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Examination of the use of synthetic Zeolite NaA–X blend as backfill material in a radioactive waste disposal facility: Thermodynamic approach

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Abstract

The underground disposal of radioactive waste is based upon a multibarrier concept. For long-term performance assessment of radioactive repositories, knowledge concerning the sorption of radionuclides in backfill materials is required. As a part of the multibarrier system for effective isolation of radioactive waste in a repository, Zeolite NaA–X blend was prepared from fly ash, characterized, and evaluated to be used as a backfill material. In this concern, the sorption behavior of Cs^+ on the prepared material as a function of pH, initial ion concentration and temperature was studied by batch technique. The sorption isotherm data was interpreted by Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models. The application of the Langmuir isotherm yielded monolayer capacity of 1546 mmol/kg at 298 K while the maximum sorption capacity predicted by D–R isotherm was of 2446 mmol/kg. Thermodynamic parameters for the sorption system were determined at three different temperatures. The enthalpy (ΔH°), entropy (ΔS°) and free energy (ΔG°) of sorption at 298 K were found to be 25.43 kJ/mol, 93 J/mol K and −2.316 kJ/mol, respectively. The positive value of ΔH° corresponds to the endothermic nature of the sorption process. The numerical value of ΔG° decreases with an increase in temperature indicating that the sorption was spontaneous and more favorable at higher temperatures.

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Keywords: Backfill material; Synthetic zeolite; Cesium; Sorption isotherms

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1. Introduction

The fundamental safety concept for the disposal of radioactive wastes is to isolate the waste from the accessible environment for a period sufficiently long to allow substantial decay of the radionuclides and to limit release of residual radionuclides into the accessible environment [1]. The long-term safety of repository sites relies on a series of engineered and natural barrier systems. The purpose of the engineered barrier is to contain the wastes for a period of time such that short-lived nuclides have decayed and then to limit the release rate of surviving radionuclides. The purpose of the natural barrier is to retard radionuclides migration so that the radioactive inventory is substantially reduced by decay and dilute the concentration of the most long-lived nuclides [2]. The engineered barrier system (EBS), which includes the waste itself along with associated overpacks and backfill/buffer, is designed to ensure complete containment for the period when the waste is most hazardous [3].

Backfill material is an important component of a multibarriered disposal facility for low and intermediate level radioactive wastes. Backfills are used for a number of purposes: void filling to avoid excessive settlement, limitation of water infiltration, sorption of radionuclides, and precipitation of radionuclides. Typical materials used, either singly or as admixtures, include clays, cement grout, rock, and soil. It is important to select the appropriate backfill, barrier and cover materials and to engineer them in the most appropriate manner to backfill, seal and cover the disposal facilities. The extent to which this should be done depends on the types and properties of the wastes and site characteristics [4]. Selections of backfill materials for radioactive waste disposal have been derived from a much data on adsorption behavior of radionuclides on several natural and synthetic materials. Because of their ion exchange properties, low permeability and easy workability clay minerals and zeolites are candidate backfill minerals for radioactive waste repositories located in a variety of geological environments [5]. For long-term performance assessment of radioactive repos-

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itories, knowledge concerning the migration of radionuclides in the backfill materials is required [6]. Sorption reactions are expected to retard the migration of radionuclides thereby reducing the potential radiological hazard to humans resulting from disposal of radioactive waste. Sorption models are required to quantify the extent to which this hazard can be reduced [7]. Various candidate materials were examined by many authors [8–14] in terms of their thermal and radionuclide sorption properties for their potential use as backfill materials in radioactive repositories.

In this study fly ash (FA), obtained from an Egyptian thermal electric power station as by-product, was used as raw material for synthesis of Zeolite NaA–X blend by alkaline fusion and SiO_2 extraction at laboratory scale. To evaluate the feasibility of using synthetic Zeolite NaA–X prepared from FA as backfill material in the proposed radioactive waste disposal facility in Egypt. The sorption behavior of cesium, as one of the most important radionuclides commonly encountered in Egyptian waste streams, was studied as a function of initial metal ion concentration, pH, and temperature. The sorption data were interpreted using Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherms and various thermodynamic parameters were determined.

2. Materials and methods

The FA used in this study was obtained from an Egyptian thermal electric power station. The bulk chemical composition of the used FA was determined by XRF (X-ray fluorescence vacuum spectrograph, Philips) and is listed in Table 1. The morphological structure of the raw FA and the prepared zeolitic material were obtained by using scanning electron micrograph (JEOL, JSM-5400). Samples were mounted on suitable substrates using a conductive glue and were then coated with a thin layer of gold. The total surface area of synthesized powder was measured using Standard Volumetric Method by nitrogen adsorption at 77 K and application of BET equation by means of Nova 3200 BET instrument, Quantachrome Corporation, USA.

All chemicals and reagents used were of AR grade. The reactive amorphous SiO_2 content in FA was used as silicon source. Sodium aluminate (Riedel-De-Haen AG) and sodium hydroxide (Merck) were used as aluminium and sodium sources in zeolite preparation mixture, respectively. Cesium chloride was BDH product.

Table 1
Chemical composition of raw fly ash

Oxide	wt.%
SiO_2	43.81
Al_2O_3	23.18
Na_2O	0.87
MgO	0.80
P_2O_5	0.49
SO_3	15.68
Cl	4.01
K_2O	2.72
CaO	6.10
TiO_2	2.31
Fe_2O_3	0.01

2.1. Synthesis of pure NaA–X zeolite blend

The fusion method used for silica extraction comprises of two stages. In the first, 10 g of grinded FA was mixed and grounded with 10 g NaOH to obtain a homogeneous mixture; this was then heated in a crucible in air at 550 °C for different time intervals (15, 30, 45 and 60 min) to explore the effect of this parameter on the amount of extracted silicon and aluminium. Secondly, the fusion product was ground and mixed with 170 ml distilled water, followed by vigorous shaking in a shaking water bath at room temperature for 30 min however, under extended period of time and higher temperatures, it led to the formation of zeolite phase on the outer surface of FA particles, thus, the amount of Si extracted from FA was limited. At the end of the process the solid is separated by filtration and the process was repeated three times to ensure that all available amounts of Si and Al were leached in the filtrates. The collected filtrates were analyzed by conventional wet chemical technique [15]. SiO_2 and Al_2O_3 were analyzed using spectro-photometric methods at wavelengths 640 and 475 nm, respectively. All analyses were estimated using a series of international and reference standards. These collected filtrates were used as starting solutions to optimize the pure NaA–X zeolite blend synthesis using the molar oxide ratios of $SiO_2/Al_2O_3 = 2.1$, $Na_2O/SiO_2 = 1.4$ and $H_2O/Na_2O = 39.0$, based on the methodology devised by Saez [16]. Sodium aluminate solution was used externally to adjust the SiO_2/Al_2O_3 ratio to the desired value. A gelification stage for 2 h at 80 °C and an ageing stage for 24 h at room temperature were done. The resulting mixture was crystallized for 8 h at 90 °C. At the end of the process the solid is separated by filtration, washing several times with distilled water (until the solution reached pH 10) and then dried overnight at 105 °C. X-ray powder diffraction measurements were performed using a Shimadzu (Japan) diffractometer. The conditions of these measurements were set to use Cu Kα radiation and Ni filter. Analysis of the diffraction patterns was made by the whole-powder pattern-fitting computer program intraconnected to the system.

2.2. Sorption studies

The parametric effects of the initial ion pH on the sorption processes were investigated. The initial pH was adjusted to values ranging from 2 to 8 using dilute solution of hydrochloric acid or sodium hydroxide.

The sorption of cesium on Zeolite NaA–X (250 μm particle size) was studied by batch technique at different temperatures (298, 313, and 333 K) to obtain the equilibrium isotherms. For isotherm studies a known weight of the sorbent (10 mg) was agitated with 10 ml of cesium chloride solution of varying concentrations, 7.5×10^{-4} to 7.5×10^{-3} M. After the established contact time (3 h) was reached, aliquots of supernatant was withdrawn and the amount of the metal ion retained in the solid phase

q_e (mmol/kg) was estimated by

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_0 is the initial concentration (mmol/m^3), C_e the equilibrium solution concentration of sorbate (mmol/m^{-3}), V the volume (m^3) and m is the weight of the sample (kg).

3. Results and discussion

3.1. Characterization of materials

The X-ray diffraction pattern of raw FA is shown in Fig. 1(a). From this figure it was found that quartz and mullite exists as crystalline substances, as identified by the sharp peaks, while the presence of amorphous phases were identified by board diffraction peak (near $2\theta = 24°$) [17]. The obtained XRD for the prepared zeolite (b) showed that the optimized experimental conditions by Sáez [16] allowed the synthesis of pure zeolite from the SiO_2 extracts of FA. $SiO_2/Al_2O_3/Na_2O$ ratios were adjusted by combining SiO_2 extracts with additional sources of $NaAlO_2$ and NaOH.

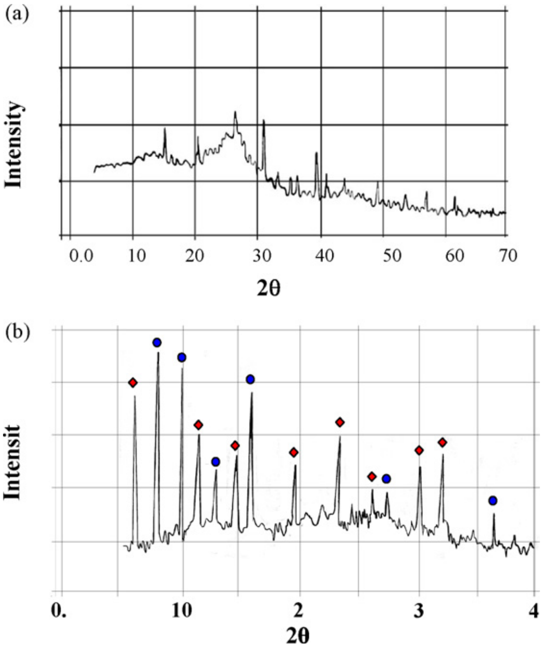

Fig. 1. X-ray diffraction pattern for (a) raw fly ash and (b) synthesized Zeolite NaA–X [◆ Zeolite X and ● Zeolite A].

The dissolution of FA during the fusion reaction was also confirmed by SEM. Fig. 2 depicts the SEM pictures of untreated FA and fused FA at time intervals from 15 to 60 min. The original FA is seen to consist of smooth and spherical particles interspersed with a small fraction of aggregates of crystalline compounds which may correspond to α-quartz and mullite [18]. The fine spherical particle seems to be glassy due to the surface coverage with amorphous aluminosilicates [19]: (a) when FA is fused with sodium hydroxide (1:1) for 15 min the amorphous aluminosilicates in fly ash were dissolved, small surface cracks appeared and

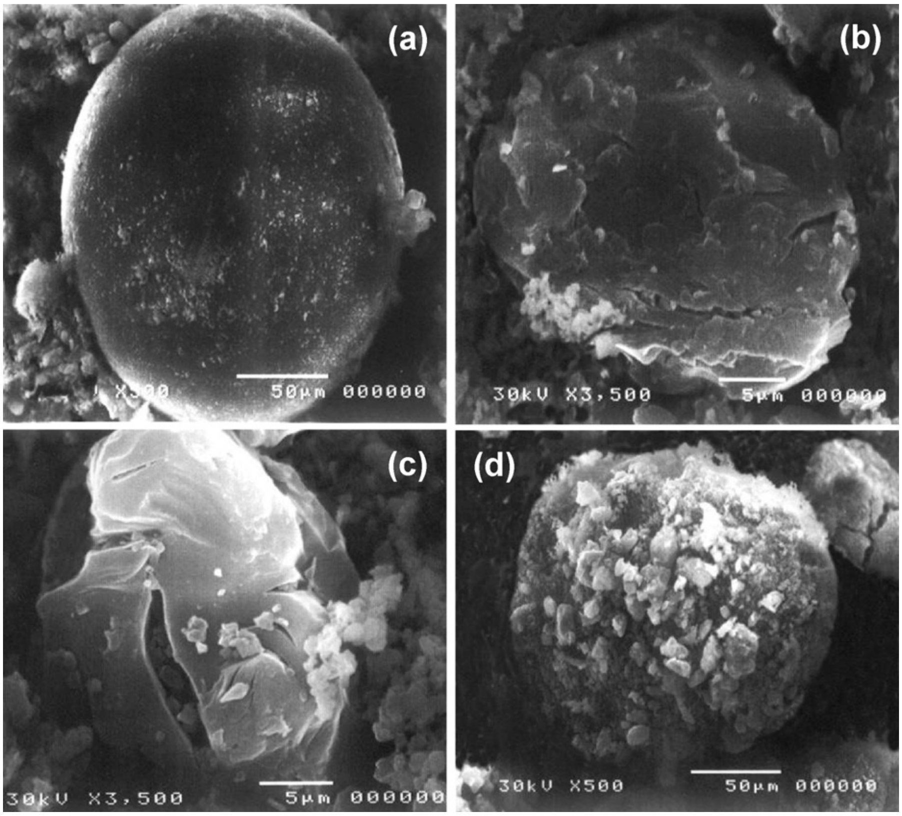

Fig. 2. SEM micrograph for raw FA (as received) and fused FA at different intervals.

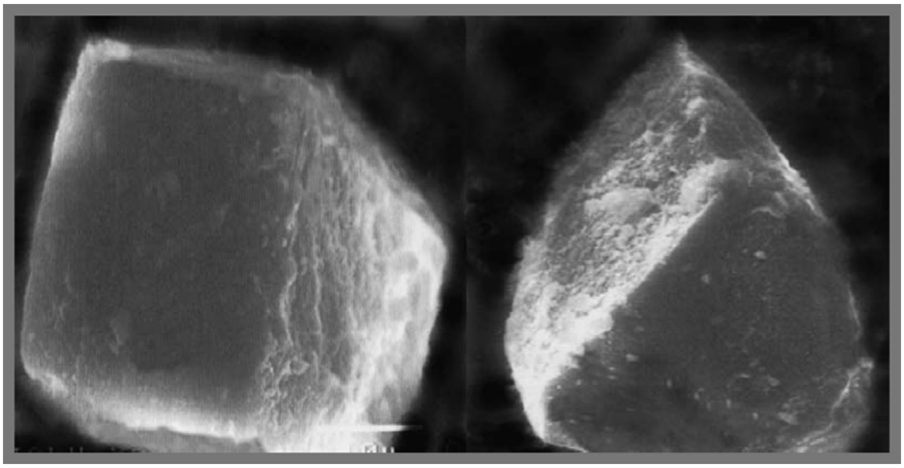

Fig. 3. SEM micrograph for synthetic Zeolite NaA–X blend.

the particle surface changed, like unevenness; (b) upon increasing the fusion time to 30 min the surface of FA plerosphere became rough, burst and larger cracks were appeared librating small aggregates; (c) at 60 min fusion time, small cenosphere appeared and several crystalline materials were precipitated onto the surface of FA particle (d). The formation of Na–A and Na–X zeolites was also confirmed by SEM observation. Fig. 3 shows the SEM picture of the synthesized zeolite blend providing an evidence for cubic crystal characteristic for Na–A zeolite and the pyramidal octahedral crystal of Na–X zeolite [20]. It was shown from the elemental analysis of synthesized Zeolite A–X blend (wt.%) (Table 2) that the percentage of sulphur was significantly reduced compared with that present in raw fly ash. This may be due to the fusion process used in the dissolution of fly ash. Fusion process made a flash burn of fly ash. This flash burn may be due to the burn of sulphur when contacted with air. The specific surface area (m^2/g) of the synthesized solid powder was measured and the results indicated that the synthetic A–X zeolite blend has specific surface area of 593.64 m^2/g.

3.2. Effect of pH

The effect of pH on the sorption of Cs^+ ions from aqueous chloride solutions using prepared Zeolite NaA–X material was investigated over the pH range from 2.0 to 8.0. It was observed that the acidic medium has an inhibitory effect on the sorption process. This may be due to the competition behavior between hydrogen ions and studied ions for sorption onto the synthesized powder. The uptake was continuously increased from 18.6% to 62.6% with the increase in pH value and the maximum uptake was found to be 64.1% and it was observed at pH range from 6.0 to 8.0 (figure omitted). It was also known that mineral acids affect the structure of zeolites. In the zeolite framework, the Si–O–Al is weaker than Si–O–Si and can be easily be attached by H^+ ions affecting the zeolite structure. This defect is more so in case of zeolites with low Si/Al ratios such as Zeolite A and X types [21]. The extent of damage to their structure depends on pH of the solution. The structure of zeolites, particularly with low Si/Al ratios, may collapse in the presence of solutions with pH lower than 5.0, but the severity would be more below pH 3.0. In fact, pH less than 5.0 is not recommended for zeolites [22]. So, all sorption experiments in the present study were carried out at initial pH value of 6.0. Also it was observed that sorption of Cs^+ caused the decrease of the final pH from 6 to 5.5.

Table 2
Elemental analysis of synthesized Zeolite A–X blend (wt.%)

Element	wt.%
Na	27.79
Al	33.41
Si	38.34
Ca	0.067
Ti	0.081
Mg	0.062
Fe	<0.01
S	0.002
K	0.056
P	0.004
Other elements	<0.1

Si/Al = 1.15 in the range of both A and X zeolite types.

3.3. Sorption isotherms

The equilibrium sorption isotherms are one of the most important data to understand the mechanism of the adsorption [23]. In this concern, the sorption isotherms of Cs^+ ions from aqueous chloride solutions onto Zeolite NaA–X sorbent at three different temperatures were determined and shown in Fig. 4(a–c). The isotherms are regular, positive, and concave to the concentration axis. These results reflect the efficiency of Zeolite NaA–X for the sorption of Cs^+ ions from aqueous solution in a wide range of concentrations. The uptake of ions increased with the increase in temperature thereby indicating the process to be endothermic. The isotherm parameters were evaluated using Langmuir, Freundlich, and D–R isotherm models.

3.4. Langmuir isotherm model

Langmuir sorption isotherm models the monolayer coverage of sorption surfaces and assumes that sorption occurs on a

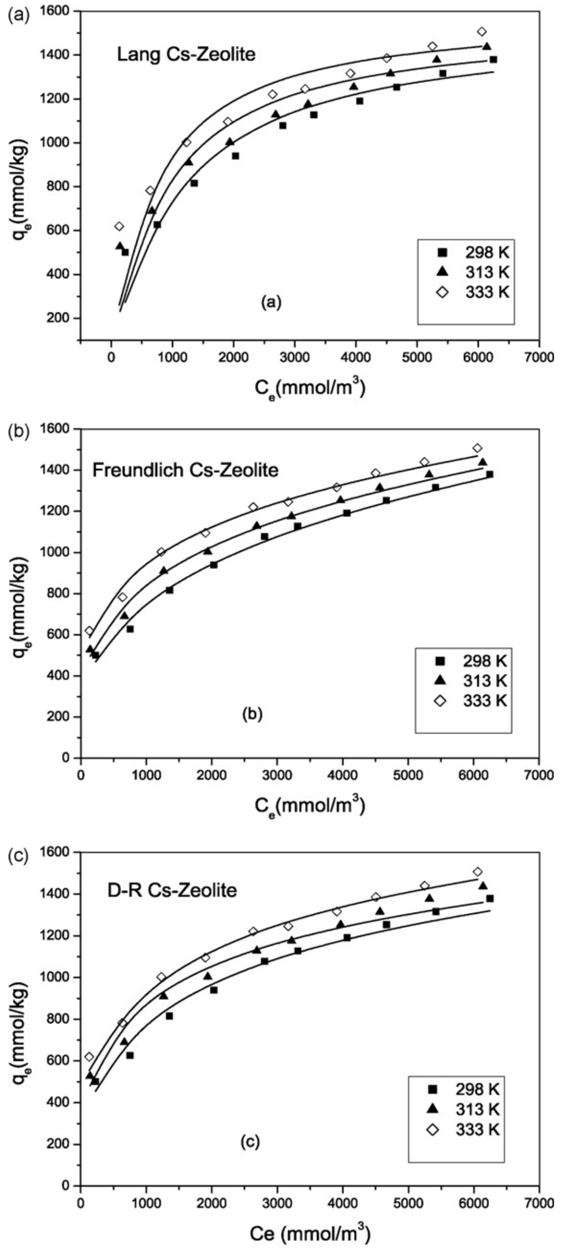

Fig. 4. Sorption of Cs^+ on Zeolite NaA–X at different temperatures. The solid lines represent the fitting of data by (a) Langmuir; (b) Freundlich; (c) D–R isotherms.

structurally homogeneous adsorbent and all the sorption sites are energetically identical. The linearized form of the Langmuir equation is given by the following formula:

$$\left(\frac{C_e}{q_e}\right) = \left(\frac{1}{Q^0 b}\right) + \left(\frac{1}{Q^0}\right) C_e \tag{2}$$

where C_e is the equilibrium concentration of metal ion in equilibrium solution (mmol/l), q_e the amount of metal ion sorbed per unit weight of sorbent (mmol/kg), Q^0 the monolayer adsorption capacity (mmol/kg) and b is a constant related to the free energy of adsorption ($b \propto e^{-\Delta G/RT}$).

The graphic presentations of C_e/q_e versus C_e give straight lines for Cs^+ ions sorbed onto Zeolite NaA–X, as represented in Fig. 5(a), confirming that this expression is indeed a reasonable representation of chemisorption isotherm. The numerical value of constants Q^0 and b evaluated from the slope and intercept of each plot are given in Table 3. The value of saturation capacity Q^0 corresponds to the monolayer coverage and defines the total capacity of the sorbent for Cs metal ion. As it can be seen from Table 3, the monolayer sorption capacity (Q^0) values define the total capacity of the prepared Zeolite NaA–X towards Cs^+ ions. The Langmuir constants Q^0 and b for sorption of Cs^+ ions increased with temperature showing that the sorption capacity and intensity of sorption are enhanced at higher temperatures. This increase in sorption capacity with temperature suggested that the active surfaces available for sorption have increased with temperature [24]. One of the essential characteristics of the Langmuir model could be expressed by dimensionless constant

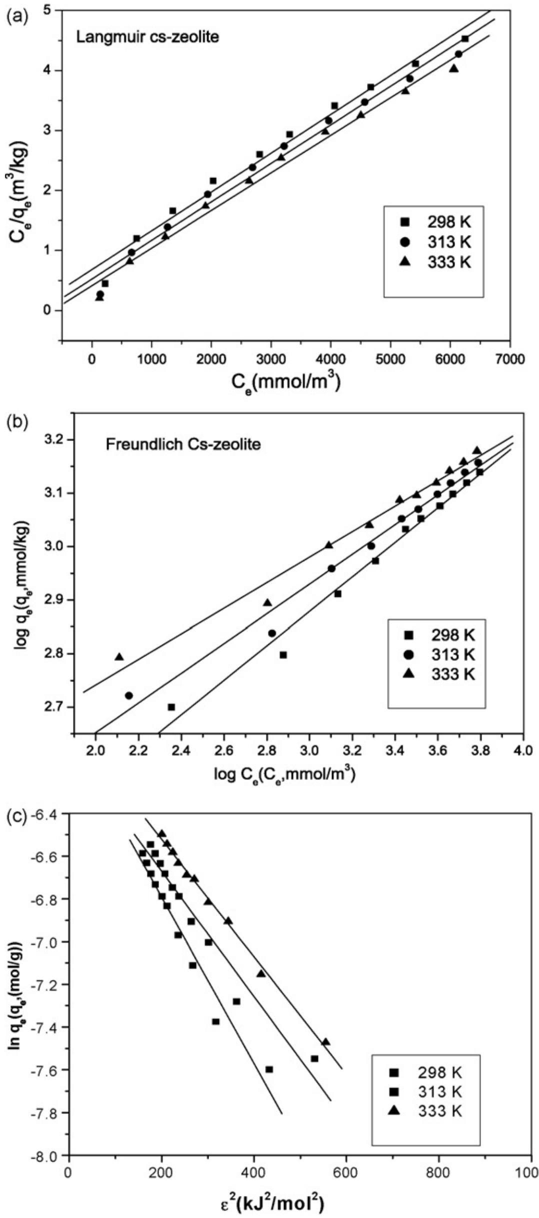

Fig. 5. Isotherm plots of Cs^+ ions sorbed onto synthetic Zeolite NaA–X blend: (a) Langmuir; (b) Freundlich; (c) D–R.

Table 3
Langmuir and Freundlich isotherm

	Freundlich		R^2	R_L	Temperature (K)		Langmuir R^2
	Q (mmol/kg)	b (L/mmol)			$1/n$	K_f (mmol/kg)	
298	1546.0	0.948	0.995	0.123	0.3222	81.73	0.985
313	1556.7	1.223	0.995	0.098	0.2779	124.79	0.985
333	1595.6	1.517	0.996	0.087	0.2386	183.81	0.982

called equilibrium parameter R_L [25]:

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

where C_0 is the highest initial metal ion concentration (mg/L). The value of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). All the R_L values (Table 3) were found to be less than 1 and greater than 0 indicating the favorable sorption isotherms of metal ions.

3.5. Freundlich isotherm model

Freundlich equation is derived to model the multilayer sorption and for the sorption onto heterogeneous surfaces. The logarithmic form of Freundlich equation may be written as

$$\log\, q_e = \log\, K_f + \left(\frac{1}{n}\right) \log\, C_e \tag{4}$$

where K_f is constant indicative of the relative adsorption capacity of the sorbent (mmol/kg) and $1/n$ is the constant indicative of the intensity of sorption process. The pictorial illustration of $\log q_e$ versus $\log C_e$ is shown in Fig. 5(b), which suggests that sorption of Cs^+ onto Zeolite NaA–X obeys Freundlich isotherm over the entire range of sorption concentration studied. The numerical values of the constants $1/n$ and K_f are computed from the slope and intercepts, by means of the linear least square fitting method, and given in Table 3. The $1/n$ value is usually dependent on the nature and strength of sorption process as well as on the distribution of active sites. The numerical values of K_f represent sorption capacity of Cs^+ sorbed onto Zeolite NaA–X of a narrow sub-region having equally distribution energy sites towards cesium ions.

3.6. Dubinin–Radushkevich (D–R) isotherm model

D–R isotherm describes sorption on a single type of uniform pores. In this respect, the D–R isotherm is an analogue of Langmuir type but it is more general because it does not assume a homogeneous surface or constant sorption potential [26]. The D–R isotherm is given with the following equation:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{5}$$

where q_m is the maximum amount of ions that can be sorbed onto unit weight of sorbent, i.e., sorption capacity (mmol/kg), β a constant related to the sorption energy (mol^2/kJ^2); and ε the Polanyi potential $\varepsilon = RT\ln(1 + 1/C_e)$, where R the gas constant (kJ/mol K), and T is the absolute temperature.

The mean free energy of sorption is the free energy change when one mole of ion is transferred to the surface of the sorbent from infinity in the solution, and it is calculated from

$$E = (-2\beta)^{-1/2} \tag{6}$$

The magnitude of E can be related to the reaction mechanism. If E is in the range of 8–16 kJ/mol, sorption is governed by ion exchange [27] In case of $E < 8$ kJ/mol, physical forces may affect the sorption mechanism.

The D–R plots of $\ln q_e$ versus ε^2 for sorption of Cs^+ ions onto studied sorbents at different temperatures are given in Fig. 5(c), these linear plots indicate that the D–R isotherm expression is followed for Cs^+ ions. Linear regression analysis using $\ln q_e$ and ε^2 resulted in derivation of q_m, β, E and the correlation factor (R^2). The correlation factor is a statistical measure of how well the data points fit the regression line. These D–R parameters, evaluated for sorption of Cs^+ ions at different temperatures, are presented in Table 4. The maximum sorption capacities of Zeolite NaA–X (q_m) are in the ranges of 2445.9–2550.9 mmol/kg. The values of the mean free energy, E, of sorption in all cases is in the range of 8–16 kJ/mol, which are within the energy ranges of ion exchange reaction.

3.7. Effect of temperature

In order to gain insight into the thermodynamic nature of the sorption process, several thermodynamic parameters for the present system were calculated. The Gibbs free energy change, ΔG°, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative quantity.

The free energy of the sorption reaction is given by the following equation:

$$\Delta G^\circ = -RT\, \ln\, K_c \tag{7}$$

where K_c is the sorption equilibrium constant, R the gas constant and T is the absolute temperature (K). The values of thermodynamic equilibrium constant at different studied temperatures were determined by plotting $\ln q_e/C_e$ against q_e and extrapolating to zero q_e according to the method of Khan and Singh

Table 4
D–R isotherm parameters of Cs^+ ions sorbed onto Zeolite NaA–X

Temperature (K)	β (mol^2/kg^2)	q_m (mmol/kg)	R^2	E (kJ/mol)
298	−0.00389	2445.9	0.966	11.337
313	−0.00293	2278.0	0.963	13.063
333	−0.00275	2550.9	0.958	13.48

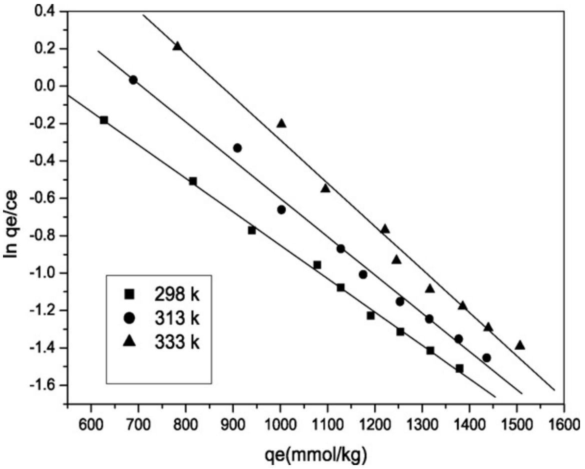

Fig. 6. Plot of $\ln(q_e/C_e)$ vs. q_e for sorption of Cs^+ ions sorbed onto synthetic Zeolite NaA–X blend.

Table 5
Values of thermodynamic parameters for sorption of Cs^+ ions onto Zeolite NaA–X

Temperature (K)	K_c	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
298	2.547	−2.316		
313	4.241	−3.670	25.43	93
333	7.500	−5.570		

[28] as shown in Fig. 6. The variation of K_c with temperature, as summarized in Table 5, showed that K_c values increase with increase in sorption temperature, thus implying a strengthening of adsorbate–adsorbent interactions at higher temperature. Also, the obtained negative values of ΔG° confirm the feasibility of the process and the spontaneous nature of the sorption processes. Other thermal parameters such as enthalpy change (ΔH°), and entropy change (ΔS°) were calculated using the relationship:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{8}$$

The values of enthalpy change (ΔH°) and entropy change (ΔS°) calculated from the slope and intercept of the plot of $\ln K_c$ versus $1/T$ (Fig. 7) are also given in Table 4. The change in ΔH° for Cs^+ ions in Zeolite NaA–X was found to be positive confirming the endothermic nature of the sorption processes. ΔS° values were found to be positive due to the exchange of the metal ions with more mobile ions present on the sorbent, which would cause increase in the entropy during the sorption process. In the case of physisorption, which may also contribute to the total sorption process, water molecules released from the hydrated metal ions or from the sorption surface may also cause an increase in the entropy.

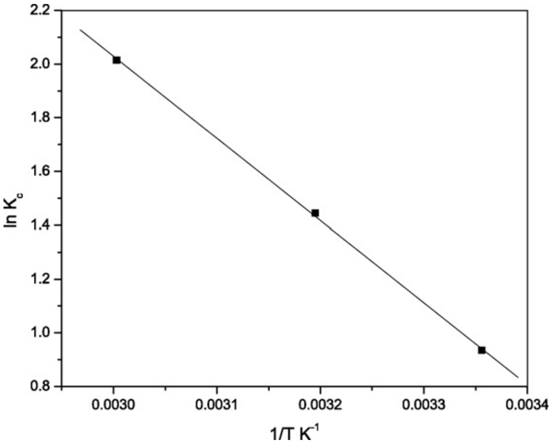

Fig. 7. Plot of $\ln K_c$ vs. $1/T$ for the sorption of Cs^+ ions sorbed onto synthetic Zeolite NaA–X blend.

4. Conclusion

Zeolite NaA–X was tested as sorbent material for the sorption of cesium ions from chloride waste solutions. Equilibrium isotherms have been determined and tested for different isotherm expressions and the sorption data were successfully modeled using Langmuir, Freundlich, and D–R approaches. Based on the D–R model expression, the maximum sorption capacity and the mean free energy of the studied Cs^+ have been determined. The values of the mean free energy, E, of sorption at the studied temperatures is in the range of 8–16 kJ/mol, which are within the energy ranges of ion exchange reaction. The sorption of Cs^+ ions is an endothermic process and the results show that the prepared zeolite can be fruitfully used as backfill materials in the proposed shallow disposal facility in Egypt.

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