorbents and adsorbates. Temkin model includes the following conditions: (i) the adsorption heat of all molecules present in the layer linearly decreases with the coverage due to the adsorbent-adsorbate interactions; (ii) to characterize the adsorption, a

uniform distribution of binding energies, up to the maximum binding energy, is used. The Temkin isotherm suggests that the decrease in the heat of adsorption is more linear than the logarithmic form as already expressed implicitly by the Freundlich equation. The Temkin isotherm is commonly used in the form of the following equation [45]:

$$q_e = B \ln(K_T C_e) \quad (11)$$

where $B = (RT / A_T)$ and K_T is the Temkin constant.

The above equation is often rearranged in a linear form given below to simplify plotting and calculation of Temkin constant. The B and K_T values are calculated using the linear plot of q_e against $\ln(C_e)$.

$$q_e = B \ln K_T + B \ln C_e \quad (12)$$

The linearized form of the Temkin adsorption isotherm (Equation (12)) was employed to analyze the equilibrium data given in Table 2.

3. 7. 4. The Dubinin-Radushkevich Isotherm

To determine the nature of the adsorption process namely physisorption and/or chemisorption, the Dubinin-Radushkevich (D-R) [46-48] isotherm was used. The linear form of this model is given as the following equation:

$$\ln(q_e) = \ln(q_m) - \beta \varepsilon^2 \quad (13)$$

where q_e is the amount of strontium adsorbed per unit dosage of the adsorbent (mg/g); q_m denotes the monolayer capacity; β indicates the activity coefficient related to the mean sorption energy and finally ε is the Polanyi potential expressed as:

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \quad (14)$$

The values of β and q_m were determined from the slope and intercept of the linear plot using the plots of $\ln q_e$ versus ε^2 . Table 2 presents the statistical results together with the isotherm constants. Results suggest that the strontium adsorption by acid treated zeolite can be matched using the Langmuir equation. Also, the D-R equation suggests there is a considerable correlation factor. It can be understood from the D-R isotherm that the heterogeneity of energies is close to the adsorbent surface. The quantity is related to the mean sorption energy, E , which is the free energy for the transfer of 1 mole of strontium from the infinity to the surface of the adsorbent [49]. The following equation shows how the mean free energy of adsorption (E , kJ/mol) is calculated [46, 50, 51]:

$$E = (2 \beta)^{-0.5} \quad (15)$$

It is clear that we can use the E magnitude to estimate the adsorption type. If this value goes below 8 kJ/mol, the adsorption type is expressed by the physical adsorption and between 8 and 16 kJ/mol the adsorption

type can be explained by ion exchange. In this study, the E values were below 8 kJ/mol. This reveals that the adsorption of strontium onto zeolite was in fact a physical adsorption [33, 51,52].

TABLE 2. Isotherm constants for strontium adsorption

	K_L (min ⁻¹)	q_m (mg/g)	R_L	R^2
Langmuir equation				
Type 1 $\frac{C_e}{q_e} = \frac{1}{(q_m K_L)} + \left(\frac{1}{q_m}\right) C_e$	0.4128	27.10	0.0462- 0.0159	0.9998
Type 2 $\frac{1}{q_e} = \frac{1}{(q_m K_L C_e)} + \left(\frac{1}{q_m}\right)$	0.4394	27.027	0.0435- 0.0149	0.9756
Type 3 $q_e = q_m - \left(\frac{1}{K_L}\right) \frac{q_e}{C_e}$	0.4499	26.96	0.0426- 0.0146	0.9661
Type 4 $\frac{q_e}{C_e} = K_L q_m - K_L q_e$	0.4346	27.057	0.044- 0.0151	0.9661
Freundlich equation	K (min ⁻¹) 16.4627	n 8.7642		R^2 0.8863
Temkin equation	K_T 413.208	B 2.5885		R^2 0.9181
D-R equation	β 2×10^{-6}	q_m 25.6		R^2 0.9372

TABLE 3. The effect of temperature on the removal efficiency.

Temperature (°C)	Removal efficiency of strontium (%)
20	90.22
35	92.69
50	95.36

TABLE 4. Thermodynamic parameter for adsorption

$\Delta H \left(\frac{Kj}{mol} \right)$	$\Delta S \left(\frac{Kj}{mol.k} \right)$	T(°C)	$\Delta G \left(\frac{Kj}{mol} \right)$	R^2
20.916	0.089	20	-5.4153	0.9079
		35	-6.5074	
		50	-8.1216	

3. 8. Effect of Temperature

The adsorption studies were conducted at 20–50 °C, pH 6 and an adsorbent dosage of 0.25g in a 100 mL solution to examine the thermodynamics of adsorption. The equilibrium contact time for adsorption was kept constant at 80 min. The adsorption percentage increased with the rise in temperature from 20 to 50 °C. Results suggested that the adsorption process had an

endothermic nature. Table 3 explains the effect of temperature on the removal efficiency. To determine the changes in Gibbs free energy (ΔG), heat of adsorption (ΔH) and entropy (ΔS) of the adsorption of strontium from aqueous solutions, the data given in Table 3 were used.

3. 9. Effect of Temperature on Thermodynamics

Different thermodynamic parameters such as the enthalpy change ΔH , free energy change ΔG and entropy change ΔS were calculated using Equations (16) to (18) in order to study the thermodynamics of adsorption of strontium on zeolite. Table 4 presents these parameters values. Using the following equations, the thermodynamic parameters ΔH , ΔS and ΔG for strontium on zeolite system were calculated as follows:

$$K_c = \frac{F_e}{1-F_e} \quad (16)$$

$$\log K_c = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \quad (17)$$

$$\Delta G = -RT \ln K_c \quad (18)$$

where F_e is the fraction of strontium sorbed at equilibrium. The values of these parameters are given in Table 4. It shows that the enthalpy change ΔH is positive (endothermic) because of the increase in adsorption on successive increase in temperature. The negative ΔG values revealed that the sorption is thermodynamically feasible and spontaneous. The positive value of ΔS indicates the increased randomness at the solid–solution interface during the fixation of the ion on the active sites of the sorbent.

4. CONCLUSION

In the synthesis experiments with NaOH solution sodalite zeolite crystals were successfully synthesized. Results indicated that the acid treated sodalite zeolite had considerable potential for the removal of strontium from aqueous solutions. The conditions of sorption were found to be: a sorbent dose of 0.25 g in 100 mL of solution, contact time and pH 80 min and 6, respectively. The kinetic data shows that the adsorption process is controlled by pseudo- second order kinetic model (type 2). The results obtained from this study were given by the theoretical Langmuir (type 1). Thermodynamic studies were indicative of a negative ΔG and positive ΔS and ΔH . Results showed that the sorption had an endothermic nature. The negative ΔG values suggested that the sorption had a thermodynamically feasible and spontaneous nature. The positive value of ΔS revealed the increased randomness at the solid–solution interface during the fixation of the ion on the sites of the sorbent.

5. REFERENCES

- Chakraborty, D., Maji, S., Bandyopadhyay, A., Basu, S., "Biosorption of cesium-137 and strontium-90 by mucilaginous seeds of *Ocimum basilicum*", *Bioresource Technology*, Vol. 98,(2007), 2949-2952.
- Chegrouche, S., Mellah, A., Barkat, M., "Removal of strontium from aqueous solutions by adsorption onto activated carbon: kinetic and thermodynamic studies", *Desalination*, Vol. 235,(2009), 306-318.
- Zhang, A., Wei, Y., Kumagai, M., "Synthesis of a novel silica-based macroporous polymeric adsorption material containing 4, 4', (5')-di (tert-butylcyclohexano)-18-crown-6 functional group and its adsorption mechanism for strontium", *Reactive and Functional Polymers*, Vol. 61,(2004), 191-202.
- Grahek, Z., Macefat, M.R., "Determination of radioactive strontium in seawater", *Analytica Chimica Acta*, Vol. 534,(2005), 271-279.
- Moon, J.-K., Jung, C.-H., Lee, E.-H., Kim, H.-T., Shul, Y.-G., "Preparation of PAN-zeolite 4A composite ion exchanger and its uptake behavior for Sr and Cs ions in acid solution", *Korean Journal of Chemical Engineering*, Vol. 19,(2002), 838-842.
- Hassaninejad-Darzi, S.K., Rahimnejad, M., "Electrocatalytic oxidation of methanol by ZSM-5 nanozeolite-modified carbon paste electrode in alkaline medium", *Journal of the Iranian Chemical Society*, Vol. 11,(2014), 1047-1056.
- Li, L., Li, W., Sun, C., Li, L., "Fabrication of Carbon Paste Electrode Containing 1: 12 Phosphomolybdic Anions Encapsulated in Modified Mesoporous Molecular Sieve MCM-41 and Its Electrochemistry", *Electroanalysis*, Vol. 14,(2002), 368-375.
- Felsche, J., Luger, S., Baerlocher, C., "Crystal structures of the hydro-sodalite $\text{Na}_6 [\text{AlSiO}_4]_6 \cdot 8\text{H}_2\text{O}$ and of the anhydrous sodalite $\text{Na}_6 [\text{AlSiO}_4]_6$ ", *Zeolites*, Vol. 6,(1986), 367-372.
- Kalantari, N., Vaezi, M.J., Yadollahi, M., Babalu, A.A., Bayati, B., Kazemzadeh, A., "Synthesis of nanostructure hydroxy sodalite composite membranes via hydrothermal method: support surface modification and synthesis method effects", *Asia-Pacific Journal of Chemical Engineering*, Vol. 10,(2015), 45-55.
- Buhl, J.-C., Gesing, T.M., Rüscher, C., "Synthesis, crystal structure and thermal stability of tetrahydroborate sodalite $\text{Na}_8 [\text{AlSiO}_4]_6 (\text{BH}_4)_2$ ", *Microporous and Mesoporous Materials*, Vol. 80,(2005), 57-63.
- Ogura, M., Morozumi, K., Elangovan, S., Tanada, H., Ando, H., Okubo, T., "Potassium-doped sodalite: A tectoaluminosilicate for the catalytic material towards continuous combustion of carbonaceous matters", *Applied Catalysis B: Environmental*, Vol. 77,(2008), 294-299.
- Sabriye, Y., Sema, E., "Adsorption characterization of strontium on PAN/zeolite composite adsorbent", *World Journal of Nuclear Science and Technology*, Vol. 2011,(2011).
- Ahmadi, S.J., Akbari, N., Shiri-Yekta, Z., Mashhadizadeh, M.H., Hosseinpour, M., "Removal of strontium ions from nuclear waste using synthesized $\text{MnO}_2\text{-ZrO}_2$ nano-composite by hydrothermal method in supercritical condition", *Korean Journal of Chemical Engineering*, Vol. 32,(2015), 478-485.
- Rao, S., Paul, B., Lal, K., Narasimhan, S., Ahmed, J., "Effective removal of cesium and strontium from radioactive wastes using chemical treatment followed by ultra filtration", *Journal of Radioanalytical and Nuclear Chemistry*, Vol. 246,(2000), 413-418.
- Pecher, C., "Biological Investigations with Radioactive Calcium and Strontium", *Experimental Biology and Medicine*, Vol. 46,(1941), 86-91.
- Manos, M.J., Ding, N., Kanatzidis, M.G., "Layered metal sulfides: Exceptionally selective agents for radioactive strontium removal", *Proceedings of the National Academy of Sciences*, Vol. 105,(2008), 3696-3699.
- Azizi, S.N., Asemi, N., "Parameter optimization of the fungicide (Vapam) sorption onto soil modified with clinoptilolite by Taguchi method", *Journal of Environmental Science and Health Part B*, Vol. 45,(2010), 766-773.
- Shukla, A., Zhang, Y.-H., Dubey, P., Margrave, J., Shukla, S.S., "The role of sawdust in the removal of unwanted materials from water", *Journal of Hazardous Materials*, Vol. 95,(2002), 137-152.
- Aslan, S., Turkman, A., "Simultaneous biological removal of endosulfan ($\alpha + \beta$) and nitrates from drinking waters using wheat straw as substrate", *Environment International*, Vol. 30,(2004), 449-455.
- Yusan, S., Gok, C., Erenturk, S., Aytas, S., "Adsorptive removal of thorium (IV) using calcined and flux calcined diatomite from Turkey: evaluation of equilibrium, kinetic and thermodynamic data", *Applied Clay Science*, Vol. 67,(2012), 106-116.
- El-Kamash, A., "Evaluation of zeolite A for the sorptive removal of Cs^+ and Sr^{2+} ions from aqueous solutions using batch and fixed bed column operations", *Journal of Hazardous Materials*, Vol. 151,(2008), 432-445.
- Mimura, H., Yokota, K., Akiba, K., Onodera, Y., "Alkali hydrothermal synthesis of zeolites from coal fly ash and their uptake properties of cesium ion", *Journal of nuclear Science and Technology*, Vol. 38,(2001), 766-772.
- Ouznadji, Z.B., Sahmoune, M.N., Mezener, N.Y., "Adsorptive removal of diazinon: kinetic and equilibrium study", *Desalination and Water Treatment*, (2014), 1-10.
- Azizi, S.N., Samadi-Maybodi, A., Fatemi, M.H., Asemi, N., "Using Taguchi Experimental Design to Develop an Optimized Synthesis Procedure of Sodalite Prepared by Microwave and Ultrasonic Assisted Aging", *Caspian Journal of Chemistry*, Vol. 2,(2013), 1-7.
- Treacy, M.M., Higgins, J.B., Collection of Simulated XRD Powder Patterns for Zeolites Fifth (5th) Revised Edition, Elsevier, (2007).
- Arieli, D., Vaughan, D., Goldfarb, D., "New synthesis and insight into the structure of blue ultramarine pigments", *Journal of the American Chemical Society*, Vol. 126,(2004), 5776-5788.
- Vadapalli, V.R., Gitari, W.M., Ellendt, A., Petrik, L.F., Balfour, G., "Synthesis of zeolite-P from coal fly ash derivative and its utilisation in mine-water remediation", *South African Journal of Science*, Vol. 106,(2010), 62-68.
- Ren, T.-Z., Yuan, Z.-Y., Su, B.-L., "Surfactant-assisted preparation of hollow microspheres of mesoporous TiO_2 ", *Chemical Physics Letters*, Vol. 374,(2003), 170-175.
- Schnabel, K.-H., Finger, G., Kornatowski, J., Löffler, E., Peuker, C., Pilz, W., "Decomposition of template in SAPO-5 and AIPO 4-5 molecular sieves studied by IR and Raman spectroscopy", *Microporous Materials*, Vol. 11,(1997), 293-302.
- Rao, G.P.C., Satyaveni, S., Ramesh, A., Seshiah, K., Murthy, K., Choudary, N., "Sorption of cadmium and zinc from aqueous solutions by zeolite 4A, zeolite 13X and bentonite", *Journal of Environmental Management*, Vol. 81,(2006), 265-272.
- Trgo, M., Perić, J., "Interaction of the zeolitic tuff with Zn-containing simulated pollutant solutions", *Journal of Colloid and Interface science*, Vol. 260,(2003), 166-175.
- Mondal, P., Mohanty, B., Majumder, C.B., "Removal of Arsenic from Simulated Groundwater Using GAC-Ca in Batch Reactor: Kinetics and Equilibrium Studies", *CLEAN-Soil, Air, Water*, Vol. 40,(2012), 506-514.

33. Esfandian, H., Javadian, H., Parvini, M., Khoshandam, B., Katal, R., "Batch and column removal of copper by modified brown algae *Sargassum bevanom* from aqueous solution", *Asia-Pacific Journal of Chemical Engineering*, Vol. 8, (2013), 665-678.
34. Metcalf, E., Wastewater engineering: treatment and reuse, in, McGraw-Hill, (2003).
35. Weber, W.J., Morris, J.C., "Kinetics of adsorption on carbon from solution", *Journal of the Sanitary Engineering Division*, Vol. 89, (1963), 31-60.
36. Lagergren, S., "About the theory of so-called adsorption of soluble substances", (1898).
37. Ciesielczyk, F., Bartczak, P., Jesionowski, T., "A comprehensive study of Cd (II) ions removal utilizing high-surface-area binary Mg-Si hybrid oxide adsorbent", *International Journal of Environmental Science and Technology*, 1-14.
38. Javadian, H., Ahmadi, M., Ghiasvand, M., Kahrizi, S., Katal, R., "Removal of Cr (VI) by modified brown algae *Sargassum bevanom* from aqueous solution and industrial wastewater", *Journal of the Taiwan Institute of Chemical Engineers*, Vol. 44, (2013), 977-989.
39. Limousin, G., Gaudet, J.-P., Charlet, L., Szenknect, S., Barthes, V., Krimissa, M., "Sorption isotherms: a review on physical bases, modeling and measurement", *Applied Geochemistry*, Vol. 22, (2007), 249-275.
40. Langmuir, I., "The adsorption of gases on plane surfaces of glass, mica and platinum", *Journal of the American Chemical Society*, Vol. 40, (1918), 1361-1403.
41. Subramanyam, B., Das, A., "Linearized and non-linearized isotherm models comparative study on adsorption of aqueous phenol solution in soil", *International Journal of Environmental Science & Technology*, Vol. 6, (2009), 633-640.
42. Esfandian, H., Jafari, M., Alizadeh, M., Rahmati, H.T., Katal, R., "Synthesis of polyaniline nanocomposite and its application for chromium removal from aqueous solution", *Journal of Vinyl and Additive Technology*, Vol. 18, (2012), 250-260.
43. Esfandian, H., Parvini, M., Khoshandam, B., Samadi-Maybodi, A., "Artificial neural network (ANN) technique for modeling the mercury adsorption from aqueous solution using *Sargassum Bevanom* algae", *Desalination and Water Treatment*, (2015), 1-14.
44. Freundlich, H., "Of the adsorption of gases. Section II. Kinetics and energetics of gas adsorption. Introductory paper to section II", *Transactions of the Faraday Society*, Vol. 28, (1932), 195-201.
45. Temkin, M., Pyzhev, V., "Recent modifications to Langmuir isotherms", (1940).
46. Dubinin, M., Radushkevich, L., "Equation of the characteristic curve of activated charcoal", *Chem. Zentr*, Vol. 1, No. 1, (1947), 875-883.
47. Ghazy, S., El-Asmy, A., El-Nokrashy, A., "Separation of chromium (III) and chromium (VI) from environmental water samples using eggshell sorbent", *Indian Journal of Science and Technology*, Vol. 1, (2008), 1-7.
48. Goharshadi, E., Moghaddam, M., "Adsorption of hexavalent chromium ions from aqueous solution by graphene nanosheets: kinetic and thermodynamic studies", *International Journal of Environmental Science and Technology*, (2004), 1-8.
49. Naiya, T.K., Bhattacharya, A.K., Das, S.K., "Adsorption of Cd (II) and Pb (II) from aqueous solutions on activated alumina", *Journal of Colloid and Interface Science*, Vol. 333, (2009), 14-26.
50. Bhattacharya, A., Naiya, T., Mandal, S., Das, S., "Adsorption, kinetics and equilibrium studies on removal of Cr (VI) from aqueous solutions using different low-cost adsorbents", *Chemical Engineering Journal*, Vol. 137, (2008), 529-541.
51. Katal, R., Baei, M.S., Rahmati, H.T., Esfandian, H., "Kinetic, isotherm and thermodynamic study of nitrate adsorption from aqueous solution using modified rice husk", *Journal of Industrial and Engineering Chemistry*, Vol. 1, (2012), 295-302.
52. Katal, R., Ghiass, M., Esfandian, H., "Application of nanometer size of polypyrrole as a suitable adsorbent for removal of Cr (VI)", *Journal of Vinyl and Additive Technology*, Vol. 17, (2011), 222-230.

Removal of Strontium Ions by Synthetic Nano Sodalite Zeolite from Aqueous Solution

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در این تحقیق، نانو زئولیت جدید سودالیت سنتز شده و ساختار زئولیت، توسط آنالیزهای XRD، SEM و FTIR مورد بررسی قرار گرفته است. زئولیت ساخته شده به عنوان جاذب در آزمایشات ناپیوسته جذب استرانسیوم از محلول آبی بر روی زئولیت اسید شویی شده با اسید سولفوریک بکار برده شده است شرایط بهینه بدست آمده برای جذب استرانسیوم توسط زئولیت شامل ۰/۲۵ گرم در ۱۰۰ میلی لیتر محلول استرانسیوم (۵۰ ppm) زمان تعادل، pH و دما به ترتیب ۸۰ دقیقه، ۶ و ۲۰ درجه سانتیگراد بوده است. از مدل های سینتیکی موریس ویر، شبه مرتبه اول و شبه مرتبه دوم برای بررسی سینتیک فرآیند استفاده شد. نتایج نشان داد بررسی سینتیک جذب استرانسیوم توسط زئولیت نشان داد که داده های آزمایشگاهی بهترین تطابق را با مدل سینتیکی شبه درجه دوم دارند. همچنین مطالعه مدل های ایزوترم توسط چهار ایزوترم لانگمیر، فرنلچ، دابینین رادشکوچ و تمکین جهت بررسی مکانیزم جذب استرانسیوم توسط زئولیت نشان داد که این فرایندها شامل واکنش جذب فیزیکی می باشند. مقادیر پارامترهای ترمودینامیکی ΔH ، ΔS و ΔG محاسبه شد. نتایج امکان پذیر، خودبه خودی و گرماگیر بودن واکنش جذب استرانسیوم از محلول آبی توسط زئولیت را نشان داد.

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