Evaluation of the possible use of a Bulgarian clinoptilolite for removing strontium from water media

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ABSTRACT: The sorption of Sr^{2+} ions by natural clinoptilolite was investigated using the batch method. The effects of pH, contact time and strontium concentrations were tested and the optimal conditions for sorption were determined. The process was very fast initially and equilibrium was reached within 24 h. Kinetic sorption data were fitted to pseudo-first-order, pseudo-second-order and intra-particle diffusion models. The simple pseudo-second-order rate model provides good agreement with the experimental data for Sr^{2+} uptake. The respective rate constants, k_2, calculated at different initial Sr^{2+} concentrations, were obtained. The equilibrium data were analysed by applying the Langmuir, Freundlich and Dubinin−Raduchkevich isotherm models. The Langmuir model describes the observed Sr^{2+} uptake most accurately and the value of the monolayer sorption capacity is 32.81 mg Sr^{2+}/g. The effect of Na^+ ions and the effectiveness of uptake from low saline groundwater simulated solutions were also studied and discussed.

KEYWORDS: clinoptilolite, Sr^{2+} uptake, ion exchange, kinetics, equilibrium.

Strontium radionuclides in the environment originate from two main sources; either from the improper release of radioactive waste from reprocessing and recovery of uranium and plutonium or via leaching from rocks by natural water movement, which can result in low concentrations that can be detected even in potable water far away from radioactive waste depositories.

The stable isotopes of strontium are harmless, but the harmful, long-lived radioisotopes ^{90}Sr and ^{89}Sr are now distributed widely in the environment and are harmful. Strontium can mimic calcium in biological systems and health damage can occur when the isotope ^{90}Sr replaces calcium in the body; especially in the long bones, as they contain the blood forming cells and the radioactivity can cause genetic changes, leukaemia and other diseases. For these reasons the strontium content should be controlled and limited by selective removal prior to the final disposal of wastes.

Among the different techniques used for removing harmful or recovering useful elements from solution, sorption by inorganic adsorbents such as natural zeolites is most appropriate for removal of radionuclides. From the technological point of view zeolites are convenient because of their great adsorption efficiency over a relatively large pH range, their fast adsorption kinetics and their chemical, radiological and thermal stability. In addition they are common low-cost minerals. Zeolites that have been investigated for this purpose are mordenite (Rajec *et al*., 1977), chabazite (Mimura & Kanno, 1985) and, especially, natural or modified clinoptilolite or clinoptilolite-containing composites (e.g. concretes) (Rajec *et al*.,

1977; Faghihian *et al.*, 1999; Marinin & Brown, 2000; Smičiklas *et al.*, 2007; El-Kamash, 2008; Yusan & Erenturk, 2011; Hossein *et al.*, 2013; Huang *et al.*, 2013). Variations in the chemical composition of clinoptilolites from different deposits, together with the substantial differences in their sorption properties often necessitate individual investigation of a particular source material for application in concrete technology (Langella *et al.*, 2000; Petrus & Warchol, 2005).

The objective of this study was to determine the kinetics and sorption equilibria of strontium from model natural waters by Bulgarian clinoptilolite in order to derive mathematical models for the processes. The equations obtained may aid the estimation of metal-cation-sorption equilibrium and kinetic parameters for prediction of optimum conditions for using zeolites for purification of drinking water and wastewater treatment. The ultimate aim of this study was the application of clinoptilolite as a permeable reactive barrier for removal of Sr^{2+} contamination from groundwater.

MATERIALS AND METHODS

The clinoptilolite sample used in the study is a clinoptilolite-rich tuff from the volcano-sedimentary deposit at Beli Plast (Eastern Rhodopes, Bulgaria), denoted herein as "natural clinoptilolite". The material was crushed, ground, sieved and the <75 μm fraction was isolated for further use. The mineralogical composition of the natural clinoptilolite sample was determined by powder X-ray diffraction (XRD) using a D2 Phaser diffractometer (Bruker) in Bragg−Brentano geometry with Ni-filtered Cu-*K*α radiation.

The elemental composition of the natural clinoptilolite sample was determined by atomic adsorption spectrophotometry (AAS), using a Perkin-Elmer 30-30 instrument. Silicon was determined gravimetrically.

The cation exchange capacity (CEC) was measured by exhaustive exchange of the zeolite (0.2 g) extra-framework cations with aqueous ammonium ions (50 mL 0.5 mol L^{-1} NH$_4$NO$_3$ solution) at 60ºC over 3 days; the exchange solution being separated and replenished daily (Bogdanova *et al.*, 1995). The CEC was calculated from the difference in elemental composition before and after the NH$_4^+$ exchange procedure, which allows determination of the extra-framework cation content.

Sorption experiments

As these experiments can be best understood by considering the relative concentrations of cationic charges, concentrations will usually be expressed as Normality (N), which equals the molarity (M, mol L^{-1}) multiplied by the cation charge (N = mol L^{-1} × charge). A stock solution of Sr^{2+} cations (~0.1 N (mol L^{-1} × 2)) was prepared from reagent-grade SrCl$_2$.6H$_2$O (Merck) and the exact concentration determined by AAS. Appropriate dilutions of the stock solution were used for the batch adsorption experiments. A solid-to-solution ratio of 1:200 (0.1 g natural clinoptilolite to 20 ml of Sr solution) was used in all room-temperature experiments in screw-capped polyethylene centrifuge tubes. The pH of the experimental solutions was adjusted by addition of dilute HCl or NaOH solutions (Consort C833 pH meter), as appropriate. The suspensions were shaken at room temperature on a horizontal shaker (amplitude of 20 mm, 150 oscillations/min). Each sorption experiment was carried out in duplicate and after the end of the adsorption time the suspension was centrifuged for 15 min at 5000 rpm. The pH values of the recovered solutions were measured and their strontium concentrations measured by AAS. The concentration of sorbed strontium in the solid phase was calculated from the difference between the concentrations of Sr added and that remaining in the equilibrium solution using the mass-balance equation:

$$q_e = [(C_0 - C_e)\, V]/m \qquad (1),$$

where: q_e (mg/g) is the concentration of metal ions in the solid phase, C_0 and C_e (mg/L) are the initial and equilibrium concentrations in the experimental solutions, respectively, V (L) is the volume of strontium solution and m (g) is the sorbent mass.

The sorption effectiveness ($E\%$) was calculated using equation 2:

$$E\% = 100 m_s/(V C_0) \qquad (2)$$

where: C_0 (mg/L) is the initial concentration of Sr^{2+} ions in the solution, m_s (mg) is the mass of the metal sorbed and V (L) is the volume of solution from which the sorption occurs.

Effect of the experimental conditions on the Sr^{2+} uptake

The effect of pH on the strontium sorption was investigated in a similar manner to that described above using 100 mg/L Sr solutions at pH 2.0−6.0,

by stirring the suspensions for 24 h at room temperature.

Kinetic runs were performed to determine the adsorption rate of the Sr^{2+}. Strontium uptake as a function of time was determined with batch experiments using 17.95 and 200 mg/L initial Sr^{2+} concentrations at initial pH 5.4. The contact time varied between 15 min and 24 h, after which the strontium concentration and the pH in the recovered solutions were determined.

The effect of the initial Sr^{2+} concentrations on the amounts of sorbed metal at equilibrium, at optimal pH and contact time, was studied further. Strontium uptake isotherms were obtained from batch equilibrium experiments. The initial Sr concentrations were $10-2500$ mg/L, the pH was 5.4 and the contact time was 24 h at room temperature.

The distribution coefficient K_d was determined from equilibrium tests with solutions containing 1×10^{-3} N (43.8 mg/L) Sr^{2+}, by the equation:

$$K_d = 1000\, q_e/C_e \qquad (3)$$

where: K_d is expressed in ml/g and C_e (mg/L) and q_e (mg/g) are the concentrations of Sr^{2+} ions in the solution and the solids, respectively.

Modelling of ion exchange kinetics and equilibrium data

The kinetics of strontium uptake by clinoptilolite was studied by applying the pseudo-first- and pseudo-second-order kinetic models (Wu *et al.*, 2001; Reddad *et al.*, 2002). In their integrated linear forms for the boundary conditions $t = 0$ to t and $q_t = 0$ to q_t the models can be expressed by equations 4 and 5, respectively:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)\, t \qquad (4)$$
$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)\, t \qquad (5)$$

where: k_1 is the apparent pseudo-first-order rate constant (min^{-1}), k_2 is the apparent pseudo-second-order rate constant (g/(meq min)) and q_t and q_e are the quantities of sorbed element (in meq/g), respectively, at time t and at equilibrium.

There is one more parameter — the initial sorption rate, h, that can be derived and defined from the linear form of the second-order rate equation (Ho & Ofomaja, 2006).

Equation 5 could be re-written as:

$$q_t/t = h/(1 + kq_e t) \qquad (6)$$

where: $h = k_2 q_e^2$. Consequently, h (meq/(g min)) can be considered as the initial sorption rate q_t/t, when t approaches 0.

The adsorption isotherms describe the equilibrium established between the ion concentration in solution and the sorbed amount at different initial concentrations. The basic adsorption models that were applied were those of Langmuir (equation 7), Freundlich (equation 8) and Dubinin–Raduchkevich (equation 9).

$$C_e/q_e = 1/q_m b + C_e/q_m, \qquad (7)$$
$$\log q_e = \log K_F + 1/n \log C_e \qquad (8)$$
$$\ln q_e = \ln q_m - k_{DR}\, \varepsilon^2 \qquad (9)$$

where: C_e (meq/L) and q_e (meq/g) are the equilibrium Sr concentrations in the aqueous phase and the solid phase, respectively, and q_m (meq/g), represents the maximum ion exchange capacity. The Langmuir parameter b (L/meq) is the site energy factor, describing the equilibrium constant (affinity term), where K_F $(meq/g)/(meq/L)^{1/n}$ and n (dimensionless) are Freundlich parameters; k_{DR} (mol^2/kJ^2) relates to the free energy of ion exchange and ε (kJ/mol) is the Polanyi potential.

The kinetic and equilibrium data were fitted by regression analysis to the kinetic and isotherm models. The applicability of isotherm-model equations was estimated by the correlation coefficients and the accord between the calculated and the experimentally determined parameters.

RESULTS AND DISCUSSION

Material characterization

The zeolite tuff consists of ~85 wt.% clinoptilolite and a small amount of opal-CT (~15 wt.%) (Fig. 1). The chemical composition of the clinoptilolite sample was: 66.58 SiO_2, 10.74 Al_2O_3, 0.28 Fe_2O_3, 0.27 TiO_2, 3.16 CaO, 0.86 MgO, 0.67 Na_2O, 2.95 K_2O (wt.%) with 13.84 loss on ignition.

The cation exchange capacity (CEC), the measure of the real availability of extra-framework cations for exchange, is 1.97 meq/g or 86.46 mg Sr/g. The individual exchangeable cations are: Ca^{2+} 1.16, Mg^{2+} 0.22, Na^+ 0.15 and K^+ 0.45 meq/g.

Ion exchange experiments

Effect of pH. The pH of the suspension is an important parameter controlling the ion uptake efficiency. The type of ions and their behaviour in
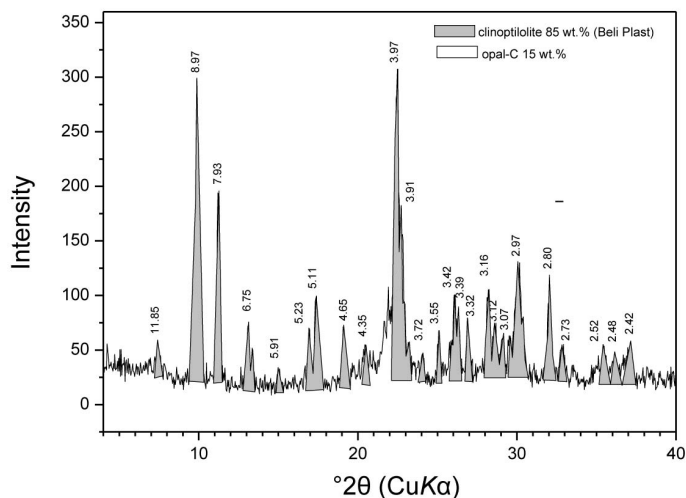
FIG. 1. Powder XRD pattern of the clinoptilolite used.

solution are determined by the pH value, which can induce hydrolysis, precipitation and formation of different ionic species and complexes of the studied element. Strontium is stable as a divalent cation over a wide range of pH values. The pH may affect the surface sites of the sorbent provoking dissolution; hence the interaction between the sorbed ions and the sorbent is highly dependent on the initial pH. On the other hand, the final pH depends on the ions taken up and gives information about the nature and mechanisms of reactions.

Figure 2 shows the removal of Sr in mg per g of sorbent and the corresponding values of pH at the end of adsorption, for initial pH values 2.0–6.1. At pH = 2 the ion exchange of strontium is limited, due to competitive adsorption of H^+ ions. As the pH increases to 3 the amount of sorbed strontium increases, reaching a plateau, which remains until the last experiment at pH 6. The final pH (pH_{fin}) of the solution follows the same trend. According to hydrolysis constants, strontium is in the form of Sr^{2+} in the pH range 2–8. At pH values up to 11, a
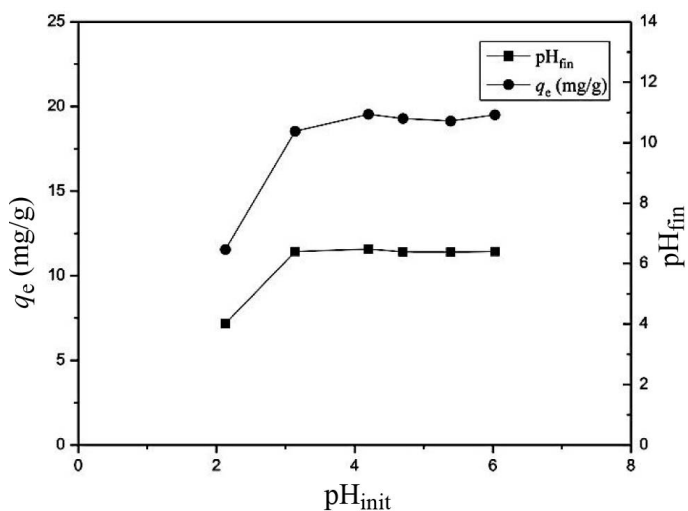

FIG. 2. Effect of initial pH values on the final pH and the sorbed amount of Sr (q_e) by natural clinoptilolite (0.1 g sorbent, 20 mL Sr 100 mg/L, t = 24h).

small amount of Sr(OH)$^+$ forms and this species predominates above pH = 13 (Yavari *et al.*, 2010). Based on these results the pH of the suspension was fixed to 5.4 for the adsorption experiment.

Effect of interaction time and kinetics of Sr^{2+} ion exchange. The rate and degree of uptake for two increasing initial Sr^{2+} concentrations are shown in Fig. 3. For the lower concentration of 17.95 mg/L the Sr^{2+} concentration decreased sharply within the first 10 min and then slowly over the next 6 h, after which the system reached equilibrium. At the Sr^{2+} concentration of 200 mg/L, after the first fast adsorption within 15 min, the Sr^{2+} concentration decreased slowly over the next 2 h and then approached equilibrium within 24 h. These results are in accord with previous studies that reported equilibrium being reached after 6 h (Smičiklas *et al.*, 2007) and 20 h (Yang *et al.*, 2013). The pH$_{fin}$ after adsorption increased with increasing contact time to 6.4−6.8 and 5.4−5.6, for Sr^{2+} concentrations 17.95 and 200.0 mg/L, respectively, with the lowest values corresponding to the initial contact time. The uptake from the higher initial concentration resulted in a greater final equilibrium concentration in the suspension and the approach to equilibrium was slower. This could be due to the greater occupation of the exchangeable sites of the sorbent resulting in a decrease in the number of accessible sites for the uptake. At the lower initial concentration almost all of the Sr^{2+} was sorbed within the first 10 min of interaction. In addition, the expected decrease in

selectivity for Sr^{2+} with increasing solution concentration, might also explain the observed trend. These trends are useful in column experiments where fast kinetics are required. Thus, for the following experiments, 24 h was selected as sufficient time to reach equilibrium.

Application of the kinetic models (outlined above) for the Sr^{2+} uptake by natural clinoptilolite shows that the pseudo-second-order model fits very well with the experimental data (R^2 >0.999) for each concentration. The pseudo-first-order model is a less adequate fit for the experimental data (Table 1). The theoretical values of $q_{e,calc}$ predicted by the pseudo-second-order model are in good agreement with the experimental values $q_{e,exp}$, estimated from the plateaus of the kinetic curves for both concentrations, the differences being within 3%. These results indicate that the overall sorption rate is controlled by chemical sorption (Ho & McKay, 1999) and that the rate of uptake is determined by the availability of the ion-exchange sites and to a lesser degree by the concentration of ions (Coleman *et al.*, 2009).

The rate constant k_2 is larger for the lower initial concentrations. Similar dependencies have been described for the ion exchange of Sr^{2+} in the synthetic zeolite Na A-X (Abdel Rahman *et al.*, 2010) and for the ion exchange of Pb^{2+} onto zeolite tuffs (Günay *et al.*, 2007). The initial sorption rate h was 0.0315 and 0.221 meq/(g min) for Sr concentrations 17.95 and 200 mg/L, respectively.
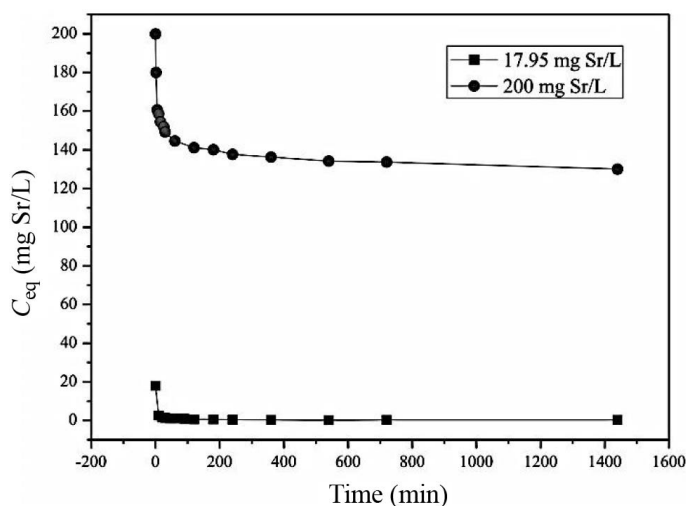

FIG. 3. Kinetics of the Sr^{2+} cation exchange for the natural clinoptilolite (0.1 g of sorbent, 20 mL Sr^{2+} solution, pH$_{init}$ = 5.4)

TABLE 1. Parameters of the kinetic models for Sr^{2+} uptake by natural clinoptilolite.

Initial conc. of Sr^{2+} (mg/L)	Pseudo-first-order model			Pseudo-second-order model				
	R^2	k_1 (min^{-1})	$q_{e,calc.}$ (meq/g)	R^2	k_2 (g/(meq min))	h (meq/(g min))	$q_{e,calc}$ (meq/g)	$q_{e,exper.}$ (meq/g)
18.0	0.7509	0.0029	0.0014	0.9999	4.79	0.032	0.081	0.081 ± 0.003
200	0.9544	0.0077	0.113	0.9995	0.22	0.221	0.313	0.302 ± 0.009

The parameter h is greater for the higher initial concentration studied. A similar trend was observed for the ion exchange of Sr^{2+} by natural clinoptilolite (Smičiklas *et al.*, 2007), by synthetic zeolite Na A-X (Abdel Rahman *et al.*, 2010) and for the ion exchange of Pb^{2+} by zeolite tuffs (Günay *et al.*, 2007).

In order to define the actual mechanism of uptake, the equation of intra-particle diffusion and liquid film diffusion was used (Gupta & Bhattacharyya, 2006). This equation takes into account surface homogeneity, transport effects (such as diffusion of the cations to the surface and within the channels) and chemical reactions like hydrolysis, all of which can affect the kinetics. The plots obtained are not linear, but consist of three parts. The intercept is not zero as required by the models, even when the data were grouped in parts for different time periods. This indicates a more complex process of uptake and suggests that different factors may contribute to the control of the kinetics and the sorption/exchange mechanisms at different time intervals. In the plot for the 200 mg Sr/L suspension (Fig. 3) the Sr^{2+} ion exchange is fast in the first 15 min, due to exchange at the surface sites. Then, the slow decrease of the solution concentration and the slow attainment of equilibrium indicate slow exchange into the channels of the sorbent.

The equilibrium capacities derived from the ion-exchange kinetic studies were 3.53 mg/g and 13.23 mg/g for initial Sr^{2+}-solutions of 17.95 and 200 mg/L respectively. The amount of Sr^{2+} sorbed at equilibrium from the initial Sr^{2+}-solution of 200 mg/L is comparable to that reported by Smičiklas *et al.* (2007) (11.76 mg/g, C_o = 300 mgSr/L) and Huang *et al.*, (2013) (16.95 mgSr/g, C_o 200 mg/L). These studies considered a pseudo-second-order kinetic model also for describing the strontium uptake by clinoptilolite or by clinoptilolite-containing materials. However, the k_2 constants in these studies are approximately three times smaller than those obtained in our work.

Ion exchange equilibrium. The sorption isotherm of Sr^{2+} by natural clinoptilolite at different initial concentrations is shown in Fig. 4. The experimental equilibrium data were fitted to the Langmuir, Freundlich and Dubinin−Radushkevich isotherm models. The parameters of the equations obtained and the calculated equilibrium uptake values are listed in Table 2.
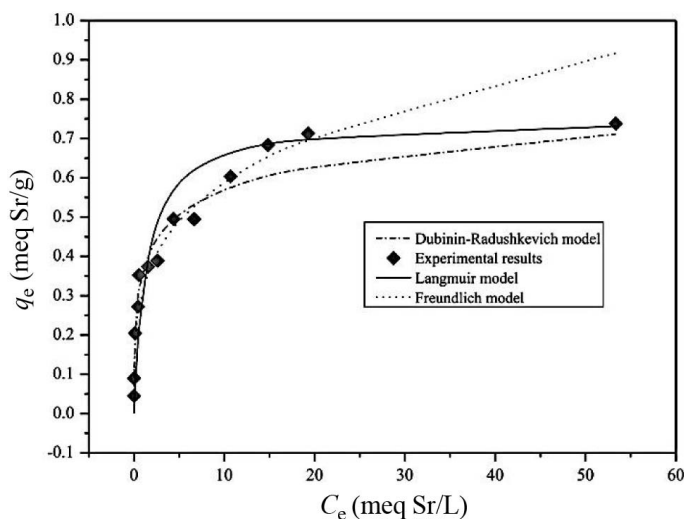
FIG. 4. Sorption isotherm of Sr by natural clinoptilolite (0.1 g of sorbent, 20 mL Sr^{2+} solution, pH_{init} = 5.4, t = 24 h)

The best correlation was found with the Langmuir isotherm model (R^2 = 0.994), although the other models also fit the experimental data points adequately. The fit of the theoretical isotherm-model equations to the experimental data are plotted in Fig. 4. The applicability of the Langmuir model means monolayer coverage of the sorption surface and structural and energetic homogeneity of the sorbent. The maximum sorption capacity, which estimates the efficiency of the natural clinoptilolite to remove Sr at conditions of saturation q_{max}, was 32.81 mg/g. This value is smaller than the theoretical exchange capacity (CEC) and shows that under the experimental conditions studied, the Sr^{2+}-exchange is not complete. This could be explained by the radius of the hydrated Sr^{2+} ions, the size of the clinoptilolite channels and also by the inherent structure of the natural clinoptilolite, the positions of the cations in the framework structure and the electrostatic repulsion by the neighbouring cations, which depend on the ion-exchanged cations and the available sites. In addition, the time allowed for equilibrium (24 h) might not be adequate for maximum Sr^{2+}-exchange.

The Dubinin–Raduchkevich isotherm may be used to determine the nature of the uptake process. The parameter k_{DR} from the Dubinin-Raduchkevich model was applied to calculate the mean free energy of reaction, E:

$$E = (-k_{DR})^{-1/2} \qquad (9)$$

where: E represents the energy change for the transfer of one mole of sorbate to the surface of the sorbent and is related to the mechanism of the uptake reaction (Helferich, 1962). The value of E

TABLE 2. Langmuir, Freundlich and Dubinin−Radushkevich isotherm parameters for Sr^{2+} sorption by the natural clinoptilolite.

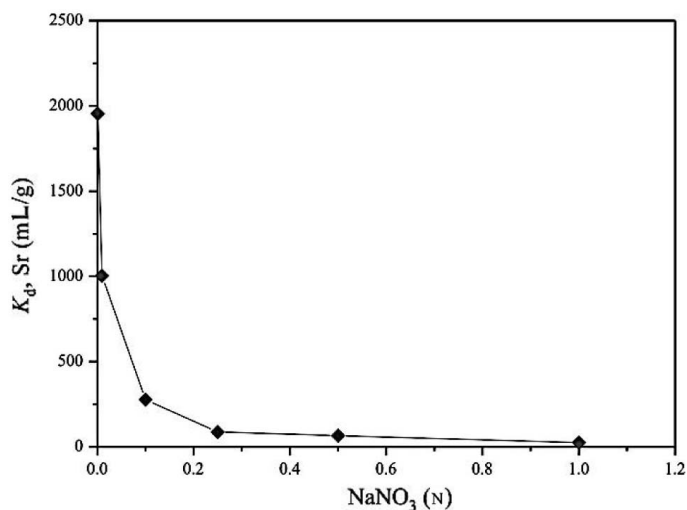|				
Langmuir model	R^2	$q_{max,calc.}$ (meq/g)	b (L/meq)	
	0.9940	0.749	0.756	
Freundlich model	R^2	$1/n$	K_F meq/g $(meq/L)^{-1/n}$	
	0.9734	0.263	0.322	
Dubinin−Raduchkevich model	R^2	$q_{max,calc.}$ (mmol/g)	β (mol^2/kJ^2)	E (kJ/mol)
	0.9847	0.433	−0.0027	1414

FIG. 5. Strontium distribution coefficient K_d (mL/g) as a function of sodium concentration (0.1 g sorbent, 20 mL 0.001 N Sr^{2+}, pH_{init} 5.4, t = 24 h)

(14.14 kJ/mol) obtained was in the range 8−16 kJ/mol and indicates an ion exchange mechanism.

The performance of the clinoptilolite for Sr^{2+} uptake in the present study was compared with similar studies in the literature, which were described most closely by the Langmuir isotherm model and the maximum capacities ranged from 9.80 to 32.5 mg/g (Rajec *et al.*, 1977; Smičiklas *et al.*, 2007; Yusan & Erenturk, 2011; Huang *et al.*, 2013). The capacity for Sr^{2+} exchange in mordenite is smaller (8.7−13.4 mg/g, Rajec *et al.*, 1977), whereas in synthetic zeolite A it is considerably larger (303 mg/g, El-Kamash, 2008). These differences in Sr-uptake are attributed to the different ion-exchange capacities (different Si/Al ratios) and the different sizes of the framework channels of the various zeolite species.

Adsorption studies for Sr^{2+} in model solutions

Effect of Na^+ ions. In order to study the ability of clinoptilolite to remove strontium from radio-nuclide-containing solutions under real conditions, the influence of different concentrations of $NaNO_3$ (0.001−1.0 N) on the distribution coefficient K_d was examined (Fig. 5). The initial value of K_d decreases sharply even at 0.01 N Na^+-concentration (K_d is ~1000 mL/g, i.e. value decreases by approximately half) and then, for $NaNO_3$ concentrations >0.25 N it remains virtually constant. At such high concentra-tions of Na^+ the exchange sites are becoming saturated and blocked by sodium ions, resulting in small distribution coefficients for sorption of the Sr^{2+} cations. These very small values of K_d imply that clinoptilolite might be useful for nuclear waste treatment only in cases of low Na^+-concentrations.

Effect of the salt composition of the simulated groundwater. The competition with other cations present in a solution of simulated groundwater containing 0.001 N Sr^{2+} (43.82 mg/L) was studied. The composition of the model groundwater (mg/L) was: Ca 60.0, K 3.0, Na 10.5, Mg 16.5, Zn 0.83 and Ni 0.63. The main cation was Ca^{2+} (0.003 N) and the total concentration of ions in the solution was small (~0.005 N). In dilute solutions calcium affects the ion exchange of strontium and the K_d values decrease to less than half the original ones (Table 3). However, the efficiency of Sr^{2+} removal still remains high (>80%). Thus, it can be concluded that the natural clinoptilolite is effective in removing Sr^{2+} from model groundwater and is potentially applicable as a permeable barrier for groundwater remediation processes.

CONCLUSIONS

The ion exchange of Sr^{2+} by natural clinoptilolite tuff from the Beli Plast deposit, Bulgaria was studied systematically under various experimental conditions. The optimal pH was 5−6 and the time to reach equilibrium was 24 h. The cation exchange

TABLE 3. Distribution coefficient, K_d, and efficiency of Sr^{2+} ion exchange in simulated groundwater.

Studied system	K_d (mL/g)	Efficiency (*E*%)
Clinoptilolite + Sr $1.05.10^{-3}$ N	1980 ± 200	91.4
Clinoptilolite + Sr $1.05.10^{-3}$ N + simulated groundwater	920 ± 66	82.1

was described by the pseudo-second-order kinetic model with a large k_1 value. The equilibrium process was described adequately by the Langmuir isotherm, although the experimental data also fitted well with the Freundlich and Dubinin–Raduchkevich models. The maximum adsorption capacity, calculated from the Langmuir model, is 32.81 mg/g, which can be attributed to monolayer sorption. The mean free energy of sorption *E*, derived from the Dubinin–Raduchkevich model is 14.1 kJ/mol, which is indicative of an ion exchange mechanism. The presence of Na^+ ions affects the Sr^{2+} exchange considerably at Na^+ concentrations exceeding 0.1 N, but the sorbent performs well with a simulated groundwater. This result, in addition to the fast exchange kinetics, shows that the natural clinoptilolite from Beli Plast could serve in groundwater remediation as a permeable barrier.

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