

CHARACTERIZATION AND STABILITY OF THERMAL MODIFIED ZEOLITIC FILTER FROM WATER TREATMENT

¹Karmen Margeta, ¹Štefica Cerjan Stefanović, ²Branka Vojnović

¹University of Zagreb, Faculty of Chemical Engineering and Technology,
Marulićev trg 20, 10000 Zagreb, Croatia

²University of Zagreb, Faculty of Textile Technology,
Prilaz baruna Filipovića 28a, 10000 Zagreb, Croatia

E-mail: kmargeta@fkit.hr

INTRODUCTION

Former research of natural and modified zeolites in wastewater contaminated with metal ions have shown their efficiency and technological application [1,2]. Natural zeolites have a strong affinity towards water molecules and belong to the group of highly hydrophilic materials. Stability of natural zeolites is determined by the structure, physical and chemical properties [3]. Thermal processing and chemical surface modification may affect their stability, as well as their adsorption, catalytic and ion-exchange properties. Calcination at the high temperature depend on the solid sample and temperature used, can enlarge pore volume by removing water molecules and organics from the pore channels. Natural zeolite-clinoptilolite is cation exchanger whose surfaces can be chemically modified by inorganic salts (e.g., FeCl₃) under different concentration, pH and temperature [4].

This paper shows the characterization of natural and chemically modified zeolites with thermal processing. Thus prepared zeolite filters can be used for the purification of water which was contaminated by arsenic ions.

EXPERIMENTAL

The raw zeolite (PZ) in this study, with particle size in the range of 0,064-0,100 mm, was obtained from a large deposit (Zlatokop) in Vranjska Banja, Serbia. Zeolite was dried at 105°C and stored in desiccator for future modifications.

The chemical modification consisted of the following two steps. In the first step, 50 g of PZ was treated with 0.1 M HCl. The mixtures was stirred for 24 h by a magnetic stirrer at 30°C. After filtering and rinsing PZ was treated for five days with 2 M NaCl at 40° C, and obtained modified zeolite – Z2. Also, 50 g of PZ treated with 2 M NaCl for five days and strried at 40° C gives modified zeolite Z1. In a second step Z2 and Z1 were treated with 0.1 M FeCl₃ in acetate buffer. The mixtures were stirred for 24 h by a magnetic stirrer at 70°C. Obtained modified zeolites were named Z2A and Z1A. Prepared samples PZ, Z1A and Z2A were calcined in a muffle furnace at different temperatures (100, 300, 600 and 900°C) for 1 h. The chemical stability of the samples was tested by heating at elevated temperatures. Hydrolysis of samples PZ, Z1A and Z2A were conducted in deionized water. The amount of iron was determined using atomic absorption spectrometry (AAS). Chemical composition of samples was made by the classical chemical analysis, while phase composition and quantitative values were determined using a combination of XRPD and EDXS.

RESULTS AND DISCUSSION

The chemical composition of natural and modified zeolites was determined by classical chemical analysis and shown in Table 1. The amount of calcium (3.21%) in the sample PZ

was greater by about 2% than the other exchangeable cations, which is in accordance with previous examinations., Therefore, sample PZ is calcium rich zeolite. Ratio of Si/Al obtained by elementary analysis was 4.78. In the sample Z1 amount of sodium was increased for 5.68% compared to the PZ. The amount of aluminum in the samples Z1 and Z2 was increased approximately for 2.5% and the amount of iron around 6.5% with respect to the PZ.

Table 1 The chemical composition of PZ and modified zeolites (w%)

Components	PZ	Z1	Z2	Z1A	Z2A
SiO ₂	65,63	67,75	67,74	60,40	61,01
Al ₂ O ₃	12,97	13,32	12,36	15,87	15,71
Fe ₂ O ₃	1,48	1,04	1,84	8,38	8,92
CaO	3,21	1,40	0,75	2,08	2,02
MgO	1,41	1,21	0,61	0,40	0,15
Na ₂ O	1,2	6,88	-	0,37	0,43
K ₂ O	1,33	0,14	-	1,27	1,05
Loss of ignition	12,96	11,31	10,39	13,06	13,17

Mineralogical analysis of samples PZ and modified zeolites were determined by XRPD method (Fig. 1). Diffractograms show the characteristic peaks for clinoptilolite in 2θ range of 10 – 40°. Peaks typical for clinoptilolite are at 9.9, 22.4, 26, 30.5 and 32°. Diffractograms of modified zeolites (Z1A, Z2A) do not show significant differences compared to natural zeolite. For quantitative phase analyses, XRPD were combined with the results of EDXS elemental analyses for all detected phases. The phase composition of natural zeolite sample was: clinoptilolite 73 %, feldspar 14 % and quartz 13 %.

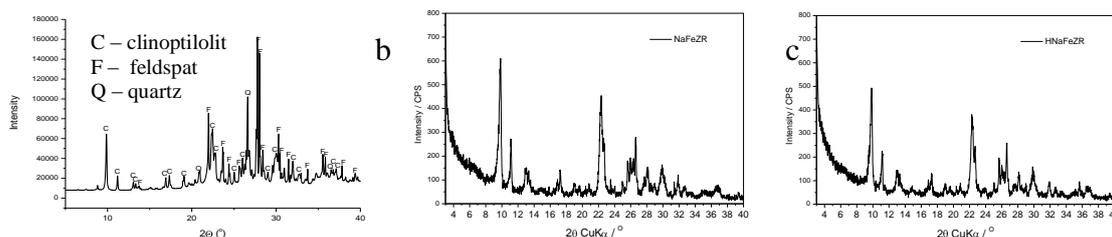


Figure 1. XRPD patterns of: a) natural zeolite (PZ), and modified zeolites b) Z1A and c) Z2A.

IR spektra of PZ and modified zeolite are shown in Fig. 2. The results of FTIR analysis confirm that the samples of natural and modified zeolite were clinoptilolite. Characteristics peaks for clinoptilolite are: bending H₂O at 1640 cm⁻¹, T-O stretching at 1060 cm⁻¹ and out to stretching at 790 cm⁻¹ (T = Si, Al), external and internal vibrations of the double ring at 610 cm⁻¹. The samples modified by FeCl₃ show the peak at 1450 cm⁻¹, which proves the presence of carbonate compounds.

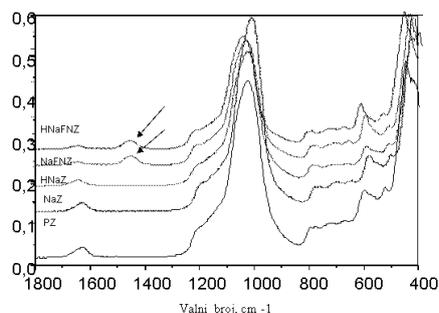


Figure 2. IR spectra of natural and modified zeolite

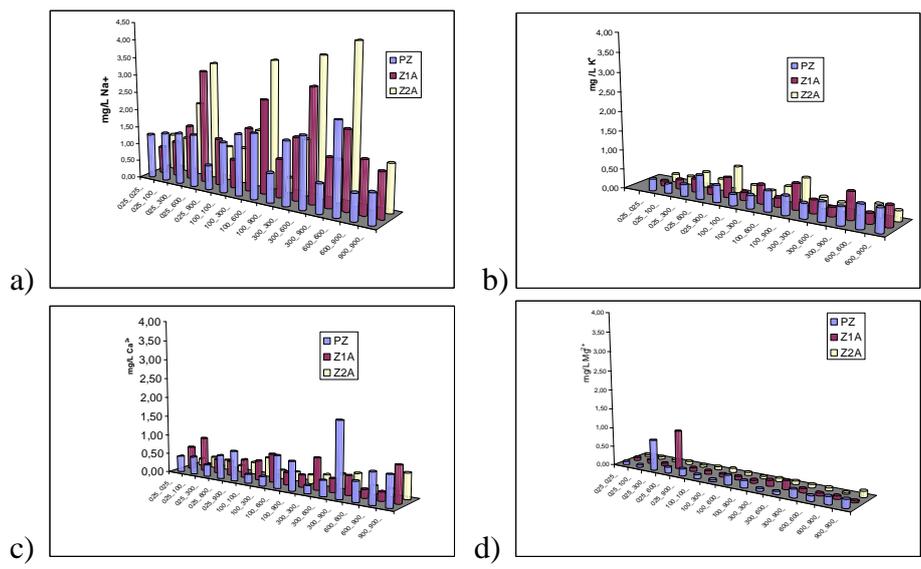


Figure 3. Quantity of exchangeable ions a) Na⁺ b) K⁺ c) Ca²⁺, d) Mg²⁺ in samples heated at different temperatures (25 – 900°C)

Hydrolysis of natural and modified zeolites (Fig. 3) were conducted on samples that were treated at all temperatures: 25°C, 100°C, 300°C, 600°C and 900°C. The results show an increase of concentration of exchangeable ions (Na⁺, K⁺, Ca²⁺ and Mg²⁺) in samples heated up to the 600°C. Further heating up to the 900°C shows a fast decline. This is in accordance to previous research of zeolite structure stability, which decreases above 750°C [5]. Concentrations of Ca²⁺, K⁺ and Mg²⁺ ions were in eluates 1-3 times lower compared to the Na⁺ ions. The results (Fig. 4) show higher pH value for samples PZ due to the larger number of hydroxyl groups which appears during hydrolysis of zeolite. Samples of modified zeolites, thermally treated at 300°C, shows a decrease in pH values and increase of iron ions concentration in eluates with respect to the samples processed at other temperatures (Fig. 5).

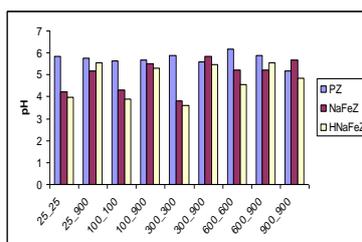


Figure 4. pH values of thermally treated samples PZ, Z1A and Z2A

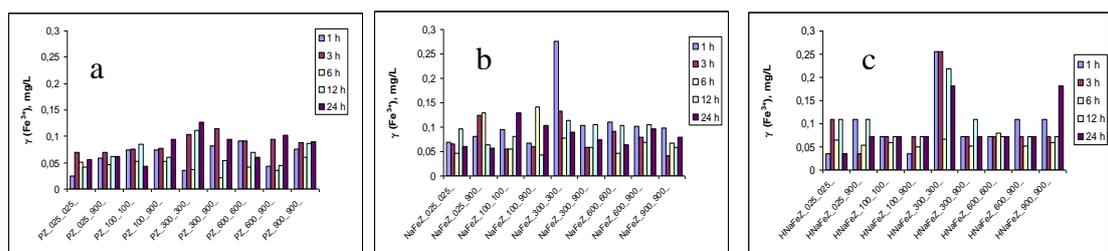


Figure 5. The amount of iron ions in the PZ (a) and modified zeolites (b, c) after the balance with water depending of thermally treated and the time of contact

The external surface of modified zeolites Z1 and Z2 becomes more charged, due to the modification by FeCl₃ solution. The iron ions can be adsorbed in the form of iron oxy-hydroxide on the surface of zeolite, depending on the pH, temperature and concentration of iron salts used. Further heat treatment at higher temperatures (>300°C) turns Fe-hydroxides into more stable iron oxides.

CONCLUSION

Modification of the zeolites with FeCl₃ does not change zeolite framework structure but it covers external surface of zeolite crystals with iron-oxy-hydroxides. Such prepared surface is suitable for adsorption of arsenic species.

Heating of modified samples with Fe-oxy-hydroxide above 300°C transform them into stable Fe-oxide.

As expected, amounts of exchangeable cations in eluates were lowest at samples treated at 900°C, due to irreversible transformation into nonzeolitic close framework structure. In order to define optimal conditions for the preparation of zeolitic filter, it is necessary to conduct further research related to the adsorption of anion species and ion-exchange properties of zeolites.

Acknowledgment

This article is made with financial support from the European project EU! 4208 EUREKA-PUREWATER

REFERENCES

- [1]. Š. Cerjan Stefanović, N. Zabukovec Logar, K. Margeta, N. Novak Tušar, I. Arčon, K. Maver, J. Kovač, V. Kaučič, Structural investigation of Zn²⁺ sorption on clinoptilolite tuff from the Vranjska Banja deposit in Serbia, *Microporous and Mesoporous Materials* 105 (2007) 251–259.
- [2]. M. Šiljeg, S. Cerjan Stefanović, M. Mazaj, N. Novak Tušar, I. Arčon, J. Kovač, K. Margeta, V. Kaučič, N. Zabukovec Logar, Structure investigation of As(III)- and As(V)- species bound to Fe-modified clinoptilolite tuffs, *Microporous and Mesoporous Materials*, 118 (1- 3) (2009), 408 – 415.
- [3]. Eng-Poh Ng, S. Mintova, Nanoporous materials with enhanced hydrophilicity and high water sorption capacity, *Microporous and Mesoporous Materials*, 114 (2008), 1-26.
- [4]. Z. Liang, Jinren Ni, Improving the ammonium ion uptake onto natural zeolite using an integrated modification process, *Journal of Hazardous Materials*, 166 (2009) 52-60.
- [5]. O.C. Duvarcı et al., *Ceramics International*, 33 (2007) 795–801.