



## **Effects of Hydrochloric and Acetic Acid Modification on the HTAB and K<sup>+</sup> Adsorption Characteristics of Natural Zeolites**

### **Hidroklorik ve Asetik Asit Modifikasyonunun Doğal Zeolitlerin HTAB ve K<sup>+</sup> Adsorpsiyon Karakteristikleri Üzerindeki Etkileri**

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#### **Abstract**

In this study, the effects of hydrochloric acid (HCl) and acetic acid (HAc) modification on the hexadecyl trimethyl ammonium bromide (HTAB) and K<sup>+</sup> adsorption characteristics of a natural zeolite were investigated. Electrokinetic evaluations showed that the zeta potential values of acid-modified samples were considerably more negative compared to natural zeolite. Additionally, the pH regulation behavior of the acid-modified samples was found to differ from the natural zeolite sample and it was in agreement with the results of zeta potential measurements. It was clear that the acid modification processes positively affected the surface properties and improved the cation exchange capacity (CEC) of natural zeolite. The results for the adsorption studies showed that the adsorption density of zeolite increased at elevated HTAB and K<sup>+</sup> concentrations. Moreover, following the zeta and pH profile results, a considerable difference in the adsorption ability between natural and acid-modified zeolite samples is present in terms of HTAB and K<sup>+</sup> adsorption characteristics. It is concluded that acid modification can be used in the enhancement of the adsorption ability of zeolites.

**Keywords:** Zeolite, Acid Modification, Adsorption, HTAB, Potassium

#### **Özet**

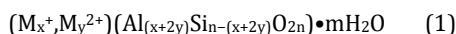
Bu çalışmada hidroklorik (HCl) ve asetik asit (HAc) modifikasyonunun doğal zeolitlerin HTAB ve K<sup>+</sup> adsorpsiyon karakteristikleri üzerindeki etkileri araştırılmıştır. Yapılan elektrokinetik değerlendirmeler asitle modifiye edilmiş örneklerin zeta potansiyeli değerlerinin doğal zeolite kıyasla önemli derecede daha negatif olduğunu göstermiştir. Buna ek olarak, asitle modifiye edilmiş örneklerin pH davranışının zeta potansiyeli ölçümü sonuçları ile uyumlu bir şekilde doğal zeolit örneklerinden farklı olduğu bulunmuştur. Asit modifikasyonu işlemleri doğal zeolitlerin yüzey özelliklerini ve kation değişim kapasitelerini olumlu olarak etkilemiştir. Adsorpsiyon çalışmalarının sonuçları zeolit adsorpsiyon yoğunluğunun yüksek HTAB ve K<sup>+</sup> konsantrasyonlarında arttığını göstermiştir. Ayrıca, zeta ve pH profili sonuçlarını takiben HTAB ve K<sup>+</sup> adsorpsiyonu açısından doğal ve asitle modifiye edilmiş örnekler arasında adsorpsiyon yeteneği açısından kayda değer bir farklılık bulunduğu belirlenmiştir. Asit modifikasyonunun doğal zeolitlerin adsorpsiyon yeteneğinin geliştirilmesinde kullanılabileceği sonucuna varılmıştır.

**Anahtar Kelimeler:** Zeolit, Asit Modifikasyonu, Adsorpsiyon, HTAB, Potasyum

## 1. Introduction

Zeolites are porous crystalline aluminosilicates that contain a channel structure that providing size and shape selectivity for guest molecules. These cation containing (i.e. Na<sup>+</sup>) channels compensate for the negative charge within the structure of zeolites. Moreover, zeolites can absorb water and desorb it upon heating without destruction of the crystalline structure [1-2]. Due to these properties zeolites have found widespread application as heterogeneous catalysts, absorbents, and ion-exchangers [3].

There are more than 80 types of zeolites with different crystalline structures and morphology found in Earth's crust [4]. The general formula of a zeolite is given in Eq. 1.



In Eq. 1, M<sup>+</sup> and M<sup>2+</sup> are monovalent and divalent cations such as Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, n is half of the number of oxygen atoms and m is the number of water molecules [5-6].

The application of natural zeolites for wastewater treatment is still a promising technique in environmental cleaning processes owing to their adsorption/desorption abilities. On the other hand, natural zeolites have several disadvantages compared to synthetic zeolites such as lower adsorption capacity for heavy metal ions and smaller pore sizes which prevent the sorption of larger molecules, which limit the range of potential applications [7-8]. For these reasons, nowadays, there have been many studies on natural zeolites [9].

To adsorb both anions and cations, natural zeolites can be modified by different treatment methods such as heating and chemical modification, which affect the cation location and pore opening. Zeolites usually gain cations such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> during the acid modification process by interaction with the solution due to their ion exchange and adsorption abilities. Additionally, the acid modification can provide the dissolution of some amorphous materials that block the pores of natural zeolites [10-12]. The effects of the crystal size, morphology, and chemical composition of zeolites should be considered for the

understanding of their cation exchange capacities and adsorption properties [13].

As known from the literature, one of the important parameters which affect the adsorption process is the Si/Al ratio that corresponds to the electronegativity of the zeolite pore surfaces due to a lower Si/Al ratio [14-15].

Active sites with a broad diversity of chemical functionalities as well as the surface properties of zeolites can be modified for a specific application in adsorption. The ion exchange method used cationic surfactants to change the surface properties of zeolites [16-17].

The monovalent (Na<sup>+</sup>, K<sup>+</sup>) and divalent cations (Ca<sup>2+</sup>, and Mg<sup>2+</sup>) in zeolites can be replaced by compounds such as hexadecyl trimethyl ammonium (HTAB) that can make the charge of the zeolite surface positive. Thus, the adsorption of anions such as chromate and nitrate became possible by zeolite.

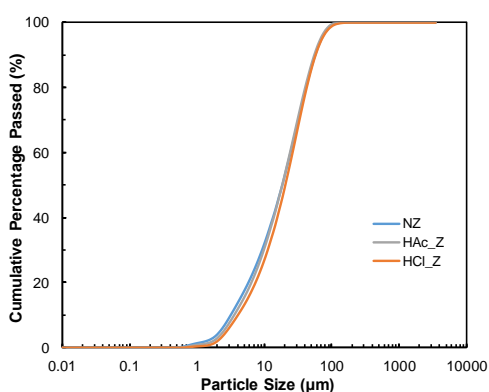
Moreover, industrial and municipal wastewaters contain heavy metal ions such as Pb, Cu, Zn, Cd, Hg, and NH<sub>4</sub><sup>+</sup>. Therefore, they may cause serious environmental problems due to the toxic effects of these elements. Therefore, there is a need for treatment techniques for water resources [18-19]. Additionally, natural spring waters contain the dissolved cations such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup> including possible anions such as HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, SiO<sub>3</sub><sup>2-</sup> which are related to the hardness against these cations [20]. Zeolite can also be used to adsorb both inorganic anions and cations after the modification process [10, 19, 21].

In this context, this study aimed to investigate the effects of hydrochloric acid (HCl) and acetic acid (HAc) modification on the hexadecyl trimethyl ammonium bromide (HTAB) and K<sup>+</sup> adsorption characteristics of a natural zeolite from Manisa Gördes region, Turkey. Moreover; the effects of acid activation on the changes in surface properties of acid (HAc and HCl) treated zeolite samples were evaluated using electrokinetic measurements.

**2. Material and Method**

**2.1. Materials**

In this study, the zeolite sample obtained from Gördes region of Manisa province, Turkey was used for the experimental studies. The zeolite sample was hand crushed and milled using a mortar grinder before the characterization, modification, and adsorption studies. The particle size distribution of the ground zeolite sample was determined with Mastersizer 3000 (Malvern, USA) instrument. The particle size distribution (PSD) of the sample is shown in Fig. 1. According to Fig. 1, the  $d_{10}$ ,  $d_{50}$ , and  $d_{90}$  sizes of the samples were determined as approximately 7  $\mu\text{m}$ , 20  $\mu\text{m}$ , and 57  $\mu\text{m}$ , respectively.



**Figure 1.** PSD graph of the sample.

The reference chemical composition of the sample was obtained from the producer and presented in Table 1. As seen in Table 1, the sample mainly consists of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{K}_2\text{O}$  with a trace amount of other major oxides.  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio is  $\sim 6.3\%$  and the major elemental impurity is Fe. According to the reference XRD information, clinoptilolite group minerals are consisting 85% of the sample [22].

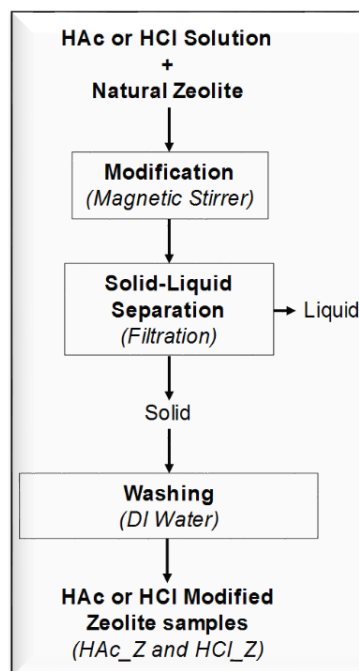
**Table 1.** Chemical composition of the zeolite sample

Oxide	Assay Value (%)	Oxide	Assay Value (%)
$\text{SiO}_2$	71.6	$\text{Na}_2\text{O}$	0.86
$\text{Al}_2\text{O}_3$	11.3	$\text{TiO}_2$	0.08
$\text{Fe}_2\text{O}_3$	1.39	$\text{P}_2\text{O}_5$	0.01
$\text{CaO}$	2.27	$\text{MnO}$	0.02
$\text{MgO}$	0.86	Others	0.03
$\text{K}_2\text{O}$	3.67	LOI	7.90

**2.2. Methods**

**2.2.1. Acid Modification**

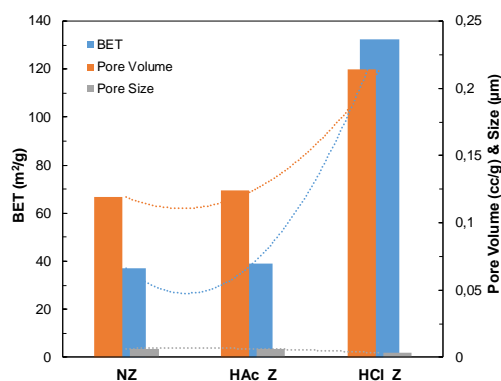
The acid modification of the natural zeolite was carried out using reagent grade HAc and HCl solutions (Merck, USA). Firstly, the modification process was performed in a glass beaker by mixing a sample of 30 g at the rate of 500 rpm for 30 min with 1 M solutions (100 mL) of HAc and HCl using a magnetic stirrer.



**Figure 2.** Acid modification process for zeolite sample.

Then, the solid-liquid separation was performed for the samples. To remove acid remnants on the surfaces, obtained filter cakes were washed until the pH value of the filtrate reached the natural pH value (5.7). The flowsheet of the modification process is shown in Fig. 2.

Also, the BET values of all samples were obtained, and the results are shown in Fig. 3. As seen in Fig. 3, BET values of the acid-modified zeolite samples increased compared to the natural zeolite sample.



**Figure 3.** BET values of the natural and acid-modified zeolite samples.

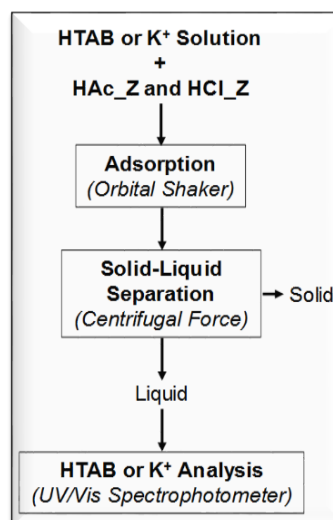
### 2.2.2. Electrokinetic Properties

To determine the electrokinetic properties of zeolite samples, the zeta potential measurements were carried out using a ZetaPlus zeta potential analyzer (Brookhaven, USA). pH values of the suspensions, which were prepared at 0.5% solids ratio, were adjusted with 0.1 M NaOH or 0.1 M HCl solution and the suspensions were mixed for 6 min to reach equilibrium before the measurements. Then, the suspensions were allowed to settle down for 3 min to eliminate the coarse particles that can affect the measurement. Subsequently, about 4 mL aliquots were sampled and transferred to the measurement cell. For each pH value, 20 measurements were taken to calculate the average zeta potential of particles.

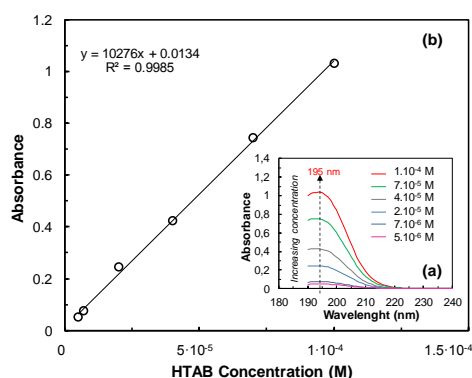
Second, the pH profile measurements of the zeolite suspensions were carried out as a function of time to investigate the buffering properties of zeolite samples. The change in the pH values of the suspensions prepared at different pH conditions was recorded automatically (Hanna Instruments, USA). The suspensions prepared at a 1% solids ratio were mixed using a magnetic stirrer at room temperature (24°C) for 1 h. Finally, the pH profiles of the suspension were recorded until the pH values reached the plateau.

### 2.2.3. Adsorption Experiments

The HTAB and K<sup>+</sup> ion adsorption experiments were carried out with natural and acid-modified zeolite samples as a function of HTAB and K ion concentration using an orbital mixer.



**Figure 4.** Adsorption process for HTAB and K<sup>+</sup> ions.



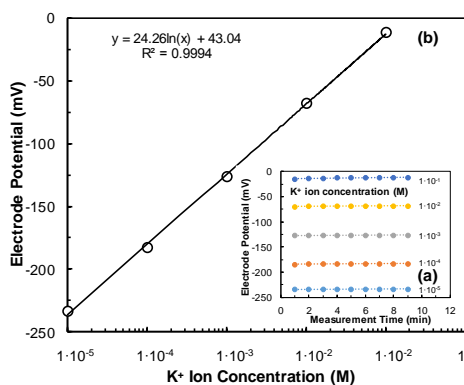
**Figure 5.** Spectrums of different HTAB concentrations (a) and HTAB calibration curve (b).

The parameters for the experiments were a 5% solids ratio, 400 rpm mixing speed, and 50 min adsorption time. For this purpose, first, the solid-liquid separation was performed at 5000 rpm for 5 min with a centrifuge. Then, 4 mL aliquots were taken from the clear portions of the filtrates. The flowsheet for the adsorption process is shown in Fig. 4.

Finally, an equilibrium concentration of the solutions was determined using Tetra T80+ UV/VIS spectrophotometer. To determine an equilibrium concentration for each solution after the adsorption experiments, the HTAB-UV calibration curve was obtained at different HTAB concentrations as seen in Fig. 5a. The results

indicated that each curve for HTAB concentrations gave the peak at 195 nm wavelength. Then, an HTAB-UV calibration curve was obtained using these values (Fig. 5b).

In the case of K ion adsorption behavior of natural and acid-modified zeolite samples, an equilibrium concentration of K ions was determined using Thermo multi-meter (Denver, USA) and K<sup>+</sup> ion probe. Firstly, electrode potentials of each concentration were determined as a function of time shown in Fig. 6a. As seen there was no significant change in the values, 5 min was taken as an optimum time. Then, the calibration curve was obtained from different KCl solutions shown in Fig. 6b.



**Figure 6.** Time-dependent electrode potentials of KCl solutions (a) and K<sup>+</sup> (b) calibration curves.

Finally, the density of adsorption was calculated according to Eq. 2:

$$\Gamma = \frac{(C_i - C_e) \cdot V}{S \cdot m} \quad (2)$$

Where  $\Gamma$  is the adsorption density (mol/m<sup>2</sup>),  $C_i$  and  $C_e$  are the initial and the equilibrium concentration (mol/L), respectively,  $V$  is the volume of the solution (L),  $S$  is the BET value of the sample, and  $m$  is the amount of zeolite sample (g).

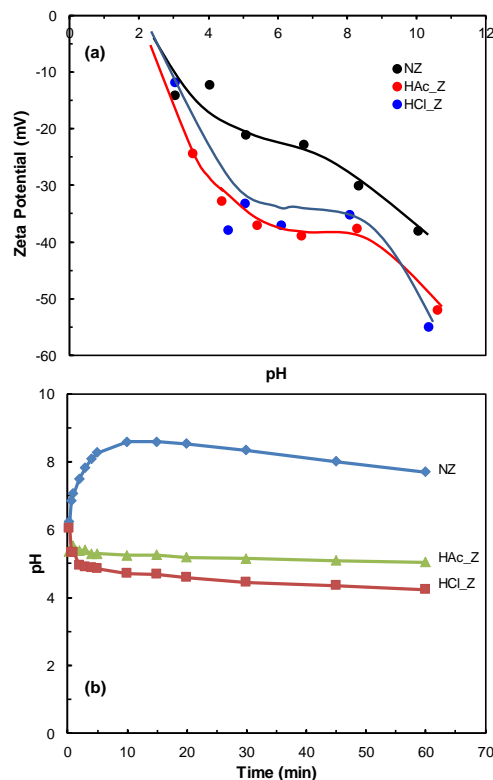
Analytical grade reagents and DI (18 M $\Omega$  × cm) water were used in all experiments.

### 3. Results

#### 3.1. Electrokinetic Properties of Zeolite Samples

To determine the electrokinetic properties of natural and acid-modified zeolite samples, first,

the zeta potential measurements were carried out, and the results are shown in Fig. 7a.



**Figure 7.** pH-dependent zeta potential (a) and time-dependent pH (b) profiles of natural (NZ), HAc modified (HAc\_Z) and HCl modified (HCL\_Z) zeolite samples.

While the natural zeolite sample showed a negative charge at all pH values and would have zero point of charge (zpc) around pH 2, the zeta potential values of acid-modified samples were more negative considerably as a function of pH (Fig. 7a). This can be attributed to the ion exchange process at the zeolite surfaces most importantly the increase in the number of charged sites in the zeolite crystal structure. Although both acids had similar trending effects on the zeta potential of natural zeolite surfaces, HCl showed a more prominent effect at higher alkaline conditions compared to HAc. This could be attributed to the higher dissociation constant of HCl, which resulting in a stronger positive charge deficiency on the zeolite surface.

In a previous study [23] surface charge of natural zeolite, which had a negative surface charge at all pH values as seen in Fig. 7a, became positive

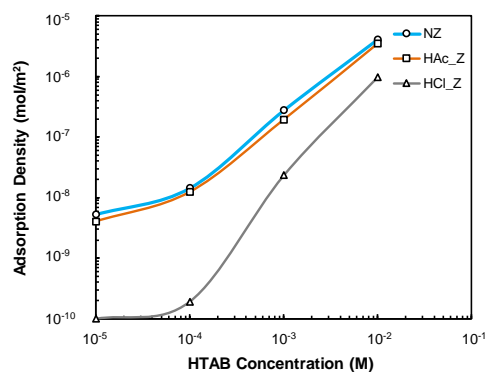
after the modification due to the electrostatic adsorption of positively charged amine molecules to the zeolite surface. In another study, it was found that the zeta-potential profiles of the modified zeolite samples had more negatively charged surfaces compared with the unmodified zeolites. Accordingly, the affinity of the unmodified zeolite to anionic solutions had increased after the modification [24].

Additionally, the pH profiles of the samples were obtained as a function of time to determine the electrokinetic behavior of the samples. As seen in Fig. 7b, the pH profile of initial pH values of the suspensions for the natural, HAc modified and, HCl modified samples were around 6.23, 5.36, and 6.05, respectively. The natural zeolite showed a buffering effect depending on time, which can be explained by the reaction of  $H^+$  ions in the suspension with the oxygen atoms at sites of the broken Si-O-Si bonds on the zeolite surface to decrease the positive charge deficiency [25-26]. On the other hand, HCl and HAc modified samples almost showed a stable trend. This finding indicates that the acid treatment has induced surface protonation of the zeolite, which was also observed in a previous study [27] where an  $H_2SO_4$  modified zeolite sample was able to regulate the solution pH value at acidic pH levels.

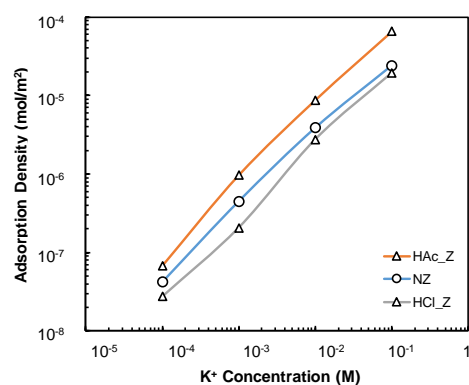
Therefore, it can be said that the zeolite samples were neutralized by the acid modification in terms of surface ion exchange and the electrokinetic properties of the acid-modified zeolites are differs from the natural zeolite.

### 3.2. Adsorption Experiments

First, the adsorption experiments were carried out with the natural and acid-modified samples for HTAB. As seen in Fig. 8, the adsorption density increased as a function of the HTAB concentration. However, there was no significant difference between the natural and acid-modified zeolite samples. The results clearly showed that several such as the solids ratio, the adsorption time, and the conditions of modification must be optimized in terms of adsorption kinetics.



**Figure 8.** HTAB adsorption isotherms for natural (NZ) and acid-modified (HAc\_Z and HCl\_Z) zeolite samples.



**Figure 9.**  $K^+$  adsorption isotherms for natural (NZ) and acid-modified (HAc\_Z and HCl\_Z) zeolite samples.

Next, the adsorption experiments were continued for  $K^+$  ion. As seen in Fig. 9, the adsorption density for all samples showed an increase as a function of  $K^+$  ion concentration. Similar to the HTAB adsorption experiments, it was concluded that investigation of the solids ratio, adsorption time, modification conditions would be necessary for terms of the optimization of the  $K^+$  adsorption kinetics.

Additionally, the resulted slight difference between the adsorption properties of natural and acid-modified zeolite samples can be associated with the relatively high molarity of acidic solutions used in the acid modification process that have some possible undesirable effects on the structure and size distribution of pores within the zeolite particles.

#### 4. Discussion and Conclusion

In this study, the effects of hydrochloric acid (HCl) and acetic acid (HAc) modification on the hexadecyl trimethyl ammonium bromide (HTAB) and K<sup>+</sup> adsorption characteristics of a natural zeolite from Manisa Gördes region, Turkey were investigated. Moreover, the effects of acid activation on the changes in surface properties of acid (HAc and HCl) treated zeolite samples were evaluated using electrokinetic methods.

According to the results of the electrokinetic evaluation of the acid-modified samples, it was found that the electrokinetic properties of the acid-modified zeolites were different from the natural zeolite.

In HTAB adsorption studies, acid modification showed no significant effect on the improvement of the organic molecule adsorption ability of the natural zeolite. To provide a better understanding of the underlying mechanism behind the obtained results, pore/channel and chemical (Si, Al, and impurities such as Fe) properties of the acid modified samples should be investigated in future studies as they have considerable effects on the adsorption capacity of the acid-modified samples.

In the case of the adsorption experiments with K ions, similar results were obtained as the HTAB adsorption results, where the K ion increased in parallel with the increase in the ionic adsorption density. On the other hand, in contrast to the results of the HTAB adsorption studies, the acid modification resulted in a slight improvement in terms of the inorganic ion adsorption ability of the natural zeolite.

The results obtained in this study clearly showed that the acid modification process can be used to improve the inorganic ion adsorption ability of natural zeolites. However, there needs more investigation for the optimization of several parameters such as the zeolite solids ratio, adsorption time as well as the modification conditions to increase adsorption efficiency, and reveal the detailed adsorption kinetics of the acid-modified zeolites.

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