Modeling the Sorption Kinetics of Cesium and Strontium Ions on Zeolite A

K. M. Abd El-Rahman,*a M. R. El-Sourougy,a N. M. Abdel-Monem,b and I. M. Ismailb

*aHot Laboratory Center, Atomic Energy Authority, P.O. 13759, Cairo, Egypt
bChemical Engineering Department, Faculty of Engineering, Cairo University, Giza, Egypt

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Zeolite A was chemically synthesized and characterized using X-ray diffraction, X-ray fluorescence, and thermal analysis. The sorptive removal of cesium and strontium ions from aqueous waste solution using synthetic zeolite A was investigated. Experiments were carried out as a function of pH, solute concentration, and temperature (298–333 K). Analysis of the respective rate data in accordance with three kinetic models revealed that the intraparticle diffusion was the rate determining step for the sorption of both studied ions. Values of the pseudo first order and pseudo second order rate constants and the particle diffusion coefficients were determined from the graphical representation of the proposed models. Activation energy and thermodynamic parameters of free energy (ΔG*), enthalpy (ΔH*), and entropy (ΔS*) of activation for each sorption process were calculated from the linearized form of Arrhenius equation.

1. Introduction

The treatment of aqueous radioactive waste solutions requires the concentration of dissolved metal ions followed by recovery or secure disposal.1 Radionuclides of cesium and strontium, because of their greater yield in the nuclear fission process and longer half-lives, are among the most hazardous radionuclides in the nuclear waste effluents for the environment.2 Different techniques such as chemical precipitation, ion exchange, and evaporation are used for the treatment of aqueous waste solutions containing these ions. Ion exchange seems to be an attractive method because of its simplicity, selectivity, and efficiency.3 Synthetic aluminosilicate zeolites act as an efficient porous exchange media and its cation exchange properties are widely used for agriculture, nuclear industry, detergent industry, and environmental protection.4,5 The potential applications of zeolites and other selective ion exchangers have been well documented by Dyer.6 These materials possess high exchange capacity, element selectivity and specificity, and good resistant properties to radiation and heat.6,7,10 The aim of this work is to examine the efficiency as a cation exchanger of the prepared zeolite A for the removal of cesium and strontium ions from waste solutions. The effect of various parameters such as initial metal concentration, contact time, and temperatures are examined. The kinetics of an exchange reaction is also evaluated using the light of current known models and the relevant parameters were determined.

2. Experimental

2.1. Chemicals and reagents. All the reagents used were of AR (Analytical Reagent) grade chemicals. Stock solutions of the test reagents were prepared by dissolving CsCl, SrCl2·6H2O, CaCl2, and MgCl2·6H2O in distilled water.

2.2. Preparation and characterization of zeolite A. The zeolite A having aluminosilicate structure was synthesized by mixing the aqueous solutions of NaAlO2, Na2O SiO2, and NaOH.11 Sodium aluminate (13.5 g) and sodium hydroxide (25 g) are dissolved in 300 mL of water, then stirred and boiled. The aluminum solution is added, with vigorous stirring, to the hot solution of sodium metasilicate (14.2 g in 200 mL water) in a 1 L beaker. The entire mixture was heated with stirring at about 90 °C for 2 hours until the suspension settled quickly when stirring was stopped. The suspension is then filtered and the solid washed many times with bidistilled water and dried overnight in an oven at 110 °C.12

The inorganic product was sieved to obtain particles less than the size 0.25 mm. The crystallinity and chemical composition of the prepared material were investigated using X-ray diffraction (XRD), X-ray fluorescence (XRF), and thermal analysis. Also, the total surface area of zeolite A was measured by means of NOVA 3200 Series, Quantachrome Inc., USA using nitrogen adsorption method at 77 K, and application of the Brunauer, Emmett, and Teller (BET) method.

2.3. Kinetics studies. The effect of solution pH on uptake of the two ions by zeolite A was studied at room temperature to understand a maximum removal efficiency. For these investigations, a series of 50 mL test tubes were employed. Each test tube was filled with 10 mL of a 100 mg/L metal ion solution and adjusted to the desired pH from 2.0 to 8.0 by pH meter. The pH of the solution was adjusted using dilute solution of hydrochloric acid or sodium hydroxide. A known amount of zeolite A (10 mg) was added into each test tube. The tubes were shaken for 24 hours to attain an equilibrium. The obtained suspension was centrifuged to separate the solid from the liquid phase. The obtained clear liquid phases were diluted to an appropriate concentration range for the elemental analysis by atomic absorption spectroscopy.

In the experiments of the kinetic investigation, 10 mg of zeolite A was contacted with 10 mL solution containing known concentration of cesium and strontium ions. Kinetic studies were carried out with the different initial concentrations (50, 100, and 150 mg/L). The temperature of the system was kept steady at 25°C. The time of the experiment was set at 24 hours. The concentration of the metal ion in the liquid phase was measured by atomic absorption spectroscopy. The amount sorbed at time t, qt (mg/g), was determined as follows

\[ q_t = \frac{(c_0-c_t)V}{W}, \] (1)
Figure 1. X-ray diffraction pattern of prepared zeolite A.

Table 1: The strongest three peaks in XRD pattern of synthesized zeolite A

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>2θ angle (deg)</th>
<th>Spacing (d/Å)</th>
<th>Crystallinity (H/Lo)</th>
<th>Intensity (kCPS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>27.057</td>
<td>12.29</td>
<td>100</td>
<td>1.945</td>
</tr>
<tr>
<td>8</td>
<td>29.777</td>
<td>8.71</td>
<td>69</td>
<td>1.938</td>
</tr>
<tr>
<td>10</td>
<td>23.997</td>
<td>7.11</td>
<td>35</td>
<td>1.832</td>
</tr>
</tbody>
</table>

Table 2: Quantitative elemental analysis of prepared zeolite A using X-ray fluorescence spectroscopy

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>27.79</td>
</tr>
<tr>
<td>Al</td>
<td>39.43</td>
</tr>
<tr>
<td>Si</td>
<td>32.14</td>
</tr>
<tr>
<td>Ca</td>
<td>0.076</td>
</tr>
<tr>
<td>Ti</td>
<td>0.026</td>
</tr>
<tr>
<td>Mn</td>
<td>0.008</td>
</tr>
<tr>
<td>Fe</td>
<td>0.015</td>
</tr>
</tbody>
</table>

where \( c_0 \) and \( c_t \) are the liquid phase concentrations at the time \( t = 0 \) and \( t \), respectively (mg/L), \( V \) is the volume of the solution (L), and \( W \) is the weight of the solid used (g).

3. Results and discussion

3.1. Characterization of material. The powder XRD pattern of the prepared material is shown in Figure 1. The XRD patterns revealed that the synthesized material exhibits crystalline pattern. The strongest three peaks in XRD patterns were \( d = 12.29 \) Å at \( I/I_0 = 100 \), \( d = 8.71 \) Å at \( I/I_0 = 69 \) and \( d = 7.11 \) Å at \( I/I_0 = 35 \) as shown in Table 1. These values are characteristic for zeolite A as reported in the literature of structure \( Na_2O \ Al_2O_3 \ 1.85 SiO_2 \ 5.1 H_2O \).\(^{11,12}\)

X-ray fluorescence is a suitable method that can be used for quantitative elemental analysis. Table 2 listed the results of the elemental analysis of the prepared zeolite A material. Silicon to aluminum ratio (Si/Al) gives the expected zeolite type. Based on Table 2 the prepared zeolite has Si/Al ratio of about 0.82 within the range of zeolite A reported in the literature, i.e. 0.7 to 1.2.\(^{13}\)

Thermal analysis of the prepared material was carried out with a heating rate of 5 °C/min to determine the thermal behaviour of the prepared zeolite A. Differential thermal analysis (DTA) is shown in Figure 2. The peak at 180 °C shows endothermic reaction derived from loss of combined water. Thermal gravimetric analysis for the 3.213 mg prepared zeolite A in its sodium form was performed in the range from 25–800 °C as shown in Figure 3. The total weight loss is 1.161 mg equivalent to 36.134% of the initial weight of the sample. The greater portion of weight loss occurred before 16.70 min at 180 °C and then the rest of weight loss occurred until 71.07 min. The final loss occurs at 800 °C. This weight loss shows that all combined water molecules was lost at this temperature. Results from thermal analysis mostly agreed with those reported by Yu et al.\(^{13}\)

Based on the XRD and the thermogravimetric results, the oxide chemical composition of the synthetic zeolite A can be expressed via the formula: \( Na_2O \ Al_2O_3 \ 1.85 SiO_2 \ 5.1 H_2O \). The theoretical cation exchange capacity (CEC) of synthetic zeolite A in \( Na^+ \) form equals to 5.45 meq/g on the basis of the chemical formula. The BET surface area measured of the zeolite A in sodium form after the thermal treatment for two hours at 473 K was 634.52 m\(^2\)/g.

3.2. Effect of pH. In order to investigate dependence of maximum removal efficiency on pH, experiments were conducted in the pH range 2 to 8 and the results are depicted in Figure 4. The recovery (%) of the metal ions by the prepared zeolite A increases gradually with an increase in pH value. In the subsequent studies, experiments were performed in the solution pH value of 6 to avoid any possible hydroxide precipitation.\(^{13}\)

3.3. Effect of initial concentration. The effect of initial concentration were investigated on a sorption process at a fixed temperature. The experiments were performed at the initial
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3.4. Kinetic studies. Preliminary investigations on an adsorption rate of the studied ions by the zeolite A indicated that the process is quite rapid and typically 60–80% adsorption of the equilibrium value for each ion occurred within 30 min. The initial rapid sorption takes place in the initial stage (0–30 min) and then gradually increases slowly to reach an equilibrium value in approximately 90–120 min.

The amounts of both cesium and strontium ions exchanged at the different time intervals, for the fixed concentration of 100 mg/L and at (298, 313, and 333 K), are plotted in Figure 6. The data showed that the amount of the sorbed Cs⁺ and Sr²⁺ increases with the increase in temperature. This indicate an endothermic nature of the process and the required time to reach equilibrium remained practically unaffected. Also, the amount recovery of each ion from the solution increases with time, and attained equilibrium with 90 min for cesium and 120 min for strontium. The equilibrium time was independent of the initial metal ion concentration in this study. The recovery amount versus time curves are monotonously increasing to an equilibrium, suggesting that the metal ions might cover on the surface area of the adsorbent.

Most sorption processes take place by a multistep mechanism comprising (i) diffusion across the liquid film surrounding the solid particles (a process controlled by an external mass transfer coefficient), (ii) diffusion within the particle itself assuming a pore diffusion mechanism (intraparticle diffusion), and (iii) physical or chemical adsorption at a site.

To describe the changes in the sorption of metal ions with time, several kinetic models were tested. The rate constant of each metal ion for removal reaction from the solution by zeolite A was determined using pseudo first order and pseudo second order rate models. The Lagergren first order rate expression is written as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t ,$$  

where $q_e$ and $q_t$ are the amount of an ion sorbed onto the zeolite A at equilibrium and at time $t$, respectively (mg g⁻¹) and $k_1$ is the rate constant of pseudo first order equation (min⁻¹). The slopes and intercept of the plots of $\log(q_e - q_t)$ versus $t$, as shown in Figure 7, were used to determine the first order rate constant $k_1$. It was observed that the sorption of both the ions followed the Lagergren equation over the range within 30 min and the values of the first order rate constants almost did significantly not change with temperature as listed in Table 3. A considerable deviation between the experimental and calculated $q_e$ values occurred (see Table 3), this confirms that it is not appropriate to use Lagergren kinetic model to predict the sorption kinetics of the studied ions on the zeolite A for the entire sorption period. Also, in the most cases in the literature, the pseudo first order equation of Lagergren does not fit well with the whole range of contact time and is generally applicable over
Figure 7. Lagergren plots for the sorption of (a) Cs\(^+\) and (b) Sr\(^{2+}\) ions from aqueous solutions onto zeolite A.

Figure 8. Pseudo second order kinetic plots for the sorption of (a) Cs\(^+\) and (b) Sr\(^{2+}\) ions from aqueous solutions onto zeolite A.

### TABLE 3: Pseudo first order rate constants of Lagergren plots for Cs\(^+\) and Sr\(^{2+}\) ions sorbed onto zeolite A

<table>
<thead>
<tr>
<th>Temp, K</th>
<th>(q_{t_0}^{\text{eq}}/\text{mg g}^{-1})</th>
<th>(q_{t_0}^{\text{st}}/\text{mg g}^{-1})</th>
<th>(k_1/\text{min}^{-1})</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>69.0</td>
<td>59.74</td>
<td>0.0647</td>
<td>0.968</td>
</tr>
<tr>
<td>313</td>
<td>71.7</td>
<td>58.29</td>
<td>0.0721</td>
<td>0.975</td>
</tr>
<tr>
<td>333</td>
<td>73.8</td>
<td>55.20</td>
<td>0.0771</td>
<td>0.968</td>
</tr>
</tbody>
</table>

### TABLE 4: The calculated parameters of the pseudo second order kinetic models

<table>
<thead>
<tr>
<th>Temp, K</th>
<th>(q_e/\text{mg g}^{-1})</th>
<th>(h/\text{mg g}^{-1} \text{ min}^{-1})</th>
<th>(k_2/\text{g mg}^{-1} \text{ min}^{-1})</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>76.92</td>
<td>8.881</td>
<td>0.0015</td>
<td>0.993</td>
</tr>
<tr>
<td>313</td>
<td>77.52</td>
<td>12.018</td>
<td>0.0020</td>
<td>0.991</td>
</tr>
<tr>
<td>333</td>
<td>78.13</td>
<td>15.997</td>
<td>0.0026</td>
<td>0.995</td>
</tr>
</tbody>
</table>

The initial stage (20 to 30 min) of the sorption process.\(^{17,18}\)

The pseudo second order rate model is expressed as\(^{17,19}\)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \tag{3}
\]

where \(k_2\) is the rate constant of pseudo second order equation (g mg\(^{-1}\) min\(^{-1}\)).

The kinetic plots of \(t/q_t\) versus \(t\) for Cs\(^+\) and Sr\(^{2+}\) sorption at different temperatures are presented in Figure 8. The relation is linear, and the correlation coefficient \(R^2\) suggests a strong correlation between the parameters and also explains that the ion exchange process of each ion follows pseudo second order kinetics. The product \(k_2 q_e^2\) is the initial sorption rate \(h\) represented as \(h = k_2 q_e^2\). From Table 4, it can be shown that the values of the initial sorption rate and rate constant were increased with the increase in temperature. The correlation coefficient \(R^2\) has an extremely high value (>0.99), and its calculated equilibrium exchange capacity \(q_e\) is consistent with the experimental data. These results explain that the pseudo second order sorption mechanism is predominant and that the over all rate constant of each ion exchange process appears to be controlled by the chemical sorption process.\(^{18,19}\)

Other simplified model is also tested because the above two
models equations cannot give definite mechanism. It is also known that at an intensive stirring of the sorptive system, the intraparticle diffusion of the solute sorbed from the solution into the sorbent pores could be a rate controlling mechanism. In this study, a quantitative treatment of the data based on the model suggested by Helferich was applied. Parameters were calculated using the following expressions as given by Boyd et al.:

\[ F(t) = 1 - \frac{6}{\pi^2} \sum_{n=1} \frac{1}{n^2} \exp(-D_i n^2 t/r_o^2), \quad (4) \]

\[ = 1 - \frac{6}{\pi^2} \sum_{n=1} \frac{1}{n^2} \exp(-n^2 Bt), \quad (5) \]

\[ B = \frac{\pi^2 D_i}{r_o^2}, \quad (6) \]

where \( F \) is the fractional attainment of equilibrium at time \( t \) \((F=q_i/q_e)\), \( B \) is the time constant, \( D_i \) is the effective diffusion coefficient of metal ion, and \( r_o \) is the radius of the solid particle.

The \( Bt \) values in eq 5 for values of \( F \) were obtained from Reichenberg's table. The linearity test of \( Bt \) versus time plots is employed to distinguish between film and particle diffusion controlling sorption process. If the plot is a straight line passing through the origin, then the sorption rate is governed by particle diffusion mechanism otherwise it is governed by film diffusion. Figure 9 depicts the \( Bt \) versus time plots for Cs\(^+\) and Sr\(^{2+}\) at different temperatures. The plots are linear and pass through the origin for both the ions studied, indicating the sorption process to be particle diffusion at all the studied temperatures. The values of \( D_i \) calculated at different temperatures for Cs\(^+\) and Sr\(^{2+}\) ions are presented in Table 5.

Plotting of \( \ln D_i \) versus \( 1/T \) (Figure 10) showed a straight line. This proves the validity of the Arrhenius equation:

\[ \ln D_i = \ln D_0 - \left( \frac{E_a}{RT} \right), \quad (7) \]

where, \( D_i \) is a pre-exponential constant analogous to Arrhenius frequency factor. The activation energies for both the ions, \( E_a \) were calculated from the slope of the straight lines in Figure 10 and the obtained values were presented in Table 5. Such a low value of the activation energy for the sorption of each metal ion indicates a chemical sorption process consisting of weak interaction between sorbent (zeolite A) and solute (Cs\(^+\) and/or Sr\(^{2+}\)) and illustrate that each sorption process has a low potential energy. The Arrhenius equation would be also used to calcu-
TABLE 6: Kinetic parameters and normalized standard deviations for the sorption of Cs$^+$ and Sr$^{2+}$ onto zeolite A

<table>
<thead>
<tr>
<th>Kinetic constants</th>
<th>Cs$^+$</th>
<th>Sr$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298 K</td>
<td>313 K</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pseudo-first-order rate model</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_1$ /min$^{-1}$</td>
<td>0.0647</td>
<td>0.0721</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.977</td>
<td>0.975</td>
</tr>
<tr>
<td>$\Delta q$ (%)</td>
<td>10.2</td>
<td>14.6</td>
</tr>
<tr>
<td>Pseudo-second-order model</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_2$ /g mg$^{-1}$ min$^{-1}$</td>
<td>0.0015</td>
<td>0.0020</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.993</td>
<td>0.991</td>
</tr>
<tr>
<td>$\Delta q$ (%)</td>
<td>7.9</td>
<td>6.5</td>
</tr>
<tr>
<td>Helfferich model</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_i \times 10^3$ m$^2$ s$^{-1}$</td>
<td>6.448</td>
<td>7.211</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.993</td>
<td>0.995</td>
</tr>
<tr>
<td>$\Delta q$ (%)</td>
<td>5.7</td>
<td>5.4</td>
</tr>
</tbody>
</table>

late $D_o$ which in turn is used for the calculation of activation entropy, $\Delta S^*$, of the sorption process using

$$D_o = 2.72 (k T d^2 / h) \exp \frac{\Delta S^*}{R},$$

where $k$ is the Boltzmann constant, $h$ is the Planks constant, $d$ is the average distance between two successive positions, $R$ is the gas constant, and $T$ is the absolute temperature. Assuming that the value of $d$ is equal to $5 \times 10^{-8}$ cm, the values of $\Delta S^*$ for both the ions were calculated and presented in Table 5. The negative values of activation entropy obtained for the sorption of both the ions normally reflect that no significant change occurs in the internal structure of the zeolite solid matrix during the sorption of ions.$^{21}$

The Gibbs free energy of activation, $\Delta G^*$, was calculated from the well known equation: $^{24}$

$$\Delta G^* = \Delta H^* - T \Delta S^* = E_a - RT - T \Delta S^*,$$

where $\Delta H^*$ is the activation enthalpy.

The estimated values of $\Delta H^*$ and $\Delta G^*$ were presented in Table 5. The positive $\Delta G^*$ values suggest the existence of an energy barrier and that the reaction is non-spontaneous process.$^{24}$ The positive values of $\Delta H^*$ indicate the endothermic nature for the diffusion process.

In order to compare the validity of each model more efficiently, a normalized standard deviation, $\Delta q$, is calculated using the following equation$^{25}$

$$\Delta q(\%) = 100 \times \frac{\sum [(q_{\text{exp}} - q_{\text{calc}})/q_{\text{exp}}]^2}{n-1},$$

where the superscripts 'exp' and 'calc' mean the experimental and calculated values respectively, and $n$ is the number of measurements. Based on the $\Delta q$ values, as given in Table 6, the uptake of both Cs$^+$ and Sr$^{2+}$ from aqueous solutions using zeolite A can be well described by the intraparticle diffusion model given by Helfferich. A good correlation of the rate data in this model can support the mechanism. Previous workers reported that the diffusion coefficient, $D_i$, values in the range of $10^{-11}$ to $10^{-13}$ m$^2$/s for intraparticle diffusion is considered to be the rate limiting step for the sorption of metal ions.$^{26-28}$ As per this, the rate controlling mechanism appears to be particle diffusion since the $D_i$ values are in the order of $10^{-12}$ m$^2$/s. The increase in values of the kinetic parameters with increasing temperature is mainly due to (i) the increase of the mobility of the ion and a decrease in retarding forces acting on the diffusing ion and (ii) a consequence of forming the ion hydration shell and a reduction of the limitation for diffusion in the inner part of the pore system caused by the effective size of ion.$^{29}$

4. Conclusions

In this study, the kinetic sorption of cesium and strontium ions were investigated and the following conclusions can be obtained.

1. The recovery of the metal ion was increases with the increase in the initial concentration and the amount uptake of strontium is greater than that of cesium ions in all studied concentrations.

2. The amount of the sorbed cesium and strontium ions increases with the increase in temperature, indicating an endothermic nature of the process.

3. Analysis of the respective rate data in accordance with three kinetic models revealed that the intraparticle diffusion was the rate limiting step for the sorption of cesium and strontium. Also, the obtained kinetic data provide valuable information about the exchange mechanisms.

References

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(22) D. Rechenberg, J. Am. Chem. Soc. 75, 589 (1953).