

## Removal of Ammonia Gas Using Chabazite Type Natural Zeolite

Aytaç GÜNAL<sup>1</sup>, Burcu ERDOĞAN<sup>2</sup>

<sup>1</sup>Eskişehir Teknik Üniversitesi, Lisansüstü Eğitim Enstitüsü, 26555, Eskişehir, Türkiye

<sup>2</sup>Eskişehir Teknik Üniversitesi, Fen Fakültesi, Fizik Bölümü, 26555, Eskişehir, Türkiye

(Alınış / Received: 18.06.2021, Kabul / Accepted: 24.01.2022, Online Yayınlanma / Published Online: 20.04.2022)

### Keywords

Adsorption,  
Ammonia,  
Chabazite

**Abstract:** In this study, chabazite (CHA) from Bala and that of cation ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) exchanged and hydrochloric acid activated forms were investigated to demonstrate their possible usability in the ammonia removal from the environment. Cation exchanged and acid activated forms were prepared using 1.0 M solutions of  $\text{KNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$  and 0.1 M and 1.0 M solutions of HCl at 90 °C for 5 h, respectively. The thermal and structural properties of all samples were characterized by TG-DTA, XRD and XRF methods. BET surface areas ( $231\text{-}448\text{ m}^2\text{ g}^{-1}$ ), micropore surface areas ( $216.2\text{-}421.3\text{ m}^2\text{ g}^{-1}$ ) and micropore volumes ( $0.086\text{-}0.169\text{ cm}^3\text{ g}^{-1}$ ) of the chabazite samples were calculated by  $\text{N}_2$  adsorption isotherms at 77 K. Ammonia adsorption isotherms were obtained at 25 °C by 3Flex-Micromeritics equipment volumetrically. Ammonia adsorption capacities of the chabazite samples ( $5.699\text{-}8.931\text{ mmol g}^{-1}$ ) were compared in terms of the induced textural and structural changes as a result of cation exchange and acid activation processes, respectively.

## Şabazit Tipi Doğal Zeolit Kullanılarak Amonyak Gazının Uzaklaştırılması

### Anahtar Kelimeler

Adsorpsiyon,  
Amonyak,  
Şabazit

**Özet:** Bu çalışmada, Bala'dan elde edilen şabazit (CHA) ve katyon ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  ve  $\text{Mg}^{2+}$ ) değiştirilmiş ve hidroklorik asitle aktifleştirilmiş formları, ortamdaki amonyak giderimindeki olası kullanılabilirliklerini göstermek amacıyla incelendi. Katyon değiştirilmiş ve asitle aktifleştirilmiş formlar sırasıyla, 1.0 M'lık  $\text{KNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$  ve 0.1 M ve 1.0 M'lık HCl solüsyonları kullanılarak 90 °C'de 5 saat süreyle hazırlandı. Tüm numunelerin termal ve yapısal özellikleri TG-DTA, XRD ve XRF yöntemleri ile belirlendi. Şabazit numunelerinin BET yüzey alanları ( $231\text{-}448\text{ m}^2\text{ g}^{-1}$ ), mikro gözenek yüzey alanları ( $216.2\text{-}421.3\text{ m}^2\text{ g}^{-1}$ ) ve mikro gözenek hacimleri ( $0.086\text{-}0.169\text{ cm}^3\text{ g}^{-1}$ ) 77 K'de elde edilen  $\text{N}_2$  adsorpsiyon izotermi ile hesaplandı. Amonyak adsorpsiyon izotermi 3Flex-Micromeritics cihazı ile 25 °C'de volumetrik olarak elde edildi. Şabazit numunelerinin amonyak adsorpsiyon kapasiteleri ( $5.699\text{-}8.931\text{ mmol g}^{-1}$ ), sırasıyla katyon değişimi ve asit aktivasyon işlemlerinin neden olduğu içeriksel ve yapısal değişiklikler açısından karşılaştırıldı.

### 1. Introduction

Ammonia ( $\text{NH}_3$ ) is a colorless alkaline gas with an irritating odor. This gas is used in refrigeration, fertilizer production, metal industries, the petroleum, chemical and rubber industries, domestic cleaning agents and water purification [1]. Ammonia gas is irritating to the eyes, respiratory tract and mucous membranes. Clearly at high concentrations (1700 ppm) ammonia lead to serious coughing, and bronchial spasms and <30 min exposure may be fatal [1, 2]. In addition to human life, ammonia is also highly poisonous to fish [3]. The allowable exposure limit for  $\text{NH}_3$  set by the United States Occupational

Safety and Health Administration (OSHA) is 25 ppm on average in an eight-hour workday [4]. For these reasons, controlling of this pollutant essentially is necessary. Apart from membrane technology, (500-2000 ppm  $\text{NH}_3$ , [5]), biological processes, (16 ppm  $\text{NH}_3$ , [6]), scrubbing processes (45 ppm  $\text{NH}_3$ , [7]) and catalytic oxidation (500 ppm and 180 ppm  $\text{NH}_3$  [8, 9], respectively) methods, ammonia can be removed from environment using low-cost natural zeolites

Zeolites are porous, crystalline and hydrated aluminosilicates. Their frameworks have channels and interconnected cavities occupied by the cations and the water molecules [10, 11]. Chabazite is the

\*Corresponding author: burcuerdogan@eskisehir.edu.tr

commonly natural zeolite and its framework structure consists of parallel stacks of six-membered double rings [12]. The largest channels are limited to the 8-membered rings with approximate dimension  $3.1 \times 4.4 \text{ \AA}$  (dehydrated) [13, 14]. For control and removal of the ammonia gas, many adsorbents such as 4A, 5A, 13X, faujasite, pentasil, ordered mesoporous carbon, activated carbon, MOFs, mordenite and clinoptilolite [15-28] are used. On the other hand, studies investigating the use of abundant, low-cost and naturally occurring chabazite to remove ammonia are still lacking. The aim of present study is to investigate the influence of the cation exchange and the acid activation methods on the ammonia adsorption properties of natural chabazite.

## 2. Material and Method

Chabazite (CHA) from Bala was sieved and the less than  $63 \mu\text{m}$  fractions were used. Five grams of each chabazite were exchanged by refluxing with 100 mL of 1.0 M  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{NaNO}_3$  and  $\text{KNO}_3$  solutions at  $90 \text{ }^\circ\text{C}$  for 5 h. Acid activated forms (01H-CHA and 1H-CHA) were obtained using a 0.1 and 1.0 M HCl solutions at the same temperature and during the time, respectively. After filtered and washed several times with hot de-ionized water, chabazite samples were dried in an oven at  $110 \text{ }^\circ\text{C}$  for 20 h. The obtained samples were named as X-CHA, which the X indicate the type of exchanged cation. All chemicals supplied by Merck Company.

XRD patterns of chabazite samples were obtained using a D8 Advance Bruker equipment, with  $\text{CuK}\alpha$  radiation at 40 kV and 30 mA, in the  $2\theta$  from  $5^\circ$  to  $40^\circ$ . The chemical analyses were carried out using Rigaku ZSX Primus equipment. DTA and TG analysis were done with a Setsys Evolution Setaram instrument in the temperature range of  $30\text{-}1000 \text{ }^\circ\text{C}$ , the heating ratio was  $10 \text{ }^\circ\text{C}/\text{min}$ .  $\text{N}_2$  adsorption measurements were conducted at 77 K using Autosorb 1. Specific surface area and micropore data of samples were determined using B.E.T. ( $P/P_0$ : 0.05–0.35) and t-plot ( $P/P_0 > 0.10$ ) methods respectively. Ammonia adsorption isotherms were obtained at 298 K using 3Flex-Micromeritics equipment. All the samples were degassed at  $300 \text{ }^\circ\text{C}$  for 10 h before nitrogen and ammonia gas adsorption measurements.

## 3. Results

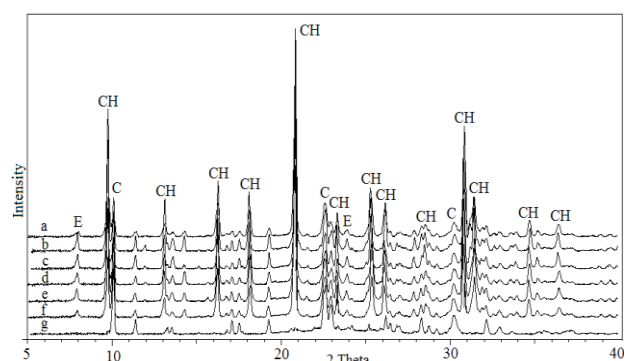
### 3.1. Elemental composition

The chemical analysis of the natural (CHA) shows that calcium and magnesium are main cations (Table 1). In addition, iron is also present as impurity. Expected increases in exchangeable cation amounts were observed compared to the raw sample (CHA) depending on the salt solution chosen. After the chabazite was activated with increasing acid molarity, the percentages of all cation components except  $\text{SiO}_2$ ,

due to its insolubility, decreased gradually. This result showed that silica remained and its content increased with increasing acid concentrations whilst exchangeable cations and framework aluminum gradually eliminated from the structure and passed into solution. When the concentration of HCl solutions was increased from 0.1 to 1.0 M, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of CHA increased from 4.0 to 4.3 and 15.8 in the 01H-CHA and 1H-CHA samples, respectively, in accordance with the XRD data (Fig. 1). XRF results confirmed that there are significant changes in the chemical composition of chabazite depending on the acid concentration.

### 3.2. X-ray diffraction analysis

Figure 1 shows the powder XRD patterns of all the chabazite samples. Raw CHA contains chabazite predominantly with the characteristic peaks at  $2\theta = 9.40^\circ$ ,  $15.90^\circ$ ,  $22.98^\circ$  and  $30.50^\circ$ . The presence of small amounts of erionite (E) and clinoptilolite (C) was also observed [29]. As seen from Figure 1, chabazite is not resistant to acid treatment. For this reason, the main chabazite peaks disappeared in 1H-CHA sample due to the partial collapse of its structure (Figure 1-g).



**Figure 1.** X-ray diffraction patterns of the CHA (a), Na-CHA (b), K-CHA (c), Ca-CHA (d) Mg-CHA (e), 01H-CHA (f) and 1H-CHA (g) (CH:chabazite, C: clinoptilolite, E:erionite).

### 3.3. Nitrogen adsorption

Nitrogen adsorption isotherms of the chabazites are presented in Figures 2 and 3. All the isotherms are of type-II [30]. B.E.T. surface areas and micropore data of the chabazites are given in Table 2. Although there is no significant difference in BET surface area values on the basis of cations, they show the  $\text{Ca} > \text{Na} > \text{Natural} > \text{Mg} > \text{K}$  series. Among the cation exchanged forms, it was found the K-CHA has the lowest micropore data and specific surface area. This can be attributed to its amount and massive size (Table 1). A significant decrease in nitrogen adsorption data was observed in the sample activated with 1 M HCl solution. The specific surface area and micropore surface area decreased from 426 and  $396.9 \text{ m}^2\text{g}^{-1}$  for CHA to 274 and  $249.3 \text{ m}^2\text{g}^{-1}$  for 1H-CHA, respectively. This can be explained by the dealumination and the partial collapse of the chabazite structure, in accordance with the XRF results (Table 1) and the XRD data (Fig. 1-g).

**Table 1.** Chemical analyses of chabazite samples.

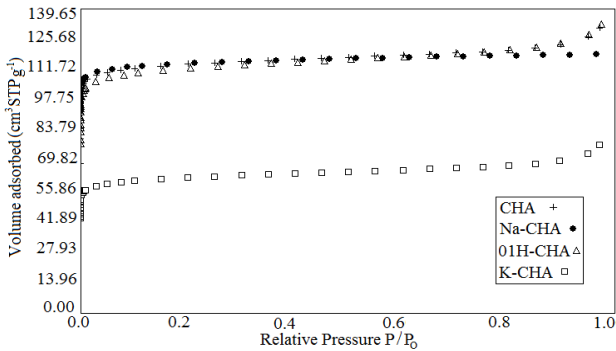
| Sample/ (%) | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MgO   | CaO   | Na <sub>2</sub> O | K <sub>2</sub> O | LOI    |
|-------------|------------------|--------------------------------|--------------------------------|-------|-------|-------------------|------------------|--------|
| CHA         | 61.417           | 15.298                         | 0.644                          | 3.133 | 2.668 | 1.450             | 1.402            | 13.873 |
| Na-CHA      | 62.771           | 15.590                         | 0.792                          | 2.381 | 0.957 | 4.693             | 1.040            | 11.688 |
| K-CHA       | 61.998           | 15.385                         | 0.796                          | 2.258 | 0.751 | -                 | 9.165            | 9.487  |
| 01H-CHA     | 64.848           | 14.948                         | 0.751                          | 2.633 | 2.053 | 0.544             | 1.369            | 12.836 |
| 1H-CHA      | 84.215           | 5.333                          | 0.262                          | 0.693 | 0.817 | -                 | 0.419            | 8.174  |
| Ca-CHA      | 61.578           | 15.214                         | 0.796                          | 2.213 | 5.104 | 0.440             | 1.321            | 13.221 |
| Mg-CHA      | 62.058           | 15.425                         | 0.798                          | 4.456 | 1.566 | 0.773             | 1.435            | 13.397 |

**Table 2.** Nitrogen adsorption data of chabazite samples

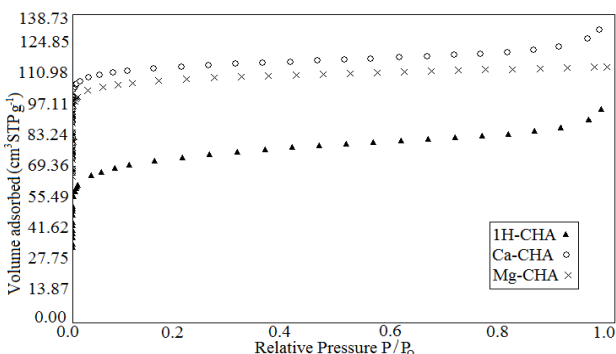
| Sample  | BET surface area (m <sup>2</sup> g <sup>-1</sup> ) | Micropore surface area (m <sup>2</sup> g <sup>-1</sup> ) | Micropore volume (cm <sup>3</sup> g <sup>-1</sup> ) | Total pore volume (cm <sup>3</sup> g <sup>-1</sup> ) |
|---------|--|--|---|--|
| CHA     | 426  | 396.9  | 0.165   | 0.203  |
| Na-CHA  | 443  | 421.3  | 0.169   | 0.185  |
| K-CHA   | 231  | 216.2  | 0.086   | 0.199  |
| 01H-CHA | 415  | 360.5  | 0.140   | 0.206  |
| 1H-CHA  | 274  | 249.3  | 0.106   | 0.149  |
| Ca-CHA  | 448  | 270.6  | 0.161   | 0.205  |
| Mg-CHA  | 403  | 280.4  | 0.158   | 0.179  |

**Table 3.** Mass losses (%) of the chabazite samples.

| Sample  | 30-200 °C | 200-400 °C | 400-600 °C | 600-800 °C | 800-1000 °C | Total mass loss (%) |
|---------|-----------|------------|------------|------------|-------------|---------------------|
| CHA     | 6.16      | 7.52       | 1.22       | 0.26       | 0.01        | 15.17               |
| Na-CHA  | 7.47      | 6.80       | 0.98       | 0.25       | 0.03        | 15.53               |
| K-CHA   | 5.04      | 5.41       | 0.89       | 0.25       | 0.03        | 11.62               |
| 01H-CHA | 5.51      | 6.93       | 1.40       | 0.39       | 0.43        | 14.46               |
| 1H-CHA  | 6.93      | 3.04       | 1.96       | 0.86       | 0.22        | 13.01               |
| Ca-CHA  | 5.91      | 6.91       | 1.35       | 0.40       | 0.02        | 14.59               |
| Mg-CHA  | 5.10      | 8.52       | 1.60       | 0.40       | 0.05        | 15.67               |



**Figure 2.** Nitrogen adsorption isotherms of CHA, Na-CHA, K-CHA and 01-HCHA.

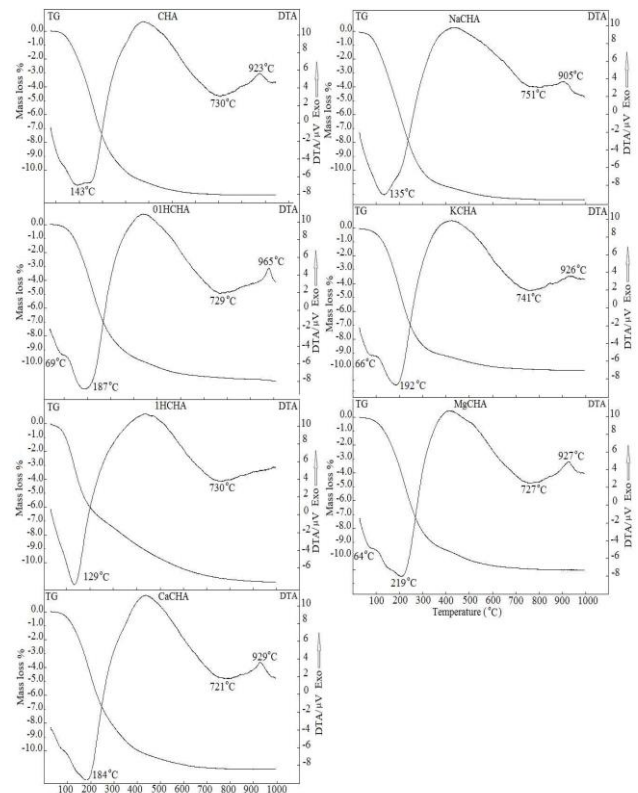


**Figure 3.** Nitrogen adsorption isotherms of Ca-CHA, Mg-CHA and 1H-CHA.

### 3.4. Thermal analysis (TG-DTA)

The TG/DTA curves for all chabazite samples are shown in Fig. 4. The DTA curves of chabazite samples showed the endothermic peaks between 30 and 400

°C due to the dehydration. In addition, these samples had the exothermic peaks at about 900 °C as a result of the destruction of the framework. The TG curves exhibit that water losses of the samples continue up to 800 °C.

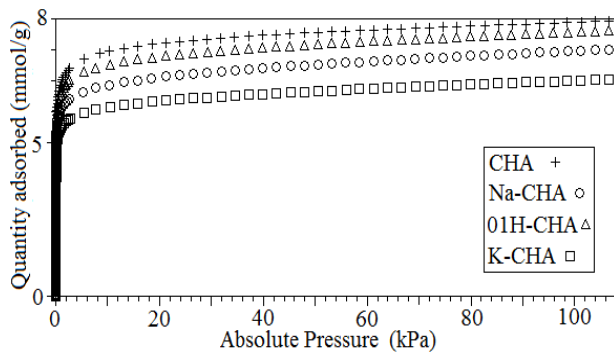


**Figure 4.** TG-DTA curves of the chabazite samples.

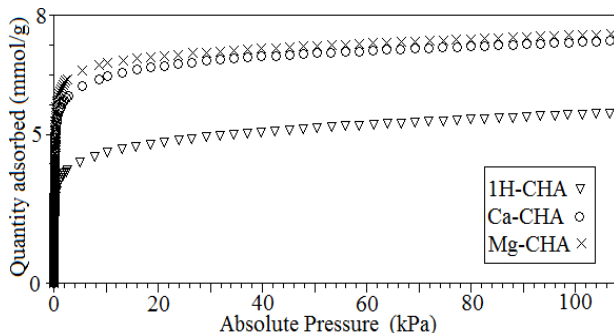
Mg-CHA samples was found to have higher mass loss value compared to other modified forms (Table 3). Similar thermal behavior caused by cation exchange in chabazite type zeolite has been observed in other studies [31,32].

### 3.5. Adsorption of NH<sub>3</sub>

Ammonia adsorption isotherms for raw (CHA), cation exchanged and acid-treated chabazites were obtained volumetrically at 298 K. As seen from Figures 5 and 6, all the ammonia isotherms are classified as type I [30]. Among the chabazite samples, ammonia adsorption capacity of CHA was found to be highest (8.931 mmol g<sup>-1</sup>). For the CHA sample, none of the cations are dominant. A partially blockage of the channels should be responsible for this phenomenon. The ammonia adsorption capacity of K-CHA was found to be lower than those of other cation exchanged forms. This can be explained by the large cation size of K<sup>+</sup> and the partial pore blockage of the eight-ring windows of chabazite. On the other hand, 1H-CHA had the lowest NH<sub>3</sub> retention owing to the collapse of the zeolitic structure (Figure 1-g). Obviously, gas adsorption on zeolites depends on many parameters such as their framework structure, size and distribution of the exchangeable cations within their channels, and features of the adsorbate (its size, geometry and polarity etc.).



**Figure 5.** Ammonia adsorption isotherms of CHA, Na-CHA, K-CHA and 01-HCHA at 298 K.



**Figure 6.** Ammonia adsorption isotherms of Ca-CHA, Mg-CHA and 1H-CHA at 298 K.

The high adsorption for ammonia can be attributed to the strong interaction of the permanent dipole moment (1.47 debye) of this molecule with the cations within the adsorbent pores.

**Table 4.** Ammonia adsorption on various materials.

| Sample                 | Temp (K) | Ads. capacity (mmol g <sup>-1</sup> ) | Ref. |
|------------------------|----------|---------------------------------------|------|
| Cu-MOF-74              | 298      | 3.4                                   | [17] |
| Zs                     | 295      | 6.30 mg g <sup>-1</sup>               | [20] |
| alumina 1597           | 298      | 3.008                                 | [21] |
| silica gel 40          | 298      | 6.250                                 | [21] |
| clinoptilolite         | 298      | 5.904                                 | [21] |
| 13X                    | 298      | 9.326                                 | [21] |
| mesoporous carbon      | 298      | 6.39                                  | [22] |
| HKUST-1 (MOF)          | 298      | 6.8                                   | [24] |
| natural clinoptilolite | 298      | 12.2 mg g <sup>-1</sup>               | [27] |
| 4A                     | 298      | 8.717                                 | [21] |
| CHA                    | 298      | 8.931                                 |      |
| Na-CHA                 | 298      | 8.016                                 |      |
| K-CHA                  | 298      | 7.039                                 |      |
| 01H-CHA                | 298      | 8.622                                 |      |
| 1H-CHA                 | 298      | 5.699                                 |      |
| Ca-CHA                 | 298      | 8.134                                 |      |
| Mg-CHA                 | 298      | 8.373                                 |      |

As seen from Table 4, retention of ammonia gas by sample CHA (8.931 mmol g<sup>-1</sup>) was higher than that for clinoptilolite from Mud Hills (CA), USA (5.904 mmol g<sup>-1</sup>, [21]), alumina 1597 (3.008 mmol g<sup>-1</sup>, [21]), silica gel 40 (6.250 mmol g<sup>-1</sup>, [21]), mesoporous carbon (6.39 mmol g<sup>-1</sup>, [22]), Cu-MOF-74 (3.4 mmol g<sup>-1</sup>, [17]) and HKUST-1 (MOF) (6.8 mmol g<sup>-1</sup>, [24]) but lower than 13X zeolite (9.326 mmol g<sup>-1</sup> [21]) and 4A (8.717 mmol g<sup>-1</sup> [21]). This result can be explained by the differences in the structural and textural properties of these adsorbents such as origin and impurity content. Although synthetic zeolites such as 13 X and 4A show higher ammonia adsorption capacities than natural zeolites due to their homogeneous structure, they are more expensive than natural zeolites found in large reserves in nature. The abundance and the high specific surface area of chabazite-type natural zeolite provide low-cost and efficient solutions for gas adsorption and environmental applications. As a result, natural chabazite from Bala can be used for the removal of ammonia gas from the air in livestock facilities.

### 4. Discussion and Conclusion

Ammonia adsorption capacities of raw chabazite and that of cation exchanged and acid treated forms were compared in terms of structural and textural differences. TG/DTA analysis demonstrated that the thermal behavior of these zeolites is influenced by the dominant cation present in the structure. For cation exchanged forms, ammonia adsorption capacity decreased with the increase of the cation radii. On the other hand, experimental results indicate that the treatment of natural chabazite tuff with salt and acid solutions did not lead to an increase of NH<sub>3</sub> retention. Due to its abundance and low cost, natural CHA sample can be recommended as a potential adsorbent for ammonia removal from indoor environments such as poultry houses.

## Acknowledgment

This research was supported by the Anadolu University Commission of Scientific Research Project under Project No1602F072.

## Declaration of Ethical Code

*In this study, we undertake that all the rules required to be followed within the scope of the "Higher Education Institutions Scientific Research and Publication Ethics Directive" are complied with, and that none of the actions stated under the heading "Actions Against Scientific Research and Publication Ethics" are not carried out.*

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