

## CHEMICAL BEHAVIOR OF IRON MODIFIED ZEOLITE AT DIFFERENT pH VALUES OF AQUEOUS SOLUTIONS

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### ABSTRACT

The sample of natural zeolite originating from the Vranjska Banja deposit has been used in preparation of iron modified zeolite (IMZ), which has shown a significant increase of adsorption capacity towards heavy metal ions. This paper examines the chemical behavior of IMZ in the IMZ - ultrapure water system at different initial pH values in the range from 1.71 to 5.08. The results show that a rapid increase of pH is observed in the time interval up to 300 min in the pH range from 2.85 to 5.08. This can be attributed to the OH<sup>-</sup> ions released during the process of exchange of H<sup>+</sup> ions from water with Na<sup>+</sup> and other exchangeable cations from the zeolitic structure. At pH=1.71, the suspension pH was unchanged during 24 hours, when partial dissolution and degradation of the aluminosilicate structure have been observed.

Keywords: iron modified zeolite, clinoptilolite, chemical behavior

### INTRODUCTION

Natural zeolites are porous aluminosilicate minerals characterized by a large surface area, and the properties of adsorption and ion exchange. In order to increase the capacity of natural zeolites, a variety of modifications are performed, and one of them is treatment with aqueous solutions containing iron (III) salts [1]. As adsorption and ion exchange processes occur in aqueous media, it is necessary to examine the chemical behavior and stability of these materials at different pH values. The interaction of these materials with the H<sup>+</sup> and OH<sup>-</sup> ions present in solutions, depending on their concentration, can lead to hydrolysis and partial dissolution [2,3]. In addition, the presence of the Brønsted and Lewis acid/base sites affects the chemical behavior of the zeolites particle surface in aqueous solutions [3]. The aim of this paper is to examine the chemical behavior and stability of IMZ at different pH values.

### EXPERIMENTAL

The natural zeolite originating from the Vranjska Banja deposit (Serbia) was used in preparation of iron modified zeolite. The particle size of the sample used in this experiment was 0.6-0.8 mm. The sample was rinsed in ultrapure water in order to remove possible impurities. After drying at 60°C, the samples were stored in the desiccator.

*Preparation of iron modified zeolite (IMZ).* The 20.0 g of natural zeolite sample was mixed with 100 ml of freshly prepared 0.1 M Fe(NO<sub>3</sub>)<sub>3</sub> · 9 H<sub>2</sub>O in an acetate buffer at pH = 3.6, for 2 h at room temperature. The sample was filtered and 90 ml of 1 mol/l NaOH solution was added to the solid phase. The suspension was shaken for an hour and filtered. Thereafter, the zeolite was shaken at 50°C for an hour with 50 ml 4 % NaNO<sub>3</sub> solution. After filtering, the sample was washed with ultrapure water (until the negative test for NO<sub>3</sub><sup>-</sup> ions) and shaken with 50 ml of 50% ethanol for an hour at 50°C. The sample was filtered and after drying for 24 hours at 40°C, kept in a desiccator [1,4,5]. The chemical analysis of natural and iron modified zeolite has been performed by classic chemical analysis of aluminosilicates.

*The chemical behavior of iron modified zeolite.* 5g of IMZ has been mixed with 500 ml ultrapure water in a 700 ml closed glass vessel with a double wall, at 200 rpm and  $20 \pm 1^\circ\text{C}$ . Initial pH values of the ultrapure water (pH = 5.08; 3.80; 2.85; 1.71) were adjusted by addition of 0.1 M HCl. Measurements of pH values of suspensions were conducted continuously during 24 hours. At defined time intervals, portions of 10 ml of the suspension were taken, centrifuged and analyzed. The total amount of suspension taken did not exceed 5 % of the entire volume suspension. The amounts of exchangeable  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  cations were determined by ion chromatography and those of  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  were determined by UV-ViS spectrophotometry.

## RESULTS AND DISCUSSION

Figure 1 shows the experimental results of continuous measurements of pH during the interaction between the IMZ and ultrapure water at different initial pH values.

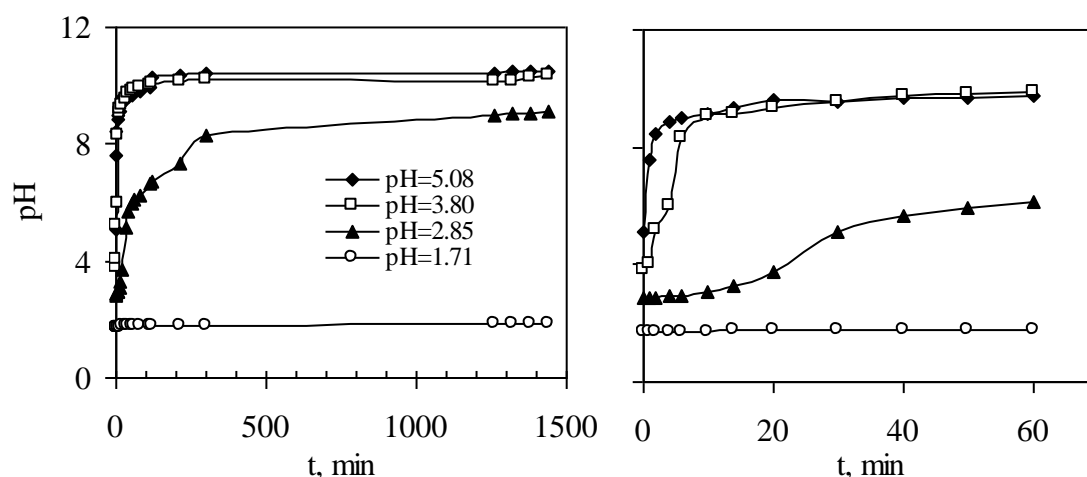


Figure 1. Continuous measurement of pH in the IMZ - ultrapure water system for different initial pH values.

As can be seen from Figure 1, at pH=5.08 and 3.80 rapid increase of pH values is observed. The equilibrium pH is reached after 100 minutes. This can be attributed to the process of exchange of  $\text{H}^+$  ions from water with exchangeable cations from the zeolite structure according to reaction (1) [6].



where:

$\text{M}^{n+}$  -  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$

Z - zeolite.

Among all exchangeable ions,  $\text{Na}^+$  ions are represented in a significant amount, which is confirmed by chemical analysis and the corresponding empirical formula for natural and iron modified zeolite which is presented in Table 1.

Table 1. Empirical formula of natural and iron modified zeolites.

Natural zeolite	$\text{Na}_{0.842}\text{K}_{0.407}\text{Ca}_{1.104}\text{Mg}_{0.368}\text{Al}_{4.780}\text{Fe}_{0.470}\text{Si}_{18.944}\text{O}_{24} \cdot 10.724 \text{H}_2\text{O}$
Iron modified zeolite	$\text{Na}_{2.108}\text{K}_{0.354}\text{Ca}_{1.219}\text{Mg}_{0.352}\text{Al}_{4.841}\text{Fe}_{0.494}\text{Si}_{18.560}\text{O}_{24} \cdot 11.405 \text{H}_2\text{O}$

At lower pH values of 2.85, the amount of Na<sup>+</sup> released by exchanged ions increases, while released OH<sup>-</sup> ions are partially neutralized and the equilibrium pH=8 is reached in 300 min (Figure 2).

At pH=1.71, the suspension pH remained unchanged during 24 hours. This is due to the affect of H<sup>+</sup> ions on the aluminosilicate framework of the zeolite, which leads to the rupture of the Al-O bonds and detachment of Al and Si species. This partial degradation and dissolution of zeolite particles is reflected in the increased amount of exchangeable cations and Al at pH of 1.71, which is shown in Figures 2 and 3 [3].

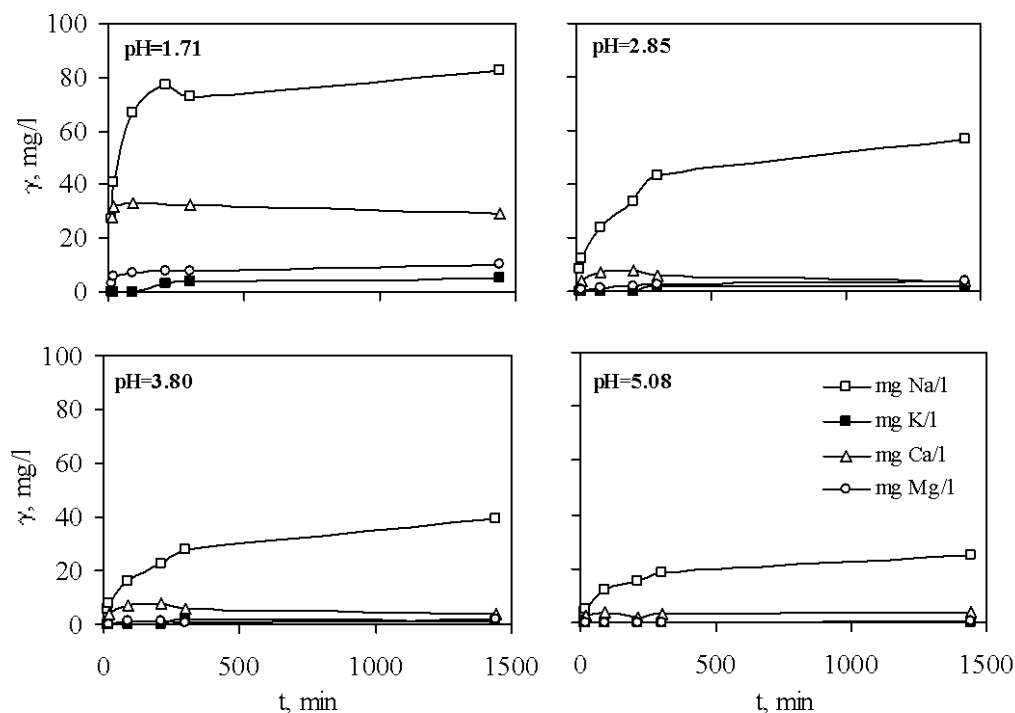


Figure 2. Concentrations of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, in the IMZ - ultrapure water system during 24 hours for different adjusted initial pH values.

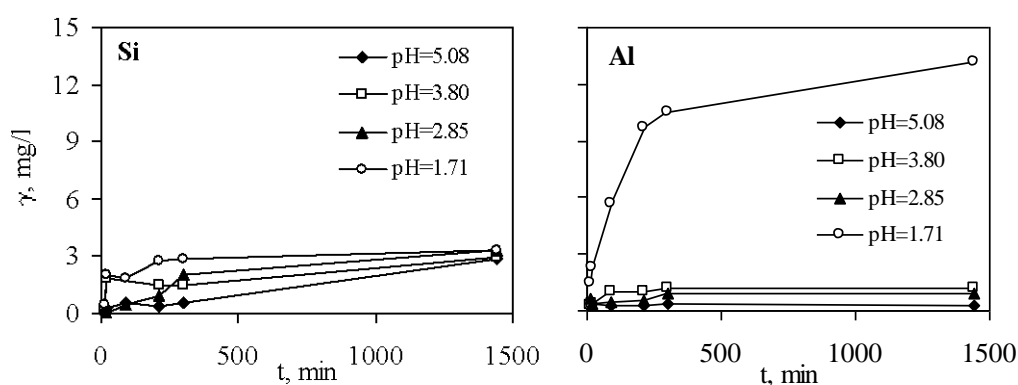


Figure 3. Concentrations of Si<sup>4+</sup> and Al<sup>3+</sup> in the IMZ - ultrapure water system during 24 hours for different adjusted initial pH values.

In a strong acid medium, elimination of exchangeable cations takes place, as well as dealumination accompanied by the degradation of the zeolitic structure according to the scheme shown in Figure 4 [7].

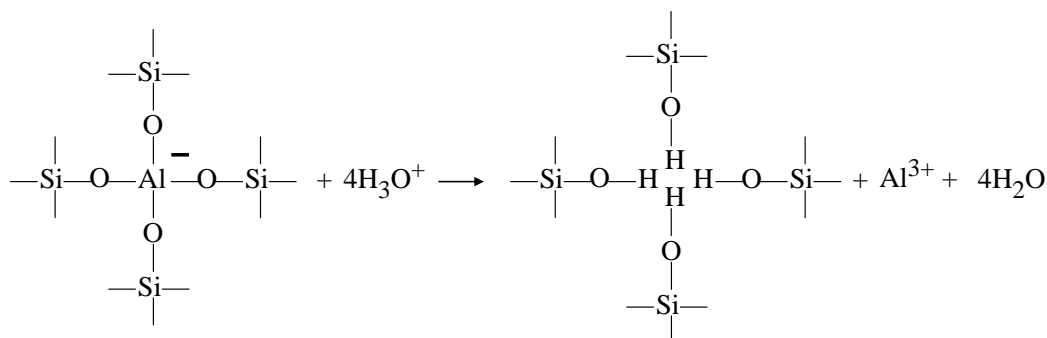


Figure 4. Dealumination of the zeolitic structure in a strong acid medium.

## CONCLUSION

The continuous measurement of pH values in a suspension of the IMZ - ultrapure water system in the pH range from 2.85 to 5.08 shows a rapid increase of pH in the time interval up to 100 min. The main exchangeable cation from zeolite structures is Na<sup>+</sup>, due to the method used for preparation of IMZ. At pH=1.71, the suspension pH is unchanged during 24 hours, which can be attributed to the processes of partial dissolution and degradation of the aluminosilicate structure.

Research into the chemical behavior in the IMZ - ultrapure water system is valuable for understanding the mechanism of binding of heavy metal ions from wastewater.

## ACKNOWLEDGEMENT

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