



## Original Article

Competitive Adsorption of  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  Ions on Phillip Site/Chabazite Zeolitic Tuff from Jordan

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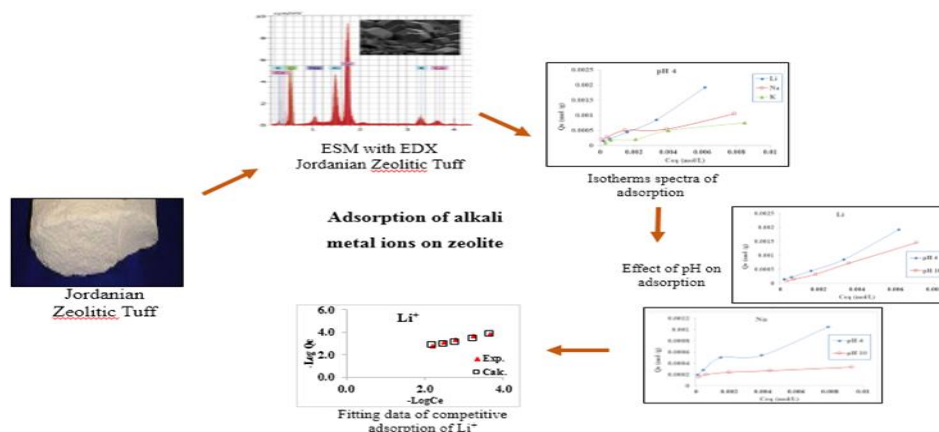
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## ABSTRACT

The adsorption of alkali metal ions on zeolite has no such possibility of precipitation. In the current work, we have studied the adsorption isotherms, and the effect of pH and temperature on the adsorption of alkali metals ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) onto Jordanian zeolitic tuff (phillipsite and chabazite) using batch adsorption method. Fitting the data using the competitive Langmuir adsorption model indicates that adsorption capacity of  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  are 4.9, 3.4, and 2.7 mmol/g, respectively. The results showed that adsorption of alkali metals on zeolite decreases with increasing pH and temperature which is a distinct behavior from that of heavy metals. The  $\Delta H$  values of adsorption process are -85.6, -23.4, and -41.5 kJ/mol for initial concentrations of  $\text{K}^+$ ,  $\text{Li}^+$ , and  $\text{Na}^+$ , respectively.

The calculated  $\Delta S$  values are -0.285, -0.081, and -0.132 J/mol.K, for the same list of metals, respectively. The negative and decreasing entropy values associated with the adsorption process indicate that zeolite may encapsulate alkali metal ions in pores rather than ion exchange. The current investigation suggests the possible use of natural zeolite for seawater's desalination by trapping alkali metals in the pores.

## GRAPHICAL ABSTRACT



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## Introduction

Jordan is a rich country in natural resources including rocks and minerals. The zeolitic tuff is widely distributed in Jordan, the first zeolite deposit (Phillipsite) was discovered in 1987 [1].

Zeolites are minerals that are found naturally or can be synthesized. They have cavities and channels in their internal structure coupled in molecular dimensions and where compensatory cations enable ion exchange. Zeolites may be modified in a variety of ways to increase their activity and selectivity in the removal of various compounds [2]. It is a class of hydrated aluminum-silicates of alkaline earth metals with high resistance to alteration and cheap mining costs [3]. XRF analysis results of zeolitic tuff were listed in Table 1 [4].

Natural zeolites have received substantial research as potential cleaning agents for the environment. They are widely available as geo-resources, affordable, and environmentally acceptable adsorbents, with high cation exchange capacities, physicochemical stability, and outstanding hydraulic features. These are their key benefits for water treatment procedures [5].

Natural zeolite is found in different areas of Jordan and it possesses a high surface area that makes it an excellent adsorption material [6]. It possessed physicochemical properties that help to be used as a sorbent in a variety of processes for the water treatment. It contains minerals that can be used to adsorb a range of organic and inorganic chemicals, including clinoptilolite, phillipsite, mordenite, and chabazite [7]. It has been shown that phillipsite ( $[(Ca, Na_2, K_2)_3Al_6Si_{10}O_{32} \cdot 12H_2O]$ ) and to a less extent chabazite ( $[(Ca, Na_2, K_2, Mg) Al_2Si_4O_{12} \cdot 6H_2O]$ ) are the main constituents of Jordan Zeolitic Tuff (JZT) [8]. The Si/Al ratio is between 2.56 and 2.72. Broad Si/Al ratios are highly desired, which can change zeolites' activity, selectivity, and durability. This might be a goal for the next study, making a modification of the structure of zeolites by controlling Al and Si distributions, to enhance of cation exchange capacity of zeolites and their ability for adsorption. The reported value for cation exchange capacity (CEC) of

phillipsite/Chabazite zeolitic tuff is (180 meq/100 g) [8].

Chemical analysis of phillipsite crystals by the SEM-EDX shows that phillipsite and chabazite comprises variable amounts of Na, K, Mg, and Ca ions in the molecular structure. In general, the high surface area of phillipsite resulting from the porous structure comprising many cavities and channels makes it an outstanding adsorbent material [9]. Moreover, zeolites are also characterized by low mining cost, nontoxicity, availability, bulk density, and high resistance to alteration [10, 11].

Al-Jarrah showed in his work the major properties of Jordanian natural zeolite and useful to use in capturing gas such as  $H_2S$ . Al-Jarrah found that the natural Jordan zeolites have effectively captured  $H_2S$  at pressures of 5 atm or higher while the adsorption does not take place at pressures lower than 5 atm. In addition, he found the capacity of adsorption of zeolite is found approximately 0.24 g  $H_2S$ /g zeolite for pressures of 6 atm or higher, when a rise in pressure, he further observed a weak or no effect on adsorption. Therefore, he concluded that the optimal pressure for Jordanian natural zeolite to capture  $H_2S$  is around 6 atm [6].

Treatment of wastewater is one of the oldest and the most applicable uses of natural zeolites adsorption of heavy metal ions contaminating wastewater like  $Pb^{2+}$ ,  $Cr^{3+}$ , and  $Cu^{2+}$  water on JZT or clinoptilolite has been emphasized recently as an alternative low-cost method for the removal of such metals [12, 13].

Omar *et al.* used natural JZT to estimate the adsorption of total organic carbon from industrial wastewater. They used different sizes of JZT in their study and various parameters were calculated. Likewise, they used different models such as Bohart-Adams, Thomas, Yoon-Nelson, and Wolborska to analyze the measured breakthrough curves and compared them with experimental values [14].

JNZ (Jordanian Natural Zeolite) was successfully used as an exchangeable material in a batch experiment to extract  $Ni^{2+}$  from aqueous models.

Table 1: XRF analysis results of zeolitic tuff

Chemicals	Al <sub>2</sub> O <sub>3</sub>	CaO	Cl	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO
wt. %	11.2	7.39	0.17	13.10	1.090	10.30
Chemicals	MnO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	TiO <sub>2</sub>
wt. %	0.180	1.96	0.413	38.3	0.102	3.12

Ni(II) adsorption on zeolite was significantly influenced by pH, concentration of Ni(II), adsorbent mass, and other parameters. Various thermodynamic parameters are also calculated such as free energy, enthalpy, and entropy and it is found the process of removing dye is exothermic and spontaneous [3].

The study conducted by Al-Mashaqbeh *et al.* used pure zeolitic and modified zeolite tuff to measure the removal of carbamazepine which is one of the pharmaceuticals residues. They used different techniques to investigate the goal of this study such as FTIR, XRF, XRD, and others. They found the efficacy of using pure zeolitic or modified zeolite tuff for removing carbamazepine from wastewater [7].

Desalination using zeolites as a sorbent material is considered as an eco-desalination technology due to the low operational cost and being environment friendly [15].

The current investigation was designed to study the adsorption isotherms, effect of pH and temperature on the adsorption of alkali metals (Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) onto Jordanian zeolitic tuff (phillipsite and chabazite) using batch adsorption method.

Materials and Methods

Collections of phillipsite/chabazite zeolitic tuff samples

The phillipsite tuff was collected from Jabal Al-Hala, east of Tafila, Jordan, and taken from different locations of Jabal Al-Hala.

Materials and characterization techniques

All chemicals used in this study including NaCl, KCl, and LiOH were purchased from Riedel-deHaën (Germany). A water-shaking bath (Memmert, Germany) was used to incubate samples at a specific temperature. Sample analysis was performed using Flame Photometer (Sherwood- United Kingdom). To monitor the pH

of solution, a portable pH meter 3110 (WTW - Germany) was used.

Samples characterization zeolitic tuff

To study the morphology of phillipsite/Zeolitic Tuff, the Scanning Electron Microscope (SEM) (FEI- Inspect F50 High Vacuum 6×10<sup>-4</sup> Pa, Eindhoven, NB, USA, University of Jordan) equipped with Shimadzu X-ray diffractometer (Energy dispersive X-ray spectroscopy (EDX)) MAXIMA 700, Shimadzu, Japan).

Preparation of natural phillipsite as an adsorbent

After collecting the samples, they were initially washed well by ultrapure water to remove any material or dirt sticking to the samples. Then, the samples were crushed by a Jaw crusher, and then subjected to a mechanical mortar to be milled. After that, the powder samples of phillipsite were sieved by a sieve of 60-120 mesh, and lastly, the obtained powder (with size 90 μm) was kept in an electrical oven at 200 °C for 24 hours and the final powder was ready to use as adsorption.

Preparation of stock solutions

A 0.01 M stock solution of all ions (Na<sup>+</sup>, Li<sup>+</sup>, and K<sup>+</sup>) was prepared and the stock solution was diluted to a series of solutions as (10 mM, 5 mM, 1 mM, 0.5 mM, and 0.1 mM) to establish the calibration curves. The adsorption capacity of phillipsite for each solution was measured using a batch experiment. The different masses (0.500 g, 1.000 g, and 1.500 g) of phillipsite were introduced into (50.0 mL standard solutions of Na<sup>+</sup>, Li<sup>+</sup>, and K<sup>+</sup> ions at three different pH values (4, 7, and 10). Each sample was shaken for 24 hours and the temperature of samples was adjusted at different temperatures (20, 30, 40, and 50 °C). Each sample was in contact with the adsorbent for 24 hours (the optimum time adsorption, the removal efficiency was the maximum 96.6%) and the experiment was

repeated three times to obtain more accurate results.

## Results and Discussion

### Characterization of natural phillipsite/ Zeolitic Tuff

The SEM image of phillipsite-zeolites shows spherulitic crystals with average lengths from 30 to 100  $\mu\text{m}$  and pseudo-orthorhombic prismatic crystals (Figure 1).

The EDX study displays the presence of elements such as Si, Al, Ca, K, and Na being rich in potassium. The chemical analysis of the phillipsite indicates the K-rich type with similar Na/K and Ca/K ratios and has a small variation in the Si/Al ratio (Figure 1).

### Effect of adsorbent concentration

In the adoption isotherm, the adsorption capacity ( $Q_e$  (mg/g)) was calculated using Equation 1:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

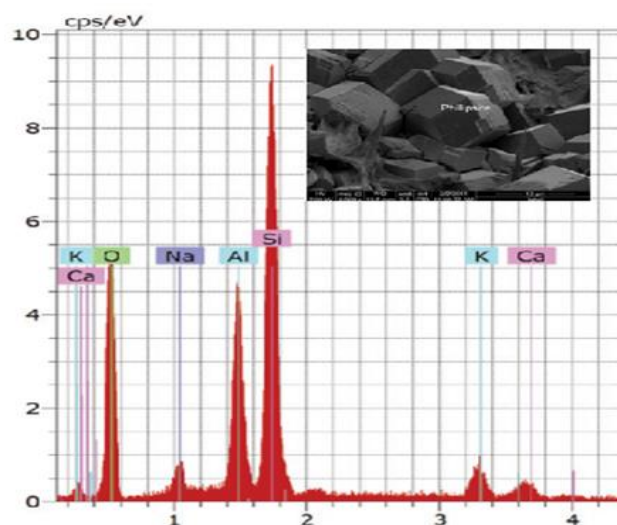
Where,  $C_0$  and  $C_e$  are the initial and final adsorbate concentrations of  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$ , respectively,  $V$  is the volume of meal ions (mL), and  $m$  is mass of adsorbent used (g) [16].

The competitive adsorption isotherms of  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  on Natural Jordanian zeolitic tuff (JZT) are given in Figure 2. At pH 4, the visual trend observed for adsorption was  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$  and at

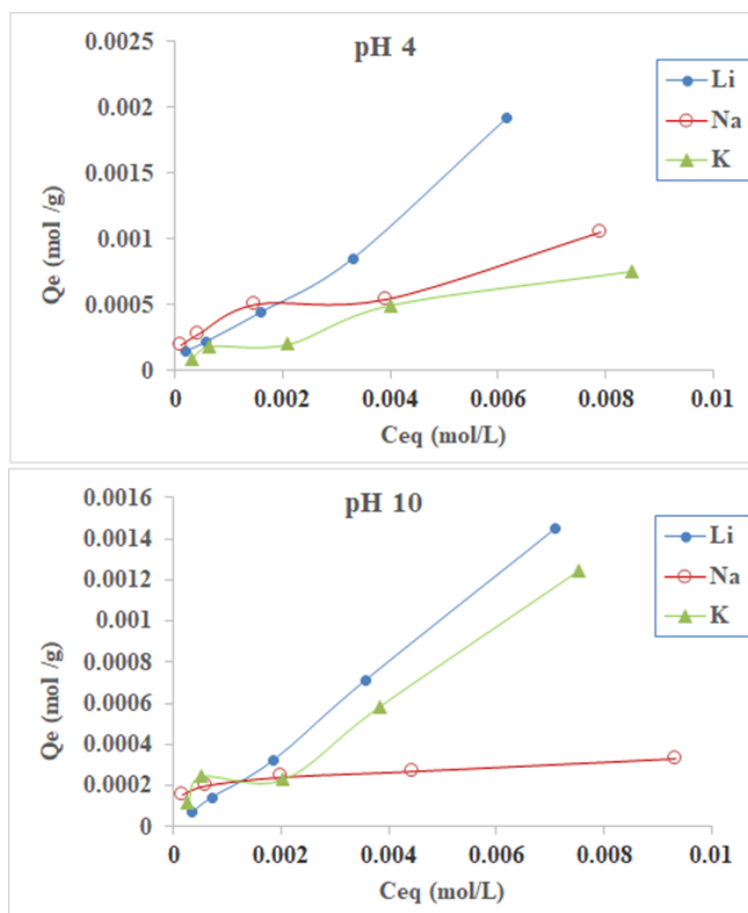
pH 10, the general trend observed was  $\text{Li}^+ > \text{K}^+ > \text{Na}^+$ . These trends reflected the importance of charge: size ratio of metal ions, where  $\text{Li}^+$ , having the smallest size among these metals, was found to have the highest adsorption, whereas the adsorbed of  $\text{Li}^+$  in both pH values (4 and 10) are 0.002 and 0.0015, respectively. This trend agrees with result that obtained by Rohmah and his team [17]. Furthermore, the adsorption isotherms of alkali metals, especially  $\text{Li}^+$  are almost linear (Figure 2). Moreover, it was noticed that adsorption did not reach the saturation stage (plateau) as usually observed in the adsorption of heavy metals like  $\text{Ni(II)}$ ,  $\text{Pb(II)}$ ,  $\text{Cd(II)}$ ,  $\text{Cu(II)}$ , and  $\text{Cr(III)}$  on JZT [18, 19].

Therefore, the adsorption of metals on a surface depends on numerous of physical and chemical factors such as molecular weight, ionic radius, electronegativity, and so forth [20].

When the concentration of adsorbent is low, a linear isotherm is usually expected [21]. However, in this study, the concentrations of alkali metals employed are relatively high (up to 0.01 M). Langmuir shapes (concave to the concentration axis) were observed in the case of adsorption of  $\text{Pb(II)}$ ,  $\text{Cd(II)}$ ,  $\text{Cu(II)}$ ,  $\text{Zn(II)}$ ,  $\text{Fe(III)}$ , and  $\text{Mn(II)}$  on clinoptilolite [22]. Thus, the adsorption behavior observed here for alkali metals on JZT is different from that for heavy metals.



**Figure 1:** Energy dispersive X-ray analysis of phillipsite crystals, and the inset figure show SEM of phillipsite/zeolitic tuff



**Figure 2:** Adsorption isotherms of Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup> on JZT

It is worth mentioning that the isotherms in Figure 3 were successfully obtained despite the fact that adsorption of any metal cation on zeolite should be associated by the release of exchangeable ions like Na<sup>+</sup> and K<sup>+</sup> from JZT as is observed in the case of adsorption of heavy metals on clinoptilolite [22].

The release of metal ions such as Na<sup>+</sup> and K<sup>+</sup> was significantly detected in the solution in the same way of the obtained result by Yuan of the adsorption of Pb(II) and Cd(II) on clinoptilolite [23]. Therefore, the results of the present study suggest that alkali metals may be adsorbed in the pores of JZT according to charge, shape, and concentration, and not on the ion exchange sites.

#### Effect of pH

Since pH is one of the major factors controlling the sorption process [24], altering both the surface charge of sorbent and the speciation of metal ions [25]. To study the effect of pH on the capacity of adsorption  $Q_e$ , two points of pH were taken, one at the acidic level at pH 4 and the other

at a basic level at pH 10. The pH degree was adjusted using a diluted HCl solution and the obtained solution was shaken for 2 hours at 200 rpm.

The active site load from the adsorbent's surface is affected by pH and Figure 2 displayed the effect of pH on the adsorption isotherms of Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup> on JZT.

The adsorption of Na<sup>+</sup> ion decreased by increasing the pH environment which may help to enhance adsorption on the zeolites surface, but the adsorption of Li<sup>+</sup> ion shows a slightly decreased by increasing the pH environment. This means that there is neither competition between H<sup>+</sup> ions and Li<sup>+</sup> nor Na<sup>+</sup> ions for the active sites of zeolites.

The opposite results were found in the case of K<sup>+</sup>, where, [26] found that the adsorption of K<sup>+</sup> ions on clinoptilolite increased in the pH range of 2 to 6 and decreased in the pH range of 6 to 12. The addition of zeolite to the solutions of metal ions was reported to raise the pH of solutions to 6-7 in the case of JZT [27] and 9.4 in the case of



clinoptilolite [23]. The difference in selective adsorption of  $K^+$ , and  $Na^+$  is attributed to the hydration energy changes, the electrostatic attractions, and the complexation between the alkali metal ions and the zeolite tuff. The ion exchange selectivities were determined by differences in hydration radii of the cation, because the smaller ionic hydration radii allow them to diffuse more easily into the solid-solution interface. As pH increases,  $H^+$  ions are removed from the cation exchange sites of zeolite. This gives the opportunity for binding of  $K^+$  more available for binding  $K^+$  because the effective ionic radius of  $K^+$  ions easily enters the tunnel structure of phillipsite zeolitic tuff [27]. In addition, the adsorption of  $Pb(II)$ ,  $Ni(II)$ ,  $Zn$ , and  $Cd(II)$  on JZT was reported to decrease with decreasing pH and was attributed to the increase in competition between heavy metals ions and  $H^+$  ions [28-30]. Furthermore, the adsorption of  $Cu(II)$ ,  $Zn(II)$ , and  $Mn(II)$  on clinoptilolite increased with pH increase [13].

Modeling of competitive adsorption

Competitive Langmuir model [31-33] was used to fit the competitive adsorption data of  $Li^+$ ,  $Na^+$ , and  $K^+$  components:

$$Q_i = \frac{Q_{m_i} K L_i C_i}{1 + \sum K L_i C_i} \quad (2)$$

Where,  $Q_i$  is the amount of metal ( $Li^+$ ,  $Na^+$ , and  $K^+$ ) adsorbed (mol metal/g zeolite) from the multicomponent system,  $C_i$  is the amount of metal  $i$  remained in solution (mol/L),  $K L_i$  is the Langmuir affinity constant, and  $Q_{m_i}$  is the maximum adsorption capacity (mol metal/g zeolite). Results are presented in Table 2. As illustrated in Figure 4, the experimental and calculated results of adsorption capacity were matched and fitted with the Langmuir model, and the Langmuir affinity constant was evaluated at pH 4 and 10 (Table 2). In addition, this model shows good descriptions of adsorption behavior.

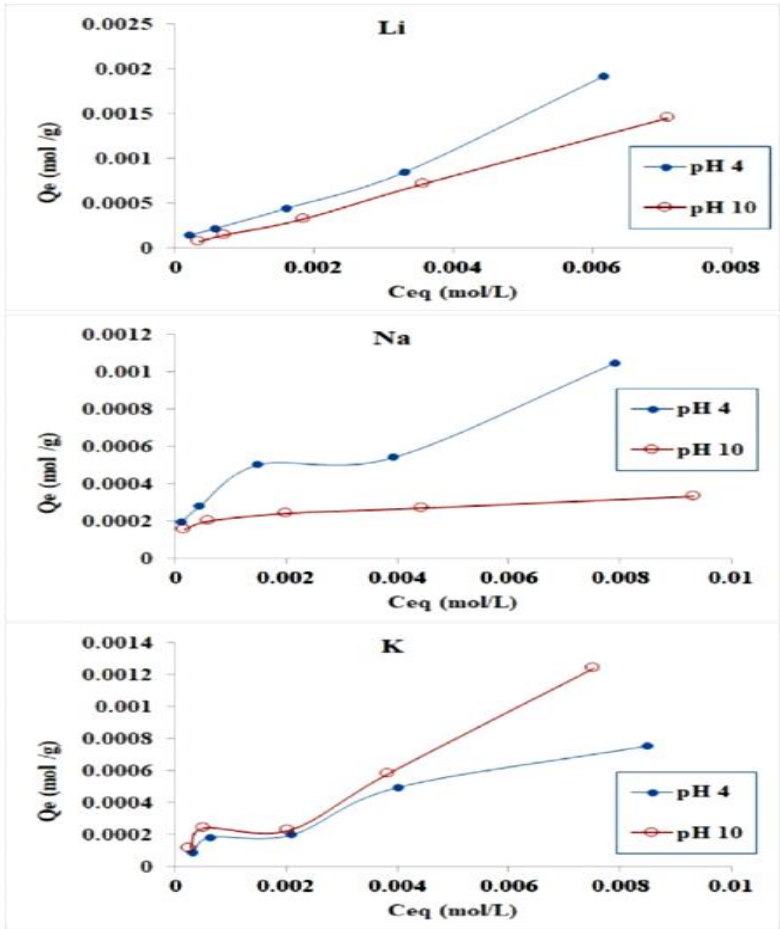
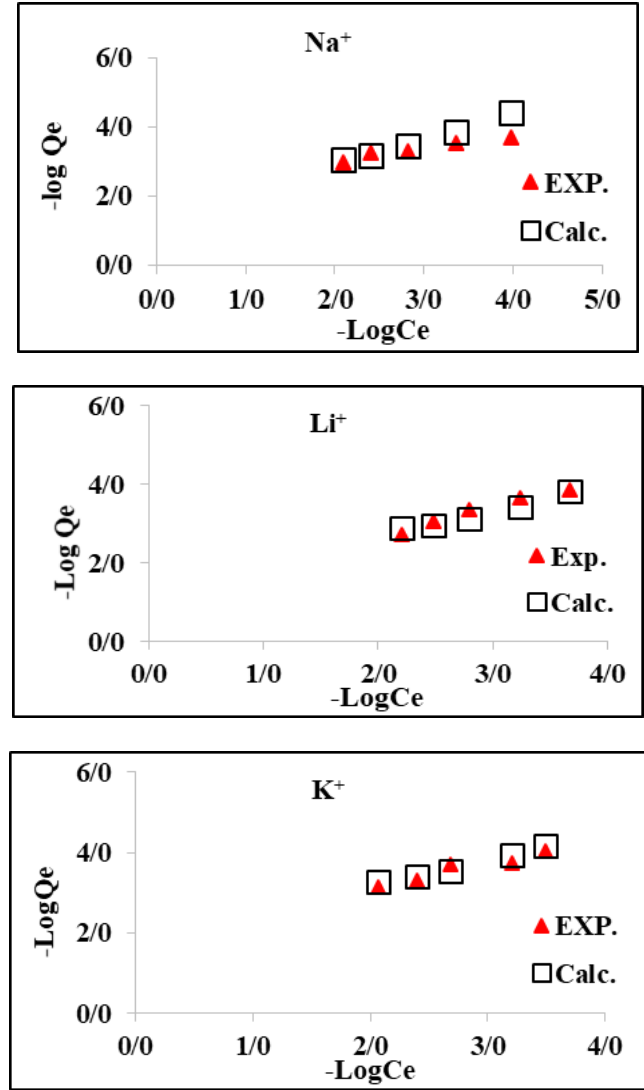


Figure 3: The effect of pH on the adsorption isotherms

**Table 2:** Langmuir adsorption capacity  $Q_m$  (mol/g) and affinity constant  $K_L$  (L/mmol) obtained from modeling the data using competitive Langmuir model with the maximum buffer capacity (MBC) = 0.033

Ion		pH 4	pH 10
$\text{Li}^+$	$Q_m$	$4.9 \times 10^{-3}$	-
$\text{Na}^+$	$Q_m$	$3.4 \times 10^{-3}$	-
$\text{K}^+$	$Q_m$	$2.7 \times 10^{-3}$	-
$\text{Li}^+$	$K_L$	155.4535	90.70534
$\text{Na}^+$	$K_L$	110.4985	27.21169
$\text{K}^+$	$K_L$	82.22693	125.3583
Standard error*		$2.4 \times 10^{-4}$	$1.9 \times 10^{-4}$

\*Standard error =  $\sqrt{\frac{\sum (y_i - \hat{y}_i)^2}{n - 2}}$ ,  $y_i$ : experimental, and  $\hat{y}_i$ : predicted.



**Figure 4:** The results of fitting the data of competitive adsorption of  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  on phillipsite at pH 4

The results of the model (Figure 4 and Table 2) are consistent with visual observations described in the previous sections (3.2 and 3.3), the Langmuir sorption isotherm displays the monolayer coverage of sorption surfaces and assumes a homogeneous surface [34].

The trend of adsorption capacity ( $Q_m$  (mol/g) zeolite) and affinity constant ( $K_L$ ) follows the order:  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$  at pH 4. Furthermore, the  $K_L$  values at pH 4 are higher than those at pH 10 in the case of  $\text{Li}^+$  and  $\text{Na}^+$ , but

not in the case of  $K^+$ . Thus, the model captures the general features of adsorption isotherms. The  $Q_m$  and  $KL$  values for adsorption of  $Li^+$ ,  $Na^+$ , and  $K^+$  on JZT are compared with those reported for heavy metals in Table 3. The  $Q_m$  value of  $K^+$  in the case of JZT (105.6 mg/g) is higher than that obtained in the case of clinoptilolite (66.67 and 32.80 mg/g). However, the  $KL$  value of  $K^+$  (0.0021 L/mg) is close to that of clinoptilolite (0.0033) [26] and 0.0020 L/mg [34]. Furthermore, the  $Q_m$  and  $KL$  values for  $Li^+$  adsorption in agreement with the reported values [24].

The  $Q_m$  values for adsorption of alkali metals on JZT are, in general, higher than those reported for adsorption of  $Pb(II)$ ,  $Cd(II)$ ,  $Cu(II)$ , and  $Zn(II)$  on JZT and clinoptilolite (Table 3). On the other hand, the  $KL$  values for adsorption of alkali metals on JZT are lower than those of heavy metals (Table 3). This is due to different sizes of atom isotherms (linear in the case of alkali metals) and concave (to the concentration axis) shape in the case of heavy metals.

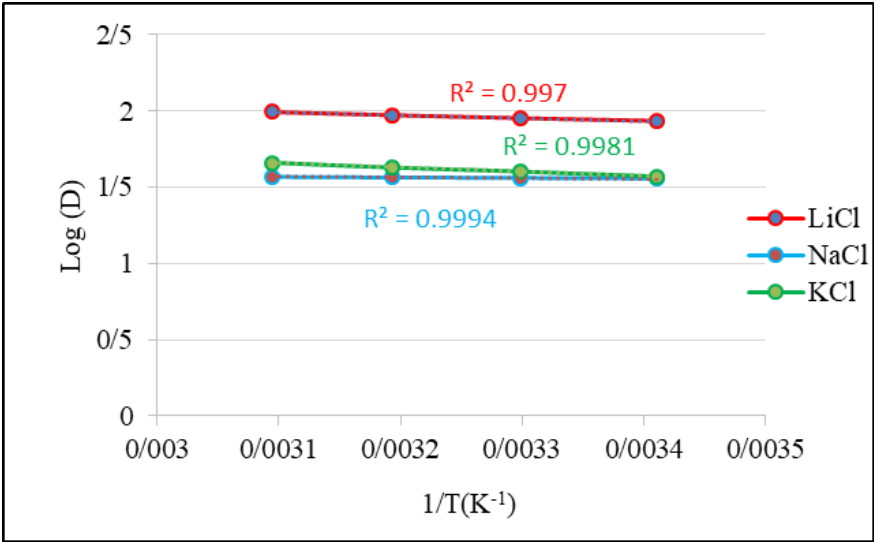
**Table 3:** Comparison of the Langmuir parameters of the present work with those reported for heavy metals

	Qm (mg/g)	KL(L/mg)	Adsorbent	Reference
$Li^+$	34.00	0.0224	JZT	Present work
$Na^+$	78.20	0.004806	JZT	Present work
$K^+$	105.60	0.002103	JZT	Present work
$K^+$	66.67	0.0033	Clinoptilolite	[26]
$K^+$	32.80	0.001967	Clinoptilolite	[35]
Cd(II)	25.9 IN LITERATURE	9.5	NJ zeolite	[19]
Cu(II)	14.30	7.36		
Zn(II)	41.84	0.059	JZT	[36]
Cu(II)	44.25	0.479	JZT	[8]
Fe(II)	0.417	-	NJ volcanic tuff	[29]
Cr(II)	0.151			
Pb(II)	56.82	0.629	Natural phillipsite tuff	[30]
Cd(II)	25.78	0.636		
Cr(III)	19.60	0.13	JZT	[18]
Cd(II)	38.9	0.35	Raw Zeolitic Tuff	[37]
Cu(II)	3.37	0.11	Clinoptilolite	[13]
Zn(II)	5.38	0.02		
Pb(II)	193.94	-	Clinoptilolite	[23]
Cd(II)	31.81	-	Clinoptilolite	[23]
Pb(II)	161.62	-	Chabazite	
Cd(II)	51.60	-	Chabazite	
Cu(II)	23.50	-	Chabazite	
Cu(II)	8.95	0.018268	Clinoptilolite	[38]
Zn(II)	8.70	0.012999	Clinoptilolite	[38]
Cu(II)	25.69	0.0336	Clinoptilolite	[39]
Pb(II)	48.07	-	Clinoptilolite-rich tuff	[31]
Cd(II)	4.88	0.0776	Clinoptilolite	[32]
Pb(II)	109.9	3.250	Synthesized Zeolite from coal fly ash	[40]
Cd(II)	53.476	1.222		
Cu(II)	57.803	0.700		
Zn(II)	36.765	0.324		
Co(II)	12.240	0.075		
Co(II)	22.12	0.354	Zeolite	[24]
Li(I)	31.12	0.019		



**Table 4:** Effect of temperature on distribution coefficients (D) of competitive adsorption of metal ions on phillipsite

Initial Concentration (mmol/L)		Temperature (°C)				Linear plot of D versus temperature	
		20	30	40	50	Slope	R <sup>2</sup>
5 × 10 <sup>-4</sup>	Li <sup>+</sup>	0.600	0.143	0.000	-0.200	-0.025	0.932
	Na <sup>+</sup>	0.900	0.550	0.023	-0.116	-0.033	0.998
	K <sup>+</sup>	0.880	0.411	0.129	0.013	-0.029	0.931
5 × 10 <sup>-3</sup>	Li <sup>+</sup>	0.381	0.261	0.036	-0.065	-0.016	0.978
	Na <sup>+</sup>	0.114	0.083	-0.025	-0.093	-0.007	0.963
	K <sup>+</sup>	1.021	0.640	0.340	0.118	-0.030	0.986
1 × 10 <sup>-2</sup>	Li <sup>+</sup>	0.262	0.206	0.025	-0.035	-0.011	0.950
	Na <sup>+</sup>	0.063	0.052	-0.010	-0.029	-0.003	0.926
	K <sup>+</sup>	5.815	2.963	0.953	0.150	-0.190	0.944
Solubility (g/100 g water) (Lide, 2005)	LiCl	86.2	89.8	94.0	98.4		
	NaCl	36.1	36.4	36.7	37.0		
	KCl	37.2	40.1	42.6	45.8		



**Figure 5:** Linear plots of log D versus 1/T for adsorption of K<sup>+</sup>, Na<sup>+</sup>, and Li<sup>+</sup> on JZT

*Effect of temperature*

The effect of temperature on competitive adsorption of Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup> ions on phillipsite is listed in Table 4 and showed a decrease in the values with increased temperature. Distribution coefficient (D), which refers to the concentration ratio of metal adsorbed per metal remaining in solution, was taken as a representative of the efficiency of adsorption. Negative D values obtained at high temperatures, especially at 50 °C (Table 4), were due to the release of small amounts of metal ions from phillipsite itself.

The release of exchangeable ions like Na<sup>+</sup> and K<sup>+</sup> was further observed in the case of the adsorption of Pb(II) and Cd(II) on clinoptilolite [23]. The results in Table 4 indicate that D values of alkali metals decreases with increasing temperature due to the exothermic nature of the adsorption process and the smallest size atom has the highest hydrated layer. The exothermic nature is further confirmed from the linear plots of log D versus 1/T (K<sup>-1</sup>) for adsorption of K<sup>+</sup>, Na<sup>+</sup>, and Li<sup>+</sup> on JZT (Figure 5). The thermodynamic parameters like Gibb's free energy, entropy, and enthalpy of the adsorption of metals ion were calculated using next

equations that help to understand the adsorption mechanism:

$$\Delta G^{\circ} = -RT \ln K_c \tag{3}$$

$$\ln K_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \tag{4}$$

Where,  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$ , and  $\Delta S^{\circ}$  are changes in the Gibbs free energy, change in enthalpy and change in entropy, respectively, T is temperature (K), R is gas constant (8.314 J/mol K), and K<sub>c</sub> is distribution coefficient.

Table 5 indicated the values of Gibbs free-energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and the entropy ( $\Delta S$ ). Table 5 presents the positive value of change in free energy for K<sup>+</sup>, Na<sup>+</sup>, and Li<sup>+</sup> indicating the adsorption spontaneously. In addition, the negative value of enthalpy referred to the adsorption process on the JZT is an exothermic [41, 42] and the negative value of entropy indicate that the effectiveness of adoption

process was decreases by an increase in the temperature [43], as shown also in the Table 4.

The calculated  $\Delta S$  values are 0.285, 0.081, and 0.132 kJ/mol.K for Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>, respectively. These values indicated that the entropy is decreasing in the adsorption process.

Guo *et al.* reported the K<sup>+</sup> adsorption on clinoptilolite had  $\Delta H$  and  $\Delta S$  values of -2.85 KJ/mol and  $\Delta S$  -2.85 J/mol.K, respectively [26]. However, the adsorption was endothermic in other cases. Jaskūnas and his team observed an increase in K<sup>+</sup> adsorption on clinoptilolite when temperature increased. Likewise, they found that, clinoptilolite adsorbed 13.4 mg/g of K<sup>+</sup> at 5 °C compared with 19.4 and 28.8 mg/g at 40 °C and 65 °C, respectively [35].

In the case of heavy metals, Lee and Moon found an endothermic nature of adsorption of Pb(II) on clinoptilolite which is opposite to the reported of Jaskūnas [22].

Table 5: Calculated thermodynamic parameters

	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ kJ/mol.K
Li <sup>+</sup>	-23.3	-23.4	-0.285
Na <sup>+</sup>	-41.5	-41.5	-0.081
K <sup>+</sup>	-85.5	-85.6	-0.132

The sensitivity of distribution coefficient values to the change in temperature can be deduced from the slope of plots of D as a function of temperature (K). The high negative slope of plots in the case of K<sup>+</sup> and to less extent Li<sup>+</sup> reflects the high sensitivity of K<sup>+</sup> and Li<sup>+</sup> adsorption to temperature. On the other hand, Na<sup>+</sup> has very small slope indicating that adsorption is independent on temperature.

It is interesting to correlate these observations with the solubility of LiCl and KCl which increases with increasing temperature from 20 to 50 (Table 4). However, the NaCl solubility is almost independent on temperature (Table 4).

Conclusion

In the present investigation, the importance of using zeolitic was explained as a sorbent toward alkali metal ions and the novelty behavior of natural zeolitic tuff was appeared. In addition, it

was demonstrated that zeolite may encapsulate alkali metal ions in pores in contrast to the heavy metals which exert ion exchange. JZT has possible to tune the adsorption selectivity depending on pH and temperature. Consequently, the adsorption of alkali metals is exothermic and associated with entropy increase. Thus, natural zeolite may be used for the desalination of seawater by trapping alkali metals in the pores.

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## Authors' Contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

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