

## ADSORPTION OF TOXIC METALS BY IRON (III) MODIFIED CLINOPTILOLITES

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### INTRODUCTION

The contamination of water resources with toxic metals (copper, zinc, cadmium, lead, chromium, nickel, mercury, etc.) can cause serious problems to human beings, animals and plants. In the recent years, the levels of these toxic metals in surface waters have been increasing due to the pollution caused by industrial wastewaters discharges. Wastewaters from mining operations, electroplating plants, power-generating plants, electronic appliance factories and tanneries contain several toxic metals [1, 2].

Various treatment methods such as ion exchange, ultrafiltration, adsorption, coagulation-precipitation, etc. have been proposed for removal of toxic metals from waters. Among others, one of the most effective method for the removal of toxic metals from waters is their adsorption by low cost adsorbent materials [3-5]. Zeolites, crystalline aluminosilicates with defined structures that consist of a framework formed by tetrahedral of SiO<sub>4</sub> and AlO<sub>4</sub>, have been widely used in toxic metals adsorption experiments. Recently, iron-overexchanged clinoptilolite (Clino-Fe) was tested for removal of Mn<sup>2+</sup> ions from drinking water and in Cu<sup>2+</sup> ions adsorption from KCl solutions at different pH values [6, 7]. It was reported that Clino-Fe system had much higher adsorption capacity for Mn<sup>2+</sup> and Cu<sup>2+</sup> ions than unmodified clinoptilolite.

In this paper, the natural zeolitic tuff with high content of clinoptilolite was modified with different amounts of iron (III) ions, and the obtained materials were tested for adsorption of copper, zinc and nickel.

### EXPERIMENTAL

Natural zeolitic tuff from the Zlatokop deposit (Vranjska Banja, Serbia) was used as the starting material. The mineralogical composition of the natural zeolitic tuff was primarily clinoptilolite (minimum 85%) with small amounts of feldspar, quartz and pyrite determined by X-ray powder diffraction analysis (XRPD). Raw zeolitic tuff was sieved to yield particles below 43 μm. The cation exchange capacity (CEC) of the starting material was 146 mmolM<sup>+</sup>/100g measured by 1M NH<sub>4</sub>Cl method.

Iron (III) modified clinoptilolites were obtained by treatment of the starting material with three different concentrations of iron (III) chloride (Fe<sup>3+</sup> was added in amounts of 0.6, 1.5 and 2 CEC of the starting zeolitic tuff), using the following procedure: 100 g of the natural zeolitic tuff and 50 mL of each FeCl<sub>3</sub> solution were mixed, as well as, the pH of the mixture was adjusted to 10.0 using 0.1M NaOH [8]. The suspensions were stirred in laboratory mixer at 60°C for 180 min. After the reaction time, the suspensions were rinsed with distilled water until Cl<sup>-</sup> ions were no longer detected and dried at 60°C. The products were denoted as

Fe(0.6)-Z, Fe(1.5)-Z and Fe(2)-Z. The starting zeolitic tuff and the three iron (III) modified clinoptilolites were characterized by chemical analysis and XRPD analysis.

Chemical composition of samples was determined by atomic absorption spectrophotometry (AAS) using Perkin-Elmer 703 instrument. XRPD analysis was performed on a Philips PW-1710 diffractometer with monochromatic Cu-K $\alpha$  radiation, in the range of 4-50° 2 $\theta$ , with a step scan of 0.02°.

For adsorption of toxic metals (Cu<sup>2+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup>), the certain amount of the starting zeolitic tuff and the three iron (III) modified clinoptilolites (1.0 g) was shaken with 50 mL of each toxic metal solution with concentration of ~7 mmol/L. The suspensions were mixed for 24 h at room temperature (20°C) and then filtered. The initial and equilibrium concentrations of each cation in supernatants were determined by AAS.

## RESULTS AND DISCUSSION

An iron (III) modified clinoptilolites were obtained by treatment of the natural zeolitic tuff with different concentrations of iron (III) chloride solution (Fe<sup>3+</sup> was added in amounts of 0.6, 1.5 and 2 CEC of the starting zeolitic tuff) under strongly basic solution. Chemical composition of the starting zeolitic tuff and iron (III) modified clinoptilolites Fe(0.6)-Z, Fe(1.5)-Z and Fe(2)-Z is presented in Table 1.

Table 1. Chemical composition of the starting zeolitic tuff and iron (III) modified clinoptilolites.

	Content, %							
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	IL
Starting zeolitic tuff	66.57	13.13	2.30	3.85	0.56	1.27	1.17	11.05
Fe(0.6)-Z	64.58	12.55	5.00	2.45	0.68	0.45	4.58	9.36
Fe(1.5)-Z	62.72	12.57	7.91	2.10	0.71	0.67	5.06	7.87
Fe(2)-Z	61.00	12.36	9.20	3.15	0.72	0.64	5.20	7.81

Results of chemical analysis (Table 1) showed that major constituents of starting zeolitic tuff and the three iron (III) modified clinoptilolites are silicon and alumina. The content of Fe<sub>2</sub>O<sub>3</sub> in starting zeolitic tuff was 2.30% (calculated Fe<sup>3+</sup> content is 1.60%). For iron (III) modified clinoptilolites, the iron (III) content increased with increasing the amount of Fe<sup>3+</sup> used for modifications (3.49%, 5.54% and 6.43% of iron (III) in Fe(0.6)-Z, Fe(1.5)-Z and Fe(2)-Z, respectively). At the same time, the amount of sodium and silicon decreased with increasing the initial amount of iron (III). Compared to the starting zeolitic tuff, the lower amount of silicon in iron (III) modified products indicate slight dissolution of clinoptilolite in basic solution (pH 10). It is also observed that modification process caused increase of potassium content in all modified samples.

XRPD patterns of the starting zeolitic tuff and iron (III) modified clinoptilolites are presented in Figure 1. All three iron (III) modified clinoptilolites are characterized by lower crystallinity than the starting material. It seems that the iron (III) modified clinoptilolites maintain the main characteristic peaks of clinoptilolite which are present in the spectrum, but with the significantly lower intensity. The additional Fe oxidic or oxo-hydroxidic crystalline phases were not observed at X-ray diffractograms.

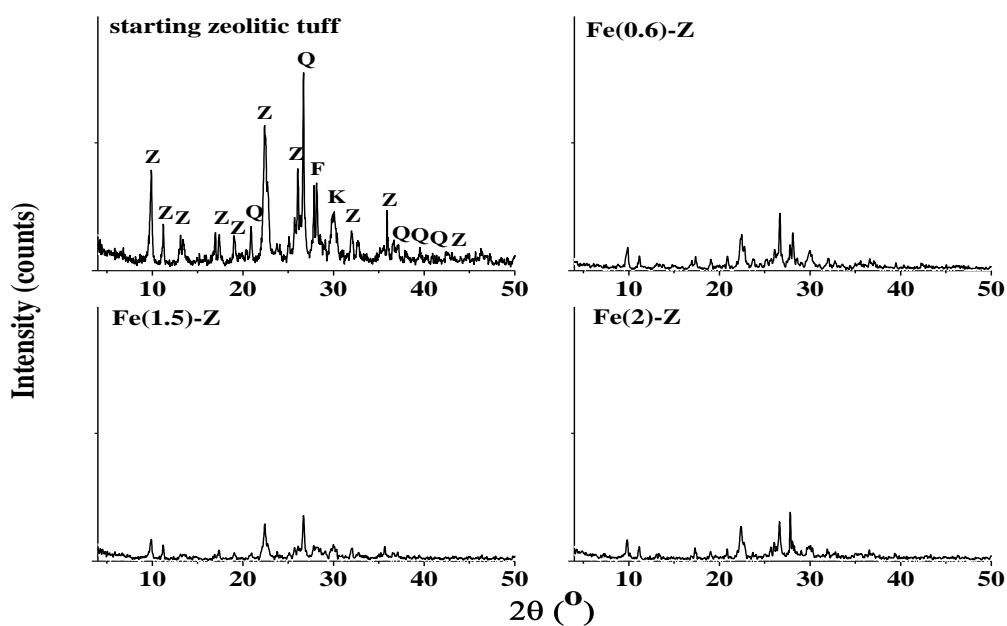


Figure 1. XRPD patterns of starting zeolitic tuff, Fe(0.6)-Z, Fe(1.5)-Z and Fe(2)-Z.

Results of copper, zinc and nickel adsorption by the starting zeolitic tuff and Fe(0.6)-Z, Fe(1.5)-Z and Fe(2)-Z are presented at Figure 2.

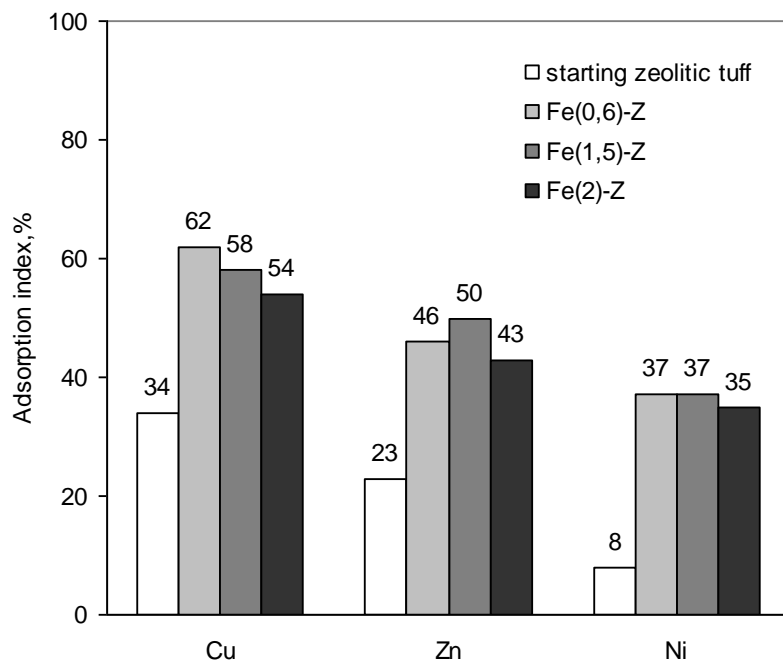


Figure 2. Adsorption of toxic metals (Co = 7 mmol/l) by starting zeolitic tuff and iron (III) modified clinoptilolites.

Results presented at Figure 2 showed that compared to the starting zeolitic tuff presence of iron (III) in clinoptilolite increased the adsorption of copper, zinc and nickel. Copper

adsorption was highest for Fe(0.6)-Z, and increase of iron (III) content in clinoptilolite slightly decreased the copper adsorption (copper adsorption index was 62% for Fe(0.6)-Z, 58% for Fe(1.5)-Z and 54% for Fe(2)-Z). Zinc adsorption increased with increasing the iron (III) content in clinoptilolite up to the 1.5 CEC of the starting zeolitic tuff (sample Fe(1.5)-Z) and then decreased (zinc adsorption was 46%, 50% and 43% for Fe(0.6)-Z, Fe(1.5)-Z and Fe(2)-Z, respectively). Nickel adsorption was low by starting zeolitic tuff (adsorption index – 8%), and the presence of iron (III) in all three modified clinoptilolites increased the adsorption of this toxic metal (nickel adsorption index was ~ 37%).

## CONCLUSION

The effect of iron (III) content in clinoptilolite mineral on adsorption of copper, zinc and nickel was investigated. Results showed that presence of iron (III) in clinoptilolite increased the adsorption of all three toxic metals. The clinoptilolite with the lowest amount of iron (III) - Fe(0.6)-Z was best adsorbent for copper. The highest adsorption of zinc was achieved by Fe(1.5)-Z. Nickel adsorption by iron (III) modified clinoptilolites was independent on the amount of iron (III) in clinoptilolite. In further investigations, in order to investigate the mechanism of adsorption of toxic metals by iron (III) modified clinoptilolites, the adsorption isotherms will be determined.

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