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## **INFLUENCE OF ACID ACTIVATION ON THE ION-EXCHANGE PROPERTIES OF MANISA-GÖRDES CLINOPTILOLITE**

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**Abstract.** In this study, the possibilities of using Manisa-Gördes district tuffs having important deposits rich of clinoptilolites have been investigated for the removal of heavy metal ions from industrial wastewaters. Adsorption of ammonium and metal cations such as  $Pb^{++}$ ,  $Cu^{++}$ ,  $Cd^{++}$  and  $Zn^{++}$  ions from aqueous solution onto sulphuric, hydrochloric and nitric acid activated samples were studied. Experimental data were obtained from batch equilibrium tests on samples activated at different acid concentrations at two different size fractions. It has been found that selectivity of the zeolite is sequentially  $Pb^{++} > NH_4^+ > Cu^{++}$ ,  $Cd^{++} > Zn^{++}$ . Experimental results show that the  $NH_4^+$  ion exchange capacity of 95 meq/100 g for the raw material can be increased to 140 meq/100 g after activation with sulphuric acid. In general, acid activation was observed to increase the ion exchange capacity, sulphuric acid responding better than hydrochloric and nitric acids.

*keywords: zeolite, clinoptilolite, acid activation, ion exchange*

### **1. Introduction**

Natural zeolite minerals are hydrated aluminosilicates of alkaline and alkaline-earth cations with indefinitely extending three dimensional network of (Si, Al) $O_4$  tetrahedral linked to each other by sharing all of the oxygen. Their structure contain channels and pores that are occupied by mobile cations and water molecules. Due to their structural characteristics, natural zeolites especially clinoptilolites are used for many purposes related with their ion exchange, adsorption, dehydration and rehydration properties (Castaldi et al., 2008; Girgin et al., 1996; Englert and Rubio, 2005; Wang and Peng, 2010, Cincotti et al., 2001; Korkuna et al., 2006).

Clinoptilolites are capable of exchanging alkaline and alkaline-earth cations in aqueous solutions and studies have been conducted on the waste water and nuclear waste treatment for the removal of some harmful cations (Ata and Girgin, 1994; Erdem et al., 2004; Curkovic et al., 1997; Toprak and Girgin, 2000; Gunay et al., 2007; Motsi et al., 2009; Ouki and Kavannagh, 1999; Abusafa and Yucel, 2002; Borai et al., 2009). They offer advantages over organic-ion exchangers due to their high chemical, thermal and radiation stabilities. Their ion-exchange and adsorption

properties can be improved by thermal and acid activation methods (Girgin et al., 1996; Wang and Peng, 2010; Curkovic et al., 1997; Inglezakis, 2005; Modale et al., 1995; Toprak and Girgin, 1999).

This study was aimed at determining the cation-exchange capacity of Manisa-Gördes clinoptilolites for  $Pb^{+2}$ ,  $NH_4^+$ ,  $Cu^{+2}$ ,  $Ca^{+2}$  and  $Zn^{+2}$  after activation with  $H_2SO_4$ , HCl and  $HNO_3$ .

## 2. Experimental

### 2.1. Chemicals and reagents

Merck grade HCl,  $H_2SO_4$  and  $HNO_3$  were used in the acid-activation experiments. Solutions used in ion exchange tests were prepared using  $CH_3COONH_4$ ,  $Cu(CH_3COO)_2 \cdot H_2O$ ,  $Pb(CH_3COO)_2 \cdot 3H_2O$ ,  $Zn(CH_3COO)_2 \cdot 2H_2O$ ,  $Cd(CH_3COO)_2 \cdot 2H_2O$  and KCl (analytical grade Merck reagents).

### 2.2. Preparation and characterization of the sample

Clinoptilolite-rich tuff samples taken from Manisa-Gördes region was used in the experiments. Representative samples were crushed using jaw, cone and roll crushers, and then wet screened to -0,3 mm. After washing with distilled water and acetone, -707 +595  $\mu m$  and -500 +298  $\mu m$  fractions were obtained in ion-exchange experiments.

The chemical composition of the sample determined by XRF analysis (Rigaku RIX-3000 Spectrometer) is given in Table 1.

Table 1. Chemical composition of the sample used

Component	%
SiO <sub>2</sub>	71.29
Al <sub>2</sub> O <sub>3</sub>	13.55
Fe <sub>2</sub> O <sub>3</sub>	1.15
CaO	2.45
MgO	0.70
Na <sub>2</sub> O	0.60
K <sub>2</sub> O	3.50
LOI	6.43

XRD analysis (Rigaku Geiger Flex X-ray) shows that the main mineral is clinoptilolite and cristobalite is present in minor quantities (Fig. 1a). XRD patterns of the sample treated between 100-1000°C (Fig. 1b) show lowering in the peak intensities of clinoptilolite lattice concentration and thermal collapse of the framework at 800°C. The TG/DTA data (Rigaku TAS 100 Thermo flex TG 8110) is in agreement with the

XRD results showing continuous hydration up to 700°C with release of water and an exothermic event at around 924°C due to the collapse of the structure (Fig. 2).

Considering the K, Na, Ca, Mg contents of the sample, theoretical cation exchange capacity was calculated as 120.74 meq/100g. Also, specific surface area, pore diameter, pore volume and the density (Quantachrome Nova 2000) of the sample were determined as 43.91 m<sup>2</sup>/g, 0.018 μm, 0.1717 cm<sup>3</sup>/gr, 2.12 g/cm<sup>3</sup>, respectively.

Figure 3 shows the electronmicroscopic view of the sample (FEI Qanta 400 MK2 electronmicroscope) where macro and micropores can clearly be seen between the clinoptilolite crystals (Fig. 3d).

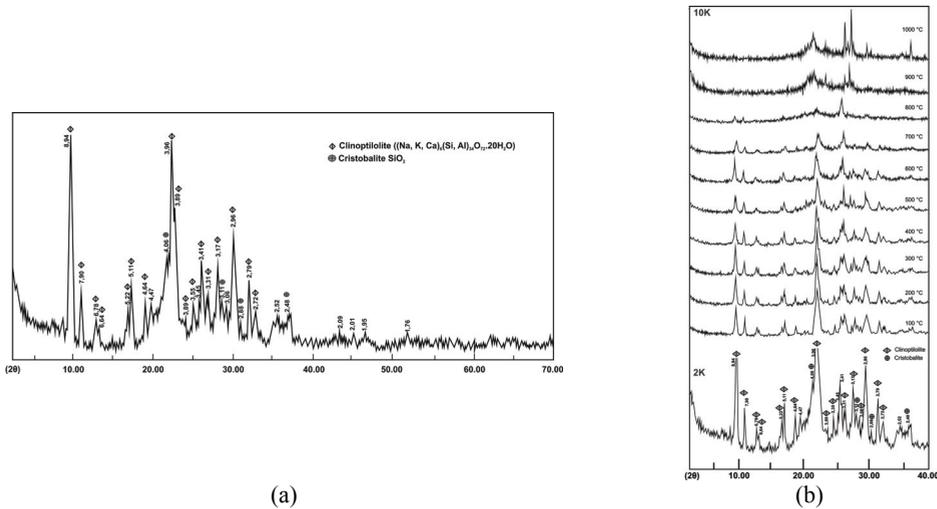


Fig. 1. a)XRD pattern of the sample b) XRD patterns of the sample between 100–1000°C

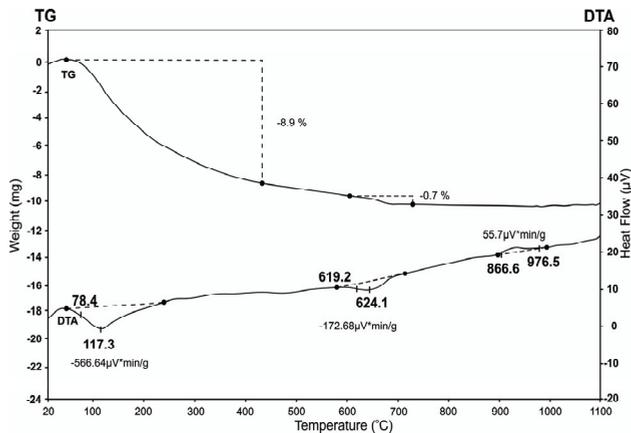


Fig. 2. TG/DTA curves of the sample

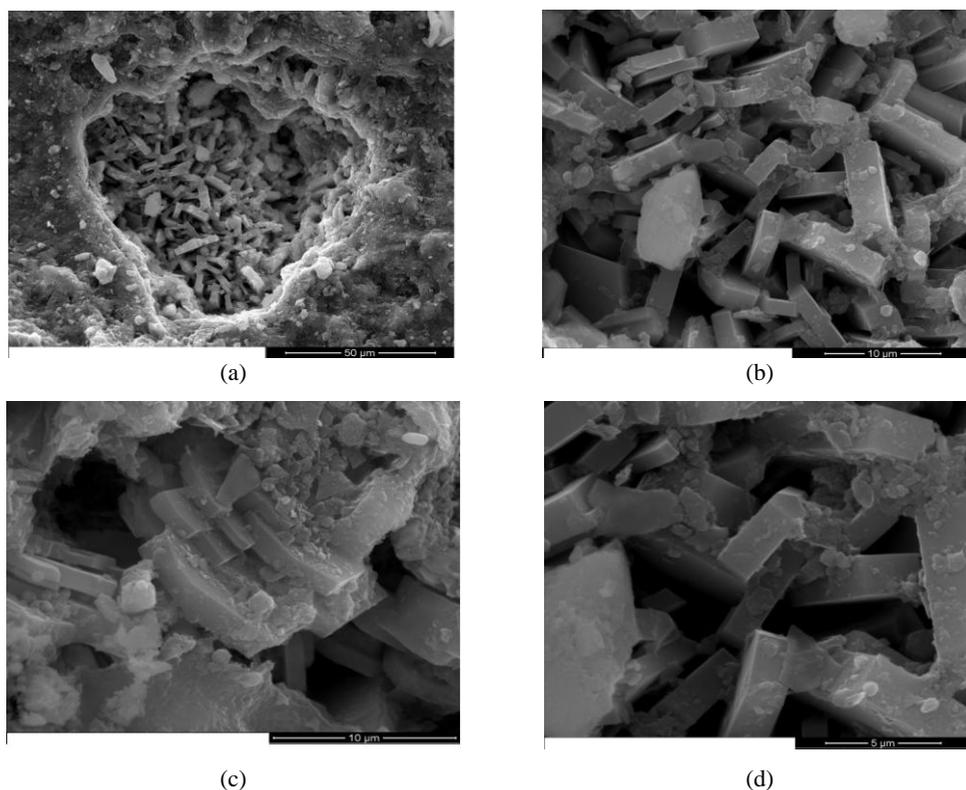


Fig. 3. An electronmicroscopic view of Manisa-Gördes clinoptilolite (a) ~1000x magnification, (b) ~4000x magnification, (c) ~6000x magnification, (d) ~8000x magnification

### 2.3. Acid activation and ion exchange tests

In the acid activation experiments, the sample was treated with acid solutions of varying concentrations (0.1, 0.5, 1.0, 2.0 M) for one hour at room temperature. Following filtration, the samples were washed with water, then with acetone and finally were dried at 105°C for 24 hours.

In the cation exchange tests, 1 gram of sample was treated with 100 cm<sup>3</sup> of solution for 8 hours in a 250 cm<sup>3</sup> beaker with mechanical agitation at constant speed to keep all the particles in suspension. After completion of the reaction, the samples were separated by filtration and rinsed with methanol. For the stripping of exchanged cations, loaded samples were treated with 100 cm<sup>3</sup> of KCl solution for 8 hours, filtered and the solutions were analyzed. As the adsorption of Pb<sup>+2</sup> on clinoptilolite was irreversible, the samples were exchanged with K<sup>+</sup> before treatment with Pb<sup>+2</sup> solution and the extent of Pb<sup>+2</sup> exchange was determined by K<sup>+</sup> analysis in the solution.

Ammonium ion was determined by colorimetric method and the other ions were analyzed using the atomic absorption spectrophotometric method.

The batch technique was used for measurement of cation exchange capacity of samples (Sub-Committee, 1994) and the cation exchange capacities (CEC) in meq/100g were determined using equation:

$$\text{CEC (meq/100g)} = (\text{milimoles of sorbed ion} / 100\text{g sample}) \cdot (\text{cation valence}).$$

### 3. Results and discussion

The  $\text{NH}_4^+$  exchange capacities for the raw sample were determined as 94 meq/100g and 100 meq/100 g for sample sizes of +595  $\mu\text{m}$  and +298  $\mu\text{m}$ , respectively. The effect of particle size and acid concentration were considered in the ion exchange experiments and the results for acid activated samples are given in Fig. 4.

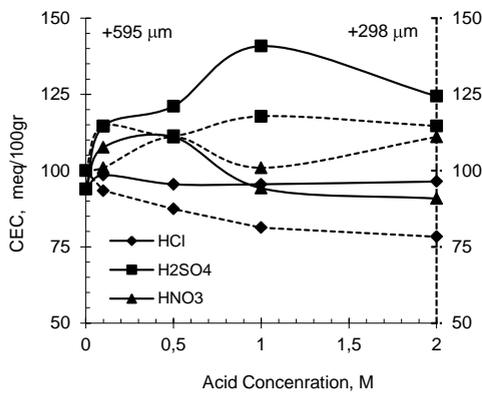


Fig. 4.  $\text{NH}_4^+$  exchange capacity of the acid activated samples

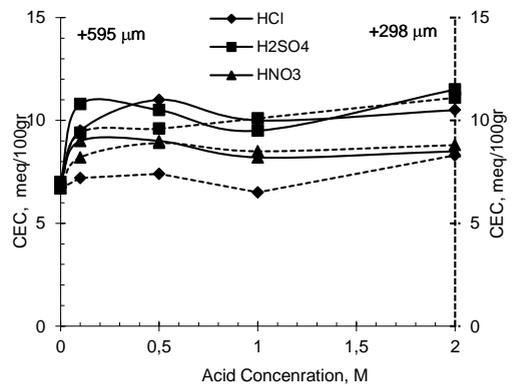


Fig. 5.  $\text{Zn}^{2+}$  exchange capacity of the acid activated samples

Although HCl does not have a significant effect on the ion exchange capacity for +595  $\mu\text{m}$  sample, ion exchange capacity decreases from 93.4 meq/100 g to 78.3 meq/100 g for +298  $\mu\text{m}$  sized sample. The highest value obtained for 0.1 M HCl activated sample for both sizes was determined as 98.5 meq/100 g. Ion exchange capacity values for +595  $\mu\text{m}$  sample activated with 0.1 and 0.5 M  $\text{HNO}_3$  were reached to 107.6 meq/100 g and 111 meq/100 g, respectively. But, upon increase of the acid concentration in the activation, ion exchange capacities were decreased considerably. Compared to others, better results were obtained with the sample activated using 1 M  $\text{H}_2\text{SO}_4$  and the CEC value was reached to 140.8 meq/100 g for both sizes.

$\text{Zn}^{++}$  exchange capacity of the raw sample for both sizes were quite close to each other being around 7 meq/100 g. Considering the  $\text{Zn}^{++}$  exchange capacities for acid activated samples (Fig. 5) HCl and  $\text{HNO}_3$  activated samples showed slight increases in the exchange capacities. Best results again were obtained with  $\text{H}_2\text{SO}_4$  activated sample and the highest value reached was 11.5 meq/100 g for +595  $\mu\text{m}$  size when the

activation was done using 2 M H<sub>2</sub>SO<sub>4</sub>. For all the acid activated samples better results were obtained for +595 μm sample.

Pb<sup>++</sup> exchange capacities for the raw samples were determined as 25.6 meq/100 g for +595 μm and 26.7 meq/100 g for +298 μm sizes. It can be seen from Fig. 6 that acids did not show big differences. The values varied between 27 meq/100 g to 31.3 meq/100 g on 595 μm sample, except 0.1 M HCl with which the value reached was 20.1 meq/100 g. It seems that particle size does not have any effect on ion exchange capacity for Pb ion. The best value obtained on +595 μm sized sample was around 31.3 meq/100 g for samples activated with 0.1 M HNO<sub>3</sub> and 2 M H<sub>2</sub>SO<sub>4</sub>.

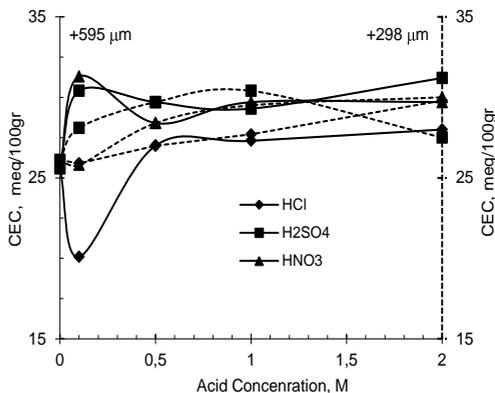


Fig. 6. Pb<sup>++</sup> exchange capacity of the acid activated samples

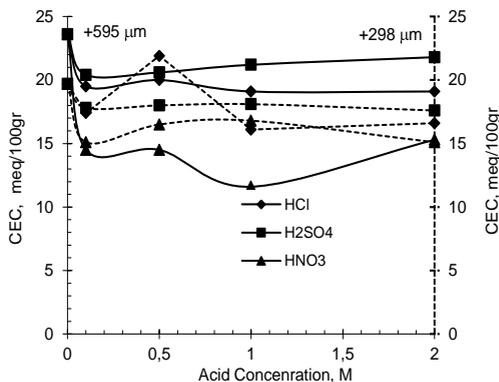


Fig. 7. Cu<sup>++</sup> exchange capacity of the acid activated samples

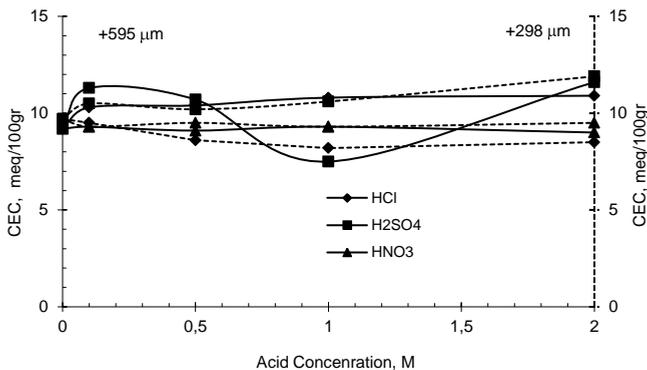


Fig. 8. Cd<sup>++</sup> exchange capacity of the acid activated samples

For Cu<sup>++</sup> ion, ion exchange capacity was 23.6 meq/100 g for +595 μm raw sample which was better than that of +298 μm sample. Also, this value was the highest compared to the acid activated ones (Fig. 7). Accordingly, although H<sub>2</sub>SO<sub>4</sub> activation gives better results, acid activation does not improve the Cu<sup>++</sup> exchange capacity of the raw material.

$\text{Cd}^{++}$  exchange capacities for the raw material were found as 9.2 meq/100 g for +595  $\mu\text{m}$  and 9.7 meq/100 g for +298  $\mu\text{m}$  sizes. No significant changes were observed for acid activated samples (Fig. 8) and a value of 11.9 meq/100 g with +298  $\mu\text{m}$  sample was reached for the sample activated using 2 M  $\text{H}_2\text{SO}_4$ .

#### 4. Conclusions

Ion exchange tests using  $\text{NH}_4^+$ ,  $\text{Zn}^{++}$ ,  $\text{Pb}^{++}$ ,  $\text{Cu}^{++}$  and  $\text{Cd}^{++}$  ions show that Manisa-Gördes clinoptilolites have exchange capacities for these ions in the order  $\text{Pb}^{++} > \text{NH}_4^+ > \text{Cu}^{++}$ ,  $\text{Cd}^{++} > \text{Zn}^{++}$ . This determination is very similar to what had been stated for heavy metals before (Concotti et al. 2001, Modela et al. 1995).

Acid activation generally affected the cation exchange capacities positively. If it is necessary to take a concise look to the results obtained separately, better cation exchange capacity values were reached at both particle sizes with every three acids for  $\text{NH}_4^+$ , except one that the cation capacity values decreased as M concentration of HCl increased at 298  $\mu\text{m}$  sample. After acid activation, while the cation exchange capacities for Pb and Zn increased, the values somewhat dropped for Cu, especially when  $\text{HNO}_3$  used. On the other hand, it can be said for Cd that activation showed just very slight effect. It can be concluded that better results were usually obtained with  $\text{H}_2\text{SO}_4$ .

The results obtained in the batch experiments are worthy. However, in order to determine the industrial applicability, pilot size tests should also be conducted.

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