

## REMOVAL OF HEAVY METALS FROM AQUEOUS SOLUTION USING NATURAL AND Fe(III) OXYHYDROXIDE CLINOPTILOLITE

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**Abstract**—The increasing levels of industrial wastewater released to the environment present a serious threat to human health, living resources, and ecological systems. Fe-modified zeolites were developed and tested for removal of Cu<sup>2+</sup> and Zn<sup>2+</sup> from contaminated water. The surfaces of the naturally occurring zeolite, clinoptilolite, were modified with Fe(III) oxyhydroxides using three different methods, denoted I, II, and III (FeCli<sub>1</sub>, FeCli<sub>2</sub>, and FeNaCli<sub>1</sub>, respectively). The oxyhydroxides were prepared in Method I using 0.1 M FeCl<sub>3</sub>·6H<sub>2</sub>O in an acetate buffer (pH = 3.6); in Method II, using 10% FeCl<sub>3</sub>·6H<sub>2</sub>O solution in 0.1 M KOH (pH = 10); and Method III was the same as Method I except the clinoptilolite was pretreated with NaCl. Newly synthesized materials from these three methods were then tested for their ability to enhance the sorption capacity for Cu and Zn compared to the natural sample (Cli). Powder X-ray diffraction measurements and the chemical composition of these modified samples confirmed that clinoptilolite maintained its structure while amorphous Fe<sup>3+</sup> species were synthesized. The specific surface area (BET method) of both the natural and modified clinoptilolite increased by 2 and 7.5 times for Methods I and II, respectively. Scanning electron microscopy and energy dispersive X-ray spectroscopy revealed that CaO was formed during Method I (FeCli<sub>1</sub>). Throughout the adsorption process, the hydrolysis of CaO and the release of OH<sup>−</sup> caused the precipitation of Cu and Zn hydroxide, which made the determination of the sorption capacity of FeCli<sub>1</sub> impossible. This phenomenon was avoided in Method III (FeNaCli<sub>1</sub>) because of the absence of exchangeable Ca<sup>2+</sup>. The adsorption experiments with Method II resulted in double-enhanced adsorption capacity. Laboratory batch experiments revealed that the sorption capacities increased in the following order: Cli < FeCli<sub>2</sub> < FeNaCli<sub>1</sub>, for Cu: 0.121 mmol/g < 0.251 mmol/g < 0.403 mmol/g and for Zn: 0.128 mmol/g < 0.234 mmol/g < 0.381 mmol/g.

**Key Words**—Copper, Fe-modification, Sorption Capacity, Zeolite, Zinc.

### INTRODUCTION

Heavy metals (Cu, Zn, Pb, Fe, Mn, Cd, Co, Mo, Ni) occur naturally in the environment over a wide range of concentrations and comprise some of the most widespread contaminants in the ecosystem. Anthropogenic sources of heavy metals have also been introduced. Zinc is a raw material suitable for corrosion-resistant alloys and brass, as well as for galvanizing steel and iron products (Shek *et al.*, 2009). Copper is used widely in electroplating, in light industry, in the mechanical manufacturing industry, and in architecture, *etc.* (Han *et al.*, 2009).

Mining operations and various chemical-processing industries produce waste containing heavy metals that are non-biodegradable (Šljivić *et al.*, 2009). Heavy metals tend to accumulate in living organisms causing disease and disorders. Therefore, wastewater that contains heavy metals needs to be treated prior to its discharge into the environment (Shek *et al.*, 2009).

In order to develop less expensive, more effective, and environmentally friendly technologies several approaches have been taken in recent times. Membrane filtration (ultrafiltration, nanofiltration, reverse osmosis) has received considerable attention for treatment of inorganic effluent because it is capable of removing inorganic contaminants such as heavy metals. The disadvantages of this process are the large operational costs and the problem of membrane fouling (Barakat, 2011). Among common purification techniques, adsorption has gained much recent attention because it is an eco-friendly, cost-effective, and straightforward operating technology.

Adsorption by ion exchange is a mass-transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by the physical and/or chemical interactions (Kurniawan *et al.*, 2006a, 2006b). Much recent research attention has been focused on the selection and/or production of low-cost adsorbents with good metal-binding capacities (*e.g.* Wan Ngah and Isa, 1998; Crini, 2005; Ajmal *et al.*, 2000; Amana *et al.*, 2008). The adsorbents may be of mineral, organic, or biological origin. Organic and biological adsorbents, such as agricultural waste, industrial by-products, biological waste, and biopolymers

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(Kurniawan *et al.*, 2006a, 2006b), have significantly larger metal-adsorption capacities than those of minerals such as zeolites and clay minerals. The great disadvantages of these adsorbents are the small pH range (Ahluwalia and Goyal, 2008), secondary pollution (Šćiban *et al.*, 2007), and insufficient quantities available for industrial application.

Natural materials, *e.g.* zeolites, have attracted significant interest, mainly because of their good metal-binding capacity, local availability in large quantities (and, therefore, at low cost), avoidance of secondary pollution, potential for regeneration, and potential for creating value-added products from the recovered adsorbed metal. Zeolites have been used widely in heavy-metal adsorption experiments because of their unique physical and chemical properties (crystallinity, thermal stability, well defined cage structure of molecular size, ion exchange, good hydrodynamic properties, *etc.*) (Doula *et al.*, 2002). Clinoptilolite is the most abundant natural zeolite and is a common alteration product of vitroclastic sediments that have been altered diagenetically in subaerial and marine environments (Passaglia and Sheppard, 2001). Zeolites are hydrated aluminosilicates of alkali and alkaline earth elements with unique crystal structures. The primary building units of the aluminosilicates are the  $TO_4$  tetrahedra, where  $T$  is Si or Al. The tetrahedra are linked in such a way that zeolites contain many channels and cavities (Gottardi and Galli, 1985). The primary structural units,  $AlO_4$  or  $SiO_4$  tetrahedra, in most zeolite structures are assembled into secondary building units which may be simple polyhedra such as cubes, hexagonal prisms, or cubo-octahedra. Each tetrahedral Al ion in the zeolite framework yields a net negative charge (Doula, 2006). This porous, negatively charged surface of zeolite can be used to adsorb metals such as Cu and Zn. The negatively charged surface is balanced by mono and divalent exchangeable cations such as Na, Ca, K, and Mg which give zeolites a large cation exchange capacity (CEC) (Kragović *et al.*, 2009).

Although zeolite has moderate adsorption capacity for heavy metals, many researchers have modified the zeolite substrates in order to obtain an adsorbent with greater retention capacity than that of the parent material (Dimirkou *et al.*, 1996, 2008; Doula, 2006, 2007). Attempts were made by those authors to synthesize mixed systems of Fe oxides and clay minerals or zeolites and those systems were proved not only capable of adsorbing large amounts of inorganic species, but also to improve the catalytic properties of the zeolites in the case of the Fe-zeolite systems (Morturano *et al.*, 2001). Both the chemical nature and large specific surface areas of submicroscopic Fe-oxide particles make them efficient sorbents and, therefore, sinks for inorganic and organic anions and metal cations. With respect to the zeolite channel size, Fe-oxide active sites are located on the external surface of the zeolite crystallites. The

formation of an Fe-oxide phase on zeolite increases the number of active sites on the adsorbent because of the presence of the Fe-OH groups. Modified zeolites should, therefore, have significantly greater adsorption capacity than the untreated version.

The purpose of the present research was to develop different Fe(III)-modified zeolites (Fe-modified clinoptilolite 1 – FeCli<sub>1</sub>; Fe-Na-modified clinoptilolite 1 – FeNaCli<sub>1</sub>; and Fe-modified clinoptilolite 2 – FeCli<sub>2</sub>), and to test their effectiveness in the removal of  $Cu^{2+}$  and  $Zn^{2+}$  ions from aqueous solution.

## EXPERIMENTAL

### *Clinoptilolite*

A clinoptilolite-rich zeolite tuff was obtained from the Zlatokop deposit in Vranjska banja, Serbia. According to semi-quantitative powder X-ray diffraction (PXRD) analysis, the clinoptilolite content is ~75% of the crystalline phase. The other crystalline minerals are quartz, feldspar, and carbonate. The total CEC of the zeolitic tuff was 146 meq/100 g, measured using 1 M  $NH_4Cl$  (Sigma Aldrich, Munich, Germany). Calcium (85 meq/100 g) was the dominant exchangeable ion but Na (23.5 meq/100 g), Mg (22 meq/100 g), and K (15.5 meq/100 g) were also present in the starting zeolitic tuff. For the adsorption experiments and synthesis of the Fe-clinoptilolite systems, a natural zeolitic tuff (Cli) was ground and sieved to particle sizes of <0.043 mm.

### *Synthesis of Fe(III)-modified clinoptilolite*

*Preparation of Fe(III)-modified clinoptilolite, Method I (FeCli<sub>1</sub>).* 100 g of Cli was saturated with 500 mL of freshly prepared 0.1 M  $FeCl_3 \cdot 6H_2O$  in a sodium acetate buffer (pH = 3.6) for 1 h in a magnetic stirrer at room temperature. The saturated sample was filtered, treated with 4% NaOH solution (450 mL), stirred for 1 h, treated with 4% NaCl solution (250 mL), and stirred for 1 h at 50°C. The mixture was rinsed by filtration with distilled water (until  $Cl^-$  ions were no longer detected) and dried (Habuda-Stanić *et al.*, 2008).

### *Preparation of Fe(III)-modified clinoptilolite, Method II (FeCli<sub>2</sub>).*

The clinoptilolite-Fe system was synthesized by combining the method for preparation of pure goethite (Mustafa *et al.*, 2004) with that for preparing Fe-coated zeolite (Jeon *et al.*, 2009). Briefly, 50 g of Cli was mixed with 25 mL of freshly prepared 10%  $FeCl_3 \cdot 6H_2O$  solution and 700 mL of 0.1 M KOH (pH = 10) in a 2 L polyethylene container. The container was capped and the suspension aged for 20 days at room temperature. During the reaction period, the suspension changed from a red brown suspension of ferrihydrite to a compact, yellow-brown precipitate of goethite (Mustafa *et al.*, 2004). After 20 days, the suspension was filtered, washed (until  $Cl^-$  ions were no longer detected), and dried for 24 h at 40°C.

*Preparation of Fe(III)-modified clinoptilolite, Method III (FeNaCli<sub>1</sub>).* The FeNaCli<sub>1</sub> was prepared using the same procedure as Method I (FeCli<sub>1</sub>), except the Cli was first washed with 1 M NaCl prior to Fe precipitation in order to obtain the monoionic form of clinoptilolite. The importance of this pretreatment is made clear below.

All of the chemicals used during the modification treatments were obtained from Sigma Aldrich, Munich, Germany.

#### Sample characterization

The chemical compositions of both natural and Fe(III)-modified clinoptilolite were determined by atomic absorption spectrophotometry (AAS) using the Spekol 1300 instrument (Analytic Jena, Jena, Germany).

X-ray diffraction was used to determine the phase composition. The XRD patterns were obtained using a PW 1710 automated diffractometer (Philips, Eindhoven, The Netherlands) using a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted-beam curved graphite monochromator and a Xe-filled proportional counter. The diffraction data were collected over the range 4–65°2 $\theta$ , counting for 0.5 s (qualitative identification) per 0.02° step. The divergence and receiving slits were fixed at 1 and 0.1, respectively. All the XRD measurements were performed at room temperature in a stationary sample holder.

A JSM-6610LV Scanning Electron Microscope (SEM) (JEOL, Tokyo, Japan) equipped with energy dispersive X-ray spectroscopy (EDS) was used for electronic scanning of the samples. For SEM analysis, the samples were coated with Au films to improve conductivity prior to imaging.

Adsorption and desorption isotherms of N<sub>2</sub> were measured on zeolite samples, at –196°C, using the gravimetric McBain method (ISO 9277, 2010). The specific surface area ( $S_{\text{BET}}$ ), pore-size distribution (PSD), mesopore space including external surface area ( $S_{\text{meso}}$ ), and micropore volume ( $V_{\text{mic}}$ ) of the samples were calculated from isotherms as detailed by Baretta *et al.* (1951). The PSD was estimated by applying the BJH method (Barrett *et al.*, 1951) to the desorption branches of the isotherms. The values of  $S_{\text{meso}}$  and  $V_{\text{mic}}$  were estimated using the high-resolution  $\alpha_s$  plot method (Kaneko *et al.*, 1992, 1998; Kruk *et al.*, 1997). The value of micropore surface,  $S_{\text{mic}}$ , was calculated by subtracting  $S_{\text{meso}}$  from  $S_{\text{BET}}$ .

#### Sorption experiments

Uptake of Cu and Zn was investigated by shaking 1 g of Cli, FeCli<sub>1</sub>, FeNaCli<sub>1</sub>, or FeCli<sub>2</sub> with 50 mL of aqueous solution of ZnSO<sub>4</sub>·6H<sub>2</sub>O and CuSO<sub>4</sub>·5H<sub>2</sub>O (Sigma Aldrich) with various initial Cu and Zn concentrations (1–14 mmol/L of Cu<sup>2+</sup> and Zn<sup>2+</sup>). Experiments were performed at room temperature using the batch technique for 24 h. After equilibration all suspensions were centrifuged at 19,006 × g for 10 min and the concentrations of the remaining Cu and Zn in supernatants were determined using AAS.

## RESULTS AND DISCUSSION

The chemical composition (Table 1) of a natural zeolitic tuff (Cli) and its Fe(III)-modified zeolites (FeCli<sub>1</sub>, FeCli<sub>2</sub>, and FeNaCli<sub>1</sub>) indicated that none of the modification processes significantly altered the chemical composition of the Cli framework. Even though these modifications were carried out under strictly basic conditions, no notable decrease in Si content in FeCli<sub>1</sub>, FeCli<sub>2</sub>, or FeNaCli<sub>1</sub> was observed.

The modifications did result, however, in different levels of exchanged (extra-framework) cations. Fe(III)-zeolites obtained during the modification by Method I, for example, contained more Na than the original sample, due to ion exchange by the Na added after initial reaction with Fe(III). Ion exchange during that treatment was only partial, however, as about half of the initial cations remained unchanged, particularly the Ca<sup>2+</sup> ions.

Unlike in FeCli<sub>1</sub>, pretreatment of Cli with NaCl by Method III resulted in almost complete cation exchange in the FeNaCli<sub>1</sub> sample. The residual amounts of Ca, Mg, and K measured in FeNaCli<sub>1</sub> may not all have been cations retained on the exchange complex of the clinoptilolite, but some could have been resident in the accessory minerals and, thus, inaccessible for ion exchange. Support for this hypothesis was found in the EDS chemical analysis, which showed that the residual Ca, K, and Mg ions were indeed absent from the clinoptilolite (Figure 1).

Due to modification treatment Method II, FeCli<sub>2</sub>, unsurprisingly, has a large K content. The sum of exchanged cations is slightly greater than the amount of K<sup>+</sup> ions introduced into the FeCli<sub>2</sub> structure, indicating

Table 1. Chemical composition (wt.%) of Cli, FeCli<sub>1</sub>, FeNaCli<sub>1</sub>, and FeCli<sub>2</sub>.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	LOI*
Cli	67.26	11.73	2.24	3.36	1.11	1.35	1.02	11.93
FeCli <sub>1</sub>	66.96	11.51	3.07	2.56	0.81	0.94	2.54	11.55
FeNaCli <sub>1</sub>	66.87	11.49	3.54	1.04	0.76	0.71	3.86	11.31
FeCli <sub>2</sub>	66.44	11.31	4.59	2.10	0.86	4.36	0.40	9.88

\* LOI: loss on ignition

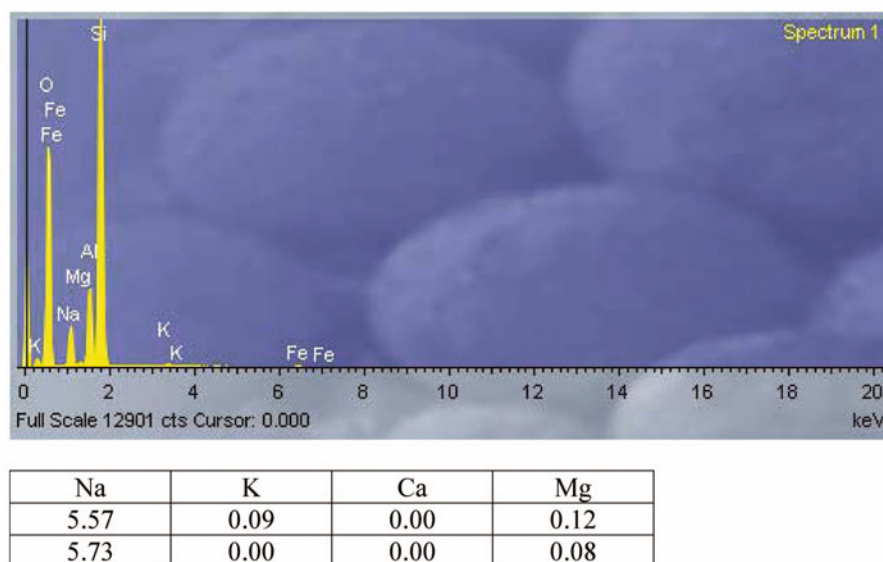


Figure 1. Qualitative and quantitative EDS analysis of FeNaCl<sub>1</sub>.

that ion exchange with K was almost complete. The amount of Fe in the modified samples was greatest in those prepared by this method (II). According to EDS analysis of a single clinoptilolite crystal, the Cli sample contained no structural Fe, so all of the Fe in the untreated Cli originated from the associated minerals. Using the same analysis, the level of the Fe in the FeNaCl<sub>1</sub> and FeCl<sub>2</sub> were 0.46 wt.% and 0.81 wt.%, respectively. This means that only some of the Fe penetrated the channel structure of the clinoptilolite while the rest of it was distributed in a form of oxyhydroxide over the external surface area.

Modification methods were carried out under strictly basic (pH consistently >9) conditions during which the surface groups lost their hydrogen and became negatively charged. These negatively charged sites were occupied by Fe<sup>3+</sup> ions that formed different Fe-species. Fe-species are linked by hydrogen bonds to the surface of the sample (Doula, 2007). The color of all three samples FeCl<sub>1</sub>, FeNaCl<sub>1</sub>, and FeCl<sub>2</sub> was yellowish-brown. The PXRD analyses (Figure 2) confirmed that the starting material was clinoptilolite. The tuff also contains small amounts of associated minerals such as quartz, feldspar, carbonate, and volcanic glass.

The Fe(III)-modified Cli samples were of lower crystallinity than the original zeolite. In the FeCl<sub>1</sub> and FeCl<sub>2</sub> samples no changes in the zeolite diffraction peaks were noted (Figure 3). The XRD trace of the FeNaCl<sub>1</sub> was the same as that of FeCl<sub>1</sub>. The absence of additional peaks in both Fe-clinoptilolite systems indicated that only amorphous and not crystalline Fe-phases were formed at the clinoptilolite surface site.

Nitrogen adsorption isotherms for the zeolites, the amount of N<sub>2</sub> adsorbed as a function of relative pressure

at -196°C, are given in Figure 3. The results below which are related to the specific surface areas of the samples of FeCl<sub>1</sub> and FeNaCl<sub>1</sub> were almost the same and so are presented together.

According to the IUPAC classification (Sing *et al.*, 1985), the isotherms are of type IV with a hysteresis loop which is associated with mesoporous materials. The shape of the hysteresis loop is of type H4 which indicates narrow slit pores and a large number of micropores (Lowell *et al.*, 2004). Specific surface areas (*S*<sub>BET</sub>) calculated by the BET equation, together with the porous parameters for the Cli, FeCl<sub>1</sub>, FeNaCl<sub>1</sub>, and FeCl<sub>2</sub> (Table 2), revealed that Fe oxyhydroxide at the zeolite surface significantly increased the overall specific surface area, especially during modification Method II (FeCl<sub>2</sub>).

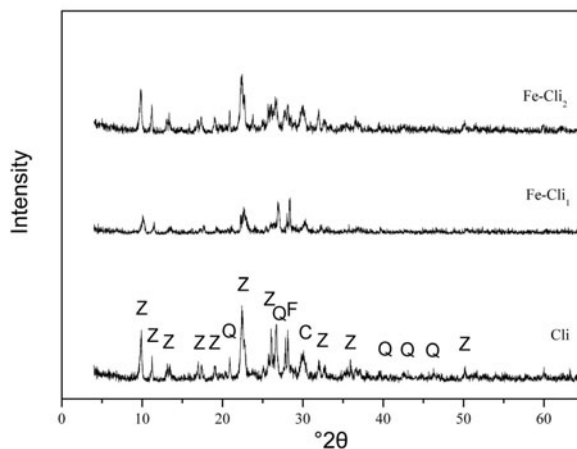


Figure 2. PXRD patterns for samples Cli, FeCl<sub>1</sub>, and FeCl<sub>2</sub>.

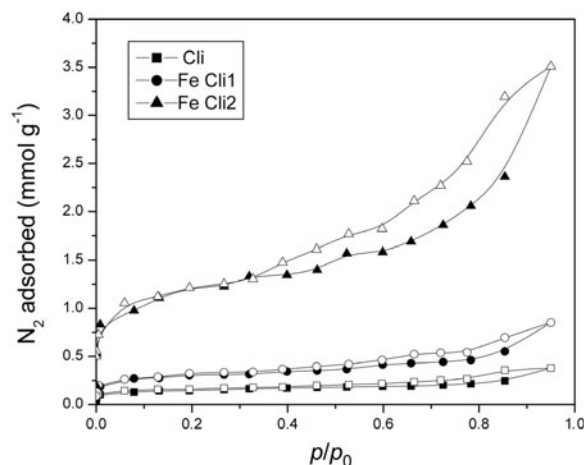


Figure 3. N<sub>2</sub> adsorption isotherms for samples Cli, FeCli<sub>1</sub>, and FeCli<sub>2</sub>. Solid symbols – adsorption, open symbols – desorption.

The PSD values of the samples (Figure 4) showed that the PSD was discontinuous where the samples were mostly mesoporous with a certain amount of micropores and the pore radius of the average sample was 2–3 nm.

The  $\alpha_s$  plot (Figure 5), obtained from the standard nitrogen adsorption isotherm, revealed a straight line in the high- $\alpha_s$  region. From this relationship the external mesoporous surface area,  $S_{\text{meso}}$ , was determined from the slope, and the micropore volume,  $V_{\text{mic}}$ , was given by the intercept. Calculated porosity parameters ( $S_{\text{meso}}$ ,  $S_{\text{mic}}$ ,  $V_{\text{mic}}$ ) (Table 2) confirmed that samples were mesoporous with a certain number of micropores. Sample FeCli<sub>2</sub> had a significantly larger mesoporous surface area compared with Cli, FeCli<sub>1</sub>, and FeNaCli<sub>1</sub>.

All samples were analyzed by SEM. Micrographs of FeNaCli and FeCli<sub>2</sub> (not shown) did not differ from the original sample. The images of Cli and FeCli<sub>1</sub> indicated the presence of small cubes at the surface of FeCli<sub>1</sub> (Figure 6), which were absent from the image of Cli. Energy dispersive X-ray spectroscopy mapping of the FeCli<sub>1</sub> (Figure 7) identified large quantities of calcium (62.32%) and oxygen (31.15%), and the well shaped isometric crystals along with the Ca/O ratio support the notion that these cubes are new crystalline structures of CaO which have been formed.

The FeNaCli<sub>1</sub> was prepared in almost the same way as the FeCli<sub>1</sub>. The absence of CaO cubes at the surface of the FeNaCli<sub>1</sub> supports the theory that modification

Table 2. Pore properties of zeolites.

Sample	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$S_{\text{meso}}$ (m <sup>2</sup> /g)	$S_{\text{mic}}$ (m <sup>2</sup> /g)	$V_{\text{mic}}$ (cm <sup>3</sup> /g)
Cli	12	6	6	0.002
FeCli <sub>1</sub>	23	15	8	0.003
FeCli <sub>2</sub>	91	57	34	0.018

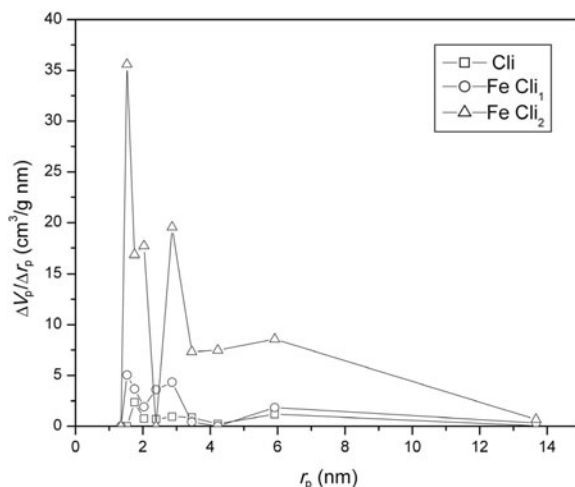


Figure 4. Pore-size distribution (PSD) for samples Cli, FeCli<sub>1</sub>, and FeCli<sub>2</sub>.

Method I liberated the Ca in the form of CaO from the zeolite. Due to the pretreatment with NaCl in modification Method III, complete extra-framework Ca<sup>2+</sup> was exchanged, which meant that none of these crystalline species was formed at the surface of the zeolite. In addition, the elemental mapping showing the spatial distribution of the elements also indicated uniform distribution of Fe over the surface of all modified samples. The EDS analysis results of the Fe content were in the following order: Cli (1.63%) < FeCli<sub>1</sub> (2.76%) < FeNaCli<sub>1</sub> (3.12%) < FeCli<sub>2</sub> (7.42%).

Copper and Zn adsorption by Cli, FeCli<sub>1</sub>, FeNaCli<sub>1</sub>, and FeCli<sub>2</sub> was examined using a range of initial Cu and Zn concentrations. The experimental data from the equilibrium studies were analyzed using Langmuir and Freundlich sorption models. The Freundlich model provided the better fit of the experimental data (Table 3).

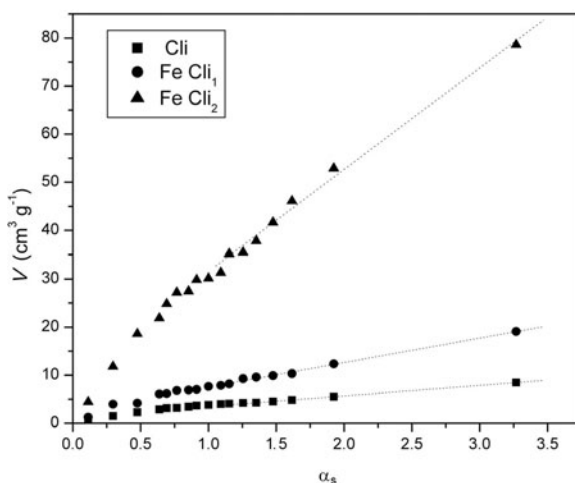


Figure 5.  $\alpha_s$  plots for N<sub>2</sub> adsorption isotherms for samples Cli, FeCli<sub>1</sub>, and FeCli<sub>2</sub>.

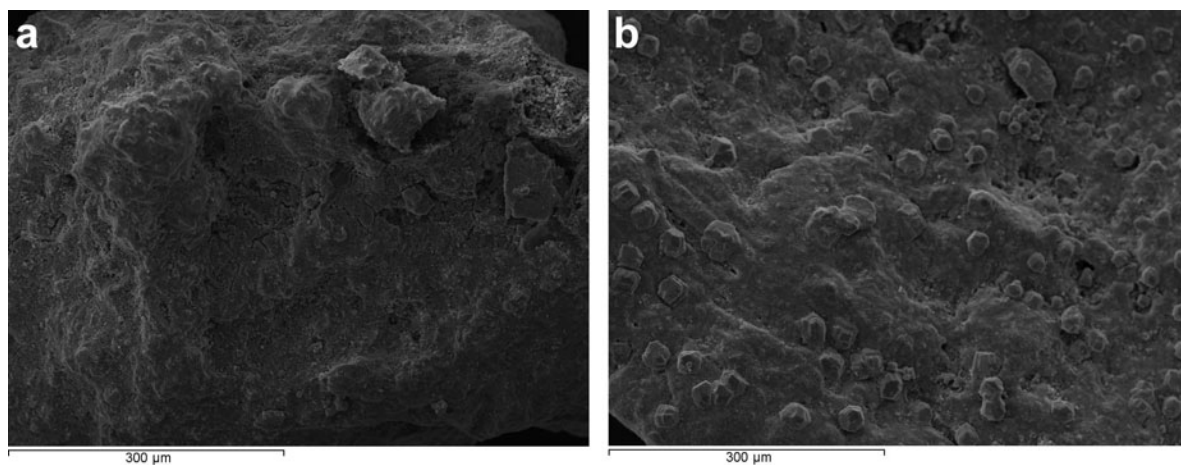


Figure 6. Micrographs of (a) Cli and (b) FeCl<sub>11</sub>.

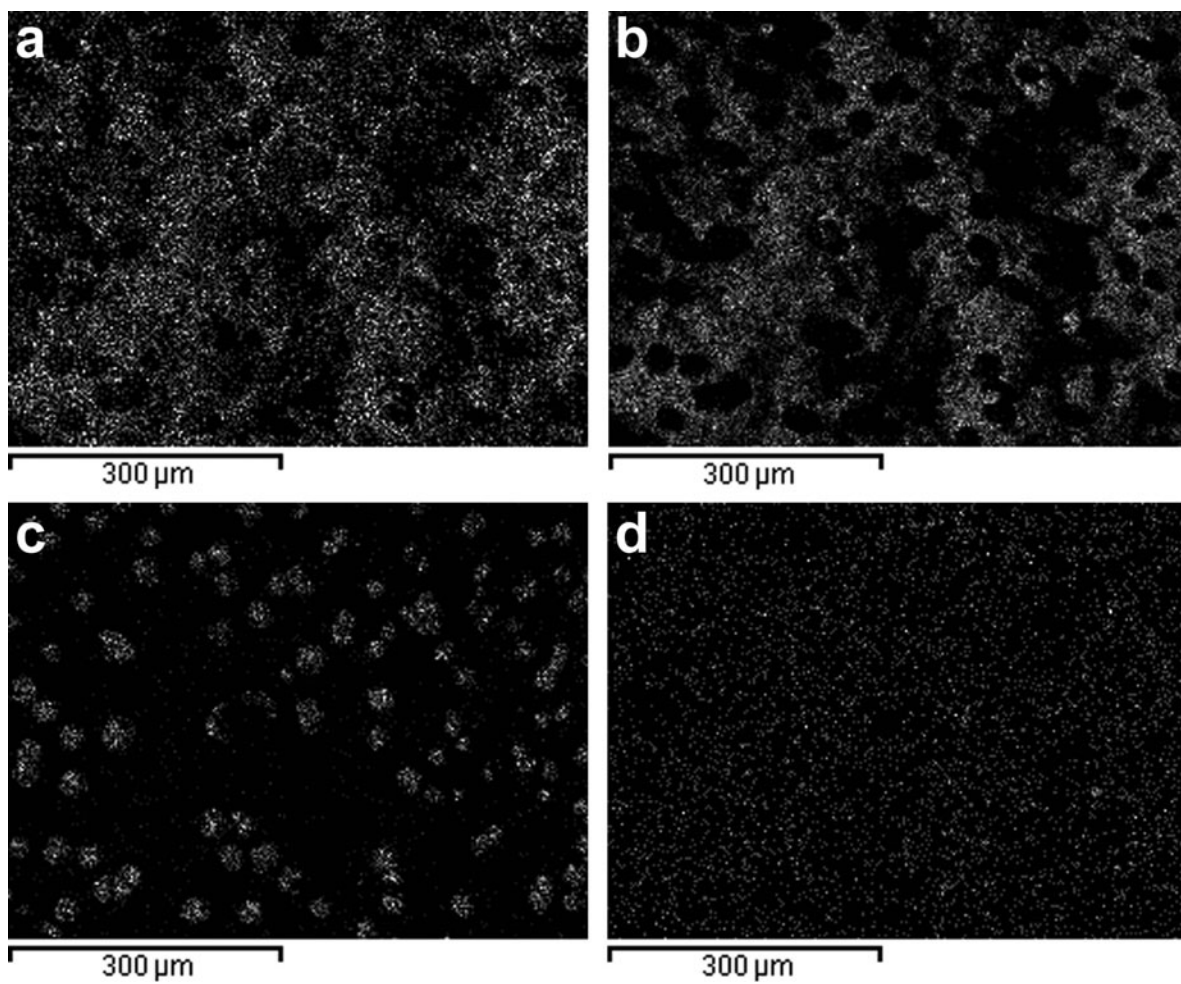


Figure 7. EDS mapping of the FeCl<sub>11</sub>: (a) Al; (b) Si; (c) Ca; (d) Fe.

Table 3. Freundlich parameters for the sorption of Cu and Zn onto Cli, FeNaCli<sub>1</sub>, and FeCli<sub>2</sub>.

		$r^2$	K (L/mg)	$\beta$
Cu	Cli	0.971	0.223	0.078
	FeNaCli <sub>1</sub>	0.990	0.290	0.156
	FeCli <sub>2</sub>	0.936	0.177	0.163
Zn	Cli	0.952	0.232	0.078
	FeNaCli <sub>1</sub>	0.983	0.260	0.174
	FeCli <sub>2</sub>	0.959	0.182	0.157

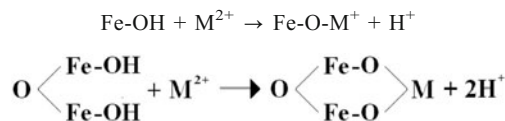
Preliminary kinetic experiments showed that most of the contaminants were sorbed on a natural zeolite within the first 30 min, while the plateau was achieved after 60 min (Kragović *et al.*, 2010). Therefore, a reaction time of 120 min was considered sufficient to reach equilibrium in all experiments (Figure 8).

The sorption capacity,  $Q_m$ , which is a measure of the maximum sorption capacity corresponding to complete monolayer coverage, showed values for Cu<sup>2+</sup> and Zn<sup>2+</sup> on Cli to be 0.116 mmol/g and 0.132 mmol/g, respectively. Similar capacities for other natural zeolite particle sizes were also found by Ugrina *et al.* (2010) confirming that ion exchange is the main mechanism for the removal of these ions from solution.

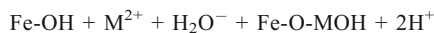
The ionic radii of the contaminant atoms are important because of the 3-dimensional framework of the zeolites. Water related to the metal ions and the radius of the hydration cation is a factor in the exchangeability of a given cation (Palmer and Gunter, 2001). In general, the hydrated radius is directly proportional to the charge density of the cation (charge:radius ratio), which means that it is inversely proportional to the cationic radius of like-charged ions (Top and Ülkü, 2004). The charge densities for hydrated Cu<sup>2+</sup> and Zn<sup>2+</sup> (Khaled and Stucki, 1991) are 3.70 and 4.65, respectively, which explains the greater adsorption of Zn<sup>2+</sup> over Cu<sup>2+</sup>.

The sorption capacity of FeCli<sub>2</sub> for Cu<sup>2+</sup> and Zn<sup>2+</sup> was 0.251 mmol/g and 0.234 mmol/g, respectively, which was about double that for the untreated Cli. The increase in sorption capacity ( $Q_{m\text{Fe-Cli}_1}/Q_{m\text{Cli}}$ ) was 2.2 for Cu and 1.8 for Zn, indicating that the synthesized Fe(III) oxyhydroxide has a greater affinity for Cu than for Zn. This result is opposite the trend in the untreated Cli. Based on the literature (Dixon and Weed, 1989), heavy metals are adsorbed by goethite in the order Cu > Pb > Zn > Cd > Co > Ni > Mn. The greatest influence on the extent of adsorption is pH. Earlier studies by the present authors have shown that for all pH values the sorption of heavy metals follows the same order as given above so copper can be adsorbed at the highest level for all pH values.

The structure of the surface complex between the functional groups of the Fe oxide and the heavy metal is not known fully. From the measured release of between one and two protons per metal atom adsorbed, several reactions have been proposed (in which mono- or binuclear complexes may form):



As the pH of the system increases, MOH<sup>+</sup>, the hydroxo species, rather than M<sup>2+</sup> will be adsorbed:



The strong effect of heavy-metal adsorption, which was also found for soils, is of great relevance for the mobility of toxic heavy metals in the soil mantle and thus for groundwater pollution.

Experimental data obtained using FeCli<sub>1</sub> are difficult to explain. During the contact time (for even <60 min), a blue precipitate of Cu(OH)<sub>2</sub> was generated and Cu was not detected in the supernatants after the suspensions had been centrifuged, irrespective of how high the starting concentration was. The new crystalline structures of the

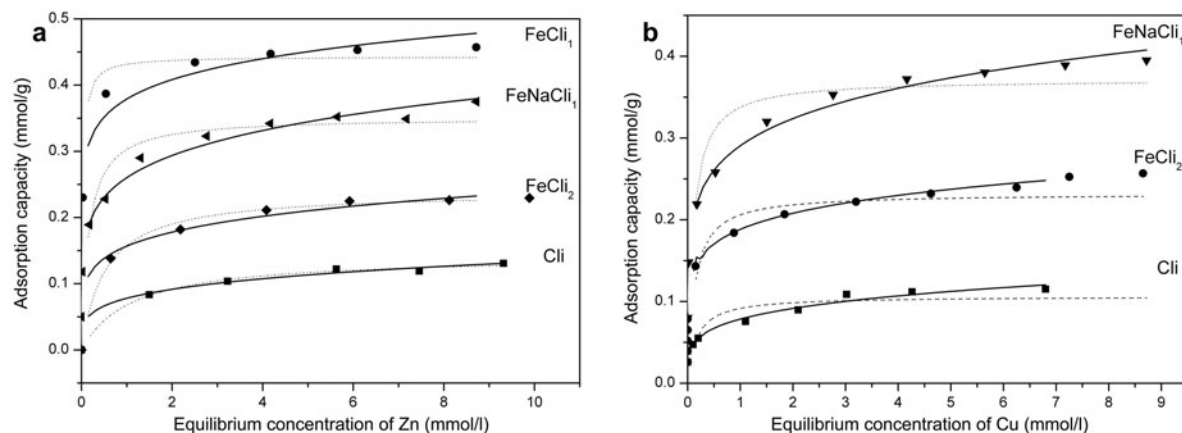


Figure 8. Sorption isotherms of (a) Zn and (b) Cu uptake on natural and Fe-modified clinoptilolite.

CaO hydrolyzed during the contact period released the  $\text{OH}^-$  and were responsible for the formation of the Cu hydroxide precipitate making it impossible to determine the mass capacity for  $\text{Cu}^{2+}$  uptake by  $\text{FeCl}_1$  through the adsorption mechanism.

Under the same experimental conditions for Zn, the maximum amount sorbed was 0.443 mmol/g. Assumptions were made that  $\text{Zn}(\text{OH})_2$  was also generated, which explains the enhanced sorption capacity but the color of the precipitate was white and, therefore, less easy to notice. Furthermore, the solubility product for the  $\text{Cu}(\text{OH})_2$  ( $4.8 \times 10^{-20}$ ) is much less than that for  $\text{Zn}(\text{OH})_2$  ( $3.0 \times 10^{-17}$ ) [http://www.ktf-split.hr/periodni/en/abc/kpt.html, visited 15 December 2013]. The  $\text{Cu}(\text{OH})_2$  probably precipitated completely, while the Zn remained in solution. The precipitation phenomenon cannot be explained absolutely, considering the fact that the pH of the solution after the reaction period was between 5 and 5.5.

Unlike  $\text{FeCl}_1$ ,  $\text{FeNaCl}_1$  did not exhibit this behavior. No blue precipitate was detected and the sorption capacities for Cu and Zn were 0.4032 mmol/g and 0.3811 mmol/g, respectively. These results indicate significantly greater sorption capacity than either Cl or  $\text{FeCl}_2$ .

The EDS analysis results of the  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  content in  $\text{FeCl}_1$ ,  $\text{FeNaCl}_1$ , and  $\text{FeCl}_2$  supported the notion that enhanced removal by  $\text{FeCl}_1$  is a result of precipitation and not of improved sorption capacity. The amounts of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  in  $\text{FeNaCl}_1$  and  $\text{FeCl}_2$  were between 2 and 3%, *i.e.* 0.30–0.40 mmol/g. These results were consistent with the adsorption results with little variation. On the other hand, the Zn content in the  $\text{FeCl}_1$  varied by between 15 and 30%, *i.e.* 2.3–4.5 mmol/g, a significant deviation from the adsorption results. This significant difference indicated non-homogenous distribution of the Zn at the zeolite surface, probably due to precipitation.

## CONCLUSIONS

The clinoptilolite-Fe systems were synthesized under strictly basic conditions. The XRD results confirmed that amorphous Fe species had been formed at the clinoptilolite surface.

The conditions for the modification did not alter the chemical composition of the starting materials significantly, *i.e.* framework or structural cations (Si and Al). The composition of the extra-framework cations changed upon exposure of the original sample to concentrated solutions of KOH or NaOH. This exchange was incomplete and  $\text{Ca}^{2+}$  that remained in the structure of the  $\text{FeCl}_1$  caused side effects later, during the adsorption experiments. Therefore, modification Method I was combined with NaCl pretreatment with the result that the  $\text{FeNaCl}_1$  sample obtained had no  $\text{Ca}^{2+}$  in the extra-framework positions.

Both chemical composition results and the EDS analysis showed the greater Fe content in all three

modified zeolites, especially in the  $\text{FeCl}_2$ . In addition, the specific surface area, calculated using the BET equation, was much greater in the  $\text{FeCl}_2$  adsorbent.

The Cl,  $\text{FeCl}_1$ ,  $\text{FeNaCl}_1$ , and  $\text{FeCl}_2$  were used in the adsorption of Cu and Zn from water solutions. The results obtained were in the following order:

Cu: Cl (0.121 mmol/g) <  $\text{FeCl}_2$  (0.251 mmol/g)  
<  $\text{FeNaCl}_1$  (0.4032 mmol/g)

Zn: Cl (0.128 mmol/g) <  $\text{FeCl}_2$  (0.234 mmol/g)  
<  $\text{FeNaCl}_1$  (0.3811 mmol/g) <  $\text{FeCl}_1$  (0.443 mmol/g)

The Fe-modified samples had significantly greater sorption capacities for Cu and Zn than the unmodified sample. The  $\text{Cu}^{2+}$  uptake increased, indicating that the synthesized  $\text{Fe}^{3+}$  species did have greater affinity for Cu, in accordance with the work of Dixon and Weed (1989, see above). The main mechanism for Cu and Zn removal by Cl is by cation exchange. In the modified systems, however, identifying the precise mechanism of removal is very difficult. Greater sorption capacity is the result not only of the negative surface charge, but also of the Fe clusters located at the surface and the greater specific surface area.

In this particular study, the results indicated that the affinity of the  $\text{Fe}^{3+}$  species in the cluster for certain cations had a greater influence than the specific surface area. The  $\text{FeNaCl}_1$  had greater sorption capacity than the  $\text{FeCl}_2$ , regardless of the fact that  $\text{FeCl}_2$  had a much larger specific surface area.

Analysis by SEM/EDS showed that during modification Method I, CaO crystals were formed at the surface of the zeolite, from exchanged structural  $\text{Ca}^{2+}$ . This CaO hydrolyzed throughout the adsorption experiments and the high  $\text{OH}^-$  concentration was responsible for the formation of  $\text{Cu}(\text{OH})_2$  and  $\text{Zn}(\text{OH})_2$ . Because of this reaction,  $\text{FeCl}_1$  cannot be considered as an improved adsorbent but would be useful in wastewater treatments as a precipitation agent. The benefit of using  $\text{FeCl}_1$  for precipitation is the pH value. Precipitation achieved by chemical reagents is usually followed by a very high pH value but in this case precipitation was achieved with the pH at <6.

Which Fe(III) oxyhydroxides were synthesized is still unclear and this will be the subject of future investigations.

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