



Efficient removal of cesium from low-level radioactive liquid waste using natural and impregnated zeolite minerals

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ABSTRACT

The objective of the proposed work was focused to provide promising solid-phase materials that combine relatively inexpensive and high removal capacity of some radionuclides from low-level radioactive liquid waste (LLRLW). Four various zeolite minerals including natural clinoptilolite (NaNCl), natural chabazite (NaNCh), natural mordenite (NaNM) and synthetic mordenite (NaSM) were investigated. The effective key parameters on the sorption behavior of cesium (Cs-134) were investigated using batch equilibrium technique with respect to the waste solution pH, contacting time, potassium ion concentration, waste solution volume/sorbent weight ratio and Cs ion concentration. The obtained results revealed that natural chabazite (NaNCh) has the higher distribution coefficients and capacity towards Cs ion rather than the other investigated zeolite materials. Furthermore, novel impregnated zeolite material (ISM) was prepared by loading Calix [4] arene bis(-2,3 naphtho-crown-6) onto synthetic mordenite to combine the high removal uptake of the mordenite with the high selectivity of Calix [4] arene towards Cs radionuclide. Comparing the obtained results for both NaSM and the impregnated synthetic mordenite (ISM-25), it could be observed that the impregnation process leads to high improvement in the distribution coefficients of Cs⁺ ion (from 0.52 to 27.63 L/g). The final objective in all cases was aimed at determining feasible and economically reliable solution to the management of LLRLW specifically for the problems related to the low decontamination factor and the effective recovery of monovalent cesium ion.

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1. Introduction

Natural zeolites are important aluminosilicates in sorption processes [1,2] because of their low cost and selectivity. The selectivities of zeolites arise from their unique structures. In the zeolite structure, three relatively independent components are found: the aluminosilicate framework, exchangeable cations and zeolitic water. The aluminosilicate framework is the most conserved and stable component and defines the crystalline structure. A most remarkable feature of zeolites, and one which practically defines the specific properties of these minerals, is the presence of a system of voids and channels, in their structures. At present, more than 100 different zeolite structures are known. For sorption, the dimensions and locations of the channels, through which the molecules diffuse into the inter-crystalline free volume, are of great importance [3,4].

In environmental applications, natural zeolites have been studied extensively to remove harmful substances from wastewater by adsorption and ion exchange processes [5–7]. However, impuri-

ties are present in natural zeolites, which can markedly decrease their adsorption and ion exchange efficiency. For example, there are impurities like quartz in most of the clinoptilolite deposits. These factors reduce the uptake of metal ion onto natural clinoptilolite. However, investigations showed that there is a significant increase in pollutants uptake when natural zeolites are pre-treated with aqueous solutions containing sodium cations (activation stage), which improve materials reactivity or sorption potential [8–10].

Natural zeolites that have been considered also for radioactive waste-treatment include mordenite, erionite, chabazite, and clinoptilolite [11–13]. Due to their high cation-exchange capacities and selectivities for Cs, Ba and Sr was, as demonstrated first by Ames [14,15], clinoptilolite and mordenite containing rocks can retard the migration of radionuclides occurring in solution as simple cations and thus are considered as potential hosts for radioactive waste disposal [16–18]. Cement encapsulation is the preferred waste for zeolite loaded with Cs and Sr radioisotopes, and some work on clinoptilolite/cement composites has described the importance of the presence of calcium ions to the leaching characteristics of this waste [19–22]. All these applications, which involve zeolites, require a better understanding of behavior of different cationic forms of zeolites for sorption of trace concentrations of radioisotopes.

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Moreover, zeolites can be modified by the introduction of new functional groups in order to improve its activity and selectivity for the removal of several substances [23–28]. Calixarene-crowns or calixcrown, macrocyclic compounds that combine calixarene and polyether units, are being studied intensively in many laboratories as hosts for selective ion recognition. Calix [4] arene-R14 is a weak-polar macrocycle compound. Calix [4] arene-R14/SiO₂-P has also some attractive advantages such as minimal organic solvent utilization, less waste accumulation, compact equipment, simple operation, simultaneous separation of multi-components, and low capital cost. The direct impregnation and immobilization of Calix [4] arene-R14 into the pores of the SiO₂-P particles is difficult. Tri-n-butyl phosphate, TBP is used as a molecular modifier. It was used to increase the polarity of Calix [4] arene-R14 and improve the affinity of SiO₂-P particles for Calix [4] arene-R14 [29].

Radioactive Cs-137 with the half-life of 30.28 years is a harmful fission product (FP) contained in low-level radioactive liquid waste (LLRLW). Another Cs-isotope, Cs-135 (half-life 2 million years) has a potential long-term adverse impact on environment because of its mobility in final repository [30]. Furthermore, Cs-137 is a source of beta radiation, which is called heat generator. From the viewpoint of minimizing the long-term radiological risk and facilitating the management of LLRLW, effective partitioning and recovery of Cs are highly requested. In this respect, the present work was oriented to prepare new impregnated zeolite material that combines high capacity as well as high selectivity towards cesium ion. This combination could be successively applied for sufficient treatment of low-level radioactive liquid waste with considerably low cost.

2. Theoretical considerations

2.1. Selectivity coefficient

Selectivity coefficient is usually used to measure the ion exchange equilibrium. For the Cs/Na exchange, for example, the selectivity coefficient $k_{Cs/Na}$ is defined as:

$$k_{Cs/Na} = \frac{[Cs]_S [Na]_L}{[Cs]_L [Na]_S} \quad (1)$$

where subscript letters S and L refer to the equilibrium ion concentrations in the solid and in the liquid phases, respectively. Selectivity coefficient may depend on the degree of loading of Cs in the exchanger.

2.2. Distribution coefficient

Especially in radionuclide removal, the efficiency of an ion exchanger is often measured by distribution coefficient, K_d , i.e.

$$K_d = \frac{[Cs]_S}{[Cs]_L} \quad (2)$$

Combining Eqs. (1) and (2) and substituting $[Na]_S = Q - [Cs]_S$ followed by rearranging gives:

$$K_d = \frac{Q}{[Na]_L / k_{Cs/Na} + [Cs]_L} \quad (3)$$

where Q is the ion exchange capacity.

In low-level waste streams, the activity concentration of Cs-137 is typically in the range of 0.1–10 $\mu\text{Ci/L}$. This corresponds to a chemical cesium concentration of about 10^{-11} to 10^{-9} mol/L. Concentration of sodium is almost always very much higher than that of cesium ($>10^{-3}$ mol/L) so that $[Na]_L / k_{Cs/Na} \gg [Cs]_L$ in Eq. (3). Under these circumstances, concentration of cesium does not have effect on the value of K_d , and Eq. (3) can be presented in a familiar logarithmic form:

rithmic form:

$$\log K_d = \log(k_{Cs/Na} Q) - \log [Na]_L \quad (4)$$

This means that in this case (uni-univalent exchange, cesium present as trace), K_d is inversely proportional to the concentration of sodium in the solution and directly proportional to ion exchange capacity Q and selectivity coefficient $k_{Cs/Na}$.

3. Experimental

3.1. Chemicals and reagents

All chemicals and reagents used in this study were of analytical grade purity and were used without further purification. Calix [4] arene bis(-2,3 naphtho-crown-6) with a purity of 95% was produced by Acros Organics, Belgium. Tri-n-butyl phosphate (TBP) with purity more than 98% was purchased from Kanto chemical Co., Inc., Japan.

Natural clinoptilolite and mordenite originated from Japan, Futatsui (Akita prefecture) and Kawarago (Miyagi prefecture), respectively. Synthetic mordenite (Zeolon 900 H) with the size 10–14 mesh was from Norton Company, USA. Chabazite sample used for these investigations was marketed as AW-500 (Linde corporation), which was the forerunner of Ionsiv IE-96 (presently supplied by UOP).

Standard solution of Cs-134 (2.280×10^4 Bq/L) originally existed in the form of CsCl solution.

3.2. Instrumentation

Measurements of the gamma radioactivity of Cs-134 radionuclide in the tested samples were identified and determined using a typical non-destructive γ -ray spectroscopic technique using Wallac WIZARD-1480 automated gamma-analyser with a well type NaI (TI) detector.

3.3. Preparation of impregnated zeolite material

3.3.1. Activation of natural and synthetic zeolites

Each zeolite powder was crushed to a size of <0.15 mm. 3.0 g of each zeolite powder was continuously refluxed with 100 mL of 1.0 M NaCl at room temperature (R.T) for 24 h. The mixture was filtered and the powder was then washed with 300 mL of distilled water (D.W). The pH of the natural and synthetic zeolites was adjusted to be 5.75, 5.41, 5.13 and 4.94 for natural clinoptilolite, natural chabazite, natural and synthetic mordenite, respectively. The powder was activated by mechanical shaking with 25 mL of methanol twice for 60 min. The powder was filtered and dried at 50 °C for 3 h. Activated zeolite samples were designated NaSM (synthetic mordenite), NaNM (natural mordenite), natural clinoptilolite (NaNCl) and NaNCh (natural chabazite).

3.3.2. Pretreatment and impregnation of synthetic mordenite

Tri-n-butyl phosphate (TBP) was used specially as a hydrophilic modifier to improve significantly the affinity of zeolites for Calix [4] arene. 25×10^{-4} M of Calix [4] arene bis(-2,3 naphtho-crown-6) was mixed with 50×10^{-4} M of TBP. Both of them were dissolved in 10 mL of 1,2 dichloroethane as solvent. The mixture was added to 0.5 g of the pre-activated NaSM and heated at 100 °C for 1.0 h with continuous stirring at 750 rpm. The impregnated NaSM was dried at 50 °C for 1.0 h.

The selection of 1,2 dichloroethane as solvent was based on the published observation that showed the solvent extraction distribution coefficient (D_{Cs}) values in different diluents following the order: nitrobenzene > dichloroethane > octanol > decanol >

chloroform > benzene–toluene ≫ dodecane, which can be correlated with their dielectric constants [31].

3.4. Characterization of zeolite samples

Crystal structures of the zeolite samples were identified from X-ray diffraction (XRD) patterns recorded with analytical X'pert Pro MPD X-ray diffraction system using X'pert High Score Plus software. The surface morphology was examined by Hitachi S-4800 field emission scanning electron microscope (FESEM). Coarse elemental analyses were carried out from energy-dispersive X-ray spectroscopy (EDX) spectra recorded by Oxford INCA 350 micro-analysis system connected to a Hitachi S-4800 field emission scanning electron microscope (FESEM) and using INCA suite version 4.05 software. Five punctual analyses were carried out for each zeolite sample. Powdered samples without casting in polymer and surface polishing were used. Thus, due to the uneven sample surfaces, the method was likely to give only coarse elemental compositions. Moreover, natural zeolite samples containing impurities were expected to be inhomogeneous in elemental composition.

3.5. Batch equilibrium experiments

Batch equilibrium experiments were performed at 298 K and at zeolite to solution ratio as 0.1 g:10 mL. 0.1 g of the impregnated synthetic mordenite was only used as a solid-phase was mixed with 10 mL of Cs-134 standard solution (2.280×10^4 Bq/L) that was originally dissolved in simulated aqueous solution which has total dissolved solids, TDS = 0.7 g/L to mimic the Egyptian low-level radioactive waste. This waste was collected from various laboratory research activities in the hot laboratories center, located at Inshas site, Egypt [32].

The zeolite–solution mixtures were rotated in a custom-made mixer at 8 revolutions per minute for 24 h till equilibrium was reached. This time is much longer than the equilibrium times determined earlier from typical kinetic experiments (Section 4.2.2). To prevent the presence of colloidal particles that may carry Cs-134, the supernatant was filtrated by 0.2 μm EiChrom ACRODISC-13. The phases were separated and aliquots (5 mL) of aqueous solution were withdrawn, with micropipette into 10 mL polyethylene empty bottle then subjected to radiometric measurement. All measurements were carried out in duplicates with relative standard deviation of ±0.03%.

The distribution coefficient (K_d) of radionuclides, the percent removal (R) as well as amount of metal ion sorbed onto the zeolite materials at any time, q_t (mg/g) were calculated from the following equations:

$$K_d = \frac{A_o - A_e}{A_e} \times \frac{V}{m}, \quad (\text{mL/g}) \quad (5)$$

$$R(\%) = \frac{A_o - A_e}{A_o} \times 100 \quad (6)$$

$$q_t = \left(\frac{A_o - A_e}{A_o} \right) C_o \frac{V}{m} \quad (7)$$

where A_o and A_e are the initial and equilibrium activities per unit volume for the corresponding radionuclide, respectively, V is the volume of the aqueous phase (mL), and m is the weight of the zeolite material (g). The error (relative standard deviation) of A_o and A_e was obtained directly from the Wallac analyser and was usually well below 1%. Relative error accumulated for R (Eq. (6)) was thus less than 2%. However, due to the mathematical form of Eq. (5), the relative error of K_d became very large when there was very high Cs-134 uptake and the sample count rate for A_e approached that of background. Thus at 95% removal, the relative error of K_d was about 6% and approached 50% at 99% removal.

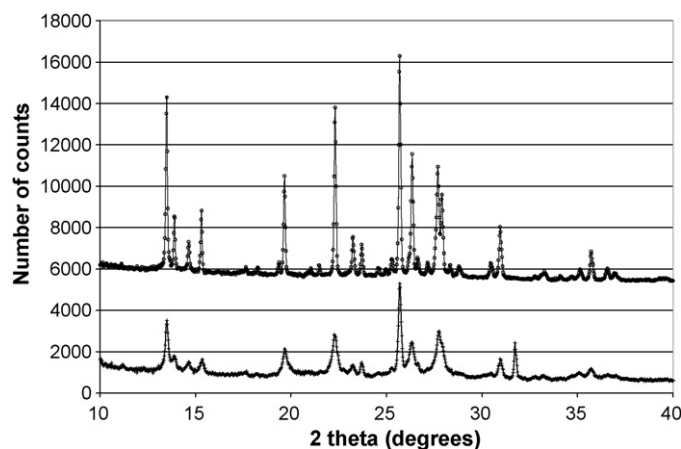


Fig. 1. XRD patterns of synthetic mordenite NaSM (upper line) and natural mordenite NaNM (lower line). Zero count level for NaSM is at 5000 counts.

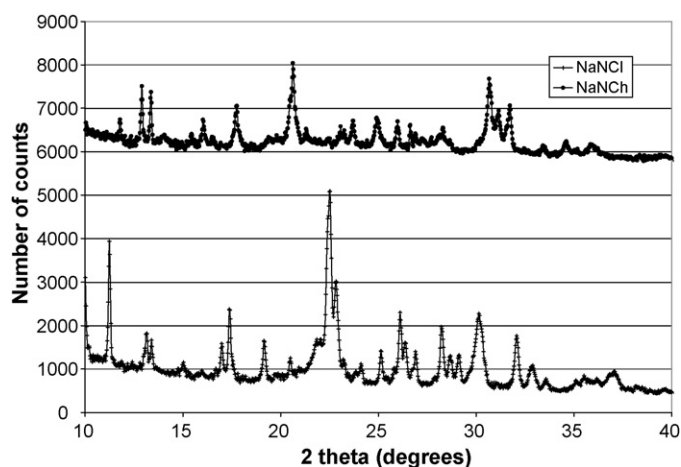


Fig. 2. XRD patterns of natural clinoptilolite NaNCI (upper line) and natural chabazite NaNCh (lower line). Zero count level for NaNCI is at 5000 counts.

4. Results and discussion

4.1. Characterization of natural, synthetic and impregnated zeolites

The XRD diffractograms showed that the zeolite materials were structurally pure mordenite, clinoptilolite and chabazite (Figs. 1 and 2).

Traces (<1%) of Cl, Fe, Mg, Ca and K were found in most samples. Considering the accuracy of the EDX method, the Si/Al-ratio of synthetic mordenite (Si/Al = 5.4) was reasonably close to the ideal value of 5 (Table 1). As could be expected, there was more discrepancy from the ideal Si/Al-ratios in the natural zeolite samples. The ideal ratios are given for the synthetic zeolite structures and the

Table 1
Coarse chemical composition of zeolite samples analysed by EDX.

Zeolite	Element %			Si/Al	Ideal Si/Al
	Na	Al	Si		
NaNCI	3.2	8.6	35.7	4.15	3.5
NaNCh	3.4	7.5	35.7	4.76	2.0
NaNM	5.0	8.0	33.9	4.24	5.0
NaSM	3.8	6.5	35.1	5.4	5.0
Impregnated synthetic mordenite	2.2	3.8	35.9	9.45	5.0

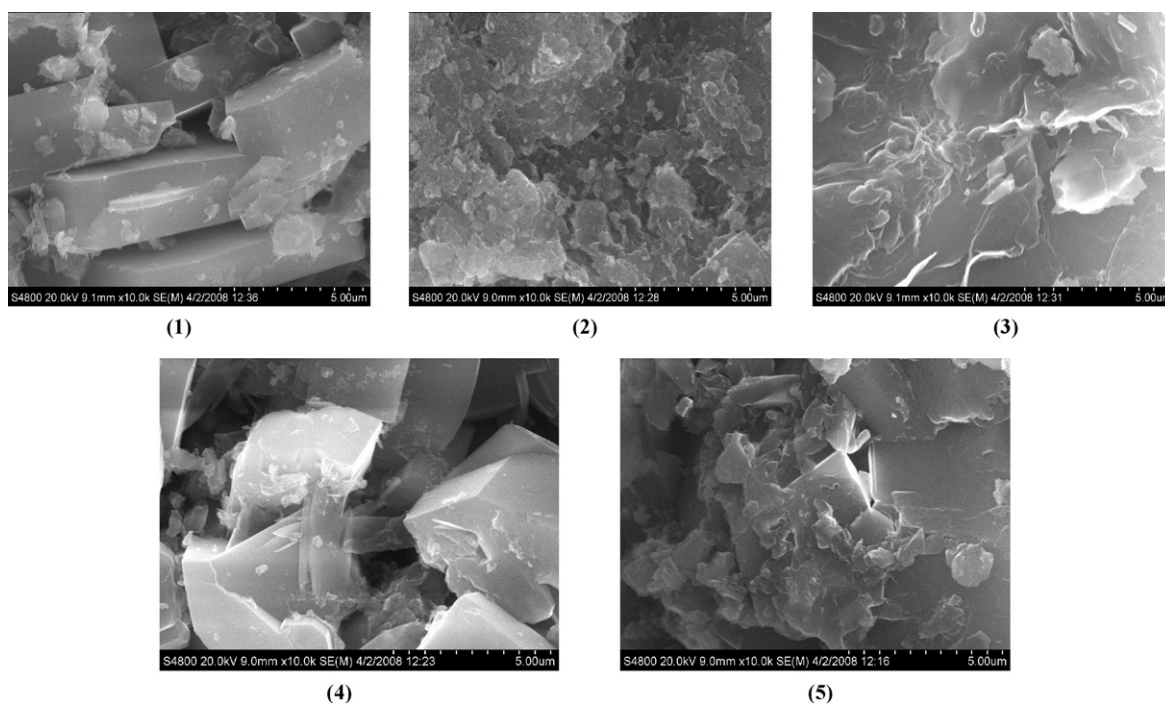


Fig. 3. SEM micrographs of the zeolite samples. 1 = natural clinoptilolite, NaNCI; 2 = natural chabazite, NaNCh; 3 = natural mordenite, NaNM; 4 = synthetic mordenite, NaSM; and 5 = impregnated synthetic mordenite, ISM.

natural counterparts are subjected to leaching of Al in the natural environment. There is a marked feature in the composition of the impregnated mordenite. The Al and Na contents are abnormally low, which is an indication that de-alumination of the zeolite framework has taken place in the impregnation, most likely due to the ability of Calix [4] arene to extract Al from the zeolite framework.

SEM micrographs revealed that there was a marked change in the morphology of natural mordenite after the de-alumination. The rectangular crystallinity was lost and replaced by irregular surface as shown in Fig. 3.

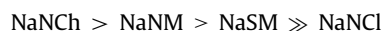
4.2. Adsorption studies

The adsorption behavior of the different zeolite materials for Cs-134 radionuclide was tested using batch equilibrium technique. The influence of parameters such as shaking time, pH of the waste solution, radioactivity levels and adsorbent weights were tested to evaluate the best zeolite material that has the various chemical and crystallographic characteristics as a function of radionuclide species.

4.2.1. Matrix effect

Analytical characterization of Egyptian low-level radioactive waste showed that TDS = 0.7 g/L because of the presence of sodium and potassium ions. In this respect, two simulated waste solutions were prepared separately with 0.0119 M of NaCl and KCl to test the effect of either Na⁺ or K⁺ ion on the sorption process of Cs⁺ on the various zeolite materials. As shown in Table 2, the distribution coefficients and the corresponding uptake percentages of Cs-134 are highly affected (decreases) by potassium rather than sodium ions in the waste solution. This may be due to the close similarity in ionic radii between Cs⁺ and K⁺ rather than that between Cs⁺ and Na⁺. Therefore K⁺ ion could compete more with Cs⁺ ion during the sorption process. Furthermore, it could be observed that the distribution coefficients of Cs-134 on different zeolite materials follow

the following sequence:



4.2.2. Effect of shaking time

The effect of shaking time on Cs-134 distribution is used to clarify its insights into reaction kinetics. The sorption kinetics of Cs-134 on the four zeolite materials was studied at different time intervals ranging from 30 min to 24 h and constant $V/M = 100$. As shown in Fig. 4, the equilibrium for Cs-134 is reached in 6 h for all zeolites except NaNCI, respectively. The data indicate that there is no significant change in the sorption rate between natural chabazite, synthetic and natural mordenite and that they represent a relatively fast reaction compared to natural clinoptilolite.

Although, clinoptilolite is a silica-rich zeolite, the kinetic data confirmed that the relatively low reaction rate of natural clinoptilolite is mainly attributed to its common impurity, quartz, its mineralogical characteristics as well as low ion exchange capacity of clinoptilolite. These factors reduce the uptake of Cs-134 ion onto natural clinoptilolite.

4.2.3. Effect of volume/weight ratio

The effect of waste solution volume to sorbent weight ratio (V/M) on the distribution coefficient and the corresponding uptake percentage of Cs-134 is studied in the range from 100 to 400 mL/mg.

Table 2

Effect of sodium and potassium ions on the distribution coefficients and the corresponding uptake percentages of Cs-134 using activated zeolite materials at constant $V/M = 100$ and pH = 5.0.

Zeolite name	Cs-134 in 0.0119 M NaCl		Cs-134 in 0.0119 M KCl	
	K_d (L/g)	Uptake (%)	K_d (L/g)	Uptake (%)
NaNCI	3.87	97.59	1.91	90.63
NaNCh	4.97	98.10	4.80	96.10
NaNM	4.89	98.07	4.51	95.74
NaSM	4.82	97.98	3.86	95.09

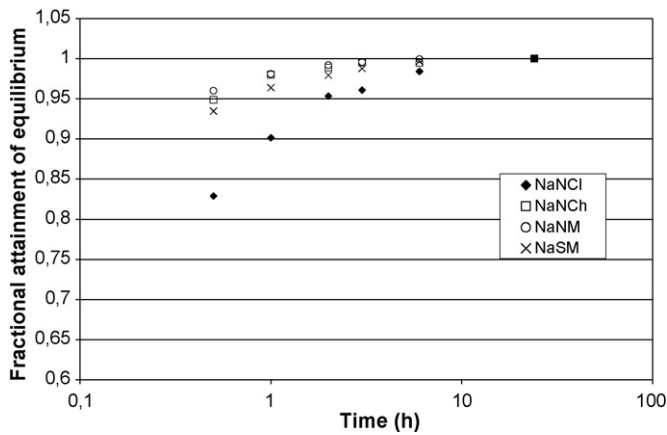


Fig. 4. Effect of shaking time on the fractional attainment of equilibrium for Cs-134 uptake on the zeolite materials at constant potassium ion concentration, 0.0119 M and $V/M = 200$ and $pH = 5.0$.

This is to evaluate the optimum resin weight that could be used to achieve high removal capability. As shown in Table 3, the uptake percentage decrease insignificantly as V/M increases from 100 to 200. Further decreasing of V/M from 200 to 400 leads to considerable decrease of the uptake percentage. Thus, the optimum V/M ratio was chosen to be 100 mL/g because it gives the maximum uptake percentage of Cs-134 with minimum resin weight.

4.2.4. Effect of potassium ion concentration

Based on the previous data in Table 2, that demonstrated that the sorption of Cs-134 is highly affected by potassium ion in the waste solution, the effect of potassium ion concentration on Cs-134 distribution was tested at different concentrations ranging from 0.0119 to 0.125 M. The data show that the uptake percentage decreases significantly as $[K^+]$ increases within the investigated concentration range. This findings confirmed that K^+ ion compete and reduce the sorption of Cs^+ ion on the four different types of zeolite materials. The slope of the logarithmic plots $\log K_d$ vs. $\log [K]$ was between -0.86 and -1.10 (see Eq. (3), Fig. 5), indicating that uptake of cesium was uni-univalent Cs^+/K^+ exchange. The selectivity of the zeolites for Cs^+ over K^+ could be estimated from the intercept values of the logarithmic plots and was found to decrease in the order:

$$NaSM \geq NaNM > NaNCh \gg NaCl$$

Thus, both natural and synthetic mordenite had the highest selectivity order for Cs(I). This may be due to the structural details

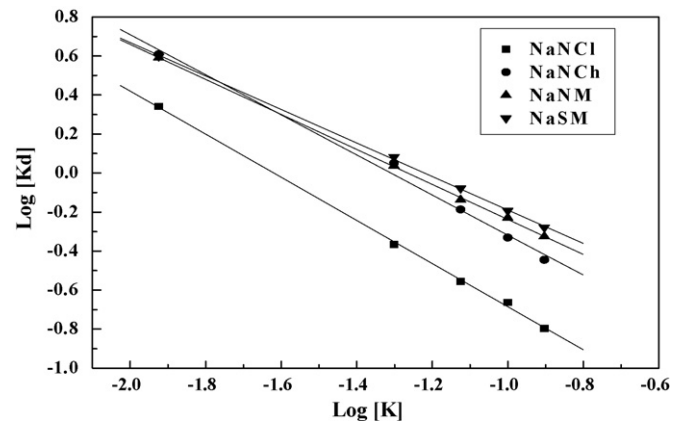


Fig. 5. Effect of potassium ion concentration on the distribution coefficient of Cs-134 on zeolite materials at constant $V/M = 100$ and $pH = 5.0$.

of the zeolites. The radius of the bare Cs^+ ion is 3.40 \AA [33] and is therefore easily accommodated by the large (smallest diameter 6.5 \AA) 12-ring cavities in their mordenite structure. The apertures in the chabazite 8-ring cavities have a diameter of 3.8 \AA , which is still accessible to Cs^+ . In clinoptilolite (i.e. heulandite structure), the smallest cavity diameter is 3.6 \AA , i.e. very close to that of Cs^+ , and may provide steric hindrance for the entry of the Cs^+ ions.

4.2.5. Effect of pH

The adsorption of Cs-134 radionuclide was investigated at different values of pH ranging from 3 to 9. As shown in Table 4, the general trend shows that the uptake percentage of Cs(I) does not change with the change in solution pH. This means that the adsorption of Cs(I) is highly independent on the surface characteristics of the zeolite materials at various pH values.

As can be seen, the independence of the distribution coefficient (K_d) on the solution-pH may be due to the considerable weak hydrolysis of monovalent Cs ion, which might originate from the lack of affinity of Cs(I) with the hard oxygen atom contained in the aluminosilicate zeolite structure.

4.2.6. Sorption isotherm

Sorption isotherm is mainly used to describe sorption equilibrium, which reflects the degree of interaction between the amounts of adsorbate on the adsorbent. Hence, the maximum affinity of the sorbent at fixed temperature and pH could be evaluated. In this respect, the sorption isotherm for the removal of Cs-134 ion from

Table 3
Effect of volume/weight ratio on the distribution coefficients and the corresponding uptake percentages of Cs-134 at constant potassium ion concentration, 0.0119 M and $pH = 5.0$.

V/M (mL/g)	NaCl		NaNCh		NaNM		NaSM	
	K_d (L/g)	Uptake (%)	K_d (L/g)	Uptake (%)	K_d (L/g)	Uptake (%)	K_d (L/g)	Uptake (%)
400	1.72	81.22	4.29	91.57	4.77	92.46	4.89	92.38
200	1.95	90.79	4.78	96.08	4.49	95.73	4.48	95.87
133	1.92	93.56	4.51	97.12	4.13	96.92	4.22	96.97
100	1.91	90.63	4.80	96.10	4.51	95.74	3.86	95.09

Table 4
Effect of pH on the distribution coefficients and the corresponding uptake percentages of Cs-134 at constant potassium ion concentration, 0.0119 M and $V/M = 100$.

pH	NaCl		NaNCh		NaNM		NaSM	
	K_d (L/g)	Uptake (%)	K_d (L/g)	Uptake (%)	K_d (L/g)	Uptake (%)	K_d (L/g)	Uptake (%)
3	1.93	90.60	5.06	96.20	4.17	95.43	4.68	95.97
5	1.95	90.78	4.78	96.08	4.48	95.87	4.49	95.73
7	2.04	91.22	4.77	96.05	4.15	95.42	4.65	95.89
9	1.95	90.85	4.92	96.18	4.12	95.42	4.63	95.92

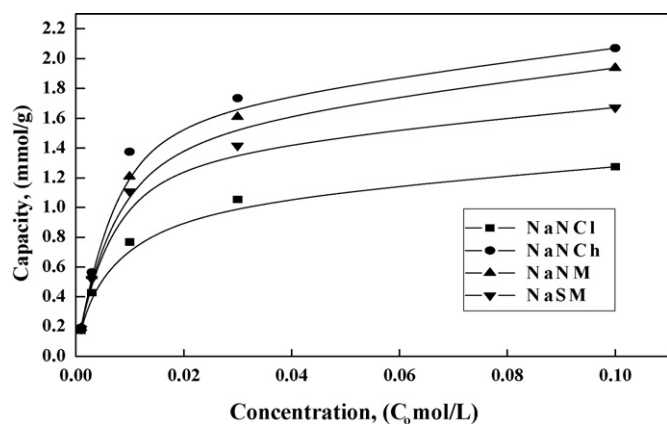


Fig. 6. Sorption isotherm of Cs^+ ion on various zeolite materials at different Cs^+ concentrations and at constant potassium ion concentration, 0.0119 M, $V/M = 100$, pH = 5.0.

LLRLW on the four investigated zeolite materials was determined. Various concentrations of non-radioactive CsCl ranging from 0.001 to 0.1 M were used as carrier for radioactive Cs-134 . Fig. 6 shows that the isotherms are regular concave curves to the concentration axis. The amount of Cs sorbed increases significantly at the low concentration range, then increases gradually at high Cs ion concentrations. These results reflect the efficiency of the zeolite materials towards Cs radionuclide. The experimental apparent capacities at high CsCl concentration (0.1 M) were found to be 1.27, 2.07, 1.93 and 1.67 mmol/g for NaNCl , NaNCh , NaNM and NaSM , respectively, i.e. natural chabazite has the highest capacity towards Cs radionuclide.

4.2.7. Impregnation of Calix [4] arene on synthetic mordenite

Different amounts (25, 50 and 100 mg) of Calix [4] arene bis(-2,3 naphtho-crown-6) were individually impregnated on the pre-activated SM. The effect of Calix [4] arene concentration on the distribution coefficients of Cs^+ ion was evaluated particularly at high potassium ion concentration (0.125 M) to testify their co-adsorption and the degree of selectivity of the impregnated synthetic mordenite (ISM) towards Cs^+ . The two empirical equations of Langmuir and Freundlich isotherm models were applied using the solver add-in with Microsoft Excel program to evaluate the experimental results. The data in Table 5 showed that in Langmuir model, coefficient q_{max} represents the maximum sorbed amount. Furthermore, K_f in Freundlich model is an index to the sorption capacity of sorbent. Both values for q_{max} and K_f indicated that ISM-50 has higher sorption capacity than that of NaNCl and NaSM and lower sorption capacity than that of NaNCh and NaNM . As shown in Table 6, comparing the obtained results for both NaSM and ISM-100, it could be observed that the impregnation process leads to high improvement in the distribution coefficients of Cs^+ ion (from 0.52 to 3.79 L/g). Furthermore, considerable improvement in the distribution coefficients of Cs^+ ion (from 3.79 to 27.63 L/g) was achieved by lowering the amount of Calix [4] arene from 100 to 25 mg even at high potassium ion concentration (0.125 M).

Table 5
The isotherm parameters obtained from non-linear analysis of Cs .

Model	Parameter	NaNCl	NaNCh	NaNM	NaSM	ISM-50
Freundlich	K_f	2.35	3.57	3.46	2.97	3.26
	n	0.237	0.201	0.218	0.213	0.256
	r^2	0.966	0.937	0.953	0.938	0.975
Langmuir	q_{max}	1.201	1.865	1.786	1.542	1.558
	K_a	454.6	1741.8	849.4	985.3	420.0
	r^2	0.943	0.952	0.948	0.960	0.913

Table 6

Effect of Calix [4] arene bis(-2,3 naphtho-crown-6) concentration on the distribution coefficients and the removal capacity of Cs-134 at constant potassium ion concentration, 0.0119 M, $V/M = 100$, pH = 5.0 at room temperature.

Zeolite material	Distribution coefficient K_d (L/g)	Uptake (%)
NaSM	0.52	84.13
ISM-25 mg Calix [4] arene	27.63	99.64
ISM-50 mg Calix [4] arene	6.70	98.53
ISM-100 mg Calix [4] arene	3.79	97.44

Table 7

Comparison between distribution coefficient (K_d) of cesium ion on various sorbents.

Sorbent	Distribution coefficient, K_d (L/g)	References
ISM-25 mg Calix [4] arene	27.63	Present work
A-X zeolite	0.19–0.39	El-Naggar et al. [2]
Natural zeolite, Turkey	3.75–4.45	Osmanlioglu [21]
Phenol-formo-phenolic resins	0.08	Dumont et al. [36]
Resorcinol-formaldehyde	0.23	Dumont et al. [36]
Catechol formo-phenolic resin	0.11	Dumont et al. [36]
Phloroglucinol-formo-phenolic	0.06	Dumont et al. [36]
Resorcinol-formaldehyde- Na^+	5.0	Faver-Reguillon et al. [37]
Antimony silicate	1.0	Al-Attar et al. [38]
Potassium nickel hexacyano-ferrate (II)	72	Nilchi et al. [39]
Tin (IV) phosphate	50–200	Bortun et al. [40]
Tin ferrocyanide	0.08–0.31	Zakaria et al. [41]
Titanium ferrocyanide	0.008–0.61	Zakaria et al. [41]

These findings could be interpreted as follows: Calix [4] arene bis(-2,3 naphtho-crown-6) has been found to be size selective complex-one for Cs^+ and therefore, capable of replacing the water molecules from the inner-sphere hydration of the metal ions during complexation. The expected mechanism may be through the incorporation of the metal ion inside the pore cavity, providing a hydrophobic exterior, which enables the sorption of the resulting complex cation onto the zeolite material. Further increases in Calix [4] arene concentration may lead to either steric hindrance and/or blocking of the interior pores that overall retard the sorption process of Cs^+ ion.

Alternatively, the decrease of Cs uptake with increased Calix [4] arene loading may be a consequence of increased de-alumination of zeolite, which was evident from the elemental analysis and which would decrease the amount of adsorption and ion exchange sites within the zeolite framework.

In view of similar observations in the present studies, it can be stated that the sorption mechanism of Cs(I) follows ion-pair formation due to the interaction of Cs^+ ion with the 'O' atoms of the Calix [4] arene rather than ion exchange process with the microporous aluminosilicates of mordenite mineral [34,35].

The obtained distribution coefficients of cesium have been compared with different sorbent materials [36–41]. As shown in Table 7, the data reflect that impregnated synthetic mordenite (ISM-25) has a high removal capability for cesium in simulated low-level radioactive liquid waste.

5. Conclusion

The obtained results revealed that natural chabazite (NaNCh) has the higher distribution coefficients as well as the highest capacity towards Cs ion rather than the other investigated zeolite materials. However, the slope analysis of the logarithmic plots $\log K_d$ vs. $\log [K]$ indicating that both natural and synthetic mordenite had the highest selectivity order towards Cs(I) .

Polytopic system was constructed by combining two binding sites together within the same architecture. They exhibit superior recognition ability towards radioactive cesium ion by the

cooperative effects of zeolite material and Calix [4] arene bis(2,3 naphtho-crown-6) moieties. Comparing the obtained results for both NaSM and the impregnated synthetic mordenite (ISM-25), it could be observed that the impregnation process leads to high improvement in the distribution coefficients of Cs⁺ ion (from 0.52 to 27.63 L/g). This combination could be successively applied for sufficient treatment of low-level radioactive liquid waste with considerably low cost.

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