

# The effect of HCl treatment on water vapor adsorption characteristics of clinoptilolite rich natural zeolite

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## Abstract

In this study, water vapor adsorption properties of the clinoptilolite rich zeolite tuff, from Bigadic (Turkey), and its modified forms were examined. The modified forms were obtained by treating the tuff with HCl solutions (0.032, 0.16, 0.32, 1.6 or 5 M) at 25, 40, 75 and 100 °C for 3 h. Infrared spectroscopy and water vapor adsorption were used for the characterization of the zeolites. Langmuir, BET and Dubinin–Rudushevich methods were applied in the analysis of water vapor adsorption data. Applications of Dubinin Rudushevich equation to the water adsorption data displayed that the super-micropore volume was not very sensitive to acid treatment. It was found out that the Langmuir surface area and ultra-micropore volume depend on the degree of the removal of aluminum from the structure.

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## 1. Introduction

Zeolites are crystalline, hydrated alumina silicates of group 1 and 2 elements, consisting of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra linked by oxygen atoms to compose the framework. In the zeolite framework, each aluminum atom introduces one negative charge on the framework which must be balanced by an exchangeable cation ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , etc.). The exchangeable cations located within the framework play a crucial role in adsorption and thermal properties of the zeolites. Clinoptilolite, one of the most commonly observed natural zeolite mineral, is a member of the heulandite group [1]. Its framework structure consists of three channels. The channel A and B, 10-member and 8-member rings, respectively; are parallel to each other while the channel C, 8-member

ring, intersects the channel A and B. Strong specific interaction of the cationic sites with water vapor, due to high dipole moment of the water leads to selective adsorption of water by the zeolites. Based on this strong water–clinoptilolite interactions, several processes with different applications of water adsorption could be mentioned such as air drying [2,3], corn drying [4,5], energy storage [6,7], hydrocarbon drying [8] applications. In separation (gas or liquid) technology, the existence of water hinders the adsorption of the others since it is selectively adsorbed by various adsorbents, especially by the zeolites. On the other hand the presence of water determines the product obtained in catalytic reactions [9,10].

Adsorption of small water molecule (molecular diameter: 2.66 Å) is also used to obtain information regarding the impurities in natural zeolite tuff [11] and characterize the microporous adsorbents such as microporous carbon and zeolite. The water vapor adsorption on cation exchanged natural zeolite [12,13], HZSM-5 [14] and carbon [15] have been studied in the analysis

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of the interaction mechanism between water and energetically heterogeneous surface.

The treatment of the natural zeolitic tuff with HCl causes the dealumination (hydrolysis of Al–O–Si bonds) besides of the exchange of the cations by hydronium ions ( $\text{H}_3\text{O}^+$ ). The study [16] of water vapor adsorption on dealuminated fuajosite showed that the change in the shape of the adsorption isotherm and the existence of correlation between the micropore volume accessible to water and the framework Si/Al ratio. Similarly, Sano et al. [17] obtained linear relationship between the number of framework aluminum of ZSM-5 zeolite and limiting pore volume estimated by water vapor adsorption. In both studies, the water molecule was used as probe molecule for understanding the dealumination degree. In the study presented hereby the aim was to prepare the HCl treated forms of the natural zeolitic tuff and investigate the effect of the HCl treatment parameters (temperature and concentration) on the water vapor adsorption properties of natural zeolite.

## 2. Experimental

The natural zeolitic tuff used in this study originated from the deposite in Bigadiç, Turkey. The major impurity in the tuff was quartz. The tuff was crushed and sieved to obtain 4–5 mm fractions, washed with distilled water at 25 °C to remove the water soluble impurities. This washed zeolite (CLI) was dried in a vacuum oven at 180 °C and used to prepare the acid treated forms. The chemical composition of CLI was (in oxide wt%):  $\text{SiO}_2$ , 71.75;  $\text{Al}_2\text{O}_3$ , 10.91;  $\text{Fe}_2\text{O}_3$ , 0.54;  $\text{MgO}$ , 1.08;

$\text{CaO}$ , 2.3;  $\text{Na}_2\text{O}$ , 1.19;  $\text{K}_2\text{O}$ , 4.3;  $\text{TiO}$ , 0.17;  $\text{MnO}$ , 0.0008 and  $\text{H}_2\text{O}$ , 7.77. This result showed that with an Si/Al ratio of 6.22 and  $(\text{Na} + \text{K}) \geq \text{Ca}$ , the CLI zeolite is fine within the composition range of high-silica clinoptilolite [18].

Acid treated forms were prepared by treating 5 g of CLI with 100 ml of 0.032, 0.16, 0.32, 1.6 and 5 M HCl solutions in a shaker at 25, 40, 75 and 100 °C for 3 h. Then it was washed until no  $\text{Cl}^-$  ions were detected in the washing water by using  $\text{AgNO}_3$  solution. The acid extracts were analyzed for Na, K, Al, Ca, Mg and Fe elements by using atomic absorption spectrophotometer (X Orian 10BQ).

In the characterization of the CLI and its acid treated forms, infrared and water vapor adsorption data were used. The infrared spectra of the zeolites were taken by using KBr pellet technique with Shimadzu IR 470 spectrometer. Water adsorption isotherms (at 25 °C) were measured using volumetric apparatus (Omnisorp 100cx) by static technique. Prior to isotherm acquisition, the CLI were outgassed for 16 h by heating at 160, 250, 400 or 600 °C under vacuum of higher than  $10^{-5}$  mbar.

## 3. Results and discussion

### 3.1. Acid treatment studies

The cation content of the acid extracts was used to calculate the chemical composition of the zeolites used in this study and presented in Table 1. The exchange degree ( $X_i$ ) of each cation ( $i$ ) which is the removal percent of the initial amount of the cation into zeolite was also

Table 1  
Chemical composition of the acid (HCl) treated zeolites used in this study

HCl treatment conditions		% $\text{Al}_2\text{O}_3$	% $\text{Fe}_2\text{O}_3$	% $\text{Na}_2\text{O}$	% $\text{K}_2\text{O}$	% $\text{CaO}$	% $\text{MgO}$	% $\text{SiO}_2$
Concentration (M)	Temperature (°C)							
0.032	25	10.81	0.54	1.15	4.17	2.15	1.07	68.90
	40	10.70	0.54	1.15	4.13	2.07	1.04	71.20
	75	10.70	0.54	1.12	4.04	2.12	1.08	70.50
0.16	25	10.57	0.53	1.12	3.99	2.05	1.04	70.49
	40	10.22	0.54	1.11	3.95	1.95	0.98	71.05
	75	10.28	0.52	1.11	3.77	1.78	0.86	72.18
	100	9.13	0.48	1.09	3.67	1.85	0.88	73.45
0.32	25	10.43	0.53	1.13	3.94	1.99	1.03	70.20
	40	9.88	0.53	1.12	3.86	1.76	0.85	71.64
	75	8.72	0.48	1.10	3.66	1.59	0.78	73.63
1.6	25	10.00	0.53	1.10	3.73	1.94	0.88	70.78
	40	9.58	0.52	1.11	3.73	1.79	0.92	71.84
	75	8.02	0.30	1.11	3.54	1.36	0.59	74.84
	100	6.41	0.26	1.09	3.38	1.10	0.83	74.65
5	25	9.68	0.51	1.15	3.85	2.05	1.01	71.20
	40	9.58	0.50	1.14	3.78	1.82	0.90	70.46
	75	4.68	0.31	1.12	3.66	1.20	0.23	78.51
	100	2.58	0.05	1.13	3.56	0.96	0.15	79.31

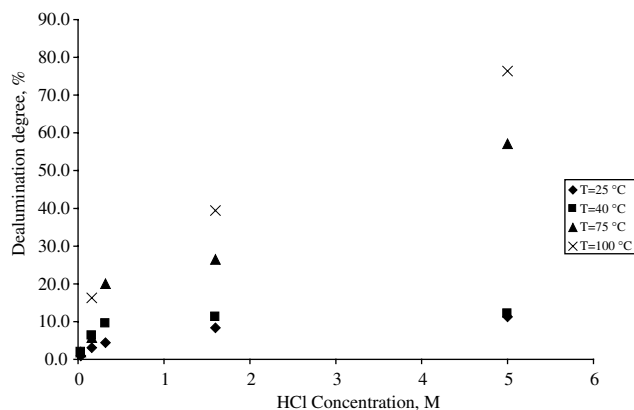


Fig. 1. The change in dealumination degree with HCl concentration.

calculated to compare the effect of the HCl treatment on each cation. As can be seen from Table 1, the cation content of the zeolite decreased with increasing HCl temperature and concentration but the removal of cation and aluminum was incomplete. The monovalent cations, such as  $\text{Na}^+$  and  $\text{K}^+$  ions content of the zeolite slightly changed during the acid treatment applied in this study. The exchange degree of the  $\text{Na}^+$  and  $\text{K}^+$  ions ( $X_{\text{Na}}$  and  $X_{\text{K}}$ ), is low (<10% and 20%, respectively) for the temperatures of 25, 40, 75 and 100 °C and changes a little with acid concentration. However temperature and HCl concentration were very effective in the removal of  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  cations and their exchange degrees reached to 90%, 57% and 85% at 100 °C, respectively. Table 1 becomes also clear that the removal of silicon atom hardly takes place during acid treatment indicating the high stability of clinoptilolite rich natural zeolite in the HCl solution. As seen from the Fig. 1 the dealumination ( $X_{\text{Al}}$ ) gradually increased with HCl concentration and reached to 57% and 75% at 75 and 100 °C, respectively; whereas,  $X_{\text{Al}}$  was low (10%) and not influenced by HCl concentration at 25 and 40 °C.

### 3.2. IR Studies

The IR spectra (at the 400–1200  $\text{cm}^{-1}$  region) of the representative acid treated zeolites are shown in Fig. 2(a) and (b). For the zeolites prepared the strong bands at 1056 and 451.2  $\text{cm}^{-1}$ , assigned to a T–O asymmetric stretching and T–O bending vibrations of the internal tetrahedra, respectively, and the weak bands at 790 and 604.8  $\text{cm}^{-1}$  wave numbers assigned to external symmetric stretching and double ring vibrations, respectively, were observed.

The effect of dealumination was observed with the shift in the wave numbers of the IR bands. Fig. 2(a) shows the change in the spectrum with the HCl concentration at 75 °C. As seen from the figure the position of the vibrations at 1056  $\text{cm}^{-1}$  (the asymmetric stretching mode involving mainly the tetrahedral atoms) is very

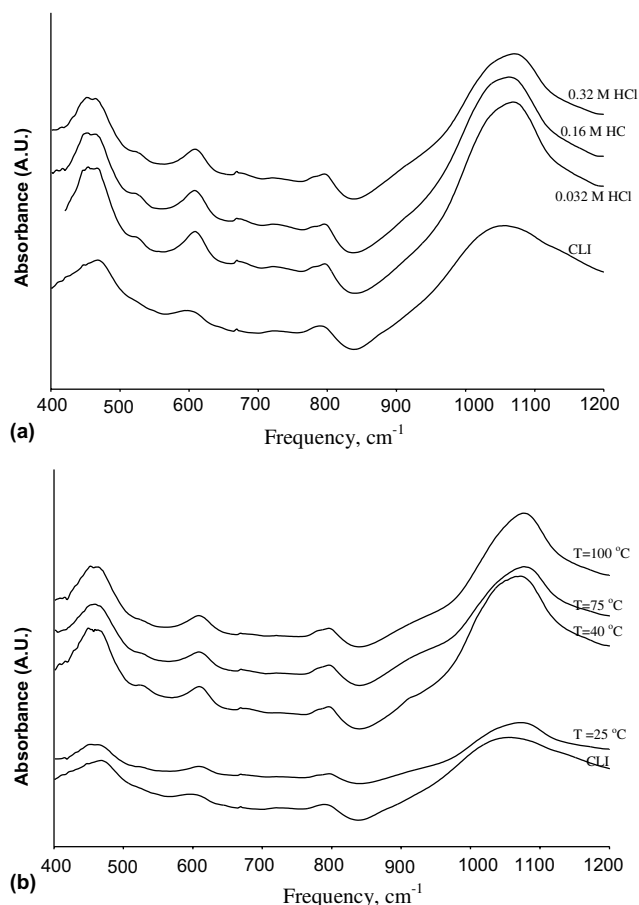


Fig. 2. (a) Infrared spectra of CLI and acid treated natural zeolite at 75 °C. (b) Infrared spectra of CLI and acid treated natural zeolite with 1.6 M HCl solutions.

sensitive to the dealumination degree and this zeolitic band shifted to 1080  $\text{cm}^{-1}$  as the dealumination degree increased from 20.1% to 57.1% depending on the increase in HCl concentration from 0.032 to 0.32 M. Similarly the effect of acid treatment temperature on the HCl concentration of 1.6 M can clearly seen from the Fig. 2(b) as shift in the position of the vibration at 1056  $\text{cm}^{-1}$  to 1081  $\text{cm}^{-1}$  with increase in the dealumination degree from 8.3% to 39.4% with increasing temperature from 25 to 100 °C. The shifting of the 1056  $\text{cm}^{-1}$  wave number of T–O–T bond to the higher values is attributed to the dealumination of zeolite framework and the change in the bond strength and Si–O–Si angle [19].

### 3.3. Adsorption studies

Fig. 3 shows the effect of outgassing temperature on the water vapour adsorption isotherms for CLI. The gradual increase in the amount adsorbed was observed for the zeolites outgassed up to 400 °C. As the outgassing temperature further increased, the amount of water vapor adsorbed by the zeolite decreased owing to

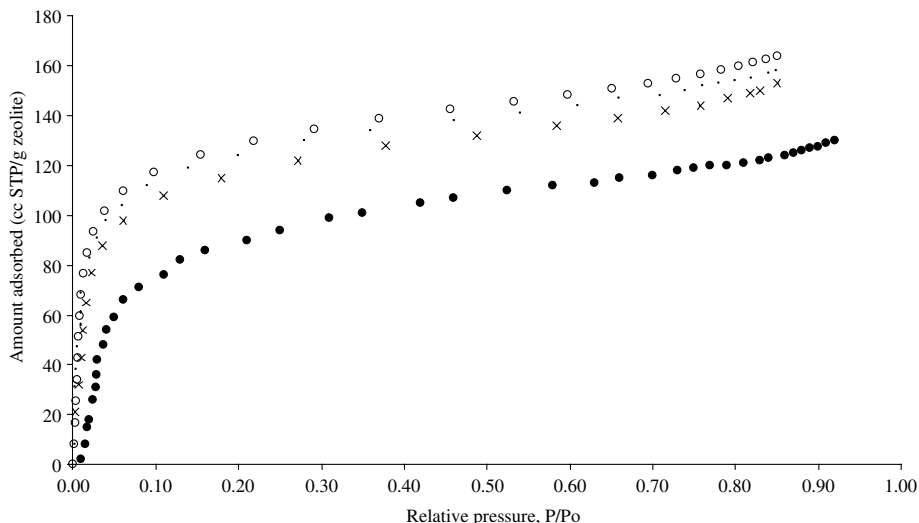


Fig. 3. Water vapor adsorption isotherm of the CLI outgassed at 160 °C (×), 250 °C (·), 400 °C (O) and 600 °C (●).

collapse of the framework. Therefore, the outgasing of CLI and acid treated zeolites was performed at 400 °C. The water vapour adsorption isotherms of the CLI zeolite and its representative acid treated forms are given in the Fig. 4. The isotherms are of type 1. However a slight increase in adsorption at high relative pressure was observed relating the presence of the impurity or

extraframework formation on the crystal surface as expected for natural zeolites [20]. The isotherms are very similar for the zeolites treated at 25 °C. However the adsorption at the zeolites treated at 100 °C diminished as a result of decrease in polar nature of the zeolite crystal.

The surface area of the zeolites was determined by using BET and Langmuir equations from isotherm data and presented in the Table 2. Although the Langmuir surface area is more commonly reported for monolayer adsorption on microporous solids, BET method was also used for understanding the strength of interaction between zeolite surface and water vapor. Surface areas are lower when calculated with the BET equation, indicating that the formation of second adsorption layer may occur before the surface could be covered completely by the adsorbate, since the desorption occurs depending on the high amount of heat which has evolved during water vapor adsorption. This can also be understood from the high BET C values calculated (Table 2). BET C values are related to the strength of H<sub>2</sub>O–adsorbent interactions and the positive values indicating the enthalpy of first adsorbed layer was higher than the latent heat of water vapor. As seen from Table 2, the BET C values are very high meaning that monolayer is instantly formed and multilayering starts immediately.

The Dubinin–Radushevich curve ( $\ln W$  vs  $\ln(P_0/P)^2$ ) is plotted with experimental data in the range of relative pressure up to around 0.1 and presented in Fig. 5. As seen from the figure the Dubinin–Radushevich (D–R) plots presents two linear parts. The first one, in the low relative pressure range (high  $\ln(P_0/P)^2$ ), corresponds to the adsorption of water on specific sites (balancing cation) in narrow pores (ultra-micro pores) and the second one, in the high relative pressure range

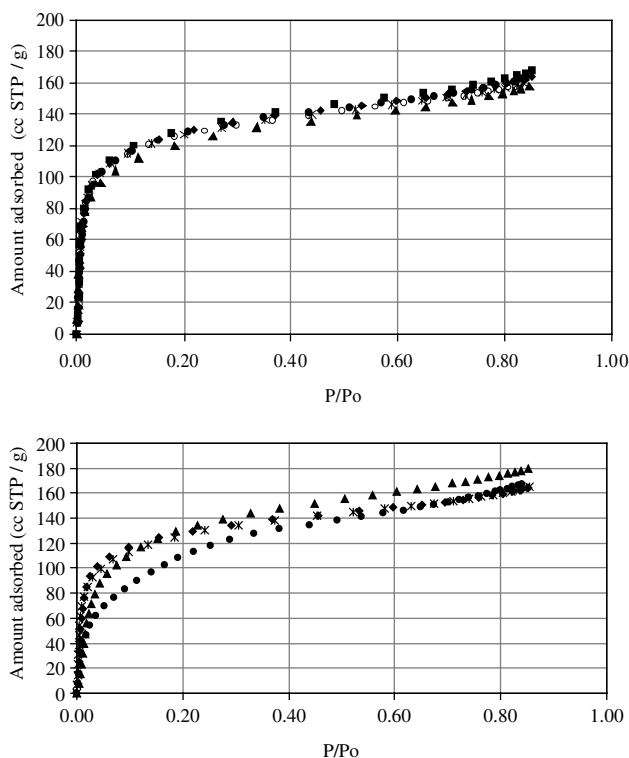


Fig. 4. Water vapor adsorption isotherm of the CLI (◆) and its acid treated forms at 25 °C (upper) and 100 °C (lower). HCl Concentrations (M): (O) 0.032; (\*) 0.16; (■) 0.32; (▲) 1.6; (●) 5.

Table 2  
Water vapour adsorption properties of the acid treated clinoptilolite rich tuff

Temperature (°C)	HCl concentration (M)	$A_L$ (m <sup>2</sup> /g)	$A_{BET}$ (m <sup>2</sup> /g)	$C$	$W_{01}$ (cc/g)	$W_{02}$ (cc/g)	$W_0$ (cc/g)	$V_{max}$ (cc/g)
CLI		384	299	684	0.0570	0.065	0.122	0.13
25	0.032	384	298	431	0.060	0.063	0.122	0.13
	0.16	381	298	496	0.054	0.067	0.120	0.13
	0.32	388	297	6907	0.058	0.065	0.122	0.14
	1.6	370	279	856	0.040	0.070	0.111	0.14
	5	388	279	519	0.053	0.069	0.112	0.14
40	0.032	361	271	360	0.052	0.058	0.111	0.13
	0.16	359	260	1828	0.050	0.057	0.106	0.12
	0.32	369	293	2007	0.050	0.056	0.106	0.13
	1.6	359	280	117	0.050	0.073	0.122	0.13
	5	402	326	110	0.062	0.067	0.128	0.13
75	0.032	362	279	567	0.050	0.049	0.099	0.12
	0.16	410	317	96	0.059	0.061	0.199	0.14
	0.32	372	297	106	0.044	0.060	0.104	0.13
	1.6	350	287	52	0.049	0.052	0.101	0.13
	5	197	239	31	0.023	0.054	0.077	0.11
100	0.16	383	298	327	0.045	0.059	0.104	0.13
	1.6	395	319	65	0.054	0.059	0.116	0.15
	5	306	273	37	0.026	0.063	0.089	0.14

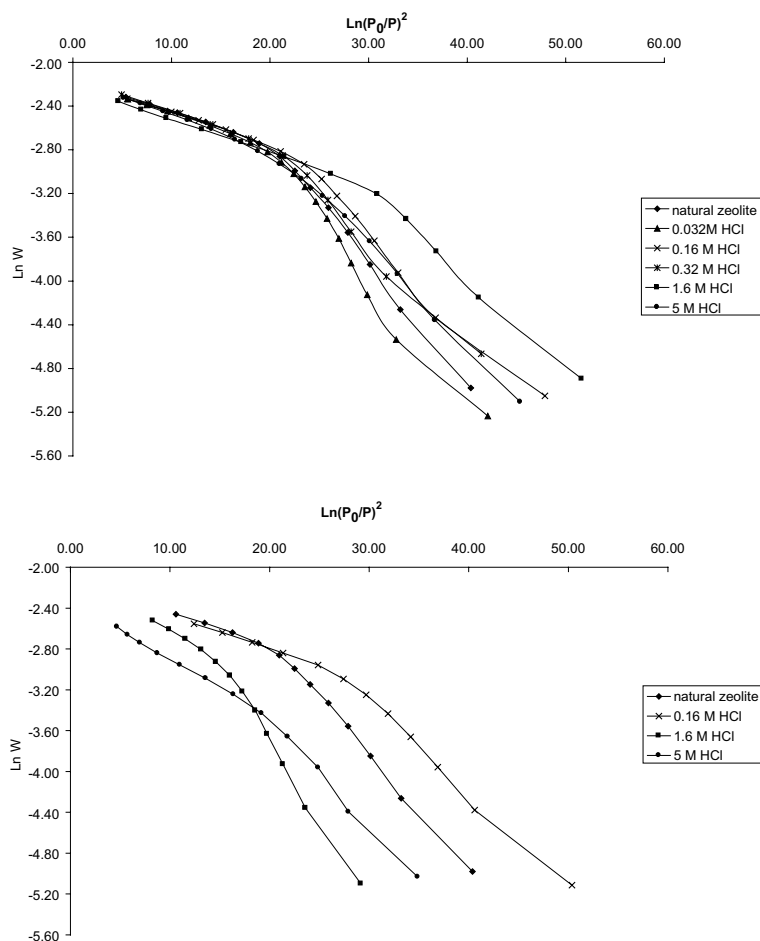


Fig. 5. Dubinin–Radushevich plots of the CLI and its acid treated forms at 25 °C (upper) and 100 °C (lower).

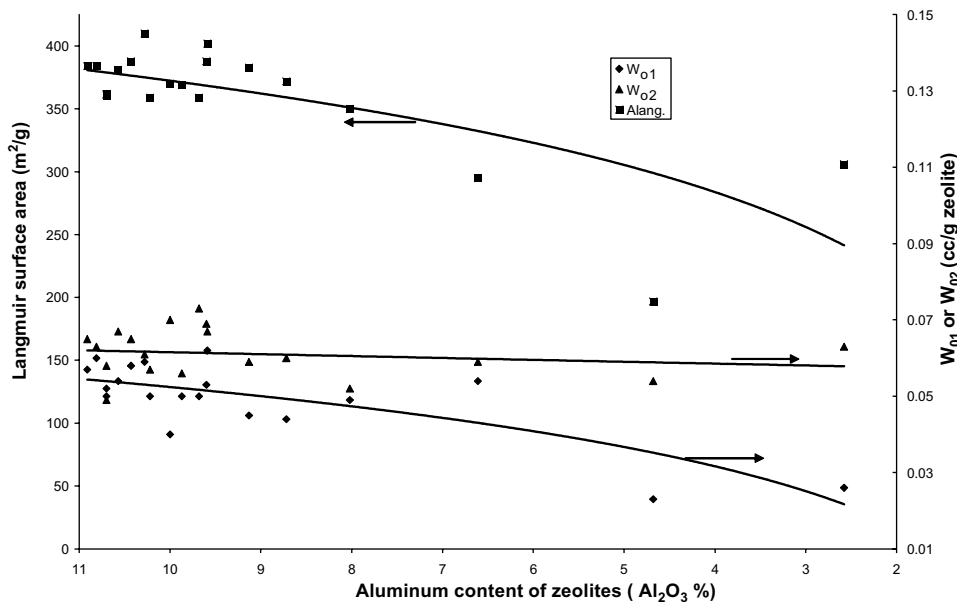


Fig. 6. The change in the specific surface area and the micropore volumes with aluminum content of zeolite.

(low  $\text{Ln}(P_0/P)^2$ ), related to filling of wide pores (super-micropores) with non-specific sites under the effect of dispersion interactions. For that reason, in the analyses of the D–R plots the two-term Dubinin–Radushkevich equation [21],

$$W = W_{01} \exp \left( - \left( \frac{RT}{E_1} (\text{Ln}(P_0/P)) \right)^2 \right) + W_{02} \exp \left( - \left( \frac{RT}{E_2} (\text{Ln}(P_0/P)) \right)^2 \right) \quad (1)$$

was used, where  $W$  is the amount adsorbed (cc/g) at relative pressure ( $P/P_0$ ) and  $E_1$  and  $E_2$  are characteristic energy of adsorption in ultra-micropore and super-micropore, respectively.  $R$  is gas constant and  $T$  is adsorption temperature. Adsorption characteristic energy can be calculated from the slope of the D–R plots. As seen from Fig. 5, in the high relative pressure (low  $\text{Ln}(P_0/P^2)$ ) range the D–R plots have almost similar trends but are scattered in low relative pressure range (high  $\text{Ln}(P_0/P^2)$ ) at 25 °C HCl treatment. This shows that HCl treatment altered only the adsorption mechanism in ultra-micropores. However the adsorption mechanism in super and ultra-micropore was influenced by the HCl treatment at 100 °C. On the other hand, the extrapolation to  $\text{Ln}(P_0/P)^2 = 0$  of D–R plots leads to the determination of the specific total micropore volume,  $W_0$ . The volume at the intersection of the two linear lines (at about 0.06 of relative pressure) is used to calculate ultra-micropore volume,  $W_{01}$ . The super-micropore volume,  $W_{02}$  was obtained by subtracting of  $W_{01}$  from  $W_0$  and presented in Table 2. As seen from the table, the ultra-micropore volumes,  $W_{01}$  are influenced by

the acid treatment depending on HCl temperature and concentration. However  $W_{02}$  values of the zeolites practically did not change (ca. 0.06 cc/g) during the acid treatment. Similarly the maximum adsorption capacity,  $V_{\text{max}}$  (amount adsorbed at  $P/P_0 = 0.85$ ) at adsorption temperature, 25 °C did not significantly change. The effect of the acid treatment can be explained with the change in the  $\text{Al}_2\text{O}_3$  content of zeolite. Fig. 6 shows the change in Langmuir surface area,  $A_L$  and micropore volumes with the aluminum content (as  $\text{Al}_2\text{O}_3\%$ ) of zeolite. The surface area,  $A_L$  and ultra micropore volume,  $W_{01}$  did not significantly change when aluminum content was higher than 8% (i.e., dealumination degree was 40%). Further dealumination was reflected as decrease in  $A_L$  and  $W_{01}$ . For example the zeolites treated with 5 M HCl at 75 and 100 °C, which have 57.1% and 76.1% dealumination degree, respectively, have the smallest  $W_{01}$  values, ca. 0.025 cc/g. This decrease may be due to the removal of aluminum from the framework.

#### 4. Conclusion

This study in which the effect of acid (HCl) treatment on the water vapor adsorption properties of clinoptilolite rich zeolitic tuff was investigated, concentration and temperature of HCl solution were not effective in the removal of monovalent cation such as Na and K. However, the increase of both temperature and concentration caused an increase in the removal of univalent cations such as Mg, Fe and Ca. Removal of the aluminum was very sensitive to HCl solution concentration at high treatment temperature. During this removal

the super-micropore volume did not significantly change (about 0.06 cc/g). The ultra-micropore volume and the Langmuir surface area decreased approximately to 0.026 cc/g and 300 m<sup>2</sup>/g when dealumination degree reached to  $\geq 40\%$ . This can be explained with the removal of framework aluminum with the above percent where the specific interaction was dominant.

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